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CERTAINTEED FY-2000 G-PLUS PROJECT

[*Full Report*]

Titled: **Dependence of Boron and Sodium in Flue Gas From a Borosillicate Glass Melting Furnace on Oxygen to Natural Gas Ratio**

CertainTeed Originator: Terry Berg
Sandia Investigators: Peter M. Walsh, Howard A. Johnsen and David K. Ottesen

The CertainTeed furnace engineers believed the oxygen to gas ratio of the furnace gas burners affected the NO_x and particulate matter emissions in melting a borosilicate insulating glass. Sandia scientists had successfully used laser-induced breakdown spectroscopy (LIBS) to measure sodium in flue gas at the Gallo Glass Co. plant in Modesto, California. This G-PLUS project plan was to use LIBS to measure the sodium, boron and other volatile metals in the flue gases while the furnace burner adjustments were made to vary the oxygen to natural gas ratios from 1.6 to 2.0.

The volatilization of boron was independent of this ratio. Sodium volatilization increased about 40 percent over the same interval. The boron mass flow at the exit from the electrostatic precipitator decreased 30 percent over the range of oxygen to natural gas ratios from 1.6 to 1.85 then increased slightly at the higher ratios of 1.95 to 2.0. The NO_x emission at a ratio of 1.9 was 49.6 lb./hour; at a ratio of 1.85, it was 38 to 46 lb./hour.

From the viewpoint of NO_x and particulate matter emissions, the oxygen to natural gas ratio of 1.85 appears to be very close to true optimum.

CORNING FY-2000 G-PLUS PROJECT

[*Full Report*]

Titled: **Construction and Performance Testing of an aerosol Generation System for Quantitative Calibration of In-Situ Laser Induced Breakdown Spectroscopic Measurements**

Corning Originator: Frederic Quan
Sandia (Livermore) Investigators: Howard Johnsen and David Ottesen

An aerosol generation system has been constructed and tested. This system will be used primarily to calibrate Laser Induced Breakdown Spectroscopy (LIBS) measurements for elemental species of interest to the glass industry. Where the environment of in-situ measurements can be simulated in the generated aerosol flow, the calibration will be quantitative. In other process environments (typically either high temperature or containing toxic or reactive species) the system serves as a developmental environment for designing optimum LIBS measurement parameters. In this case, the in-situ optical emission data are calibrated by independent off-line methods for process characterization and control.

In this report we describe an aerosol generation system that enables the production of precise mass flow streams of well characterized, submicron sized aerosol particles. The construction and testing of this system has been carried out in cooperation with Corning, Inc. Particle characterization, including detection of low-concentration contaminants, and new on-line process monitoring technologies may serve as important enabling technologies. These and other application needs served as the motivation for development of an aerosol generation system for calibrating in-situ laser diagnostic measurements.

LIBS spectra were recorded for Ca, Si, Al, K, Mg, and B. A representative spectrum, corresponding to the average of 1000 laser pulses at different concentrations. Calibration curves were calculated for calcium, silicon, aluminum, potassium, magnesium and boron.

A linear least-squares regression analysis of these data yields a correlation coefficient of 0.999.

The nebulization of aqueous solutions enables the generation of a reasonably large range of overall mass concentrations. This aerosol generator system is well suited for the development, assessment and calibration of LIBS (as well as other laser-based diagnostic techniques) for a variety of in-situ process measurements.

VISTEON FY-2000, 2001 & 2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Strength of Glass with Holes Including Stress Corrosion Cracking**

Visteon Originator: Ed Boulos and M. Brennan
Pacific Northwest Investigators: F.A. Simonen, M.E. Dahl and A.D. Guzman

These G-PLUS projects created data using annealed but not tempered glass specimens. The tests included samples with holes and samples without holes, and included a range of fabrication procedures to produce the holes. The testing focused on conditions of high loading rates which included static fatigue tests with a water environment.

The long range objective of the three projects was to develop a design procedure, including recommendations for limits on design stresses, for automotive glazing subject to strength reductions caused by hole penetrations. The proposed design approach was to have a probabilistic basis which can relate proposed design stresses to defined levels of failure probabilities.

Tests have been performed to establish strengths of glass specimens for which the breaking strengths have been degraded by the presence of a drilled hole. The drilled hole introduces a stress concentration that elevates the local stress at the hole, and introduces a distribution of small flaws around the edges of the hole. Tests of specimens under sustained loads in the presence of a water environment showed a significant reduction in breaking loads compared to the loads for fracture of the specimens for short-term loading conditions. Fracture mechanics calculations were performed to predict failure times associated with the growth of small flaws at the edges of the holes by the mechanism of stress corrosion cracking. These predictions predicted failure loads and failure times that were consistent with the static fatigue tests of the present study. The fracture mechanics calculations and results of short-term strength tests of specimens degraded by static fatigue loadings showed minimal interactions between the failure modes of static fatigue and failure due to short-term loading. A method for the design of automotive glazing is proposed. This method sets independent limits on sustained and short-term stresses, and assumes that interaction effects between the two failure modes can be neglected.

The test result data were used in the fourth G-PLUS project (FY-2003) titled “Strength of Tempered Glass with Holes Including Stress Corrosion Cracking”.

CERTAINTEED FY-2001 G-PLUS PROJECT

[*Full Report*]

Titled: **Dependence of Boron and Sodium in Flue Gas From a Borosillicate Glass Melting Furnace on Conditions in the Caustic Spray Tower and Electrostatic Precipitator**

CertainTeed Originator: Terry Berg
Sandia Investigators: Peter M. Walsh, Howard A. Johnsen, David K. Ottesen and Shane Sickafoose

Laser-induced breakdown spectroscopy (LIBS) will be used to define the relationships between the concentrations and volumes of caustic chamber reactants to maximize the collection of emissions from the waste gas stream for a furnace melting a borosilicate glass used for home insulation. This project is a continuing investigation of the influence of process and flue gas treatment conditions on the flow rates of boron and sodium in the exhaust from an oxygen/natural gas fired borosilicate glass melting furnace. The purpose of this investigation was to determine the effects of caustic soda and spray tower conditions, in particular the solution concentration, flow rate, and spray quality on the collection of boron in the electrostatic precipitator, with a view to optimizing the treatment of flue gas.

The data collected was scattered due to process variations of melting the borosilicate batch, volatilization of boron and alkali, treatment of the flue gas and the LIBS testing equipment. Also the electrostatic precipitator and the spray tower are exposed to the outside, so, another variable is the temperature at the precipitator outlet which varies with the ambient temperature and intensity of sunlight.

One set of data showed a systematic decrease in the flow rate of boron leaving the precipitator with increasing temperature at the outlet from the precipitator. Boron leaving the precipitator decreased by 15 percent over the range of outlet temperatures from 454 to 487 ^{o}F. The equilibrium calculations predict that the orthoboric acid vapor concentration passes through a minimum at 490°F, then increase with further increase in temperature. The boron leaving the precipitator also depends upon the time of day.

The water used to dilute the caustic soda serves to reduce the temperature of the flue gas. When the precipitator outlet temperature is below 490 ^{o}F, a low flow rate of more concentrated caustic soda is expected to provide slightly better boron capture than a higher flow rate of more dilute solution.

Variation of the atomizing air pressure at the caustic soda spray nozzle had no significant effect on the flow rate of boron leaving the precipitator.

OSRAM SYLVANIA FY-2001 G-PLUS PROJECT
[*Full Report*]

Titled: **Analysis of Refractory Metal Needles Formed During Glass Extrusion**

Osram Sylvania Originator: Bill Yellenik
Oak Ridge Investigators: Roberta A. Peascoe, Evan K. Ohriner and Camden R. Hubbard

Quartz tubes are melted and fabricated in refractory metal furnace. The lifetime of this furnace is limited due to metallic crystals nucleating and growing just below the orifice, inside the cooling area where the molten quartz is formed into a continuous quartz tube. Thus this study is to investigate the nucleation, growth and source of the metallic crystals in hopes of determining methods for controlling crystal growth and extending the lifetime of the quartz melter.

Samples of metallic crystals were examined using various techniques: X-ray diffraction (XRD), optical microscopy and the scanning electron microscope (SEM).

Thermodynamic calculations, supported by analysis of specimens, indicate the source of molybdenum oxides present below the orifice are from inside the molten quartz container. The most likely pathway is for the oxidized molybdenum vapor species from the melter container to pass through the orifice either as a gas layer between the molybdenum surface and the molten quartz, as bubbles in the molten quartz, or as a dissolved component of the molten quartz. As the molten quartz passes through the orifice the glass begins to cool and any absorbed gas species or bubbles would escape from the just formed quartz tube. If the gas forms a layer between the solid molybdenum surface and the molten glass it would easily cool after passing through the orifice. If a gas interface is formed, it may assist the flow of molten glass through the orifice. Once the molybdenum oxides from the melt container pass through the orifice it is exposed to an Ar/H2 atmosphere. In this environment, molybdenum oxides reduce to molybdenum and condense out as crystals preferentially on a cooler molybdenum (111) surface.

Analysis of specimens found that the molybdenum crystals on the bottom of the orifice and skirt are formed when molybdenum oxide vapors are reduced to Mo(S) by the Ar/H2 gases below the orifice. Upon cooling, molybdenum then condenses out of the vapor phase and deposits on the cooler surfaces. Nucleation of molybdenum crystals occurs on single grains and crystals grow is in a preferred direction.

The formation of molybdenum crystals on the orifice and skirt of the quartz melter is the main reason for failure and subsequent shutdown of quartz melters. Considering the finding above, two potential methods to extend quartz melter lifetime can be considered. The first is to eliminate molybdenum crystal formation. The second is to control the location and or direction of crystal growth.

OWENS CORNING FY-2001 G-PLUS PROJECT

[*Full Report*]

Titled: **Thermophysical Properties of Glasses**

Owens Corning Originator: Christopher Q. Jian
ORNL Investigators**:** Hsin Wang, Wally D. Porter and Ralph B. Dinwiddie

Thermophysical properties of glass are very important for the glass melting and forming processes. These properties are needed for modeling of the glass tank temperature distribution. More importantly, a good understanding of the thermophysical properties will also affect the productivity, energy and raw material cost.

It has been well documented that thermophysical properties data of the glasses are difficult to measure, especially into the melt region. In this project, we tested glass samples provided by Owens Corning for thermal diffusivity, thermal conductivity, specific heat and thermal expansion from room temperature to Tg and above. The thermal conductivity measurements into the glass melt (above 1000ºC) were not achieved using the current laser flash technique and other available instruments. A specially designed probe is needed for measurement in melt of 1200-1600ºC. As far as we know, there has been no commercial testing device that can accurately measure thermal conductivity of glass melts. Thermal expansion and heat capacity results both showed the glass transition temperature consistently. All the measurements indicated Tg near 780ºC.

Thermal properties of Owens Corning glass were studied. The laser flash method, DSC and thermal expansion results all indicated the same glass transition region. Thermal properties into the melt were only achieved to 1000ºC. At higher temperatures, all the current experimental setup could not be used. Special thermal conductivity probe has to be designed to measure thermal conductivity of the glass melt. Heat capacity of the glass melt could be measured when proper sample container is chosen.

SCHOTT FY-2001 G-PLUS PROJECT

[*Full Report*]

Titled: **High Temperature Thermocouple Degradation Study**

Schott North America Originator: Alfred Thorne
Idaho Investigator: Arthur D. Watkins

Glass manufacturers use precious metal 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. The primary indication of thermocouple degradation is EMF (voltage) drift as a function of time when the thermocouple is immersed at a constant temperature. Most tests described in the literature consisted of holding thermocouples at different high temperatures (e.g approximately 1300 to 1700 °C) for an extended period of time and then testing the thermocouples for EMF output at a single, lower reference temperature (e.g. 860 °C.) The EMF change from the original thermocouple output is drift and is normally associated with compositional changes in the "legs" or junction of the thermocouple. These resistance and EMF changes generally result from contamination (impurities) contained in the furnace atmosphere or ceramic protection tubes, from exchange of alloying elements at the welded junction, or from preferential volatilization of one metal (or oxide) from the alloy leg. Sometimes volatilization or embrittlement (in association with stresses on the thermocouple) will lead to breakage of the thermocouple wire.

The Idaho National Engineering and Environmental Laboratory performed a literature search, integrated a self-verifying temperature sensor into their furnace control system, calibrated and exposed five commercially available precious metal thermocouples, supplied by Engelhard-CLAL, to approximate temperatures of 1400 °C and 1610 °C for a period of 2 months. Trending, drift, and metallurgical analyses were performed on all and/or selected thermocouples and the results published in a final report.

The Pt-10%Rh vs Pt and Pt-6%Rh vs Pt-30%Rh thermocouples with high purity Al_2O_3 insulation construction (#810 and #811) did not exhibit drift at any of the holding temperatures.

Two other thermocouples showed drift with slightly more at the higher temperature.

The Pt-30%Rh vs Pt-40%Rh thermocouple with high purity Al_2O_3 insulation construction (#812) failed as the furnace temperature was increased from 1399 °C to 1610 °C and exhibited drift at the lower holding temperature. Evaluation of drift at the higher holding temperature was not evaluated because of the failure.

This G-PLUS project recommended a follow up experiment to expose another set of thermocouples to a single elevated temperature for an extended period of time (6 to 12 months). The results are in the FY-2003 Schott INEEL G-PLUS report.

SGSP FY-2001 G-PLUS PROJECT

[*Full Report*]

Titled: **Reduction in Corrosion of Refractories Using Encapsulated Glass Additives**

Society for Glass Sciences & Practices Originator: James Kroner (Kopp Glass)
Argonne Investigator: J.P. Singh

Fundamental to the manufacture of quality glassware using either a tank or pot, is the efficient inclusion of various additives. Also fundamental to the melting procedure is the best selection of refractory material with which to construct a tank so as to minimize the corrosion nature of molten glass on the refractory surface. Much of the interactive decision-making regarding the type of tank refractory relative to the type of encapsulated batch additive still needs to be appreciated.

The project objective was to characterize the corrosion behavior of refractories in molten borax glass and to evaluate the effect of pelletization on the corrosion behavior of refractories.

This research project proposes to theoretically as well as experimentally evaluate particular tank refractory materials based on an assessment of the corrosion effects of various additives using different encapsulated techniques. Vision Tile and RESERV® 70 from North American Refractories Company were two of the refractories tested. Refractory bricks from L. E. Smith Glass Company and the Vision Tile constituents were alumina, zirconia and silica, while the primary constituents of RESERV® 70 were chromic oxide and alumina. These refractories were in the shape of rectangular bricks. Two batches of anhydrous borax glass (sodium tetraborate, $Na_2B_4O_7$) were received from Kopp Glass, Inc., to characterize their effect on refractory corrosion. Among the two glass batches, one was prepared using powdered cadmium sulfide (unpelletized), while the other was prepared using pelletized cadmium sulfide.

The corrosion testing of the three refractories with pelletized and unpelletized glasses was performed in air at 1371 and 1460°C for 10 to 100 h. No corrosion damage occurred for the three refractories tested at 1371°C for 10 to 50 h. However, refractories tested at 1460°C for 100 h exhibited varying degrees of corrosion. For testing performed at 1460°C for 100 h, Vision Tile exhibited the maximum corrosion, while the L. E. Smith refractory exhibited little or no corrosion. Corrosion depth was ~10 mm for the Vision Tile and ~3 mm for the RESERV® 70 refractory. The depths of corrosion for each refractory was observed to be similar in both pelletized and unpelletized glasses, suggesting that there is no significant effect of pelletization on the corrosion behavior of the refractories exposed to the two glasses.

CERTAINTEED FY-2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Glass Properties Determination**

CertainTeed Originator: Terry Berg
Berkeley Investigators: Jeffrey A Reimer

The purpose of the proposed testing is to try to determine the differences in glass properties from fibers produced in different plants using essentially the same batch composition and identify the most likely causes of these differences. This project would give a National Laboratory the opportunity to show what tests they can perform on glass and the limits of detectablility of these tests.

CertainTeed would provide "virgin" fiber samples from four different plants making the same product by the same processes. These fibers could then be tested as fibers or pulverized and re-melted and tested as bulk glass. If desired, the raw materials could be provided and melts made to compare glass properties before the fiberizing process begins.

Berkeley National Laboratory used Nuclear Magnetic Resonance (NMR) experiments on the sodium (^{23}Na) nuclei in the provided fiberglass samples (CertainTeed) to find differences in the submitted samples. The spectra were obtained using the Hahn spin-echo pulse sequence during magic angle spinning (MAS) in a 200 MHz magnet, spun at about 28 kHz. A 0.1M NaCl solution was used as a standard. Magic angle spinning was performed on these samples in order to narrow the line width of the spectra in case multiple peaks were present that may have been hidden within the broad spectrum obtained previously without spinning.

Our conclusion from these studies is that further analysis of the structure and composition of these fiberglass samples will require more extensive NMR techniques, as well as investigations of other nuclei. At the present time the CertainTeed partners consider such further investigations outside the scope of the G-PLUS program.

CORNING FY-2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Development of New Control Software for Integration of an Echelle Grating Spectrometer for use in Laser Induced Breakdown Spectroscopic Measurments**

Corning Originator: Preston S. Clemons
Sandia (Livermore) Investigators: Shane Sickafoose and Robert Steinhaus

A custom instrument control and data acquisition software package has been developed, in cooperation with Corning, Inc. to integrate an echelle grating spectrometer into an existing Laser Induced Breakdown Spectroscopy (LIBS) instrument. The LIBS instrument has been and will be used in a variety of projects with relevance to the glass industry. The application of an echelle grating spectrometer to the LIBS instrument introduces the ability to simultaneously collect spectral information for the entire spectral range from the ultraviolet to the near-infrared (200 nm to 900 nm). This will afford the continuous, simultaneous, in situ monitoring of most atomic elements of interest to the glass industry for process characterization and control.

In this report we describe the development of control software for integration of an echelle grating spectrometer, the Mechelle 7500, into an existing Laser Induced Breakdown Spectroscopy (LIBS) instrument. The key to process and emission characterization and control is the continuous and simultaneous monitoring of all relevant elements in the process or exhaust stream. The unique optical arrangement of an echelle spectrometer enables the simultaneous acquisition of a wide range of wavelengths. The software developed under this program is a significant improvement beyond the original commercial software, but still is restricted by the state of driver development from the manufacturer.

Some of the features that we implemented in this version include: automated file naming and saving, front panel display and control of timing functions, and cursor bars that permit marking and monitoring. Ongoing development will continue to refine the control software to fit the niche requirements of a field test oriented instrument.

This G-PLUS project was the second of three projects. Corning is using their LIBS unit in process control and problem solving to optimize the glass manufacturing processes and the specialty glass being produced.

FIRE & LIGHT FY-2004 G-PLUS PROJECT

[*Full Report*]

Titled: **Using Colored Cullet for Making Beautiful Glassware**

Fire & Light Originator: John McClurg
Pacific Northwest Investigators: Dong-Sang Kim and Josef Matyas

Eight colored glasses from Fire and Light Originals (FLO) and three container cullet glasses were characterized for the viscosity, density, and thermal expansion, glass transition temperature, dilatometer softening temperature, color chromaticity, Fe(II)/Fe(total) redox ratio, and chemical composition. The results of the characteriza-tion were used to evaluate the options for the glass formulation development of colored glasses aimed at increasing the use of recycled container glass cullet. Out of several options considered, the possibility of using clear cullet for FLO's Citrus colored glass was selected and investigated in this study. It was shown that it is possible to use clear cullet to produce Citrus glass at the cullet oxide ratio of 90 mass% and the final color can be adjusted by controlling the nitrate level and alkali concentrations. From the present study, recommendations for further development efforts are provided to increase the container cullet usage or to replace partially or entirely the clear cullet by the amber cullet.

One of the major efforts of the Environmental community for the glass industry is to recover and recycle 100 percent of available post-consumer glasses. Currently, Fire and Light Originals (FLO) (http://www.fireandlight.com) uses recycled cullet from clear glass containers to make beautiful glassware of various colors. Cullet from green and amber containers is not used. Batch raw materials without cullet are used for some of its special colored products. The purpose of this project is to develop the glass formulations that can lead to increased usage of recycled container glass cullet.

The first step of this project was to characterize the properties of FLO's current products and container glasses by measuring the viscosity, density, and thermal expansion and glass transition temperature by dilatometer, color chromaticity, redox, and chemical composition. Eight colored glasses distributed in the following three source categories: (1) colors produced from clear container cullet and additional batch raw materials, (2)colors produced from 100 percent batch raw materials, and (3) color produced from the scrap of stained glasses.

The results from the study for the Citrus glass development suggest that the similar development for Lavender glass will be possible. There are no anticipated major obstacles for producing lavender color using clear container cullet. It is also recommended that the formulation development to replace partially or entirely the clear cullet by the amber cullet for the current "Clear cullet" glasses be performed. It is suggested that the development of the Olive glass that uses Fe_2O_3 as a colorant is the first option to start with, and then the development efforts can be expanded to other colors. The use of amber cullet will provide some cost benefits and will become very helpful, especially, in case there is a difficulty to provide enough supply of clear cullet.

LIBBEY FY-2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Batch Reactions of a Soda-Lime Silicate Glass**

Libbey Originator: James McGaughey
Pacific Northwest Investigators: Dong-Sang Kim and Josef Matyas

The purpose of this project is to develop the batch reaction data for a soda-lime-silicate glass needed to improve the batch part of the glass-furnace model being developed for the glass industry. Evolved gas analysis combined with batch expansion measurement and thermal analysis was successfully applied to obtain batch reaction data. The heat-capacity measurement by differential scanning calorimetry (DSC) was suggested as a promising method to derive the heat-of-fusion data inexpensively for many different technical glass batches. More tests on a variety of glass batches and parametric studies of the suggested methods are needed for validation. The experimental methods for batch reaction studies and the methodology for obtaining inexpensive heat-of-fusion data developed in this study can also be applied to various types of other technical glasses.

From the study of batch expansion and TGA-DTA combined with evolved gas analysis, the batch-reaction data on a soda-lime-silicate glass composition have been obtained including the effect of the cullet ratio on the reaction rate of cullet-containing batches. The batch-reaction data obtained in this study can be incorporated into the batch part of the glass furnace model. The methodology developed during this study with a soda-lime glass batch can be applied to other technical glass batches. It was suggested that test methods should be modified for the detailed study of refining by refining agents.

It has been suggested that DSC can be used to measure the heat capacity of the glass cullet and the batch of raw materials, and this measurement can be used to estimate the heat of fusion needed for the batch model. With the improvement of measurement accuracy and the validation of the assumptions involved in the calculations, the combined method of applying DSC *Cp* measurements and thermochemical calculation would become a valuable tool for obtaining data for batch model calculation for many different technical glass batches.

OSRAM SYLVANIA FY-2002 G-PLUS PROJECT
[*Full Report*]

Titled: **Analysis of Refractory Metal Needles Formed During Glass Extrusion II**

Osram Sylvania Originator: Mark Fieldsend
Oak Ridge Investigators: Roberta A. Peascoe , Ted Besmann , Evan K. Ohriner, Sudarsanam S. Babu and Camden R. Hubbard

This project is the second one to study a problem in the manufacture of quartz tubes melted in refractory metal furnace. The lifetime of this furnace is limited due to metallic crystals nucleating and growing just below the orifice, inside the cooling area where the molten quartz is formed into a continuous quartz tube. In the FY-2001 study, it investigated the nucleation, growth and source of the metallic crystals in hopes of determining methods for controlling crystal growth and extending the lifetime of the melter.

One potential means of reducing or eliminating crystal growth in quartz melting furnaces is to coat the internal components with another refractory metal such as rhenium or iridium. These materials have been reported to be useful as coatings in reducing metallic impurity contents in melted quartz. The purpose of this analysis is to obtain a rough estimate of coating thickness needed for long-term service at 2000° C. The coating thickness requirement is controlled by diffusion of the coating material into the molybdenum base metal.

Several thermodynamic calculations were performed. This time molybdenum, tungsten, rhenium and iridium were included to compare various refractory metals that could have potential applications in the quartz melter. The thermodynamic data available for rhenium or iridium calculations is not as extensive as for molybdenum and tungsten. Further the lack of high temperature data for some possible oxide species along with the unknown data's reliability make predictions uncertain.

Analysis of specimens from the three OSRAM Sylvania quartz melters examined at ORNL leads to the following findings. Molybdenum or tungsten crystals form on the bottom of the orifice and skirt when molybdenum or tungsten oxide vapors (MoOX or WOX) are reduced to solid molybdenum or tungsten by the Ar/H2 cooling gases circulating below the orifice.

The formation of crystals on the orifice and skirt of the quartz melter is the main reason for failure and subsequent shutdown of quartz melters. Considering the findings above, two potential approaches for extending the quartz melter lifetime can be considered. The first is to eliminate or reduce the rate of crystal formation. The second is to control the location and or direction of crystal growth. Iridium and rhenium coatings on molybdenum offer potential for reducing or eliminating crystal growth in quartz melting furnaces due to lower oxide partial pressures.

OWENS CORNING FY-2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Thermal Conductivity Measurements of Fiberglass**

Owens Corning Originator: Norman T. Huff
ORNL Investigators**:** Hsin Wang, Ralph B. Dinwiddie and Kenneth E. Wilkes

Fiberglass made by Owens Corning is being used in noise reduction of automobile exhaust system. Specifically, the glass fibers are packed inside the muffler to achieve the desired acoustic effect. A secondary benefit of the fibers is to serve as a thermal insulation. Because of this insulating property, the glass fibers can serve to reduce the temperature of the muffler shell. This in turn reduces the need for heat shields around mufflers and reduces the amount of exterior temperature accelerated corrosion of the muffler shell, especially in the winter "salt belts" where large amounts of salt are placed on highways to minimize the safety impact of snow and ice. In addition, for some applications the use of the fiberglass could allow the use of lighter weight carbon based polymer composite materials in place of steel for muffler shells. However, in order to properly design exhaust systems without heat shields or to take advantage of new materials, the thermal conductivity of the fiberglass material at operating temperatures (for some applications above 750° C) must be known.

We selected two types of Owens Corning glass fibers, 17 m and 24 m in diameter, for this study. There are some room temperature thermal conductivity data for the fiberglass, but high temperature data are not available. Based on the thermal radiation model, thermal conductivity should increase rapidly at high temperature, providing less thermal insulation. In addition, thermal conductivity depends on packing density of the glass fibers. We will study the effect of packing density on thermal conductivity. Another issue is that the glass fiber conducts heat better along the fiber, while the conduction across the fibers is poor, because thermal conduction from one fiber to another has to go through an interface with thermal resistance. In fiberglass, most fibers are not in good contact with the surrounding fibers, thus, most heat transfer is dependent on the thermal radiation effect.

Thermal conductivity of Owens Corning glass fibers were tested from room temperature to 700° C using the Hot Disk system. The general trend shows a significant increase of thermal conductivity as a function of temperature. This effect is mainly due to radiation contribution. At room temperature the effect of increased packing density only showed small a effect on the thermal conductivity. A more sensitive Heat Flow Meter system was used to measure thermal conductivities at lower temperatures. The results showed a lowering of thermal conductivity with increasing densities. The low temperature data fits and physical laws were used to extrapolate and estimate the high temperature thermal conductivity. The results showed that the Hot Disk technique needs more calibration to be used reliably for measurements of thermal insulations.

PPG FY-2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Dependence of Melting (Liquidus) Temperature for Fiberglass-Related Compositions**

PPG Originator: Cheryl Richards and Hong Li
Oak Ridge Investigators: Theodore M. Besmann

This G-PLUS project investigated glass compositional changes to reduce fiber glass emissions while maintaining the current or reduced energy consumption of the glass fiber process. A brief overview of the emissions and energy concerns follow below.

Air emission impacts from fiber glass manufacturing are nitrogen oxides (NOx) from the combustion process, particulate matter from batch raw materials, and volatilized losses of boron and fluoride from the melted glass. Efforts to reduce pollutants include end-of-process emission control devices and/or reformulation of the glass to reduce or eliminate pollutants of concern.

Reformulating glass to reduce or eliminate process pollutants however impacts energy consumption in the following ways. Boron and fluorine help to reduce the viscosity of the glass. Boron also reduces liquidus and provides desirable electrical properties while fluorine reduces surface tension. A reformulated glass with lower boron and fluoride removal, therefore, is expected to have significantly higher melting and forming temperatures.

The focus of the current effort was to explore the effects of compositional change on melting (liquidus) temperature. The objective is to mitigate the effect of increased liquidus temperature due to changing glass composition to reduce pollutants. Thus information was obtained from equilibrium phase relations calculations, particularly looking at the influence of B_2O_3, MgO, and CaO on simplified/model fiberglass compositions.

Comparison with experimental results showed substantial deviations from computed liquidus values. This highlights the need for better models in these systems than those currently available through the FactSage databases. Work is ongoing in an Industrial Materials of the Future project to address some of these needs. PPG notes that significant modeling improvements for both CaO and MgO alumino-silicate will provide invaluable assistance to the fiber glass industry in predicting the impact of composition change on fiber glass processability.

SCHOTT FY-2002 G-PLUS PROJECT

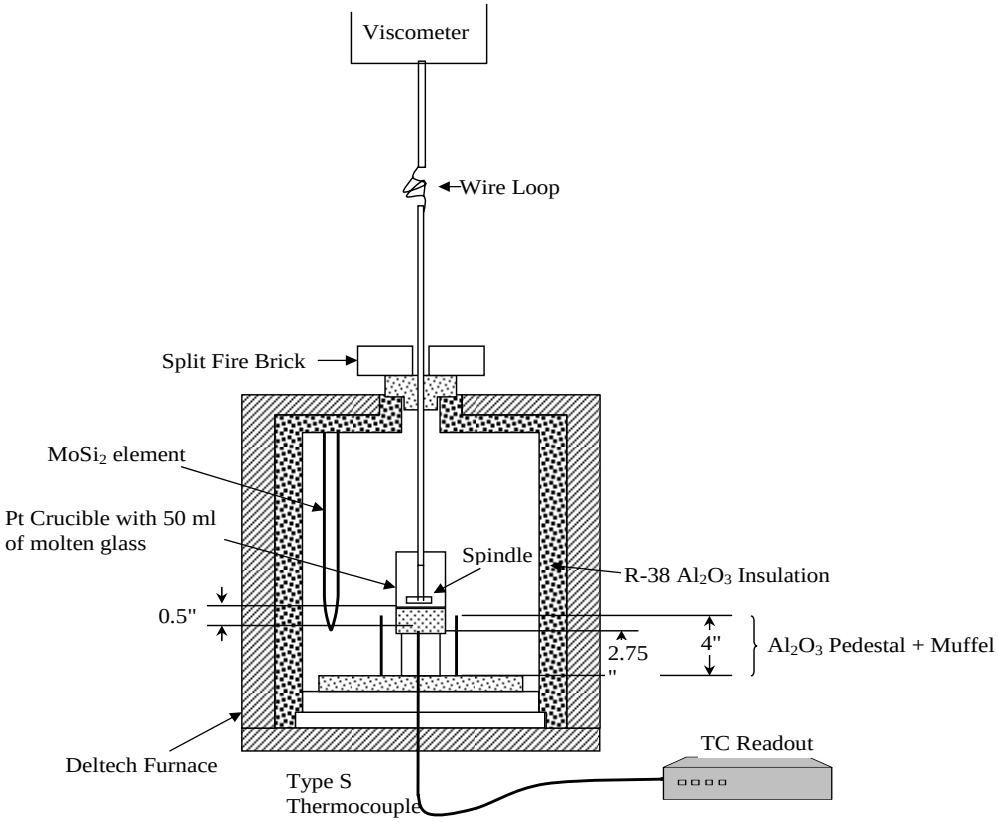
[*Full Report*]

Titled: **Viscosity of Commercial Glasses Data Package**

Schott North America Originator: Alex Marker
Pacific Northwest Investigator: C. A. See, O. P. Lam, K. B. C. Minister and P. R. Hrma

Viscosity was measured for commercial glasses fabricated at Alfred University for the DOE project "High Temperature Melt Property Database for Modeling." Rotating spindle viscometers were used at Pacific Northwest National Laboratory to obtain high-temperature data for the glass-melting temperature range (between 900°C to 1550°C); the viscosity varied from 1 Pa·s to 750 Pa·s. Arrhenius coefficients were calculated for individual glasses.

Glasses for six different types of commercial glasses were measured. These glass types are low-expansion-borosilicate glasses, E glasses, fiberglass wool glasses, TV panel glasses, container glasses, and float glasses. The total number of glasses was 150 different compositions, 25 compositions (baseline plus 24 variations) for each of the six groups.



SGSP FY-2002 G-PLUS PROJECT

[*Full Report*]

Titled: **Glass Coating Enhancement**

Society for Glass Sciences & Practices Originator: Beri Fox (Marble King)
Oak Ridge Investigator: Craig Blue

This goal of this project is to fully characterize the heating and coating process at Marble King. Once completed and implemented, this work will result in decreased energy usage through: optimization of heating, improved heating technology, and reduced scrap.
This project involves the infrared processing of glass and is relevant to industries involved in heat treating, coating or annealing of glass products.

Presently, glass marbles are being coated with Tetraisopropyl Titanate (TIPT) to enhance the marbles esthetics. The process incorporates heating of the substrates followed by room temperature aspiration of the TIPT onto the heated substrates. The Glass Technology Roadmap identifies the following needs, “increase yield/decrease rejection rate of product”, “use of process heat”, and “increase throughput and waste minimization”. Heating is presently the rate-limiting step and is not fully characterized. In some instances the substrates crack upon heating.

In the laboratory, the use of an infrared furnace to heat the marbles to the processing temperature decreased the cycle time by nearly half. Additionally, the thermal control established by the use of a direct heating method has the potential to reduce scrap by preventing overheating and by insuring uniform batch-to-batch heating. Implementation of a rotational system on the cooling bucket is expected to result in a large reduction in the scrap that was the result of uneven cooling and poor annealing.

Future work is expected to include the possible implementation of an infrared furnace at Marble King, justified by the expected increase in productivity and the decreased energy usage. Future work will also include the implementation of a rotational system on the cooling bucket as well as an analysis of the scrap reduction involved with the installation of the rotational system.

CLEVELAND STATE JOHNS MANVILLE FY-2003 G-PLUS PROJECT

[*Full Report*]

Titled: **Millimeter Wave Diagnostics for Glass Fiber Drawing**

Cleveland State Investigator: Phillip Sanger
Johns Manville Investigator: Jerry Demott
Pacific Northwest National Lab Investigator: S.K. Sundaram

The measurement of bushing temperatures and glass level inside the bushing are key glass fiber drawing process variables. However measuring the complete temperature profile on the bushing is not possible because the glass fibers themselves obstruct the line of sight. Millimeter waves (MMWs) however do not see the fibers due to their small diameter (5-10 microns) and offer a unique sensor approach not presently available in the industry. Moreover, MMWs offer the potential for the measurement of glass head pressure and glass viscosity, two other key variables to the glass fiber drawing process. The research project completed focused on setting up a MMW system at CSU on the 400 tip bushing and demonstrating the effectiveness of that technique in obtaining a clear temperature profile of the bushing. The team not only accomplished the goal of the project but also showed that MMW technology could also be used to detect fiber breakage. This letter report summarizes the technical work completed under this project during this period.

Temperature profile in the bushing has been identified as a key parameter affecting breakage which directly impacts production efficiency (Roadmap goal #1). The development of sensors and controls that improve glass production efficiency has been clearly identified as an action step in the roadmap. Furthermore improved efficiency reduces process energy (#3), reduces glass scrap (#2), and reduces environmental emissions (#4).

On-line monitoring of glass melt processing can be realized through the use of millimeter-wave (MMW) technologies. Electromagnetic radiation in the 10 – 0.3 mm (30 – 1000 GHz) range of the spectrum is ideally suited for remote measurements in harsh, optically unclean and unstable processing environments. Millimeter waves are long enough to penetrate optical/infrared obscured viewing paths through dust, smoke, and debris, but short enough to provide spatially resolved point measurements for profile information. Another important advantage is the ability to fabricate efficient MMW melter viewing components from refractory materials. The same ceramics and alloys from which the melter/furnace is constructed could be used to fabricate MMW waveguide/mirror components that go into the melter for long life survivability. Therefore, ***we chose the MMW technology for our demonstration***.

CORNING FY-2003 G-PLUS PROJECT

[*Full Report*]

Titled: **Feasibility Study: Laser-Induced Breakdown Spectroscopy (LIBS) as a Glass Melt Monitor**

Corning Originator: P. Scott Clemons
Sandia (Livermore) Investigators: Shane Sickafoose

Initially Corning purchased a LIBS system and planned to evaluate the usefulness of LIBS as a possible means for improving the glass manufacturing process rather than as an academic tool. However, Corning did not have sufficient expertise and sought outside expertise in this technical area in order to properly evaluate the technology. Through GPLUS Corning was able to access capabilities at the Sandia National Laboratory wrt knowledge of the method, design, construction, application and testing and with SNL's assistance developed improved software controls and a unique approach to calibration of the instrument. "Having access to a national laboratory with LIBS expertise was very valuable to Corning".

The first and second GPLUS projects focused on a fumed silica process in the Corning fiber division. The goal was to probe the silica particle forming process by analyzing the composition of particles as they formed in the reaction flame. The objective of the GPLUS project was to develop the software that would enable the proper use of LIBS to the various glass manufacturing processes applications. Having a pure silica powder is critical in achieving high process efficiency and yield from the continuous free glass forming process in the free fiber division. In this way, processes could be controlled and the impurity level of the silica powder monitored and controlled. Parts per million impurity levels would essentially ruin the functionality of the glass parts. Various other applications for this type of specialty glass include a) optical fiber used in communications, b) windows in high performance environments ie windows for the Space Shuttle, and c) projection lenses for photolithography production of critical semiconducting circuits.

The third LIBS project focused on testing the feasibility of LIBS to determine the composition of molten glass by analyzing vapor species immediately above the surface of the molten glass in a furnace. Typically Inductively Coupled Plasma (ICP) is utilized to measure the composition of glass by taking samples from the melt and analyzing them at a laboratory. The use of ICP is time consuming and the results cannot be easily related to the influence of various feed materials and glass melting process parameters on glass quality. LIBS could possibly provide glass compositional information at various locations in the furnace very quickly. This was a high risk technical activity and the GPLUS enabled Corning to evaluate it.

The GPLUS efforts brought a new tool to Corning that is being used in process control and problem solving to optimize the glass manufacturing processes and the specialty glass being produced.

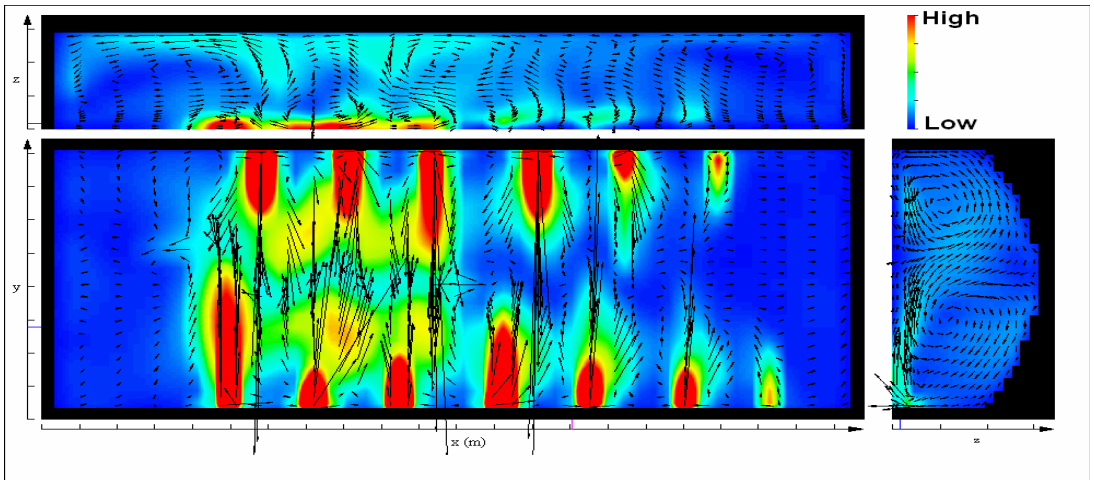
LONGHORN FY-2003 G-PLUS PROJECT
[*Full Report*]

Titled: **Application of Furnace Model to Longhorn Glass Corporation Oxy-Fuel Furnace for the Production of Amber Glass**

Longhorn Originator: Susan Jones
Argonne Investigators: Brian Golchert

The objective of this project is to apply the ANL Glass Furnace Model (GFM) to the Longhorn oxy-fuel furnace to improve energy efficiency and to investigate the transport of gases released from the batch/melt into the exhaust. The model will make preliminary estimates of the local concentrations of water, carbon dioxide, elemental oxygen, and other subspecies in the entire combustion space as well as the concentration of these species in the furnace exhaust gas. This information, along with the computed temperature distribution in the combustion space may give indications on possible locations of crown corrosion. An investigation into the optimization of the furnace will be performed by varying several key parameters such as the burner firing pattern, exhaust number/size, and the boost usage (amount and distribution). Results from these parametric studies will be analyzed to determine more efficient methods of operating the furnace that reduce crown corrosion. Finally, computed results from the GFM will be qualitatively correlated to measured values, thus augmenting the validation of the GFM.

It was shown in this work that the gases released from the batch materials have a significant impact on the combustion space flow field. These gases cool down the combustion gases in those areas in which they are released and they alter the flow field inside the chamber. To create a complete simulation of an industrial glass furnace, this effect must be accounted for in detail. The current work demonstrates, in a very simplistic manner, the need for this interchange. Once this release has been determined, one can model the transport of the corrosive species that affect crown corrosion. This work has shown that, in addition to the temperature and corrosive species concentrations, the combustion space velocity field may have a strong impact on the crown corrosion.



Velocity Field Magnitude and Direction including Batch Gases

OWENS CORNING FY-2003 G-PLUS PROJECT

[*Full Report*]

Titled: **Improvement of Oxyfuel Burner Design and Operations**

Owens Corning Originator: Christopher Q. Jian
Sandia (Livermore) Investigators: Peter M. Walsh

Conversion of a forehearth from air/natural gas to oxygen/natural gas firing has two principal advantages: (1) a substantial increase in energy efficiency, because of the reduction in waste heat loss, and (2) fewer burners are required, reducing capital and maintenance costs. In spite of these advantages, oxygen/natural gas-fired forehearths are relatively rare. This project design and tested three burners and measured the burner tip temperatures in the burner evaluation trial. This G-PLUS project complemented the burner system development work for a larger DOE project.

A venturi burner containing a converging/diverging nozzle, internally mixing oxygen with natural gas, produced satisfactory flames in open air, but was rapidly destroyed by overheating when placed in a tuyere in the forehearth simulator. The marked changes in flow and heat transfer on placing a flame in an enclosure, especially one as restricted as a forehearth burner block, make observations of the behavior of forehearth burner candidates in open air of little value in assessing the likely performance of the burners in practice.

Instrumenting the burners with thermocouples placed at the oxygen and natural gas tips provides quantitative comparison of the performance of the burners and is especially useful for evaluating the effects of operating conditions on burner performance *in situ*, where the ability to observe flames, burners, and burner blocks visually is severely limited.

A straight concentric tube-in-tube burner having equal oxygen and natural gas velocities is capable of producing, with increasing tube diameters, a range of flames from short, with high combustion intensity, to long, with low combustion intensity. A burner of the latter type performed satisfactorily in a short-term test in the forehearth simulator. Because the spatial distributions of the properties of jet flames are dominated by their nozzle diameters and initial velocities, adjustment of orifice diameters is a useful approach to the adaptation of a basic burner design to the requirements of particular applications.

A review of the burner designs described in U.S. patents and publications related to oxygen/natural-gas-fired forehearth burners indicates that wide ranges of opinion exist regarding the optimum velocities of oxygen and fuel, internal versus external mixing, and desirability of flame luminosity. This shows that no consensus on the design of forehearths and forehearth burners has yet been reached and suggests that continued research and development work can lead to further improvements in performance.

PPG FY-2003 G-PLUS PROJECT

[*Full Report*]

Titled: **Foaming of E-Glass**

PPG Originator: Cheryl Richards
PNNL Investigators: Dong-Sang Kim and Pavel R. Hrma
UCLA Investigators: Bryan C. Dutton and Laurent Pilon

The behavior of foams generated in the crucible melts was investigated to study the effect of furnace atmosphere on E-glass foaming, specifically focused on its water content to understand the effect of oxy-firing. A quartz-crucible furnace equipped with video recording was used to observe the behavior and to evaluate stability of foams generated from the PPG E-glass under various atmospheres. The present study preliminarily concluded that the higher foaming in oxy-fired furnace compared to air-fired is caused by the effect of water on early sulfate decomposition, promoting more efficient refining gas generation from sulfate (known as "dilution effect"), not by the effect of humidity on foam lamella stability. A plausible explanation for the difference between soda-lime glass and E-glass in the end result of the dilution effect on glass refining and foaming is presented. A preliminary experiment on the effect of heating rate also suggests that thermal history of glass melting can be a major factor in the rate of E-glass foaming. Approaches to develop the methods to reduce foaming in oxy-fired furnace are recommended.

Glass foams generated in glass-melting furnaces reduce energy efficiency and can lead to poor glass quality. Foaming of E-glass refined with sulfate is especially severe when processed with oxy-fuel firing. The objective of this project was to study the effects of the furnace atmosphere, mainly its water content, on E-glass foaming. The ultimate goal is to identify conditions for foam reduction during E-glass processing.

The results of foaming experiments with varying gas atmospheres conducted in this study point that the higher foaming in oxy-fired furnace (compared to air-fired) in E-glass production is not caused by the effect of water on foam stability, which contradicts the general hypothesis. The higher foaming in oxy-fired E-glass furnace can be attributed to the dilution effect of water on sulfate decomposition, discussed in the literature primarily for the soda-lime glasses. However, the difference is that the sulfate in E-glass has other function in addition to refining, which may prevent the decrease of sulfate to a sufficiently low level to compensate the increased refining gas generation in oxy-fired furnaces.

The possibility that small change of gas atmosphere may have a significant effect on foam stability was not confirmed at least within the atmospheres with varying fraction of N_2, CO_2, and O_2 tested in this study. The strong effect of heating rate on foaming was mathematically formulated, which agrees with the industry experience of higher foaming at higher throughput. A second G-PLUS project studied batches with different fining agents and variations to the furnace atmosphere.

SCHOTT FY-2003 G-PLUS PROJECT

[*Full Report*]

Titled: **High Temperature Thermocouple Degradation Study Follow Up**

Schott North America Originator: Alfred Thorne
Idaho Investigator: Arthur D. Watkins

Glass manufacturers use precious metal 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. This G-PLUS project is a continuation of the Schott FY-2001 project where five commercially available precious metal thermocouples, supplied by Engelhard-CLAL, were tested at approximate temperatures of 1400 °C and 1610 °C for a period of two months. In the Schott FY-2003 G-PLUS project, five commercial precious metal thermocouples, supplied by Engelhard-CLAL, were calibrated and exposed to approximate temperatures of 1500 °C for 6 to 7 months. Trending was performed on all of the thermocouples and the results are published in this final report.

Contamination from impurities is the most frequently cited cause of drift in thermocouples after exposure to high temperatures. In most of the testing cited in the literature, thermocouples were given positive protection from test furnace environments; thus, impurities in the ceramic components of the thermocouple assemblies were found to be the principal source of contamination. Ceramic components can include single- or double-bore electrical insulators (bores are for the wires), ceramic powder insulation, and ceramic protection tubes for isolation of the thermocouple from the furnace atmosphere. The ceramic composition generally used is high purity alumina (Al_2O_3), but high purity magnesia (MgO), and (to a lesser extent) zirconia (ZrO_2) and thoria (ThO_2) are sometimes used. Time, temperature, atmosphere, wire size, and geometry affected the magnitude of the EMF drift.

Table 1: Thermocouple Identification

ID Tag #	Type	Diameter (in.)	Composition
1066	S	0.347	Pt vs Pt-10%Rh
1067	B	0.347	Pt-30%Rh vs Pt-6%Rh
1068	S	0.347	Pt vs Pt-10%Rh
1069	S	0.125	Pt vs Pt-30%Rh
1070	B	0.125	Pt-30%Rh vs Pt-6%Rh

Evaluations of the results indicate the following:

1. Thermocouple 1067 did not exhibit any appreciable drift; its useful life was projected to be in excess of 5000 hours,
2. Thermocouples 1066 and 1068 exhibited drift and have useful lives of close to 2000 hours,
3. Thermocouples 1069 and 1070 exhibited extreme drift and have useful lives of only 200 hours.

VISTEON FY-2003 G-PLUS PROJECT

[*Full Report*]

Titled: **Strength of Tempered Glass with Holes Including Stress Corrosion Cracking**

Visteon Originator: Edward N. Boulos
Pacific Northwest Investigators: F.A. Simonen, M.E. Dahl and A.D. Guzman

This G-PLUS project built on existing data from past structural failure tests on glass specimens, which had been performed on samples of glass provided to PNNL by Visteon. The past tests included samples with holes, samples without holes, and samples using a range of fabrication procedures to produce the holes. The initial testing focused on high loading rates, whereas the more recent work provided data from static fatigue tests with a water environment. However, these prior tests were only for non-tempered glass. The work of the present report expands on the testing to address tempered glass, both for short- term loading and for long-term static fatigue loadings.

The long range objective of the past and present studies has been to develop a design procedure, including recommendations for limits on design stresses, for automotive glazing subject to strength reductions caused by hole penetrations. The proposed design approach has a probabilistic basis which relates proposed design stresses to selected levels of failure probabilities.

Results of the most recent tests for tempered glass are used to design automotive glazing systems. These tests determined the strength of tempered glass for which the strengths had been degraded by the presence of a drilled hole. The drilled hole introduced a stress concentration that elevated the local stress at the edge of the hole, and also introduced a distribution of small flaws around the edge of the hole.

The method for the design of automotive glazing as proposed for non-tempered glass should also apply to tempered glass. This method independently sets limits for sustained stresses and for short-term stresses, and assumes that interactions between the two failure mechanisms are small and can be neglected. Visteon used the results of the four G-PLUS project to develop a verified computational glass strength model that could be used in the design of holes in tempered glass sheets such that stress levels can be reduced and thus lead to the decrease or elimination of breakage in the field.

Visteon has estimate the energy savings using the results of the PNNL G-PLUS projects conducted on stress corrosion cracking of glass. The results of these studies were used as part of the justification for making a process change for a given product that resulted in a significant reduction in the number of parts needed. Based on this volume reduction, an estimated 3.4 MMBTU/year were saved. This estimate only includes the energy requirements associated with manufacturing. Additional energy savings due to reduction of shipping, handling, recycling of scrap etc. are not included.

PPG FY-2004 G-PLUS PROJECT

[*Full Report*]

Titled: **Foaming of E-Glass II**

PPG Originator: Hong Li
PNNL Investigators: Dong-Sang Kim, M. Portach, Josef Matyas and Pavel R. Hrma
UCLA Investigators: Laurent Pilon

In a previous study, the effect of the furnace atmosphere on E-glass foaming was investigated with the specific goal to understand the impact of increased water content on foaming in oxy-fired furnaces. The present study extended the previous study and focused on the effect of glass batch chemical composition on E-glass foaming. The present study also included reruns of foam tests performed in a previous study, which resulted in the same trend: the foaming extent increased nearly linearly with the heating rate and no foam was produced when CO2 + 55% H2O atmosphere was introduced at 300°C. It was shown that the lack of foaming in the test with CO2 + 55% H2O atmosphere introduced at 300°C was caused by a loss of sulfate at T <1250°C because of higher water content at the early stages of melting. The tests with new batches in the present study showed that replacing quicklime with limestone tend to decrease foaming, possibly caused by increased sulfate loss during early stages of melting in the batch with limestone. The batches where Na2SO4 was replaced with NaNO3, NaNO3 + CeO2, or CeO2, produced only very limited foaming regardless of the replacing components. As expected, the foaming extent increased as the sulfate content in the batch increased. The results of the present study suggest that foaming can be reduced by using limestone over quicklime and by decreasing the sulfate addition to a minimum required for refining.

Reruns of foaming tests with the E-glass batch used in a previous study (Kim et al. 2004) and designated as FY03 batch, resulted in the same trend as observed in a previous study: the foaming extent, measured by maximum ψ and $d\psi/dT$, increased nearly linearly with the heating rate and no foam was produced when CO2 + 55% H2O atmosphere was introduced at 300°C. The results of sulfate analyses retained in the glass after foaming tests confirmed that the lack of foaming in the test with CO2 + 55% H2O atmosphere introduced at 300°C was caused by a loss of sulfate at T <1250°C because of higher water content at the early stages of melting.

The tests with FY05 baseline batch containing more sulfate than the FY03 batch produced substantially higher foam and did not show noticeable effect of the heating rate on the foaming extent. Replacing quicklime with limestone showed a tendency to decrease foaming, possibly caused by increased sulfate loss during early stages of melting in the batch with limestone. The batches where Na2SO4 was replaced with NaNO3, NaNO3 + CeO2, or CeO2, produced only very limited foaming regardless of the replacing components. As expected, the foaming extent decreased as the replacement of sulfate by NaNO3 increased and thus the sulfate content in the batch decreased. The results of the present study with FY05 suggest that foaming can be reduced by using limestone over quicklime and by decreasing the sulfate addition to a minimum required for refining.

SGSP FY-2004 G-PLUS PROJECT

[*Full Report*]

Titled: **Spectral Analysis and Imaging of Colored Glasses**

Society for Glass Sciences & Practices Originator: Tomas Mason (Judel Products)
Oak Ridge Investigator: Hsin Wang

Redox state is one of the most important factors that affect color of glasses. Recently, optical properties and redox state of the glass melts have been studied at TNO by A.J. Faber. Spectral measurements up to 4 μm into the infrared region were taken. The focus of similar studies was on the redox state of iron. In glassware production, the control of color is mainly dependent upon the experience of the operators. When the color varies due to changes in processing conditions, batching or furnace contamination, usually little can be done but to scrap the entire batch. This can result in significant down time and waste of energy to melt and refine the glass. For small glass companies, detecting out-of-specification color variation early in the melting process means savings on labor and energy costs. In larger color glass operations, early detection may provide means to correct or save the batch.

Monitoring the redox state of the glass melt can be used to effectively control the quality of glass products. An in-line redox sensor has been tested in industrial environment. Thermal emission spectroscopy is a non-contact, real-time sensing technique. The collection of a spectrum takes only a few seconds or less. This may allow on-line analysis of the glass melt or hot glass products. For a specific glass product, a series of spectra with different processing parameters could be collected and analyzed. The sensing system would be able to detect a deviation from the normal conditions and signal the operator a change has occurred. The primary goal of this GPLUS effort is to find a practical solution for color monitoring.

In this project, we proposed to conduct initial experiments of spectral characterization of colored glasses from the designated glass industry members of the Society for Glass Science and Practices. The work plan contained three stages: 1) Obtain glass samples and use spectroscopy analysis at ORNL to measure basic spectral characteristics of various glass products; 2) collect emission spectra of the glasses using single-point spectrometers (UV to 2.5 microns) from glass melts; 3) Using a spectral imaging device (3-5 microns) at ORNL to obtain 2D hyper-spectra images to evaluate the emission of glass melts.

Spectral transmissions of colored glasses were obtained from three major Judel products using a low-cost portable spectrometer. The instrument and set up is relatively low cost and capable of detecting differences between batches and has the potential to be used as a quality control tool. Spectral emission of the different color glasses were also studied using the same spectrometer. Thermal radiation differences were observed among the three glasses. This result is consistent with the variation in radiative thermal conductivity due to redox states reported in the literature.

VISTEON FY-2004 G-PLUS PROJECT

[*Full Report*]

Titled: **Sulfate Fining Chemistry in Oxidized and Reduced Soda-Lime-Silica Glasses**

Visteon Originator: Edward N. Boulos
Pacific Northwest Investigators: Josef Matyas and Pavel R. Hrma

The experimental program included measuring silica sand dissolution and sulfate decomposition in melts from batches containing sulfate plus varied fractions of carbocite, graphite, or pyrite. Glass batches were heated at a temperature-increase rate deemed similar to that experienced in the melting furnace. Melts were terminated at different temperatures and quenched for further analyses.

Various reducing agents were used and their additions were varied to 1) increase glass quality through eliminating defects from silica scum, 2) decrease SO_x emissions through changing the kind and quantity of reducing agents, and 3) improve production efficiency through increased flexibility of glass redox control during continuous processing.

The work included measuring silica sand dissolution and sulfate decomposition in melts from glass batches. Sulfate is used in soda-lime-silica glasses as a fining agent. Its fining action is caused by the excess sulfate that decomposes, releasing SO_2 and O_2. The need to decrease the use of sulfate, thus minimizing SO_2 emissions, is especially important when mildly reduced soda-lime-silica glass is produced; in these glasses, the solubility of sulfur in glass is low, and thus more SO_2 can be evolved.

The results of the present study helped Visteon Inc. reduce the energy consumption and establish the batch containing 0.118 mass% of graphite as the best candidate for Visteon glass production. The improved glass batch has a lower potential for silica scum formation and for brown fault occurrence in the final glass product. It was established that bubbles trapped in the melt even at 1450°C have a high probability to be refined when reaching the hot zone in the glass furnace. Furthermore, silica sand does not accumulate at the glass surface and dissolves faster in the batch with graphite than in the batch with carbocite.

This G-PLUS project, along with an M-PLUS project at Oak Ridge, allowed Visteon to reduce the melting temperature in its glass furnaces which reduce their energy usage.
Visteon also had lower batch costs because they were able to eliminate a batch material.
So, their total production costs were reduce because of lower batch costs, less energy usage, and fewer defects in their float glass.