Advances in Oxy-Fuel Fired Glass Melting Technology

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About 200 commercial glass melting furnaces have been converted to or built as oxy-fuel firing worldwide over the last 15 years. The main benefits for oxy-fuel conversion are glass quality improvement, emissions reduction (NOx, SO2, particulates), productivity increase, fuel reduction, expansion of the existing furnace, and the elimination of regenerators. A review of technical differences between air and oxygen firing is provided and advances made in the oxy-fuel firing technology and potential future improvements are discussed.

(key words: oxy-fuel, glass melting, refractory corrosion, fining chemistry)

1. Introduction
In 1988 the U.S. Department of Energy awarded a program to Praxair, Inc. to demonstrate the use of oxy-fuel combustion in a large commercial glass furnace using an on-site vacuum-pressure swing adsorption (VPSA) technology. A container glass furnace at Gallo Glass Company was rebuilt in 1991 as the first large scale oxy-fuel fired furnace. The successful conversion of the furnace and the demonstration of substantial fuel savings (15%) and emissions reduction (80% NOx, 80% CO, and 30% particulates) stimulated the glass industry to adopt the new technology at a rapid rate. By 1996 about 90 commercial glass furnaces were converted to oxy-fuel firing worldwide. Today, about 200 commercial glass furnaces of various glass types, including three float glass furnaces, are fired with oxygen. A great deal of experiences have been gained through these conversions and the design and operation of oxy-fuel furnaces have improved substantially. Significant changes in the melting and fining behaviors were observed under oxy-fuel firing, due to changes in the heat transfer characteristics and the chemical changes caused by the higher water content of glassmelt under oxy-fuel firing. Most furnaces required some batch modifications to optimize the glass fining chemistry. Extensive laboratory studies and mathematical modeling have been conducted to investigate heat transfer, glass fining, alkali volatilization and refractory corrosion mechanisms. Although accelerated silica crown corrosion was experienced, especially in early conversions, improved burner and furnace designs made it possible to extended the life of the silica crown close to that of a conventional air fired furnace. In the following sections the technical understandings developed on the oxy-fuel glass melting technology are reviewed and potential future improvements are discussed.

2. Oxy-Fuel Furnace Design and Burner Placement
Since 1970’s “oxy-fuel boosting” was successfully applied to many types of air fired glass melting furnaces for production increase. In this method typically a pair of auxiliary oxy-fuel are placed either in the side walls or in the crown and angled down toward the unmelted batch areas in an air fired furnace to accelerate the melting and fining rate. In most furnaces glass pull rate increases of about 10 to 30% were achieved as compared with air only firing. The experience from these partial conversions as well as successful full oxy-fuel conversions of steel heating and aluminum melting furnaces provided important technical background to engage in full conversion of large glass melting furnaces in the 1990’s. In most full oxy-fuel furnace conversions, the furnace geometry (i.e., the melter area, the bath depth and the crown height) of the original air fired furnace was maintained to keep the same melting and fining characteristics and to avoid the extra costs of changing the structural steel beams. Yet, significant production rate increases were achieved in many conversions. In an oxy-fuel fired furnace the
temperature profile or the heat flux distribution to the furnace load is relatively easily controlled by the number and the placement of the oxy-fuel burners. This flexibility of placing a flame where it is needed is a major reason enabling the production rate increase. With a proper burner selection and placement the crown temperature is reduced at the same glass pull rate. Since the maximum glass pull rate is often limited by the peak crown temperature, a lower crown temperature enables a higher firing rate and an increased glass pull.

The crown height is an important design parameter. In general a higher crown height results in a lower average crown refractory temperature and a flatter temperature profile along the furnace length. In most conversions the original crown height was maintained. In one furnace conversion, the crown height was reduced with fused cast alumina crown in order to increase the pull rate and also to reduce side wall heat loss. In several recent conversions, the crown height was increased to reduce alkali corrosion of crown. Further discussions of the effects of furnace height are provided in the refractory corrosion section.

Since the combustion and heat transfer conditions under oxy-fuel firing are substantially different from those under air-fuel firing, retrofitting of an existing air fired furnace with oxy-fuel burners requires a careful selection of the type and number of oxy-fuel burners and their proper placement on the glass furnace walls. In general heat transfer is improved by placing a flame close to the glassmelt or angling a flame toward the glassmelt⁵. However, it also increases volatilization of alkali species, which would cause higher particulate emissions and increase the potential for refractory corrosion. Some refractory damages have been observed in early oxy-fuel conversions due to flame impingement or excessive flame momentum. Both the opposed and staggered burner arrangements have been successfully adopted. An advantage of the opposed burner configuration is the symmetry of the heat flux profile. Although some furnace designers believe that the symmetric design is critical for high quality glass production, CFD analyses of furnace heat transfer conditions indicate that similar heat flux profiles can be achieved by either method. In the symmetric burner arrangement two opposing flames meet in the center of the furnace and create an upward flow toward the crown. Accelerated corrosion of silica crown was observed in several furnaces with an opposed burner arrangement under relatively high burner momentum. The problem can be managed either by increasing the number of the burners, which reduces the individual flame momentum, or by using flat spreading flames. Thus, the optimum number and the placement of burners depend on the furnace geometry and the flame characteristics.

The location and the number of flue ports are other design issues with different opinions and experiences. In order to maximize the furnace energy efficiency, flue ports are almost always located in the coldest area of the furnace, i.e., near the charge end of a furnace. Three different flue arrangements have been successfully adopted: a single flue in the charge end wall, a single flue in a side wall, and two symmetrically arranged flue ports on the side walls. The choice for the best flue ports arrangement depends on the type of batch chargers used and the space available around the furnace.

3. Burner Type, Flame Characteristics and Heat Transfer

Traditional oxy-fuel burners are characterized by high flame temperature and intense localized heat transfer, and used for special high temperature applications such as flame polishing of glass and welding. For heating and melting applications in industrial furnaces, it is often desirable to provide uniform heat transfer in a large hearth area. Many different burner types producing different flame shapes (conical flame, flat flame, high momentum, low momentum, luminous and non-luminous flames) have been developed for both natural gas and fuel oil, and have been successfully applied in glass melting furnaces. More comprehensive discussions of industrial oxy-fuel burners are provided elsewhere⁶.

CFD simulation studies and actual measurements⁵ show that the local heat transfer from a flame is very sensitive to the flame characteristics. A short intense flame produces a localized high flame temperature, which has a tendency to create a hot spot on the adjacent glass or refractory wall surfaces. A high
momentum flame induces large furnace gas recirculation, reduces the flame temperature, and tends to push the peak flame temperature zone away from the burner. A luminous flame, like an oil flame, has a higher emissivity due to soot particles and transfers heat by flame radiation more efficiently, which reduces the peak flame temperature. Thermal NOx emissions are reduced as a result. Furnaces fired with oil flames often have lower NOx emissions than those fired with natural gas for this reason. Traditionally long and wide luminous flames covering the entire glassmelt surface area are believed to be most efficient and preferred. Oxy-fuel flames with high luminosity and wide flat flame shapes have been developed and installed in many furnaces.

Although the local heat transfer from a flame is very sensitive to the flame characteristics and the burner placement, the overall heat transfer efficiency of the oxy-fuel fired furnaces is actually very insensitive to the flame characteristics and the burner arrangement. Very seldom burner types can influence the overall fuel efficiency of an oxy-fuel fired glass furnace by more than a few per cents. This somewhat counter-intuitive statement can be understood by considering the effects of heat transfer on the sensible heat loss to flue gas. A reduction in flame heat transfer results in an increase in the flue gas temperature. Since the volume of the flue gas in an oxy-fuel fired glass furnace is reduced to 15 to 25% of that of the equivalent air fired furnace, even an increase in flue gas temperature of 100 °C causes only a few per cent increase in the sensible heat loss to flue gas.

A reduction in the flame heat transfer to a furnace load results in an increase in the local gas temperature downstream of the flame. A relatively small increase in the bulk furnace gas temperature causes a sharp increase in the gas-to-load radiative heat transfer due to the strong temperature dependence of radiative heat transfer. Thus, any loss in local heat transfer from an oxy-fuel flame is naturally compensated by an increase in the gas-to-load radiative heat transfer caused by a small increase in the bulk furnace gas temperature after the flame zone. This is especially the case in an oxy-fuel combustion because of the inherently efficiency in the radiative heat transfer, i.e., higher concentrations of CO2 and H2O in the furnace atmosphere which increase the gas emissivity and the much longer gas residence time. In the cross-fired regenerative furnace where the flame fired from a side wall port takes a straight path and exhausts from the opposite wall. The gas residence time in the centerline of the flame is only about 1 second and the furnace volume average gas residence time is about 5 to 10 seconds. In the oxy-fuel fired furnace the flue gas form oxy-fuel flames interact with other flames in the furnace and exhaust from the charge end. The average gas residence time is on the order of 30 seconds. As the hot flue gas travels over the cold batch toward the flue ports, the flue gas cools down by transferring heat to the cold batch. The final flue gas temperature exiting the furnace is more strongly influenced by the geometry of the furnace and the flue port locations in the charge area than the flame characteristics of the oxy-fuel burners in the hotter zone of the furnace.

4. Glass Quality and Effects of Water
Glass quality and production rate have improved in most oxy-fuel furnace conversions. The main reason for the quality improvement (less seeds) is the enhancement of the fining reactions with “water” dissolved in glass. All commercial glasses contain water in the form of hydroxyls, which cause significant impact on the fining behavior as well as the glass property such as viscosity. In some cases, manufacturers are controlling the amount of water in glass to assure more consistent product quality.

Oxy-fuel melting typically increases the water in glass by 30% or more, compared to air firing. The solubility of water in glass is proportional to the square root of the partial pressure of water. It is about 1100 ppm weight (expressed as H2O) with 100% water vapor in the furnace atmosphere at 1 atm. In air/natural gas fired furnace where the volume % of water vapor in the furnace atmosphere is about 16-18%, the typical water content of the soda lime glass product is about 300 to 400ppm. In oxy-fuel firing, the volume % of water vapor in the furnace atmosphere is about 50 to 55% and the typical water content becomes about 500 to 600ppm. These measured water contents represent about 70 to 90% of the
saturation level\textsuperscript{10}. The high saturation level is surprising in view of the very low diffusivity of OH in glass, but is believed to be promoted by the convective current of molten glass as well as by the mixing action caused by rising bubbles from the batch reactions and fining reactions.

Laboratory tests showed remarkable differences in the redox state, sulfate retention and foaming behaviors of the same batch melted in an oxygen fired atmosphere and that in an air fired atmosphere\textsuperscript{11}. Key findings are;

- The redox state (Fe\textsuperscript{3+)/Fe\textsuperscript{2+}) of the glass decreases as the water vapor pressure increases for a soda lime silica glass batch without reducing components.
- For batch with reducing components, water vapor seems to have oxidizing effect during the melting and/or fining process.
- A higher water vapor pressure in the furnace often will increase the formation of foam due to an increased release of fining gases.
- A water rich atmosphere improves the sulfate fining, since the extra amount of dissolved water enhances the removal of bubbles.

In early oxy-fuel conversions, redox and foaming problems were experienced in some furnaces due to the above changes in glass chemistry. These problems were solved by relatively minor batch adjustments, including a reduction in the amount of fining agents.

5. Furnace Energy Efficiency and Fuel Savings

The fuel efficiency of oxy-fuel fired furnaces is significantly better than that of the conventional air fired furnaces. Most of the efficiency gains come from the elimination of nitrogen contained in air, which constitutes about 78\% by volume, and causes a major source of the sensible heat loss in the flue gas. Another advantage of the oxy-fuel furnace is the stability of the specific fuel consumption over the life of the furnace. With an air fired regenerative furnace the efficiency of the regenerators deteriorates with the furnace life and the fuel consumption toward the end of the campaign typically increases by about 10\%\textsuperscript{12}. Fuel savings by oxy-fuel conversion depend on the conditions and the heat recovery system used in the original air furnace. For container and float glass furnaces with efficient regenerators about 15 to 20\% fuel savings have been achieved. For fiber glass furnaces with metallic recuperators fuel savings are typically in a range of 40 to 50\%. For small speciality glass furnaces, which generally do not have efficient regenerators or recuperators, fuel savings over 50\% have been achieved.

Figure 1 shows the evolution of the oxy-fuel fired furnace performance on energy and emissions, based on a few of the Praxair’s container glass furnace conversion projects. The first project was the cross fired regenerative furnace at Gallo Glass and the air baseline data on natural gas consumption and emissions of NO\textsubscript{x} and particulates in 1990 are compared with those after the conversion to oxy-fuel in 1991\textsuperscript{1}.

The baseline energy consumption of the 116 m\textsuperscript{2} (1248 sq ft) furnace was about 935 Kcal/Kg (3.74 MMbtu HHV/ton) using 152 kwh/ton of electric boost for flint glass with 10\% cullet. After the
conversion to oxy-fuel firing the energy consumption was reduced to 848 Kcal/Kg (3.39 MMbtu/ton) using 111 kwh/ton of electric boost at about the same pull. The approximate fuel consumption without electric boosting was calculated from a furnace energy balance analysis, which yielded about 1113 Kcal/Kg (4.45 MMbtu/ton) for the baseline air case and 963 Kcal/Kg (3.85 MMbtu/ton) for the oxy-fuel firing case. The baseline energy consumption of this furnace was relatively high because of the relatively low pull for the furnace size, the end of the campaign regenerator deterioration and the low cullet ratio. The furnace converted in 1996 showed energy consumption of less than 800 Kcal/Kg (3.2 MMbtu/ton) with 60% cullet in a 111 m² (1194 sq ft) furnace. The figure also shows the projected performance of 625 Kcal/Kg (2.5 MMbtu/ton) with 60% cullet for a furnace with a fully integrated batch and cullet preheater.

Since the generation of oxygen requires electric power, the overall energy consumption must consider the primary fuel consumed in the generation of electric power for oxygen. The overall energy efficiency of the oxy-fuel fired furnace without heat recovery and with the electric power required for oxygen generation, is about the same as that the best end-fired regenerative furnace today12. As shown in Figure 1, however, both fuel and oxygen consumption can be reduced by as much as 30%, if the high temperature waste heat in the flue gas is recovered. Although a fully integrated batch/cullet preheating system has not been demonstrated to date, a cullet preheater/filter has recently been demonstrated13-14. Preheating of oxygen and/or natural gas is another method for heat recovery. A prototype recuperator to preheat oxygen and oxy-fuel burners using preheated natural gas and oxygen have been developed15, but no commercial installations have been made yet. A waste heat boiler to generate steam is an alternative method of heat recovery. An oxy-fuel fired furnace with a fully integrated waste heat boiler system to generate power from the steam has been in commercial operation since 199616.

6. Emissions From Glass Furnaces

NOx Emission

Due to the high flame temperature required for glass melting significant “thermal NOx” is formed in the flame region. The rate of formation of thermal NOx is strongly temperature dependent and approximately proportional to the concentration of nitrogen in the furnace. The conversion of an air fired furnace to oxy-fuel firing typically results in NOx reduction by 80 to 90% as the nitrogen concentration in the furnace is reduced from about 70% in an air fired furnace to about 5 to 10% in a typical oxy-fuel fired furnaces. Other key factors influencing NOx emission are oxy-fuel burner design which influences the flame temperature, batch niter content, and excess oxygen17. Results of NOx emissions tests conducted on several glass furnaces fired with natural gas-oxygen are plotted in Figure 2.

Figure 2. NOx Emissions from Glass Furnaces

NOx emissions from glass furnaces equipped with conventional (high flame temperature) oxy-fuel burners increased linearly from 0.4 to 1.0 kg (as NO2) per metric ton (0.8 to 2.0 pound per short ton) as the wet basis furnace nitrogen concentrations increased from 3 to 7 percent. These furnaces were well sealed and the main source of the nitrogen in the furnace was the infiltration of side wall cooling air and ambient air form refractory gaps, chargers, view ports and others. Clearly minimizing air infiltration is a very important furnace design consideration. Although it is possible to achieve a nitrogen concentration of 3 to 5% in a very tight furnace, most oxy-fuel furnaces have furnace nitrogen concentrations of about 5 to 10, especially with the aging of the furnace. In addition, other sources of furnace nitrogen such as the nitrogen contained in
natural gas and oxygen need to be considered to estimate NOx emissions from a new oxy-fuel fired furnace. The nitrogen concentration in natural gas is typically between 1 to 3% in the U.S. In some Northern European countries, the nitrogen concentration of natural gas is as high as 11%, which increases the nitrogen concentration in the furnace by about 3 to 4%. Oxygen from a cryogenic oxygen plant or in delivered liquid is typically high purity (> 99.5%), but oxygen from the VPSA (Vacuum pressure swing adsorption) typically contains 3 to 5% nitrogen and about 4 to 5% argon. 5% nitrogen contained in oxygen will increase the nitrogen concentration in the furnace atmosphere by about 3%.

As shown in the figure the type of oxy-fuel burners is also a key factor in achieving low NOx emissions. Low NOx oxy-fuel burners are designed to produce low peak flame temperature and the NOx emission can be as low as one tenth of those form conventional oxy-fuel burners. NOx emissions in a furnace temporarily converted to permit regenerator repairs was as low as 0.05 kg/mton (0.1 lb/ton) when the wet basis nitrogen concentration in the melter atmosphere was about 1%. Air infiltration was well controlled by maintaining a high furnace pressure, and high purity liquid oxygen and natural gas with relatively low nitrogen content were used to fire the melter. Another furnace equipped with low NOx oxy-fuel burners had NOx emissions of 0.4 kg/mton (0.8 lb/ton), at a time when nitrogen concentration in the furnace was about 35 percent.

Some of the furnaces converted to full oxygen firing with low-NOx burners contained batch niter (NaNO3 or KNO3). NOx emissions from one of these furnaces were 90 percent below the air baseline levels, but were substantially well above the predicted level for thermal NOx. The discrepancy was caused by the presence of batch niter, which decomposed upon heating to form NOx. The complete conversion of the nitrogen content of niter to NO3 would have caused NOx emission of 1.35 kg/mton (2.7 lb/ton). The actual emission was 1.05 kg/mton (2.1 lb/ton), indicating conversion of some of NOx generated from batch niter to N2 with reactions with flame species and batch materials. Oxy-fuel flames could be used to chemically reduce NO produced from thermal decomposition of niter by the so called "NOx reburning" technique. The extent of NOx reduction depends on the furnace conditions. Field results from other glass furnaces fired with oxy-fuel burners indicated up to 50% reduction of NOx emissions generated from niter.

**Particulate Emissions**

Particulate emissions from glass furnaces are generated by three main sources; (1) volatilization of glass forming compounds from glass bath surface and from batch, (2) physical carryover of fine batch particles, and (3) metal oxides and sulfates from combustion of fuel oil. Flame generated particulates from oil firing are generally a very small fraction of overall particulate emissions. Previous studies have shown that carryover in modern glass furnaces typically contributes only 5 to 15% of total particulate emissions and that volatilization is the most important mechanism for gas fired furnaces. In an oxy-fuel fired furnace the average velocity of furnace gases over the unmelted batch area is reduced significantly due to the small volume of flue gas. Thus, particulate emissions caused by batch carryover are expected to be reduced further to an insignificant level with proper furnace design and burner positioning. Volatilization of NaOH is typically the main source of particulates for soda lime silicate glasses and is discussed below.

Volatilization of alkali compounds from soda-lime glass is a complex process involving heat and mass transfer, and chemical reactions. Thermodynamics and literature data show that NaOH is the predominant sodium species in the glass furnace atmosphere, and that NaOH may be formed mainly by the reactions of water vapor with sodium oxides in molten glass or with sodium carbonate in batch via the following reactions.

\[
\text{Na}_2\text{CO}_3 \text{ (batch)} + \text{H}_2\text{O} \rightarrow 2 \text{NaOH (vapor)} + \text{CO}_2 \\
\text{Na}_2\text{O} \text{ (glass melt)} + \text{H}_2\text{O} \rightarrow 2 \text{NaOH (vapor)}
\]

As the flue gas from a glass furnace cools down in the regenerator and flue ducts, NaOH vapor reacts with SO2 and O2 available in the flue gas to form Na2SO4, which subsequently condenses to form submicron size
particles in the stack. Direct volatilization of Na$_2$SO$_4$ from the glass melt surface is considered less important than the above mechanisms, but also contributes to the overall emissions.

Since a higher water vapor pressure in the furnace atmosphere increases the equilibrium vapor pressure of NaOH at the melt surface, the gas phase concentration of NaOH is expected to increase significantly under oxy-fuel firing. On the other hand, flue gas volume and the average gas velocity are reduced substantially and the higher gas phase NaOH concentration tends to reduce the mass transfer rate of NaOH from the glass melt surface to the bulk of the furnace atmosphere. In order to evaluate the relative importance of these factors, mathematical model calculations were performed based on the equilibrium vapor pressure of NaOH at glass melt surface and gas phase convective mass transfer under typical glass furnace conditions.

Figure 3 shows calculated mass particulate emissions, as Na$_2$SO$_4$, from a 200 metric TPD soda-lime glass unit melter at different glass surface temperatures. The concentration of water vapor was assumed to be 20 and 60 % for air and oxygen firing respectively. Since the equilibrium vapor pressure of NaOH at the melt surface is proportional to the square root of H$_2$O partial pressure, it is increased by 73 % for oxygen firing. The average gas velocities were assumed to be 5 and 0.8 m/s for air and oxygen firing respectively. The mass transfer rate of NaOH from the glass surface to the bulk of the furnace gas is reduced due to the lower velocity for oxygen firing.

![Figure 3. Calculated Particulate emissions (Na$_2$SO$_4$) from NaOH volatilization](image)

The net effect of converting from air firing to oxygen firing is about 50% reduction in mass particulate emissions at a constant production rate and a constant glass surface temperature in this example. NaOH vapor concentration in the furnace, however, increases about three times. As is well known, volatilization rate increases sharply with glass surface temperature due to the exponential increase of the equilibrium vapor pressure. The model predicts approximate doubling of mass emissions for each 100 °C of temperature increase for both air and oxygen firing. Impinging flames create localized areas of high glass surface temperature. Since the impinged areas are also exposed to higher gas velocities volatilization is expected to increase significantly. In actual furnace measurements impinging flames and reducing combustion atmospheres were shown to accelerate alkali vapor volatilization substantially. Reducing flame is believed to cause evaporation of metallic sodium vapor. Thus, proper burner placement and furnace atmosphere are also very important in minimizing particulate emissions.

In Figure 4 particulate emissions from both air and oxygen fired glass furnaces are correlated with the specific production rate per unit melter area. The specific production rate was compensated for electric boosting by subtracting the equivalent amount of glass produced by electric boosting. The round and square data points on particulate emissions are based on the U.S. EPA Method 5 and came from three regenerative container glass furnaces with nominal capacities of 68, 135 and 310 metric tons per day, before and after conversion to oxy-fuel firing. The data show sharp increases in particulate emissions per unit glass surface area with increasing specific production rates. This trend is consistent with higher volatilization rates of NaOH expected at high glass surface temperatures and gas velocities when the furnaces operate at high specific production rates.
A comparison of the air and oxygen data in Figure 4 shows about 20 to 30% reduction of overall particulate emissions under oxygen firing. These results are about half the reduction predicted by the simple model calculation for a unit melter in Figure 3, but are reasonable since the reduction in the average gas velocity was much less in the conversion of efficient regenerative furnaces. In these early oxy-fuel conversions, little design considerations were given to minimize the alkali volatilization and particulate emissions. In later furnace conversions, several modifications were made to the furnace design and the oxy-fuel burners based on detailed CFD studies of alkali volatilization and actual furnace measurements of the concentration of alkali species. The design improvements included lower flame velocities, a higher burner elevation and the taller crown. Some of the improved results are also plotted in Figure 4. Particulate emissions were reduced approximately by a factor of two compared to the earlier oxy-fuel furnace design. At a specific pull rate of 3 mton/day/m² particulate emissions of 0.25 kg/mton were achieved. Further reductions to 0.1 to 0.15 kg/mton seem feasible with further design improvements, especially when batch/cullet preheating is integrated to reduce the firing rate and the glassmelt surface temperature.

![Figure 4. Measured Particulate Emissions from Container Glass Furnaces](image)

**SO₂ Emissions**

In early oxy-fuel conversions, increased emissions of SO₂ were observed when no adjustments were made on the batch composition. The cause for the increased SO₂ emissions was later found to be the enhancement of the sulfate fining reactions with dissolved water in glassmelt under oxy-fuel firing. By reducing the amount of sulfate in the batch SO₂ emissions reductions greater than 50% were achieved, while maintaining excellent fining reactions. The mechanisms for SO₂ emissions in glass furnaces and the effects of oxy-fuel firing are briefly discussed in this section. More detailed discussions can be found elsewhere.

SO₂ emissions from glass melting furnaces originate from two main sources, sulfur contained in the fuel and sulfates in the feed materials. Heavy oils typically contain 0.5 to 2 %wt sulfur and increase SO₂ emissions by about 1.2 to 4.8 kg per ton of container glass produced, or about 250 to 1,000 ppm for a typical air fired regenerative furnace. Although some dissolution of SO₃ in the furnace atmosphere into molten glass is expected in the colder region of the furnace, virtually all of sulfur in the fuel leaves the furnace as SO₂. Clearly the most obvious step to reduce SO₂ emissions from a glass furnace is to reduce the sulfur content of the fuel. For furnaces fired with natural gas, the only source for SO₂ emissions is sulfates contained in the batch materials for fining of gas bubbles and redox control. SO₂ emissions from the batch sulfate are typically in a range between 1 to 2 kg per ton of container glass produced, or about 200 to 500 ppm for a typical air fired regenerative furnace. They depend on several factors including the total sulfur in the batch materials, type of glass, and firing conditions of the furnace.

The amount of sulfates added in glass batch depends on the type of glass melted. Typical ranges of sodium sulfate used per metric ton of glass product are 6 to 12kg (3.4 to 6.7kg as SO₃) for float and
oxidized plate glass, 5 to 8kg (2.8 to 4.5kg as SO$_3$) for flint bottle glass, 4 to 7kg (2.2 to 3.9kg as SO$_3$) for green bottle glass, and 5 to 10kg for textile fiber glass (E-glass). When other sulfur containing materials, such as cullet, filter dust, slag and calcium sulfate are used in the batch mixture, the amount of sodium sulfate is reduced accordingly to provide the equivalent amount of total sulfates.

In Figure 5 the typical mass balance of sulfur is shown for a flint container glass furnace fired with natural gas. 6.5 kg of sodium sulfate (4.0 kg as SO$_3$) is used per metric ton of glass product in this example. About 62% (2.5 kg as SO$_3$) of the sulfate input is retained in glass product and about 38% (1.5 kg as SO$_3$) evolves mostly as SO$_2$ gas during batch melting and fining, and exhausted from the furnace. As the flue gas cools down, some of SO$_2$ (0.15 kg as SO$_3$) reacts with NaOH, O$_2$ and H$_2$O to form condensable sulfate compounds such as Na$_2$SO$_4$, Na$_2$S$_2$O$_7$, NaHSO$_4$ and H$_2$SO$_4$ and is released as particulate emissions. The net SO$_2$ emissions in this example is 1.08 kg/t or about 220 ppm for a typical natural gas air fired container glass furnace.

In most commercial glass furnaces, the amount of sulfate in the glass batch has been adjusted to the lowest acceptable level to operate the furnace properly and to achieve good glass quality. So a further reduction in sulfate would presumably results in an increased seeds count. Gibbs and Turner suggested the theoretical minimum limit of sulfate requirement for float glass as the amount of sulfate retained in glass plus 0.05 wt % as SO$_3$ evolved at the fining zone. If we assume 0.25 wt % SO$_3$ retention in glass, the minimum sulfate requirement is 0.30 wt.% SO$_3$, or equivalent to 5.3 kg of sodium sulfate per metric ton of float glass. The underlying assumption is that 0.05 wt % of sulfate as SO$_3$ is required for proper fining of gas bubbles in the fining zone of the furnace. The actual amount of sulfate mixed in the batch materials is typically much greater since a significant fraction of SO$_3$ is released during batch melting by reacting with carbon and other compounds.

In order to reduce SO$_2$ emissions from a natural gas fired furnace, either (1) the premature release of SO$_2$ during batch melting has to be reduced, (2) a greater fraction of SO$_2$ has to be converted to condensable sulfate compounds and removed as particulates, or (3) the fining action of SO$_2$ has to be replaced with other gases. The first option requires batch and flame adjustments and offers some reduction of SO$_2$ emissions. It is known that impinging flames and reducing combustion atmospheres tend to accelerate batch sulfate reactions and result in premature release of SO$_2$ in the batch melting zone. Thus, an adjustment of the burner firing conditions and the furnace atmosphere over the batch area may reduce SO$_2$ emissions without adversely affecting the glass quality. The second option is theoretically possible by increasing volatilization of alkali species in the furnace to produce more NaOH and KOH, which react with SO$_3$ to form more sulfate particulates. However, it is not a desirable option as higher volatilization of alkali species in the furnace causes faster refractory corrosion.

Third option requires a new fining gas. Dissolved water has been shown to act as an effective fining agent to partially replace sulfate and other fining agents. During the normal sulfate fining process,
sulfate in glass melt dissociates at high temperatures to produce a fining gas mixture of \( \text{SO}_2 + \frac{1}{2}\text{O}_2 \) via the following reaction.

\[
\text{SO}_4^{2-} \text{(in melt)} = \text{SO}_2 \text{(gas)} + \frac{1}{2}\text{O}_2 \text{(gas)} + \text{O}_2^- \text{(in melt)} \quad (1)
\]

The fining gases diffuse into gas bubbles in glass melt, grow the bubbles which rise to the glassmelt surface and escape. Reaction (1) is strongly dependent on temperature and active dissociation of sulfate takes place typically in the temperature range of 1450 to 1500°C for soda lime glass. Since a significant amount of water can dissolve in glass melt as hydroxyls, water can potentially replace the fining reaction of sulfate via the following reaction.

\[
\text{OH}^- \text{(in melt)} = \text{H}_2\text{O(gas)} + \text{O}_2^- \text{(in melt)} \quad (2)
\]

Since the equilibrium constant of the above reaction change very little with temperature, water can not act alone as the fining agent in the conventional fining process which is based on the temperature change. Fortunately, reaction (2) would proceed to the right and produce water vapor when the sulfate fining reaction (1) starts and reduces the partial pressure of \( \text{H}_2\text{O} \) in bubbles. In fact both reactions (1) and (2) promote each other through the mutual dilution effect. It is thus possible to enhance the fining action of sulfate with dissolved water. If we assume that a constant volume of fining gas generation is required to achieve the same degree of fining, then 1 1/2 moles of \( \text{H}_2\text{O} \) is required per mole of \( \text{SO}_3 \). Thus, the theoretical replacement ratio of \( \text{H}_2\text{O} \) to \( \text{SO}_3 \) is 1.5 on a molar basis or 0.3375 on a weight ratio of \( \text{H}_2\text{O} \) to \( \text{SO}_3 \). In order to replace 0.05 wt. % \( \text{SO}_3 \), or to reduce about 0.4 kg of \( \text{SO}_3 \) per ton of glass, about 0.017 wt. % \( \text{H}_2\text{O} \) is required, which is relatively small compared with the maximum solubility of water of about 0.11 wt. %.

In the conventional air fired furnace, water content of glass is about 0.03 to 0.04 wt. %, while that in the oxy-fuel fired furnace is increased by about 0.02 wt % to 0.05 to 0.06 wt. %. Thus it is possible to reduce the amount of sulfate and still achieve good fining results under oxy-fuel firing. Both mathematical modeling and laboratory tests have been conducted to verify the concept. Significant reductions in \( \text{SO}_2 \) emission were achieved in container glass furnaces by reducing the amount of batch sulfate by about 30%.

7. Silica Crown Refractory Corrosion and Tall Crown Furnace Design

Accelerated silica crown refractory corrosion was observed in oxy-fuel fired furnaces, especially in early conversions. Often the most severe corrosion occurred at the joints of crown bricks, creating so called “rat holes”. Laboratory studies and furnace measurements indicated that the primary cause for the accelerated corrosion was the high concentration of alkali vapor species, especially \( \text{NaOH} \) and \( \text{KOH} \), in oxy-fuel fired furnaces. Although the rate of corrosion typically increases exponentially with temperature, actual experience varied widely. In some furnaces, most severe corrosion was observed in the charge end, i.e., the coldest area of the furnace, and in other furnaces more corrosion was observed near the hot spot area. During 1995-1998 Praxair and a consortium of several glass companies funded a series of laboratory studies and thermodynamic modeling studies at TNO Institute of Applied Physics to elucidate the corrosion mechanisms and to develop better furnace/burner designs to reduce corrosion. The key findings of the studies are as follows.

- The corrosion rates of silica bricks and joints are strongly related to the mass transfer rate of alkali vapor species to the bricks.
- The calcium rich binding phase (beta-wollastonite, \( \text{CaO} \cdot \text{SiO}_2 \)) used in the regular silica brick is preferentially attached by alkali vapor species, forming a glassy phase which penetrates through the silica grain boundaries and dissolves silica grains.
- The rate of silica brick loss appears to be controlled by “washing” of the glassy phase. At high temperatures only a relatively small amount of alkali oxides in the glassy phase is sufficient to reduce the
viscosity of slag to flow. Thus, a unit amount of alkali vapor transferred to the brick surface can “wash” a large amount of silica.

- In the colder area of the crown near the charge end below about 1475 °C, a glassy layer containing a high alkali oxides concentration (up to 14%) would form with a low enough viscosity to flow. Thus, the amount of silica loss per unit amount of alkali vapor transferred is reduced substantially. On the other hand the alkali vapor concentration and the rate of gas phase mass transfer is often higher in the charge end of the furnace. Thus, the mass transfer rate of alkali vapor to the brick, and the viscosity and temperature of the glassy phase control the rate of silica loss.

- Fused silica reacts less intensively with alkali vapor species. The initial rate of alkali vapor absorption was about ¼ of that for the regular silica brick. At temperature below about 1450 °C sodium silicate will be formed. At high temperature less alkali vapor attack is expected since sodium silicate is thermodynamically unstable. Fused silica bricks or special silica bricks with a very low calcium content are preferred over the regular silica brick for the crown.

- The silicate phase in the AZS bricks absorbs alkali vapor species and forms a low viscosity glassy phase, especially in the initial campaign due to exudation. As a crown material, AZS with a low glassy phase is recommended.

- Pure alumina and MgAlO4 spinel show very low absorption rates for alkali vapor species.

Based on these findings a goal was set to develop an improved furnace/burner design so that the silica crown life in a new oxy-fuel fired furnace becomes as long as that of the equivalent air fired furnace.

As discussed in the section on particulate emissions, the amount of alkali vaporization depends on furnace temperature, gas velocity, water vapor concentration and the flame characteristics. The total particulate emission is a good indicator of the total amount of alkali species volatilized. Figure 4 shows that the total amount of alkali volatilized in oxy-fuel furnaces is significantly less than that from the corresponding air fired furnace. The average concentration of the alkali species, however, is increased by as much as three folds due to the elimination of nitrogen from combustion air. In order to understand the differences in the NaOH profile between air and oxy-fuel firing, a 3D-furnace model was developed. The model calculated the volatilization rate of NaOH from glassmelt and the batch surface areas and the NaOH vapor concentration profile in the furnace. The results indicated that the NaOH concentrations near the crown refractory of an oxy-fuel fired furnace was an order of magnitude higher than those of a corresponding cross-fired regenerative air furnace, when the average NaOH concentration in the oxy-fuel fired furnace was three times higher19.

In a cross-fired regenerative furnace, each flame from a side wall port has a short straight path to the opposite sidewall. The NaOH vapor from the glassmelt or batch is concentrated near the melt surface and is exhausted quickly from the opposite port. As a result, the NaOH concentration near the crown is much lower than the average furnace NaOH concentration. In an oxy-fuel fired furnace, the flue gas is exhausted from one or two flue ports located near the charge end. NaOH vaporized in the discharge end of the furnace is mixed with several oxy-fuel flames as the bulk furnace gas flows toward the flue ports. As a result, the furnace atmosphere is relatively well mixed, resulting in high concentrations of NaOH near the crown refractory.
The effects of burner types and furnace geometry were studied by an alkali volatilization and corrosion model\textsuperscript{33}. As shown in Figure 6, the model predicted the areas of high alkali volatilization rates underneath each flame in an oxy-fuel fired container furnace, caused by higher glass surface temperature and higher convective velocity. As the burner elevation was increased, the alkali volatilization rate was reduced substantially. The crown temperature, however, increased as the burner height was raised. It was found that raising both the burner and the crown heights offered several advantages in reducing the crown corrosion rate while maintaining a good heat transfer characteristics\textsuperscript{34}. Both the concentration of NaOH and the convective velocity near the crown were reduced. The crown refractory temperature profile became more uniform, i.e., the charge end temperature was increased and the hot spot temperature was reduced. All of these factors contributed to the reduction of the mass transfer rate of NaOH to silica crown and the corrosion rate. Based on these model predictions, a new 350 mtpd furnace with a tall crown was built by Heye Glas, Obernkirchen, Germany in 1996\textsuperscript{23}. Measurements of alkali vapor species and particulate emissions confirmed a substantial reduction in the alkali vapor concentration. Two more furnaces were converted to oxy-fuel firing with the same tall crown design. After eight years of operation for the first furnace the silica crown is still in good condition and expected to last over 10 years, i.e. as long as the normal campaign of the original air furnace\textsuperscript{16}. Details of the tall crown furnace design and experiences will be published separately\textsuperscript{34}.

Another approach to solve the alkali vapor corrosion problem was to develop or select better refractory crown materials. Extensive studies were conducted to test different materials in laboratories and in actual furnaces\textsuperscript{30}\textsuperscript{-32}. Fused cast alumina was found to be most corrosion resistant material for crowns and was installed in oxy-fuel glass furnaces producing high quality glasses. However, the cost of an alumina crown was an order of magnitude higher than that of the conventional silica crown and it was not considered economically viable for container glass furnaces. An improved silica crown material has recently been developed for oxy-fuel firing applications. Since the calcium bonding phase of conventional silica brick was shown to be attacked preferentially, the calcium content of the new silica brick was minimized to about 0.8\%, as compared with 3+ \% used for standard silica bricks\textsuperscript{36}. A container glass furnace at Grupo Pavisa in Mexico was rebuilt with the low lime silica crown bricks in 2000 and the result to date has been reported to be excellent\textsuperscript{37}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Calculated Rate of NaOH volatilization versus Burner Elevation}
\end{figure}
Recent thermodynamic analyses with analytical models of transport phenomena for alkali corrosion of silica bricks and detailed furnace measurements of sodium species have provided further supports on the notion that the rate controlling step is the gas phase transport of NaOH to the silica crown\textsuperscript{38-39}. It is likely that the rate of silica crown corrosion can be reduced further by controlling the alkali volatilization and transfer to silica crown through the optimization of furnace/burner designs.

8. The Future of Oxy-Fuel Fired Glass Furnaces - Container Glass

In Table 1, projected characteristics of an optimized oxy-fuel fired container glass furnaces are shown. They were extrapolated from actual measurements from advanced oxy-fuel fired container furnaces with the effects of a batch/cullet preheater/filter system\textsuperscript{40}.

<table>
<thead>
<tr>
<th>Table 1. Projected Performance of Optimized Container Glass Furnace</th>
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<tr>
<td><strong>Furnace Capacity</strong></td>
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<tr>
<td><strong>Productivity</strong></td>
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<td><strong>Energy Efficiency</strong></td>
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<tr>
<td><strong>NO\textsubscript{x} Emission</strong></td>
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<td><strong>SO\textsubscript{2} Emissions</strong></td>
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<td><strong>Particulate Emissions</strong></td>
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Most of the improvements over the state-of-the-art oxy-fuel furnaces are direct or indirect benefits of batch/cullet preheating. As discussed in Section 5, up to 30\% of fuel and oxygen could be saved by fully recovering waste heat from a directly fired oxy-fuel furnace. Since batch/cullet preheating reduces the heat transfer requirement in the furnace, a higher specific production rate can be achieved, as demonstrated in air fired furnaces equipped with batch/cullet preheater. Similar to electric boosting, batch/cullet preheating reduces the glass surface temperature at a constant production rate. The reduction in the firing rate proportionally reduces the combustion gas volume and reduces the average gas velocity in the furnace. Lower glass surface temperature and lower gas velocity both help to reduce the volatilization of alkali species from glassmelt and batch. Thus, particulate emissions are reduced and the potential for silica crown corrosion is also reduced.

The net economic benefit from preheating, of course, depends on the capital investment required for the preheating equipment and its installation costs. An economic study\textsuperscript{15} showed that the total capital cost of a new oxy-fuel fired furnace equipped with a batch/cullet preheater/filter system is still significantly lower than the capital cost of the traditional regenerative air fired furnace.

9. Summary

The performance of oxy-fuel fired glass melting furnaces have improved significantly over the last 15 years. Advanced oxy-fuel burners reduced NO\textsubscript{x} emissions substantially, improved heat transfer characteristics and reduced volatilization of alkali vapors from glassmelt and batch. Oxy-fuel firing was shown to increase the water content of glass and to enhance the fining reactions, contributing to reduced seed counts. Particulates and SO\textsubscript{2} emission were reduced over 50\% in some glass furnaces as a result of reduced volatilization of alkali species and a reduced sulfate requirement for fining. Improved burner/furnaces designs have been developed to reduce corrosion of silica crown and the life of a well designed oxy-fuel fired container glass furnace is now expected to be over 10 years. Waste heat recovery systems such as a cullet preheater/filter and a waste heat boiler compatible with oxy-fuel firing have been developed and installed in a few furnaces. Further improvements are expected with full integration of heat recovery systems. The performance of an optimized oxy-fuel fired container glass furnace with full heat recovery was estimated, based on actual experiences and model predictions.
References