

1. **Project Name:** Monitoring And Control Of Alkali Volatilization And Batch Carryover For Minimization Of Particulate Emissions And Crown Refractory Corrosion In Glass Melting Furnaces
2. **Lead Organization:** Sandia National Laboratories
Combustion Research Facility
7011 East Avenue
Livermore, CA 94550
3. **Principal Investigator:** Linda G. Blevins
(925) 294-4811 phone
(925) 294-2276 fax
lgblevi@sandia.gov
4. **Project Partners:** John Neufeld
Gallo Glass Company
Modesto, CA 95354
- Shane M. Sickafoose
Sandia National Laboratories
Livermore, CA 94550
- Alejandro Molina
Sandia National Laboratories
Livermore, CA 94550
- Peter M. Walsh
University of Alabama Birmingham
Birmingham, AL 35294
5. **Date Project Initiated:** June 1, 2001
6. **Expected Completion Date:** June 30, 2004

PROJECT RATIONAL AND STRATEGY:

7. **Project Objective:** Not provided.
8. **Technical Barrier(s) Being Addressed:** Not provided.
9. **Project Pathway:** Not provided.
- 10: **Critical Technical Metrics:** Not provided.

PROJECT PLANS AND PROGRESS**11. Past Accomplishments:**

August 2001: Simultaneous records of the LIBS metals measurements and process variables for Tank No. 1.

- October 2001: Continuous monitors for carbon monoxide and oxygen content of furnace exit gas.
- November 2001: Continuous recording of furnace exit gas temperatures.
- December 2001: Continuous recording of flame and refractory radiation.
- January 2002: Synchronized records of metals, furnace exit gas properties, radiation, and the control room process variables.
- March 2002: Measurement campaign for continuous records of sodium, flue gas composition, temperatures, flame radiation, and process data.
- April 2002: Particle size distributions for sodium.
- May 2002: Identification of conditions influencing sodium volatilization and sodium carryover.
- June 2002: Identification of oxygen-to-gas ratio for maximum furnace efficiency at normal pull rates.
- August 2002: Measurement campaign for continuous records of silicon, flue gas composition, temperatures, flame radiation, and process data.
- October 2002: Measurement campaign for continuous records of calcium, flue gas composition, temperature, flame radiation, and process data. Identification of the conditions associated with lime carryover.
- December 2002: Identify conditions associated with high or low volatilization, high or low batch carryover, high or low combustion efficiency, and high or low furnace efficiency.
- April 2003: Incorporate in the LIBS instrument an echelle grating spectrometer. Determine joint size-composition distributions for particles.
- June 2003: Software needed to drive data acquisition using the broad-band, echelle-grating-based LIBS instrument.
- August 2003: Measurement campaign with signals from sodium, potassium, calcium, and silicon recorded simultaneously to determine joint particle size-composition distributions and to identify the sources of particles.
- September 2003: Determine the ratio of sodium to potassium volatilization.
- October 2003: Optimum stoichiometry for minimization of particulate emissions, minimization of corrosion, and maximization of energy efficiency.
- February 2004: Prototype of a low cost sodium and calcium monitor.
- April 2004: Control strategy and system for minimization of alkali volatilization and batch carry over, and maximization of furnace efficiency.

Extended measurement campaigns were conducted in May 2003, June 2002, and December 2001. Analysis of the data from the first and second campaigns is complete. Analysis of the data from the third campaign is mostly complete.

May 2003: Measurements were performed in the vertical flue just downstream from the furnace exit on Tank #1. Flue gas temperature and concentrations of O₂, CO, NO, and SO₂ were recorded simultaneously with LIBS signals for multiple elements. Gallo Glass systematically varied oxygen-to-gas ratio while tests were being performed.

As the average oxygen-to-gas ratio increased from 1.98 to 2.18, average O₂ concentration increased, average NO concentration increased, and average SO₂ concentration decreased. For the lowest oxygen-to-gas ratios (1.98 to 2.04), CO occasionally appeared in the exhaust.

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

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

When products of fuel-rich combustion appeared in the furnace, SO₂ concentration increased noticeably. Calcium LIBS signals remained constant in the presence of rich products. Interestingly, sodium and potassium LIBS signals from both detection systems decreased dramatically for fuel-rich conditions as well. A plausible explanation was found for the decrease of sodium and potassium signals for fuel-rich conditions: The LIBS signal is absorbed by alkali atoms appearing in the path between the spark and the LIBS receiving optics. Alkali *atoms* are more prevalent than alkali-containing *molecules* for rich conditions but not for lean conditions, according to equilibrium calculations. Laboratory experiments adding sodium to the products of a well-controlled burner verify that, for a constant sodium concentration, temperature, and background gas composition, LIBS signals are dramatically reduced for rich conditions relative to lean conditions owing to sodium atom absorption.

To address this issue, we analyzed newly selected sodium spectral lines that terminate in an energy level higher than the ground state energy level; emission from these lines should not be absorbed by ground-state sodium atoms. Sodium lines matching this requirement were found at 818.3 nm and 819.5 nm. We analyzed these lines, which were available because of the broadband nature of the echelle spectrometer. The new sodium signals proved to be less susceptible to the sodium atom absorption. Absorption calculations are underway to explain the relative trends. The effects of line broadening in a high temperature carbon dioxide/water environment are being accounted for in the calculations.

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

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

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

The largest fraction of the energy required for batch reactions and melting goes into heating the glass. Because the temperature at the throat is a set point, there is only slight variation in the sensible energy content of the glass, even with change in pull. The energy required for the batch reactions, per unit mass of glass, is completely unaffected by any of the conditions in the furnace. In contrast, the enthalpy of the batch gases depends upon the furnace exit gas temperature, but the temperature is only subject to relatively small fluctuations. The total energy required for melting is close to 50% of the total energy input at the pull rate of 322 ton/day. Calculation of furnace efficiency is not possible because the air inleakage rate is not known. Plans are in place to measure the inleakage rate during the June 2004 tests.

A plan was developed for the June 2004 tests. Our objectives are to (1) determine air inleakage rates, (2) further examine the effects of furnace stoichiometry on alkali volatilization, and (3) further examine the effects of furnace conditions on batch particles. Several improvements have been made to our instrumentation, and these will be tested in the field.

June 2002: Flue gas temperature and concentrations of O₂, CO, NO, and SO₂ in the vertical flue were recorded synchronously with sodium, potassium, calcium, and aluminum LIBS signals. Both linear and echelle spectrometers were used with the LIBS system. Natural gas and oxygen input flows for the furnace were captured in strip charts from Gallo Glass. Other operating data such as furnace

pressure, glass level, electric boost amount, and radiometric wall temperatures were also obtained from Gallo Glass. Plots of these variables as a function of time were digitized from the Gallo strip charts. Their values were interpolated so that the data points corresponded to the times associated with the LIBS measurements. Mathematical cross-correlations were performed.

Sodium and potassium concentrations in the flue were found to mathematically correlate with the north and south breast wall temperatures. Additionally, alkali concentrations correlated with exhaust oxygen and sulfur dioxide concentrations for some days but not for all days. Two different glass pull rates were examined (336 and 435 tons/day), so trends were established for different furnace loads. The oxygen to gas ratio was consistently 2.12. Alkali concentrations showed a stronger dependence on temperature than on stoichiometry. The relationship between alkali release and furnace stoichiometry may be temperature dependent. Calcium and aluminum were also observed in the flue, but at much lower concentrations than sodium and potassium. The June 2002 data hint that an optimum furnace stoichiometry will minimize alkali concentration and avoid carbon monoxide emission.

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

December 2001: LIBS measurements of sodium, potassium, calcium, magnesium, aluminum, boron, and silicon were performed using the echelle spectrometer in the furnace exhaust duct upstream of the electrostatic precipitator. At this location, the exhaust is diluted by a factor of about 3.5:1. Simultaneously, O₂, CO, NO, and SO₂ concentrations were recorded. Natural gas rate of flow, oxygen rate of flow, furnace pressure, glass level, electric boost amount, and radiometric process temperatures were captured in strip charts from Gallo Glass. The pull rate was about 430 tons/day, and the oxygen to gas ratio was about 2.16.

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

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

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

12. Future Plans:

June 2004: Specify the strategy for minimizing volatilization and entrainment while maintaining high combustion and furnace efficiency.

The final test will be held June 2-11, 2004

13. **Project Changes:** The echelle grating spectrometer does not have sufficient sensitivity for determination of element concentrations in individual laser sparks. This precludes the determination of joint particle size composition distributions. However, the apparent size distributions of individual elements can still be determined using the conventional grating spectrometer, so relatively infrequent large particles carried over from batch can be distinguished from the more uniform concentration of submicrometer particles formed from volatile species.

For the Czerny-Turner spectrometer, difficulties were encountered with determining the presence of batch particles for the alkali metals because they have high background concentrations in the furnace. Additionally, artifacts associated with the first shot of each series of shots were identified and linked to the necessary operation of the intensified camera in "shutter pre-open" mode.

Typical off-the-shelf alkali metal calibration mixtures result in alkali concentrations in the calibration rig lower than the ~200 pm expected in the field. Hence, self-prepared mixtures containing high concentrations of sodium and potassium were used for the calibrations. However, the concentrations determined from the calibrations were too large. Reasons are presently being explored. The atomization process in the calibration rig is being examined. Calculations are being performed to predict the effect of self absorption both in the pathway and in the spark on the alkali calibration curves.

A set of laboratory experiments currently underway aims to resolve the effect of temperature, background gas makeup, and particle loading on the calibration curves. A well controlled burner is being used to generate combustion product mixtures and temperatures characteristic of glass furnaces.

14. **Commercialization Potential, Plans and Activities:**

The product of the research will be the prototype of an instrument for monitoring individual elements, e.g. sodium, boron, or potassium. The potential market is all manufacturers of glass having need for, or interest in, reducing particulate emissions and slowing the rate of volatile species attack on superstructure and crown refractories.

15. **Patents, Publications, Presentations:** None