Proceedings of the

FY 2001 Glass Industry Project Review

OIT Glass Industry of the Future

Research Program

November 7-8, 2001
Richland, Washington

Proceedings of the

FY 2001 Glass Industry Project Review

November 7-8, 2001
Pacific Northwest National Laboratory
Richland, Washington

Coordinated by
Elliott Levine
U.S. Department of Energy
Office of Industrial Technologies

Proceedings of the 2001 Glass Industry Project Review

CONTENTS

1 Agenda

2 List of Reviewers

3 Project Evaluation Results and Presentations

High-Heat Transfer Low-NOx Natural Gas Combustion
Development and Validation of a Coupled Combustion Space/Glass Bath Furnace Simulation
Auto Glass Process Control
Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulates and Crown Corrosion
Molybdenum Disilicide Composites for Glass Processing Sensors
In-House Recovery and Recycling of Glass from Glass-Manufacturing Wastes
Glass Furnace Combustion and Melting Research Facility
Measurement and Control of Glass Feedstocks
Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Float Glass
Enhanced Cutting and Finishing of Handglass Using a Carbon Dioxide Laser
Electrostatic Batch Preheater System
Diagnostics and Modeling of High-Temperature Corrosion of Superstructure Refractories in Oxy-Fuel Glass Furnaces
Modeling of Glass Processes
Advanced Process Control System for Glass Production

Appendices

A Evaluation Form

B Other Presentations

GPLUS Update

C Attendees

D Completed Glass IOF and GPLUS Project Posters

1

Agenda

FINAL AGENDA

DOE GLASS PROJECT REVIEW

November 7-8, 2001

Pacific Northwest National Laboratory

Richland, Washington

Day One: Wednesday November 7, 2001

Battelle Auditorium

Time	Activity	Speaker(s)
3:40 - 4:00 pm	**REGISTRATION**	
4:00 - 4:20 pm	Welcome and Introduction	Elliott Levine Office of Industrial Technologies (DOE) Michael Greenman Glass Manufacturing Industry Council
4:20 - 4:40 pm	*GPLUS Update*	Peter Angelini Oak Ridge National Laboratory
4:40 - 5:15 pm	*High-Heat Transfer Low-NOx Natural Gas Combustion* Questions and Answers	David Rue Gas Technology Institute
5:15 pm	**Adjourn and Board Bus(es) for Reception/Dinner**	
6:15 - 7:15 pm	**RECEPTION AND WINERY TOUR AT COLUMBIA CREST WINERY**	
7:15 pm	**DINNER AT COLUMBIA CREST WINERY**	

Day Two: Thursday November 8, 2001

Battelle Auditorium

Time	Activity	Speaker(s)
7:45 - 8:00 am	**REGISTRATION**	
8:00 - 8:05 am	Opening Remarks	Elliott Levine Office of Industrial Technologies (DOE)
8:05 - 8:40 am	*Development and Validation of a Coupled Combustion Space/Glass Bath Furnace Simulation* Questions and Answers	Mike Petrick Argonne National Laboratory
8:40 - 9:15 am	*Auto Glass Process Control* Questions and Answers	Moe Khaleel Pacific Northwest National Laboratory
9:15 - 9:50 am	*Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulates and Crown Corrosion* Questions and Answers	Pete Walsh Sandia National Laboratories
9:50 - 10:05 am	**BREAK**	
10:05 - 10:40 am	*Molybdenum Disilicide Composites for Glass Processing Sensors* Questions and Answers	John Petrovic Los Alamos National Laboratory
10:40 - 11:15 am	*In-House Recovery and Recycling of Glass from Glass-Manufacturing Waste* Questions and Answers	Bassam Jody Argonne National Laboratory
11:15 - 11:50 am	*Glass Furnace Combustion and Melting Research Facility* Questions and Answers	Pete Walsh Sandia National Laboratories John Connors PPG Industries
11:50 am - 1:00 pm	**LUNCH**	

Day Two: November 8, 2001 (Continued)
Battelle Auditorium

1:00 - 1:35 pm	*Measurement and Control of Glass Feedstocks* Questions and Answers	Robert De Saro Energy Research Company Arel Weisberg Energy Research Company
1:35 - 2:10 pm	*Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Float Glass* Questions and Answers	Jill Aaron PPG Industries Mark Allendorf Sandia National Laboratories
2:10 - 2:45 pm	*Enhanced Cutting and Finishing of Handglass Using a Carbon Dioxide Laser* Questions and Answers	Steve Woodruff National Energy Technology Laboratory
2:45 - 3:20 pm	*Electrostatic Batch Preheater System* Questions and Answers	Carl Schatz BOC Gases
3:20 - 3:35 pm	**BREAK**	
3:35 - 4:10 pm	*Diagnostics and Modeling of High-Temperature Corrosion of Superstructure Refractories in Oxy-Fuel Glass Furnaces* Questions and Answers	Mark Allendorf Sandia National Laboratories
4:10 - 4:45 pm	*Modeling of Glass Processes* Questions and Answers	Tom Seward Center for Glass Research
4:45 - 5:20 pm	*Advanced Process Control for Glass Production* Questions and Answers	Chester Shepard Pacific Northwest National Laboratory
5:20 - 5:30 pm	Wrap-Up: Comments and Recommendations	Elliott Levine Office of Industrial Technologies (DOE) Michael Greenman Glass Manufacturing Industry Council
5:30 pm	**ADJOURN**	
6:30 pm	**NO-HOST DINNER**	

2

List of Reviewers

Reviewers
Glass Manufacturing Industry Council

CORE MEMBERS

CertainTeed Corporation
Terry Berg
Robert Butler

Corning Incorporated
Fred Quan

Fire and Light Originals, LP
John McClurg

Johns Manville
Kevin Schaal

Owens Corning
Tom Huff
Christopher Jian

PPG Industries
Jill Aaron
Amar Mishra
Cheryl Richards

Saint-Gobain Containers
Marvin Gridley

Saint-Gobain Vetrotex America
John Wells

Schott Glass Technologies
Carsten Weinhold

Techneglas
Robert Adams
John Chumley

Visteon
Ed Boulos

ASSOCIATE MEMBERS

Advanced Manufacturing Center
Philip Sanger

American Air Liquide
William Von Drasek

BOC Gases
Neil Simpson

Center for Glass Research
Thomas Seward

Diagnostic Instrumentation and Analysis Laboratory
John Plodinec

Eclipse/Combustion Tec
Dan Wishnick

Gas Technology Institute
David Rue

Siemens Energy and Automation
Robert Newell

3

Project Evaluation Results

HIGH-HEAT TRANSFER LOW-NO_x NATURAL GAS COMBUSTION SYSTEM

by

David Rue, Hamid Abbasi

Institute of Gas Technology

Val Smirnof, Dan Wishnick

Combustion Tec Inc. / Eclipse

2001 Project-Industry Review

Nov. 7, 2001

PROJECT TEAM - SUPPORT

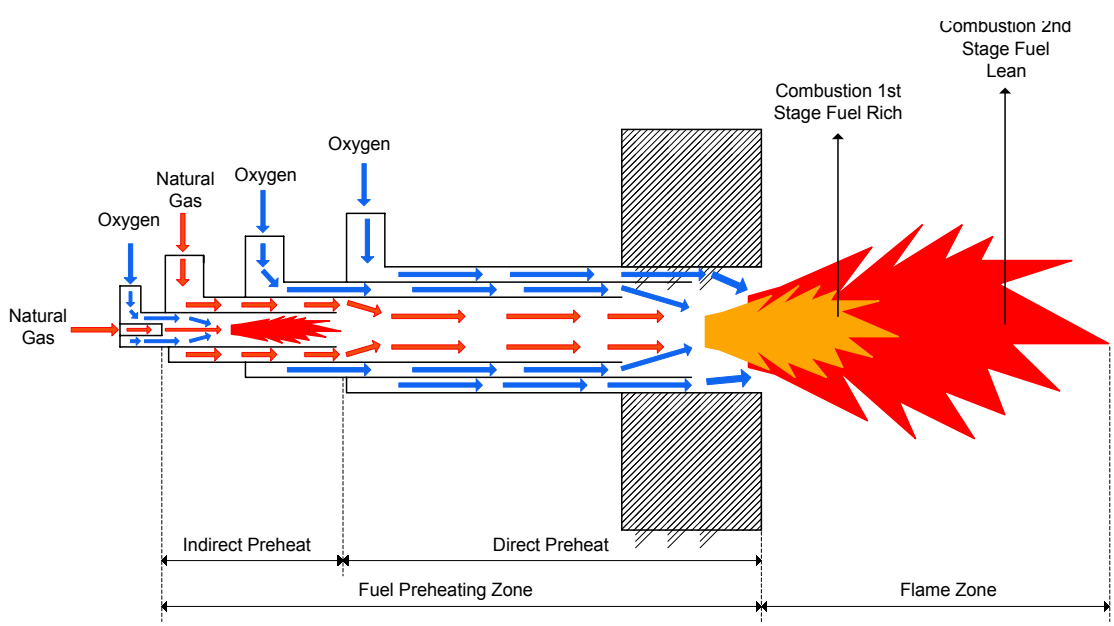
- US DOE
- IGT Sustaining Membership Program
- Gas Research Institute (now Gas Technology Institute)
  - Phase III
- NYSERDA
  - Phase III
- Eclipse / Combustion Tec
  - 20% of their efforts
- Owens Corning
  - technical review, host site, testing support

Co-funding - 20% of Phase I and II, 50% of Phase III

CONCEPT

- Soot precursor formation followed by soot production and burnout in the flame creates a highly luminous oxy-gas flame
  - radiative heat transfer to the load is increased
  - NO_x emissions are decreased because of radiative cooling of the flame
- Burner components
  - Fuel preheating zone
    - precombustion of a small fraction of the natural gas
    - direct mixing to heat natural gas and form soot precursors
  - Flame zone
    - fuel-rich combustion with soot formation
    - fuel-lean combustion with soot burnout

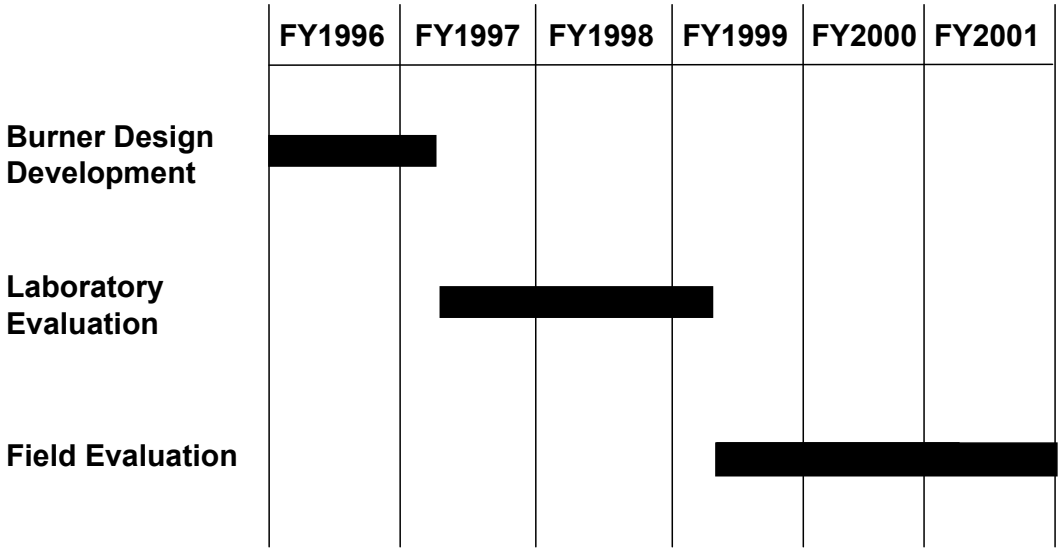
HIGH LUMINOSITY BURNER - CONCEPT



HIGH LUMINOSITY BURNER BACKGROUND

- Laboratory demonstration of luminosity increase by adding soot to a flame
- IGT laboratory verification of heat transfer and luminosity increase by adding externally generated soot (from a cracker) to a flame
- Development of High Luminosity Burner concept
- Patent on burner concept - granted March, 1998
- DOE-SMP-GRI-NYSERDA supported program in progress to develop and commercialize burner

HIGH-LUMINOSITY BURNER PROJECT SCHEDULE



HIGH LUMINOSITY BURNER PROJECT

3-Phase, project to bring burner from concept to commercialization

Phase	Activity	Length	Status
I	Burner Modeling and Design	15 mo.	Complete
II	Laboratory Testing	24 mo.	Complete
III	Commercial Demonstration	36 mo.	Began 1/99

PHASE I - MODELING RESULTS

- Soot concentrations increase from 0.1 to 2.0% at optimum Fuel Preheat Zone conditions
- Soot concentrations in fuel and furnace inlet affect furnace thermal performance
- Thermal efficiency of luminous flames can be increased by 25%
- Flames covering a large part of the glass surface enhance thermal performance
- Short flames produce non-uniform profiles
- Increasing soot concentration lowers temperature and decreases NO_x

PHASE II - LAB-SCALE BURNER TESTS

Independent Variables

- Firing rate
- Excess O2
- Natural gas to precombustor and mixing sections
- O2 to precombustor, fuel-rich combustion, and fuel-lean combustion

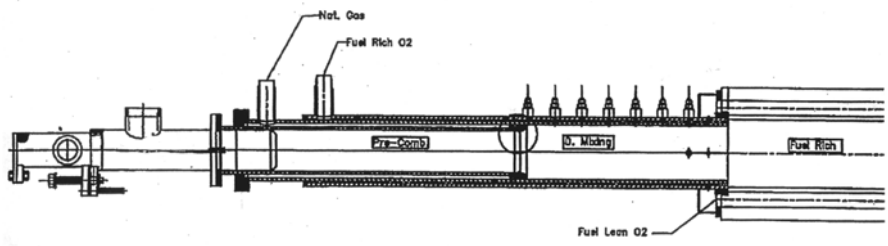
Measurements

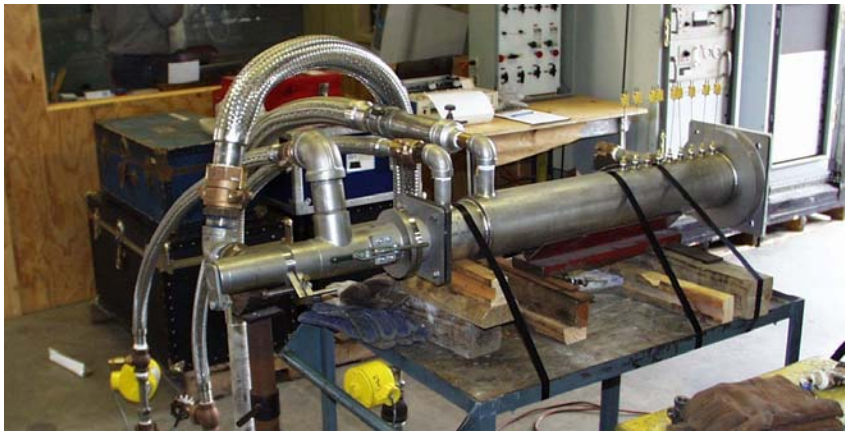
- Heat transfer to a simulated load
- Total and radiative heat fluxes
- Temperatures, pressures, and flows
- Exhaust gases (O_2, CO, CO_2, NO_x)

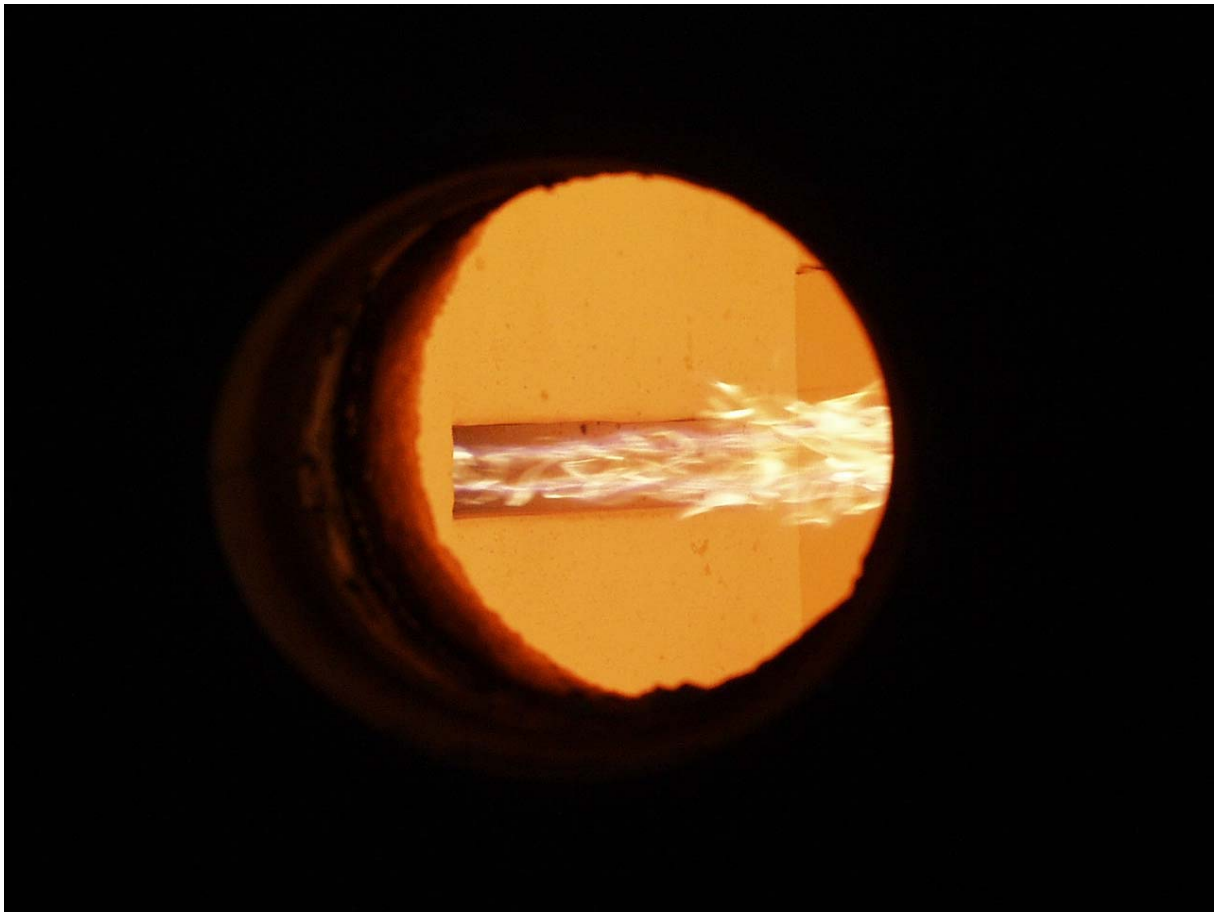
PHASE II - LAB-SCALE BURNERS

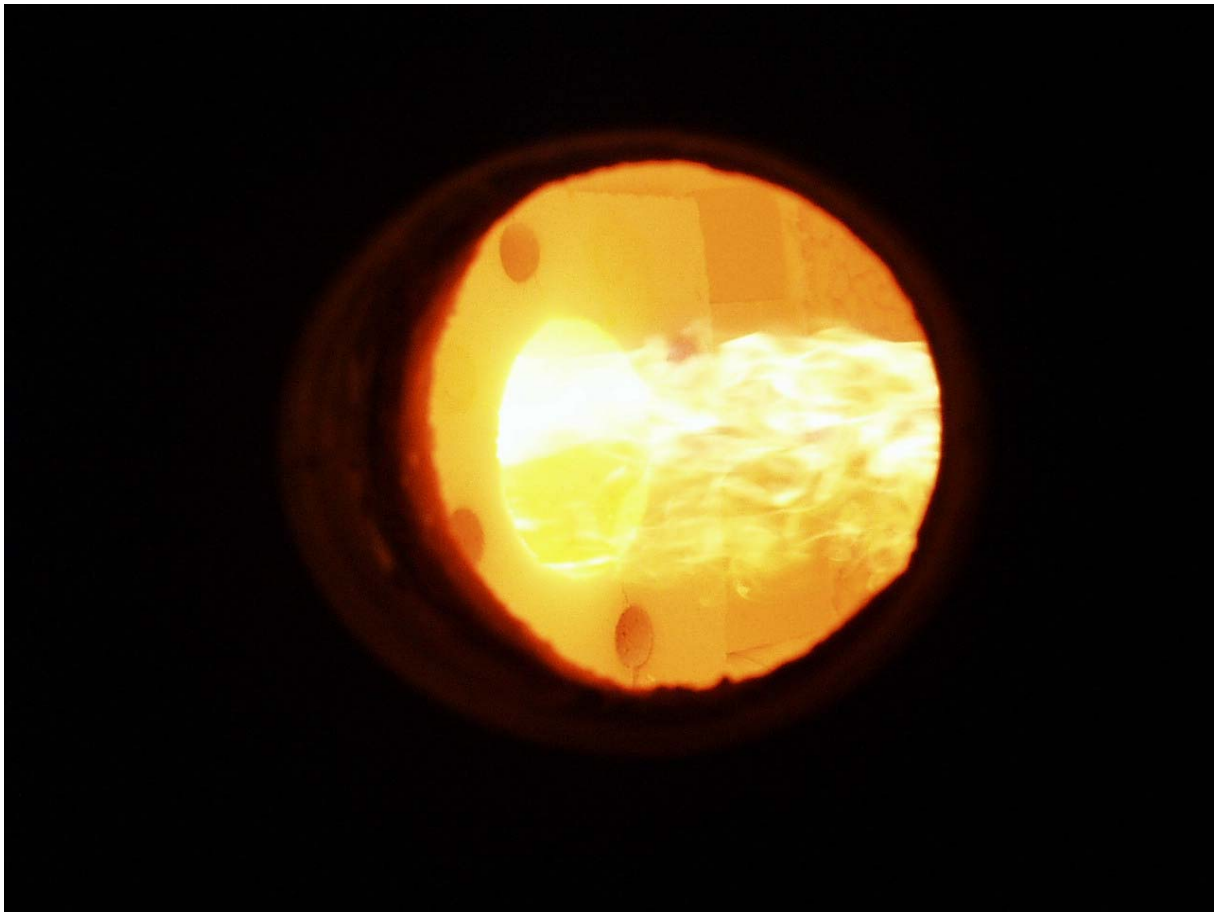
Burner	Design
1	• All zones lengths adjustable • Separate preheat zone
2	• All zone lengths fixed except for adjustable fuel-rich combustion zone • Separate preheat zone
3	• Adjustable direct mixing zone length • No fuel-rich combustion zone • Combined preheat and direct mixing zones

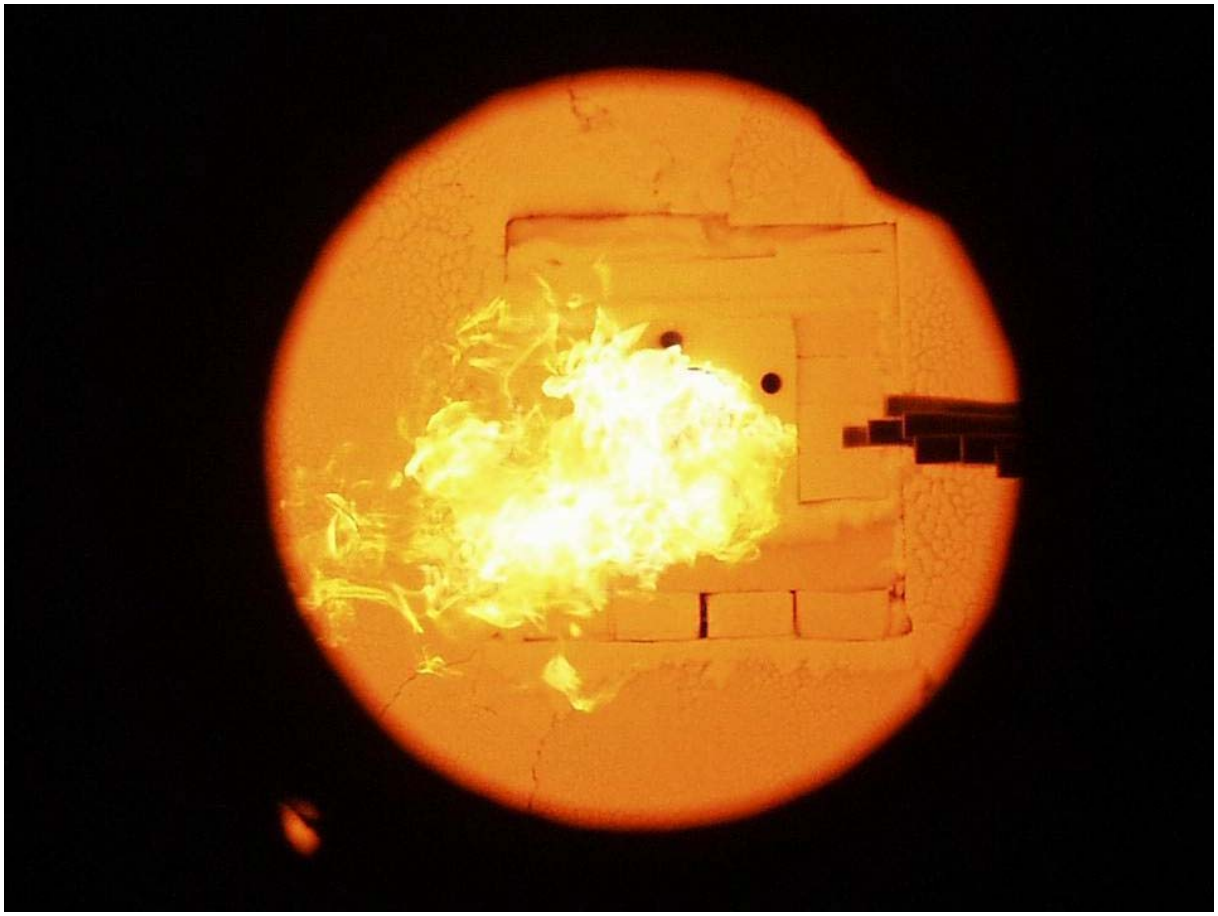
PHASE II - PILOT-SCALE BURNER











PHASE II CONCLUSIONS

- Heat transfer to simulated load increased 10-12% over baseline
  - CTI Primefire 100 used as baseline burner
  - greater increase expected for a glass load
- Total heat flux increased along with heat transfer to simulated load
- Temperature of furnace roof increased and exhaust gas temperature decreased with higher heat transfer to load
- NO_x emissions not significantly affected in the lab-scale furnace
- CO values <40 vppm for high-luminosity burner tests
- Precombustor and direct mixing zones can be combined
- Heat transfer is higher with combustion zone divided into fuel-rich and fuel-lean sections

PHASE III MILESTONES

Year, FY	Milestone	Schedule Completion Date	Done?
1999	Commercial Prototype Burner Test	Oct. 1999	Yes
1999	Demo Site Study and Selection	Oct. 1999	Yes
1999	Demo Test Host Site Agreement	mid 2000	Yes
2000	Demo Test Preparation	Mar. 2001	Yes
2000	Demo Testing - Parametric	Nov. 2001	No
2000	Demo Testing – Long Term	Nov. 2001	No
2000	Demo Testing Data Reduction and Analysis	Dec. 2001	No
2000	Industrial Adoption Plan	Dec. 2001	No
2000	Draft Phase III Final Report	Jan. 2002	No
2000	Final Report – Phases I, II and III	Feb. 2002	No

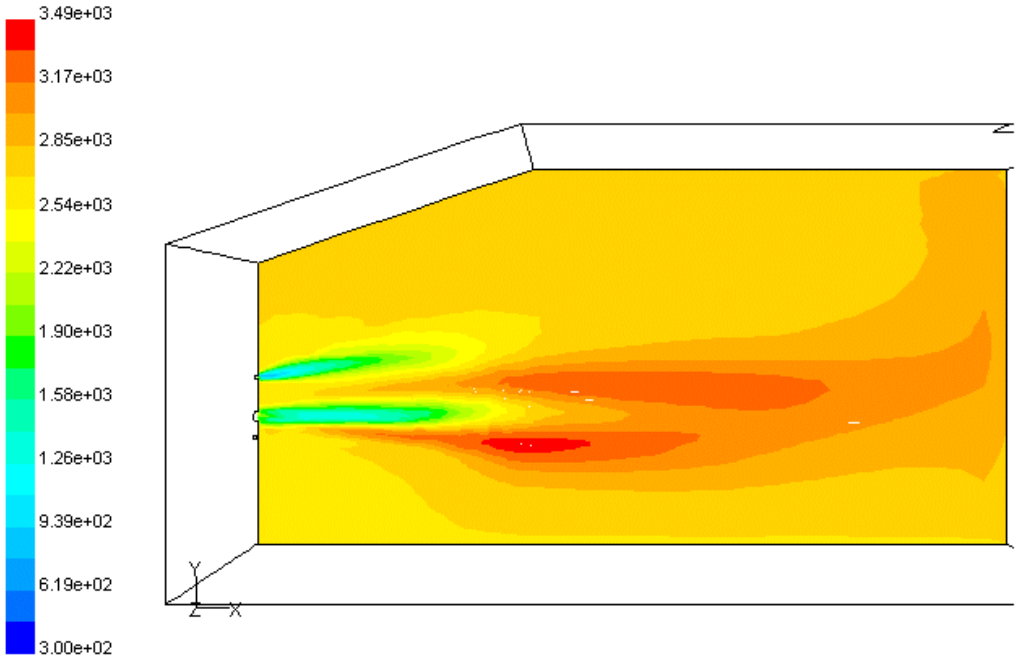
PHASE III - CURRENT STATUS

Done	• Designed commercial prototype burner • Modeled configurations of burner • Fabricated burner with two blocks
Also Done	• Testing of commercial prototype burner • Comparison of commercial burner and prototype burner with two blocks • Design changes and fabrication of burners for commercial demo tests
To Be Done	• Installation of burners for commercial demonstration tests • Parametric burner tests • Long-term burner tests • Preparation of Industrial Adoption Plan • Marketing technology to different industries

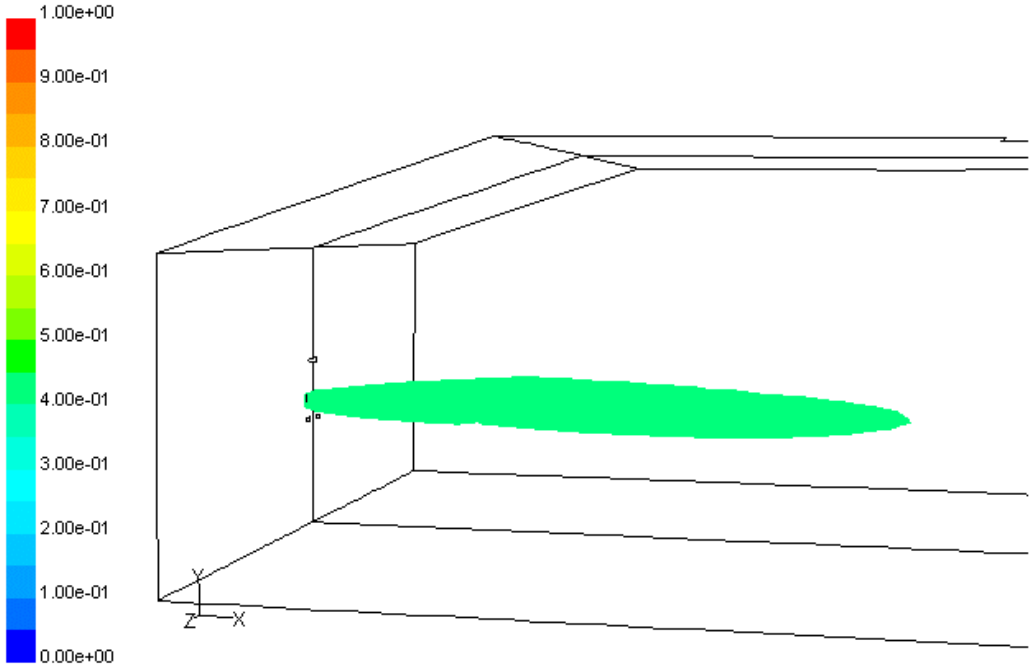
COMMERCAIL PROTOTYPE HIGH LUMINOSITY BURNER DESGIN

- Flat flame burner
- Inlets reduced to one for gas and one for O_2
- Burner length reduced by using the block as part of the direct mixing zone
- HELN 'A' multiple jets
  - Center preheated fuel slot
  - O_2 slots above and below fuel slot to create fuel-richand fuel-lean flame zones
- HELN 'B' single jet
  - Proprietary means of staging combustion using a single slot
  - Burner capacities from 1 to 20 MMBtu/h

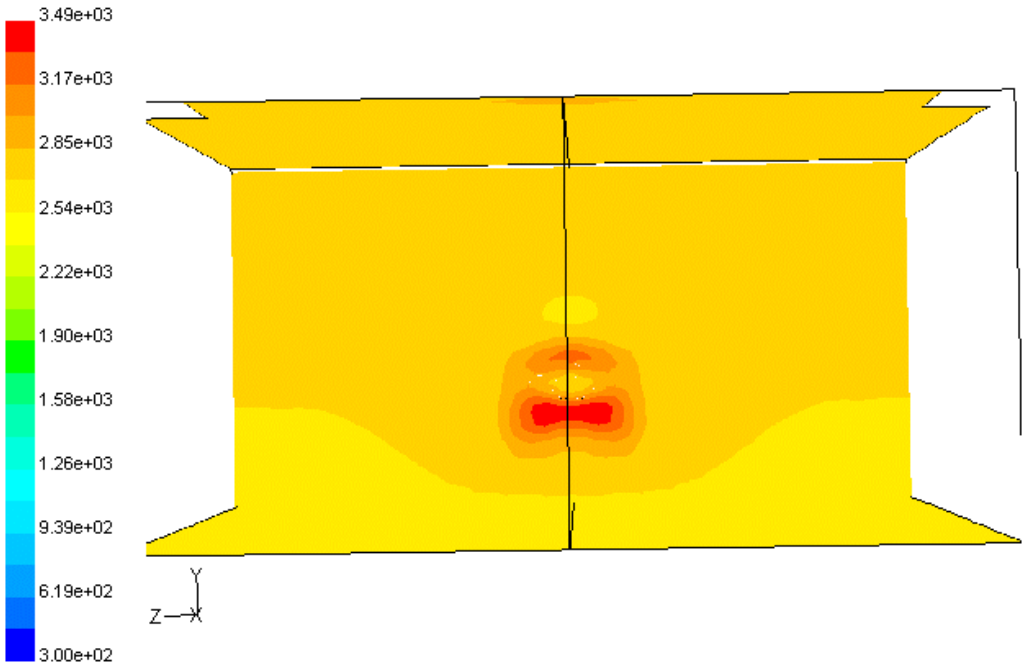
HELN 'A' TEMPERATURE PROFILE, °F



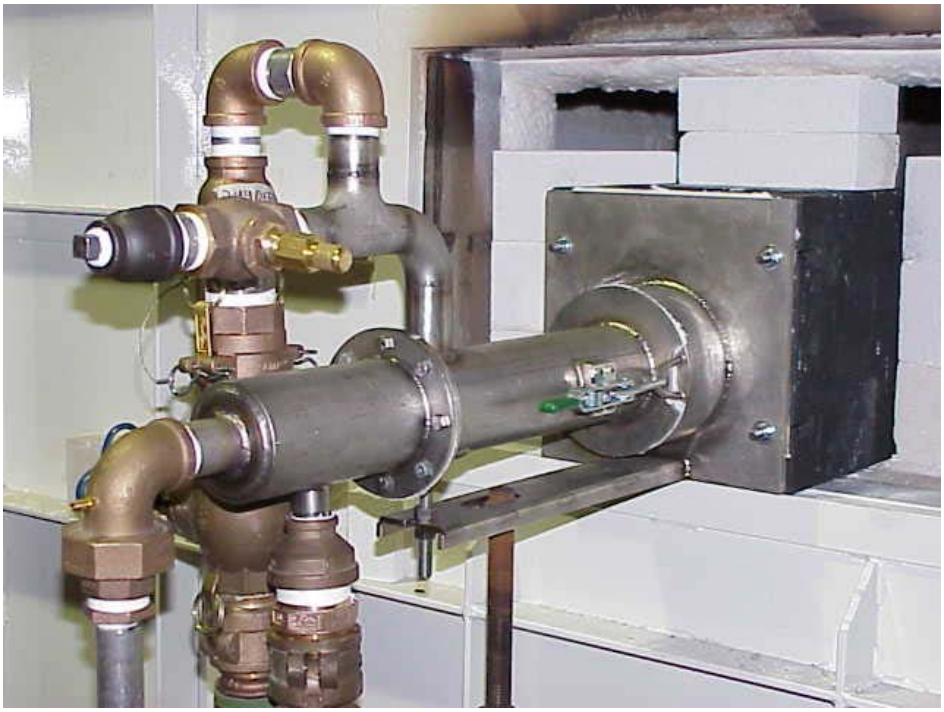
HELN 'A' FUEL-RICH ZONE



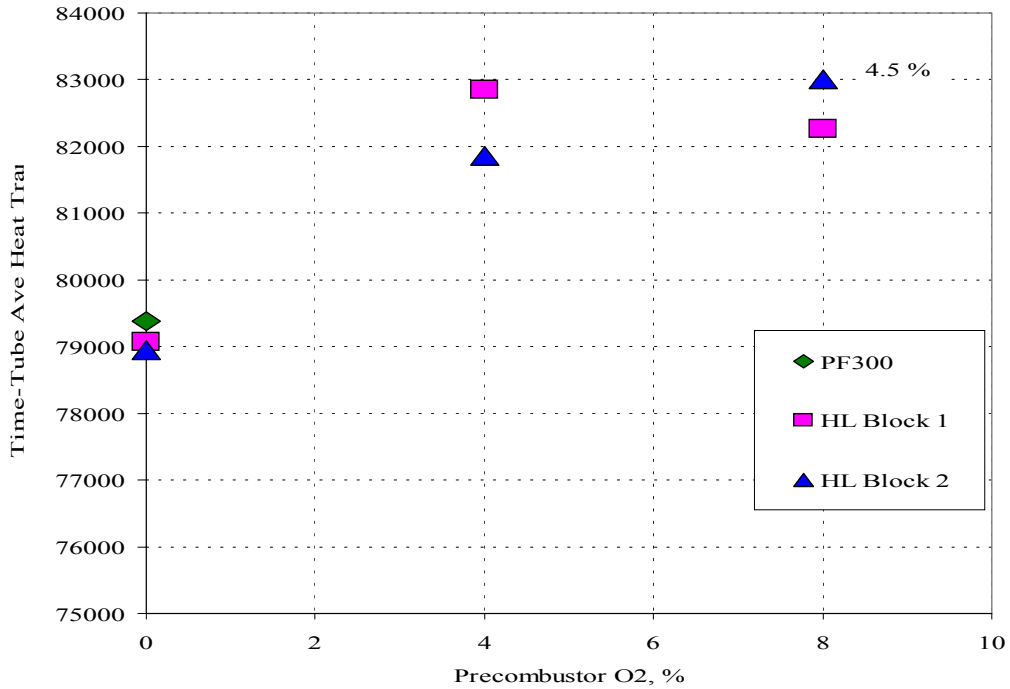
HELN 'A' TEMPERATURES, °F
PARALLEL TO BURNER FACE



DEMONSTRATION-SCALE HIGH LUMINOSITY BURNER



HEAT TRANSFER INCREASE WITH HELN 'A' BURNER



HELN 'A' PROTOTYPE BURNER TESTING RESULTS

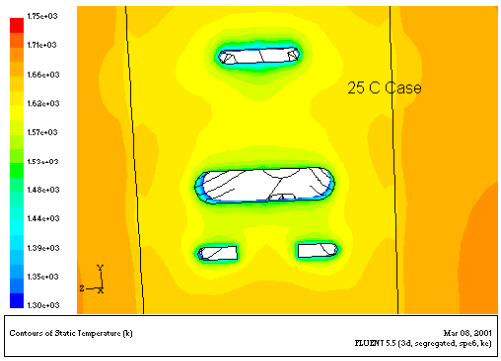
- Prototype burner heat transfer with both blocks is similar to PF 300 burner when there is no precombustion
- 4% to 8% O_2 to precombustion raises heat transfer and greatly reduces NO_x
- High luminosity burner flame is brighter, longer, and wider than the PF 300 flame
- Heat transfer increase and NO_x reduction (from combustion staging) are best with block 2 and 4 to 8% O_2 for precombustion

FLAT FLAME OXY-GAS BURNERS AT 1.75 MM/Btu/h

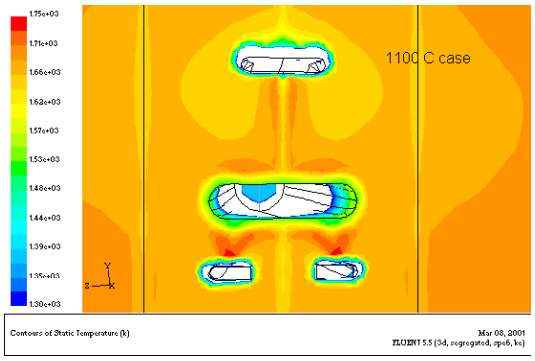
Combustion Tec
Primefire 300 burner

HELN 'A' Prototype burner
8% O_2 precombustion

HELN 'A' HOT FACE TEMPERATURES BY CFD



No precombustion

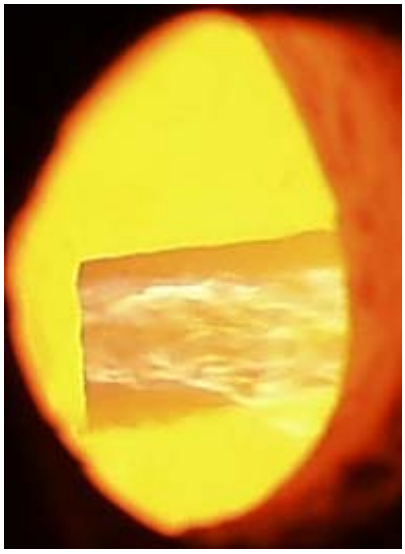


5% precombustion

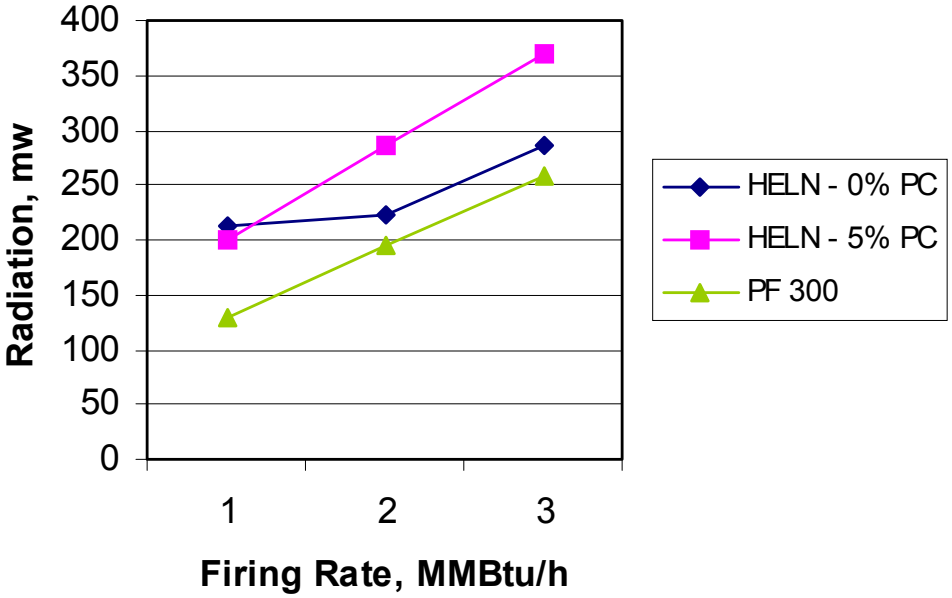
In a borosilicate glass furnace, hot face temperatures must be high enough to avoid sodium borate attack of the refractory

HELN 'B' AT 3 MMBtu/h WITH 5% O_2 PRECOMBUSTION

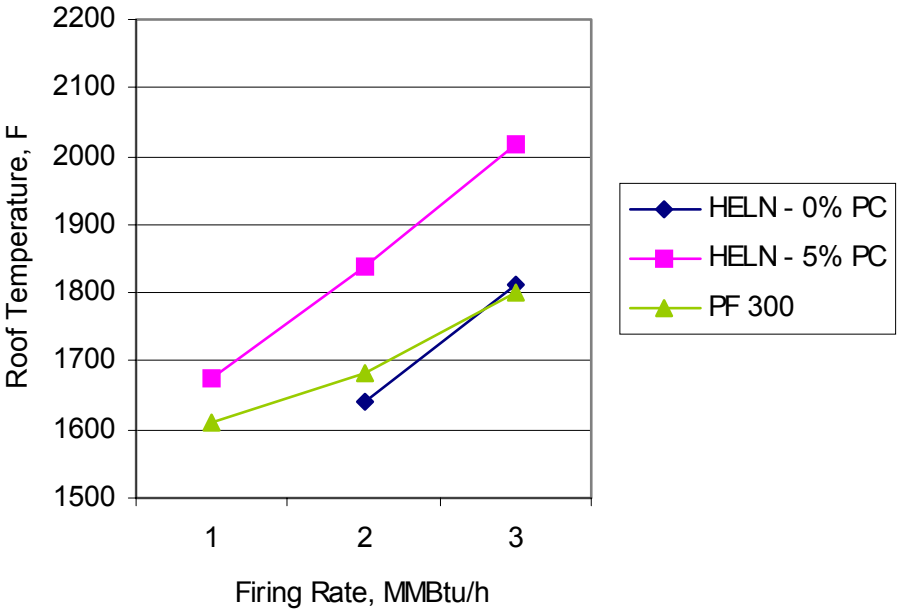
HELN 'B' HOT FACE AT 3 MMBtu/h – 5% O_2 PRECOMBUSTION



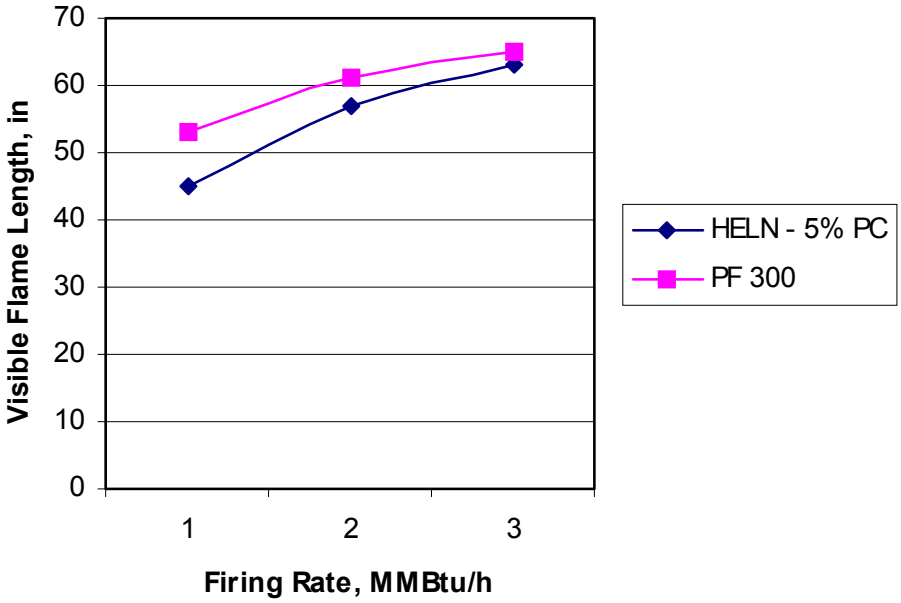
HELN 'B' AND PF300 – MEASURED TOTAL RADIATION



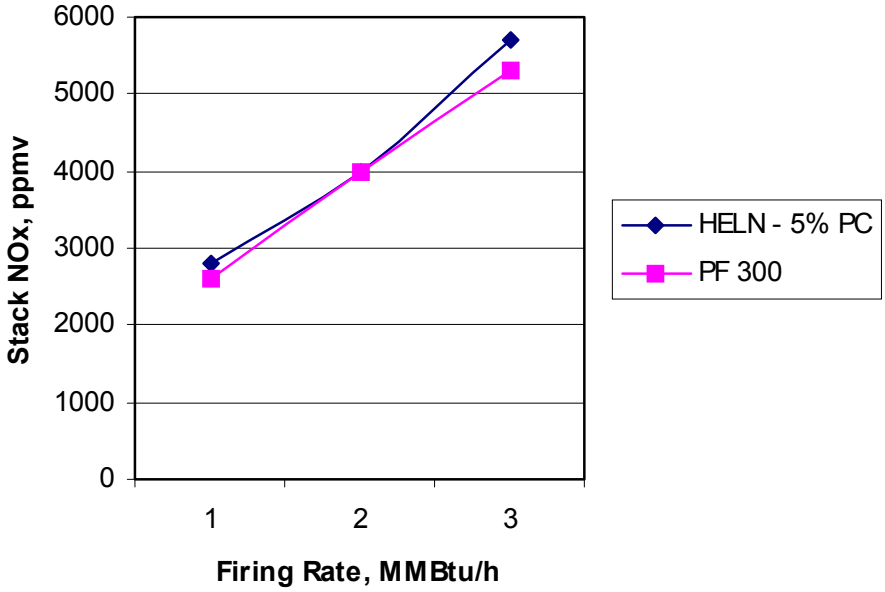
HELN 'B' AND PF300 - TEMPERATURES



HELN 'B' AND PF 300 – FLAME LENGTH



HELN 'B' AND PF 300 – MEASURED STACK NO_x



HIGH LUMINOSITY BURNER TEST PLAN – DELMAR, NY

Action	Date
Install data gathering insturments	Mon. 11/12 – in AM
Collect baseline furnace data	11/12 and 11/12
Swap out burner #2 and install the HELN 'B' burner	Wed. 11/13 – in AM
Collect furnace data with the HELN 'B' burner	11/13 and 11/14
Collect furnace data after HELN 'B' has been operating for some time	11/30 and 12/1

20 MMBtu/h HELN 'B' FIRING

10 MMBtu/h

COMMERCIALIZATION PATH

- Demonstration testing by IGT/Eclipse/OC in 2001
- Conical and flat flame versions will be available for all U.S. and non-U.S. glass furnaces from Eclipse after demonstration
  - approximately 50 U.S. oxy-gas glass melters
  - the high luminosity burner will be marketed as the high end of the Combustion Tec line of oxy-gas burners
  - royalties will be paid to IGT/SMP for patent rights
  - Combustion Tec builds, markets, installs, and services a full line of glass furnace burners
- Technology will be extended to other industries with GRI and NYSERDA support

DEVELOPMENT/VALIDATION OF AN ADVANCED MULTIPHASE GLASS FURNACE MODEL (GFM)

PRESENTORS:	Michael Petrick	ANL
	Shen Lin Chang	ANL
	John Chumley	Techneglas

COLLABORATING PRINCIPAL INVESTIGATORS:

INDUSTRY:	Christopher Jian	Owens Corning
	Ed Olson	Libbey, Inc.
	Jim McGaughey	Libbey, Inc.
	Bill Anderson	OSRAM Sylvania
	Ed Boulos	Visteon
ACADEMIA:	Ray Viskanta	Purdue U.
	Robert Cook	MSU

PRESENTATION OUTLINE

- Program Overview
  - Goals, technical approach, advances in furnace modeling, program description
  - Integration of Part I and Part II Programs
    - Part II program objectives
    - Integrated WBS
- Technical Progress/Accomplishments
  - Code Validation
  - Gaseous phase transport in glass melt
  - Extension of radiation model into glass melt
  - Development of reduced chemistry/kinetic models
  - Development of user-friendly, windows-based glass furnace (GFM) model
  - Parametric/sensitivity studies
- Technology Transfer
- Expected Progress in FY 2002

PROGRAM OVERVIEW

AND

STATUS

Program Goals

- Advance the "State of the Art" in Glass Furnace Modeling/Simulation
- Provide Industry with a Validated Furnace Model that Can be used to Analyze Different Types of Furnaces
- Make the Validated Code (Executable and Source Codes) Readily Available to Industrial Users.

Technical Approach for Achieving Program Goals

- ANL's Multiphase Reacting Flow CFD Codes (ICOMFLO, ICRKFLO) used to Develop an Advanced Glass Furnace Model
  - Incorporate advanced phenomenological models for spectral radiation heat transfer, batch melting, foam layer formation, etc.
- Construct Simulations of Selected Furnaces
- Develop/Install Diagnostics in Selected Furnaces to Acquire Data for Code Validation
- Validate Furnace Models with Data Acquired
- Demonstrate the Utility and Benefits That Can Be Derived From the Use of GFM Code
  - Conduct extensive parametric, sensitivity and optimization studies to identify opportunities to improve furnace performance

Program Description

- Two Part Program Initiated in 1998
- Ongoing Part I Program Integrated with Follow On Part II Program in 2001
  - Part I: Develop/validate a coupled combustion space/glass melt furnace simulation
  - Part II builds upon the Part I program to develop/validate an advanced multiphase Glass Furnace Model (GFM)
- Supported by Industrial Consortium
  - Techneglas, Inc. Libbey, Inc. Visteon (new member)
  - Owens Corning Osram Sylvania
- University Participants
  - Purdue University
  - Mississippi State University
- Five-Year Program Schedule
  - Part I Program completed; Part II Program initiated
- Deliverable: User Friendly, Validated, Glass Furnace Model for Use by Engineers
  - Inputs: furnace geometry, burner fuel/oxidizer flow rates, and pull rate

Part I Program Objectives

COMPLETED

- Develop/Validate Combustion Space Model
  - Incorporate rigorous spectral radiation model
  - Radiation to and from crown to glass melt
- Develop Model of Glass Melt with ANL's Multiphase CFD Code
  - Develop/incorporate multiphase batch model
- Couple Combustion Space and Glass Melt Models Through Radiation Model into an Overall Furnace Model
- Develop Diagnostics and Acquire Furnace Performance Data for Furnace Model Validation
- Conduct Initial Validation Studies

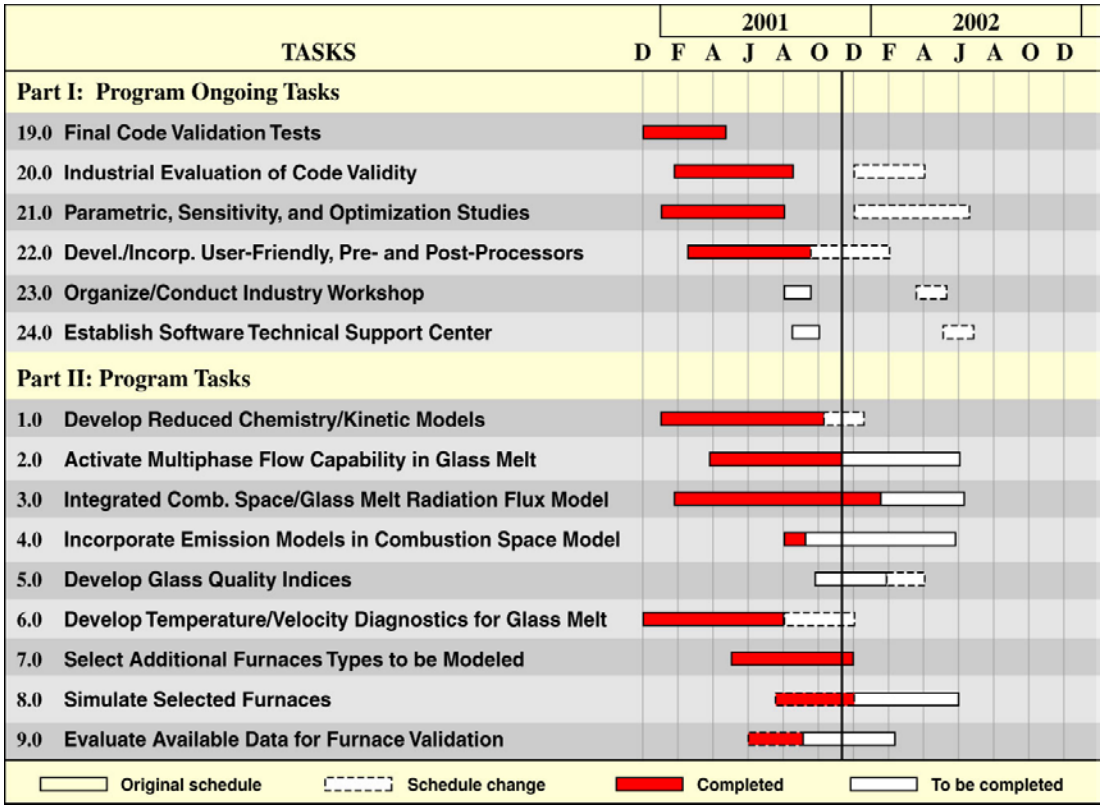
DEFERRED

- Transfer of Furnace Model to Industry Via Workshop and Establish Support Center
  - Deferred to later date with integration of Part I and Part II Programs

Part II Program Objectives

- Incorporate Glass Chemistry models into GLASS Melt
  - Compute/track key solid, gaseous, liquid species
- Activate Gaseous Phase Transport in Glass Melt Model
  - Source terms derived from chemistry models
  - Compute gaseous species production, bubble nucleation, bubble growth, dissolution, and release at glass surface
- Develop/Incorporate Glass Quality Indices into Glass Melt Model
  - Facilitate optimization studies re energy use and productivity
- Validate GFM Model on Other Types of Glass Furnaces
- Technology Transfer to the Industry
  - Release of Beta versions of code to industrial participants (ongoing)
  - Release of Demo version to GMIC Membership in late spring Workshop
  - Release of Final version to industry at program conclusion
    - Establish Support Center

PROGRAM WBS, SCHEDULE, AND KEY MILESTONES

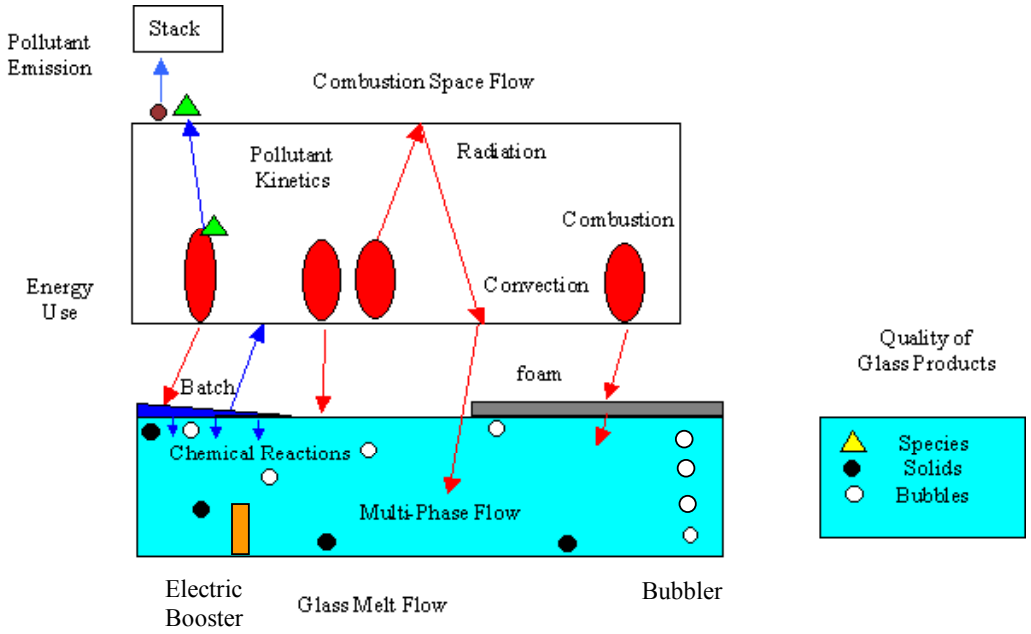


TECHNICAL PROGRESS AND ACCOMPLISHMENTS

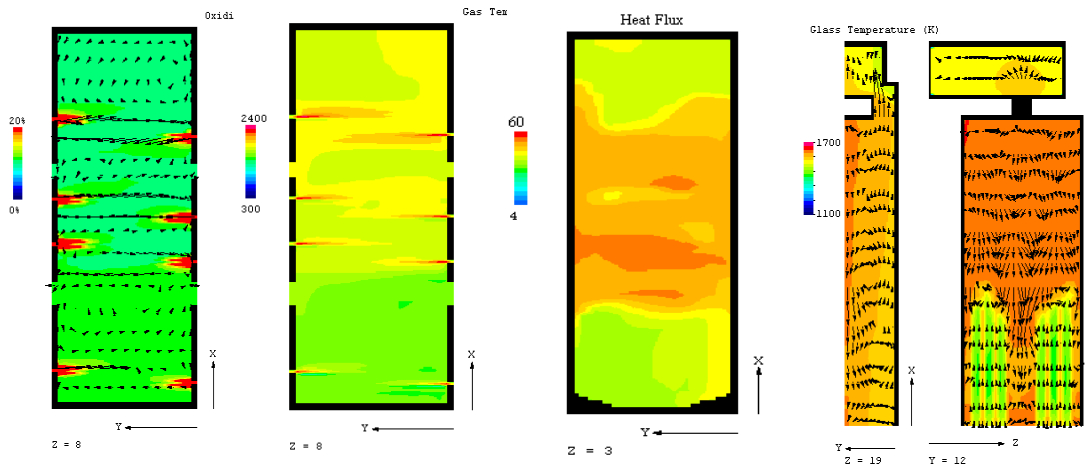
Technical Accomplishments

- Glass Furnace Model Enhancements
  - Electric Booster and Bubblers
  - Liquid/Solid/Bubble Flow in the melter
- Furnace Measurements and Code Validation
  - Temperature, Heat Flux, Velocity, and Species
  - Measurements at Two Furnaces
- **Technology Transfer**
  - Window-based GFM Processor
  - User Support Center

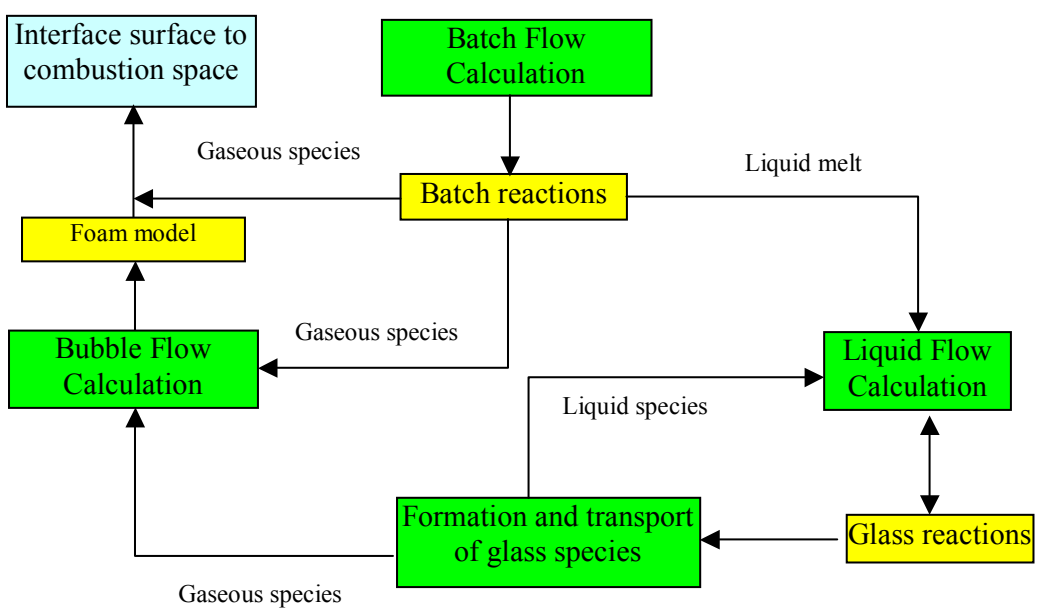
Controlling Processes in Glass Furnace



Results of Furnace Modeling



Bubble Flow Simulation



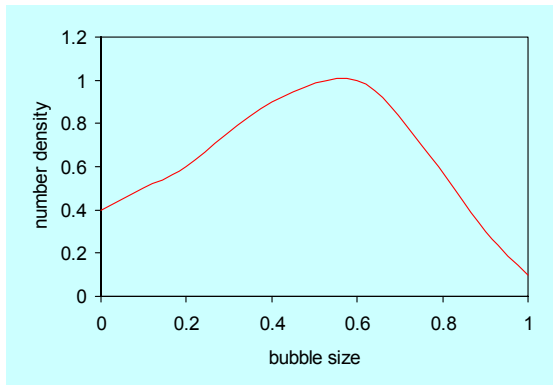
Glass Reaction and Bubble Models

- **Lumped batch melting reaction model**

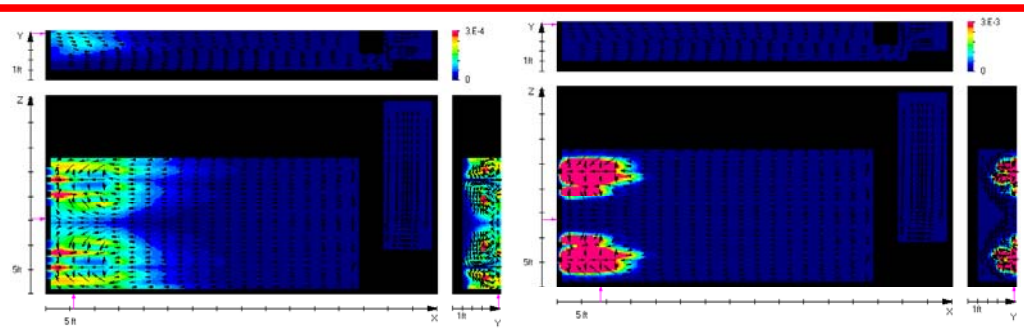
$$\text{batch} \xrightarrow{k} a_1 \text{volatile} + a_2 \text{liquid glass}$$

- **Glass refining reaction model**

$$b_1 \text{glass}_1 + b_2 \text{refining agent} \xrightarrow{k} b_3 \text{gas} + b_4 \text{glass}_2$$



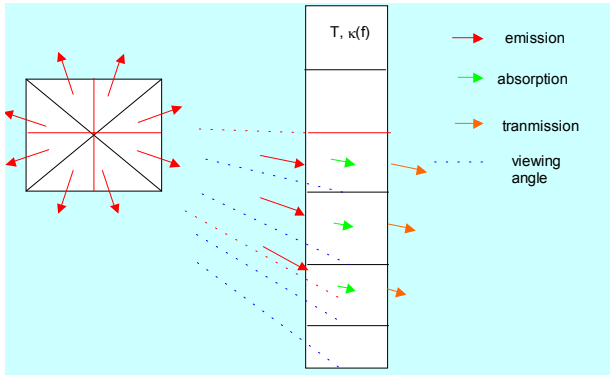
Bubble Flow in a Melter



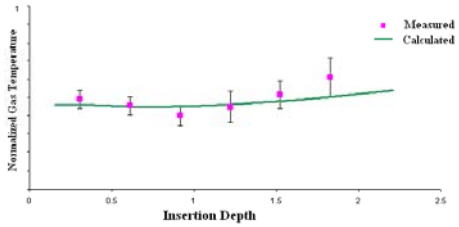
smaller bubbles larger bubbles

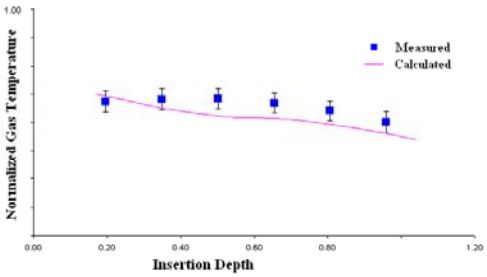
Radiation Heat Transfer in Glass Flow

- Radiation Transport Equation
- **Integral Solution Approach (3-D) in Glass Melt and Walls**
  - applicable to all grid sizes and all viewing angles

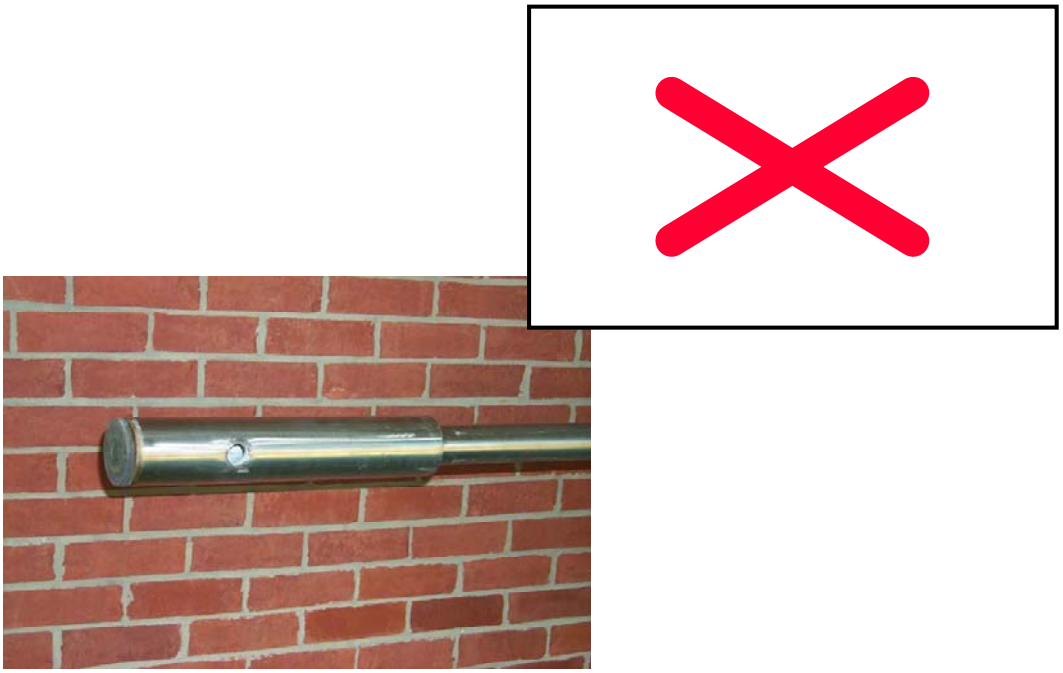


Gas Temperature Measurements and Calculations

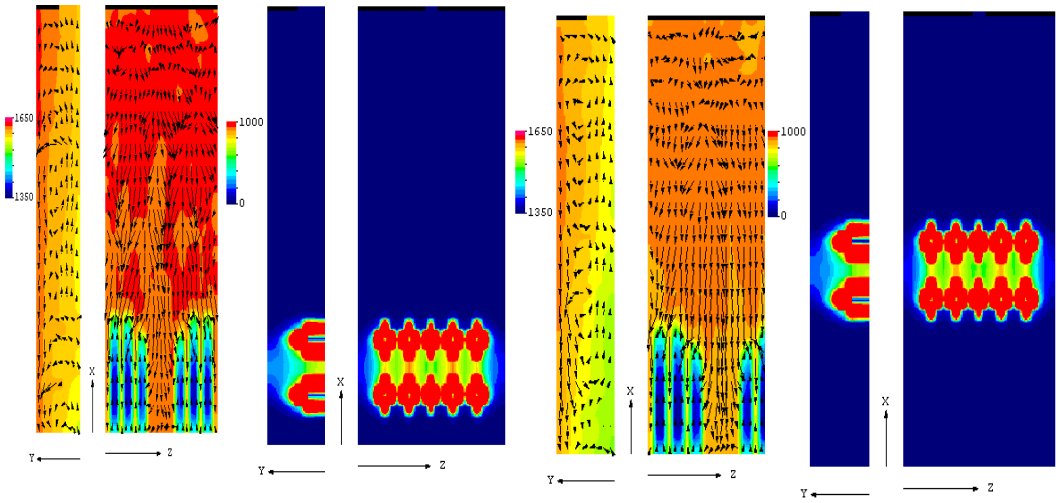




Glass Temperature Measurements and Calculations

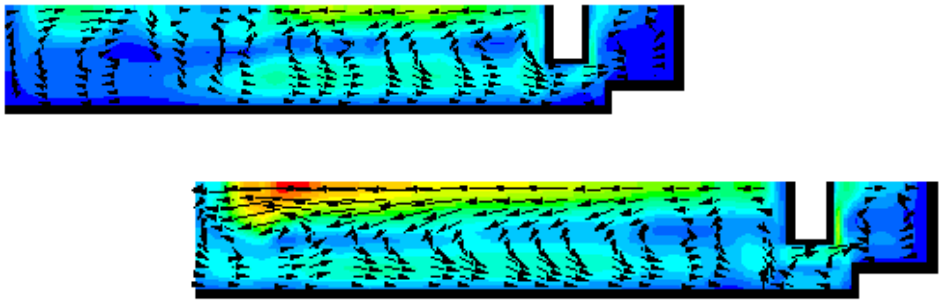


Effect of Electric Booster Locations



Effect of Heat Flux on Melter/Refiner Flow

- Firing patterns have strong impact on flow characteristics.
- **More uniform heat load can induce back flow from refining section.**



GFM Processor

- Preprocessor

  Define geometries, flow conditions, and simulation requirements for Combustion Space and Glass Melter

- Program Executables

  Runs computer program and generates associated files for exchanging data between programs.

  - **Combustion Space**
  - **Radiation Heat Transfer**
  - Glass Melt Flow

- **Post Processor**

  Plots grid and computed flow properties for Combustion Space and Glass Melter

TECHNOLOGY TRANSFER

STRATEGY FOR TRANSFER OF GFM CODE TO THE INDUSTRY

- Release of Beta Versions of Code to Industrial Participants
  - Provide feedback to code developer (ANL)
  - Participants gain experience in use of the code
    - Gain head start vis a vis other industrial users
- Hold Workshop for GMIC Membership in Late Spring, 2002
  - Release royalty free demo version to attendees
  - Instruct attendees on use of the code
  - Make available executable version of the code
- Release of Final Version of Code to Entire Glass Industry at Conclusion of the Program
  - Hold workshop
  - Establish support center

John Chumley
Techneglas, Inc.

GMF a user's view

Introduction

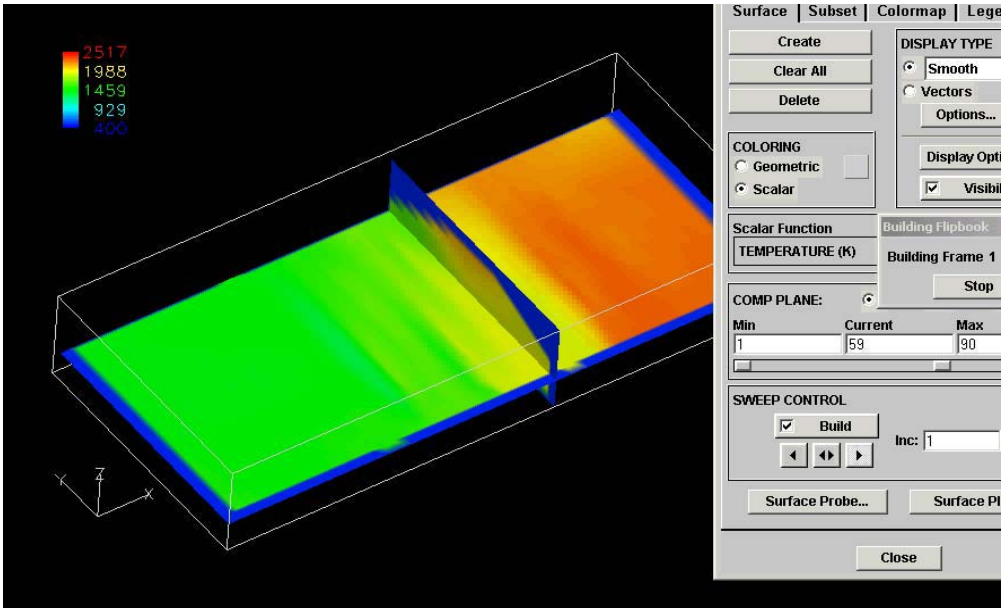
- This report examines the glass furnace model code now being developed under the sponsorship of the DOE from the perspective of an Industrial user.
- My name is John Chumley and I work for Techneglas, one of the four industrial partners working with the project.

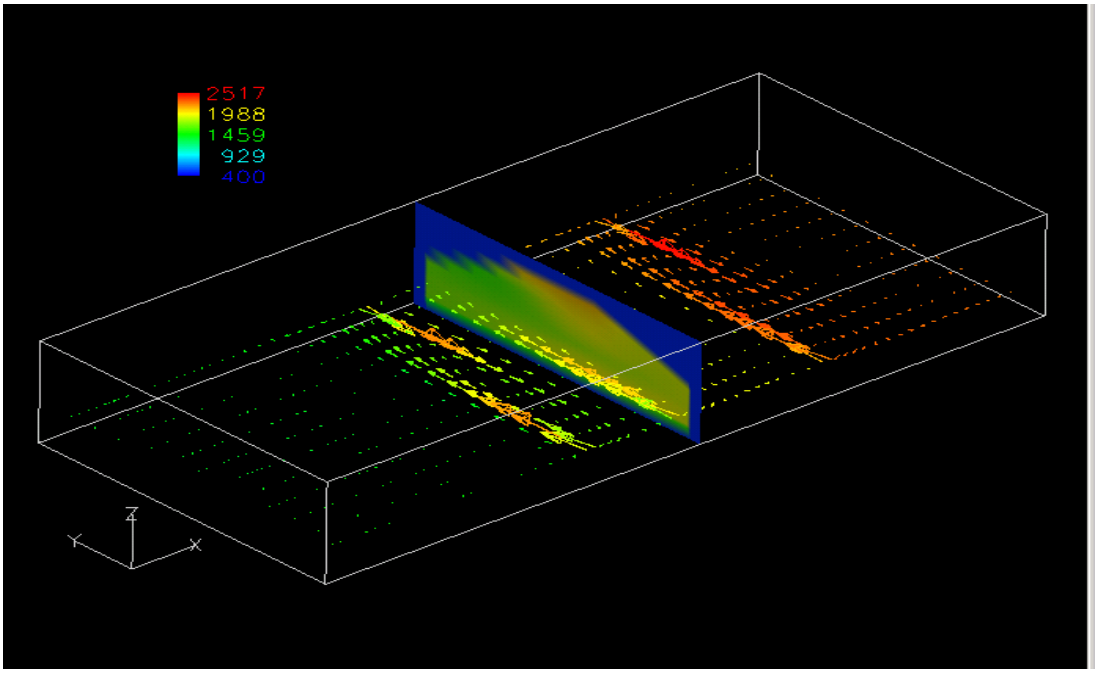
Topics of Discussion

- Since other speakers have described the capabilities of the code, my report concentrates on the mechanics of it can be applied from the users prospective.
- To help evaluate the code each of the industrial partners was asked to model a furnace unique to their operation. In fact I did three different models to illustrate different features of the code.

Columbus TV-Funnel Furnace

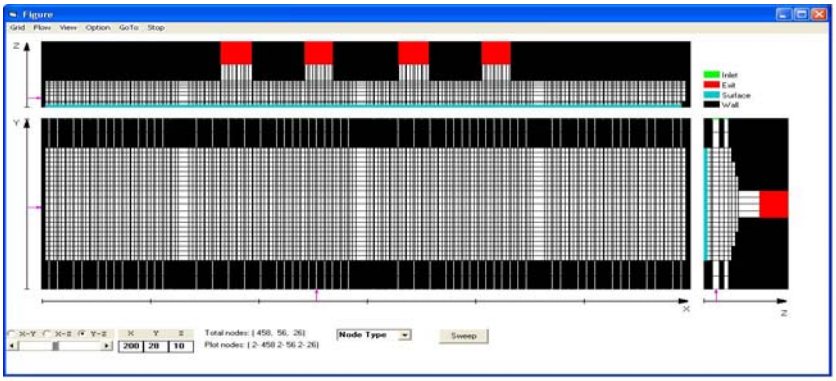
- A Columbus tv-funnel furnace is the subject of the model development and verification project, therefore, it was not necessary to rebuild the model. Instead I concentrated on interfacing the model output with a commercial post processing product, FieldView^{tm} ,by Intelligent Light Corp.
- A temperature field and a flow-field animation are presented here.

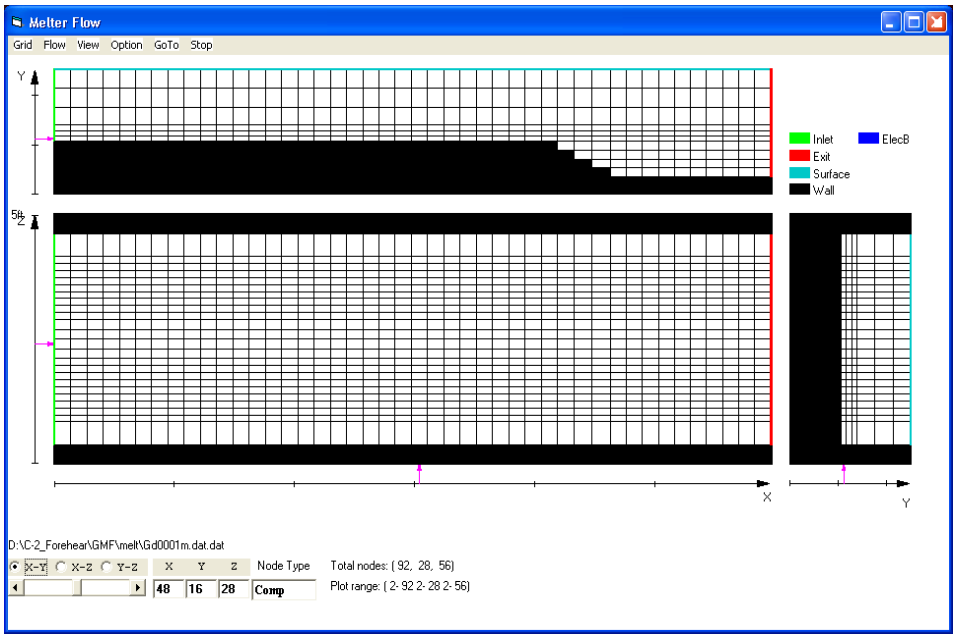

2517
1988
1459
929
400
Surface
Subset
Colormap
Lege
Create
Clear All
Delete
DISPLAY TYPE
Smooth
Vectors
Options...
COLORING
Geometric
Scalar
Scalar Function
TEMPERATURE (K)
Building Flipbook
Building Frame 1
Stop
COMP PLANE:
Min
Current
Max
1
59
90
SWEEP CONTROL
Build
Inc:
1
Surface Probe...
Close

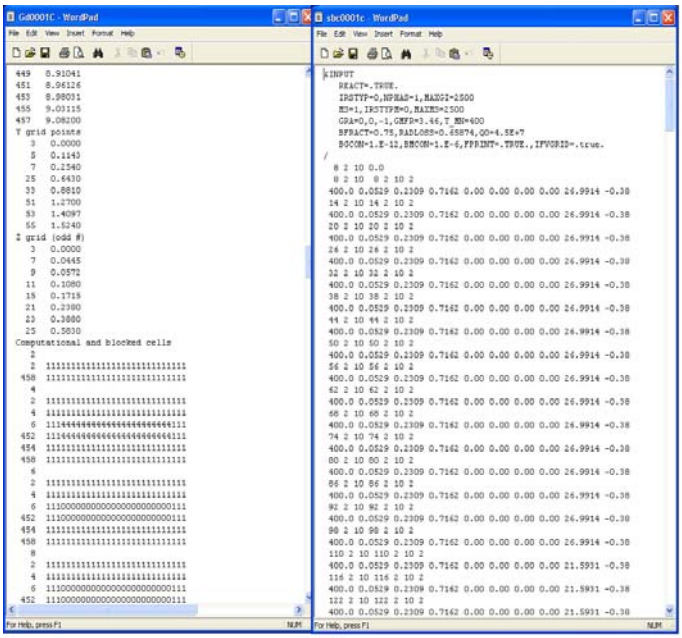

2517
1988
1459
929
400

Air-Fuel Fired Forehearth

- To extend the usefulness of the code I applied it to one of our tv-panel forehearths.
- Because of the large number of burners and the non standard configuration, it was more convenient to build the model from the the basic files.
- Included here are excerpts from the input files and some views of the model made with the graphical user interface postprocessor.

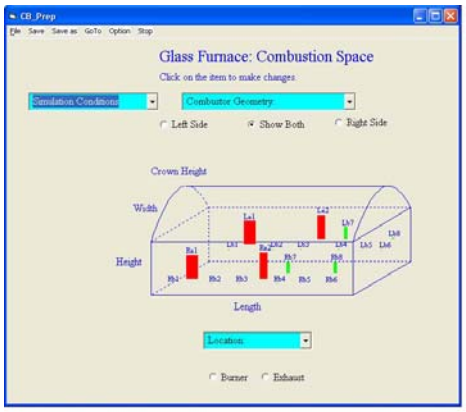


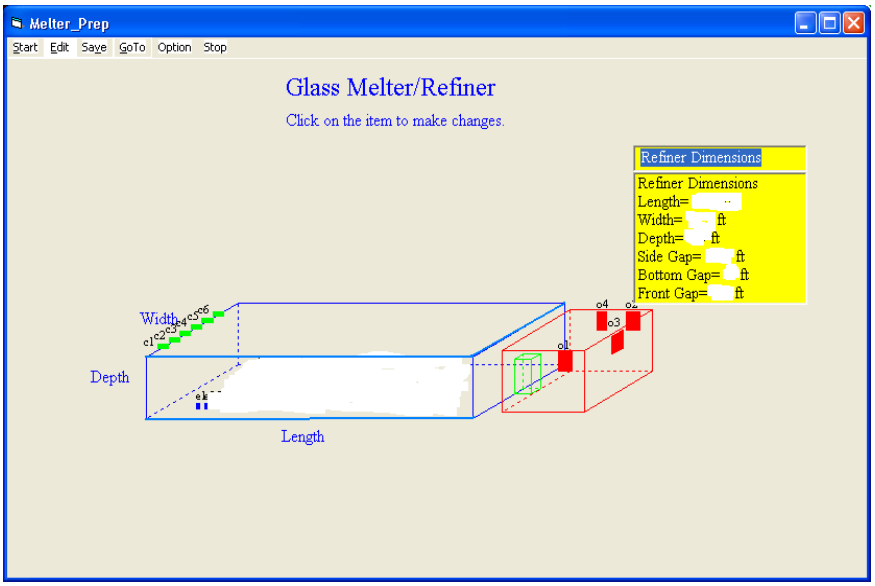

Melter Flow
Grid Flow View Option GoTo Stop
Y
Inlet
ElecB
Exit
Surface
Wall
X
Y
D:\C-2_Forehear\GMF\melt\Gd0001m.dat.dat
X-Y X-Z Y-Z
X Y Z
Node Type
Total nodes: (92, 28, 56)
48 16 28 Comp
Plot range: (2- 92 2- 28 2- 56)


Gd0001C - WordPad
stc0001c - WordPad
File Edit View Insert Format Help
For Help, press F1
NUM

Tv-Panel Glass Furnace

- Modeling a tv-panel glass tank is more interesting because of the increased complexity of the furnace design and the need to produce a higher quality product.
- The next two slides show how a model was built using the GMF graphical interface.



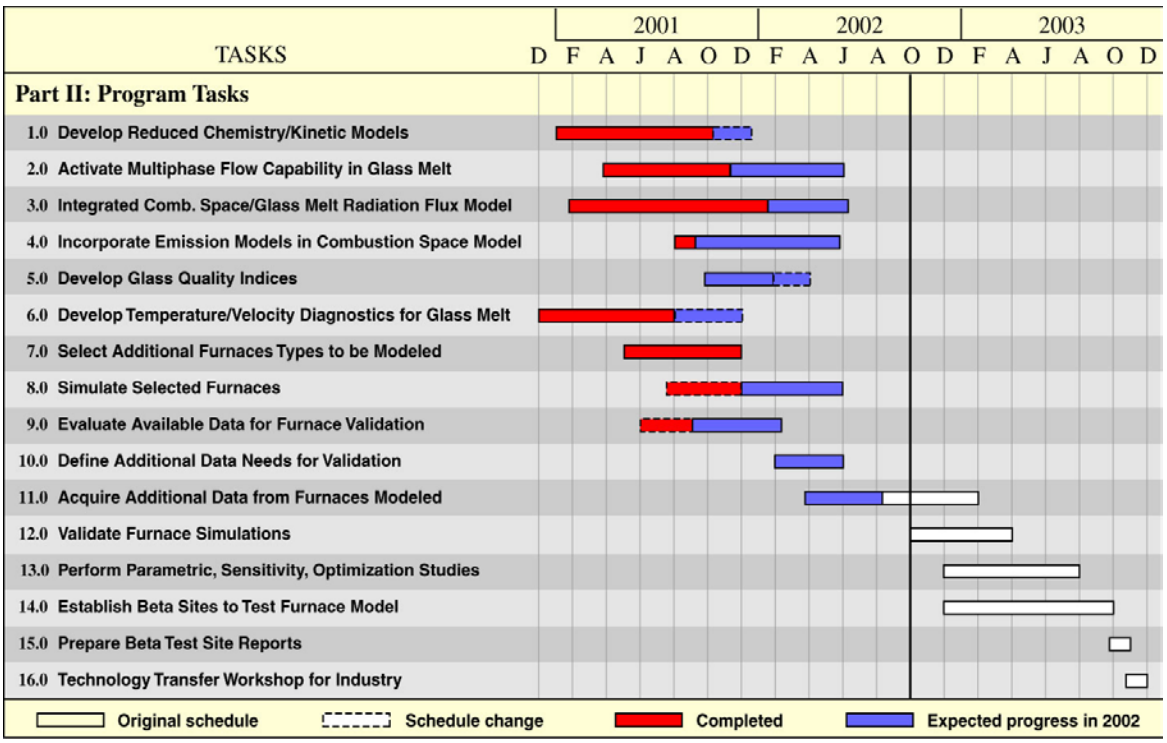


Conclusions

- While there are still problems to be resolved, the program is, in general, no more difficult to use than other commercial codes and in some cases much easier.
- As features are added, the project will advance the state of the art of glass furnace modeling while keeping the technique within the reach of the average industrial user.

EXPECTED PROGRESS IN FY2002

PROGRAM WBS, SCHEDULE, AND KEY MILESTONES



Advances/Innovations in the "State of the Art" in Furnace Modeling/Simulation in Place at the End of FY2002

- A Rigorous Treatment of Radiation Heat Transfer Throughout the Whole Furnace Volume
  - Spectral radiation from combustion species such as H_20, CO_2, and soot
  - Radiation to and from crown and glass melt
  - Radiation through foam layer
  - Global and local heat balance throughout furnace volume
- A Three-Phase (liquid,gas,solid) Reacting Flow model of the Glass Melt
  - Compute batch coverage
  - Chemical species reactions and transport
  - Evolution and transport of gas phase species
- Direct Calculation of Glass Quality Indices as a Function of Furnace Operating and Design Parameters
  - Basis for optimization of furnace performance, re throughput, energy use, and emissions
- Nucleation Models of Particulate Formation/Transport for gases Emanating from Glass Melt/Batch that Exit Furnace
- Validation of Furnace Model with a Comprehensive Database Acquired from Operating Furnaces
  - Data obtained from in situ furnace measurements

Enabling Measurement & Modeling Technologies for

Auto-Glass Process Control

MA Khaleel, BD Cannon, CL Shepard, and VN Korolev,
Pacific Northwest National Laboratory

Industrial Partners:
RE Rueter, PH Burnside
PPG Industries
MT Brennan, LR. Lyke and EN Boulos,
Visteon Automotive Systems

DOE-OIT Glass Project Review Meeting
Richland, WA
November 7-8, 2001

Project Goals

- Improved fabrication process and quality control for formed and heat treated automotive glass components through the development of:
  - optical sensors for measuring 3D stress and temperature in auto-glass.
  - methods for modeling material radiation in glass.

The Technical Approach Towards Achieving Project Goals are Contained within 2 Major Tasks

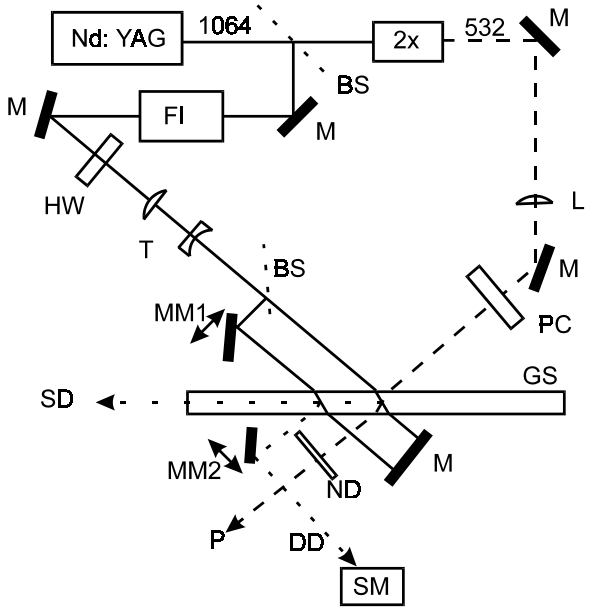
- Completion and commercialization of optical sensors for measurement of stress and temperature in formed auto glass (task 1).
- Development of modeling tools for radiation in optically thin materials, thereby allowing accurate simulation and optimization of fabrication processes (task 2).

Progress Summary

- Stress and temperature sensor concepts have been demonstrated. Patent applications have been filed.
  - Discussions with StrainOptics regarding commercialization of stress measurement
  - Visteon Automotive System and PNNL submitted a proposal to OIT Best Practices Program for plant deployment of stress measurement system
- Radiation model development has been completed (i.e. RAD3D thermal code) and experimental validation is continuing at PPG.
- Coupling radiation with MARC FEA code is completed and being implemented in actual forming processes.
- Teaming agreement with MSC Software (largest FEA vendor in the world) was signed November 2000.

Task 1 – Stress Measurement

Laboratory Arrangement for Stress Measurement in Glass



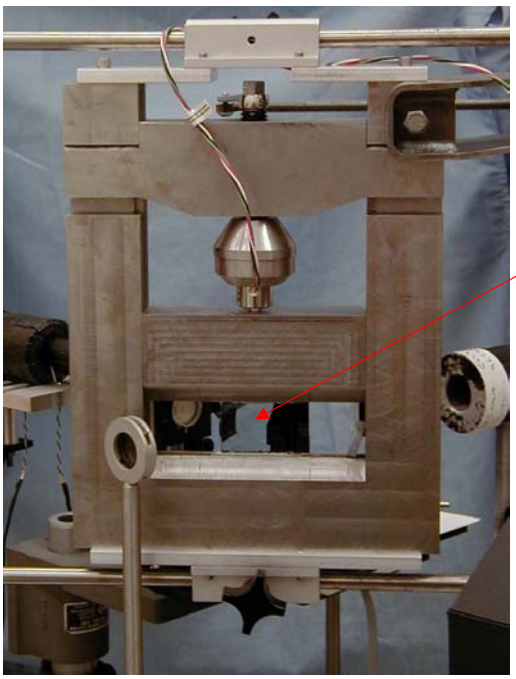
Task 1 - Non-Contact Measurement of In-Plane Stress in Tempered Glass - Past Accomplishments

- Observed and identified optical signal due to stress induced birefringence in auto glass.
- Began development of an optical stress measurement method.
- Obtained stress measurement at the mid-plane of an auto glass sample using a transient thermal grating for optical coupling.
- Obtained in-plane stress measurement with an auto-glass sample using a differential double thermal grating method.

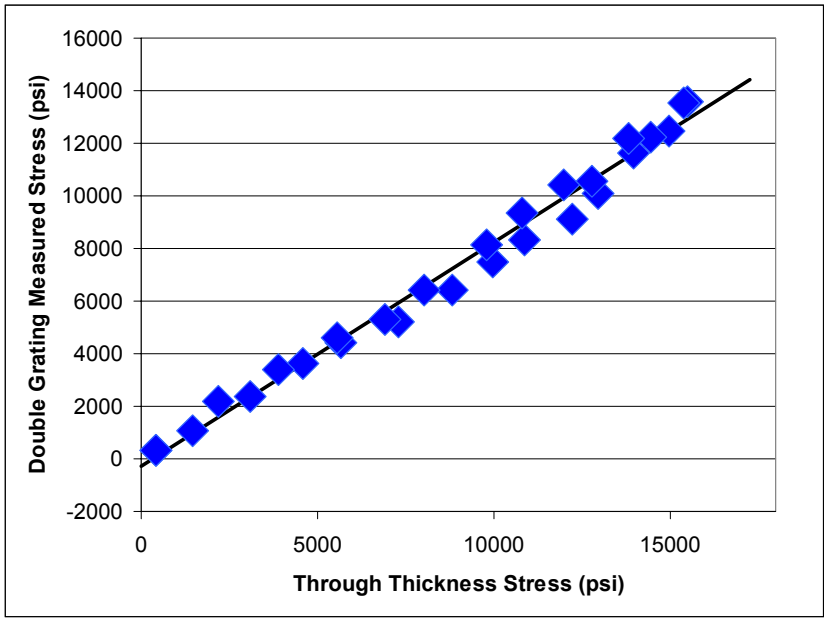
Task 1 - Non-Contact Measurement of In-Plane Stress in Tempered Glass – Past Accomplishments

- Automation was accomplished by the development of a system including:
  - Servo motors for beam scanning and signal beam control.
  - Stokes meter coupled with light detector for analysis of signal beam polarization.
  - Custom software for computer control of measurements and immediate analysis of data.
- Complete measurements at a location can be accomplished in less than 10 seconds.

Mechanical Stress was Applied in Instrument Calibration



Instrument Calibration Performed with Glass Sample under Known Stress



Task 1 - Non-Contact Sensor Development – FY 2001 Progress

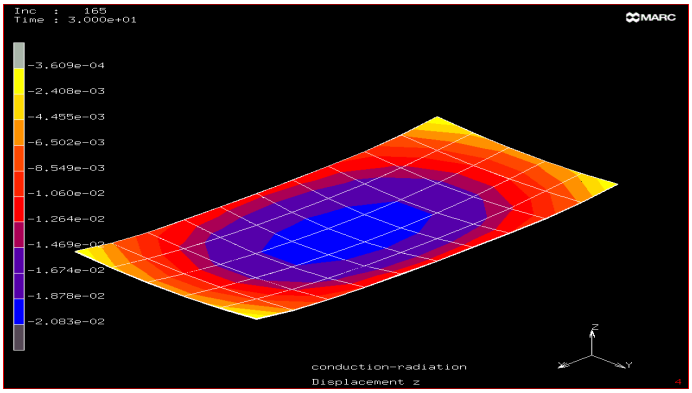
- Calibrated instrument using glass sample placed under known mechanical loading.
- Two Patent applications filed.
- Four Journal articles published:
  - BD Cannon, CL Shepard, and MA Khaleel, *Applied Optics*, **40**, 5354 (2001).
  - CL Shepard, BD Cannon, and MA Khaleel, *Int. J. of Heat and Mass Transfer*, **44**, 4027 (2001).
  - MA Khaleel, JL Woods, and CL Shepard, *Glass Technology*, **42**, 49 (2001).
  - MA Khaleel, CL Shepard, and BD Cannon, *Ceramic Industry*, **151**, 52 (2001).

Task 2 - Modeling of Heat Transfer in Optically Thin Materials - Past Accomplishments

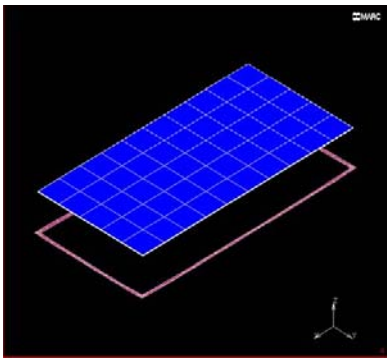
- RAD3D, a 3D heat transfer FE code with radiation, developed to obtain accurate temperature distributions within auto glass.
- RAD3D benchmarked against 1D CFD code.
- RAD3D linked with MARC code for thermal stress analysis.

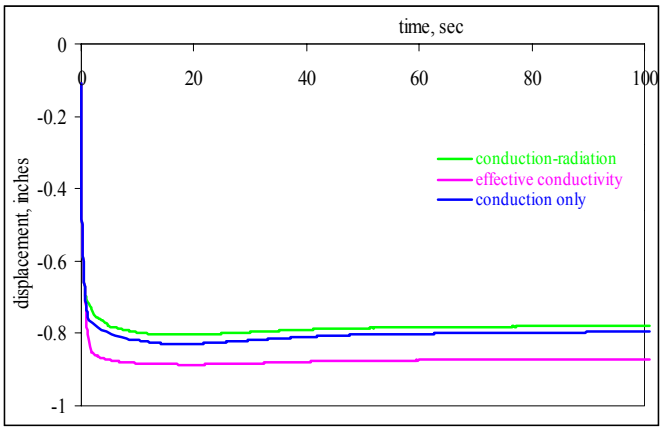
Battelle

U.S. Department of Energy
Pacific Northwest National Laboratory



DEFORMATIONS

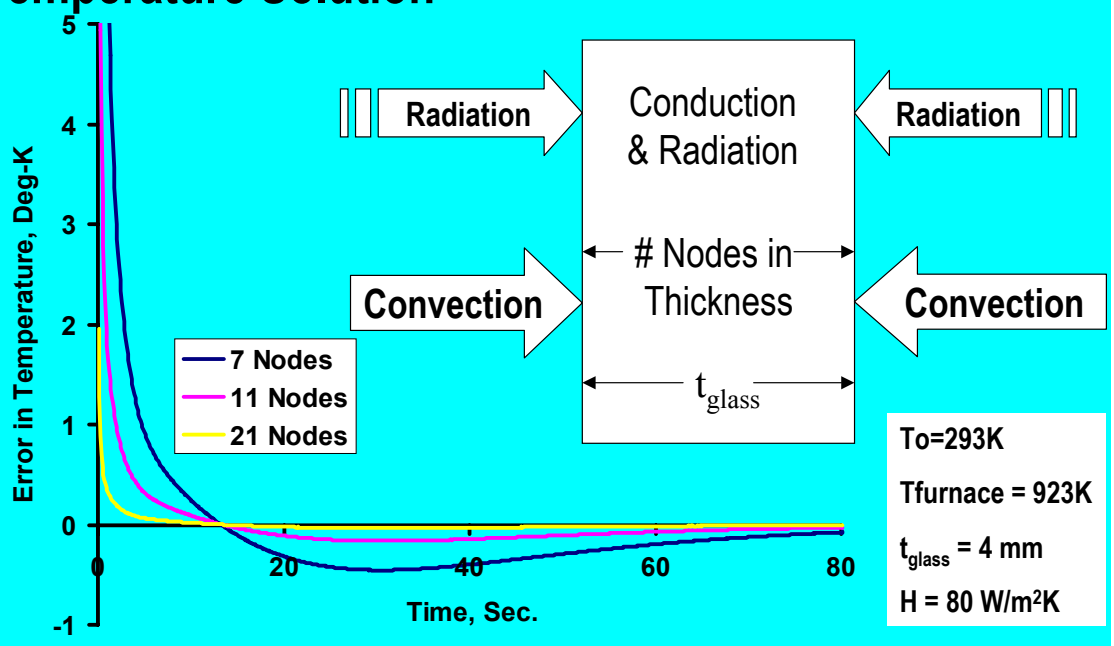


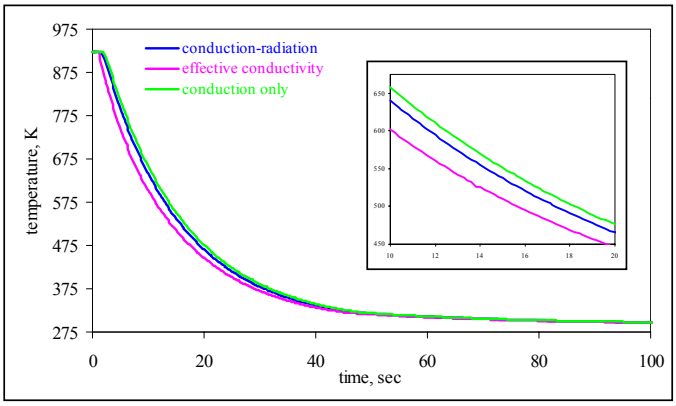


Efficient Radiation Formulations

- Efficiency needed for increased mesh refinement (accuracy) and to make real glass engineering problems solvable.
- Implemented DOM and hybrid methods that only modify the flux vector.
- Efficient mesh sweeping algorithm removes need for mesh preprocessing for the DOM implementation.

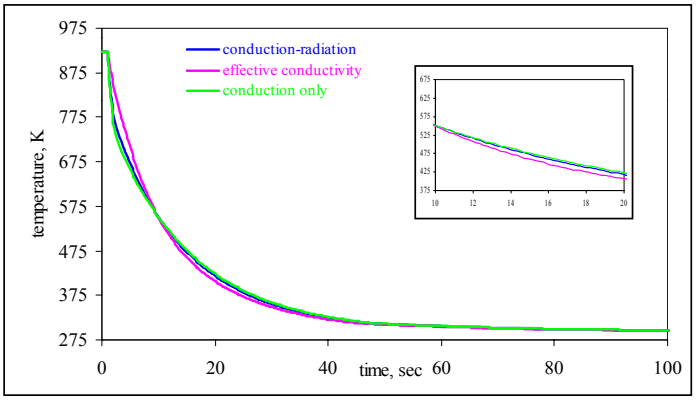
Mesh Refinement Needed for Accurate Surface Temperature Solution

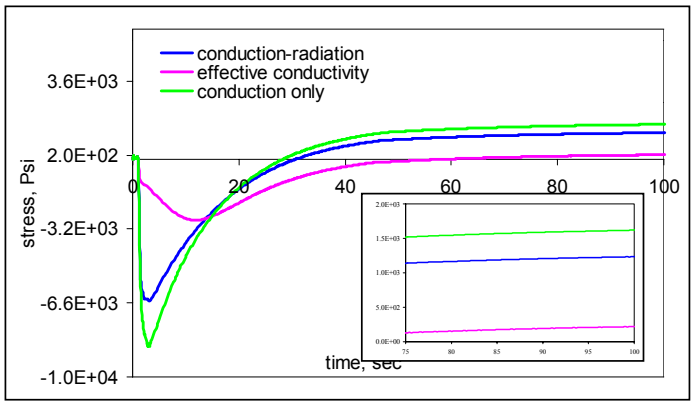




Temperature history for an internal point.

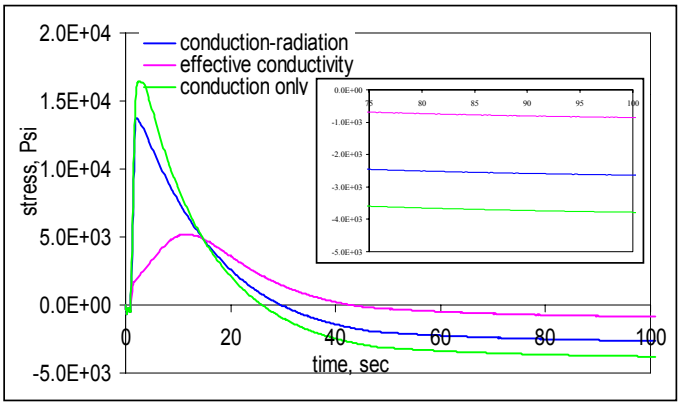
Temperature history for a point on the surface.





Residual stress history for an internal point.

Residual stress history for a point on the surface.



PPG Fluent Modeling Experience of Radiation in a Semi-Transparent Media

Advantages

- Fluent has a 3-band spectral absorption model.
- Test case showed temperature simulations are within 3°F of measured values.

Disadvantages

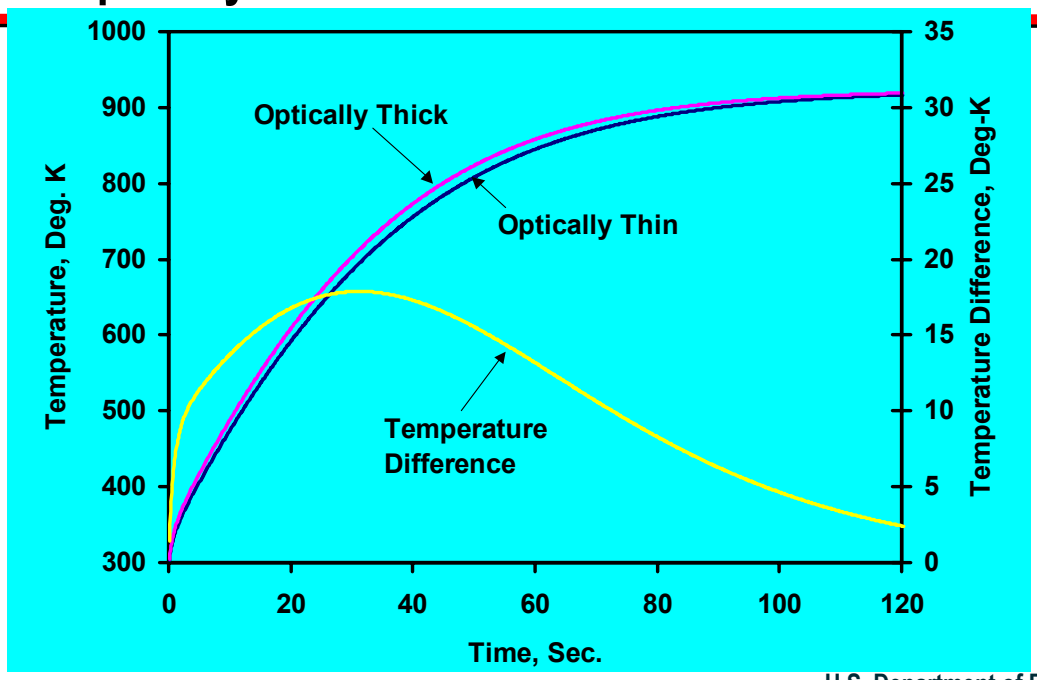
- The transient test case of a continuous ribbon took **2 weeks** to run.
- Full windshield model estimated to take **3 - 6 months** of CPU time using this method and suffers from numerical instabilities.

Conclusion: Fluent model is accurate, but run times are unacceptable.

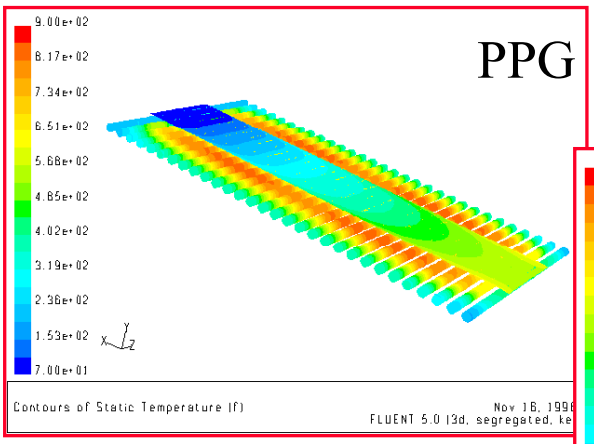
FY 2001 Progress

- RAD3D enhanced for any number of spectral absorption bands.
- Enhanced Accuracy and Numerical Efficiency - Radiation formulations modified for improved accuracy and reduced solution time and memory.
  - Discrete Ordinate Method (DOM) added to the code.
  - Parallel processing capabilities being developed.
- Working with PPG to experimentally benchmark the RAD3D code.

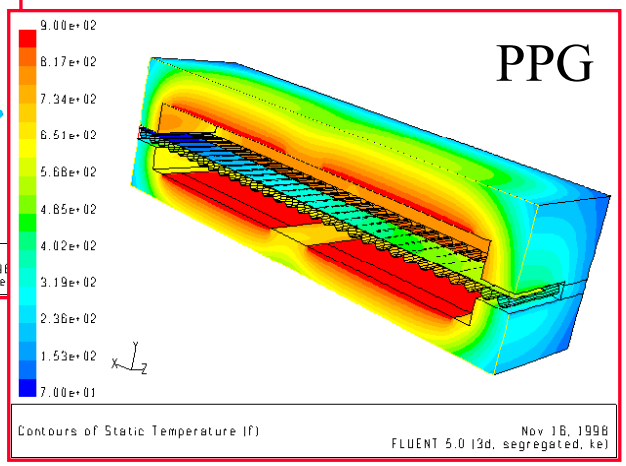
Surface Temperature Solution for Optically Thick and Optically Thin Cases



RAD3D Benchmarking: PPG Model of Radiant Heating in Glass

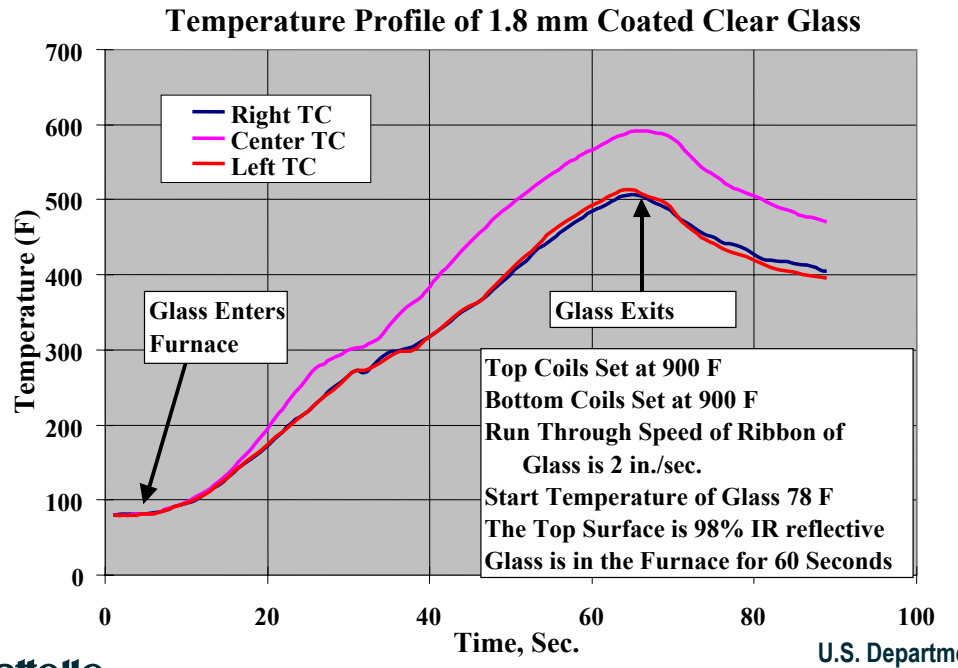


Fluent Model of PPG Single zone furnace.



Glass Temperature Increase in a Uniform Radiant Field.

RAD3D Benchmarking: Measured Glass Temperatures in Furnace



FY02 RAD3D Modeling Goals

- Complete RAD3D benchmarking against PPG data.
- Complete parallel implementation of DOM method.
- Demonstrate code for application to PPG and Visteon problems.
- Build graphical user interface for efficient stand-alone use on personal computer platforms.
- Seek opportunities to commercialize RAD3D.

Budget

- FY01 - $100K
- FY02 – Project continues, budget – unknown.

Project Expected Outcomes

- Stress instrument capable of non-contact measurement of 3D stress in glass sheets.
- Temperature instrument capable of 3D on-line measurement of temperature up to 600°C in sheet glass with excellent resolution.
- Computer software capable of modeling material radiation in glass which can be linked to any available non-linear finite element commercial code as a user subroutine (user defined function).

Broad Industry Application

- Stress measurement
  - Automotive glass (3D)
  - Flat glass (3D)
  - TV glass (Through-thickness)
  - Glass fiber (Average)
  - Bottle glass (Average)
- Temperature measurement
  - Automotive glass (3D)
  - Flat glass (3D)
  - TV glass (3D)
- Modeling tools
  - Automotive glass (fabrication – gravity sag and tempered)
  - Bottle glass (fabrication)
  - TV glass (by coupling with computational forging tools - AutoForge).
  - May be applicable to glass melting (by coupling with other CFD code).

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

Peter M. Walsh, Howard A. Johnsen, and Shane M. Sickafoose
Sandia National Laboratories
Livermore, California

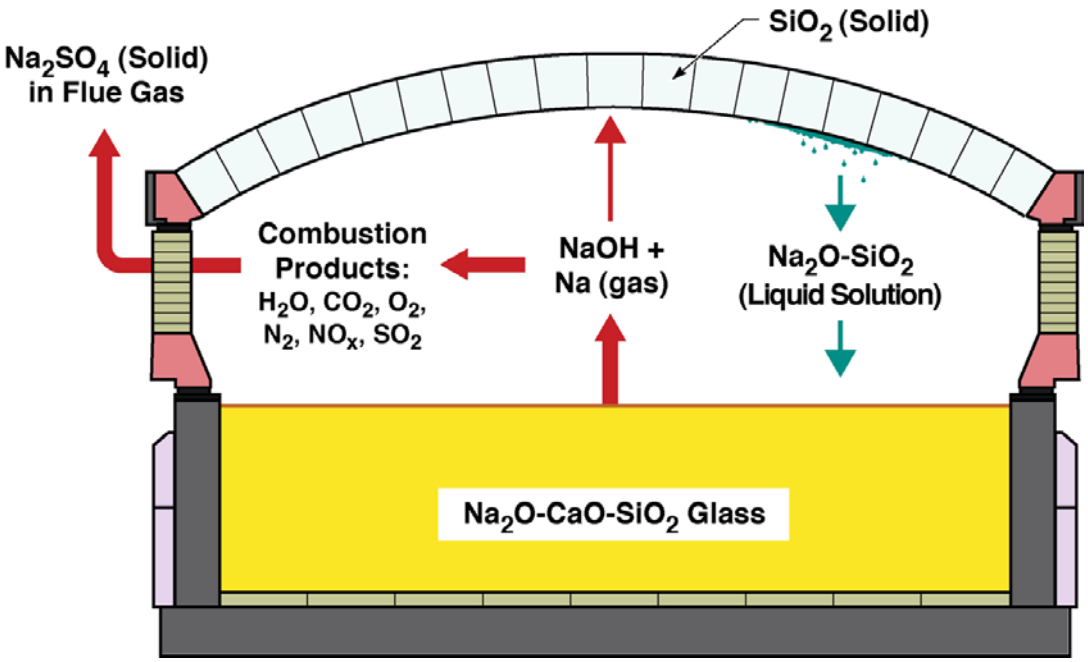
John Neufeld
Gallo Glass Company
Modesto, California

DOE/OIT Glass Industry Project Review
Pacific Northwest National Laboratory, Richland, WA
November 7-8, 2001

Technical Needs Being Addressed

- Control particulate matter emissions, from both volatilization and batch carryover.
- Minimize rates of superstructure and crown corrosion.

Fate of Volatilized Sodium



111401.01.ppt

Laser-Induced Breakdown Spectrometry (LIBS)

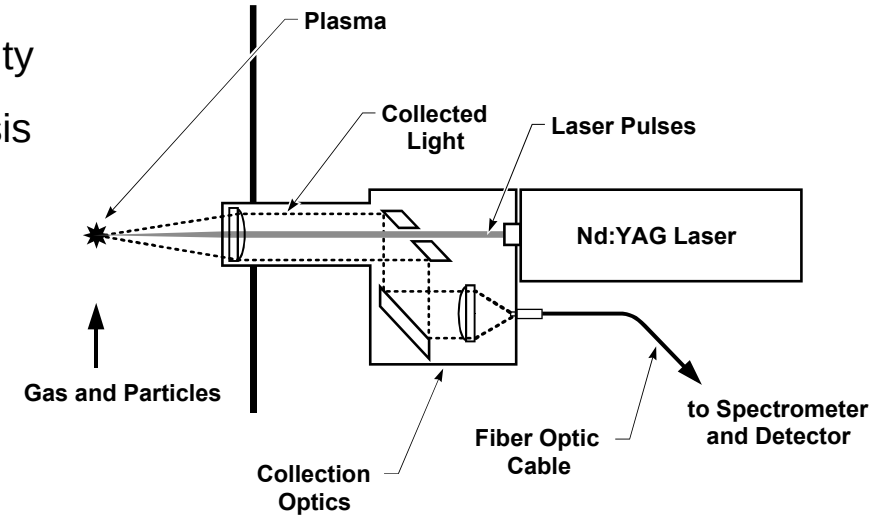
High sensitivity

In-situ analysis

Elemental signature

Good time resolution

Portable

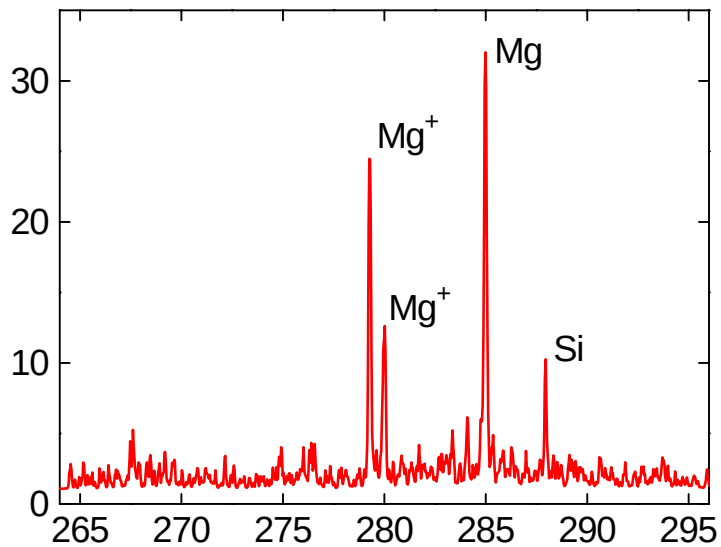


Plasma Emission Spectrum

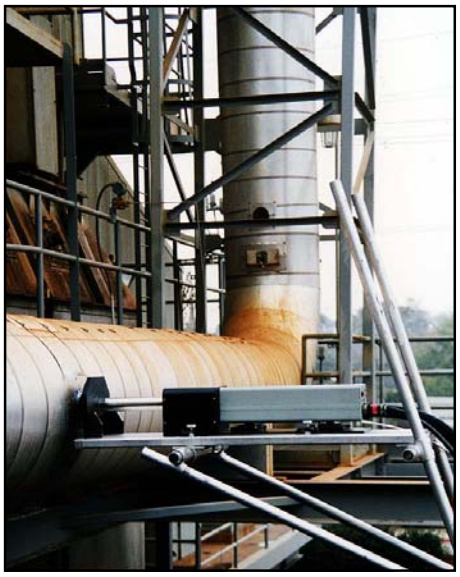
Wavelengths identify the elements present

Intensities give masses and concentrations

Typical detection limit ~ 10 x 10^{-15} g

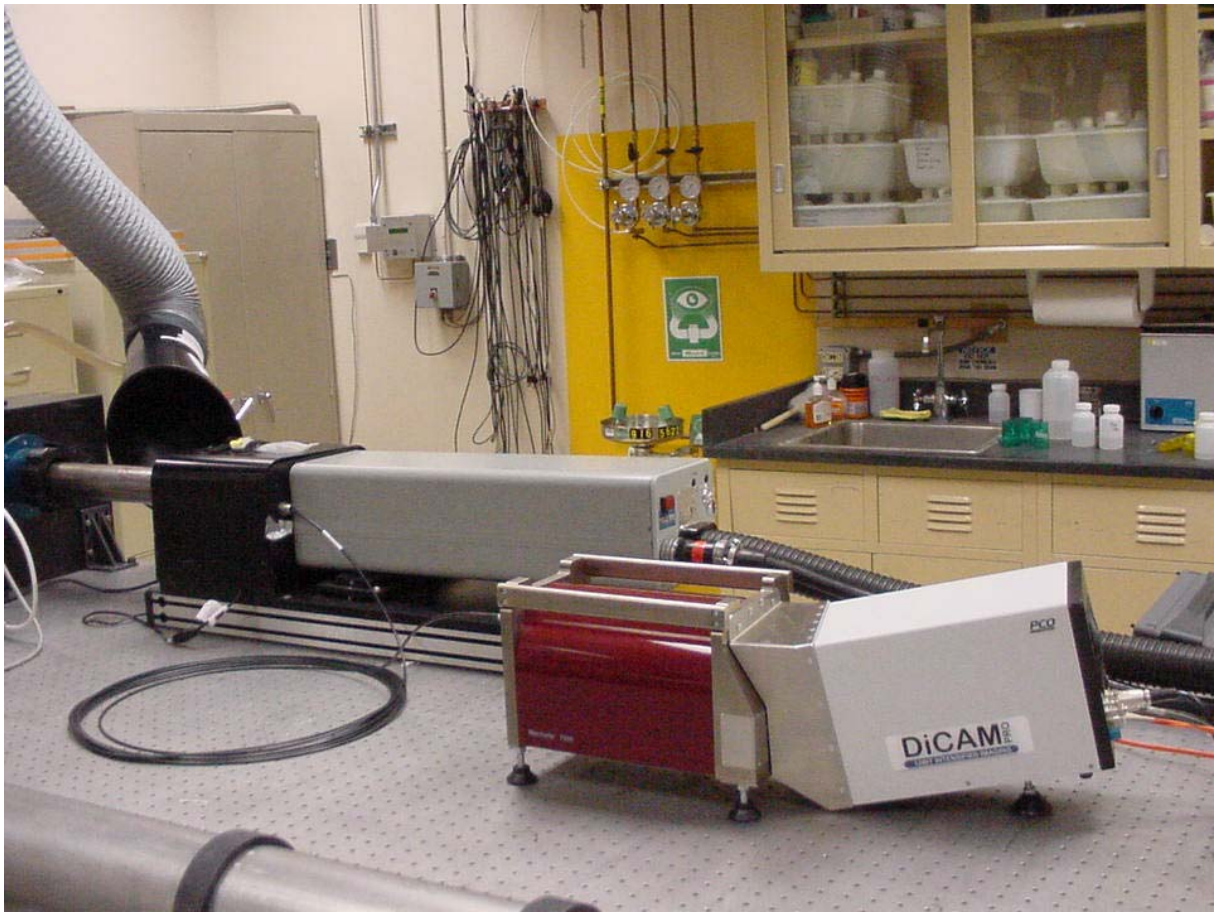


Sodium in Flue at Gallo Glass

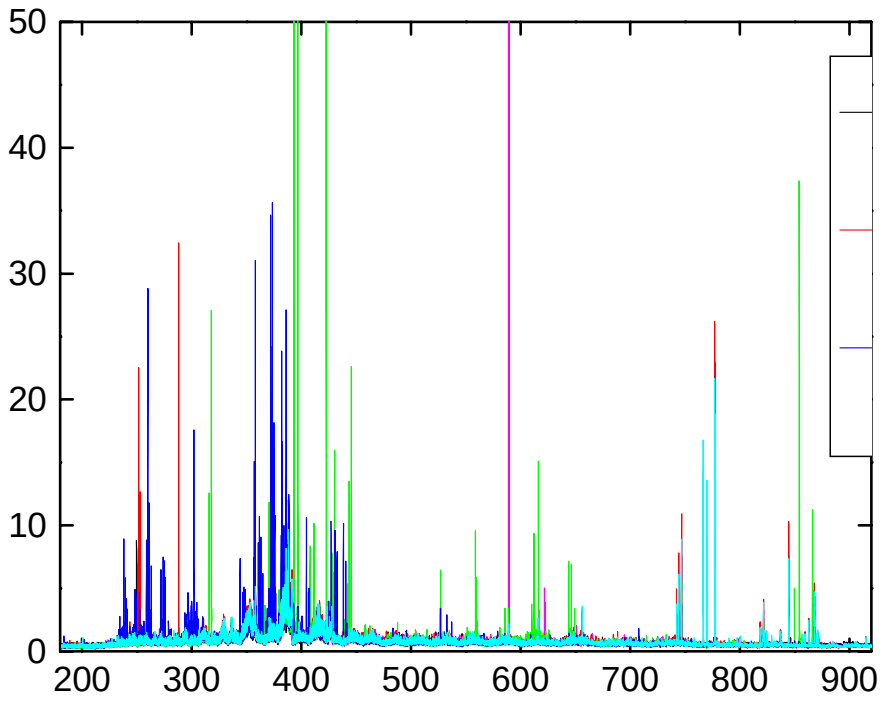


Technical Progress

- Complete elemental signature
- Determination of particle size
- Foundation for model-based corrosion control



LIBS with Echelle Spectrometer



Benefits and Market Applications

Near Term: Changes in furnace operation

Mid-term: Improvements in furnace design

Long Term: Commercial instrument for active control

Schedule

October 2001:	Assembly of LIBS instrument and software with echelle spectrometer. (Tasks 13 and 14 - complete)
December 2001:	To Gallo Glass for simultaneous measurements of Na, K, Ca, Si, Fe and process variables. (Tasks 1, 7, 15, and 16)
February 2002:	Implement measurements of furnace exit gas temperature, exit gas composition, and flame radiation. (Tasks 2, 3, 4, and 5)
June 2002:	Long measurement campaign. (Task 6)
August 2002:	Identify conditions controlling volatilization and batch carryover and their associations with NOx and efficiency. (Tasks 8 and 9)

Objectives

- Increase furnace life and reduce particulate matter emissions from glass production by providing monitoring techniques and control schemes for minimization of volatilization from molten glass.
- Identify conditions associated with batch dusting that may be avoided by furnace design, furnace operation, or batch formulation.
- No detrimental effects on glass quality, furnace efficiency, or emissions of NO_X and CO.

Molybdenum Disilicide Composites for Glass Processing Sensors

J.J. Petrovic, R.G. Castro, M.I. Peters, R.C. Hoover

Materials Science & Technology Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DOE/OIT/Glass Industry Project Review
8 November 2001

Los Alamos NATIONAL LABORATORY

Budget History

- FY-1999
  - OIT: $400K
  - Industry: $400K (in-kind)
- FY-2000
  - OIT: $400K
  - Industry: $400K (in-kind)
- FY-2001
  - OIT: $250K
  - Industry: $250K (in-kind)
- Project ended 30 September 2001

Los Alamos NATIONAL LABORATORY

Project Objectives/Goals

- Development of oxidation and corrosion resistant $MoSi_2$-based sensor protection sheaths for the glass industry
  - Protection of sensors in molten glass
  - Fabrication of tubular sheaths by plasma spraying
- Industrial interactions and technology transfer
  - Accutru International Corporation
    - Temperature sensor systems
  - Combustion Tec Inc.
    - Video monitoring sensor systems
  - Exotherm Corporation
    - Silicide plasma spray powders and combustion synthesized composite tubes
  - Plasma Processes, Inc.
    - $MoSi_2$-coated Al_2O_3 tubes

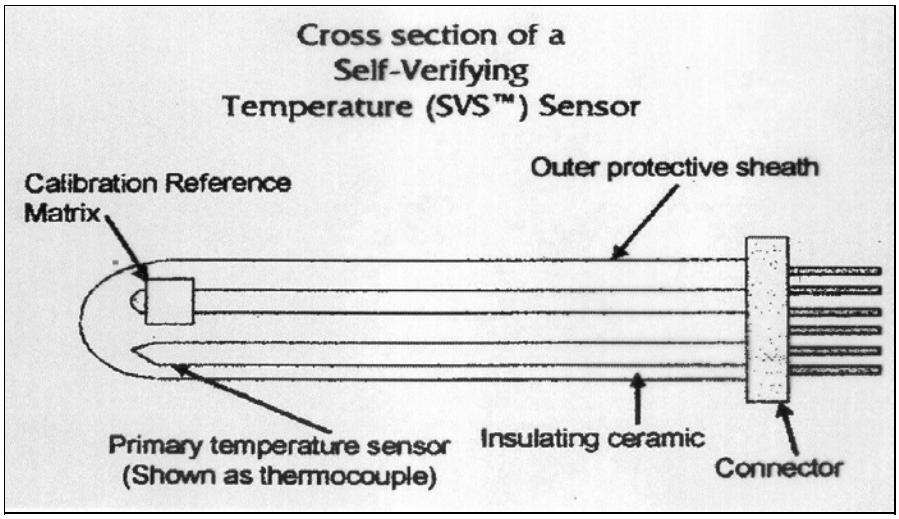
Los Alamos NATIONAL LABORATORY

U.S. Process Control Industry Needs

- Eliminate or quantify drift (in situ)
  - Accuracy
  - Repeatability
- Longer life
  - Sensor internals
  - Outer protective sheath
- Compatible with existing process control equipment
- Ease of installation and maintenance
- Protection from plant noise interference

Los Alamos NATIONAL LABORATORY

Schematic of Accutru Self-Verifying Temperature Sensor



Materials Currently Used for Sensor Protection With Molten Glass

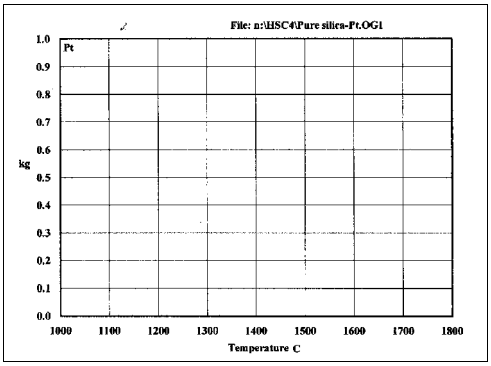
- Monolithic platinum and platinum-coated Al_2O_3 tubes for sensor sheaths inserted through the glass line
  - Thermocouple sheaths
  - Problem: Platinum is expensive
- Molybdenum
  - For hardware below the glass line
  - Problem: Molybdenum has poor oxidation resistance above the glass line
- Alumina-Zirconia-Silica (AZS)
  - Refractory ceramic applications
  - Problem: AZS has low strength

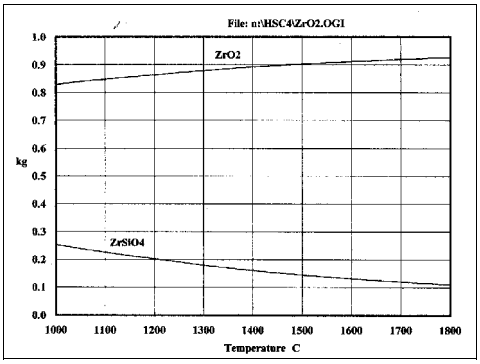
Thermodynamic Stability Calculations of Materials Stability in Different Molten Glass Compositions

- Outokumpu HSC Chemistry software employed
  - Large thermochemical database: 15,000 chemical compounds
- Introduce 1 kg of the material into 1000 kg of the glass composition
  - Calculate equilibrium amounts of species present at various temperatures
    - Minimization of Gibbs free energy of the system with respect to all possible compounds that may form
      - W.B. White, S.M. Johnson, and G.B. Dantzig, "Chemical Equilibrium in Complex Mixtures", Journal of Chemical Physics, 28, 751-755 (1958).

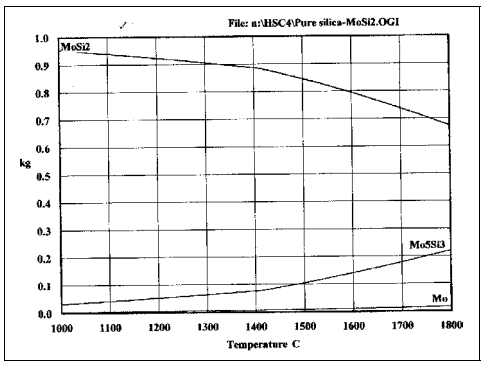
Los Alamos NATIONAL LABORATORY

Most Thermodynamically Stable Oxidation-Resistant Materials in Silica





Platinum



ZrO_2

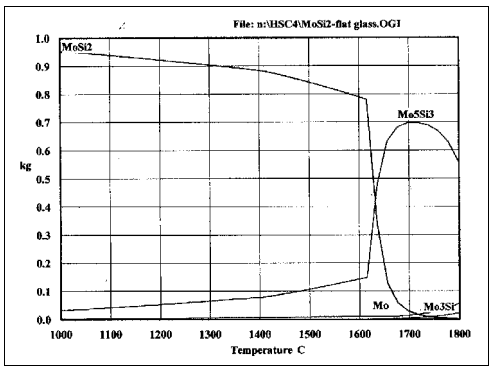
$MoSi_2$

Los Alamos NATIONAL LABORATORY

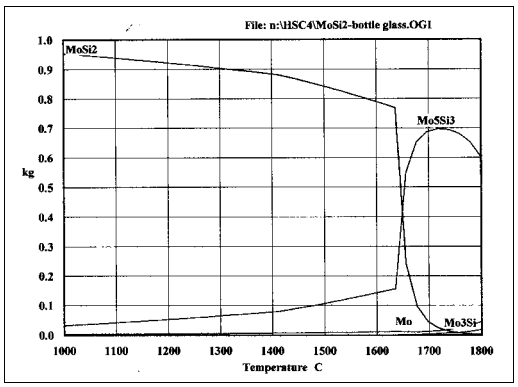
Commercial Glass Generic Compositions

- **Flat glass**
  - 71% SiO_2, 16% Na_2O, 9% CaO, 1% Al_2O_3, 3% MgO
- **Bottle glass**
  - 74% SiO_2, 14% Na_2O, 11% CaO, 1% Al_2O_3
- **Lighting glass**
  - 73% SiO_2, 15.9% Na_2O, 6.5% CaO, 1.3% Al_2O_3, 3% MgO, 0.3% K_2O
- **Fluorescent lighting glass**
  - 72.7% SiO_2, 14.6% Na_2O, 5.7% CaO, 2.6% Al_2O_3, 2.9% MgO, 1.2% K_2O, 0.3% B_2O_3
- **Domestic glass**
  - 71% SiO_2, 16% Na_2O, 5% CaO, 3% Al_2O_3, 3% MgO, 1% K_2O, 1% B_2O_3
- **Fiber glass**
  - 54.7% SiO_2, 0.5% Na_2O, 22% CaO, 14.5% Al_2O_3, 8.3% B_2O_3
- **Heat resistant glass**
  - 78.5% SiO_2, 4.5% Na_2O, 5% Al_2O_3, 12% B_2O_3

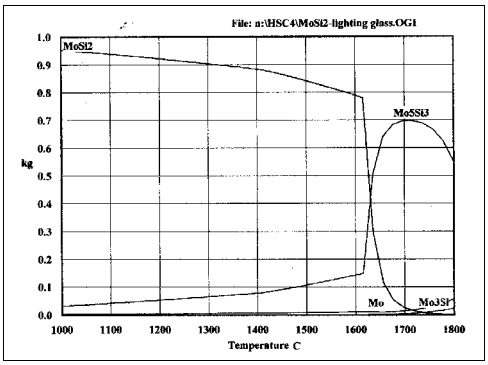
$MoSi_2$ Thermodynamic Stability in Soda-Lime Glasses



Flat glass

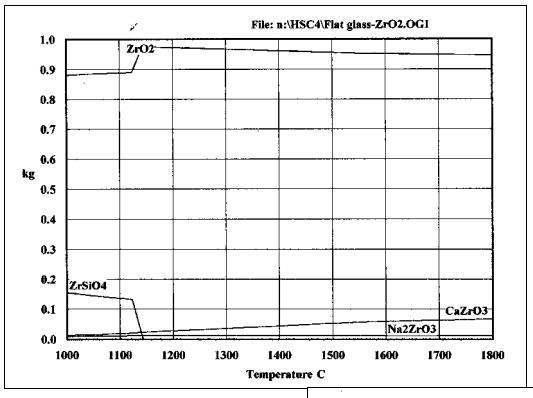


Bottle glass

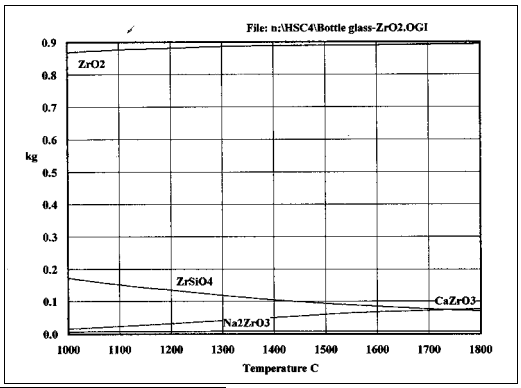


Lighting glass

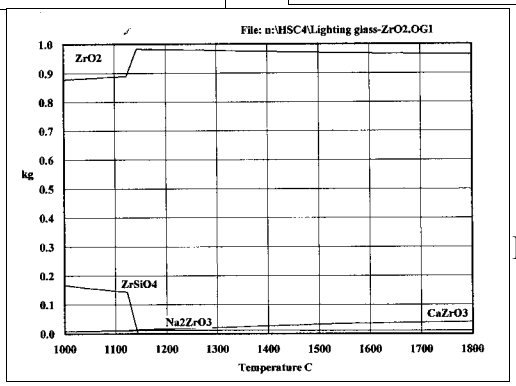
ZrO_2 Thermodynamic Stability in Soda-Lime Glasses



Flat glass

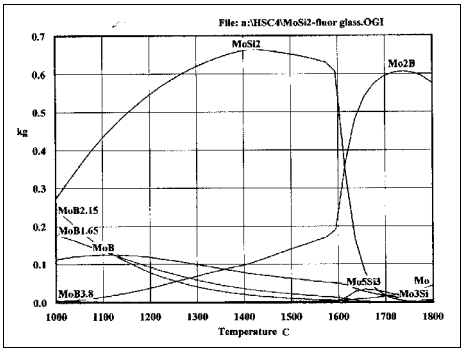


Bottle glass

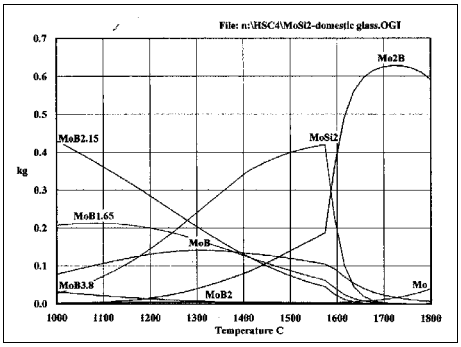


Lighting glass

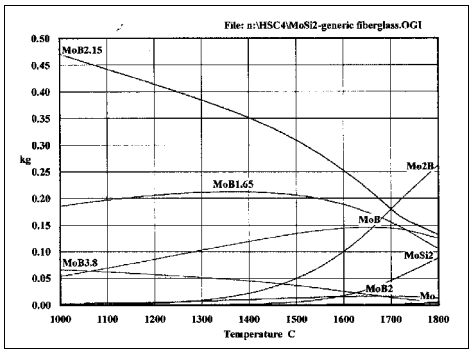
$MoSi_2$ Thermodynamic Stability in Borosilicate Glasses



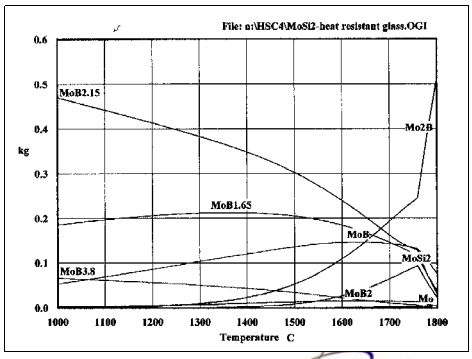
Fluorescent lighting glass: 0.3% B_2O_3



Domestic glass: 1% B_2O_3

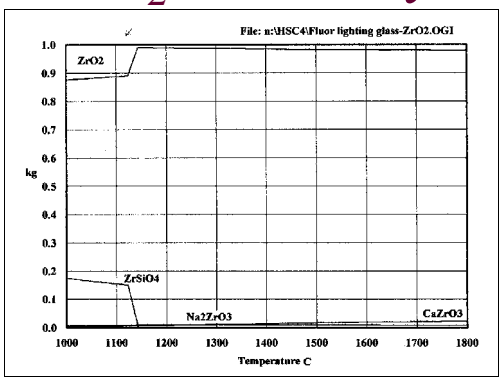


Fiber glass: 8.3% B_2O_3

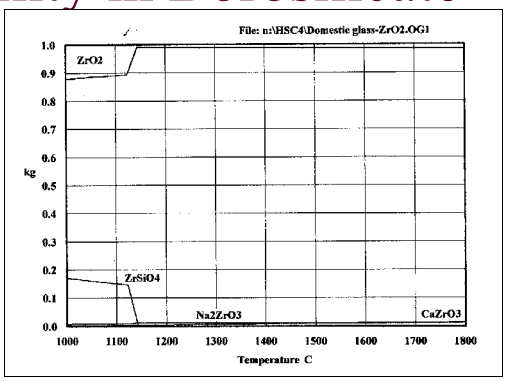


Heat resistant glass: 12% B_2O_3

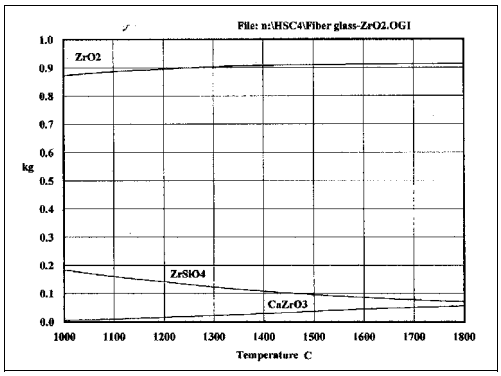
ZrO_2 Thermodynamic Stability in Borosilicate Glasses



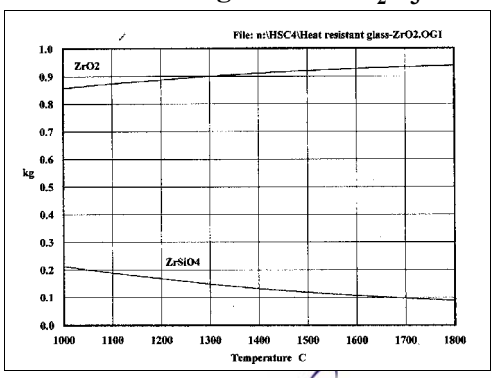
Fluorescent lighting glass: 0.3% B_2O_3



Domestic glass: 1% B_2O_3



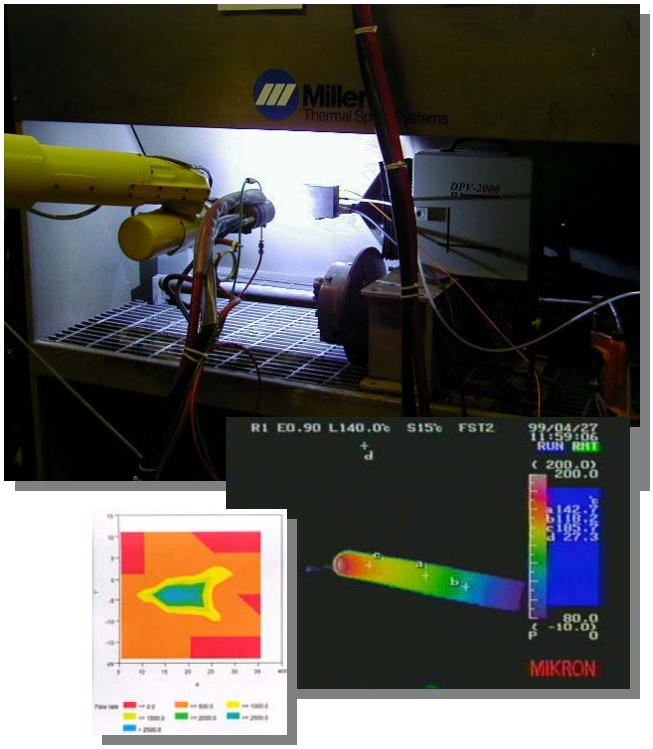
Fiber glass: 8.3% B_2O_3



Heat resistant glass: 12% B_2O_3

Los Alamos NATIONAL LABORATORY

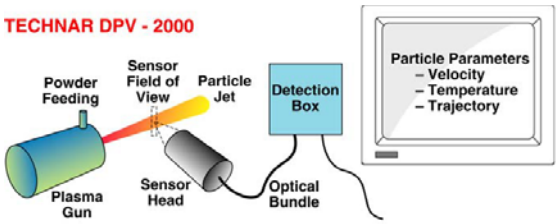
Atmospheric Plasma Spraying System



- Praxair Surface Technologies SG 100 Gun, Plasma Gas: Argon (40 slm), Powder Gas: Argon (Variable, 1-4 slm).
- Praxair Surface Technologies Model 1264 Powder Hoppers, Programmable, Speed Variable (0-1 rpm).
- Fanuc Robotics S Model 10.
- Tecnar DPV 2000 In-Flight Particle Analyzer for quality control signatures and indications.
- Mikron TH 5104 Infrared Camera.

Los Alamos NATIONAL LABORATORY

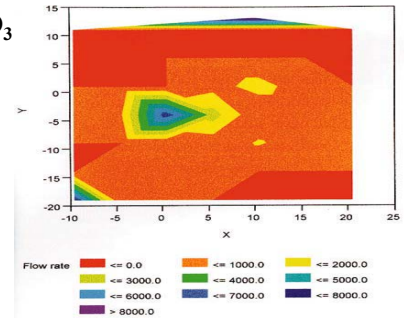
In-flight Particle Diagnostics: Quality Control for Plasma Spray Process - Particle Contour Maps



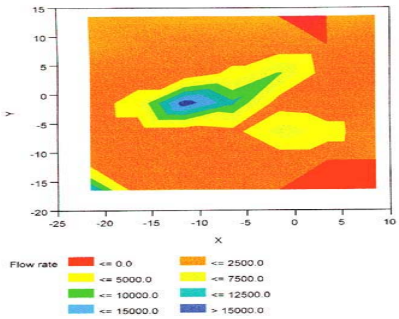
Individual Particle Measurements	
Temperature (°C) (emissivity and size dependent)	1100-4000
Velocity (M/s)	10-1200
Diameter (μm)	10-250
Maximum Analysis Rate (particles/s)	400

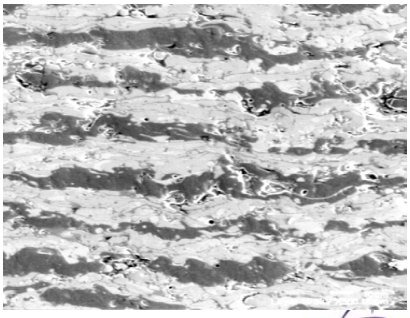
Particle Jet Measurements	
Field of View (mm)	28
Resolution (mm)	0.8
Maximum Analysis Rate	Real-Time

Al_2O_3



$MoSi_2$



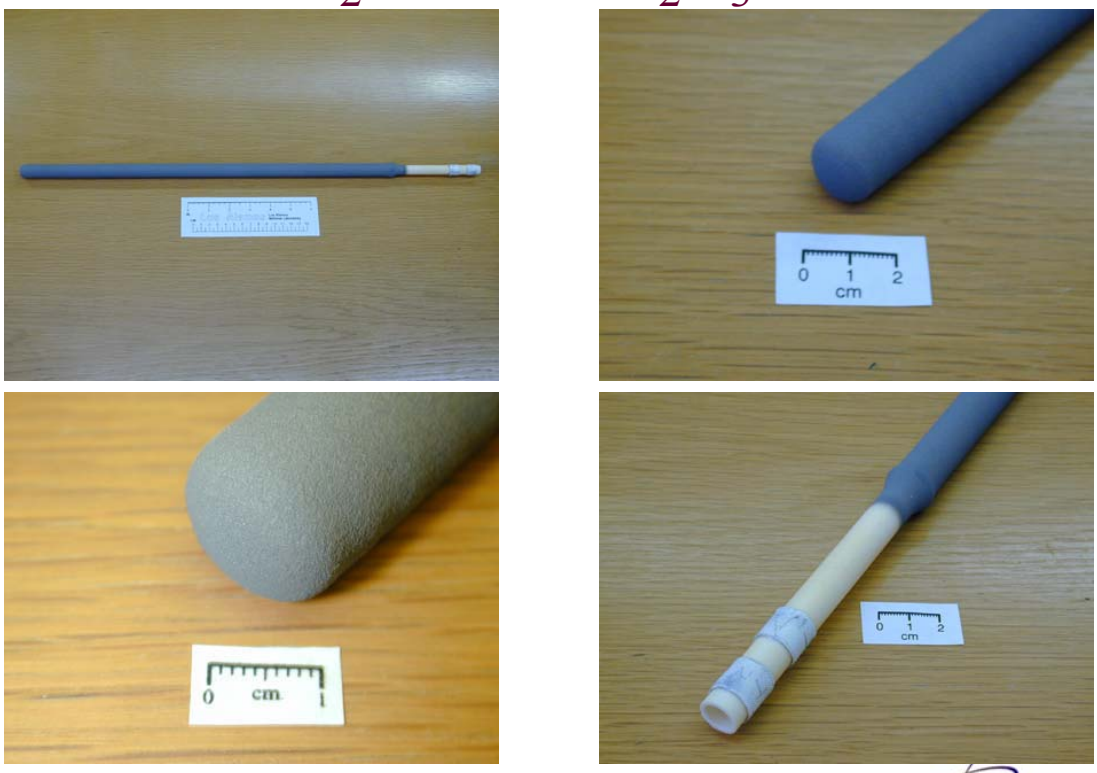


Los Alamos NATIONAL LABORATORY

$MoSi_2$-Coated Al_2O_3 Tubes Provided to Accutru International for Distribution and Testing at Various Glass Companies

Los Alamos NATIONAL LABORATORY

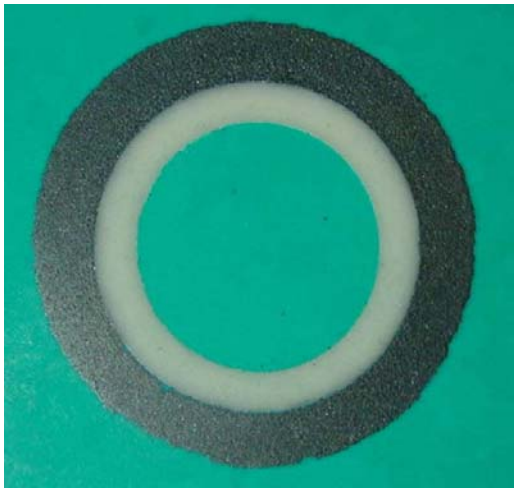
$MoSi_2$-Coated Al_2O_3 Tube



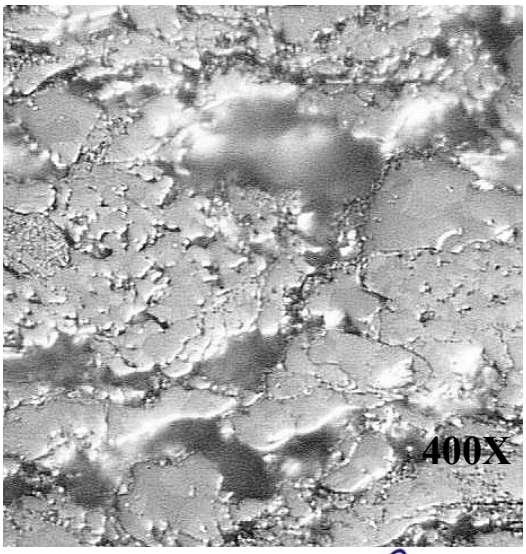
Los Alamos
NATIONAL LABORATORY

Microstructure of $MoSi_2$-Coated Al_2O_3 Tube

Cross section of $MoSi_2/Al_2O_3$ tube (mounted in resin)

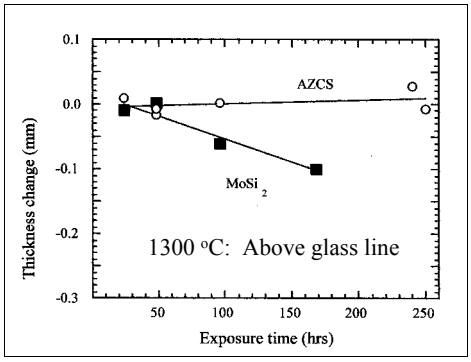


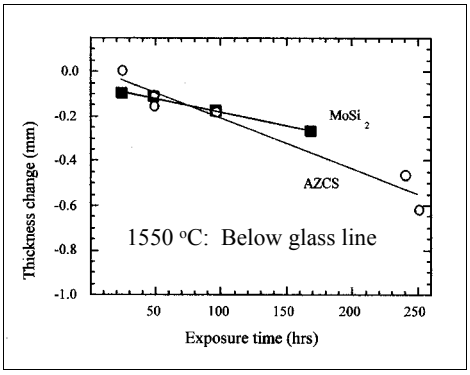
Microstructure of $MoSi_2$ coating

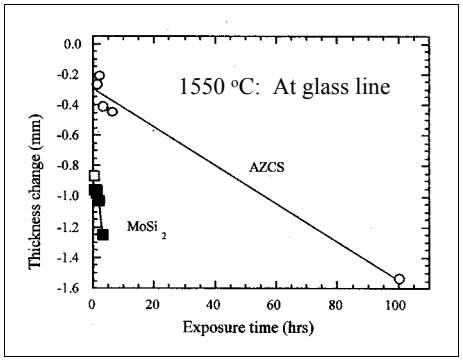


Los Alamos
NATIONAL LABORATORY

Corrosion Resistance of $MoSi_2$ in Johns Manville Fiberglass



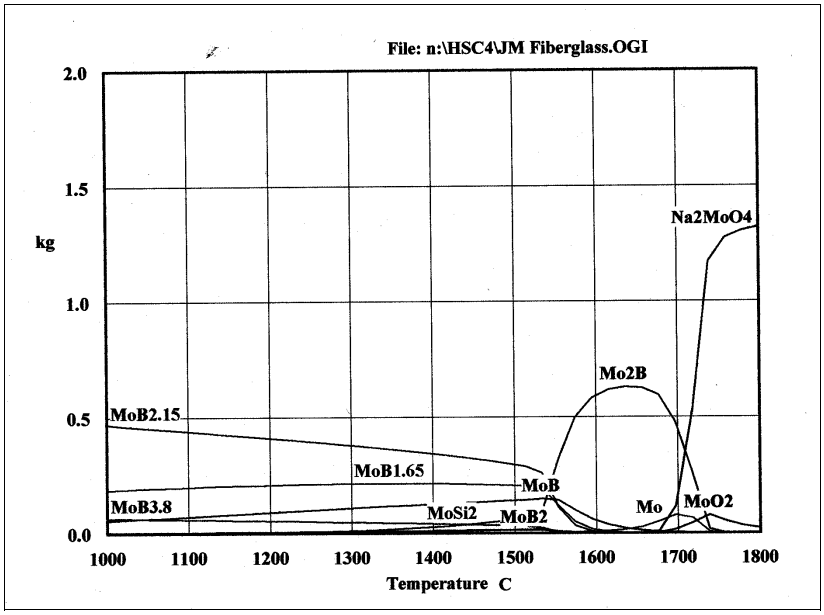




- The corrosion of $MoSi_2$ materials above and in molten glass is similar to the ceramic refractory material AZS, which is currently widely used in the glass industry
  - AZS is more corrosion-resistant than $MoSi_2$ at the glass line
- $MoSi_2$ has the following advantages over AZS
  - Electrically conductive
  - Stronger

Los Alamos NATIONAL LABORATORY

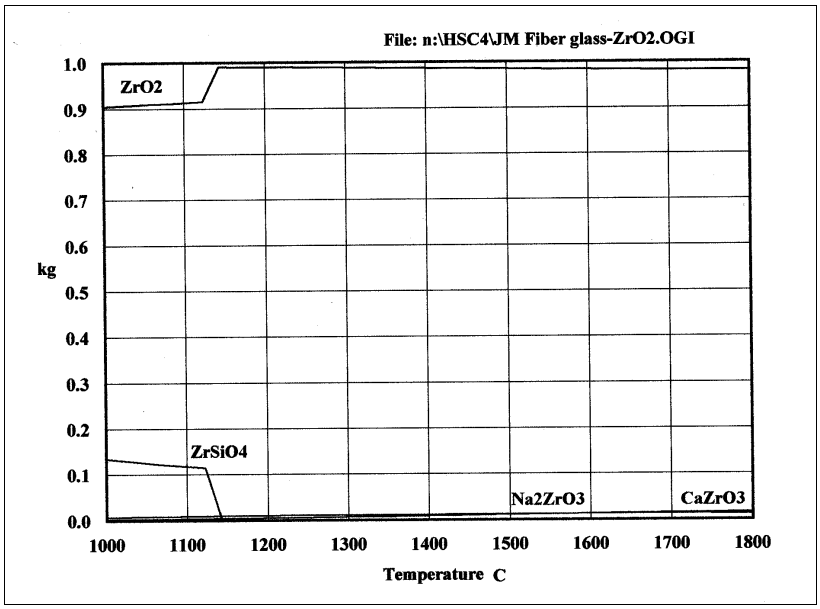
Thermodynamic Stability of $MoSi_2$ in Johns Manville Fiberglass



56.2% SiO_2, 16.7% Na_2O, 7% CaO. 4.9% Al_2O_3, 4.9% MgO, 1.1% K_2O, 8.6% B_2O_3

Los Alamos NATIONAL LABORATORY

Thermodynamic Stability of ZrO_2 in Johns Manville Fiberglass



Glass Companies Sent $MoSi_2$-Coated Al_2O_3 Tubes by Accutru

- **Thomson Consumer Electronics, Circleville, OH**
- **LOF - Pilkington, Rossford, OH**
- Corning Incorporated, Corning, NY
- PPG Fiberglass, Lexington, NC
- Ball-Foster, Muncie, IN
- Owens-Brockway, Toledo OH
- Techneglas, Columbus, OH
- Guardian Industries, Carleton, MI

TCE Glass Engineering Molten Glass Corrosion Test of $MoSi_2$-Coated Al_2O_3 Sensor Sheath

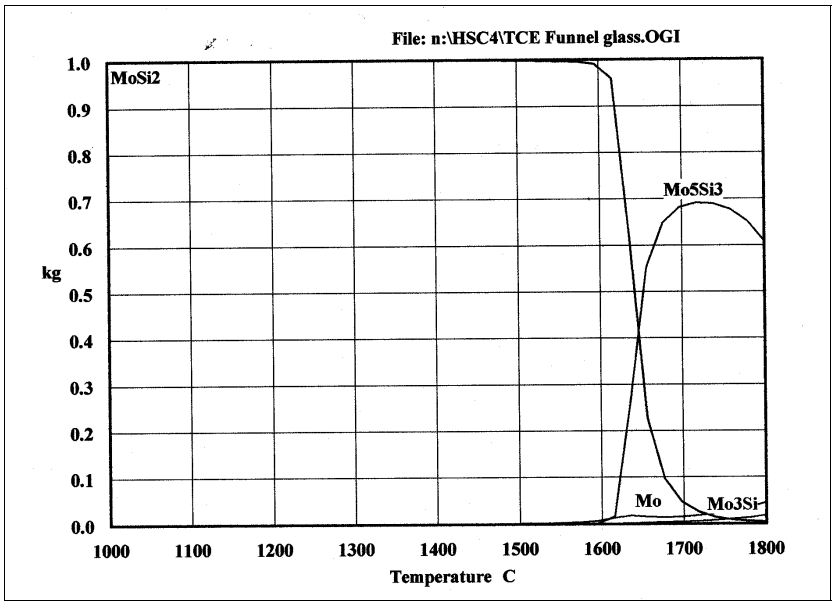
Funnel Glass

53.3% SiO_2, 22.9% PbO, 6.6% Na_2O, 3.4% CaO, 3.3% Al_2O_3, 2.4% MgO, 8.0% K_2O, 0.2% Sb_2O_3

16 hours at 1350 °C

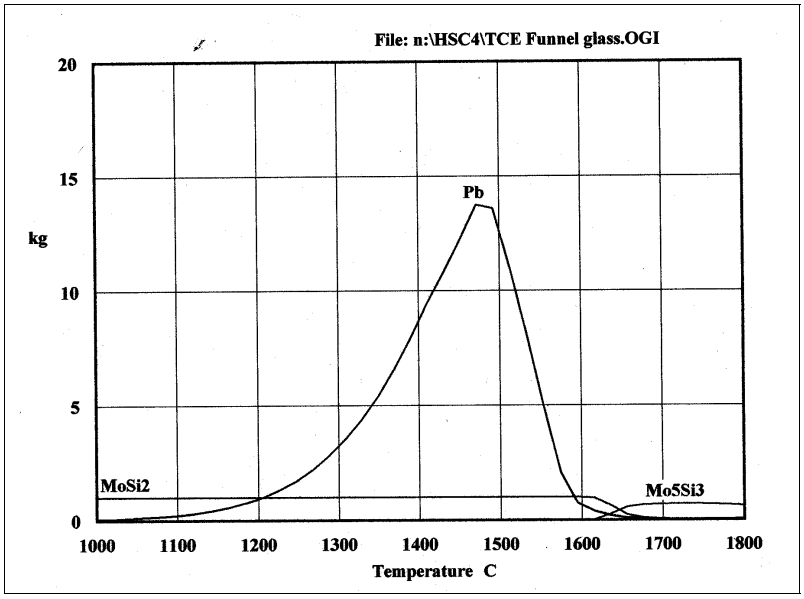
Los Alamos NATIONAL LABORATORY

Thermodynamic Stability of $MoSi_2$ in TCE Funnel Glass

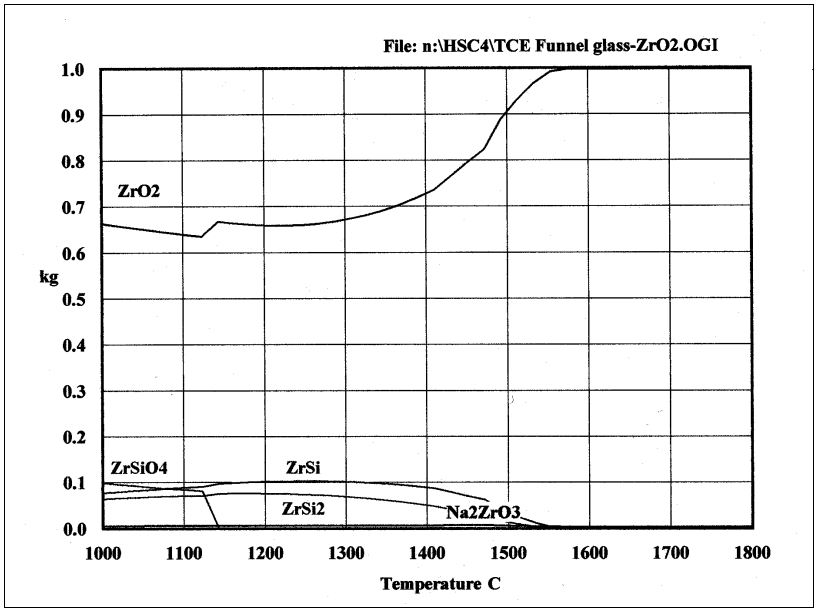


Los Alamos NATIONAL LABORATORY

Thermodynamic Stability of Metallic Lead in TCE Funnel Glass Composition



Thermodynamic Stability of ZrO_2 in TCE Funnel Glass



TCE Glass Engineering Molten Glass Corrosion Test of $MoSi_2$-Coated Al_2O_3 Sensor Sheath

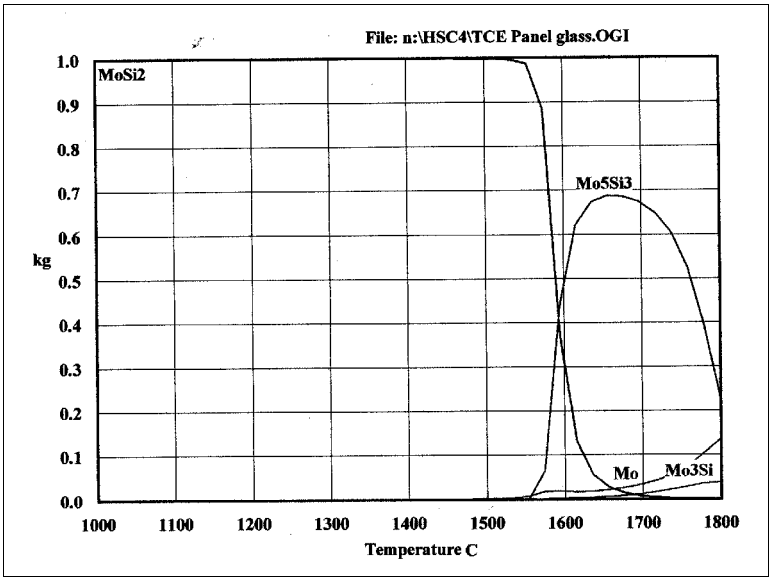
Panel Glass

63.0% SiO_2, 3.3% PbO, 8.3% Na_2O, 2.7% CaO, 2.2% Al_2O_3, 0.06% MgO, 7.1% K_2O, 8.0% SrO, 4.4% BaO, 0.4% TiO_2, 0.3% Sb_2O_3, 0.3% CeO_2

16 hours at 1350 °C

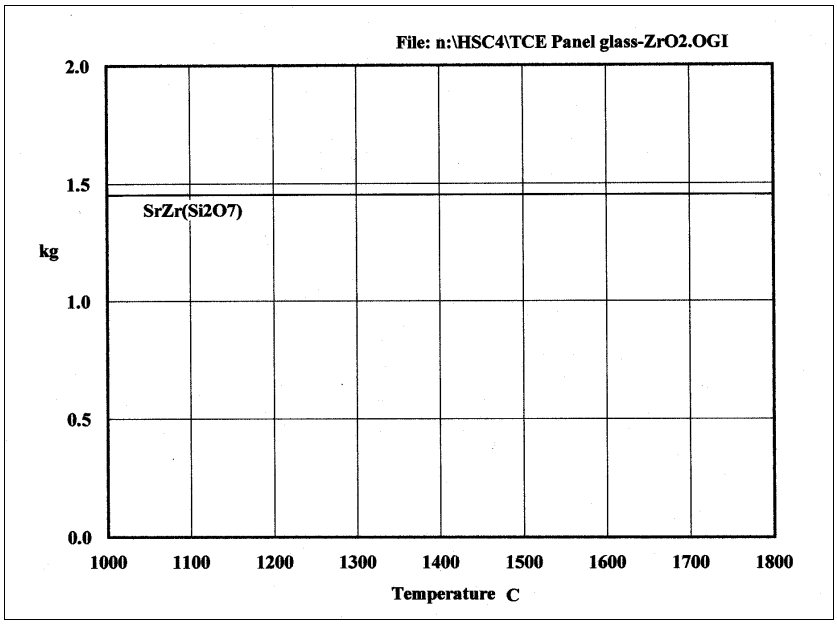
Los Alamos NATIONAL LABORATORY

Thermodynamic Stability of $MoSi_2$ in TCE Panel Glass



Los Alamos NATIONAL LABORATORY

Thermodynamic Stability of ZrO_2 in TCE Panel Glass



Los Alamos NATIONAL LABORATORY

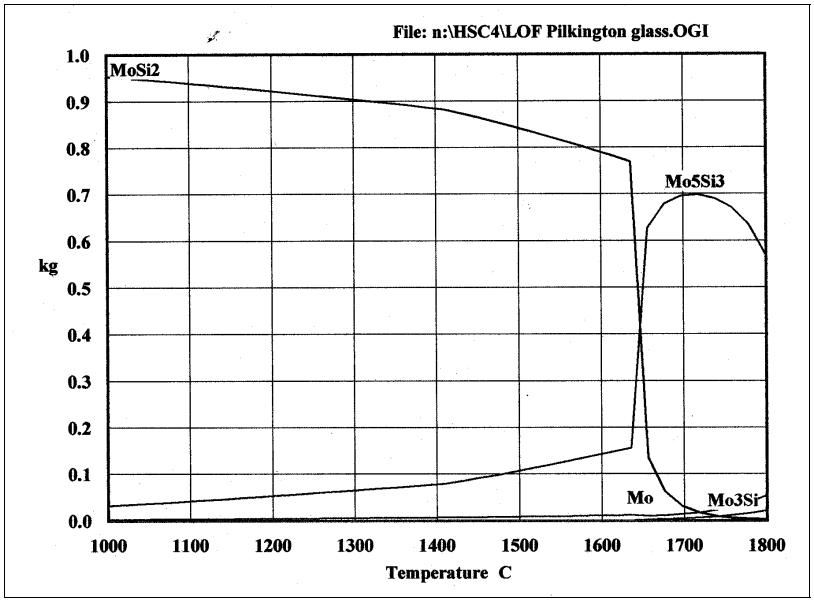
LOF-Pilkington Molten Glass Corrosion Test of $MoSi_2$-Coated Al_2O_3 Sensor Sheath

72.2% SiO_2, 13.5% Na_2O, 8.4% CaO, 1% Al_2O_3, 4% MgO, 0.6% K_2O, 0.12% Fe_2O_3

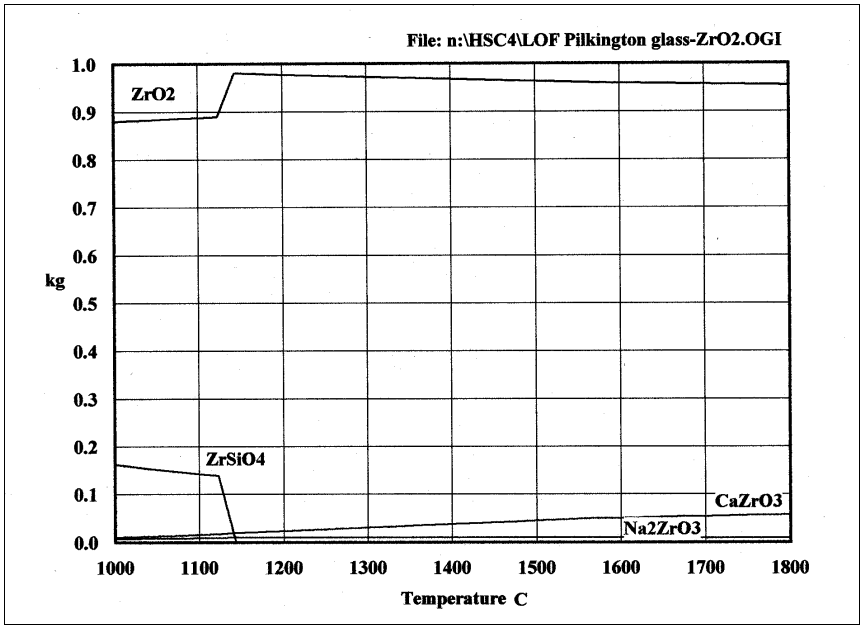
72 hours at 1400 °C

Los Alamos NATIONAL LABORATORY

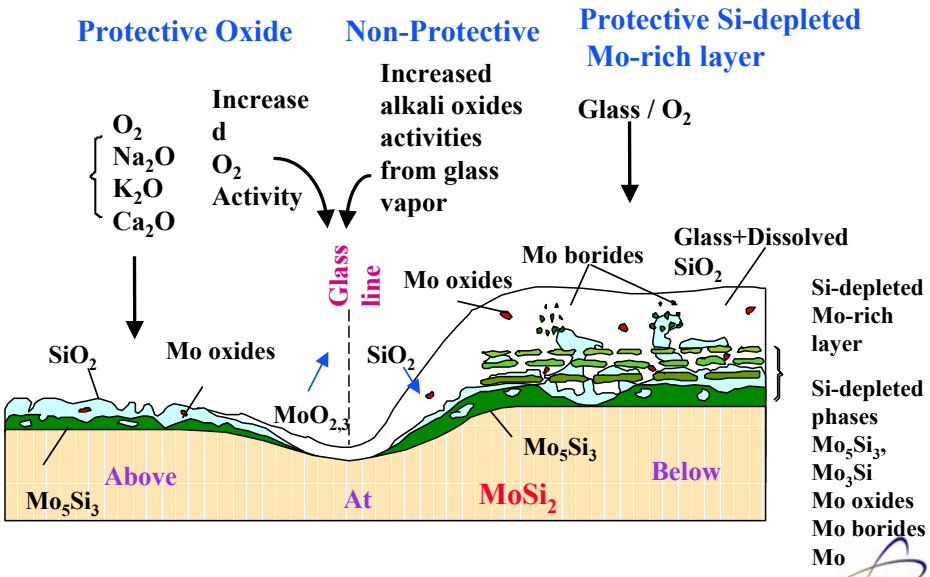
Thermodynamic Stability of $MoSi_2$ in LOF-Pilkington Glass



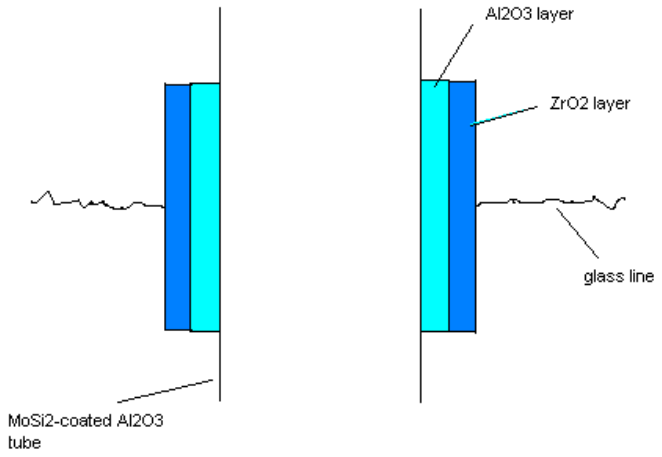
Thermodynamic Stability of ZrO_2 in LOF-Pilkington Glass



Fiber Glass Immersion Testing of Al_2O_3 Tubes Coated with $MoSi_2$



Glass Line Corrosion Protection of $MoSi_2$-Coated Al_2O_3 Tube



Summary

- $MoSi_2$ is a corrosion resistant material in many different molten glass compositions
  - Corrosion resistance is similar to AZS, except at the glass line
- It can be employed as a sensor protective sheath for immersion into molten glass
  - Reduction in the use of platinum for sensor sheaths
- The ability to produce $MoSi_2$-coated Al_2O_3 thermocouple sheaths has been demonstrated
  - Fabrication by plasma spray forming techniques
- $MoSi_2$ requires a ZrO_2 overlayer at the glass line

Los Alamos NATIONAL LABORATORY

Commercial Source of $MoSi_2$-Coated Al_2O_3 Tubes

- Plasma Processes, Inc.
  - 4914 D Moores Mill Road, Huntsville, Alabama 35811
  - Website: www.plasmapros.com
  - Phone: (256)851-7653

Los Alamos NATIONAL LABORATORY

Objective

Develop a technology to enable the glass industry to recycle its glass fiber waste

Project Team

- Argonne National Laboratory

  Sam Jody, Joe Pomykala Jr. & Ed Daniels
- Saint-Gobain Vetrotex America

  John Wells
- CertainTeed Corporation

  Terry Berg

Development of a Process for the Recycling of Glass From Glass-Manufacturing Waste

Prepared for

DOE GLASS PROJECT REVIEW

November 7- 8, 2001

Pacific Northwest National Laboratory

Richland, Washington

Presentation Outline

- Overview
- Technical Progress
- Summary & Conclusions
- Future Plans

Problem

- Waste is presently landfilled
- Earlier attempts to recycle the waste resulted in more frequent breakage of the filaments

Approach

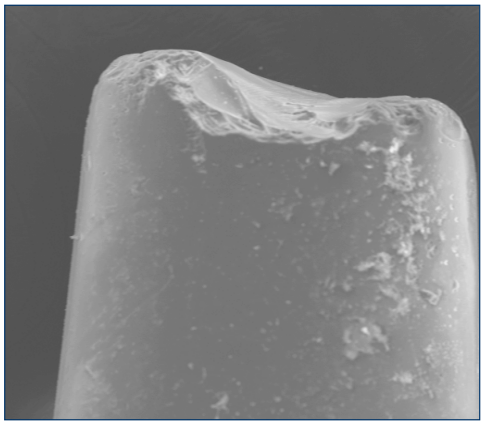
- Identify the cause for increased filament breakage
  - Identify species in the waste glass not present in the virgin glass
- Develop a process to remove these species from the waste material
- Test and demonstrate the process

Species Identification

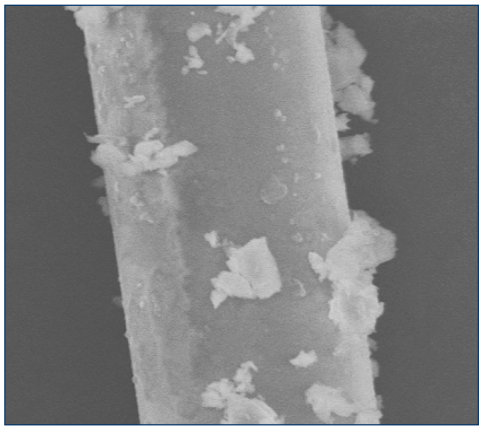
- **Qualitative Analysis**
  SEM, EDS
- **Quantitative Analysis**
  Combustible Fraction, ICP

Difference Between "Virgin" & Waste Glass Appears to be Polymeric Coating

Virgin Glass

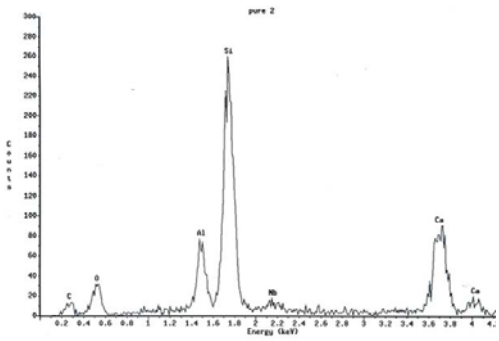


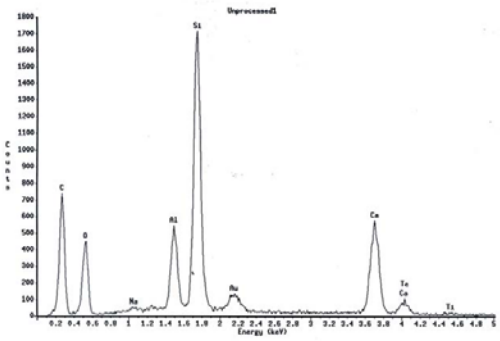
Waste Glass



Same Elements Appeared in the EDS of Both Virgin & Waste Glass

Virgin Glass **Waste Glass**





Same Elements Appeared in the EDS of Both Virgin & Waste Glass

- No elements were identified on the surface of the waste glass that are not present on “virgin” glass
- Both the “virgin” glass and the waste glass surfaces contained:

Silicon	Calcium	Carbon
Aluminum	Oxygen	Sodium

Combustible Mass Determined By Chem. Analysis Lab

Sample	Comb. wt, PPM	Comb. wt, PPM
Virgin-1	42	
Virgin-2	71	
Waste-1		2805
Waste-2		1844

[@ 1200 Deg F (650 Deg C) for 16 Hours, after drying at 220 Deg F (105 Deg C) for 16 Hours]; +/- 20 PPM. Waste samples containing as much as 25,000 PPM of combustible material were observed

Observations & Conclusions

- No elements have yet been identified in the waste glass that are not in the "virgin" glass
- The only apparent difference is the polymer coating layer

Experimental Approach to De-coat the Waste Glass

- Utilized experience in recovering carbon fibers from polymer matrix composites, we selected two methods for testing:

  Thermal Treatment

  Chemical Treatment

Thermal Treatment Method

- Oxidation of the polymer coating at elevated temperatures
- First, conduct bench-scale experiments to determine temperature and residence time
- Second, conduct continuous treatment experiments under "typical" process conditions

Results to Date Are Based on Bench-Scale Tests

Later, Tests will be Conducted in a Continuous Thermal Reactor

Thermal Treatment Appears Capable of Effective Removal of the Coating

Sample	Combustible Residual, PPM
Virgin Glass 1	42
Virgin Glass 2	71
Thermal Treat (750 F, 60 min)	0
Thermal Treat (1000 F, 10 min)	67
Thermal Treat (1000 F, 70 min)	70
Thermal Treat (1250 F, 15 min)	0

* Samples packed < 0.25 inch thick

Total Carbon Analysis of Virgin & Treated Samples Confirms Process Effectiveness

Sample	Carbon	Sulfur
Virgin	< 100 PPM	95 / 80 PPM
Treated @ 1250 F for 15 minutes	< 100 PPM	115 PPM

Packing Density Appears to Limit The Transport of the Evolving Gases

Sample	Combustible Residual, PPM
Thermal Treat (1250 F, 5 min)	324
Thermal Treat (1250 F, 15 min)	450
Thermal Treat (1450 F, 5 min)	490
Thermal Treat (1450 F, 15 min)	193
Thermal Treat (1500 F, 5 min)	437

* Samples Packed ~ 1 inch thick
* Heat/mass transfer issues when scaling-up
  (Could glass melting of coated filaments trap carbon particulates and gas bubbles?)

Observations and Conclusions Thermal Treatment Method

- Thermal treatment can remove the polymer coating off the glass filament surface
- Treatment time and process effectiveness depend on the temperature and on sample packing density

Chemical Treatment Method

- Degradation / dissolution of the polymer coating at elevated temperatures
- First, conduct bench-scale experiments to identify chemicals, determine temperature and residence time
- Second, conduct larger scale tests *if process is competitive with the thermal method*
- A few preliminary experiments were conducted

Chemical Treatment Preliminary Results

Sample	Combustible Residual, PPM
Virgin Glass 1	42
Virgin Glass 2	71
In TTEG (570 F, 15 min)/ water wash	97
In TTEG (570 F, 30 min)/ water wash	492

* Chemical treatment appears capable of removing the coating
* Washing of the treated fibers is necessary
* Generates liquid waste

Conclusions

- No additional chemical elements were found in the waste glass that are not in the virgin glass
- The coating layer is the only "contamination" observed so far in the waste sample
- Technical feasibility of the thermal and chemical methods was established
- Process-improvement studies are underway

FY 2001 Milestones & Accomplishments

*Project started on July 2nd, 2001

Milestone	Scheduled Comp. Date	Status
Identify species in the waste not present in the virgin glass	07/01	Done* (ICP Pending)
Complete thermal treatment set-up and start experiments	07/01	Done
Complete set-up for chemical treatment and start experiments	09/01	Done

2002 & 2003 Milestones

Milestone	Completion Date
Complete technical & economic evaluation of the thermal treatment method	03/02
Complete technical & economic evaluation of the chemical treatment method	05/02
Produce treated glass for testing by industrial partners	08/02
Complete evaluation and characterization of recycled products	10/02
Develop implementation/ commercialization plan & submit of final report	02/03

The Glass Furnace Combustion and Melting Research Facility

John J. Connors
PPG Industries
Glass Technology Center
Pittsburgh, Pennsylvania

Peter M. Walsh and Robert J. Gallagher
Sandia National Laboratories
Combustion Research Facility
Livermore, California

DOE/OIT Glass Industry Project Review
Pacific Northwest National Laboratory, Richland, WA
November 7-8, 2001

Project Team

PPG Industries: John Connors (PI), James Harris, Warren Curtis, David Bivins, Bill Cullum, Joseph Yu, Tom Smith

Sandia National Laboratories: Bob Gallagher, Peter Walsh (PI), Blake MacDonald

Advisors: Vince Henry and John McConnell

Furnace: A. C. Leadbetter & Son

Batch and Cullet Systems: Lilja Corp.

Charger: Merkle Engineers

Burners: Maxon Corp.

Ejector: Morgan Construction Co. (now Laidlaw Drew)

Melting Research Furnace

Firing: O_2/gas

Heat input:
8.6 x 10^6 Btu/hour

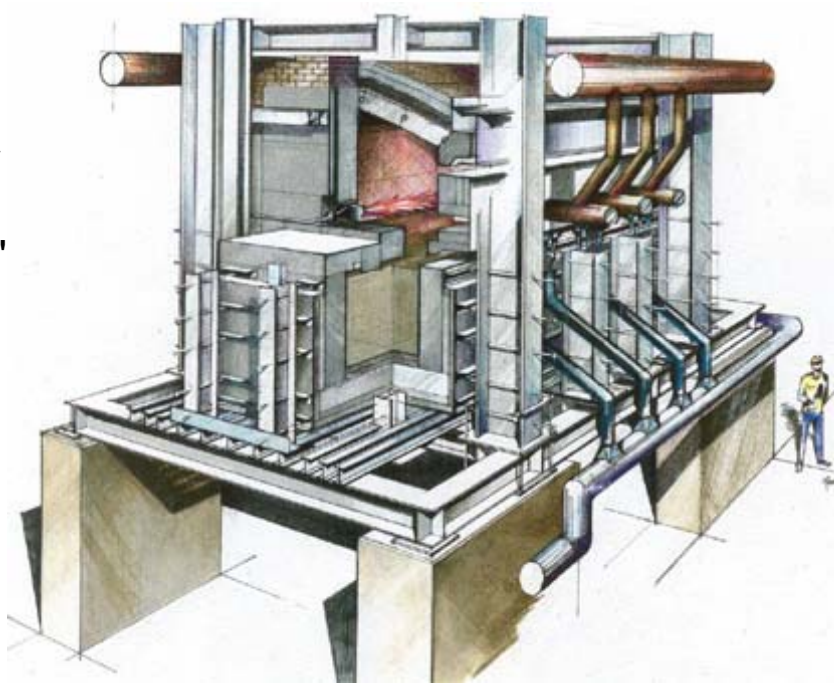
Melting area: 6' x 13'

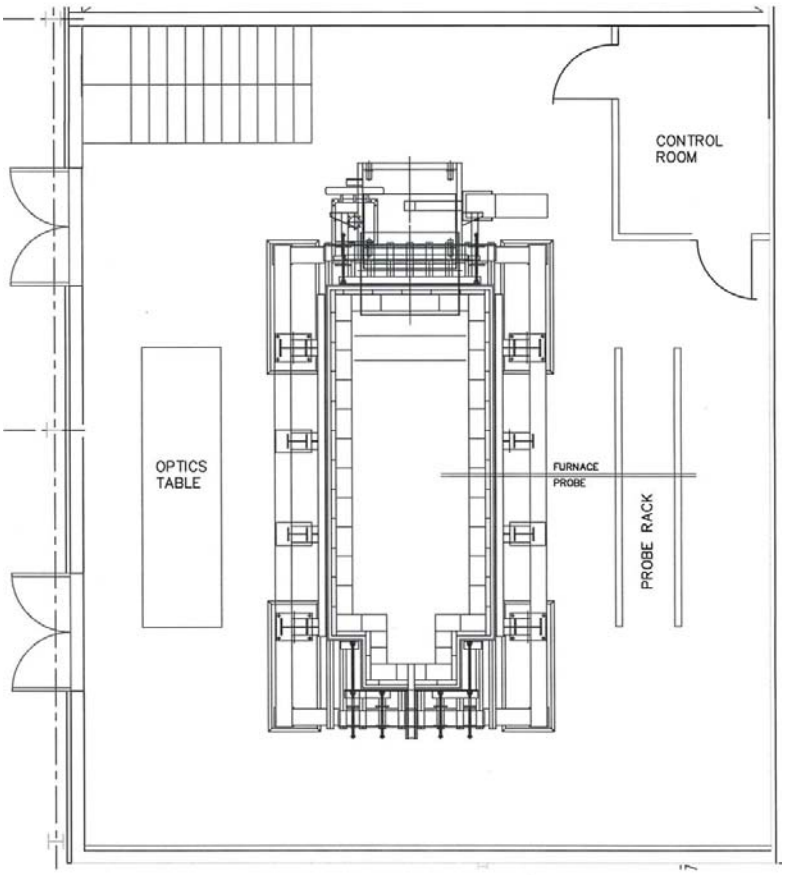
Glass depth: 3'

Maximum pull:
25 ton/day

Full width doghouse

Bubblers

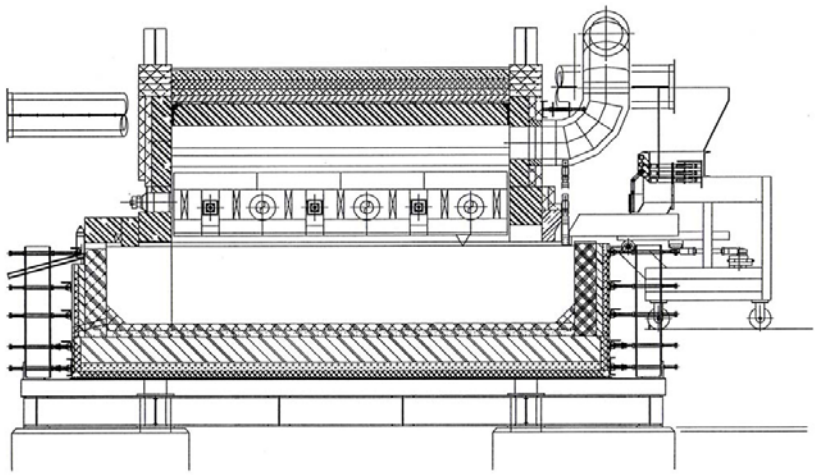




Measurements

Essential Properties:
- Temperature
- Composition
- Velocity
- Radiation

System components:
- Batch
- Foam
- Glass
- Refractory
- Flames
- Burned Gas



Measurement Techniques:
- Probes
- Optical

First Measurement Campaign - Data

Total radiation incident on glass surface

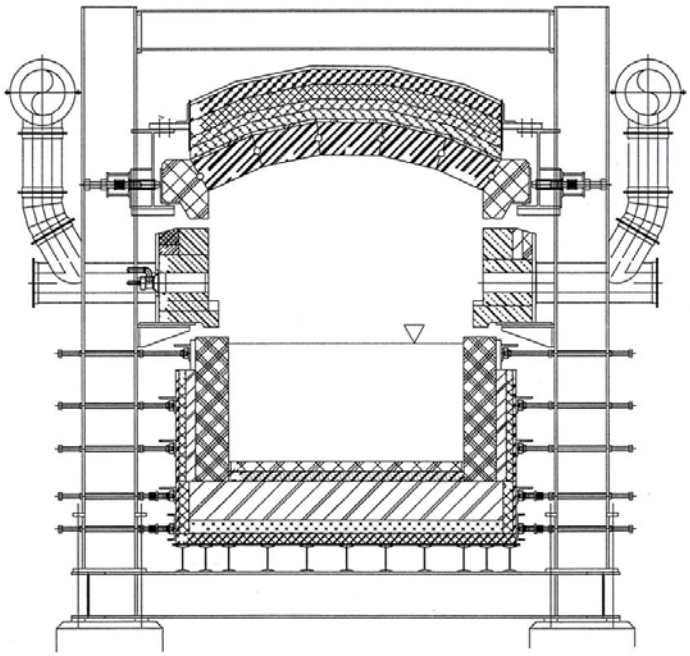
Total heat transfer at glass surface

Radiation from crown

Temperature of glass/ foam/batch vs. depth

Radiation vs. axial and radial position in flames

Gas composition and temperature vs. position in flames



Sodium concentration above glass surface

First Measurement Campaign - Variables

Burners: concentric tube, flat flame

Burner location: front wall, breastwalls

Burner flow momentum: high, low

Burner height: low, center, high

Oxygen staging: none, full

Oxygen purity: 0.5, 1, 2, 5, 10 vol% N_2

Flame luminosity: propane addition, levels to be determined

Firing rate distribution: along breastwalls, to be determined

Feed: cullet, batch

Glass: clear soda-lime, green soda-lime

Modes of Operation

Thorough characterization and comparison of performance under various operating conditions

- Quantify the influence of individual process variables
- Identify limiting conditions
- Validate models

Special tests

- Burners
- Batch formulations
- New instrumentation

Experimental Trials

- Explore radical departures from accepted practice

Modes of Operation (continued)

New Diagnostics

New measurements, e.g. glass surface temperature
Adapt laser-based techniques to monitoring and control

Develop and Refine Model-Based Control Strategies

Transient behavior

Quantify Rates and Mechanisms of Individual Processes

Batch reactions and melting
Glass circulation
Foam dissipation

Laser-Based Techniques

Laser Doppler Velocimetry (LDV or LDA)

Measurement: Gas velocity
Status: Commercial
Advantages: Non-intrusive, characterizes turbulence

Coherent Anti-Stokes Raman Spectroscopy (CARS)

Measurement: Gas temperature
Status: N_2 CARS well established
O_2 and CO_2 CARS under development at SNL by R. Farrow and P. Schrader
Advantages: Non-intrusive, no temperature limit, observes fluctuations

Laser-Based Techniques (continued)

Laser-Induced Breakdown Spectroscopy (LIBS)

Measurement: Metals (Na, K, Ca, Mg, Fe, B, Si, Al), particle size.

Status: Sandia instrument used to measure Na and B in melting tank flues.
New broad-band instrument to Gallo Glass, December 10.
Water-cooled probe under construction.

Advantages: High sensitivity,
determines particle size in-situ.

Laser-Based Techniques (continued)

Photofragment Fluorescence

Measurement: NaOH

Status: Under development at SNL by S. Rice and M. Allendorf

Advantages: Pointwise measurement, non-intrusive

Raman Scattering

Measurement: Glass surface temperature

Status: Experimental

Advantage: Non-intrusive

Schedule

Beginning with authorization and funding to proceed

Complete engineering: 1½ months

Bid package to Sandia purchasing dept.: 1 month

Bids due: 1½ months

Contract in place: 1 month

Materials to site and site preparation: 3 months

Furnace installation: 3 months

Heat up and shake down: 1 month

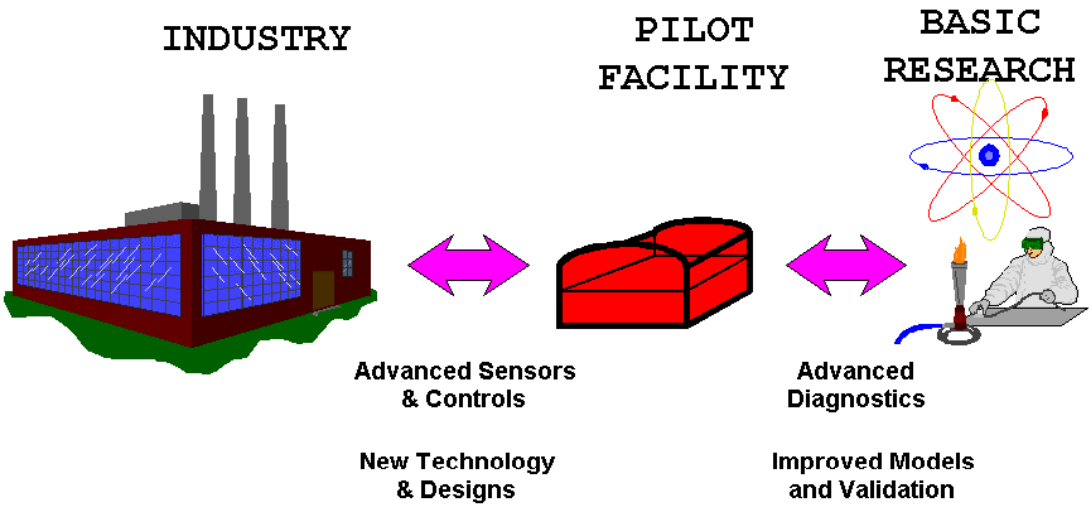
Total: 12 months

Glass Oxy-Fuel Melter Facility

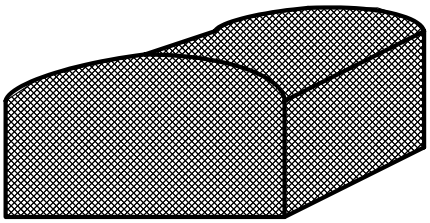
By John J Connors

11/7/01

Glass Oxy-Fuel Melter Facility



Pilot Facility Deliverables



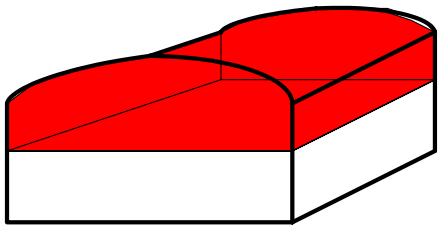
- Advanced Glass Oxy-Fuel Melter
  - State-of-the-Art Sensors and Diagnostics
  - Fully Operational and Tested
- Matrix of Results
  - Combustion vs. Glass vs. Interface
- Modeling Validation Measurements
  - Temperatures, Velocities and Concentrations
- Complete Mass and Energy Balance

Oxy-Fuel and Glass

- Control:
  - Firing Profile
  - Oxy/Fuel Ratio
- Continuous firing and coverage
  - Flame Geometry and Characteristics
- Lower emissions
- Stability

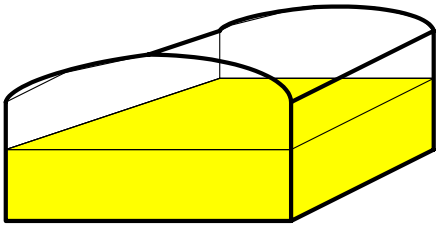
Air-Fire	Oxy-Fuel
2.5% O_2	2.5 % O_2
8 % CO_2	32% CO_2
16 % H_2O	64% H_2O
72 % N_2	3 % N_2

Combustion Space



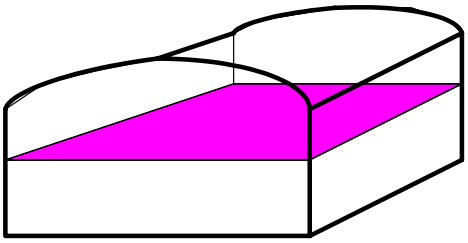
- Burner Design and Firing
  - Flat flame, staged, crown firing, etc…
  - Oxy/Fuel ratio (excess oxygen)
  - Flame velocity
- Fuel and Oxidizer
  - Fuel type and composition
  - Oxidizer purity, composition and air Ingression
- Exhaust Emissions

Glass Space



- Glass Compositions
  - Clear, automotive, other compositions…
- Glass Load
  - Melting cullet vs. batch
- Chemistry
  - Redox
  - Minor species retention

Interface



- Glass Surface
  - Batch, foam, glassy, etc…
  - Surface Temperatures
- Mass & Energy Transfer
  - Volitilization of batch (e.g. NaOH, etc…)
  - Water into glass
  - Heat transfer into glass

Advanced Diagnostics and Sensor Development

- Temperature
  - **Thermocouple matrix (crown, glass, walls,etc..)**
  - **Combustion space temperatures (CARS)**
- Gas and Glass Compositions
  - **Continuous exhaust monitoring**
  - **Combustion space sampling (LIBS, Raman, etc..)**
- Radiation Measurements (Heat Flux Probes)
- Velocity measurements (LDV, Pitot Tube, etc..)

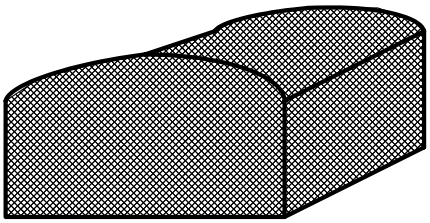
Disclosure (First Two Years)

- Furnace Capabilities
- Diagnostic, Sensors and Instrumentation
- Furnace Performance (PPG Inspections)
- Initial Test Report (Some base line quantitative data)
- Test Program Outline
- Technical Source and Cooperate with NGM program

Non-Disclosure (5 Years)

- Quantitative data
  - Flame temperatures
  - Emissions levels
- Specific process data
  - Actual glass compositions,
  - Burner designs, etc

Results



- Advanced Glass Oxy-Fuel Melter
  - State-of-the-Art Sensors and Diagnostics
  - Fully Operational and Tested
- Matrix of Results
  - Combustion vs. Glass vs. Interface
- Modeling Validation Measurements
  - Temperatures, Velocities and Concentrations
- Complete Mass and Energy Balance

Measurement and Control of Glass Feedstocks

DE-FC07-01ID14030

Dr. Arel Weisberg
Robert De Saro
Energy Research Company
www.er-co.com

DOE OIT Glass Project Review

November 7-8, 2001

Agenda

- Participants
- Brief Summary of Accomplishments
- Problem Statement
- Concept Description
- Experimental Data
- Software Developments
- LIBS Measurements in Molten Material

DOE's Office of Industrial Technologies

Glass

ERCo
Energy Research Company

Other DOE Support for Molten Work

- Sensors and Controls
- Innovation and Inventions

Other Support

- NYSERDA
- NYS DED

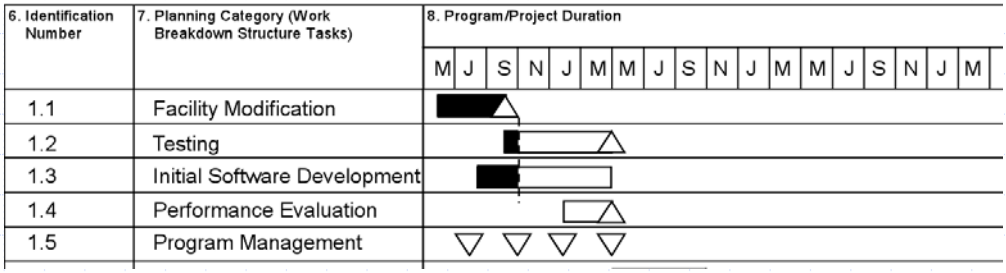
Participants in Glass Project

- DOE OIT
- Energy Research Company
- Oak Ridge National Laboratory
- Fenton Art Glass
- Mississippi State University

ERCo
Energy Research Company

Timeline & Milestones

- Program Started April 2001



- Facility Modification completed
- Testing Underway
- Initial Software Development Underway

Two Projects in Glass

- Measure Batch Formulations in Real-Time
  - Measure Oxide Concentrations
  - Determine if Batch is on Spec
- Measure Cullet in Real-Time
  - Identify Cullet Color and Contaminants
  - Remove Contaminants and Separate Color

Future Interest

- Measure Concentrations of Molten Glass in Tank in Real-Time, In-Situ

Each Project Requires Different Approach

- Batch Requires High Measurement Accuracy of Oxides and Statistical Approach
- Cullet Requires Identification of Color or Contaminant, not of Oxides
- Molten Requires High Measurement Accuracy of Oxides in Extreme Environment
- Each Uses Measured Spectra

Accomplishments

- Laboratory Apparatus Operational
- Demonstrated Technique's Utility for Batch and Cullet Analysis
- Development of Advanced Batch Analysis Algorithm Initiated
- Cullet Sorting Algorithm Being Developed and Testing Underway
- Demonstrated Technique at DOE Utah Showcase
- First LIBS Patent Underway, Glass Patent Shortly

Problem Statement

- The Glass Industry Technology Roadmap emphasizes this need for accurate process and feedstock sensors (p. 12):

  "The lack of effective in-process sensors and control systems is the most serious barrier to better production efficiency."

ERCo
Energy Research Company

Problem Statement

- Lack of Effective Way to Ensure Well Mixed, Contaminant-Free Batch
- Lack of Effective Way to Ensure Color Sorted, Contaminant-Free Cullet
- These Issues Lead to
  - Wasted Feedstock
  - Quality Problems
  - Increased Energy Use and Emissions
  - Wasted Product

Benefits of Batch and Cullet Analysis

1. Poor quality or non-uniform raw materials would not enter the furnace.
2. Contaminants can be identified prior to their entering the batch or the furnace.
3. Degree of mixing of the batch could be monitored, leading to more uniform mixtures in the furnace, and higher quality and uniformity in the final product.
4. As a result of repeatable batch formulations entering the furnace, optimal furnace parameters can found for a particular mixture, resulting in less material and energy waste.
5. Single Device Accomplishes All

ERCo
Energy Research Company

Goals

- Develop an on-line sensor for rapidly measuring overall batch composition and detecting contaminants
- Develop a sensor for color sorting cullet and identifying contaminants
  - Remove contaminants and collect color sorted glass

Glass Applications

- Glass Batch Constituents
- Cullet Color Separation
- Cullet Contaminant Identification
- Specialty and Electronic Glasses (Low Tolerance for Alkali Metals)
- Sealing Glasses (TEC Critical)

LIBS Technology

- Laser Induced Breakdown Spectroscopy
- Tightly focused laser is used to vaporize a minute amount of material resulting in a plasma
- UV and visible light emitted by the plasma is analyzed using a spectrometer
- The strength of emissions from individual elements in the spectrum are directly related to their concentration in the material

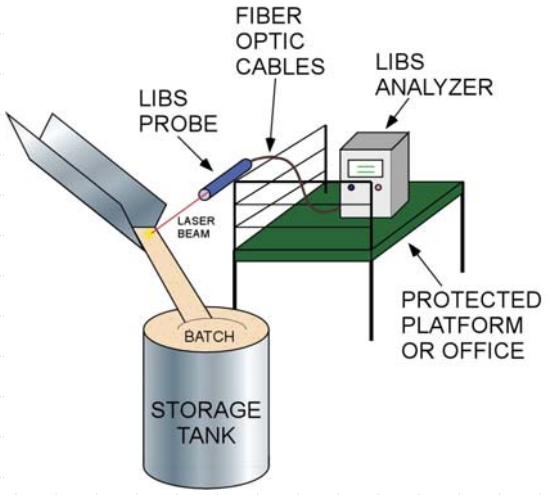
LIBS Advantages

- Fast
  - 10-50 Measurements/second up to 10 kHz with higher end lasers
- Accurate
  - Fractions of a percent to ppm
- Applicable to a wide range of materials
  - Glass, Batch
  - Metals, other solids, liquids, gases
- Proven
  - Extensive literature on use of the process in lab environments

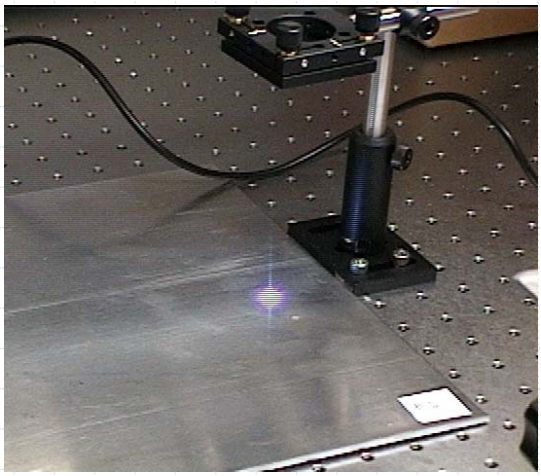
ERCo
Energy Research Company

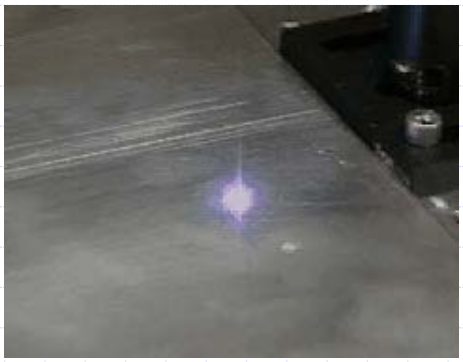
LIBS Advantages

- Use of fiber optics can remove expensive equipment from factory floor to controlled environment



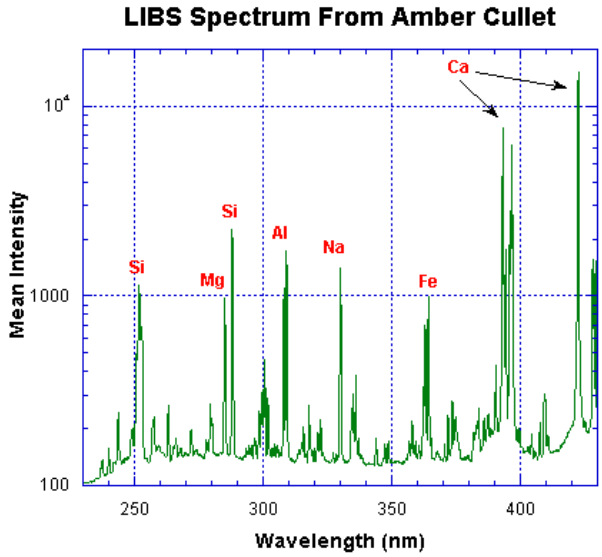
LIBS Technology





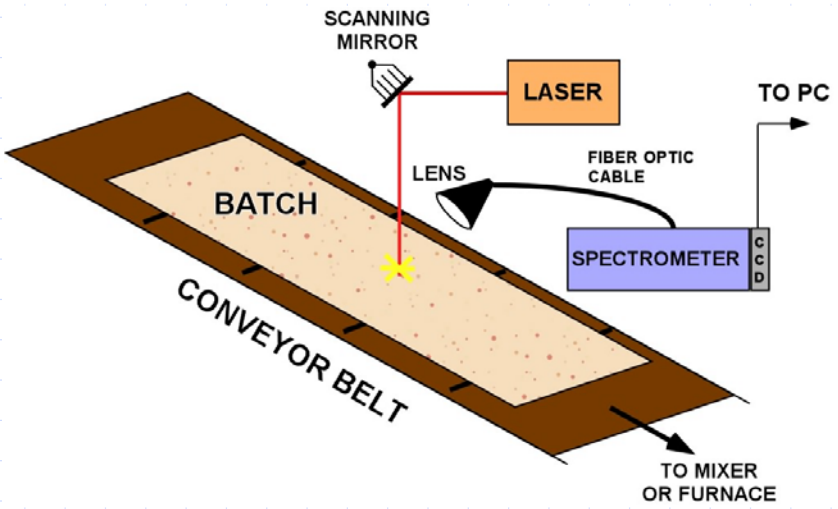
A Tightly Focused Pulsed Laser Is Used to Vaporize and Ionize the Sample Material (Solid, Liquid, or Gas)

LIBS Technology

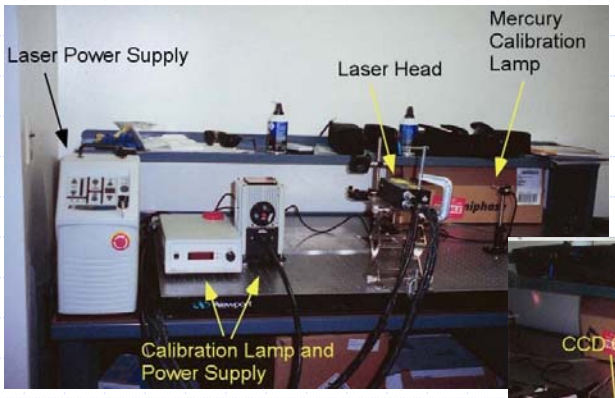


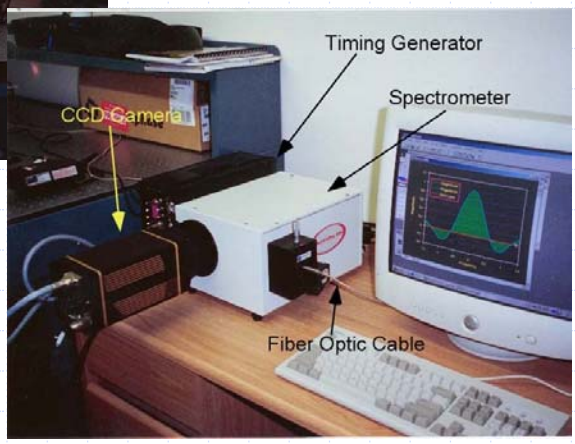
Spectrometer gathers the ultraviolet light and spreads it, like a prism, into a spectrum where the contribution of each element can be seen

LIBS Batch Analyzer



ERCo LIBS Facility





Glass Analysis

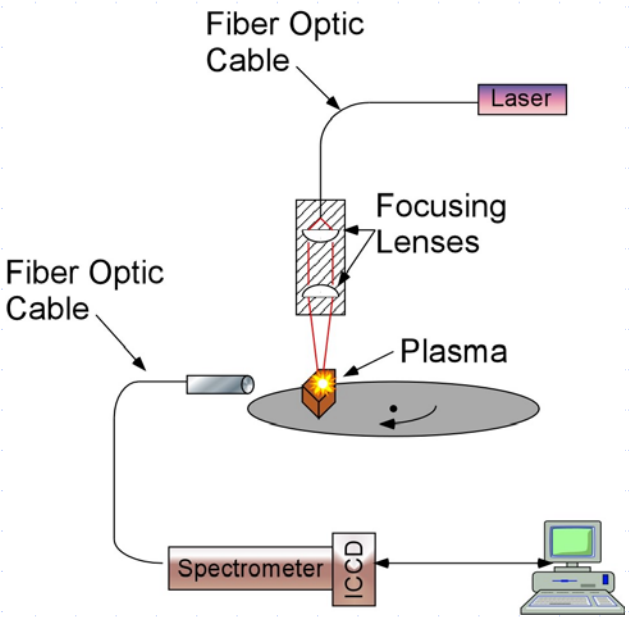
Elements in Glass Production and their Spectral Lines

Element	Spectral Line(s) (nm)
Al	394.40, 396.15
Ca	368.08, 363.10, 364.44, 364.48
Ca^+	393.37, 396.85
Fe	371.99, 373.49, 373.71,382.04, 404.58
Mg	382.93, 383.23, 383.83
Mg^+	279.55, 280.27
Mn	403.08, 403.31
Pb	368.35, 405.78
Si	251.61, 252.85, 288.16
Sr^+	407.77
Ti	365.35
K	404.414, 404.721
Na	330.3

Batch Analysis – Phase I

- Identify spectral lines useful for measuring concentrations of batch constituents and contaminants
- Statistically analyze LIBS data from granular batch
- Identify equipment specifications necessary for optimally measuring batch composition

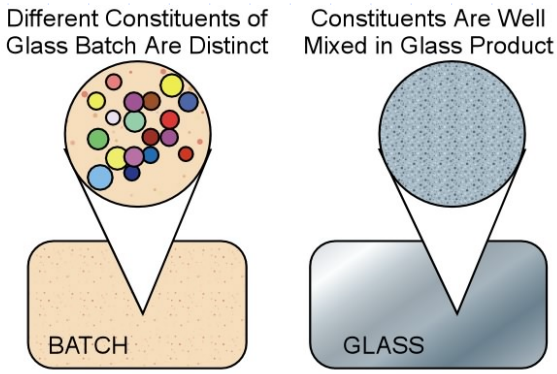
LIBS Apparatus Schematic



Batch Analysis – Phase I

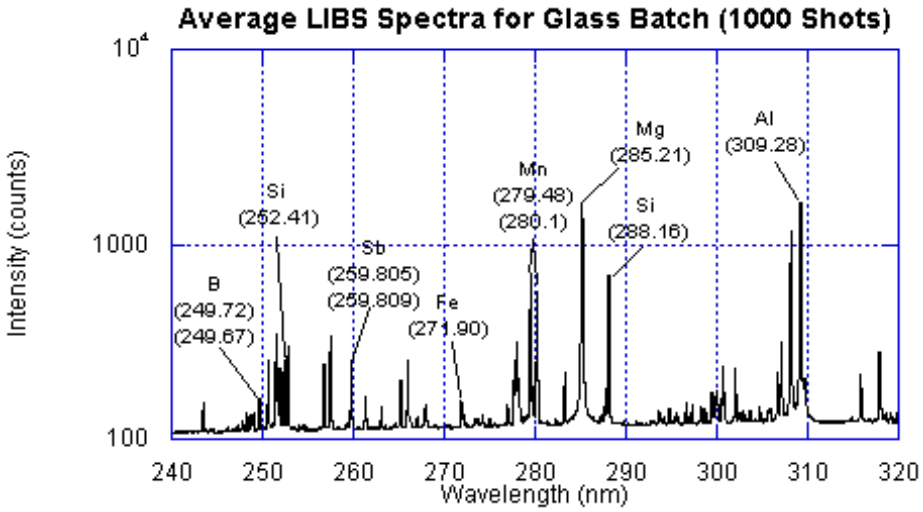
Treat Data Statistically

- Because batch is segregated many sparks are needed to ensure that all elements are sampled
- This also improves detection of trace elements since their presence is concentrated when sparked



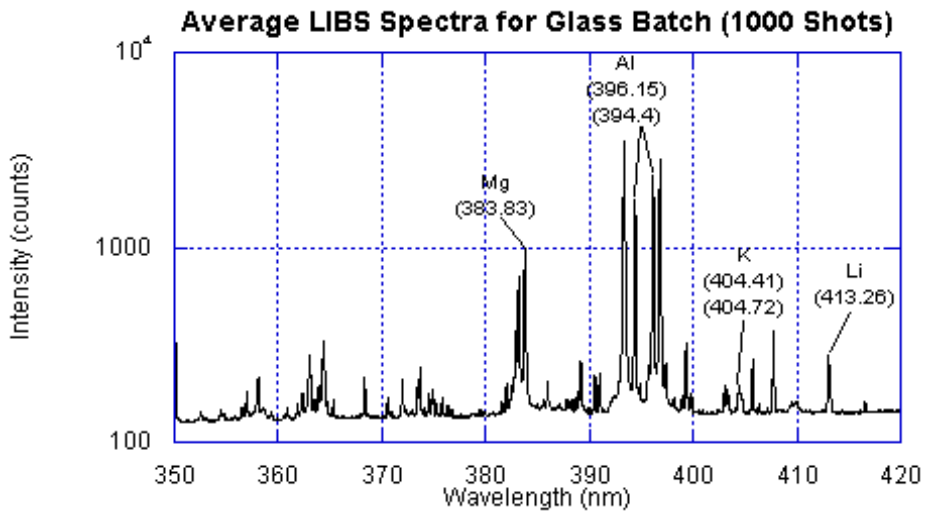
LIBS May Spark Only One Type of Grain in Batch
But Will Spark All Constituents in Glass or Metal

Batch LIBS Spectra



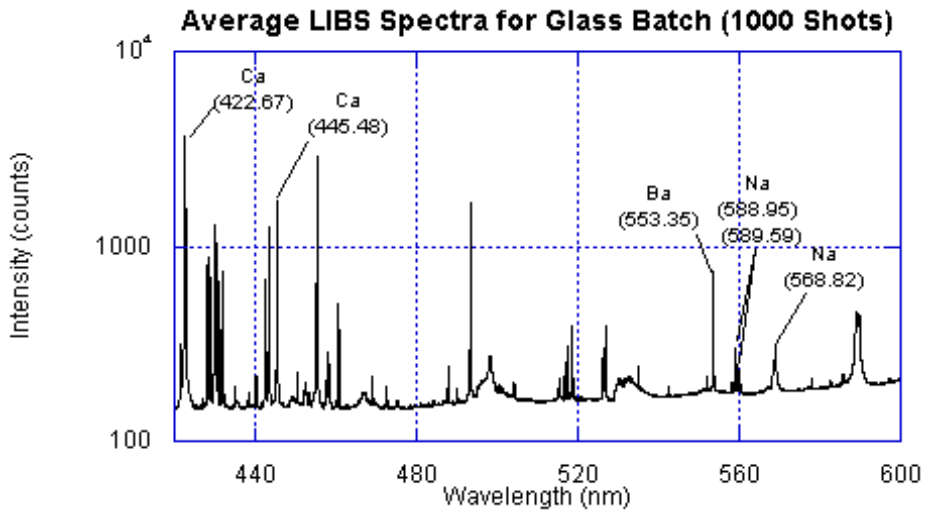
(concentrations proprietary, Fenton Art Glass)

Batch LIBS Spectra



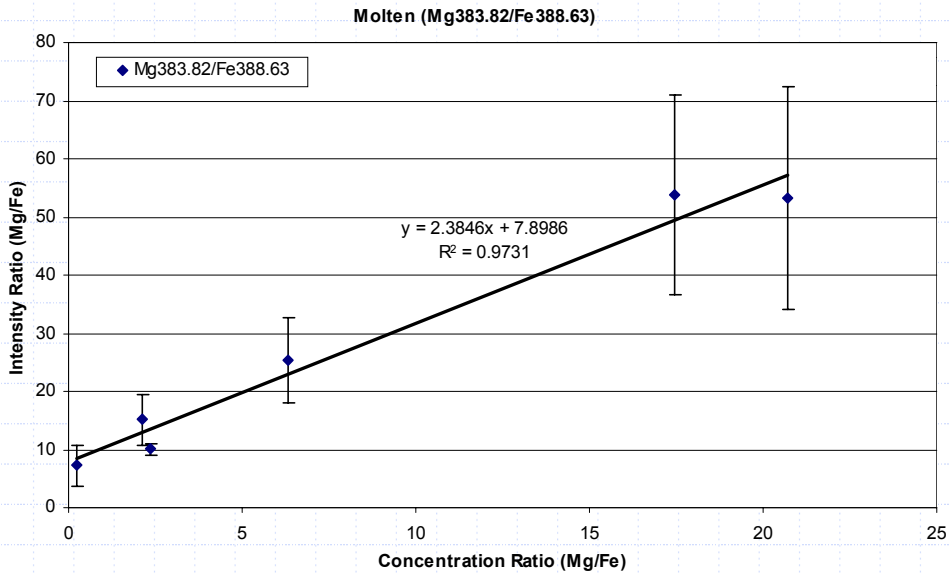
ERCo
Energy Research Company

Batch LIBS Spectra



Software Approach for Batch

Calibration Curves Difficult to Use

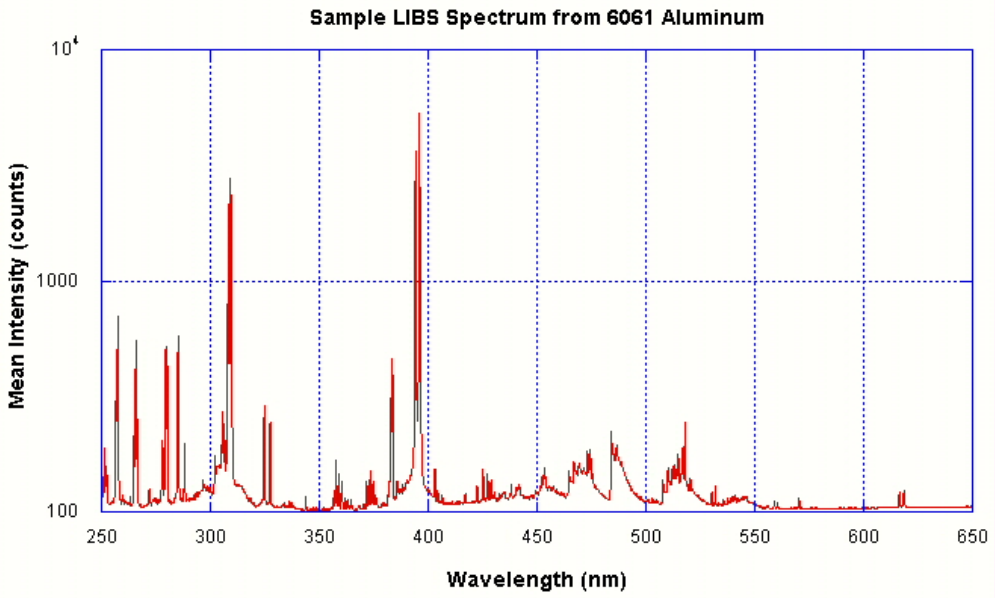


Large Uncertainties Are Characteristic of LIBS Measurements

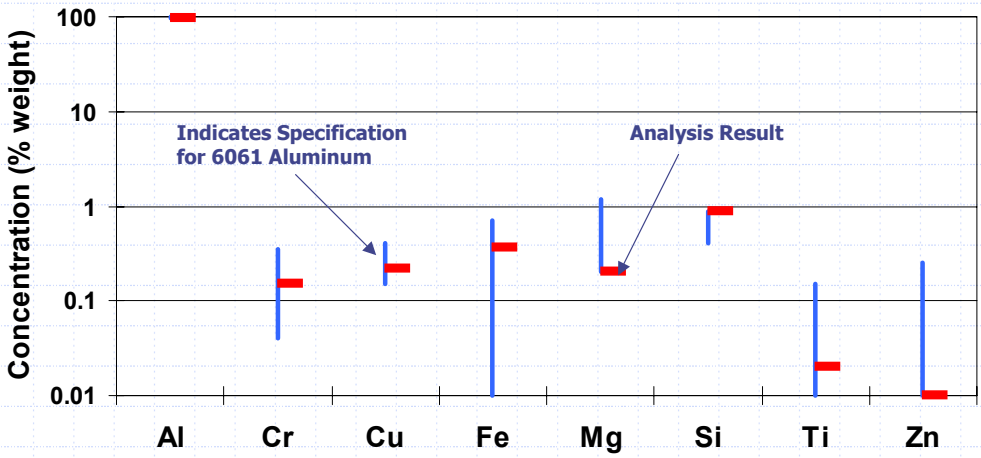
Calibrationless Software

- ERCo has Proprietary Software Using First Principles that Translates LIBS Spectra into Concentration Measurements
- Method Applies to both Molten and Solid Data
- Method is Independent of Experimental Parameters such as Laser Power
- No Calibration Data Required

Initial Software Test



Initial Software Test



Cullet Color Sortation

"The industry needs technologies that can reliably identify and eliminate non-glass materials from the stream and efficiently sort glass by color."

The Glass Industry Technology Roadmap

CLEAR AMBER GREEN

Recyclable Colors of Container Glass

Cullet Contaminants

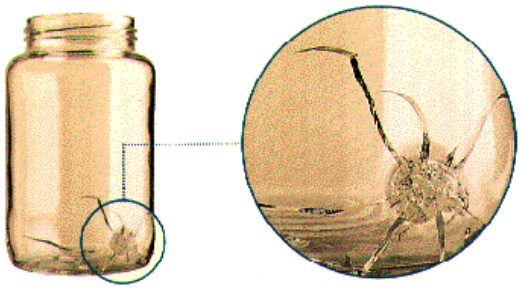
- Optical Sensors Cannot Detect Some Common Contaminants Such As Cookware and Window Glass

Visions Cookware
A Glass-Ceramic

AMBER

- A LIBS Sensor Would Easily Distinguish Between Container and Non-Container Glasses Because Of Their Different Elemental Makeup

Cullet Contaminants



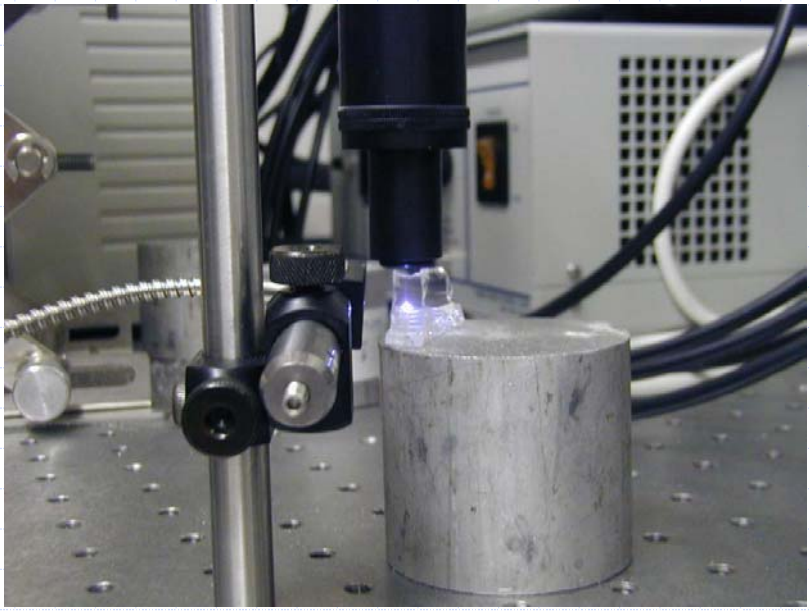
Contaminants Can Produce Severe Defects

Cullet Sorting Phase I

- Test goal is to identify color or identify contaminants with one laser pulse

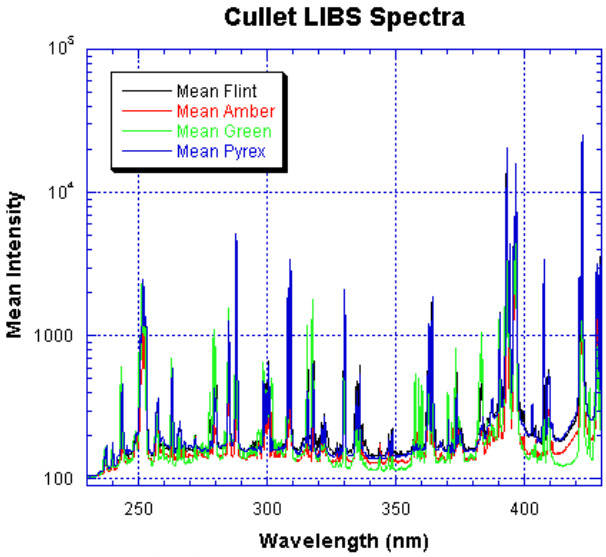
Cullet and Contaminant Samples

Cullet Sorting – Phase I



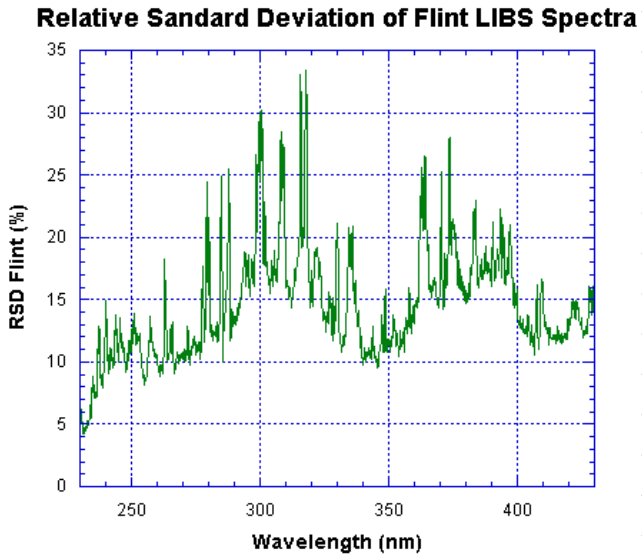
Cullet Spectra

- Spectra Exhibit Differences That Can Be Exploited In A Sorting Algorithm



Cullet Spectra

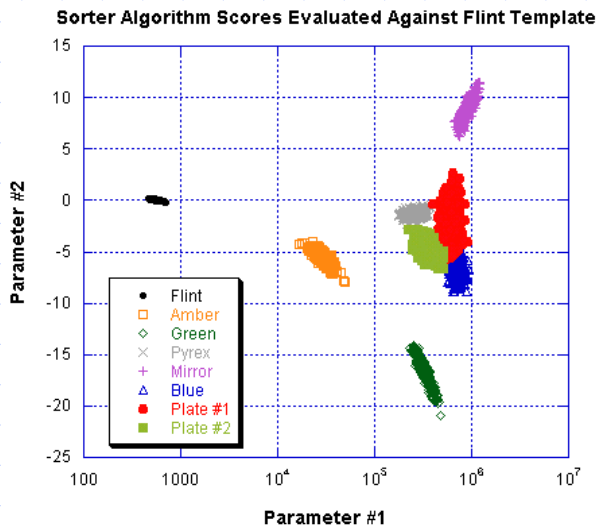
- However, LIBS Spectra Also Exhibit Large Fluctuations



Software Approach for Cullet

Software to Identify Contaminants

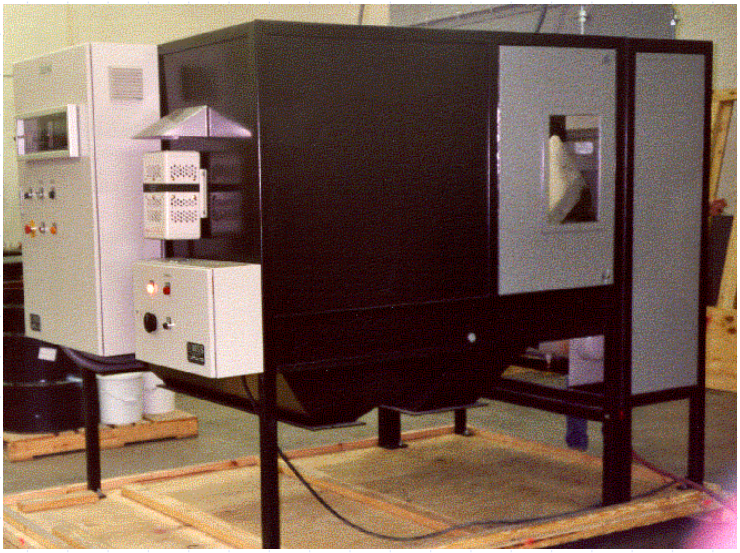
- Proprietary algorithm uses database of spectra to identify cullet color and contaminants using one laser spark



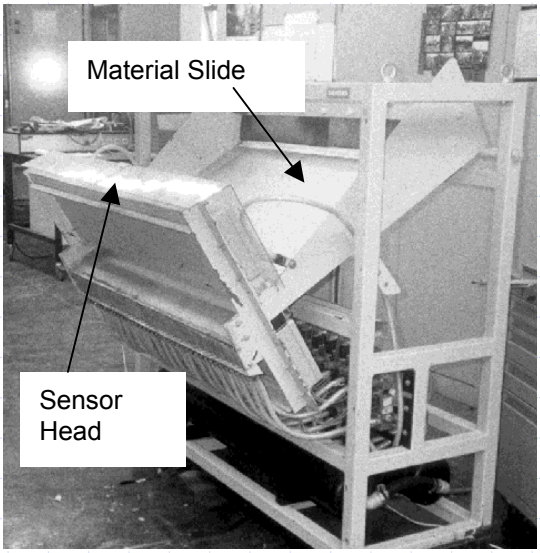
Initial Cullet Test

- All colors can be sorted simultaneously or one color can be sorted separately
- Percent of spectra correctly identified as a color of cullet: 100%
- Percent of spectra correctly identified as a contaminant: 100%

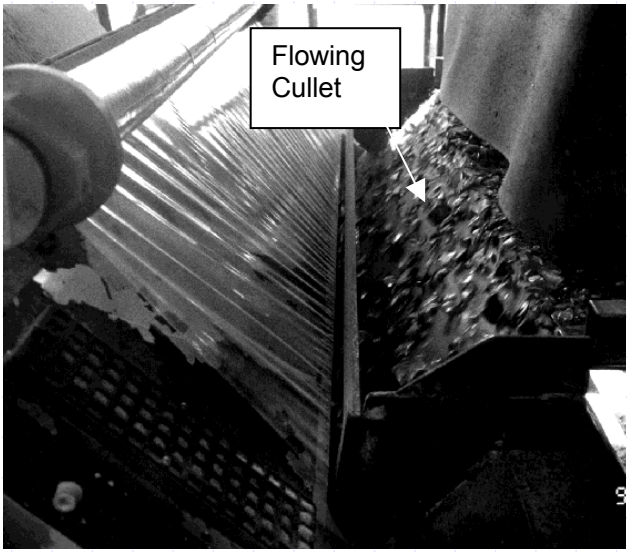
MSS Packaged Ceramic Removal



MSS Cullet Sorter



MSS Cullet Sorter



ERCo
Energy Research Company

Next Phase in Cullet Sorting

- Expand testing to include spectra from many different cullet sources (different bottles, jars)
- Expand testing to check that other contaminants are also rejected (e.g. window glass, ceramics)
- Design larger scale system for testing cullet at increasing speeds
  - High Speed Laser
  - Replace Spectrometer with Radiometers and High Speed Data Acquisition System

Other LIBS Work at ERCo

- Molten Aluminum
- Molten Steel
- Alloy Identification
- Industry Interest in Molten Glass Applications

Participants

- Oak Ridge National Laboratory
- Crucible Specialty Metals
- Alcoa
- Hydro Aluminum
- Crestwood Metals
- Mississippi State University

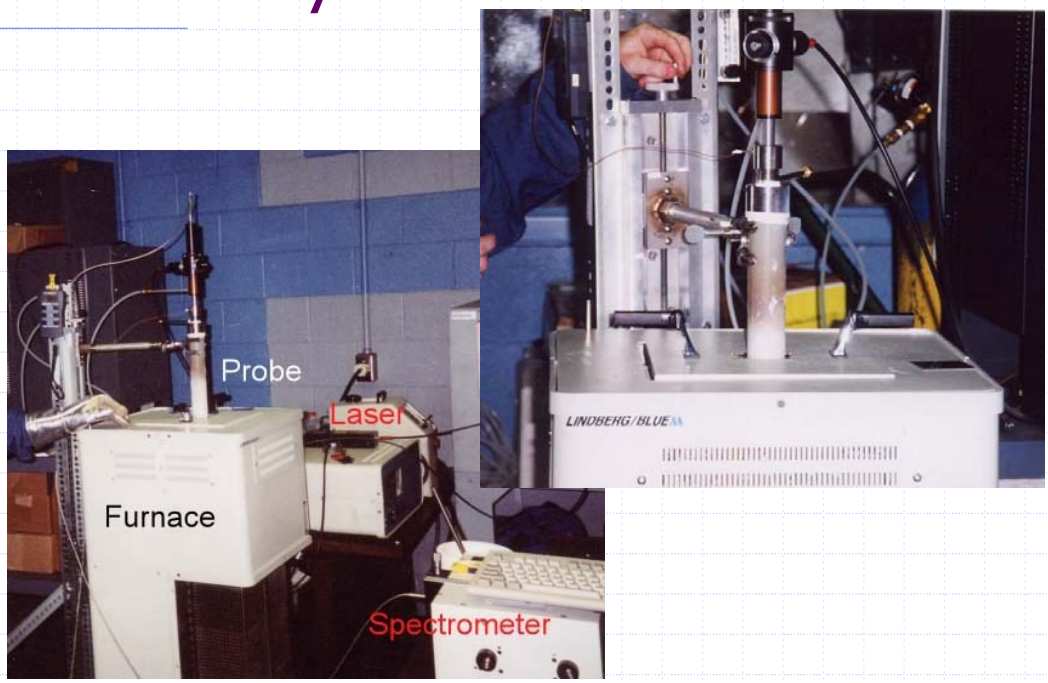
Funding Partners

- DOE
  - Sensors and Controls
  - Inventions and Innovation
- ERCo
- NYSERDA
- NY State DED
- Crucible Specialty Metals

Related Accomplishments

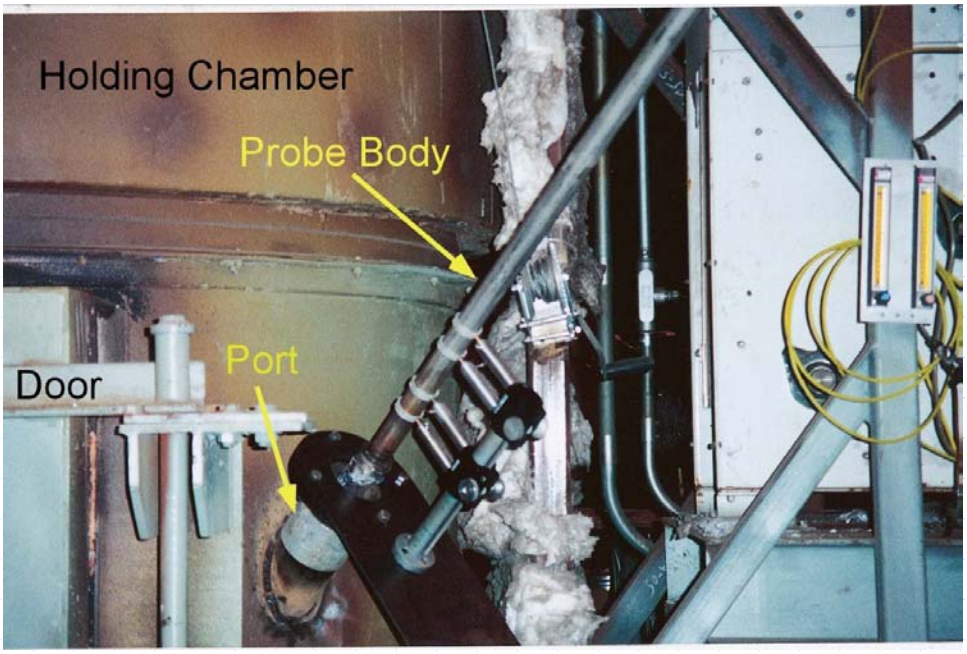
- LIBS Probe developed for in-situ analyses of molten aluminum and other materials
- Melt composition can be measured at any point below or on top of the melt surface
- Laboratory and pilot scale probes built
- First LIBS data ever recorded from within molten aluminum

Laboratory Scale Probe



Pilot-Scale Tests

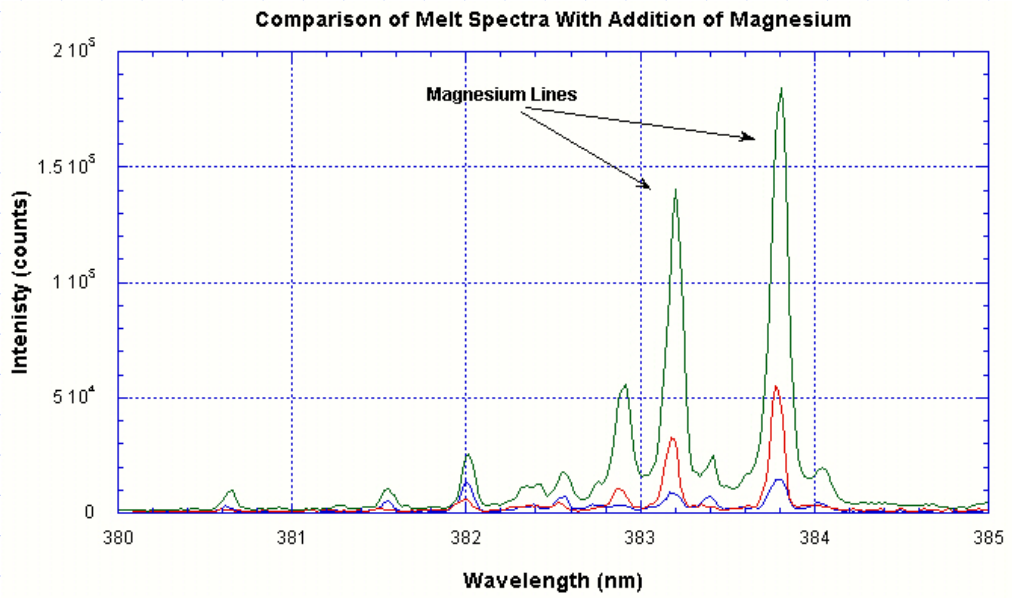
Probe at Pilot Scale Facility



LIBS Equipment at Pilot Test

Pilot Scale Testing

LIBS Data – Change in Composition



Durability

- Probe was immersed in molten aluminum for a total of 130 hours at 800 ºC (1470 ºF)
- Probe is still operable:Neither probe sheath nor the optics suffered degradation

ERCo
Energy Research Company

Aluminum Applications

- Aluminum - In-Line Alloying
- Aluminum - Continuous Furnace
- Advance Science of Furnace Modeling
- Aluminum Scrap Alloy Separation

Conclusions

- Glass LIBS Sensors' Feasibility Proven
- Initial Technology Tests Successful in Laboratory Facility
- Development Proceeding with Industry Guidance

Sandia National Laboratories
Combustion Research Facility

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

A joint project (CRADA) between
PPG Industries, Inc.
and
Sandia National Laboratories

Funded by DOE/Office of Industrial Technologies

J.M. Aaron
November 8, 2001
DOE Glass Project Review
Pacific Northwest National Laboratory

Sandia National Laboratories
Combustion Research Facility

APCVD in the Glass Industry

- Approximately 110 million ft^2/year of float glass is coated using atmospheric pressure chemical vapor deposition (APCVD).
- APCVD coated glass is used mainly for low-emissivity and solar-control windows, but other applications including solar cells, computer screens, automotive glass, and xerography glass are increasing.
- The dual pane window market for APCVD coated glass is nearly $600 million. This is only a fraction of the value of the final product considering the framing.

APCVD Process Difficulties

- Low deposition efficiencies lead to wasted chemical and the high costs associated with purchase, waste treatment, and disposal of the unconverted chemical
- Low process yields due to coating defects result in unproductive energy required for re-melting the glass
- Difficulty in scaling new APCVD processes from laboratory to manufacturing facility requires time and money for development to determine the correct parameters for the manufacturing facility

Sandia National Laboratories
Combustion Research Facility

Potential Benefits to Glass Industry

- Chemical precursor, waste treatment, and waste disposal costs add up to over $23 million per year - doubling reaction efficiency from ~11% to ~22% would halve this cost
- Approximately 4.5×10^{10} BTU per year are used to remelt glass due to coating defects – reducing the fraction of coating defects from 15% to 5% would reduce the amount of unproductive energy usage by ~3×10^{10} BTU per year

Project Objectives

- Identify modified/new APCVD coater designs that double the efficiency of reactant utilization
- Develop validated process models and use them to reduce coating defects (non-uniform coating thickness, haze, chlorine pitting, etc.)
- Generate database of fundamental thermodynamic and kinetic information for chemical precursors
- Provide enhanced understanding of underlying chemistry and physics of APCVD

Project Tasks

- Task 1: Deposition Mechanism Development (SNL)
  - **Thermodynamic Data**
  - **Gas-Phase Chemistry**
  - **Surface Mechanism**
  - **Defect Formation**
- Task 2: Reaction Rate Measurements (SNL and PPG)
  - **Gas Phase Reactions**
  - **Surface Reactions**
- Task 3: On-line Coater Effluent Analysis (SNL and PPG)
- Task 4: CFD Modeling of Coating Reactors (SNL)
- Task 5: Deposition Experiments (SNL and PPG)
  - **Model Validation**
  - **Defect Analysis**
- Task 6: Validation of Optimization Strategies (SNL and PPG)

Team Participants - SNL

- Mark Allendorf (Principal Investigator)
  - **High-temperature chemistry; thermochemistry (quantum-chemistry methods); modeling complex reacting systems**
- Yongkee Chae
  - **CVD processes and modeling**
- Bill Houf
  - **Computational simulation of fluid flow and heat transfer**
- Tony McDaniel
  - **CVD mechanisms (experiments, modeling); on-line process monitoring**
- Steve Rice
  - **Laser diagnostics in high-temperature reacting systems**

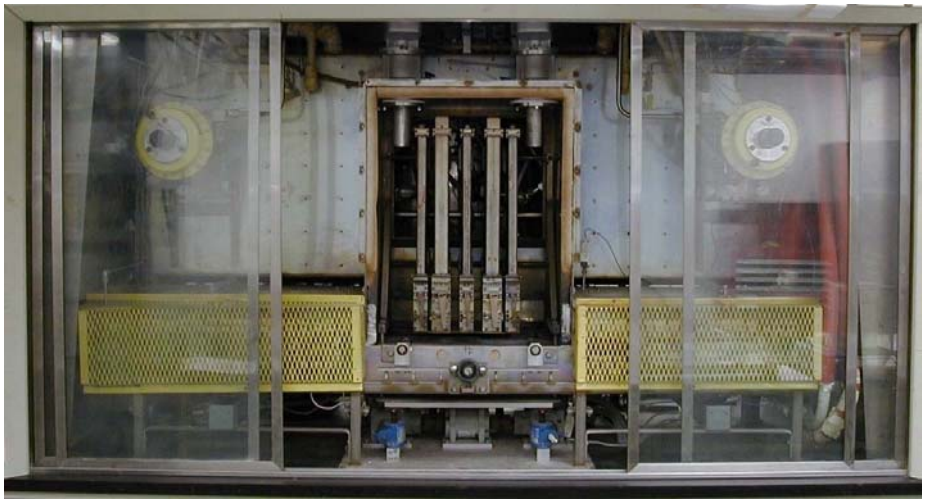
Team Participants - PPG

- Jill Aaron (Principle Investigator)
  - **Improvement, development, and maintenance of CVD processes**
- John Sopko
  - **Improvement, development, and commercialization of CVD processes and products**
- Douglas Dauson
  - **Improvement, development, and maintenance of CVD processes**

Project Kickoff

- On March 5-6, 2001, a meeting was held at PPG's APCVD coating facility in Mt. Zion, IL. Both SNL and PPG personnel were present to discuss the project, the capabilities of each organization, and the information necessary to begin work on the project. SNL personnel were given a tour of the facility.

Pilot Scale Coater at PPG



Pilot Scale Kinetics Experiments – Task 5

- An initial set of experiments varying Mono butyl Tin Trichloride concentration and temperature using only MBTC and oxygen from carrier air for deposition is planned. Data from this set of experiments will be compared with existing data from TNO.
- A second set of experiments varying MBTC concentration and temperature using MBTC, water, and oxygen from carrier air for deposition is planned following completion of the initial set of experiments.

Sandia National Laboratories
Combustion Research Facility

Pilot Scale Kinetics Experiments – Task 5 (cont.)

- A tachometer to measure glass traverse speed and infrared temperature measurement devices to measure glass temperature have been added to the pilot scale coater.
- Programming the software to control the complex system is a larger task than expected. Work is progressing, but unfortunately, it has delayed the start of experiments.

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

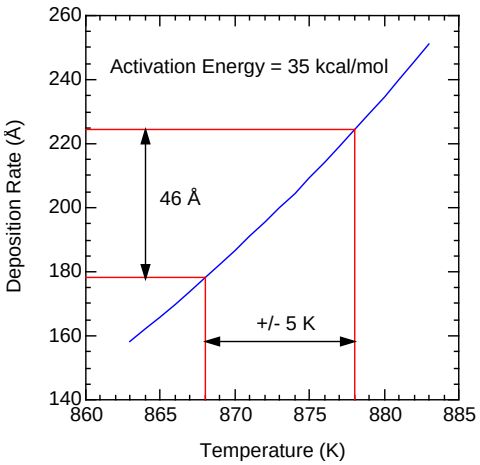
A joint project between
PPG Industries, Inc.
and
Sandia National Laboratories
Livermore, California

Funding from the U.S. DOE/Office of Industrial Technologies
Glass Industry of the Future Team

Project review meeting
Richland, WA
September 19-20, 2001

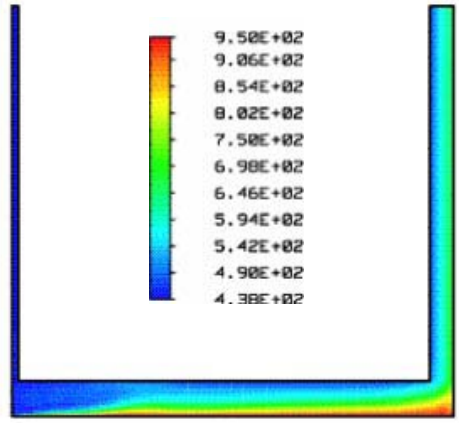
Uniformity of coating thickness is essential for achieving acceptable product quality

- **Thermal inertia of bath minimizes temperature gradients**
- **Heat loss at ribbon edges does occur**
- **Non-uniform gas temperatures can also affect thickness**
- **Typical CVD activation barriers are 20 - 35 kcal/mol**
- **Even small temperature variations (± 5 °C) can lead to major nonuniformities**



Gas-phase reactions play a key, possibly rate-limiting, role in tin oxide APCVD

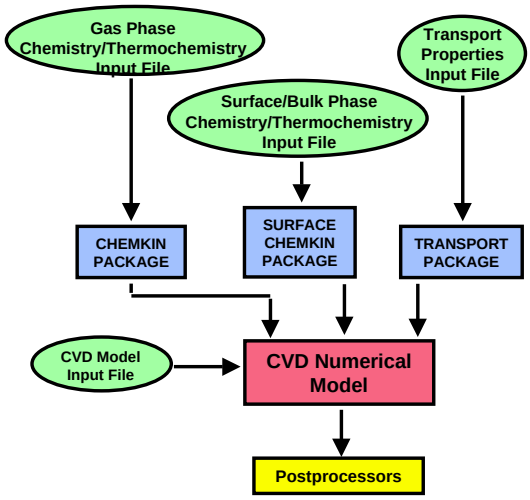
- High temperatures (600 - 700 ºC)
- Relatively weak precursor bonds
  - Sn-C bond in $Cl_3SnC_4H_9$ = 69 kcal/mol
  - C-C bond in C_2H_6 = 91 kcal/mol
- Gas preheating
- Residence times of 1-3 sec



CFD simulation of PPG pilot-scale reactor. Temperature scale is in degrees Kelvin.

Modeling chemically reacting flows requires detailed information about chemistry and transport processes

Modeling Approach using Surface CHEMKIN



- Thermochemistry
  - heats of formation
  - heat capacities
  - entropies
- Chemical kinetics
  - Arrhenius parameters (A, E_a)
  - Pressure dependence
  - Thermochemistry (to calculate reverse reaction rates)
- Mixture transport properties
  - Diffusion constants
  - Viscosities
  - Heat transfer coefficients
- Chemkin application codes:
  - 0-D : CSTR
  - 1-D : Plug-flow, stagnation-flow
  - 2-D : Boundary Layer Flow
  - 3-D : Finite Volume Reacting Flow (STARCD; collaboration with ADAPCO)

Task 1: Deposition mechanism development

Tin precursor oxidation chemistry is likely very complex

- **Fortunately, previous work provides excellent starting points:**
  - **$Sn(CH_3)_4$ and $(CH_3)_2SnCl_2$ kinetics (Gordon et al.)**
  - **Good understanding of silicon chemistry, which may be similar**
  - **Hydrocarbon oxidation chemistry is well understood**
  - **$SnCl_4$ shock-tube data (Roth et al. 2000)**

Accurate thermochemistry for tin compounds the foundation for building a deposition mechanism

- **Knowledge of related chemistry (e.g., oxidation of silicon compounds) suggests a mechanism for MBTC oxidation:**

<u>Uncharacterized reactions</u>:

$Cl_3SnC_4H_9 \leftrightarrow SnCl_3 + C_4H_9$

$SnCl_3 \leftrightarrow SnCl_2 + Cl$ (fast)

$SnCl_2 + O_2 \leftrightarrow Cl_2SnO + O$

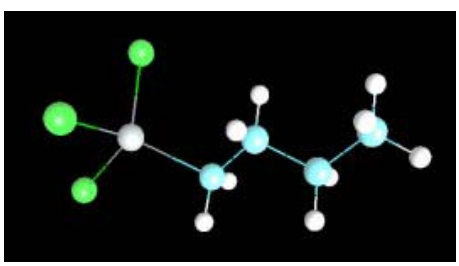
<u>Known reactions</u>:

$C_4H_9 \leftrightarrow C_2H_4 + C_2H_5$ (fast)

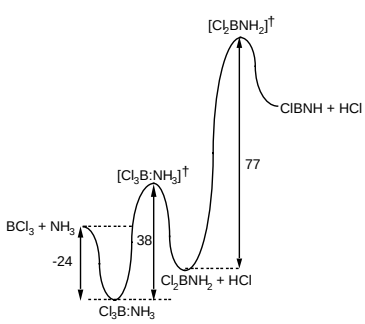
$C_2H_5 \leftrightarrow C_2H_4 + H$

C_2H_4 oxidation reactions

Key model inputs can be obtained from quantum chemistry codes when experimental data don't exist



Structure of $C_4H_9SnCl_3$ precursor



Quantum-chemistry can also predict transition-state energetics

- Bond Additivity Correction methods predict:
  - Thermochemistry
    - Heats of formation (±2 kcal/mol)
    - Entropies and heat capacities
  - Reaction kinetics
    - Activation energies
    - Transition states
- Transition-state theory (e.g., RRKM) predicts reaction rates
- Thermodynamic data for many compounds already generated by BAC method:
  - First row: B, C, N, O, F
  - Second row: Al, Si, P, S, Cl
  - Third row:: Ga, Ge, As
  - Fourth row: In
- Energies for > 60 Sn molecules calculated to date
- Corrections for Sn-H, Sn-C, Sn-Cl complete
- High-level calculations underway to establish thermochemistry of Sn-O species

Task 2: Reaction rate measurements. Year 1 activities

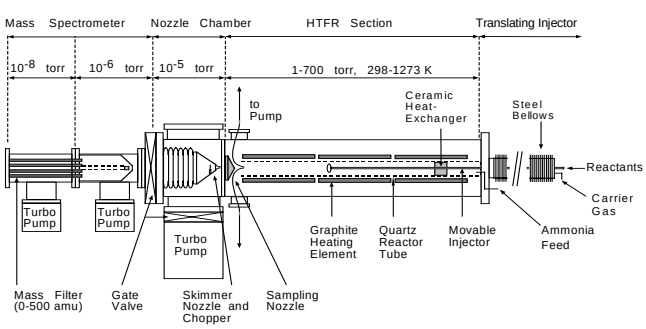
High-temperature flow-reactor measurements

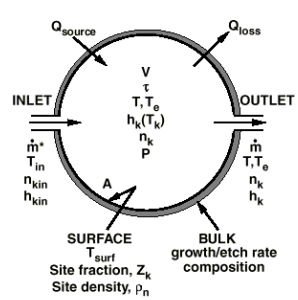
- Modify laboratory precursor delivery equipment to handle tin compounds
- Develop mass-spec detection/calibration scheme for reactants of interest
- Conduct initial scoping experiments:
  - Reactants alone (dilute conditions to avoid secondary reactions)
  - Mixtures representative of process conditions
  - Assess severity of wall reactions
  - Define regimes in which gas-phase chemistry dominates (if possible)
- Provide data for comparison with models developed in Task 1
- Assess need for additional experimental techniques:
  - Optical detection of reactants ("wall-less" conditions)
  - Reaction intermediates

Continuously stirred tank reactor (CSTR) measurements: TNO collaboration

- Limited set of experiments to provide data for MBTC + O_2 (+H_2O) gas-phase chemistry
- Deposition rates

Gas-phase reaction chemistry will be probed using several reactors





Sandia

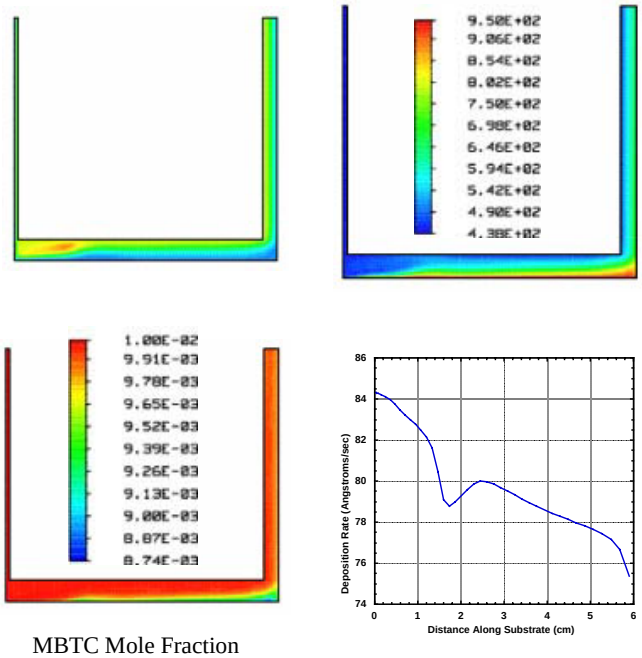
- High-temperature flow reactor
- Modulated molecular-beam mass sampling (0-500 amu) (1 ppm limit)
- 300-1273 K
- 1-100 torr

TNO

- Continuously-stirred tank reactor
- 1 atm
- FTIR species detection (0.1% limit)
- Growth rate via microbalance

Task 4: CFD modeling. Flows in the PPG pilot-scale coater are laminar and well behaved

- 2-D non-reacting calculations completed
- Stationary substrate
- Laminar flow (Re ~ 500) predicted
- Some recirculation
- Global mechanism predicts non-uniform deposition profile
- Reduced mechanisms are needed
- Collaboration with ADAPCO to beta-test StarCD-CHEMKIN for CFD modeling reacting flows



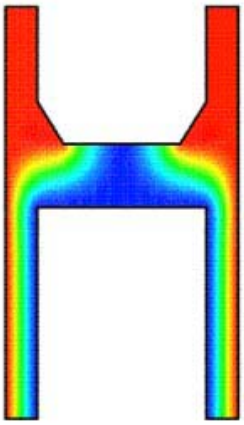
MBTC Mole Fraction

Sandia National Laboratories
Combustion Research Facility

Task 5: Deposition experiments

Model development/validation requires simple reactor geometries to separate chemistry from fluid mechanics

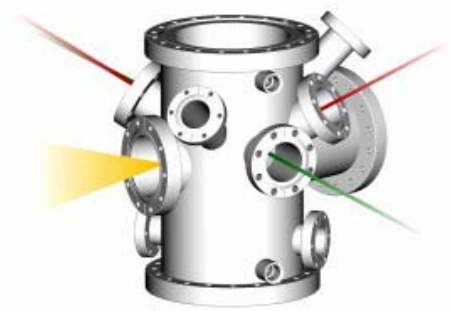
- Full-scale APCVD reactor too complex to model with detailed chemistry
- Stagnation-flow geometry provides:
  - Pseudo 1-D geometry
  - Potential to probe gas-phase with spatial resolution
  - Ability to relate downstream measurements to models (e.g., mass spectrometry)
  - Modeling with detailed chemistry possible
- SPIN/Surface-Chemkin model used to simulate experiments



Sandia National Laboratories
Combustion Research Facility

A flexible design is being adopted for a new stagnation-flow deposition reactor

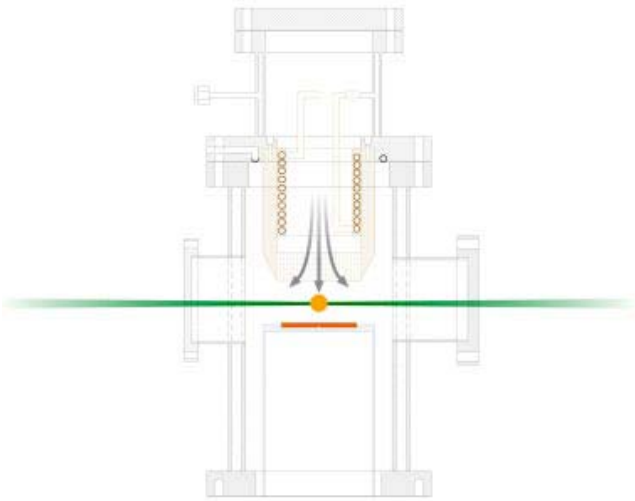
- Design patterned after reactor built at CalTech (Prof. David Goodwin)
- Variable reaction conditions:
  - Pressure (1 - 100 torr)
  - Temperature (up to 800 C)
  - Mass flow controllers for reactants
- Load lock for rapid turnover of substrates
- Complete access for gas-phase and surface optical diagnostics
- Low pressures allow gas-phase boundary layer to be probed



Sandia National Laboratories
Combustion Research Facility

Optical diagnostics provide spatial resolution of gas-phase species concentrations and temperature

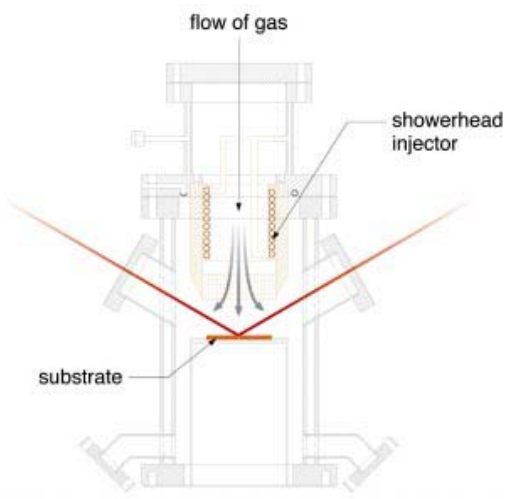
- Laser-induced fluorescence
  - Detect radical (short-lived) species
  - Examples: SnO, OH
- FTIR
  - Stable molecules
  - Line of site technique



Sandia National Laboratories
Combustion Research Facility

Optical methods can also probe the surface

- FTIR to detect adsorbed species
  - Imaging
  - Reflection
- Laser Raman scattering
  - Surface composition
  - On-line monitoring of deposition
- Light scattering
  - Surface roughness



Summary of progress to date

- Task 1: Deposition mechanism development (in progress)
  - Tin thermochemistry predictions (in progress)
  - Gas-phase mechanism (in progress)
- Task 2: Reaction rate measurements (in progress)
  - gas-phase (in progress)
  - surface
- Task 3: On-line coater effluent analysis
- Task 4: CFD modeling (in progress)
  - non-reacting pilot-scale (complete)
  - reacting pilot scale (in progress)
- Task 5: Deposition experiments (in progress)
  - PPG pilot-scale measurements (in progress)
  - CSTR measurements (underway with TNO)
  - New stagnation-flow reactor (design and fabrication underway)
- Task 6: Validation of optimization strategies

Enhanced Cutting and Finishing of Hand Glass using a CO_2 Laser

Steven D. Woodruff,
National Energy Technology Laboratory

John E. Sneckenberger
West Virginia University

In association with
Kim Larew
Rory Flemmer
Larew-Nimbl Consortium

Project Components

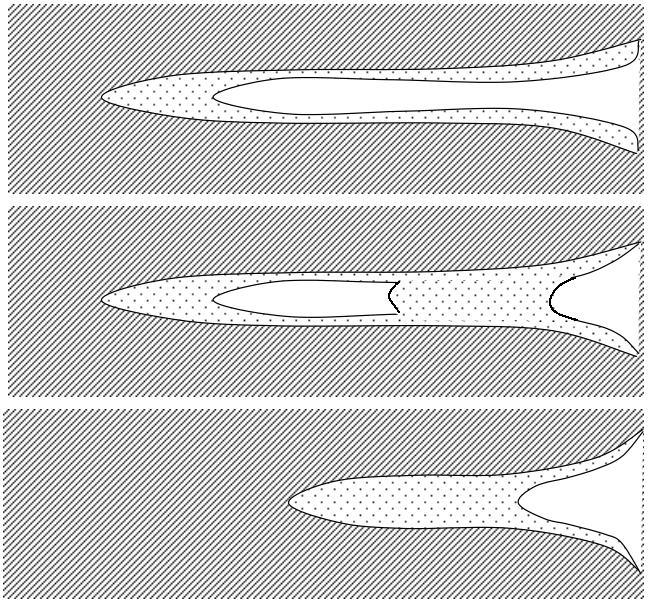
- Development of lab prototype laser-glass cutting machine
- Enhancement to laser-glass cutting process
- Development of plant prototype laser-glass cutting machine
- Factory Testing

Initial Work

Initial findings

- The Laser Glass Cutting Machine cuts glass by melting and vaporization
- The laser glass cutting machines on the market today cut by thermally cracking the glass and are applied to plate glass and circuit wafers
- The Art Glass Industry requires the more controlled cutting action offered by melting and vaporization

Melting/Vaporization Mechanisms

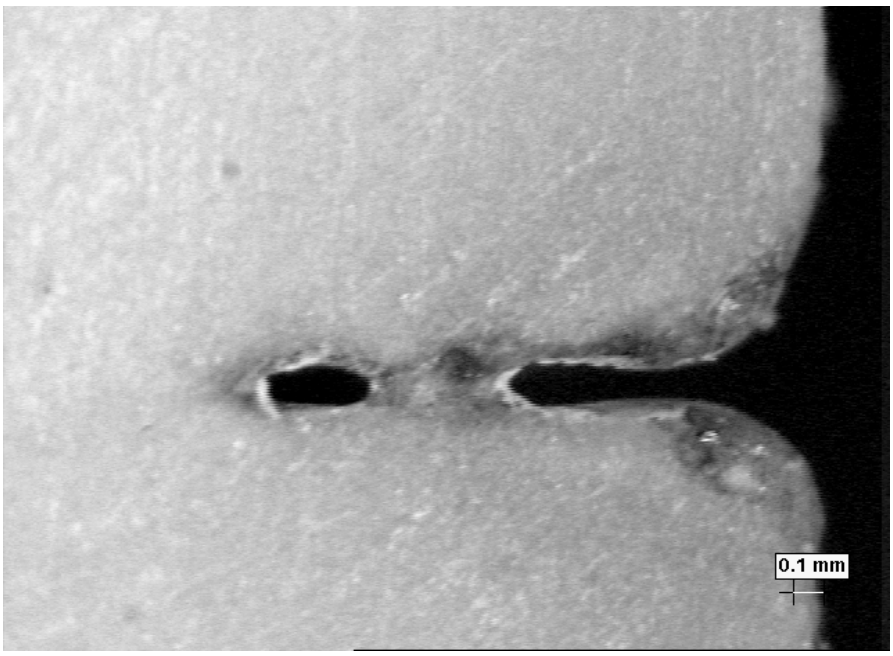


a. Ideal, no resealing

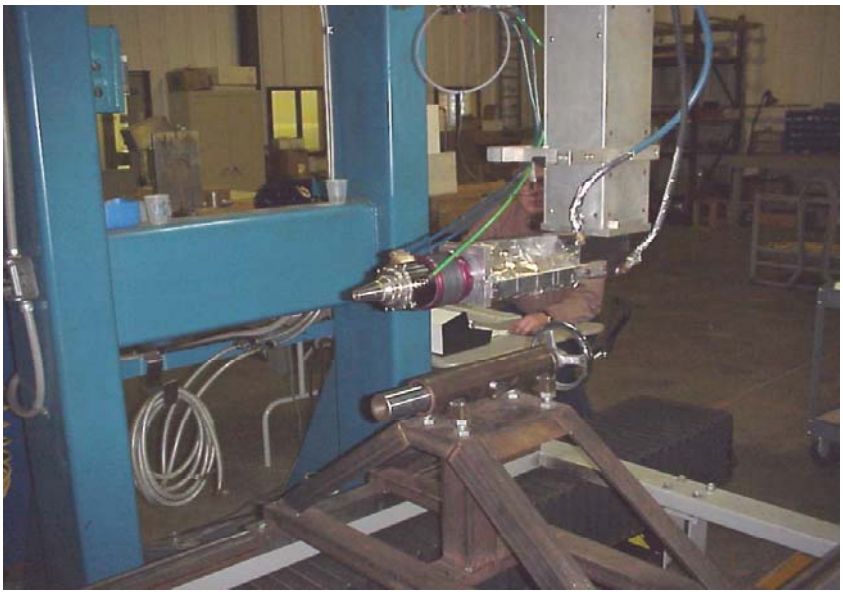
b. Resealing occurs during cutting if glass becomes too liquid from excess heat

c. Resealing prevents cutting from occuring by filling in the cut

Evidence of Resealing



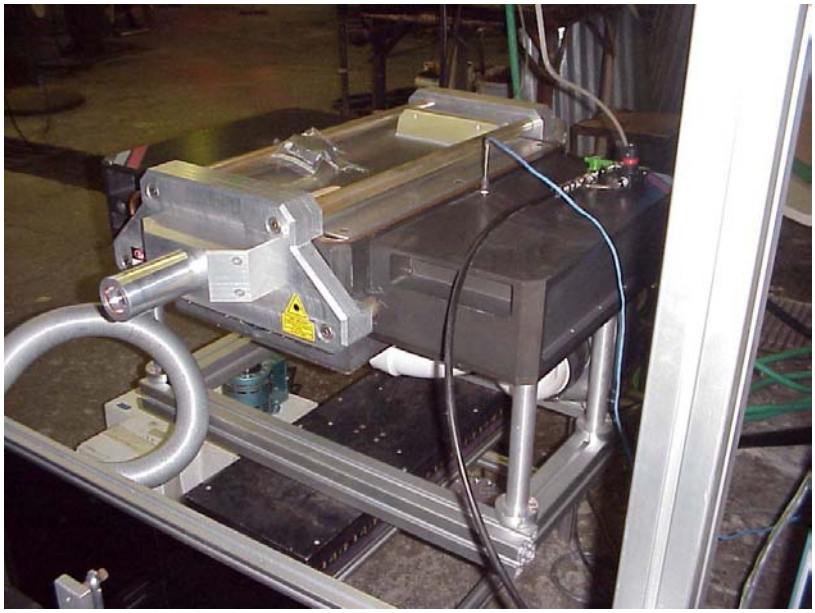
4000 Watt Laser at Laser Processing Company Morgantown, WV



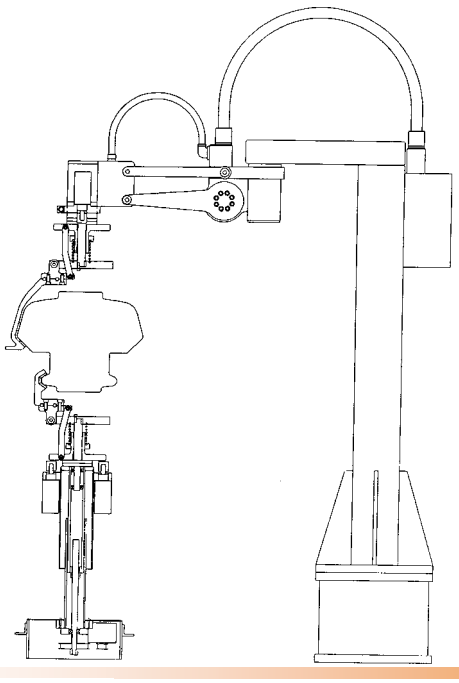
Current Status

- 1300 Watt, TEM00 CO_2 Laser, by Continental Laser Energy installed
- Robotic glass handling system developed by the Nimbl-Larew Consortium completed and installed at Davis-Lynch Glass
- The Laser and Robot will be integrated for tests at three West Virginia Glass factories

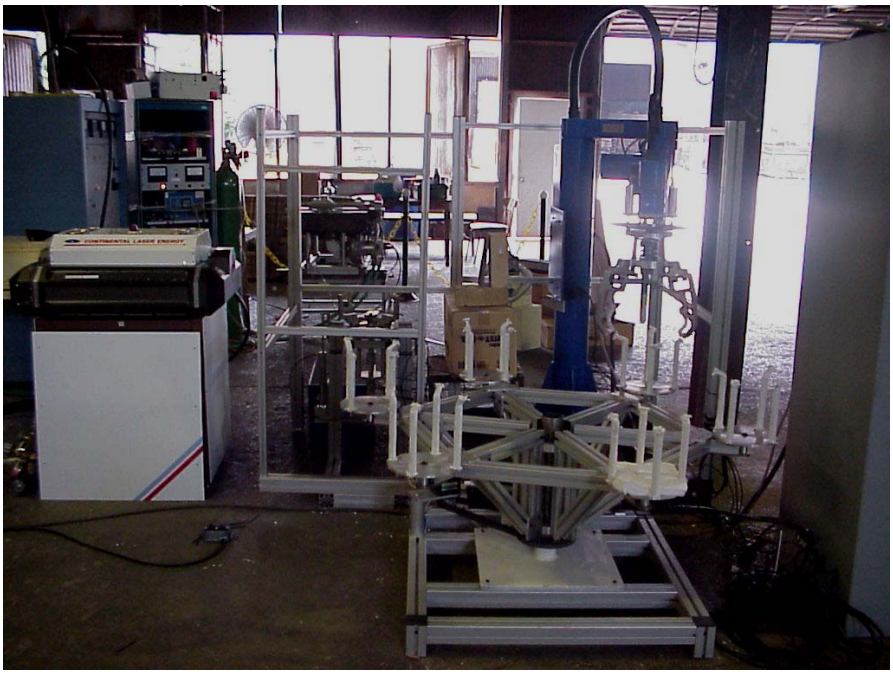
The Continental Laser Energy 1300 watt CO_2 Laser



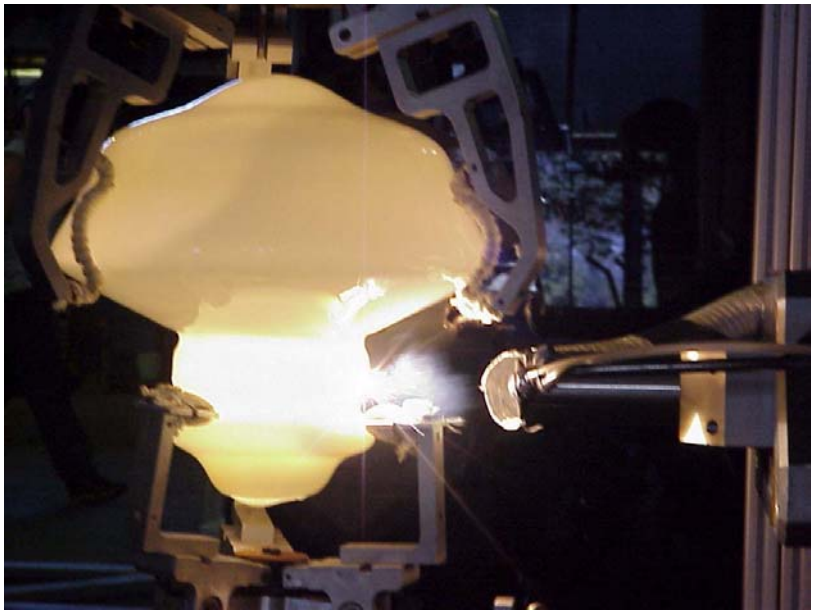
Nimbl Glass Handling Robot



Nimbl Glass Handling Robot



Laser Cutting a Schoolhouse Globe
Davis Lynch Glass, Morgantown, WV



Robot Positioning Schoolhouse Globe at Davis Lynch Glass, Morgantown, WV

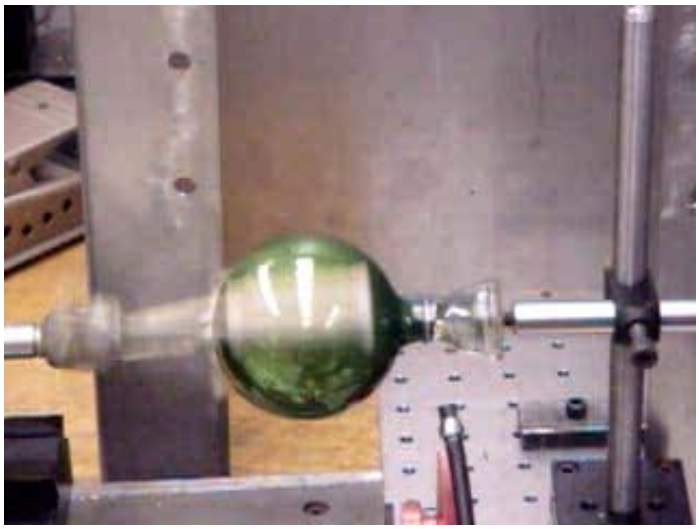
Laser Cutting Schoolhouse Globe

Factory Tests

- Davis-Lynch Glass in Morgantown, WV
  - School House Globes, Milk Glass
- Fenton Art Glass in Williamstown, WV
  - Lamp Shades, Vases, colored glass products
- Third company to be determined
- St. George Crystal
  - In-house tests on Television projection base

St. George Crystal Projector Base

Christmas Tree Bulb



Design of Experiments Results

Process Control of Laser System for Enhanced Glass Production
http//etd.wvu.edu/templates/showETD.cfm?recnum=1718

Dissertation By Liyun Zheng

Development of System Parameters for Enhanced Cutting and Finishing of Handglass Using a CO_2 Laser
http//etd.wvu.edu/templates/showETD.cfm?recnum=1347

Thesis By Chris Thompson

The End

Electrostatic Batch Preheater System Demonstration ("E-Batch")

USDOE
Office of Industrial Technologies
2001 Glass Industry Project Review

BOC GASES

Industrial Team

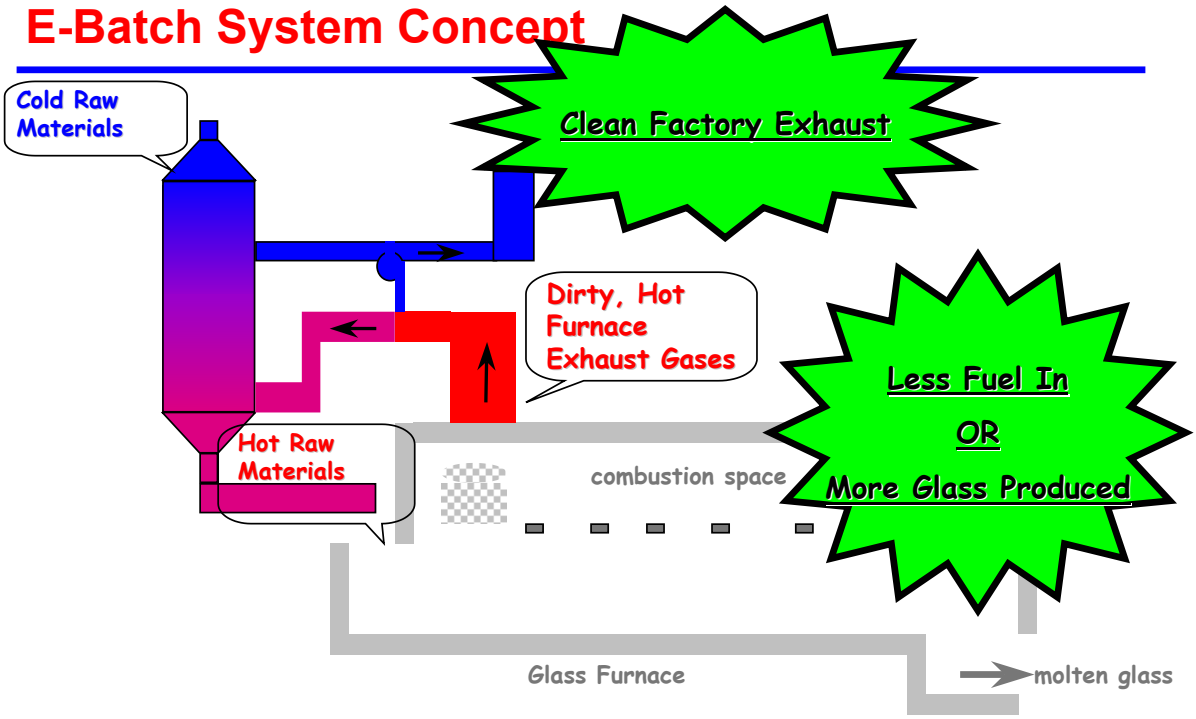
- **BOC**
  - Carl Schatz, PI
  - Neil Simpson, Project Manager
  - Dr. Jeff Alexander, Technical Manager
- **Leone Industries (Host site)**
  - Peter Leone, President
  - Larry Barrickman, Project Manager

Background Information

Pre-OIT

BOC GASES

E-Batch System Concept



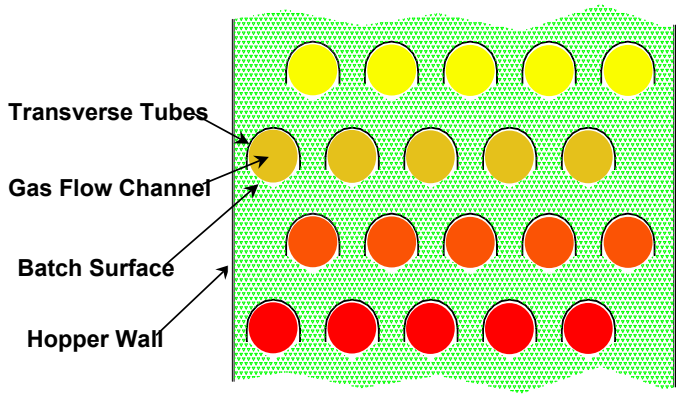
BOC GASES

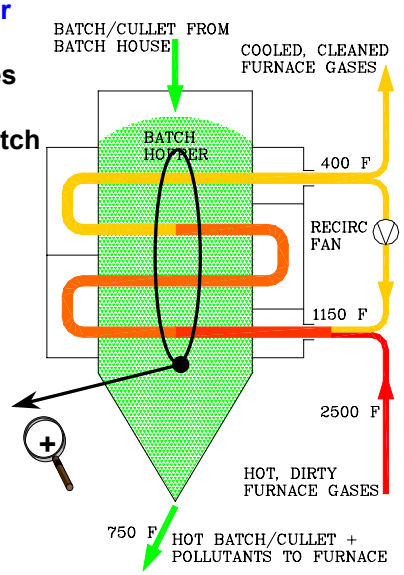
Technology Overview

- A "one box" solution integrated with furnace for :
  - Batch + cullet preheat using furnace exhaust gases
  - Particulate + SOx control
    - » *Contains integral ESP and dry SOx scrubber*
- We expect:
  - 10-25% reduction in energy use, or
  - 10-25% increase in pull rate and
  - NSPS level dust control + SOx removal
- Development Program at BOC:
  - Laboratory testing at Holbrook, UK
    - » *3 tpd - Completed March 2000*
  - Alpha unit - pilot test at Gallo Glass
    - » *12 tpd - First operated September 2000*
  - Beta unit - full scale installation at Leone Industries
    - » *nominally 200 tpd - To be completed under DOE OIT Program*

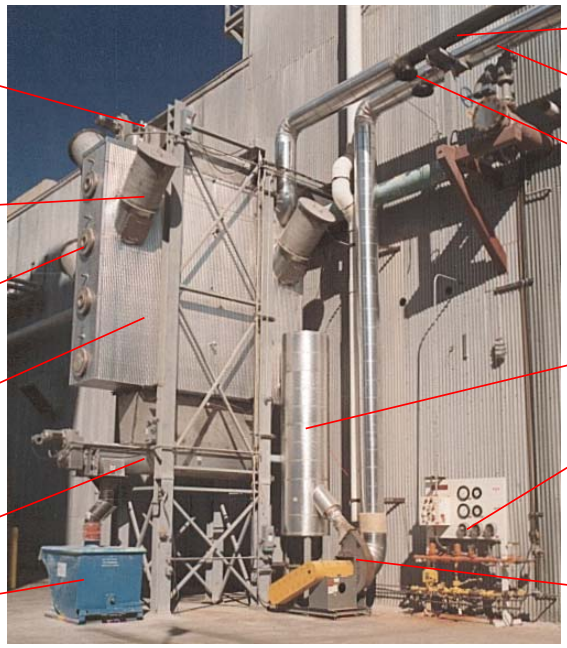
How E-Batch Works

- Hot furnace gases flow through channels in hopper
- Batch/cullet heated by direct contact with hot gases
- Pollutants captured in tubes and deposited into batch
  - uses electrostatic technology, like an EP





Gallo Glass Pilot Unit

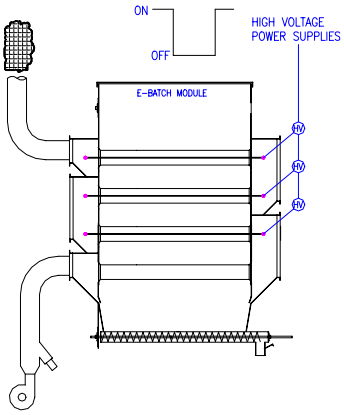


Summary of Pilot Results

- 95% particulate abatement
  - better than most electrostatic precipitators
- 56-66% SOx abatement
  - equal to most lime injection systems
  - even better results are probable
- 15-25% waste heat recovery
  - equal or better than other preheaters
  - preheat to approx 300 deg F of inlet gas temperature
- No batch segregation
- operation with 0 to 100% cullet
  - better than all other preheating systems

Video Clip of Emission Control at Pilot Unit

- Confirmed opacity with High Voltage OFF
- Zero visible discharge with High Voltage ON



--HV ON---/----------HV OFF----------/-----HV ON------

E-Batch Demonstration Project

DOE OIT

Goals of OIT Demonstration Project

- Construct a full sized system
- Operate the system long term (24 months)
  - Determine/resolve operability issues
  - Confirm basic engineering results (nuts and bolts)
  - Confirm broader engineering results (melting process interactions)
- Confirm the economics....
- Provide the fundamentals for commercializing the technology in Glass

Technical Reporting Deliverables (quarterly after startup)

- Heat recovery
  - Quantitative determination of E-Batch effect on amount of waste heat recovered from an oxy-fuel furnace and the resultant effect on the furnace's input energy.
- Emissions abatement
  - Quantitative determination of E-Batch functionality as an emission control device.
- Capacity vs size and cost data
  - Quantitative determination of E-Batch projected costs with respect to a range of furnace capacities as normally used in the glass industry and taking into account the waste heat, emission control information and as-built cost and size at Leone.
- Maintenance
  - Quantitative determination of E-Batch maintenance requirements and costs.
- Operation
  - Qualitative determination of operability issues of E-Batch.
- Effect on furnace
  - Quantitative determination of the effect of highly preheated batch on furnace operation, control, and glass quality.
  - Quantitative determination of the effect of highly preheated batch on furnace refractory structure.

Progress and Status of Work - Overview

- DOE contract awarded to BOC June 28, 2001
- Design and validation of design are 95% complete as of 9/30/01
- BOC has held two meetings with NJ environmental permitting authorities
- Delay in submitting permit application has delayed the project
- All big ticket items are on hold until Leone's permit application is submitted and approved
  - Estimate submittal December 01
  - Estimate approval March 02
  - Project schedule has been adjusted accordingly....

Work Plan - "Was" and "Is"

Item	original completion schedule	current completion schedule
Design and Build:	**Mar 02**	**Nov 02**
Finalize Process Design	Jul 01	Oct 01
Receive Permit Approval	n/a	Mar 02
Procure Materials and Services	Oct 01	Jul 02
On Site Installation	Feb 02	Nov 02
Operational Baselining (eng'g pre-startup furnace study)	Feb 02	Nov 02
Start Up and Debug:	**Jun 02**	**Mar 03**
Commissioning	Mar 02	Dec 02
Initial 90 day Operation, Inspections, and Modifications	Jun 02	Mar 03
Demonstrate, Test, & Report:	**Mar 04**	**Dec 04**
Q1 Eng'g Audit, Conference and Report	Jun 02	Mar 03
Q2 Eng'g Audit, Conference and Report	Sep 02	Jun 03
Q3 Eng'g Audit, Conference and Report	Dec 02	Sep 03
Q4 Eng'g Audit, Conference and Report	Mar 03	Dec 03
Q5 Eng'g Audit, Conference and Report	Jun 03	Mar 04
Q6 Eng'g Audit, Conference and Report	Sep 03	Jun 04
Q7 Eng'g Audit, Conference and Report	Dec 03	Sep 04
Final Eng'g Audit, Conference and Final Report	Mar 04	Dec 04

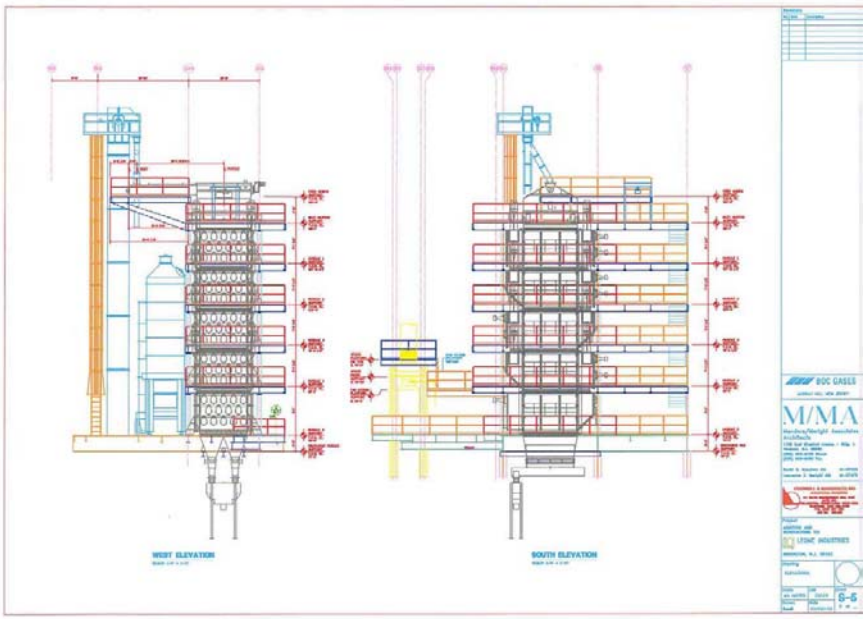
Work Completed in 2001

- Design validation
- System design and construction planning
- Cost and market understanding

System Design and Construction Planning

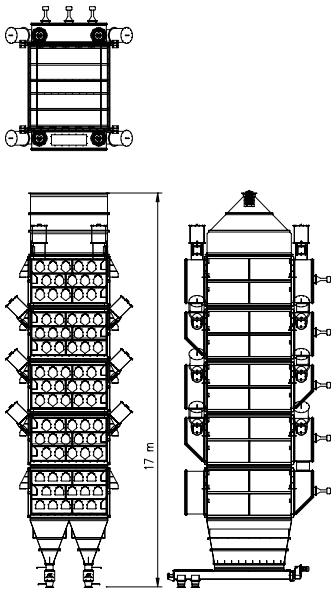
- System engineering, P&ID's
- Detail engineering
  - shop drawings
  - purchase specs
- Structural and field related design
- Process safety and hazop reviews (with Leone)
- Execution/construction plan
- Bids and cost confirmation

Elevation View



200 tpd Beta Unit Overview

- About 12 x 12 x 55 feet tall
- Constructed of 5 individual modules
  - 4 electrostatic zones, 3 required
  - bottom zone preheat only
- Holds ~200+ t. mixed batch and cullet
  - any cullet ratio
- Expect to prove that this unit will be well oversized for a 200 tpd furnace
- Expect this size to handle a 400 tpd oxy fuel furnace
  - NSPS particulate levels
  - to 800 deg F preheat

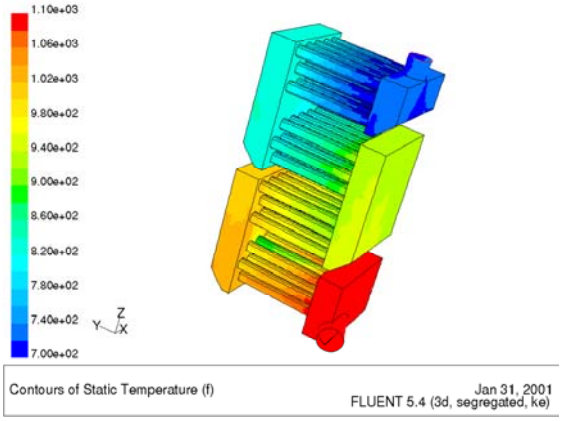


Design Validation Work

- VOC abatement tests (pilot)
  - + design optimization in lab model
- Gas flow modeling (computer)
- Moisture tolerance tests (pilot)
- Drying tests (lab study)
- Abatement vs. flow tests (pilot-Oct '01)
- Insulator design tests (pilot)
- Electrode design tests
- Electrostatic design criteria (eng'g)

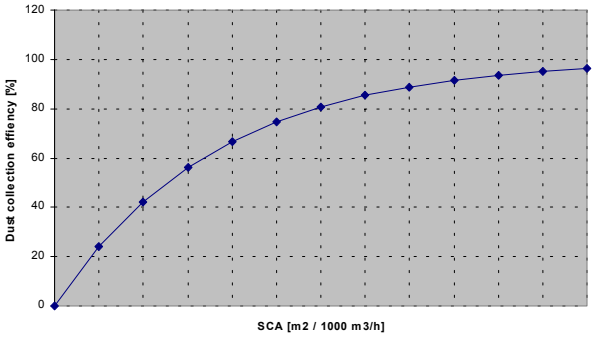
Gas Flow Optimization

- Why Important?
  - Flow balance across elements means each is fully utilized
  - Full utilization reduces excess sizing requirements
  - Smaller overall size = lower cost = economic applicability
- How done?
  - Modeled with Fluent
  - Gave flow velocity distributions
    - » *in tubes*
    - » *across groups of tubes*
  - Allowed viewing effects with design tweaks
  - Net result is balanced flow



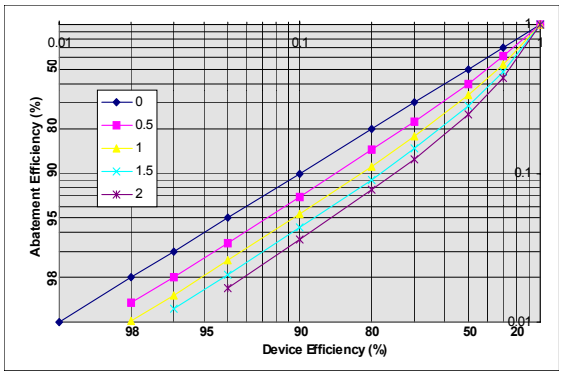
Electrostatic Precipitation -- the SCA

- **What is SCA?**
  - **"Specific Collection Area"**
  - **A measure of surface area for dust collection with respect to flow for an EP**
  - **The primary means of sizing an EP**
- **What is the E-Batch EP?**
  - **A semi-standard tubular type configuration**
    - » *better size to performance ratio than standard flat plate type normally used in glass*
    - » *therefore lower cost per performance*
- **How is the E-Batch EP sized?**
  - **Conservative SCA numbers which are consistent with EP industry practice**
  - **This is primary reason we expect to demonstrate that 200 tpd Beta unit will actually be capable of handling a 400 tpd furnace**



E-Batch System vs Unit Efficiency

- **Overview**
  - **E-Batch uses recirculated cooler gas to quench hot furnace exhaust**
  - **Therefore some of the furnace exhaust goes through the unit twice**
  - **Overall abatement performance is boosted by this recirculation**
  - **Chart shows relationship of overall abatement efficiency to basic module efficiency for several recirculation ratios**
- **Why is this important?**
  - **Furnace exhaust must be quenched anyway**
  - **Improvement in abatement reduces unit size requirement (or allows extra operating margin)**
  - **Reduced size requirement = lower cost**
  - **This is second reason we expect to demonstrate that 200 tpd Beta unit will actually be capable of handling a 400 tpd furnace**

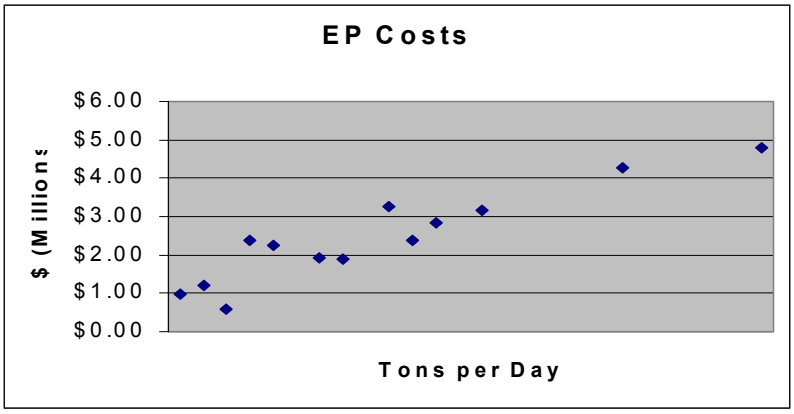


Cost and Market Understanding Work

- Initial capital and operating cost comparisons (favorable)
  - E-Batch
  - Electrostatic precipitator and dry SOx scrubber
- Initial market study (not DOE funded)
  - confirms 30-40 units
  - financial model included

Evaluated EP + Scrubber Cost Structure

- Fixed Costs
  - EP Box
  - Installation
  - Indirect Costs
- Site Specific Costs
  - Auxiliary Equipment
    - » *Ductwork*
  - Dry Scrubber



Evaluated E-Batch over EP/Scrubber Systems

- **Energy savings**
  - 15 - 25% in oxy-fuel furnaces
  - 8 - 12% in air-fuel furnaces
- **Increased productivity**
  - Believe it can be gained in trade for fuel savings
  - 15 - 25% in oxy-fuel furnaces
  - 8 - 12% in regenerative air-fuel furnaces
- **Simpler design**
  - Fewer ductwork requirements
  - No dust handling system required
- **Equivalent air pollution control**
  - 95% dust abatement
  - 56 - 66% SOx abatement

E-Batch Demonstration Project Costs ($000)

FY	OIT	BOC	Total
2001 (act.)	121.6	121.6	243.2
2002 (est.)	548.5	731.5	1280.0
2003 (est.)	528.9	701.1	1230.0
2004 (est.)	0.0	278.2	278.2
TOTALS	1199.0	1832.4	3031.4

End of Presentation

BOC GASES

Development of Models and On-Line Diagnostic Monitors of the High-Temperature Corrosion of Refractories in Oxy/Fuel Glass Furnaces

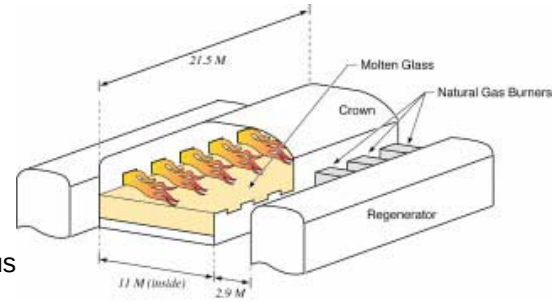
Mark Allendorf
Principal Investigator
Sandia National Laboratories, Livermore, CA
mdallen@sandia.gov

George Pecoraro
Principal Investigator
PPG Industries, Inc., Pittsburgh, PA
pecoraro@ppg.com

A project conducted with support from the
U.S. DOE/Office of Industrial Technologies
and
American Air Liquide, BOC Gases, PPG Industries, Inc., NARCO/Harbison-Walker, Monofrax Inc., University of Missouri-Rolla

The need to understand corrosion processes in oxy/fuel furnaces has several major drivers

- Melting furnaces represent major capital investments for glass manufacturers
  - Example: $10 M to rebuild a float-glass furnace
- Highly competitive industry, so reducing manufacturing costs and increasing productivity are important objectives
- Federal air-quality regulations are tightening, esp. with regard to NOx
- Some refractories used contain hazardous materials (e.g., chromium)



This project has three major objectives

- Identify factors controlling corrosion of refractories
- Develop models to predict corrosion rates based on these factors
- Develop *in-situ* optical techniques to monitor gas-phase alkali concentrations:
  - Process optimization
  - On-line monitoring

Sandia, glass manufacturers, gas suppliers, and refractory manufacturers are working together

- Current consortium members (includes both direct and in-kind cost sharing):

PPG Industries, Inc. (Project PI; furnace gas analysis; direct funding support)
American Air Liquide (CFD modeling; direct funding support)
BOC Gases (direct funding support)
Gallo Glass Co. (corrosion data)
NARCO/Harbison-Walker Refractories (refractory samples; post-mortem analysis)
Monofrax Corp. (refractory samples; corrosion tests; post-mortem analysis)
Pennsylvania State University Dept. of Materials Science and Engineering (thermodynamic calculations)
University of Missouri, Rolla Dept. of Ceramics (corrosion tests; post-mortem analysis; pilot-scale diagnostic tests)

Project Tasks

- Task 1: Experimental characterization of the corrosion process
  - — Simulate corrosion process in controlled laboratory environment
  - — Measure furnace concentrations using conventional methods
  - — Characterize samples of corroded furnace brick
- Task 2: Corrosion modeling
  - — Compile thermodynamic database for predicting corrosion chemistry
  - — Construct models describing corrosion phenomena
  - — Evaluate competition between transport and chemistry
  - — Verify model predictions
- Task 3: On-line monitors for gas-phase alkali detection
  - — Laboratory development/evaluation
  - — *In-situ* furnace testing
  - — Commercialization

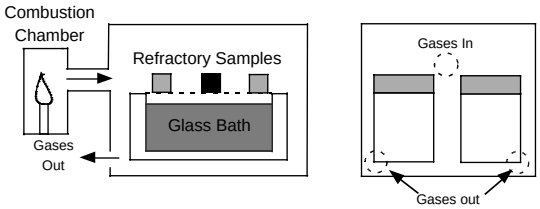
Task 1. Experimental characterization: summary of results

- Industry partners have made major in-kind contributions:
  - Praxair: oxy-fuel burners
  - Monofrax, HW, UMR: sample characterization
  - PPG: measurements of furnace gas composition; batch/cullet for tests
  - BOC: oxygen system for UMR tests
  - Gallo Glass Co.: corrosion data and furnace operating information
- Corrosion tests conducted
  - Monofrax:
    - 2 Air/fuel tests complete; 1 oxy/fuel scheduled
    - Samples: NARCO/HW Vega, Vega O2, Visil, Crownseal I
    - Postmortem analysis by Monofrax and NARCO/HW
    - Air-sampling equipment purchased to enable gas analysis
  - University of Missouri/Rolla:
    - 2 oxy/fuel tests complete
    - Samples: Vega 1, Vega 2, Gensil
    - Post-mortem analysis complete

Corrosion data from laboratory tests, furnace post-mortem analysis, and the literature is being used

- Monofrax tests (oxy/fuel and air/fuel)
- Gallo Tank #1 post mortem
  - operated oxy/fuel for 7 years
  - Furnace rebuild in 1998
  - Gallo provided:
    - Furnace operating conditions
    - Furnace dimensions
    - Photographs and video
    - Harbison-Walker post-mortem analysis of Gen-Sil brick
    - Corrosion rates
- Other data
  - PPG (air-fired)
  - TNO experiments air (1997) and oxy (1998)
  - Corning experiments
  - Paskocimas et al. (1998)

Interior of Gallo Tank 1



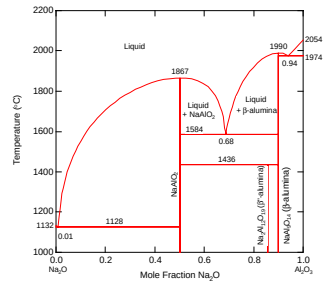
Schematic of Monofrax test facility

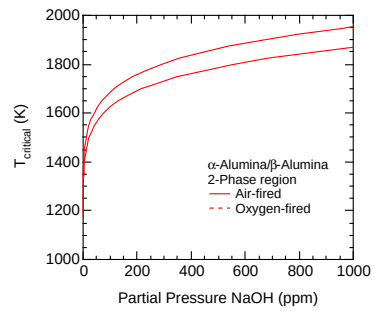
Task 2. Corrosion modeling: summary of results

- Equilibrium predictions of corrosion chemistry
  - Silica corrosion
    - Thermodynamic data for SiO_2/Na_2O and SiO_2/K_2O systems determined
    - Corrosion regimes identified as a function of
      - Temperature
      - NaOH or KOH partial pressure
      - Air/fuel vs. oxy/fuel
    - Two papers describing thermodynamic data published
  - Alumina (Al_2O_3) corrosion by NaOH
    - Thermodynamic data determined for Al_2O_3/Na_2O system
    - Equilibrium calculations completed
    - One paper published; second submitted
- Analysis of possible rate-limiting corrosion mechanisms complete:
  - Gas-phase mass-transport limited corrosion at refractory hot face
  - NaOH(gas) diffusion through pores (“In-depth” corrosion)
  - Na_2O diffusion through liquid corrosion-product layer
  - Chemical-kinetic limited reaction at SiO_2/liquid interface

Thermodynamic analysis of the Al_2O_3/Na_2O system

- Associate species model used to predict properties of liquid phases
- Corrosion reactions:
  - $\alpha \leftrightarrow \beta$-alumina, $T \leq 1974$ °C
  - $\alpha \leftrightarrow$ liquid, $T > 1974$ °C
  - $\beta \leftrightarrow \beta''$-alumina, $T < 1436$ °C
  - $\beta \leftrightarrow NaAlO_2$ at 1436 °C $< T <$ 1584 °C
  - $2\ NaOH(g) + CO_2(g) \leftrightarrow Na_2CO_3 + H_2O(g)$ can also occur
- Alumina is highly resistant to corrosion because:
  - Liquid phase formation requires T " 1584 °C
  - In contrast: liquids form in Na_2O-SiO_2 at T > 817 °C



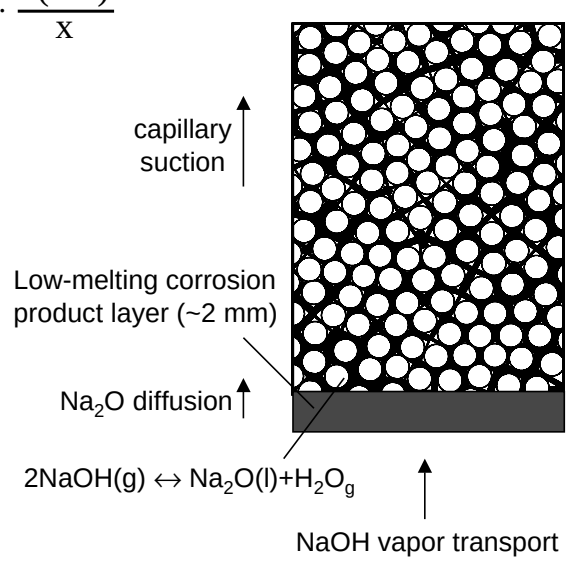


Combining thermochemistry, transport models, and test data yields insight into the corrosion mechanism

$$\frac{dl}{dt} \approx \frac{\rho_{react}}{\rho_{SiO2}}(X_{NaOH,\infty} - X_{NaOH,0}) \cdot \frac{D}{L} \cdot \frac{2(1-x)}{x}$$

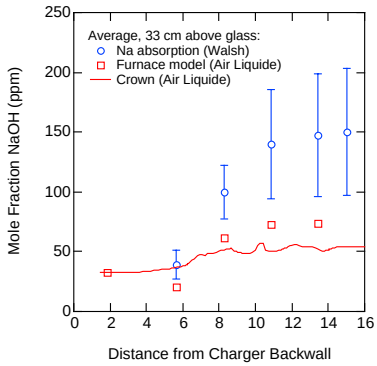
Possible rate-limiting mechanisms:

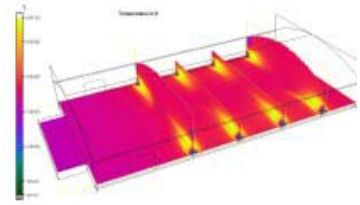
- *Gas Phase Transport:* NaOH(g) is transported from melt surface to crown surface and reacts there
- *Liquid-Phase Diffusion:* Na_2O diffuses through melt layer and reacts with silica to form liquid glass
- *NaOH transport through pores:* reaction occurs in depth via gas-phase diffusion
- *Kinetic limitations:* recession is limited by chemical reaction



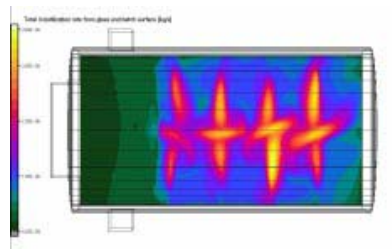
Air Liquide modeled Gallo Tank #1 using their state-of-the-art furnace code to provide critical data for modeling

- 3-D model of combustion space
- Calculations provide:
  - Gas temperatures, velocities
  - NaOH, H_2O concentrations





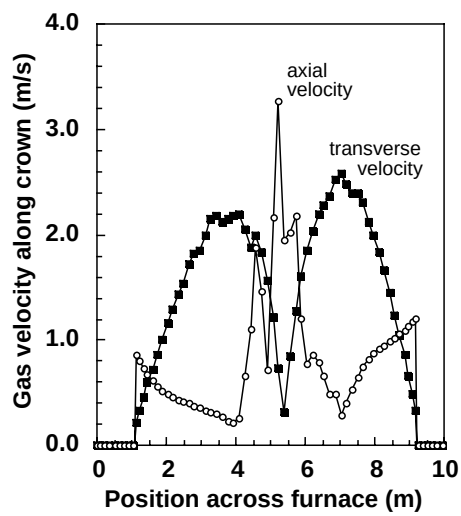
Gas temperatures



NaOH release rate from batch

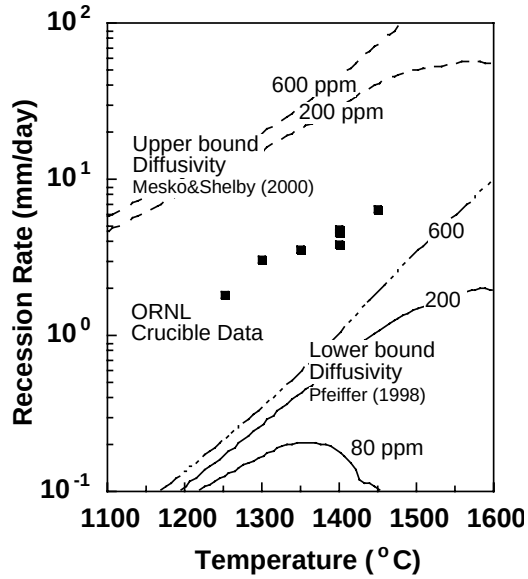
Air Liquide CFD models predict gas velocities along crown on the order of 1 m/s

- Burner jet velocities of ~ 30 m/s drive convective roll cells within furnace.
- Resulting gas speeds along crown average to ~1.5 m/s
- Axial velocities along furnace crown are also ~ 1m/s
- These velocities are used to compute NaOH transport through gas boundary layer to crown surface
- Comparable to 1-2 m/s velocities computed & observed for air/fuel furnaces



Diffusion of Na_2O through liquid product layer permits corrosion rates greatly exceeding field observations

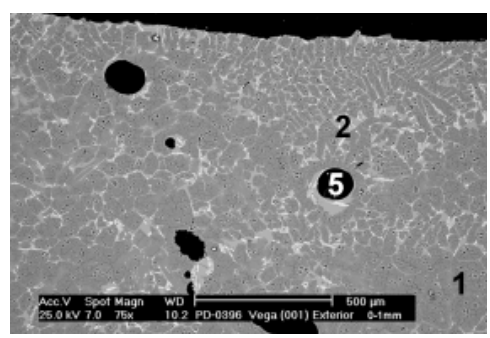
- Layer thickness, δ~3 mm, on hot face is estimated using Rayleigh Taylor stability criterion
- Recession rate is proportional to difference in Na_2O concentration, $\Delta C = C_{l,s} - C_{l,s}$, across liquid layer
  - $C_{l,g}$ in equilibrium with gas
  - $C_{l,s}$ full equilibrium
- Diffusion-limited model is consistent with rates measured in ORNL crucible tests
- Computed recession rates are about 100X greater than those observed in glass furnaces
- Conclude that diffusion through liquid layer does not limit crown corrosion



Glassy phase within bricks appears to be drawn in by capillary suction rather than being formed at depth

- Photomicrographs show:
  - small pores appear to fill first
  - large pores are not surrounded by halos of reacted material
  - brick surface appears to be sealed by liquid layer (~ 1mm thick)

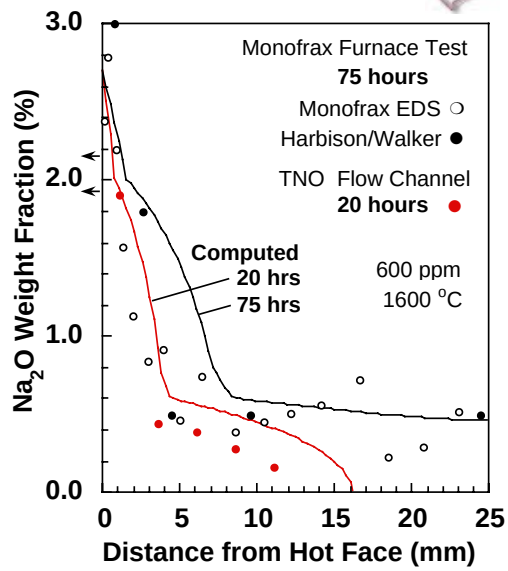
  → gas reaction is not occurring at depth
- Small pores appear to be glass filled
  - consistent with capillary infiltration
- Computed capillary uptake is sufficient to rapidly fill small pores comprising about 50% of porosity



Vega sample from Monofrax oxy/fuel test

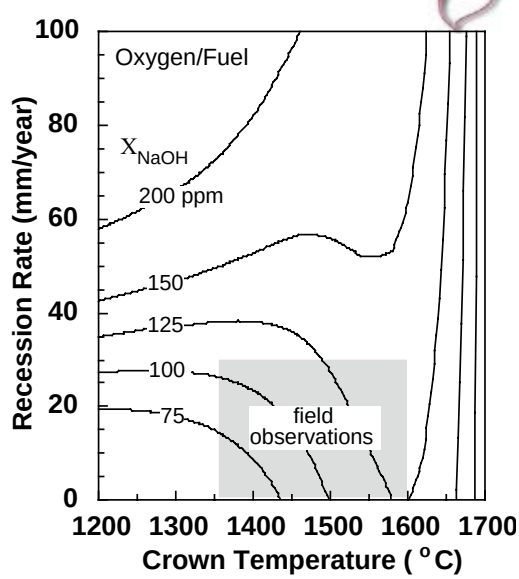
Measured penetration depths by Monofrax and TNO are consistent with capillary infiltration model

- Infiltration model describing gas/liquid flow in porous media is similar to those used in
  - hydrology
  - petroleum engineering
- Model utilizes measured data
  - Porosity and capillary pressure curves from Harbison Walker
  - Viscosity variation with temperature and Na_2O
  - 6% Na_2O in glass liquid
- Infiltration rates are comparable to those observed
  - Supports hypothesis that corrosion occurs mainly at hot face



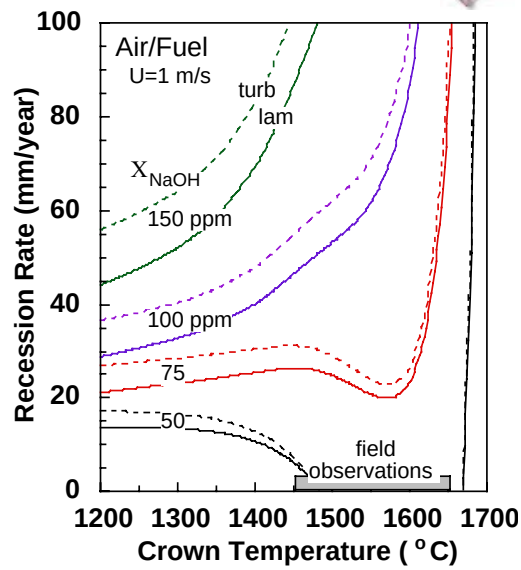
Gas transport within Oxy/Fuel furnace will support recession rates >100 mm/yr for 200 ppm NaOH

- Mass transfer through boundary layers is computed for Gallo case
  - 1 m/s gas velocity; 10 m width
  - laminar boundary layer
- Predicted corrosion rates for 200 ppm NaOH are several times greater than maximum observed rates of ~30 mm/year
- Calculations become consistent with observations if either -
  - NaOH in furnace < 125 ppm
  - Equilibrium NaOH pressures are <u>slightly</u> greater than predicted by thermodynamic models



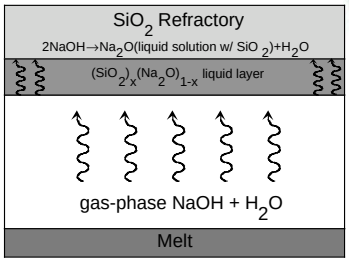
Gas transport within Air/Fuel furnace will support recession rates of 25 mm/yr for 75 ppm NaOH

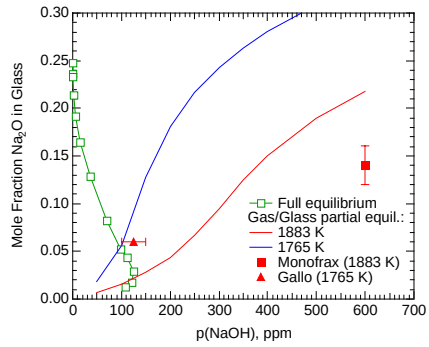
- Mass transfer through boundary layers is computed using:
  - Laminar and turbulent boundary layer models
- Predicted corrosion rates for 75 ppm are 10X greater than typical observations of ~3mm/year
- Calculations become consistent with observations if either -
  - NaOH in furnace < 60 ppm
  - Equilibrium NaOH pressures are slightly greater than predicted by thermodynamic models (off by just 5-10 ppm)



Evidence suggests silica corrosion is limited by chemical reaction at the liquid/grain interface

- Monofrax (1883 K, 600 ppm NaOH, 72 hrs):
  - Full equilibrium: ~3% Na_2O in SiO_2
  - Gas/liquid equilibrium: 22% Na_2O in SiO_2
  - Observed: 9-16 % at surface
- Gallo (125±25 ppm NaOH, T≥ 1765 K, 7 year campaign):
  - Full equilibrium: 5.5% Na_2O in SiO_2
  - Gas/liquid equilibrium: 9.0% Na_2O in SiO_2
  - Observed: ~ 6% Na_2O throughout a 25-cm brick (5 m from batch inlet)
- Data suggest:
  - Initial kinetic limitation to corrosion
  - Long-term reaction may be close to full equilibrium, but kinetic limitation is feasible
    - Requires $T_{crown} > T_{breast\ wall}$ in Gallo furnace





Reaction at liquid-particle interface

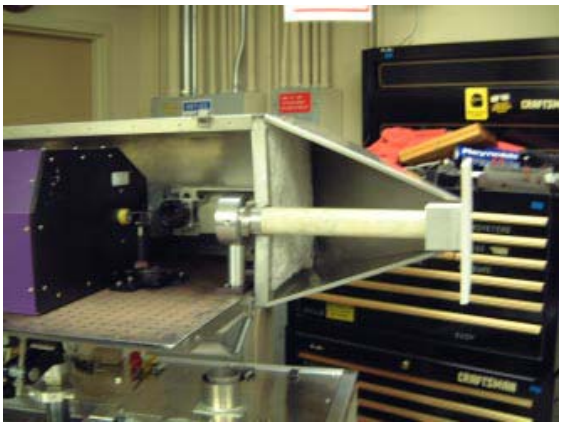
Modeling conclusions

- *"You can never prove a mechanism, you can only disprove it…" Anonymous scientist*
- Two potential rate-limiting steps have been eliminated:
  - Diffusion through product layer
  - In-depth corrosion
- Gas phase transport could be the rate-limiting mechanism, but requires either:
  - NaOH concentrations less than generally accepted
  - Predicted equilibrium NaOH pressures are slightly low
- A chemical-kinetic limitation is possible if:
  - Measured breast-wall temperatures in Gallo Tank 1 are somewhat lower than crown temperatures
- Predicted corrosion rates are very sensitive to:
  - Gas-phase NaOH concentration
  - Solubility of Na_2O in SiO_2 at equilibrium
  - Crown temperature
- Clearly, additional measurements of both NaOH and temperature would be helpful in validating model predictions

Task 3: NaOH Field Unit based on excimer-laser-induced fragmentation fluorescence (ELIF) complete

FY01 Accomplishments

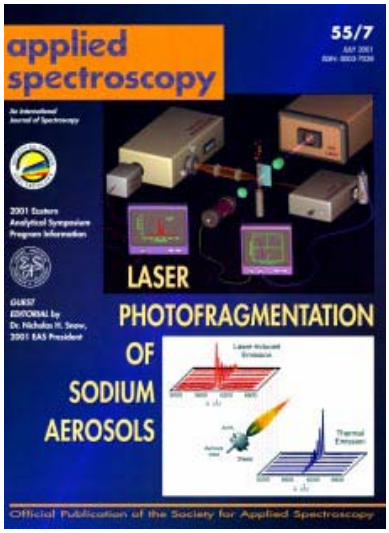
- Designed and fabricated portable Furnace Environment Sensor System
- Characterized O_2 and CO_2 attenuation up to 1600 °C
- Extended ELIF method to KOH
- Visited UM Rolla - preliminary evaluation of facility for field test
- Coordinate w/ UMR for field visit- ES&H and other admin. activities
- UMR field test scheduled for 12/03/01.



Sensor head cross section showing excimer laser (purple box), imaging optics, and heat shield.

ELIF based on new rapidly developing technology

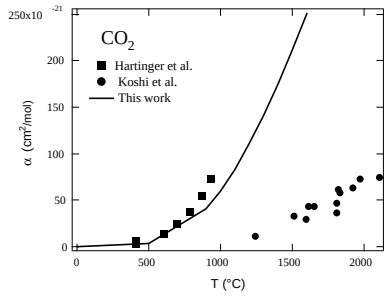
- Laser Photofragmentation, (LPF); Excimer Laser Induced Fragmentation (ELIF); Laser Induced Fragmentation Fluorescence (LIFF); & more - essentially the same method
- ELIF provides an *in-situ* measurement and effectively reduces problems associated with bright furnace background
- Method is easily made portable

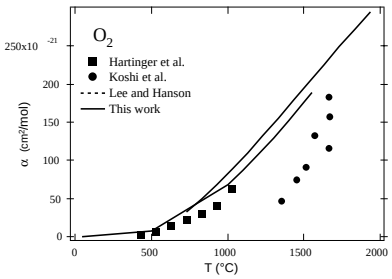


July, 2001

Completed bench-scale development spectroscopy

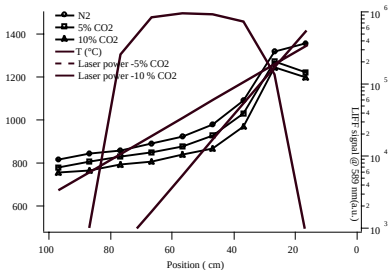
- Paper accepted by *Applied Spectroscopy* on attenuation of 193 nm UV light by O_2 and CO_2
- These results extend the recent work of Hartinger et al. to temperatures relevant to glass furnaces
- The results confirm earlier suspicions that the actual high temperature absorptivity is much greater than had been reported previously

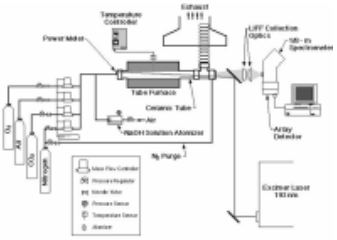




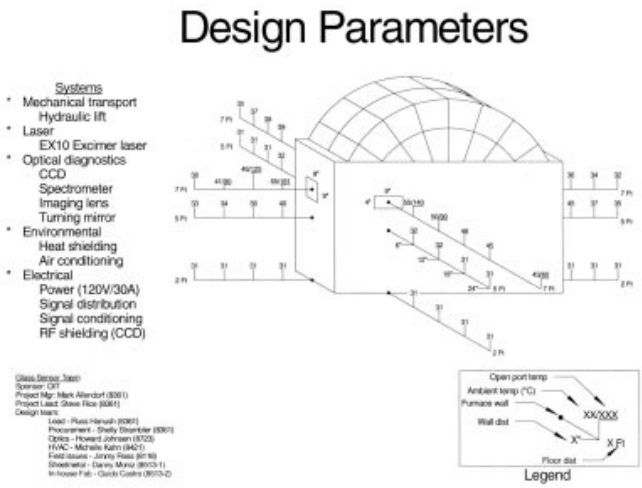
Tube furnace experiments point to the need to calibrate ELIF in a larger furnace volume

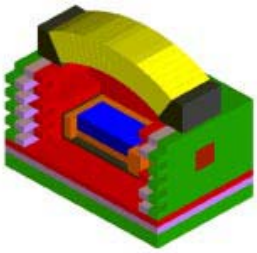
- Scatter from tube walls interferes with calibration at depths greater than 40 cm.
- UMR furnace volume will remove this interference
- Imaging hardware ruggedized for industrial environment
- Depth-of-measurement calibration procedures established for field environments are different from lab environment





Visit to UMR Rolla in 12/00 guided ELIF design for glass furnaces and portability strategy



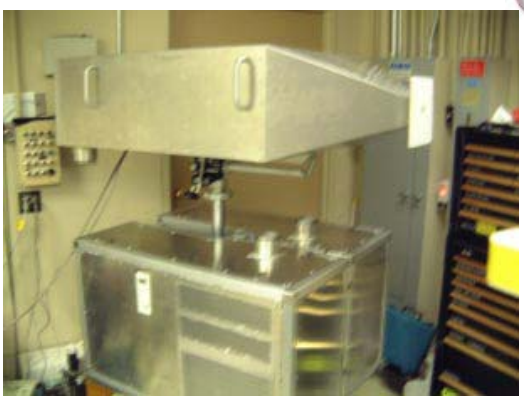


UM Rolla Furnace

Portable gas handling system

ELIF trial runs at UMR scheduled for 12/03-12/07

- UMR field test will establish field deployment logistics for full-scale field tests:
  - Crating and shipping
  - Field assembly
  - Excimer gas handling
  - Safety procedures
  - Toolbox and spare parts
  - Data collection rates
- Tests will also
  - contribute to UMR's understanding of spatial and temporal NaOH fluctuations in their experiments.
  - allow direct comparison of NaOH extractive sampling measurements with an in-situ measurement



Portable ELIF system fully assembled w/o air ducting. Electronics in lower case with dual air conditioning units. Sensor head on top with heat shield and fire-brick nose for placing adjacent to furnace port.

FY02 Activities

- Task 1
  - Complete remaining oxy/fuel corrosion testing at Monofrax
- Task 2
  - Thermodynamic modeling:
    - $SiO_2/Na_2O/CaO_2$
  - Transport modeling:
    - Develop prototype corrosion submodel software for use in CFD furnace models
- Task 3
  - Complete UMR field test
  - Schedule and two full-scale field tests, subject to UMR results
    - PPG/Fresno oxy/fuel facility
    - Gallo/Modesto container-glass facility

Acknowledgements

- Sandia National Laboratories
  - Dr. Robert Nilson (transport modeling)
  - Dr. Steven Rice (laser diagnostics)
  - Dr. Peter Walsh (technical discussions)
  - Dr. Nancy Yang (electron microscopy)
- NARCO/Harbison-Walker Refractories
  - Ed Wolfe (refractory post mortem analysis)
- Monofrax Inc.
  - Dr. Amul Gupta (corrosion testing)
- Gallo Glass Inc.: John Neufeld (furnace data)
- Pennsylvania State University: Prof. Karl Spear (thermodynamic calculations)
- American Air Liquide (CFD calculations)
  - Dr. Ovidiu Marin
  - Dr. Ben Bugeat

Melt Properties Measurements at the Center for Glass Research

Thomas P. Seward III, Director

November 9, 2001

Outline

- Project participants
- Objectives of this study
- Properties being investigated
- Methodology and example results
- Status

DOE-CGR Project at Alfred University

- Grant # DE-FG-02-96-EE41262
- Title
  - » Modeling of Glassmaking Processes for Improved Efficiency
- Sub-title
  - » High Temperature Glass Melt Property Database for Modeling

DOE-CGR Project at Alfred University

- Multi-year, multi-investigator project
- Two phases
  - » Property measurements and database generation
  - » Evaluation by industry process modelers
- Principal Investigators
  - » T.P. Seward, W.C. LaCourse, A.G. Clare, J.E. Shelby, A.K. Varshneya, D.Oksoy, D. Earl
- Sub-contracts with Thermex Company, St. Petersburg, Russia - O.H. Prokhorenko

Project Objective

- To develop a high-temperature melt properties database with sufficient reliability to allow mathematical modeling of glass melting and forming processes
- In response to melt properties measurements needs established at the DOE-CGR jointly sponsored 1996 “Modeling Workshop”

Properties Being Studied (DOE & CGR funding)

- Gas solubility and diffusion (CGR)
- Density, thermal expansion, and surface tension
- Viscosity (including non-Newtonian effects)
- Electrical resistivity
- Radiative thermal conductivity
- Redox (oxygen partial pressure)
- Glass physical properties (CGR)

Families of Glasses (Commercial Base Glasses)

Component	Container	Float	E-Glass	TV Panel	Low α Borosilicate	Wool
SiO_2	74.05	73.1	55	61.29	81	62
Al_2O_3	1.26	0.10	15	1.96	2	4.0
Fe_2O_3	0.031	0.5	0.4	0.044		0.3
TiO_2	<0.01	0.02	0.5	0.42		
CaO	10.53	8.9	18	0.06		8.0
MgO	0.20	3.8	4.0			4.0
SrO	<0.01			9.15		
BaO	<0.01			9.32		
PbO				0.03		
Na_2O	13.49	13.7	0.5	7.46	4	16
K_2O	0.27	0.1		7.59		1.0
B_2O_3			7		13	5.0
Li_2O				0.002		
As_2O_3						
Sb_2O_3				0.27		
CeO_2				0.27		
MnO_2	<0.007					
Cr_2O_3						
SO_2	0.22					0.2
ZrO_2	<0.03			1.46		
ZnO				0.48		
F_2			0.2	0.002		

All Values in Weight %

Melting and Chemical Analysis

- Composition variations statistically designed about the six base glasses
- Melting program:
  - » Phase I - 15 melts per “family”
  - » Phase II - 10 additional melts per “family”
- Phase II now complete in three of six families, almost complete in other three (approximately 100 glass melts to date)

Solubility

- Helium
  - » Measurements completed for all six commercial base glasses (1000°C - 1350°C)
- Neon
  - » Little CGR interest; low TCE borosilicate done
- Argon
  - » Measurements in progress; about 50% complete
- Nitrogen
  - » Abandoned - solubility below detection limits of the instrumentation

Solubility continued

- CO_2
  - » Work funded by CGR members
  - » Measurements complete for all six commercial base glasses
  - » Solubility much lower than in the more basic (highly modified) silicate glasses generally reported in the literature
  - » Examples follow:

Solubility continued

- Water (H_2O)
  - » Work funded by CGR members
  - » Solubility, diffusivity and extinction coefficients determined for all six commercial base glasses
  - » Some data follows:

Solubility continued

- SO_2
  - » Work funded by CGR at Thermex Company in St. Petersburg, Russia (O. Prokhorenko)
  - » Experimental techniques and analysis methods developed for solubility and diffusion
  - » Measurements completed for a commercial soda lime silica glass
  - » Predictive mathematical models for diffusion and outgassing developed

Density and Surface Tension

- Sessile and pendent drop techniques developed; algorithms written
- Atmosphere varied
- Volatility effects studied
- Measurements completed on five of the six commercial base glasses
- Some examples follow:

Viscosity

- Rotating Spindle (10^1 to 10^4 Poise)
  - » Measurements complete for all six commercial base glasses
  - » Measurements near complete for container and “wool” composition variations
  - » Plagued during 2000-2001 by equipment failures
  - » Significantly behind schedule

Viscosity continued

- Parallel Plate (10^5 to 10^9 Poise)
  - » Software rewritten
  - » Measurements started again this September with undergraduate student
- Beam Bending (10^{10} to 10^{13} Poise)
  - » Work began this year, funded by CGR
  - » Measurements complete on 13 container, 10 float, 23 E-glass, 25 TV Panel, 25 low- expansion borosilicate and 14 “wool”

Non-Newtonian Viscosity

- Installed parallel plate viscometer on hydraulic Instron™ testing machine
- Measured six base glasses at ~ 10^{10} Pa·s and seven strain rates
- Deviations from Newtonian behavior characterized
- Data being used by at least one CGR member

Electrical Resistivity

- Two-probe system operating and calibrated
- Resistivity measured between 900˚C and 1450˚C for
  - » SRM 1414 NIST standard glass
  - » All six commercial base glasses
  - » All 24 TV panel glass compositions
  - » Most of the low expansion borosilicates

Radiative Conductivity

- Work conducted at Thermex Company (St. Petersburg, Russia - O. Prokhorenko)
- High temperature (600ºC-1450ºC) spectrophotometer and sample cells constructed; Measurement techniques developed
- Measurements complete on all six commercial base glasses
- Examples follow:

Redox (oxygen partial pressure)

- Recognized need to measure oxygen partial pressure for glasses whose properties (such as radiative thermal conductivity) depend on redox state of dissolved ions
- Rapidox™ apparatus installed
- Measurements complete on five of the six commercial base glasses

Glass Physical Properties

- Physical properties measured:
  - » Density
  - » Refractive index
  - » Coefficient of thermal expansion
  - » Dilatometric softening point
  - » Glass transition temperature
  - » Dissolved water concentration
  - » Electrical conductivity (at 200˚C & 300˚C)

Status

- Measurements completed on all six commercial base glasses, for most properties
- Melting of Phase I and II glasses (with designed composition variations) is about 80% complete

Status continued

- Remaining to do:
  - Complete chemical analysis and property measurements on Phase II composition variations
  - Perform statistical analysis of data
  - Obtain evaluation of database by CGR member companies

Approximate Milestones

- October 2001 - Begin statistical analysis of available data
- November 2001 - Complete Phase II melting
- December 2001 - Complete property measurements (except viscosity); begin data transfer to member companies
- March 2002 - Complete viscosity measurements

Examples

- Glass composition ranges and examples of measurement results can be found on the CGR Web site at:
  <http://cgr.alfred.edu/meltprops/meltprops.html>

Advanced Process Control System for Glass Production

CL Shepard, MA Khaleel, KI Johnson,
A. Mendoza, and JT Munley
Pacific Northwest National Laboratory

Industrial Partner:
L Malinowski, M Ehrlich, A Hoque, and K Matin
Thomson Multimedia

DOE-OIT Glass Project Review Meeting
Richland, WA
November 7-8, 2001

Project Goals

- Enhance process control and quality assurance in the manufacture of TV glass panels through the development of:
  - Process control software based on Thomson's historical plant data and advanced sensor and modeling technologies.
  - Advanced non-contact sensors for the measurement of temperature during the forming process and stress distribution in the final product.
  - Non-linear finite element (FE) models for describing glass-metal mold interaction, optimization of the forming process,and generation of databases in support of process control.

Technical Approach for Achieving Project Goals are Contained in 4 Major Tasks

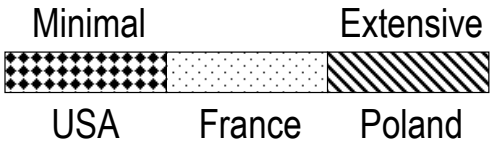
- Development of process control software for production control and quality assurance (task 1).
- Development of coupled non-linear thermal stress models for describing the stamping of TV glass and glass/mold interactions (task 2).
- Development of a sensor for measurement of stress distribution in final product (task 3).
- Development of a sensor for on-line measurement of temperature in formed panels (task 4).

Progress Summary

- Performed experimental demonstrations of optical measurement concepts for determination of:
  (1)stress
  (2)temperature
  applicable towards TV glass production.
- Have begun the collection of process temperature data at Thomson Circleville, OH plant.
- Completed thermal analysis of forming steps and initiated associated stress calculations.

Task 1 - Process Control Software Development – Historical Plant Data

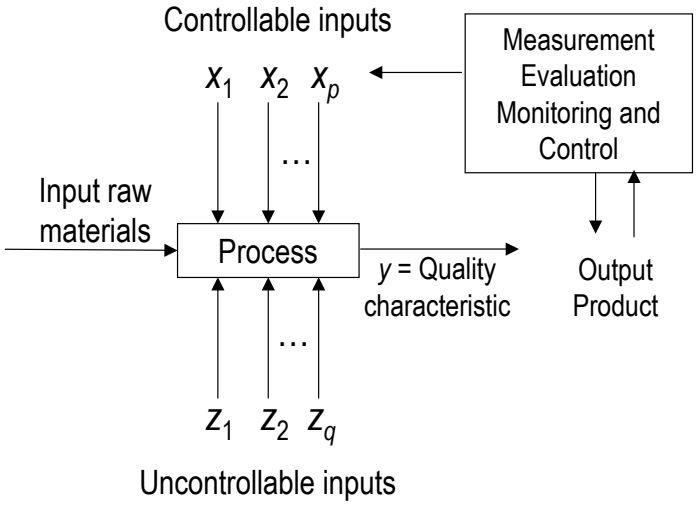
Data Collection/Control



<u>Measurements</u>
Temperatures
Gob weight/density
Die conditions
Product dimensions
Optical transmission

Statistical Process Control Approach

- Statistical analysis
  - Relates product quality to process parameters.
  - Helps identify parameters and ranks their importance.
  - Reduces product variability.
- Statistical approach
  - Multivariate analysis.
  - Coupling with databases/model results.
  - Regression analysis.
  - Time series analysis.



Task 1 - Progress

- Investigated several statistical methods appropriate for use in process control.
- Selected Multivariate Analysis as the preferred statistical approach
- Collection of temperature data at Thomson plant (Circleville, OH) has begun.
- Statistical analysis will commence when sufficient data are recorded.

Task 2 – Modeling and Simulation

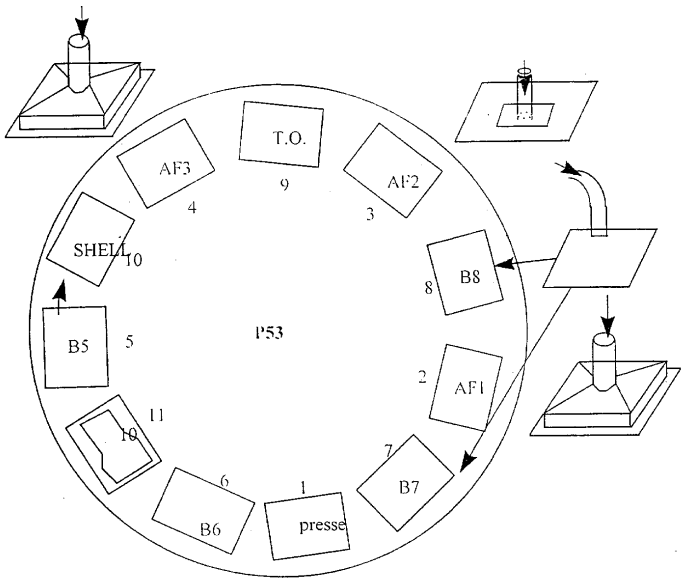
Simulate 11-step pressing cycle including 3-dimensional model with:

- Contact/separation between glass, mold, and plunger.
- Heat transfer between glass, environment.
- Radiation heat transfer within glass.
- Structural and stress relaxation in glass.

Eleven-Step Forming Process

1. Press – forms panel
2. Air former 1
3. Air former 2
4. Air former 3
5. Shell Take Off
6. Air Pipe 6
7. Air Pipe 7
8. Air Pipe 8
9. Panel Take Out
10. Shell Transfer
11. Glass gob loaded

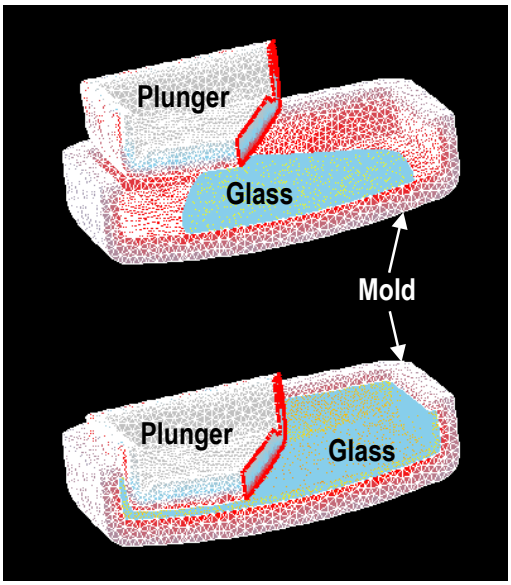
Cooling Stages



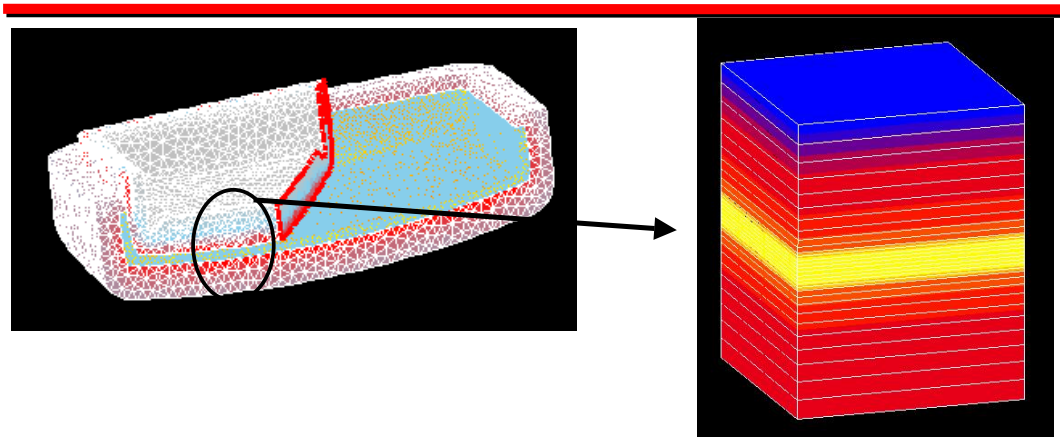
Two-Phase Modeling Approach

- Pressing Stage - Large deformation viscous glass flow.
- Thomson has successfully modeled pressing stage using the DEFORM code.
- Cooling Stage - Small strains, viscoelastic response through glass transition.
- PNNL using Thomson's pressing results as initial conditions for the cooling stage models in MARC.

Thomson's DEFORM Model

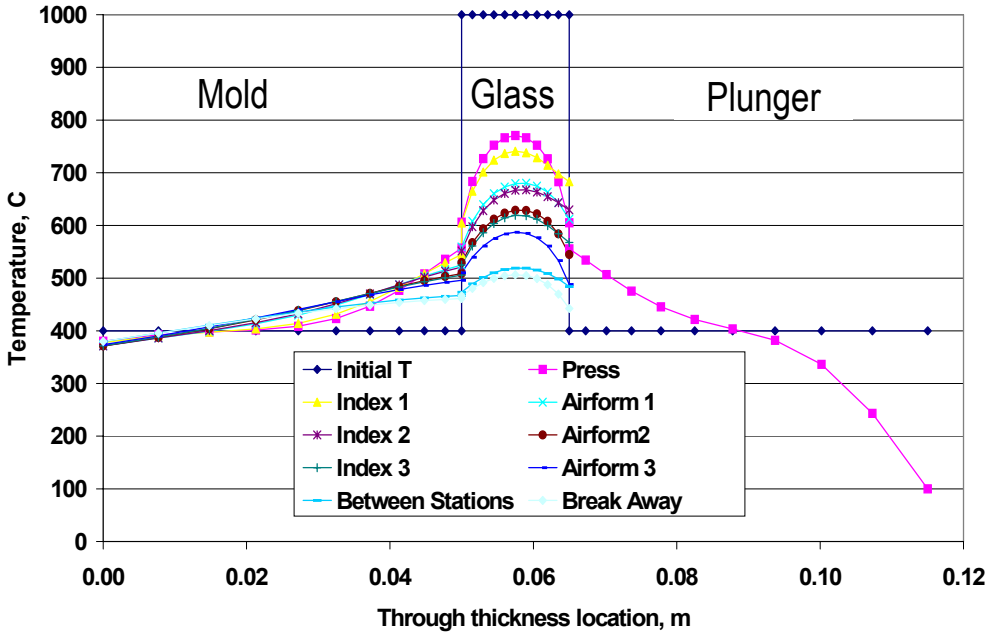


Cooling Stages - 3-D Model Development



- Develop 3-D modeling techniques on sub-model, then apply to large model of 1/2 the television panel.
- 1-D Thermlayer solution used for thermal model validation.

Thermal Results of 3-D Sub-model for all Cooling Stages

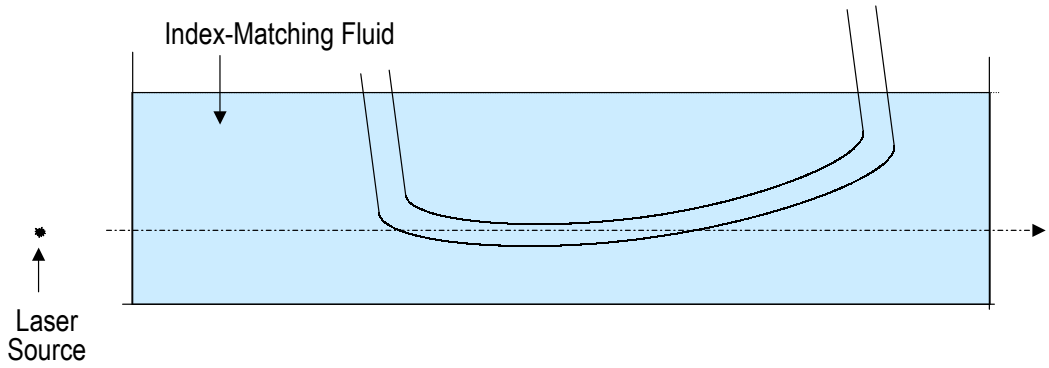


Task 3 - Development of Stress Measurement Method

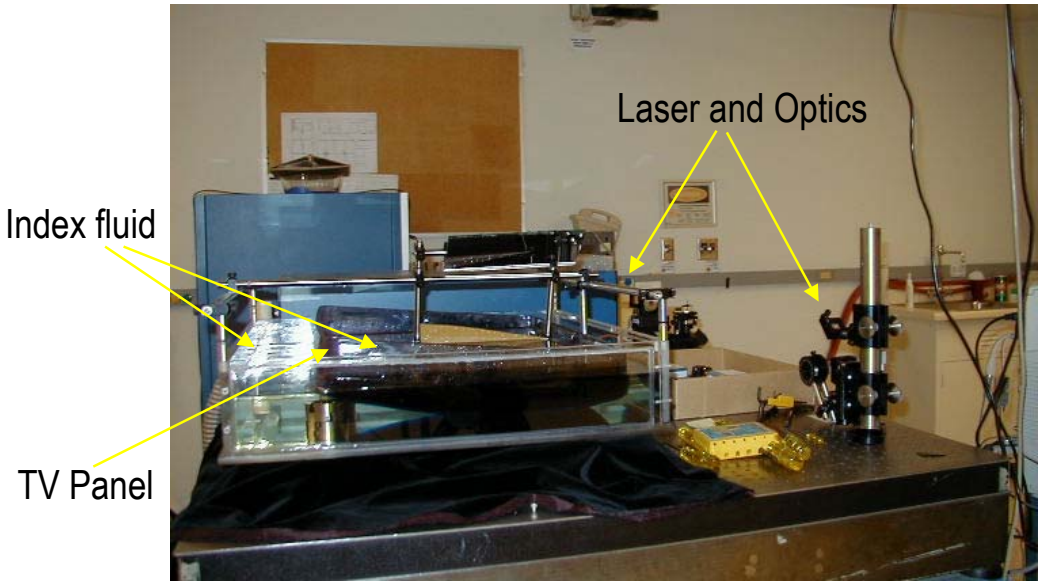
- Stress measurement method developed under an earlier project is not directly applicable due to glass geometry and surface conditions.
  - Glass is curved and of variable thickness.
  - Inner surface is not smooth.
- A new concept for stress measurement in TV glass has been developed and experimentally demonstrated.

Measurement Concept

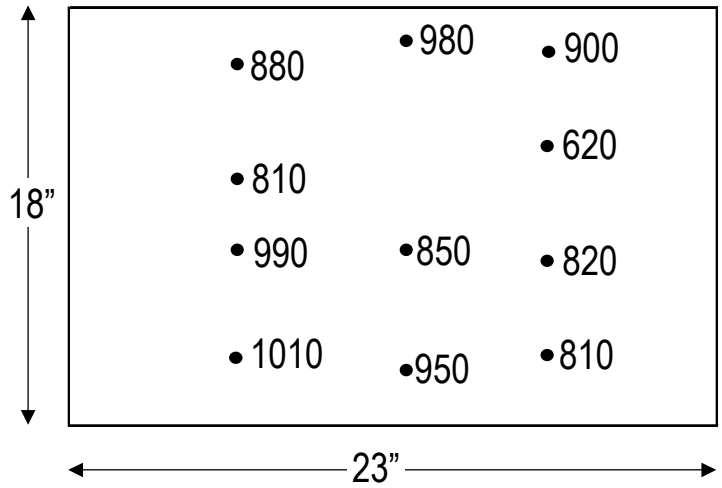
Light scattered from the laser beam is collected with mirrors and directed towards a high-speed digital video camera.



Experimental Arrangement for Stress Measurement using EMSL Alexandrite Laser



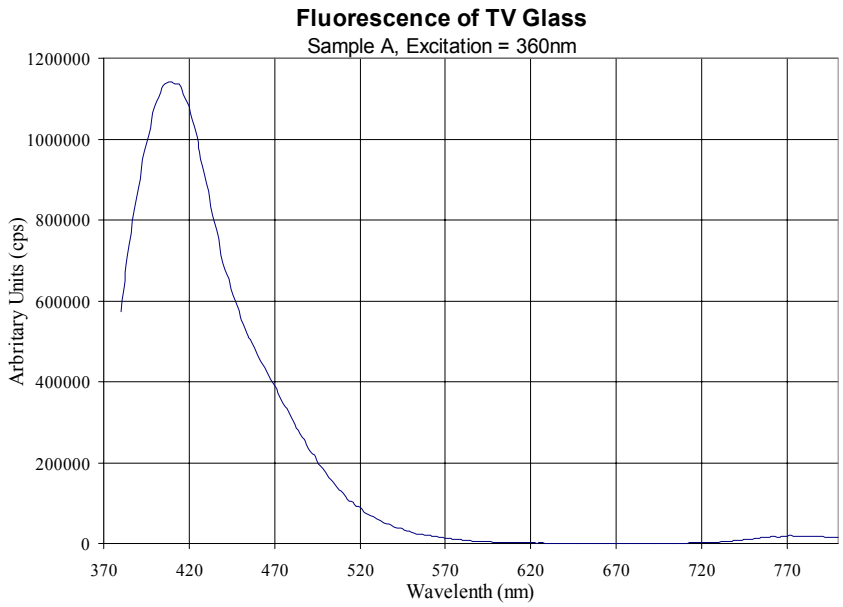
Measured Mid-Plane Stresses in TV Glass Panel (Psi)



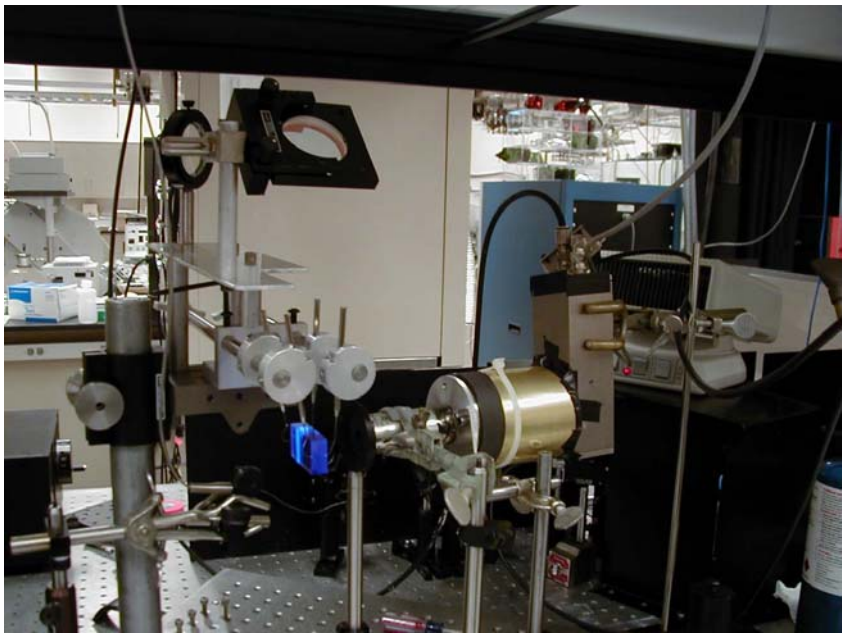
Task 4 - Development of Temperature Measurement Method

- Temperature measurement method developed in earlier project is not applicable to TV glass.
  - Very little iron is in TV glass.
- TV glass contains cerium, which provides another means to obtain temperature via fluorescence.

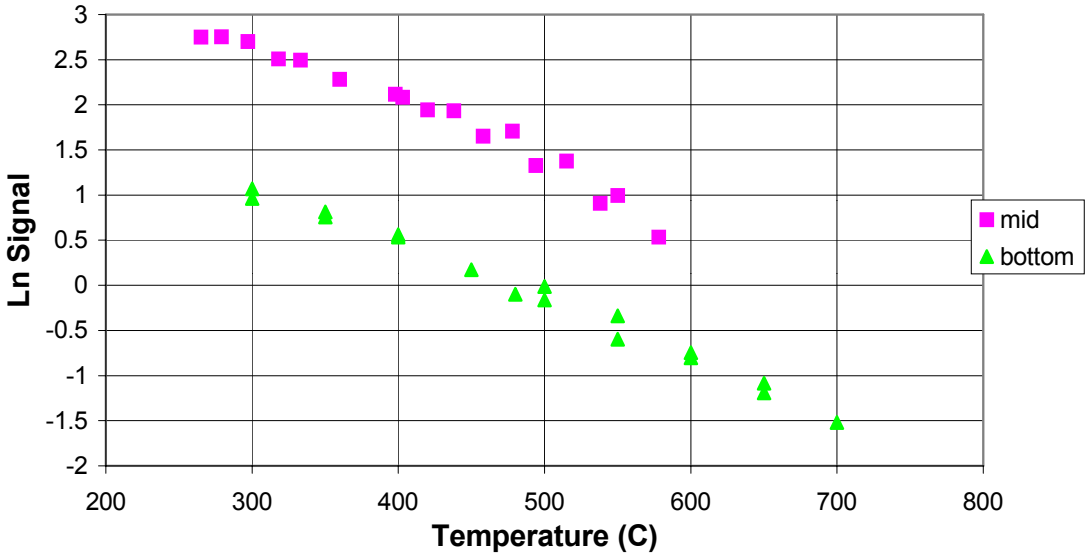
Fluorescence in TV Glass is due to Cerium



Experimental Arrangement for Observing TV Glass Fluorescence at PNNL EMSL Facility



TV Glass Fluorescence Exhibits Temperature Dependence



Temperature Sensor Based on Cerium Fluorescence Appears Promising

- Cerium is present in TV glass at about 0.25%.
- Cerium is a rare-earth element.
  - Rare-earth elements retain atomic behavior even in solids.
- Experiments show emission decreases exponentially with increasing temperature.
- Temperature resolution of about 5°C at 700°C is possible if emission can be measured to within several percent.

Progress Summary

- Task 1 - Plant data collection for process control is underway.
- Task 2 - FE modeling of the forming process is partially completed.
- Task 3 - A method for determining internal stress in glass that is applicable to plant conditions has been demonstrated.
- Task 4 - A method for measurement of internal glass temperature has been demonstrated.

Current and Future Budgets

- FY01 - $300K
- FY02 - $220K
- FY03 – Under discussion with OIT, Thomson, PNNL, and GMIC (?)

Project Expected Results

- Development of process control software for automatic control of plant operating parameters, thereby enhancing quality assurance of final products.
- Development of sensors for measurements of stress and temperature in TV glass panels for enablement of enhanced process control.
- Development of finite element models for optimization of glass fabrication and generation of additional databases in support of model based process control.

Upcoming Technical Milestones

- Tech transfer of stress and temperature measurement concepts (9/02).

  (Concerns about adequate funding)
- Completion of finite element modeling of forming process (6/02).
- Completion of statistical analysis of Thomson historical plant data (9/02).
- Develop framework for process control software appropriate for implementation in Thomson USA plant (9/02).

Plans for FY02

- Work will concentrate on the following efforts:
  - Statistical analysis of temperature data from Thomson Circleville, OH plant and process control framework.
  - Initiate technology transfer to Thomson for stress and temperature measurements.
  - Completion of FE modeling of press forming and glass/mold interaction including radiation.

Commercialization Plans

- Commercialization will follow a logical procedure.
  - Obtain patent protection.
  - Determine commercial product requirements and barriers to plant entry with help from industrial collaborators.
  - Evaluate Thomson plant experience.
  - Ensure that commercialization efforts are applicable towards several glass industries (not just TV glass).

Broad Industry Application

- Stress measurement
  - Automotive glass (3D)
  - Flat glass (3D)
  - TV glass (Through-thickness)
  - Glass fiber (Average)
  - Bottle glass (Average)
- Temperature measurement
  - Automotive glass (3D)
  - Flat glass (3D)
  - TV glass (3D)
- Modeling tools
  - Automotive glass (fabrication – gravity sag and tempered)
  - Bottle glass (fabrication)
  - TV glass (by coupling with computational forging tools - AutoForge).
  - May be applicable to glass melting (by coupling with other CFD code).

A

Appendix A

Sample Evaluation Form

PROJECT NAME:

I. Technical Merit

A. Does the project address an important technical need of the glass industry?

Low		*Medium*		*High*
1	2	3	4	5

Comment: _____

B. To what degree will this project contribute new information or technology to the knowledge base of the glass industry?

Insignificant contribution				*Significant contribution*
1	2	3	4	5

Comment: _____

C. What is the likelihood that the project will meet its technical objectives?

Very Unlikely				*Very Likely*
1	2	3	4	5

Comment: _____

II. Market Applications/Commercial Potential

A. If the successful, will the research results have direct commercial benefit in the glass industry?

None		*Moderate*		*Large*
1	2	3	4	5

Describe benefit: _____

B. Will the research results be widely applicable throughout the industry, or narrowly applicable to a particular industry segment?

Narrow				*Wide*
1	2	3	4	5

Please explain: _____

III. Budget and Schedule Considerations

A. In your opinion, is the cost of the project in line with the anticipated value of the results?

Costs seem too high				*Costs seem about right*
1	2	3	4	5

Comment: _____

B. In your opinion, is the research proceeding at a reasonable pace?

Too slow				*Quite fast*
1	2	3	4	5

Comment: _____

Please turn to reverse side ----------->

_____

Name of Reviewer:

III. Budget and Schedule Considerations (Continued)

C. Do you believe the project will meet its technical objectives as currently *budgeted* and *scheduled*?

No -- both behind				*Yes -- both ahead*
1	2	3	4	5

Comment: _____

IV. Overall Risk Assessment

A. How do you rate this project overall?

1	2	3	4	5
Poor -- little chance of producing results of any real value to the industry		*Fair -- good chance of producing results of moderate value to the industry*		*Excellent -- almost certain to produce results of high value to the industry*

V. The following changes should be made to improve this project:

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

Name of Reviewer:

B

Appendix B

Other Presentations

Status of GPLUS Efforts

Peter Angelini

GPLUS Coordinating Laboratory Main Contact

Oak Ridge National Laboratory

November 2001

Topics

- Background
- Initial projects
- FY 2001 activities
- Summary

Purpose

- **GPLUS - (Glass - Project Laboratory User Services)** program
  - Provides GMIC members access to unique capabilities of DOE National Laboratories
  - Industry defined projects ($25K per core GMIC member) - funding to participating national laboratory/ies
  - Projects - involve one or more core members, and associate members
  - Project submittals by GMIC core member

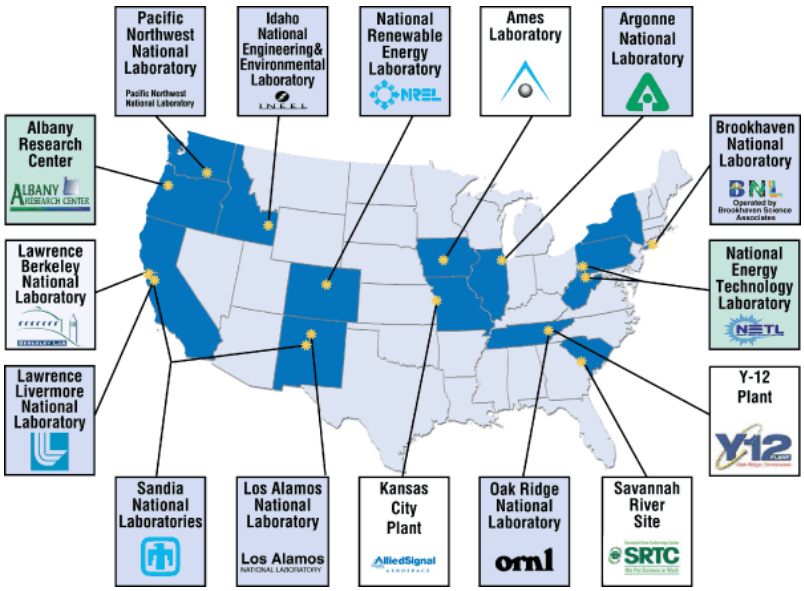
GPLUS Initiated in FY 00

- Laboratory Coordinating Council (LCC) committee worked with Michael Greenman and Theo Johnson to develop overall guidelines
- Effort completed in early 2000;
  - FY 2000 - trial period of three GPLUS projects
    - $75K made available by DOE in FY 2000 for 3 projects
  - Mode of Operation
    - industry GMIC core member submits a Project Description form
    - GMIC prepares approval form
    - both are sent to the coordinating laboratory (ORNL) for initiation of funds transfer to the participating national laboratory; Peter Angelini, Coordinator

GMIC Core Members

- Ball-Foster
- CertainTeed Corporation
- Corning, Inc.
- Fire and Light Originals L. P.
- Libbey, Inc.
- Owens Corning
- Osram Sylvania
- PPG Industries
- Schott Glass Technologies Inc.
- Society for Glass Science Practices
- Techneglas
- Visteon - An Enterprise of Ford Motor Company
- Vetrotex America

DOE National Laboratory Participants



Initial Projects in FY 00

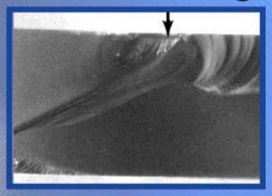
- **1. Title: Asymmetrical Windshield Construction**
  - Visteon Glass Division - K. K. Koram
  - Pacific Northwest National Laboratory - M. A. Khaleel

  - Objective: Examine windshield maximum impact resistance for three thickness combinations to (a) blunt and (b) sharp objects. Effects of windshield curvature, residual stress and interface bond properties will be examined.
  - Status:
    - project initiated in about 2 weeks after funds transfer effort initiated;
    - PNNL has made significant number of computational runs determining the effects of various size "rocks" impacting various windshield designs (thickness, glass layer types.)
    - project completed

Asymmetrical Windshield Construction

Project

The impact resistance of symmetric and asymmetric glass constructions is being evaluated to determine the effects of various glass/layer thickness, crack size, and shape of impact material.



Participants

Visteon and
Pacific Northwest National Laboratory

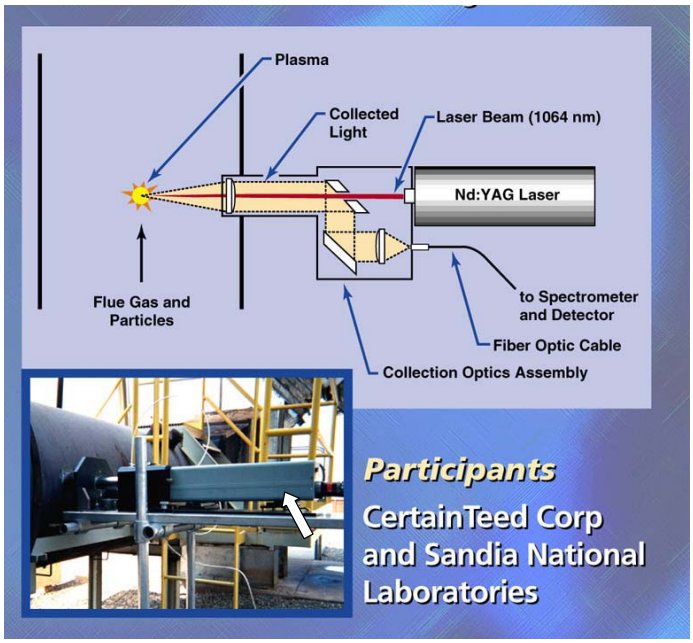
Initial Projects in FY 00

- **2. Title: Construction and Evaluation of Laser-Induced Breakdown Spectroscopy (LIBS) Instrument**
  - Corning Incorporated - Frederic Quan
  - Sandia National Laboratories, California- David Ottesen
  - Objective: A Laser Induced Breakdown Spectroscopy (LIBS) system will be evaluated to characterize the quality of glass melting furnaces, the glass formation process, and the downstream exhaust byproducts for emissions and process control
  - Status
    - Project Completed

Initial Projects in FY 00

- **3. Title: Controlling Emissions from Borosilicate Glasses**
  - CertainTeed Corporation - Terry Berg
  - Sandia National Laboratories, California - Peter Walsh
  - Objective: Identify the conditions which most limit the emissions from borosilicate type glass. The effects will be quantified by determining the effects of changing firing ratios and cullet levels on glass furnace emissions
  - Status
    - Project Completed

Laser Induced Breakdown Spectroscopy Evaluated for Controlling Emissions from Borosilicate Glass



FY 2001 Activities

- FY 2001 funding for GPLUS effort - DOE
  - DOE providing funding for one project per GMIC core member
- Direct funds transfer from DOE/HQ to ORNL
  - Recommendation - DOE to transfer all funds in one Work Authorization to ORNL; completed
  - Funds made available as Project Descriptions are submitted

Project in FY 01

- **4. Title: Windshield Coating Studies**
  - PPG Industries - K. K. Koram
  - Pacific Northwest National Laboratory - M. A. Khaleel
  - Objective: Determine failure mechanisms and durability of busbar/coating system for windshields. The durability and extended lifetime of the system will be evaluated.
  - Status
    - Project Initiated February 2001

Project in FY 01

- **5. Title: Mechanical Strength Studies of Automotive Tempered and Annealed Glass with Holes**
  - Visteon – E. N. Boulos
  - Pacific Northwest National Laboratory - M. A. Khaleel
  - Objective: Experimentally determine the strength of various annealed specimens using the ring on ring apparatus and determine the fatigue strength of glass specimens.
  - Status
    - Project Initiated March 2001

Project in FY01

- **6. Title: Effectiveness of Caustic Soda Solutions in Controlling Boron Emissions**
  - CertainTeed Corporation – Terry berg
  - Sandia National Laboratories, California - Peter Walsh
  - Objective: Define relationships between concentrations and volumes of caustic chamber reactants to maximize the collection of emissions from the waste stream.
  - Status
    - Project initiated March 2001

Project in FY01

- **7. Title: Analyses of Refractory Metal Needles Formed During Glass Extrusion**
  - Osram Sylvania – Bill Yellenik
  - Oak Ridge National Laboratory – Cam Hubbard
  - Objective: Understand and characterize needles that interfere with the flow of molten glass and that form around an orifice made of refractory metal. Results will be used in conjunction with thermodynamic modeling to address the cause of whisker formation. Solving the technical issues would result in improved processing efficiency.
  - Status
    - Project Initiated May 2001

Project in FY01

- **8. Title: Reduction of Corrosion of Refractories using Encapsulated Glass Additives**
  - Kopp Glass – James Kroner
  - Argonne National Laboratory – J. P. Singh
  - Objective: The objectives are to theoretically and experimentally evaluate particular tank refractory materials based on an assessment of the corrosion effects of various additives using different encapsulated techniques.
  - Status
    - Project Initiated June 2001

Project in FY01

- **9. Title: High Temperature Thermocouple Degradation Study**
  - Schott Glass Technologies – Alfrerd Thorne
  - Idaho National Engineering and Environmental Laboratory – Arthur Watkins
  - Objective: INEEL will perform a literature search, integrate a self-verifying temperature sensor into a laboratory furnace control system, calibrate and expose commercially available precious metal thermocouples and perform trending, drift, and metallurgical analyses
  - Status
    - Project Initiated July 2001

Project in FY01

- **10. Title: Cycle Time Reduction in the Bushing Castable Refractory Cure Sequence**
  - Owens Corning – Christopher Jian
  - Oak Ridge National Laboratory – Terry Tiegs
  - Objective: The activity will investigate materials, mix formulations and drying/curing schedules to identify opportunities to improve the castable refractory used to encase the precious metal bushings used in glass fiber manufacture. Initial emphasis will focus on curing and drying schedules and conditions for their impact on the finished properties of a castable refractory. Subsequent effort will include variations in refractory materials and mix formulations.
  - Status
    - Project in process of being initiated 2001

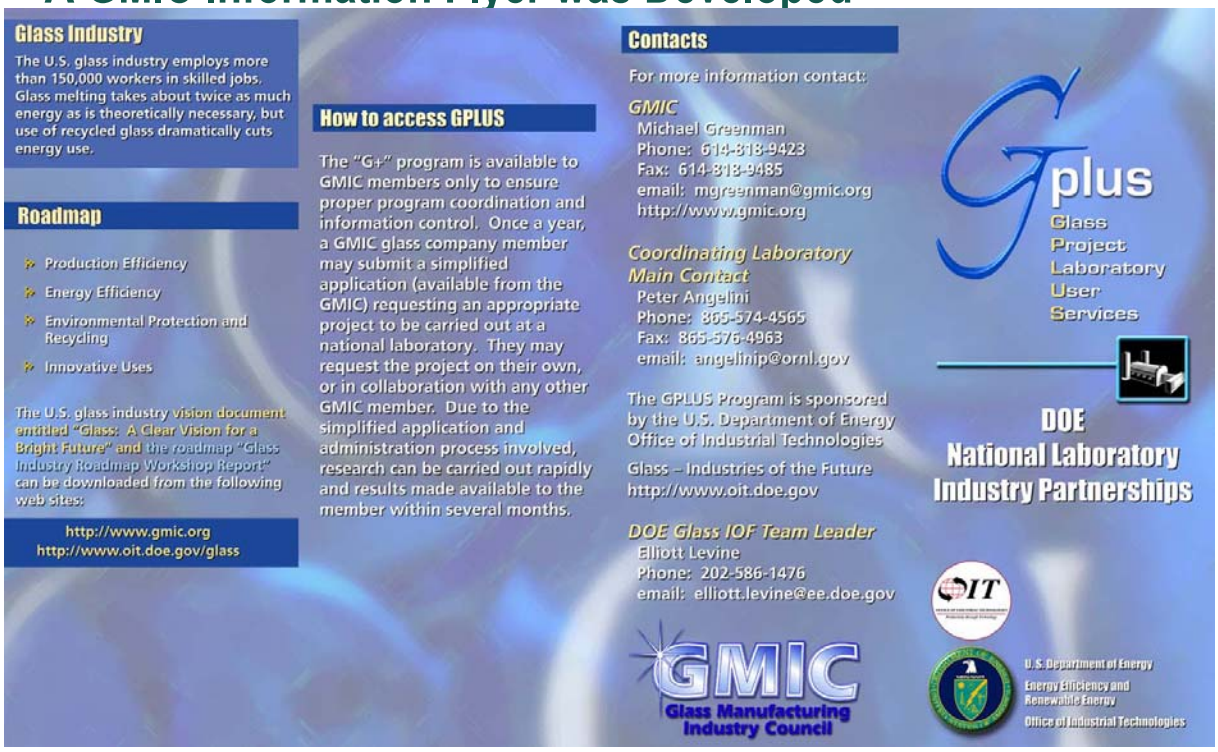
Industry has Requested Capabilities Information from Laboratories Relative to Specific Needs (in FY 01)

- **Owens Corning – (Manoj Choudhary)**
  - Topic: Acoustics
  - Responses - Ames Lab; ORNL
  - Action: capabilities did not match industry needs
- **Schott Glass - (Al Thorne)**
  - Topic: Thermocouples
  - Responses: from various labs
  - Project description developed with INEEL

Industry has Requested Capabilities Information from Laboratories Relative to Specific Needs (in FY 01)

- **Osram Sylvania (Bill Yellenik)**
  - Topic: Glass processing/ Refractory metal needle growth
  - Responses from various labs
  - Project initiated with Oak Ridge National laboratory
- **Society of Glass Science and Practices (Jim Kopp and Ed Sneckenberger)**
  - Topic: Glass Tank Refractories Glass Interactions
  - Responses from various labs
  - Project initiated with Argonne National Laboratory

A GMIC Information Flyer was Developed



Glass Industry

The U.S. glass industry employs more than 150,000 workers in skilled jobs. Glass melting takes about twice as much energy as is theoretically necessary, but use of recycled glass dramatically cuts energy use.

Roadmap

- Production Efficiency
- Energy Efficiency
- Environmental Protection and Recycling
- Innovative Uses

The U.S. glass industry vision document entitled "Glass: A Clear Vision for a Bright Future" and the roadmap "Glass Industry Roadmap Workshop Report" can be downloaded from the following web sites:

http://www.gmic.org
http://www.oit.doe.gov/glass

How to access GPLUS

The "G+" program is available to GMIC members only to ensure proper program coordination and information control. Once a year, a GMIC glass company member may submit a simplified application (available from the GMIC) requesting an appropriate project to be carried out at a national laboratory. They may request the project on their own, or in collaboration with any other GMIC member. Due to the simplified application and administration process involved, research can be carried out rapidly and results made available to the member within several months.

Contacts

For more information contact:

GMIC
Michael Greenman
Phone: 614-818-9423
Fax: 614-818-9485
email: mgreenman@gmic.org
http://www.gmic.org

Coordinating Laboratory Main Contact
Peter Angelini
Phone: 865-574-4565
Fax: 865-576-4963
email: angelinip@ornl.gov

The GPLUS Program is sponsored by the U.S. Department of Energy Office of Industrial Technologies

Glass – Industries of the Future
http://www.oit.doe.gov

DOE Glass IOF Team Leader
Elliott Levine
Phone: 202-586-1476
email: elliott.levine@ee.doe.gov

GMIC
Glass Manufacturing Industry Council

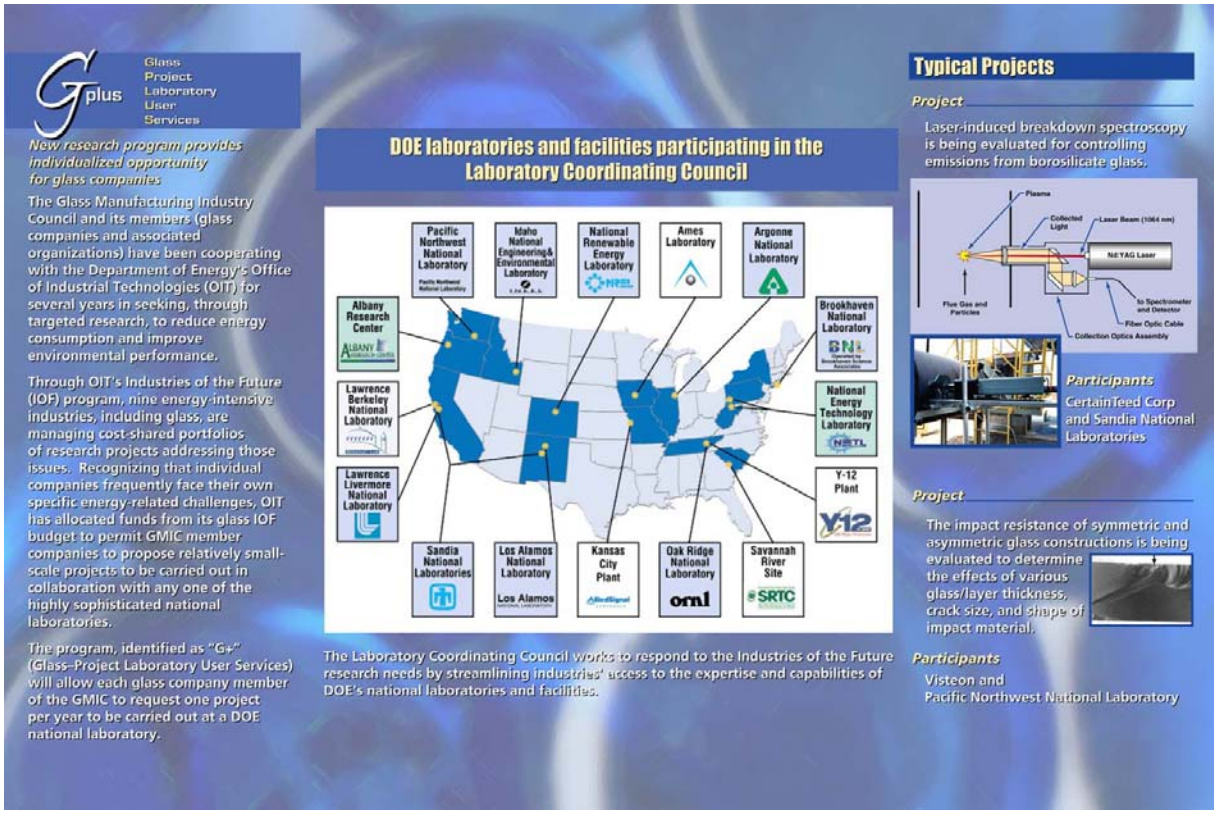
Gplus
Glass Project Laboratory User Services

DOE
National Laboratory Industry Partnerships

OIT

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Office of Industrial Technologies

A GMIC Information Flyer was Developed



Lessons Learned

- **Communication is key to timely initiation and completion**
  - Communication with lab and industry PIs is being improved
    - GMIC - notifies PIs and ORNL when the Project Description has been approved by the GMIC, and sends both to ORNL
    - ORNL notifies PIs when ORNL receives the GMIC approval form and the Project Description
    - ORNL notifies the lab PI when the funds transfer process has been initiated
    - Lab PI communicates with ORNL on funds transfer, project status, and reporting

Lessons Learned

- **Lab capabilities information requests to the GPLUS**
  - If there is a need to determine capabilities outside of GPLUS relative to proprietary efforts, the industry requestor would provide his/her name and contact information to the LCC chair; contact will be made directly between interested laboratories and the industry representative with appropriate agreements in place.

Summary

- **FY 00**
  - Three projects initiated in FY 00;
  - Two have been completed; one continuing
- **FY 01**
  - Seven projects initiated;
  - Four capabilities requests submitted by industry
    - Decision on three projects made
  - Project Description form modified to show the project "estimated costs" at the specified national laboratory to simplify procurement
  - DOE providing funding for one project per GMIC core member, and support for efforts at ORNL

Contact Information

* Michael Greenman, Director

Glass Manufacturing Industry Council

tel. - 614 818-9423

Fax - 630 982-5342

e-mail; mgreenman@gmic.org

http://www.gmic.org/

* Peter Angelini, Coordinating Laboratory Main Contact

Oak Ridge National laboratory

tel. - 865 574-4565

Fax - 865 576-4963

e-mail; angelinip@ornl.gov

C

Appendix C

Attendees

Attendees

U.S. Department of Energy

OIT GLASS PROJECT REVIEW

Richland, Washington
November 7-8, 2001

Jill Aaron
PPG Industries
(412) 820-8520
jaaron@ppg.com

Robert Adams
Techneglas
(614) 445-1698
radams@techneglas.com

Mark Allendorf
Sandia National Laboratories
(925) 294-2895
mdallen@sandia.gov

Peter Angelini
Oak Ridge National Laboratory
(865) 574-4565
angelinip@ornl.gov

Terry Berg
CertainTeed
(610) 766-1569
terry.l.berg@saint-gobain.com

Lori Bisping
Pacific Northwest National Laboratory
(509) 375-2123
lori.bisping@pnl.gov

Ed Boulos
Visteon Glass Systems
(313) 322-0173
eboulos@visteon.com

Robert Butler
CertainTeed
(610) 341-6784
bob.c.butler@saint-gobain.com

Rolf Butters
DOE - OIT
(202) 586-0984
rolf.butters@ee.doe.gov

Shen-Lin Chang
Argonne National Laboratory
(630) 252-6955
slchang@anl.gov

John Chumley
Techneglas
(614) 443-6551
jchumley@techneglas.com

Robert Cook
Mississippi State University - DIAL
(662) 325-2105
cook@dial.msstate.edu

John Connors
PPG Industries, Inc.
(412) 820-8787
jconnors@ppg.com

Edward Daniels
Argonne National Laboratory
(630) 252-5279
edaniels@anl.gov

Robert De Saro
Energy Research Co.
(718) 442-2725
rdesaro@er-co.com

Bob Gallagher
Sandia National Laboratories
(925) 294-3117
rjgalla@sandia.gov

Bob Gemmer
DOE - OIT
(202) 586-5885
bob.gemmer@ee.doe.gov

Brian Golchert
Argonne National Laboratory
(630) 252-6518
bgolchert@anl.gov

Michael Greenman
Glass Manufacturing Industry Council
(614) 818-9423
mgreenman@gmic.org

Marvin Gridley
Saint-Gobain Containers
(765) 741-7145
mgridley@sgcontainers.com

Vincent Henry
Henry Technology Solutions
(734) 623-7445
vhenry@henrytechsol.com

Tom Huff
Owens Corning
(740) 321-7556
tom.huff@owenscorning.com

Keith Jamison
Energetics, Incorporated
(410) 953-6201
kjamison@energetics.com

Christopher Jian
Owens Corning
(740) 321-8259
christopher.q.jian@owenscorning.com

Bassam Jody
Argonne National Laboratory
(630) 252-4206
bjody@anl.gov

Joe Keller
Idaho National Engineering and
Environmental Laboratory
(208) 526-1533
kellerjg@inel.gov

Hank Kenchington
DOE - OIT
(202) 586-1878
henry.kenchington@ee.doe.gov

Moe Khaleel
Pacific Northwest National Laboratory
(509) 375-2438
moe.khaleel@pnl.gov

Elliott Levine
DOE - OIT
(202) 586-1476
elliott.levine@ee.doe.gov

John McClurg
Fire & Light Originals, LP
(707) 825-7500
mcclurg@arcata.com

John McConnell
JFM Consulting
(412) 921-8535
jfmcconnell@us5.com

Matea McCray
DOE - Idaho Operations Office
(208) 526-0117
mccraymh@id.doe.gov

Amar Mishra
PPG Industries
(412) 820-8050
mishra@ppg.com

Robert Newell
Siemens Energy and Automation
(215) 646-7400 x 3021
robert.newell@sea.siemens.com

Rob Penney
WSU Energy Program
(360) 956-2053
penneyr@energy.wsu.edu

Michael Petrick
Argonne National Laboratory
(630) 252-5960
mpetrick@anl.gov

John Petrovic
Los Alamos National Laboratory
(505) 667-0125
petrovic@lanl.gov

John Plodinec
Mississippi State University - DIAL
(662) 325-2105
plodinec@dial.msstate.edu

William Pollack
Optimization Technology Inc.
(716) 359-0700
bill.pollack@optimizationtech.com

Frederic Quan
Corning, Inc.
(607) 974-3438
quanfj@corning.com

Cheryl Richards
PPG Industries
(412) 820-4942
crichards@ppg.com

David Rue
Gas Technology Institute
(847) 768-0508
david.rue@gastechnology.org

Richard Rueter
PPG Industries
(412) 820-8731
rueter@ppg.com

Phillip Sanger
Advanced Manufacturing Center
(216) 687-4565
phillip.sanger@camp.org

Kevin Schaal
Johns Manville
(303) 978-5097
schaalk@jm.com

Carl Schatz
BOC Gases
(908) 771-1228
carl.schatz@us.gases.boc.com

John Sealock
Pacific Northwest National Laboratory
(509) 375-3635
john.sealock@pnl.gov

Thomas Seward
NY State College of Ceramics
Alfred University
(607) 871-2432
seward@alfred.edu

James Shell
Shell Glass Consulting, Inc.
(614) 471-7539
jshell@columbus.rr.com

Chester Shepard
Pacific Northwest National Lab
(509) 375-3675
chester.shepard@pnl.gov

Neil Simpson
BOC Gases
(419) 897-3314
neil.simpson@us.gases.boc.com

Mike Soboroff
DOE - OIT
(202) 586-4936
mike.soboroff@ee.doe.gov

Charles Sorrell
DOE - OIT
(202) 586-1514
charles.sorrell@ee.doe.gov

Mike Thompson
Pacific Northwest National Laboratory
(509) 375-6471
michael.thompson@pnl.gov

Jud Virden
Pacific Northwest National Laboratory
(509) 375-6512
jud.virden@pnl.gov

William Von Drasek
American Air Liquide
(708) 579-7755
bill.vondrasek@airliquide.com

Peter Walsh
Sandia National Laboratories
(925) 294-3726
pwalsh@sandia.gov

Steve Weiner
Pacific Northwest National Laboratory
(202) 646-7870
sc.weiner@pnl.gov

Carsten Weinhold
Schott Glass Technologies
(570) 457-7485
cweinhold@schottglasstech.com

Arel Weisberg
Energy Research Company
(718) 442-2683
aweisberg@er-co.com

John Wells
Saint-Gobain Vetrotex America
(940) 689-3356
john.wells@saint-gobain.com

Dan Wishnick
Eclipse/Combustion Tec
(407) 299-7317
dwishnick@eclipsenet.com

Steven Woodruff
National Energy Technology Laboratory
(304) 285-4175
steven.woodruff@netl.doe.gov

Vicki Zarrell
OIT Clearinghouse
(800) 862-2086
zarrellv@energy.wsu.edu

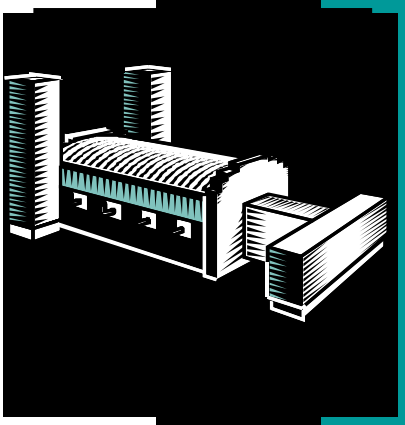
Jack Zeiger
WSU Energy Program
(360) 956-2017
zeigerj@energy.wsu.edu

Appendix D

Completed Glass IOF and GPLUS Project Posters

Glass IOF Completed Project

Characterization of Refractories for the Glass Manufacturing Industry



Project Objective and Background

• The goal of the project was to provide expertise and facilities for the thermomechanical and thermophysical properties characterization of refractory materials which are of interest to the glass industry. The relevance of this effort to the refractory and glass-making industries was ensured by coordinating our research activities (1) with the Glass Industry Advisory Committee (GIAC), comprised of recognized technical representatives from refractory vendor and glass manufacturing companies, (2) receiving input from representatives and furnace refractory specialists from the glass manufacturing community, and (3) through a subcontract with the University of Missouri-Rolla (UMR).

Accomplishments and Knowledge Gained

•During the course of this project we completed (1) a postmortem analysis of salvaged silica brick from PPG float glass and TCE TV-panel furnaces, (2) a complete thermal and mechanical characterization of mullite and fusion-cast alumina refractories, and (3) a comparison of thermal conductivity test techniques.

Potential Benefits and Impacts

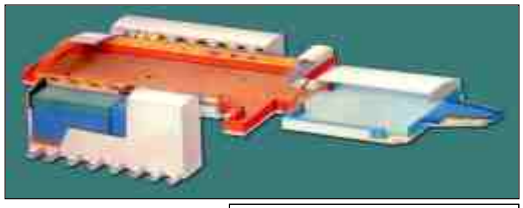
•Based on the 1998 DOE/OIT GPRA Report, approximately $202M in energy savings per year in 2005 and a $445M per year savings by 2020 can be expected with the conversion of air/fuel to oxy-fuel fired glass manufacturing furnaces. These are quoted results from the consideration that 61% and 100% furnace conversions will occur by the years 2005 and 2020, respectively. The results from this project will be used by glass manufacturers and their furnace designers to accelerate this conversion process and optimize furnace design to achieve these energy realizations.

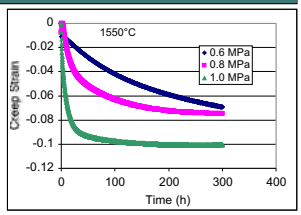
Information/Technology Transfer Potential or Plans

• The information generated in this project have been transferred to both the refractory manufacturers and glass industry

Project Participants

• Corning, Owens-Brockway, Owens-Corning, PPG, Techneglas, Corhart, Harbison-Walker, Monofrax, University of Missouri-Rolla, and Oak Ridge National Laboratory.



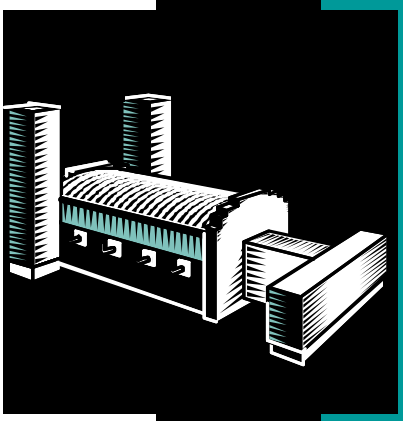


For more info, contact:
Mattison K. Ferber
Oak Ridge National Laboratory
(865) 576-0818

Glass Manufacturing Industry Council

Glass IOF Completed Project

Coupled Modeling of Glass Furnaces



Project Objective and Background

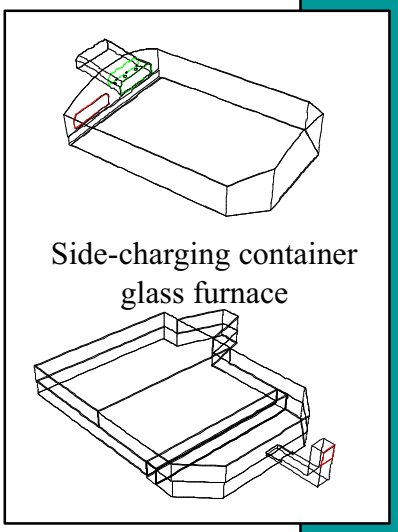
- Develop techniques for characterization of industrial furnace performance.
- Develop coupled combustion space/melt tank circulation/batch melting model.

Accomplishments and Knowledge Gained

- Industrial furnace performance has been characterized experimentally, and model validation data have been collected.
- Coupled combustion space/melt tank circulation/batch melting model has been developed and validated by comparison of model predictions with measured data in float glass environment.
- Coupled model has been extended to fiberglass unit melter, container glass furnace environments. Model predictions have driven rebuild designs.

Technology Benefits and Impacts

- Experimental effort has characterized furnace operation on energy efficiency and pollutant generation.
- Model allows economical exploration of new furnace designs.



Side-charging container glass furnace

Commercialization Plans

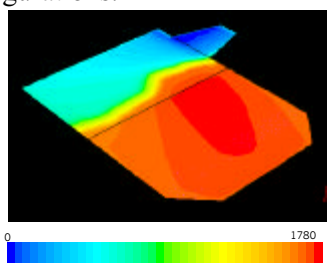
- Expertise developed for furnace characterization is available for application in other environments.
- Coupled model is available for license.

Target Markets

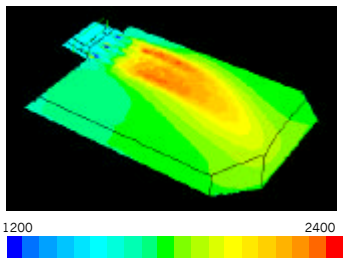
- Experimental measurement capability applicable to all segments of the glass industry.
- Coupled model has been formulated for float glass, fiberglass unit melter, and container glass furnace configurations.

Key Participants

- Brigham Young University
- Visteon Glass



Glass/batch temperature (K)

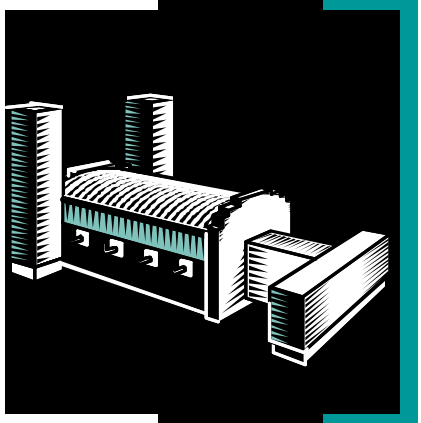


Gas temperature (K)

For more info, contact:
Prof. Brent W. Webb
Brigham Young University
(801) 378-6543

Glass IOF Completed Project

Laser Diagnostics for Oxygen-Enhanced Glass Synthesis



Project Objective and Background

There has been relatively little development of laser-based diagnostic measurements of O_2-enhanced combustion gases with low N_2 concentrations. The objective of this research is to develop coherent anti-Stokes Raman spectroscopy (CARS) thermometry using O_2 and CO_2. This technique is capable of measuring temperatures at specific locations in high-temperature flame gases, and can be applied in pure-O_2/fuel systems.

Accomplishments and Knowledge Gained

- CARS temperature measurements based on O_2 have provided accuracy and precision comparable to N_2 CARS thermometry, from 294 K to 2450 K.
- An improved spectral model for analyzing O_2 CARS data was developed and validated against measurements in a bench top furnace (see plot) and in flames.
- A similar validation effort for CARS thermometry based on CO_2 was initiated.
- A broadband CARS system, capable of a data rate > 1 s^{-1}, was built and tested.

Technology Benefits and Impacts

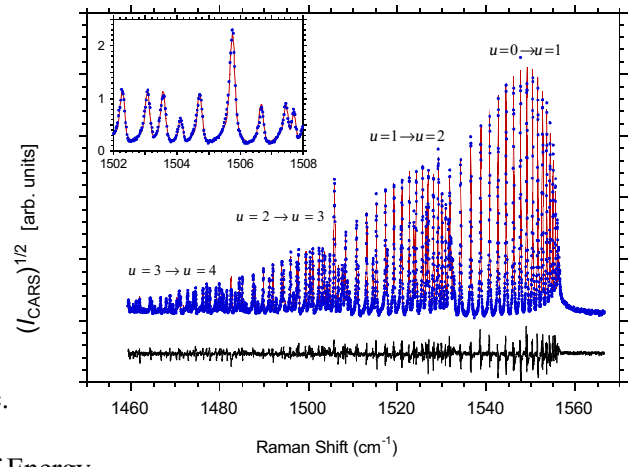
- O_2 CARS thermometry has been validated for probing the temperatures in fuel-lean O_2-enhanced environments up to 2450 K where O_2 is present in quantities of ≈10% or greater.

Commercialization Plans

- None at this time, although a miniaturized, field-capable CARS instrument based on this methodology is certainly viable.

Target Markets

- Organizations conducting research and development of oxygen-enhanced glass melters.



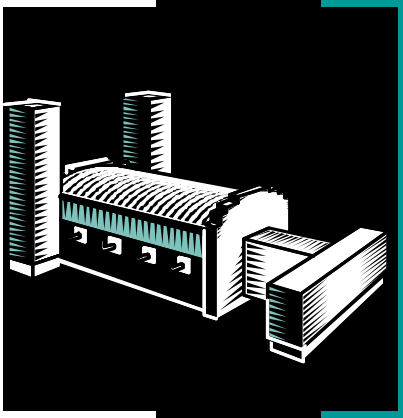
Key Participants

- Diagnostics and Remote Sensing Department, Sandia National Laboratories
- In the initial stages, this project was included in a larger project led by Air Products and Chemicals, Inc. and Techneglas.
- Partial support received from the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

For more info, contact:
Roger L. Farrow
Sandia National Labs
(925) 294-3259

Glass IOF Completed Project

On-Line Chemical Vapor Deposition of Coatings on Float Glass



Project Objective and Background

North American production of flat glass for architectural applications exceeds 2.6 million tons annually. Most of the glass produced has relatively low insulating capabilities and is therefore not energy efficient. Sandia National Laboratories and Pilkington-Libbey-Owens-Ford worked together to develop an on-line chemical vapor deposition (CVD) process for applying new, optically transparent coatings with improved insulating capabilities for architectural glass. These coatings are hard and bendable, making them easy to handle and potentially suitable for automotive windshields.

Accomplishments and Knowledge Gained

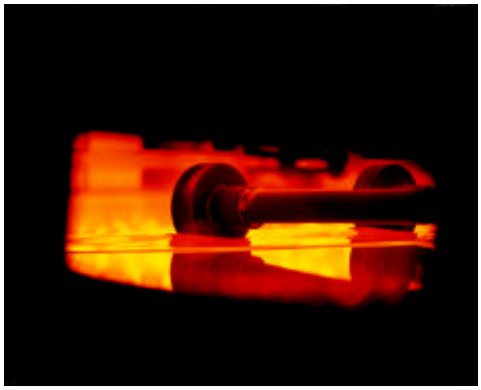
- Full-scale manufacturing processes for doped tin oxide coatings developed.
- On-line data base compiled for modeling on-line CVD processes: www.ca.sandia.gov/CRF/03_reactflow/ThermoKinData/index.html.
- Measured chemical reaction rates and thermal stability of coating chemical precursors.
- Demonstrated on-line analytical techniques for monitoring CVD process gases, based on mass spectrometry and catalytic sensor technology, in field trials.

Technology Benefits and Impacts

- Dramatically accelerated development of subsequent new products; commercialization occurred in only six months for next-generation on-line coatings.
- New processes produce fewer waste products and use reactant more efficiently by reducing side reactions in delivery lines.
- On-line monitoring techniques reduce process upsets and minimize defects associated with fluctuating reactant delivery rates.

Commercialization Plans

- Full-scale manufacturing of indium-doped tin oxide demonstrated.
- Full-scale manufacturing of antimony-doped tin oxide now on line.



Target Markets

- Flat-glass producers are the key targets.
- Also relevant to specialty glass coatings.

Key Participants

- Sandia National Laboratories (Livermore, CA)
- Pilkington-Libbey-Owens-Ford Co. (Toledo, OH)

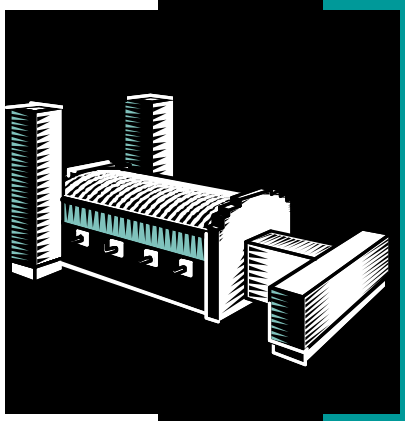
For more info, contact:
Mark D. Allendorf
Sandia National Laboratories
(925) 294-2895

Glass IOF Completed Project

On-Line Sensor System for Monitoring the Cure of Coatings on Glass Optical Fibers and Assemblies

Project Objective and Background

Polymer coatings, used on all telecom fibers, are important to the performance of modern communication systems. Undercure of the polymer coating is a common problem. The objective of this project is development of on-line, real-time monitoring technologies to prevent production of undercured coatings.



Accomplishments and Knowledge Gained

Two cure monitors were designed, built, and tested under experimental coating conditions. A transient infrared spectroscopy (TIRS) monitor was the primary project technology. The TIRS monitor response correlated well with the degree of cure. A second monitor measured the tackiness and therefore the degree of undercure of the coating surface. This tackmeter was also responsive to the degree of cure, but was less thoroughly investigated. Both technologies can increase production efficiency and product dependability by detecting undercured material during manufacturing.

Technology Benefits and Impacts

A cure monitor conserves energy by reducing the amount of glass fiber that must be scrapped because of undercure. The energy involved is considerable due to the energy intensive chemical vapor deposition and molten-glass fiber draw operations. Equally important benefits come from the improved product quality and performance of 100% fully cured product and from reduced waste.

Commercialization Plans

Further tests of a TIRS cure monitor may be needed before it will be commercially viable. Efforts are being made to interest the fiber-optic industry in the tackmeter technology, which is less costly but less proven. If sufficient commercial demand develops, a small, local company, MTEC Photoacoustics, Inc., is interested in manufacturing cure monitors.

Target Markets

These technologies are targeted at the fiber-optic industry, consisting of both single fiber and cable assembly producers. The monitors could find other markets where the cure of coatings is important to product performance and reliability.

Key Participant

- Ames Laboratory

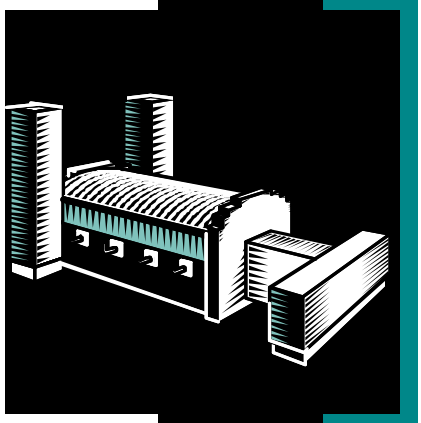
For more information, contact:
John McClelland
Ames Laboratory
(515) 294-7948

Glass IOF Completed Project

Oxygen-Enriched Air Staging (OEAS) for NO_x Reduction

Project Objective and Background

The objective is to commercialize the least expensive means to reduce NO_x in air-fired regenerative glass melters. In OEAS, air to the burners is reduced which reduces NO_x by 30-70% while CO is formed. Air or O_2-enriched air is injected into the furnace near the exhaust ports to burn out CO and recover all heat above the glass surface without generating more NO_x.



Accomplishments and Knowledge Gained

The project team has determined optimum OEAS configurations, reduced OEAS to commercial practice, made OEAS reliable and transparent to furnace operators, and reduced costs to make OEAS the most economical means to reduce NO_x. NO_x has been reduced by 30-70% to as low as 2 lb NO_x/ton of glass.

Technology Benefits and Impacts

OEAS is the lowest-cost technology available to reduce NO_x by 30-70% on air-fired regenerative glass furnaces. OEAS is rugged and industrial proven.

Commercialization Plans

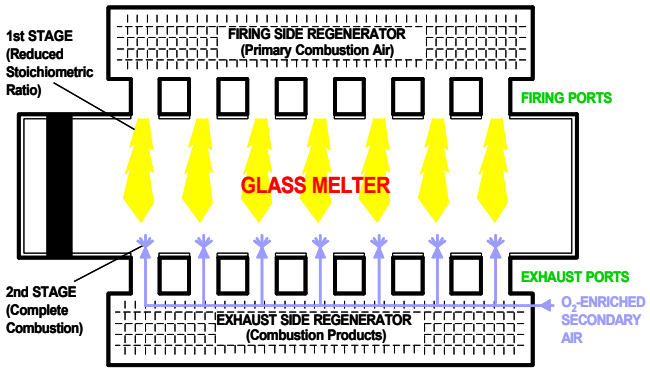
OEAS is commercialized and installed on 7 endport and 3 sideport container glass furnaces. Eclipse is actively marketing OEAS for container, flat, and specialty glass furnaces. GTI is pursuing development funding to apply OEAS to other high-temperature furnaces.

Target Markets

- Air-fired regenerative glass melters (container, flat, TV, specialty)
- Kilns (lime, cement, waste processing)
- Process heaters

Key Participants

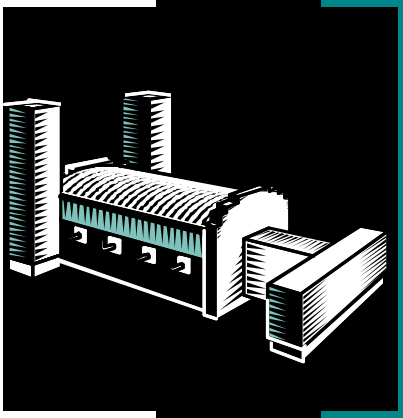
- Gas Technology Institute (GTI) – previously IGT
- Gas Research Institute (GRI)
- Southern California Gas Co. (SoCalGas)
- IGT Sustaining Membership Program (SMP)
- Eclipse – Combustion Tec
- Air Products and Chemicals, Inc. (APCI)
- Anchor Glass Containers
- Owens Brockway Glass Containers



For more info, contact:
Dan Wishnick
Eclipse/Combustion Tec
(407) 299-7317

GPLUS Completed Project

Construction of a Laser-Induced Breakdown Spectroscopy (LIBS) Instrument Calibration System



Project Objective and Background

A method is required to calibrate Laser Induced Breakdown Spectroscopy (LIBS) measurements for elemental species of interest to the glass industry. This capability will enable the LIBS technique as a research tool for characterization of particle composition, and as an on-line process monitoring method.

Accomplishments and Knowledge Gained

In this project we constructed and tested an aerosol generation system that produces a stream of submicron-sized particles. Plasma emission generated in the particle stream by a LIBS instrument allowed us to quantitatively calibrate elemental concentrations for several elements of interest to the glass industry (Na, Ca, Si, Al, B, K, Mg).

Potential Benefits and Impacts

The quantitative, real-time measurement of elemental concentration by the LIBS technique will allow the optimization and control of a wide variety of process flows in the glass industry. Measurements can be made on systems ranging from R&D bench-scale reactors to full-scale industrial production lines.

Information/Technology Transfer Potential or Plans

The aerosol generation system constructed and tested in this project was delivered to Corning, Inc., for use with their LIBS measurement systems. Detailed information on the calibration system is available for other interested industry participants.

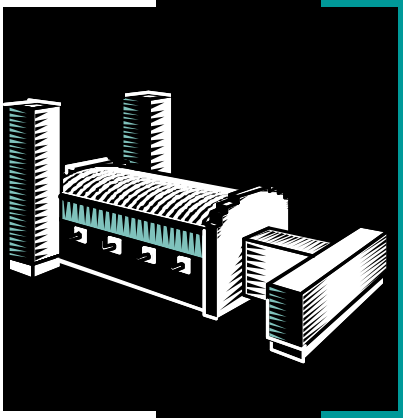
Project Participants

- Corning, Inc.
- Sandia National Laboratories

For more info, contact:
Jim Wang
Sandia National Laboratories
(925) 294-2786

GPLUS Completed Project

Controlling Boron Emissions



Project Objective and Background

One of the best ways to control emissions is to never generate them in the first place. The objective of this study was to try to quantify by direct measurement what effect the firing ratio of gas-to-oxygen has on the generation of volatile emissions. In this case, boron was chosen as the species to watch.

Accomplishments and Knowledge Gained

Using the latest LIBS technology, it was possible to monitor the changing levels of boron in the exhaust stream of an actual, operating, OXY-GAS glass furnace pulling approximately 300 MT/day. It was found that there is a dramatic increase in the Boron present in the exhaust gases whenever the fires went below the 2:1 stoichiometric ratio.

Potential Benefits and Impacts

- The cost of oxygen is a large portion of the operating equation and knowing how low you can go without adversely effecting emissions can be key to reducing costs.
- Batch costs and glass quality can better be controlled by knowing how to minimize the boron lost by volatilization.
- The energy required to handle the waste stream and landfill requirements can be reduced as fewer emissions are being generated.

Information/Technology Transfer Potential or Plans

A complete report on this work has already been released to all of the members of the Glass Manufacturing Industry Council. A summation of these results was also presented to the entire glass industry at the Glass Problems Conference at Ohio State University in October 2000.

Project Participants

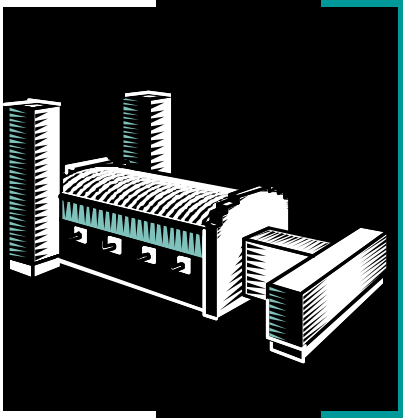
- Sandia National Laboratories
- CertainTeed Corporation

For more info, contact:
Peter Walsh
Sandia National Laboratories
(925) 294-3726

GPLUS Current Project

Analysis of Refractory Metal Needles Formed During Quartz Tube Extrusions

Project Objective and Background



- Quartz tubes for lamp applications are formed by melting high purity silica in a vertical refractory metal container and are formed through a refractory metal orifice and mandrel as a continuous tube. Typically, this process operates for long periods of time. In some cases, after an extended period of tube production, the quartz tube becomes scribed and out of round. The major cause of these defects has been shown to be large metallic crystals (see figure below) which grow on the bottom of the orifice and intercept the just formed quartz tube near the exit from the orifice.

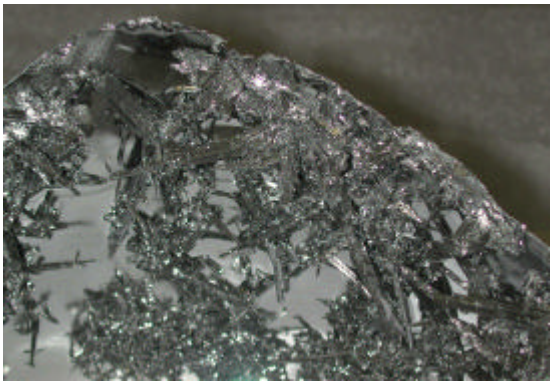
- The objective of the GPLUS project is to characterize the metallic needles and to determine the source of material, the crystal chemistry, growth habit, and the material transport mechanism that supports growth. Optical microscopy, scanning electron microscopy, x-ray diffraction, and thermodynamic modeling are to be used.

Potential Benefits and Impacts

The reduction or elimination of crystal growth would result in a substantial reduction in defective tubes and a consequential saving of both energy and capital investment for the furnace container, orifice and mandrel.

Information/Technology Transfer Potential or Plans

A project report will be prepared that summarizes the materials characterizations and thermodynamic calculations that are being performed.



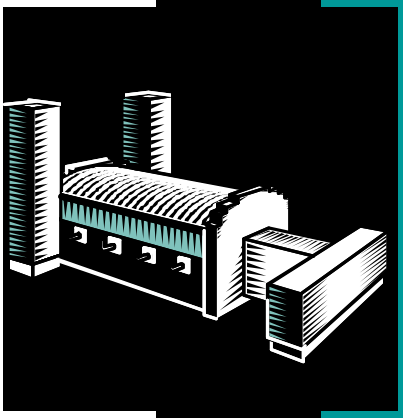
Project Participants

- Bill Yellenik, Osram Sylvania Inc, Glass Technologies, Exeter, New Hampshire
- Camden Hubbard, Evan Ohriner, and Roberta Peascoe, Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

For more info, contact:
Bill Yellenik
Osram Sylvania Inc.
603-778-4534

GPLUS Current Project

Boron Emissions Capture



Project Objective and Background

In 2000, a GPLUS project was undertaken to better control boron emissions. This project will define the best operating parameters of a caustic soda chamber to convert the boron into a compound which can be captured by an electrostatic precipitator.

Potential Benefits and Impacts

- Increased efficiency of the electrostatic precipitator will capture more boron that can be put back into the batch, thereby reducing batch costs.
- Emissions going out of the stack into the atmosphere are reduced.
- Solid waste build up in the chamber is reduced and therefore reduces the amount of waste sent to landfills.

Information/Technology Transfer Potential or Plans

The information will be made available through the GMIC after appropriate review.

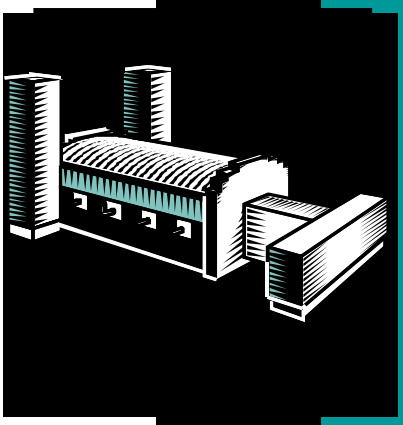
Project Participants

- Sandia National Laboratories
- CertainTeed Corporation

For more info, contact:
Peter Walsh
Sandia National Laboratories
(925) 294-3726

GPLUS Current Project

High Temperature Thermocouple Degradation Study



Project Objective and Background

• Glass manufacturers use precious metals thermocouples as the primary temperature sensors throughout the manufacturing process. It is well known that thermocouples degrade (drift) over time at high temperatures, but very little has been published that quantifies and characterizes this loss of accuracy at real operating temperatures over long periods of time.

Several commercially available precious metals thermocouples will be exposed to high temperature for a period of several months. Pre-test calibration, data trending, post-test calibration and metallurgical analyses will be used to quantify the degradation.

Potential Benefits and Impacts

• By providing quantitative information on the degradation of thermocouples, this project will increase the understanding of how and why thermocouples change while in use at high temperatures.

Information/Technology Transfer Potential or Plans

• This information will be published to help the glass industry to improve and make better use of these common temperature sensors.

Project Participants

•Schott Glass Technologies Inc. (SGT)
•Idaho National Engineering and Environmental Laboratory (INEEL)
•Engelhard-CLAL

For more info, contact:

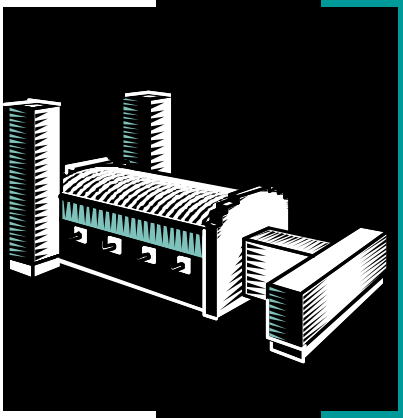
Art Watkins	Al Thorne
INEEL	SGT
(208) 526-1217	(570) 457-7485

Glass Manufacturing Industry Council

GPLUS Current Project

Reduction in Corrosion of Refractories Using Encapsulated Glass Additives

Project Objective and Background



The *Glass Industry Technology Roadmap* envisioned the development of technologies for the glass industry that would reduce manufacturing costs by 20%. Encapsulation of additives in the glass batch material and enhancement of refractory life in the melting equipment are regarded as critical steps needed to substantially reduce manufacturing costs.

Efficient inclusion of various additives in the starting glass batch material is fundamental to the manufacture of quality glassware using either a tank or pot. However, these additives may have adverse corrosive reaction with the refractory lining of the glass melting tank or pot. A clear and improved understanding of the effects of various additives in the glass batch on degradation of refractory lining of the glass melting tank will help select appropriate refractory material with improved service life and optimize glass batch composition for enhanced quality of glass.

This research project plans to theoretically as well as experimentally evaluate corrosion behavior of assorted candidate refractory materials for glass tank lining as a function of various additives in glass batch, using different encapsulated techniques. Based on the results of this study, glass batch composition with appropriate additives will be optimized and refractory lining material with improved corrosion resistance will be selected.

Potential Benefits and Impacts

Results of this study will provide information on appropriate selection of additives for improving quality of glassware and identification of refractory material(s) with improved corrosion resistance relative to the glass additives. This will result in reduced refractory wear, improved glass ware quality, and enhanced campaign life of refractory lining and melting equipment. Minimization of refractory wear will reduce refractory waste with a positive environmental impact, and enhanced campaign life will result in a substantial amount of energy savings.

Information/Technology Transfer Potential or Plans

This work will be done in close collaboration with glass industry and refractory manufacturer(s). Industrial partners will be informed of the research findings through phone conversations and written reports, if needed. At their annual symposium, the Society for Glass Sciences and Practices will partner with the Glass Manufacturing Industry Council to present a paper on the project.

Project Participants

- Society for Glass Sciences and Practices (SGSP)
- Argonne National Laboratory

For more info, contact:
J.P. Singh
Argonne National Laboratory
(630) 252-5123