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REVIEW

An overview and the recent advancement of combustion applied to glass melting furnaces

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Abstract

The glass industry stands at a critical moment in its evolution, confronted with the urgent need for decarbonization while striving to maintain operational efficiency and product quality. This paper delves into the current scenario of the glass industry, highlighting its significant contributions to global sustainability efforts while confronting substantial challenges in reducing carbon emissions. This paper looks at different ways to reduce carbon emissions in glass production, focusing on how much energy is needed to make glass and how important melting furnaces are to this process. These include using oxy-fuel, electricity, hydrogen, and possible combinations. Emphasizing the need for innovative approaches to mitigate refractory corrosion and other operational issues resulting from changes in combustion processes, the study underscores the importance of ongoing research and development in materials science and combustion technology. The paper looks at how the different parts of the furnace, its atmosphere, flame, and the refractory behave in complex ways. This helps us understand how to improve furnace performance and make them last longer so that the glass industry can be more sustainable.
Keywords: glass industry, decarbonization, oxy-fuel, hydrogen, refractory corrosion.

INTRODUCTION

THE GLASS INDUSTRY'S ACTUAL SCENERY

From ancient times to modern society, glass has served humans with various uses that make life more comfortable and allow technological advancement [1]. Due to its valuable properties and characteristics, glass has numerous applications, ranging from packaging to high-tech medical devices [2]. Some of these properties, like transparency, non-crystallinity, rigidity, environmental stability, and high transmission, combined with relatively low production costs, continuously increase the relevance of glass in the global efforts for a more environmentally friendly usage of energy [2, 3]. Glass applications are contributing not only to the transition for new renewable energy sources, like solar panels and wind turbines but also providing more efficient buildings and urban infrastructures [1, 2]. While glass is increasingly considered in the development of several low-carbon initiatives, its production faces huge challenges and duties for decarbonization. The glass industry is classified as energy-intensive, having to fulfill the CO_2 reduction targets of the Paris Climate Agreement [2, 4].

Even though glass is largely recyclable and not a hazardous material, it cannot be considered completely "green". The fabrication process consumes a significant amount of energy, with the conversion of batch raw materials into molten glass accounting for more than 50% of the total energy required [1, 2, 5]. According to the variety of glass types, the melting specific energy consumption varies in the range of 4–17 GJ/ton [4]. Between 1960 and 2010, there was a significant optimization of this consumption, but the pace of improvement has slowed down significantly [2, 4]. The "melting" process involves chemical reactions and silica dissolution. Glass furnaces, as they are commonly called, consist of a chemical reactor where batch reactions take place, activated by temperatures always above 1300 °C and very often between 1500 °C and 1600 °C [1, 2, 4-6].

Therefore, the melting furnace determines the energy intensity for the glass industry. The main source of heat supplied to glass furnaces comes from combustion technologies, using fossil fuels in the range of 75–85%, either oxy-fuel or regenerative/recuperative air-fuel. The secondary source of heat is electricity, with usage rounding 10-15% [2]. Several factors affect the energy balance of a furnace. These include the heat capacity of the fuel, the enthalpy and sensible heat of combustion, the electric power from the electrodes, the flow of air and the temperatures used for preheating it, the composition and volume of the flue gas, the furnace's losses, and more [7]. Proper manipulation of these variables is the key to maximizing furnace efficiency and energy consumption.

Fuel consumption directly correlates with CO_2 emissions, particularly in the glass industry in Europe and the USA, where natural gas is predominant [2, 4]. In China, oil and coal are still important sources of energy for glass production. Consequently, the CO_2 emissions related to energy consumption are even more significant [2, 4]. As a result, glass is among the world's most carbon-intensive industries [8]. Container and flat glass production combined

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make up about 80% of the global glass industry, with an annual carbon emission rate of over 60 Mt CO_2 [2, 4]. As a reference, 1 kg of glass produced in a furnace heated by natural gas combustion emits approximately 0,6 kg of CO_2 [2]. Combustion is the main source of these emissions. However, an estimated 25% of the CO_2 emitted comes from the dissociation of raw materials. Emissions from batches are not reversible by using "green" energy sources, but by improving raw material mix composition [2, 4]. Moreover, full electrical melting would not drop CO_2 emissions to zero, as the carbon footprint depends on the energy source used for electricity generation [8].

Fuel switching for carbon neutrality, waste heat utilization, and carbon capture are all potential pathways for decarbonizing glass furnaces [8]. To achieve a carbon neutral industry in the following 20–30 years, as committed by the European Union countries, a hybrid combination of renewable electricity and low-carbon combustion is a possible scenery under current deep research and evaluation of the applicability stage [2, 4, 8]. Meanwhile, there are commercial technologies available as intermediate steps toward decarbonization, like oxygen-enhanced combustion [2, 8]. However, in Europe, hydrogen as a fuel has emerged as a very promising alternative. Despite the controversy surrounding its economic implications and significant technical impacts, this study will delve deeper into these topics.

The new technologies that have been proposed have the potential to change the mass and energy balances, control volumes, oxidizing-fuel ratio, and mostly the composition of the products of the combustion reaction [6]. Therefore, all potential short- and long-term solutions have a significant impact on the combustion chamber and durability of the melting furnaces. Many factors in the process can cause significant changes, such as refractory surface temperatures, combustion atmosphere composition, and resultant emissions [6]. For low-carbon combustion with alternative fuels and/or oxygen-enhancing improvements, the consequent NOx, SOx, and alkaline hydroxide formation may be specific concerns, still requiring deeper investigation to evaluate their impact on the refractory lining behavior and lifetime [2, 6]. Additionally, the resultant higher temperatures in the combustion chamber are an aggravating factor [8].

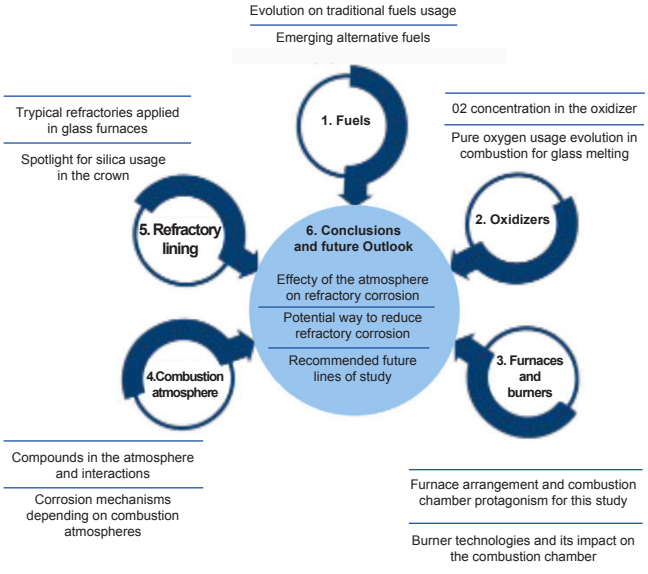

Figure 1: After introducing the current combustion scenery for the glass industry, this paper covers five main topics contextualizing the furnace conditions that favor refractory corrosion. We outline conclusions and prospects regarding the challenges that combustion decarbonization poses to the furnace's durability in the path for the energy transition.

This paper discusses recent advancements in combustion technology for industrial glass production, with a focus on the anticipated potential changes to the furnace atmosphere. These are exposed as an attempt to base a critical reflection on how prepared the glass melting processes are to keep furnaces lifetime and productive operation in the evolution to more sustainable ways to produce glass that challenges industry.

FUELS

Despite the delineation of numerous pathways for the decarbonization of glass manufacturing, combustion continues to be the most significant energy input due to the high temperatures required and the competitiveness of fossil fuel prices. Some alternative fuels considered carbon neutral are, in principle, suitable substitutes for current standard fossil fuels. Some examples are biogas, synthetic methane, and green hydrogen [4]. The adaptation to these alternative fuels represents a significant transformation in both the process and the supply chain infrastructure [2, 9, 10].

To maintain carbon neutrality, the required energy input for producing alternative fuels must also come from carbon-neutral sources. Frequently, renewable electricity derived from wind farms or solar panels serves as the primary energy source for producing carbon-neutral gaseous fuels [11]. Hubbert highlights that since antiquity, humans and creatures have relied on harnessing solar energy for survival, with the sun being the predominant source of this energy, sustaining life for billions of years. The scenario of human energy manipulation dramatically changed with the fortuitous discovery of coal in the 13th century. This potent source of manageable energy began powering steam engines, trains, and many other steam-powered devices, revolutionizing society, dynamics, and industry [12].

The advent of oil and natural gas resources accelerated the transition from exclusive dependence on solar energy. Mesopotamian ancient civilizations used crude oil for street lighting and later produced and commercialized vegetable oils. However, the industrial revolution in 1859 led to the discovery of conventional petroleum oil as we know it today. Oil, the second-largest source of fossil fuel, played a significant role in the 19th century, triggering a stronger wave of industrialization and technological innovation characterized by the development of internal combustion engines, automobiles, planes, and a multitude of other technological advances. Therefore, fossil fuels, especially

coal and oil, facilitated technological expansion by allowing industrial production rates to double approximately every few decades. These fuels have powered the majority of our daily activities and continue to do so. However, their combustion emits harmful gases like carbon dioxide (CO_2), which contributes to environmental issues such as global warming. To mitigate these effects, technological development focused on maximizing energy extraction from fossil fuels while minimizing environmental harm [9, 12, 13].

More than a secondary source, natural gas emerges as a viable substitute for coal, although its limited availability and methane leakage present obstacles. Over the past decades, enhanced global trade and partnerships between gas-rich countries and the main industrialized nations have facilitated the adoption of natural gas, primarily used in the glass industry located in the Americas and Europe [2, 4, 13]. Fossil fuels, powering over 85% of the global energy consumption, have undeniably improved quality of life but have also inflicted severe environmental damage [9, 14]. Leveraging efficient technologies has been explored in an attempt to reconcile economic growth with emission reduction goals. Transitioning from coal to natural gas brought significant challenges for international collaboration, overcome by technology transfer and financial support. Despite these challenges, we must continue to rely on fossil fuels until we perfect superior alternatives [13]. Still, the massive proportional emissions generated as a result of this energy source underscored the importance of implementing regulations to enable sustainable production practices, which culminated in consensus for CO_2 reduction targets such as the Paris Climate Agreement [2, 4, 14].

The future availability of traditional fossil fuels is also an important topic. For decades, researchers such as Hubbert, Abas, and Armanoli have highlighted the urgent need for a long-term strategy, based on the imminent depletion of finite resources, particularly coal, oil, and natural gas, at an alarming rate. Thus far, energy demand and population growth curves continue to exhibit unprecedented upward trajectories. In 2015, Abas reviewed Hubbert's prediction of resource depletion, taking into account new explorations that increased global reserves. Despite climate change and population growth challenges, living standards continue to push fossil fuel reserves, although these remain finite. The debate around fuel peaking lacks consensus; some optimist studies predict abundant oil reserves peaking in 2100, while pessimists suggest the end of the hydrocarbon era. Environmental concerns prompt the exploration of sustainable hydrocarbon fuels through CO_2 capture and sequestration processes [9, 14].

Table I shows similar natural gas challenges about peak production. Experts anticipate a peak in natural gas production within a decade of oil peaking; however, the discovery of shale gas has temporarily postponed this projection. Meakin and his coauthors provide relevant discussion around the rising significance of shale gas and its contribution to CO_2 emissions [15]. To mitigate the risk of depletion, effective consumption management remains imperative. Transitioning to renewable energy sources may contribute to long-term sustainability.

The context of traditional fossil fuels underscores long-term fuel usage's criticality due to emissions and limited availability. In a very complete review of decarbonization options for the glass industry, Zier and his coauthors introduced different promising solutions based on renewable energy technologies that can significantly contribute to increasing energy usage efficiency, reducing CO_2 footprint, and reducing dependence on finite fossil fuel reserves [4, 9]. Nevertheless, it is not new. Hubbert had already documented the urgency of transitioning to more sustainable energy sources in the late 1940s [12]. Armaroli also provided, in 2011, a deep study on the fossil fuels legacy of the earth, suggesting energy transition is probably the only way to prevent civilization's collapse [14]. The economics of the energy transition at the current prices are largely questioned, and regrettably, none of the available alternatives demonstrate likely competitiveness compared to fossil fuels. Both studies from Egerer (2024) and Zier (2021) corroborate the gap in economic viability [4, 11].

Egerer gives special focus to hydrogen as a pivotal element on the way out of fossil fuels in a broader context for Germany. However, current hydrogen production heavily relies on fossil fuels, such as natural gas and dense coal. It leads to significant CO_2 emissions, as appears in equations (A) and (B). Thus, there is a pressing demand for transitioning to low-carbon hydrogen production methods, such as electrolysis powered by renewable energy sources; this is exemplified by equation (C) and is an alternative to mitigate environmental impact [11].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \text{(A)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(B)}$$

Steam methane reforming

$$6H_2O + \text{electrical energy} \leftrightarrow 6H_2 + 3O_2 \quad \text{(C)}$$

Table I – Global fossil fuel statistic derived from verified reserves (adapted from [9]).

Fuels	Total reserves	Production / day	Projected end
Oil	1,7 trillion barrels	87 million barrels	2066
Gas	6558 trillion cubic feet	326 billion cubic feet	2068
Coal	892 billion of tons	22 million of tons	2126

Table II – Assumptions for hydrogen demand (in TWh/year) for different sectors (adapted from [11]).

Sector	Low H_2	High H_2
Cement	5,4	8,4
Lime	1,3	6,7
Glass	3,2	15,7
Pulp and Paper	-	27,1
Total	9,9	57,9

Hydrogen production by electrolysis

The high temperatures of the glass melting process present challenges for electrification, making hydrogen an attractive option. In 2023, Zier and colleagues will conduct new pathway studies for the German glass industry. While hydrogen remains a central focus, its combination with oxyfuel and preheating technologies is also a possibility [16]. The balance between electrification and hydrogen usage depends mostly on economic factors. Therefore, a common approach considered by the technical and scientific communities is the implementation of hybrid technology for future glass melting, as systematically presented by Furszyfer and colleagues in a comprehensive review of decarbonization alternatives specifically for the glass industry [2].

Although green hydrogen demonstrates the highest CO_2 reduction potentials, all-electric technology efficacy depends on further evolution in the electricity mix. Nevertheless, understanding the dynamics of hydrogen demand and the feasibility of alternative fuel adoption across industries becomes crucial in devising effective strategies for achieving climate neutrality [16]. Egerer prepared a case study for future hydrogen demand for the German glass industry, highlighting that for float production, "These plants already use hydrogen in small amounts as a protective atmosphere". This suggests considering a lower hydrogen usage limit, such as 20% of the energy demand. For the high H2 usage level, he stated, "The glass manufacturers as of today are certain that hydrogen will play a large role, especially in the melting process," assuming complete replacement of the current fossil fuels with H2 [11].

At the time of submitting this paper, there were an increasing number of initiatives underway, particularly in Europe. For instance, the HORIZON H2GLASS project, as reported in Glass Worldwide's technical news in 2023, secured 24 million euros for testing hydrogen combustion at industrial facilities, involving glassmakers and research institutes [17]. Similarly, The American Ceramic Society highlighted promising outcomes of hydrogen trials in 2023, showcasing successful demonstrations by different glassmaking groups [18]. Additionally, Glass International Magazine noted that four glass manufacturing facilities are poised to begin full-scale hydrogen trials [19]. Numerous other publicly or privately funded projects in Europe are exploring the technical feasibility of hydrogen usage. These projects are examining various hydrogen production methods, including blue, turquoise, yellow, and green hydrogen, each with different environmental impacts and cost implications. However, transitioning to hydrogen leads to changes in combustion conditions, such as higher flame temperatures and velocities, as well as potential impacts on NOx emissions and glass quality. Experimental investigations into these issues may necessitate modifications to furnace design and infrastructure elements.

The production of fundamental chemicals like methanol and ammonia, which are also considered alternative energy carriers, extensively utilizes hydrogen as a primary feedstock. As a result, there is an increase in demand for hydrogen as a feedstock. To qualify as low carbon, the production process must utilize low carbon hydrogen. Carbon capture systems provide a transitional solution, typically capturing between 60 and 95% of CO_2, although facing challenges with limited storage capacities. These advancements signify a shift in energy production and consumption paradigms. Changes in the hydrogen source would be required, primarily when transitioning to low-carbon production methods for ammonia and methanol. The synthesis of these two energy carriers or fuels, ammonia, and methanol, has no direct CO_2 emissions. Nevertheless, one ton of these fuels requires roughly 197 kg and 209 kg of hydrogen, respectively. For ammonia synthesis, nitrogen is also needed and can be obtained by an air separation unit, again powered by low-carbon electricity if intended to be claimed as renewable. The carbon source used in methanol synthesis, as well as its use, has an impact on the carbon cycle. An example of a sustainable use of methanol is in the production of biopolymers, where it can partially replace traditional fossil fuels as an energy source through the polymer synthesis process [10, 16, 20].

Synthetic methane, produced via chemical or biological processes using hydrogen and CO_2, offers a potential alternative energy source. Various process routes and reactor technologies exist, each with different investment costs and efficiencies. Additional investment costs and conversion losses may limit the long-term viability of applying synthetic methane in the glass industry, making it less competitive as a very cost-sensitive solution. While finding significant CO_2 sources for synthetic methane production is critical, availability is scarce [2, 4, 20].

Biogas is also considered a CO_2-neutral fuel, as the CO_2 emitted during combustion was previously absorbed during organic matter growth. Anaerobic digestion generates it, primarily methane (50–70%), with the remainder consisting of CO_2 and trace components. Initial tests in glass melting furnaces have shown potential for co-firing biogas without adverse effects on product quality or refractory materials. However, biogas availability is limited, and fluctuations in gas composition pose challenges for glass manufacturers. To fully leverage biogas as a sustainable energy source in the glass industry, further research and development are still necessary [2, 4].

Another option is biomass gasification. Gasification

requires a shift in the carbon source from fossil fuels to biomass [11]. Fuel switching to biomass offers an approach to mitigating emissions without requiring significant infrastructure changes. Biomass gasification processes solid biomass, such as wood, into downstream products like wood powder or syngas of CO, CO_2, and CH_4. Large-scale use of wood for glass manufacturing, despite its widespread use as an energy source, is considered unsustainable due to significant energy requirements that could potentially lead to deforestation [4, 10]. Biomass, such as fruit hulls, pits, and nut shells, can be readily utilized to replace part of the coal, with the potential for increased substitution using pre-processed biomass in the future [10]. More sustainable alternatives to biomass sources or advanced energy conversion technologies are required for direct application in the glass industry [2, 4].

In industries other than glass production, there is an equivalent growing interest in alternative fuel strategies aimed at reducing carbon emissions. Biomass fuel switching, particularly in the cement, lime, and steel sectors, emerges as a promising avenue for CO_2 emissions reduction but is highly dependent on locally available biomass resources. Nutshells and fruit stones stand out as viable alternatives to coal, which currently serves very often as the primary energy source for furnaces in these industries. Despite challenges related to regional biomass availability and pre-processing, the potential benefits in terms of emissions reduction underscore the need for further research and investment in biomass fuel technologies tailored specifically for each one of these sectors. Similarly, hydrogen fuel switching holds considerable promise for reducing CO_2 emissions for the cement, lime, and steel industries. However, the transition presents technical challenges, including the adaptation of processes and equipment [10].

As a result, decarbonization strategies focus on fuel substitution, waste heat recovery, and process optimization. Engineers could use electrical melting in a variety of ways, including combining it with hydrogen combustion [4]. Until alternative energy sources replace coal, oil, and natural gas, the engineering imperative remains unchanged: to optimize energy extraction from conventional sources while mitigating environmental impact [12, 13]. The sequence further expands certain possibilities.

OXIDIZERS

Combustion occurs when fuel interacts with oxidizers, liberating energy. Combustion can be defined as the rapid chemical reaction between a combustible substance and oxygen molecules. This reaction is characterized by the release of energy in the form of heat and light. It differs from other classical oxidation reactions, such as surface oxidation of metals, mainly due to the speed at which it occurs, regardless of the energy released in the reaction. In the glass production process, combustion gaseous products typically provide the heat for the system and exit the furnace through a chimney. For the reaction to occur, it is necessary to fulfill the classical fire triangle with the three basic components: a fuel, an oxidizer, and an ignition source. These three elements are essential for the reaction, and abstaining from one of them consequently prevents combustion from occurring [21, 22].

Oxygen (O_2) serves as the primary oxidizer in combustion reactions. Atmospheric air is composed of approximately 20,9% oxygen, making it an effective oxidizer for combustion. Under normal conditions, oxygen concentrations below 16% in the oxidizer are no longer effective at fueling combustion. However, since the combustion reaction requires only oxygen, the remaining 79,1% of nitrogen (N_2) in the air composition remains inert in the reaction. If nitrogen is eliminated, using only pure oxygen as an oxidant, combustion is called oxy-fuel, and its efficiency is significantly improved [21, 22].

The combustion ratio is a determining factor for oxidizing partially or completely the fuel molecules composed of elements such as carbon, hydrogen, and sulfur. Complete combustion is defined as the total oxidation of all oxidizable elements present in the fuel. The following equations for carbon oxidation demonstrate this.

$$C + O_2 \leftrightarrow CO_2 + 34\ MJ \quad (D)$$

$$C + 0{,}5O_2 \leftrightarrow CO + 10\ MJ \quad (E)$$

Varying the amount of available oxidizing in the reaction reflects on greater or lesser energy released, in addition to the generation of different subproducts. The setting of this variable in the combustion process has a direct relation with the efficient usage of fuels, allowing the reduction of unnecessary resource consumption and emissions. In the industrial setting, adjusting the oxidizing process to minimize carbon monoxide (CO) content is a practical measure that aids in achieving complete combustion. Some processes set the oxygen input to the combustion slightly higher than the theoretical value. The percentage difference between actual oxygen and theoretical oxygen is called excess oxygen [21–23].

Excess oxygen will impact the thermal balance of the system based on the quantities of oxidizer and fuel used (mass balance), the energy released by the reaction, the system temperature, and the amount of heat lost in the exhaust of gases through the furnace chimney. When it comes to combustion whose oxidant is atmospheric air, the impact of excess oxygen on the mass balance and, consequently, on the thermal balance is even more significant as it proportionally increases the amount of nitrogen. Nitrogen does not participate in the combustion reaction, but it is heated in the system and takes part of the energy generated through the chimney [21–23]. The main negative impact of the presence of nitrogen in combustion is the reduction of energy available in the combustion chamber of glass melting furnaces. Lower available energy is the main driver for recuperative and regenerative furnace technology usage, where elevating air entry temperature into the combustion

chamber is the target. The consequence is to reduce the energy required to raise the temperature of the oxidizing from ambient to the furnace operating temperature [21, 24].

Another technological approach is to increase the oxygen concentration in the oxidizer. This option is well established in both literature and industrial use. The process involves increasing the oxygen concentration in the air from its natural level to 100%. Oxygen concentrations above normal 20,9%, present in the air, characterize an air enriched with oxygen [21, 24]. Most combustion systems benefit from this method, as only oxygen is required for combustion. The consequent reduction or elimination of nitrogen not only reduces the formation of nitrogen oxide (NO_X), a major emission concern but also significantly increases the thermal efficiency of the system [21, 23, 24].

Elevating the oxygen concentration with pure oxygen leads to a notable increase in flame temperature, emphasizing the enhanced utilization of energy in the system [21, 25]. Eliminating nitrogen improves energy efficiency because the N_2 reduces radiative heat transfer, which leads to more energy waste during heating. Furthermore, a decrease in the concentration of N_2 in the fumes reduces the energy transfer through the chimney in the flue gases [23]. Therefore, more energy for the glass allows two ways to optimize the process. We can use the surplus available energy to either increase production or reduce fuel consumption, thereby tailoring the available energy to desired production levels. For this reason, in recent decades, oxy-combustion has emerged as a viable solution for the glass industry, improving productivity, energy use, and glass quality [21, 25-27].

The adoption of oxy-fuel firing in glass furnaces gained momentum following successful demonstrations in the early 1990s, showcasing significant fuel savings and emissions reduction. While the rate of conversions slowed, over 300 commercial furnaces worldwide now use oxygen to improve combustion, mostly in specialty glass production [23, 27]. The main benefit of oxy-combustion for glass production is the increase in available energy. Other benefits can be cited as impacts on glass quality, reduction of electricity costs, operational flexibility, increased production, and extension of furnace life. Out of all the benefits listed, the glass industry most commonly associates the increase in production rates with oxy-combustion. Oxy-fuel combustion enables the glass industry to either occasionally increase glass extraction or turn off the burner when the increased energy is no longer required. The higher radiance to the glass from oxy-fuel flames can positively contribute to convective current patterns in the glass tank, impacting also on glass quality. The cost of installing equipment for electrical reinforcement or even combustion air recovery and regeneration systems is higher than the cost of installing oxy-combustion equipment to power the furnace. Another motivator for oxy-combustion is the extension of the furnace's lifetime, significantly contributing to the maintenance of the furnace at the end of campaigns [25].

Although oxy-combustion is a well-known technology and its benefits are already well established in the glass industry, there are concerns related to the use of pure oxygen in combustion that counterbalance the assessment of this technology's applicability. Safety, emissions impacts, refractory corrosion, overheating of the glass or specific regions in the furnace, and burner deterioration are some of the main concerns. Because pure oxygen is a powerful oxidant, handling it carries risks. Several materials typically used for the pipes and combustion equipment would not combust when in contact with air; nevertheless, they may enter into the range of flammability or explosiveness upon contact with pure oxygen at the operating pressure of oxy-fuel systems. Low temperatures when storing oxygen in cryogenic form could also pose a concern. The selection of materials in contact with oxygen therefore becomes much more careful, and any intervention in the systems requires a more elaborate assessment of the risks involved. An evaluation of the operation's design and layout from the perspective of oxygen risks is required, to mitigate them. When it comes to emissions, a higher oxygen concentration in combustion leads to elevated flame temperatures, which could potentially impact NOx generation if residual nitrogen, whether from combustion or parasitic air, remains present. The combination of three factors: oxygen in higher concentrations, elevated temperature, and the presence of nitrogen, even in small concentrations, can result in this very undesirable emission from glass furnaces. This issue motivates burner developers to work on improving flame energy distribution and reducing peak temperature regions [23, 25].

Oxygen utilization in glass manufacturing offers opportunities to enhance efficiency and reduce environmental impact. We can employ various techniques to accomplish this. Overall air enrichment, use of lances, or specific oxy-fuel burners are just a few options for intermediate solutions to full oxy-fuel furnace conversions. Depending on the type of furnace, burners strategically place themselves to optimize heat transfer in conventional combustion processes [4]. The supply of oxygen for a glass furnace necessitates multifaceted considerations, including energy efficiency, initial investment outlays, and operational adaptability. More recently, with the increased usage trend of oxygen supply, the reliability and carbon footprint associated with it are also very important elements. Oxygen requirements drive the utilization of diverse supply systems. Smaller quantities typically prefer a tank-based liquid supply. Non-cryogenic generators typically supply the medium ranges using swing adsorption (VPSA). Cryogenic air separation units (ASUs) are economically viable for larger oxygen demands. Alongside on-site oxygen supply systems, reserve storage is often installed to ensure uninterrupted operation in case of process failures. Electrolysis emerges as an alternative means for oxygen production, particularly attractive when hydrogen is also needed. Electrolysis technologies offer flexibility in oxygen and hydrogen production ratios [4, 27].

Oxy-fuel combustion is seen as a promising method to improve fossil fuel combustion efficiency and is possible to combine with carbon capture technologies due to reduced

waste gas volumes for a more significant reduction of CO_2 emissions. It is particularly suitable for integration with major CO_2-emitting industries like glass factories, bringing oxygen supply technologies to play a pivotal role in advancing CO_2 neutrality objectives and enhancing industrial operational efficiency. Using O_2 instead of air in combustion improves efficiency and reduces fuel consumption, producing a high CO_2 concentration stream. It is also a great advantage for CO_2 purification via mechanical separation based on condensed temperatures downstream [16, 23, 27].

This transition to oxyfuel offers significant opportunities to enhance thermal efficiency and reduce emissions in industrial processes beyond glass production. Furnaces, kilns, and other thermal systems experience elevated flame temperatures and exhaust gas temperatures when air is replaced with oxygen, potentially reducing overall energy requirements and process time. The glass industry has extensively applied oxyfuel technology, which offers reduced energy consumption and NOx emissions, but its potential also extends to other sectors such as cement, lime, and ironmaking. Successful adoption requires consideration of refractory materials, kiln geometry, and process infrastructure modifications. Pilot projects and collaborations demonstrate the feasibility of oxyfuel technology in various industries, including adaptations for precalciner cyclones in cement production and efforts to address temperature profile challenges in blast furnaces. Despite technical hurdles, oxyfuel presents a promising pathway for achieving emissions reductions in the short and midterm, enhancing energy efficiency across diverse industrial applications [10]. However, a significant challenge lies in the additional cost of oxygen production, typically through cryogenic Air Separation Units (ASU). Efforts are underway to optimize ASU performance and reduce energy consumption [16, 23, 27]. While pressurized oxy-fuel combustion of coal shows potential for carbon capture, utilization, and sequestration, more research is necessary [23].

Implementing waste heat recovery systems from combustion gases to preheat oxygen and natural gas is a promising technology to enhance fuel efficiency in glass furnaces. Industrial installations have demonstrated the potential to save approximately 10% of fuel, leading to proportional reductions in oxygen and CO_2 emissions. The design of the heat exchange network can be customized to fulfill specific technical requirements, including the burner and control system [4, 27]. While the net economic benefit depends on the initial investment in preheating equipment, studies have shown that the total capital cost of a new oxy-fuel fired furnace with preheating systems is still lower than that of traditional regenerative air-fired furnaces [28].

The overall economic viability of oxy-fuel firing in glass furnaces relies on balancing achievable fuel savings and oxygen costs. While small furnaces can achieve significant fuel savings of 40–50%, larger furnaces typically achieve 10-15% savings. Economic incentives include capital cost savings and NOx reductions. Achieving high fuel savings and lowering oxygen costs are crucial for oxy-fuel firing to become economically favorable, particularly at higher fuel costs [27].

Oxy-hydrogen combustion emerges as a promising future option for CO_2-neutral glass production. Through electrolysis, water can be split into H_2 and O_2. The generated O_2 can potentially be employed in oxy-fuel combustion with relatively smooth integration to combine with H_2 as a fuel. However, due to the expected significant alterations in the furnace atmosphere composition, the existing oxyfuel melting systems may not readily accommodate pure oxy-hydrogen combustion concepts. These changes could impact glass chemistry and have not been adequately explored so far. Different industrial trials in the glass industry have been conducted, and, to ensure process stability, it is recommended to incrementally introduce proportions of H_2 into the fuel blend. This strategy facilitates the ongoing utilization of established burner technology while concurrently lowering CO_2 emissions [20, 27].

Gärtner's theoretical model suggests that adding H_2 to the fuel mixture in oxyfuel combustion has a less significant effect on the adiabatic flame temperature than in conventional air-fuel combustion. Furthermore, increasing H_2 content in oxyfuel may lead to a maximum 25% rise in specific energy demand for glass melting, compared to conventional oxyfuel melting [20].

FURNACES AND BURNERS

Glass melting furnaces, which are critical to glass production, operate continuously for extended periods, catering to various glass types with daily outputs ranging from 20 to over 700 tons. Typically, the lifespan ranges from 5 to 15 years, with some campaigns potentially extending to 20 years. To enhance energy efficiency, technologies like regenerators, recuperators, electrical reinforcement, and oxy-combustion have been employed [26, 29-31].

For the majority of furnace types where energy is supplied by flames, heat transfer typically occurs in the combustion chamber, which is the region bounded by the glass line and the furnace's superstructure (walls and crown). In the furnace's combustion chamber, the flames transfer the heat to the melted glass by radiation and convection. The melting tank, which is filled with molten glass melt, and the throat or spout, which connects the end of the furnace to the work-ending section, glass channels, and working zone [29, 31], are also necessary parts of the furnace that depend on the type of glass being made.

This industrial equipment enables the melting of raw materials through the radiation of flames from burner combustion while also maintaining the temperature of the molten glass. Furnace design is crucial for its durability. A proportional relation based on the furnace's width, length, glass area, and combustion chamber height determines the sizing. Various thermocouples, positioned either in the furnace superstructure to indicate refractory temperature and atmosphere or at the furnace throat to indicate molten glass temperature, frequently monitor temperatures. Different control zones can be defined, allowing for consumption

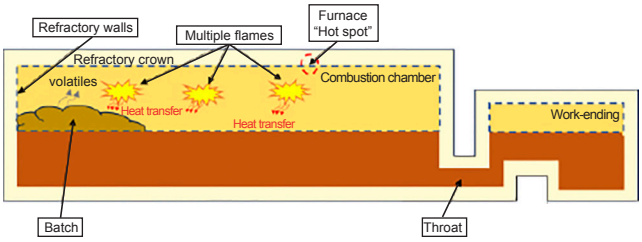

Figure 2: Schematic representation of a standard glass melting furnace, illustrating its main regions and key components.

optimization and delivering more energy near the raw material inlet. Furnace supervision is frequently based on operator experience and visual observation of burner performance. More modern facilities rely on continuous analysis programs to identify potential issues and deviations to immediately stabilize production [26, 29, 31, 32].

For smaller glass production under 10 tons per day (TPD), pot or tank furnaces are used, with pot furnaces being discontinuous and tank furnaces suitable for higher production like borosilicate. They are made with refractory bricks and interact with open flames directly. Still on the smaller-scale production up to 400 TPD, recuperative furnaces recycle heat from fumes with a double-pass metallic heat exchanger to preheated combustion air. Heat recovery ranges from 25 to 40%, and the design is relatively simple, with a fairly low construction cost. Regenerative furnaces, which dominate the industry, achieve higher production rates ranging from 100 to 1000 TPD. With regenerators, it is possible to achieve an efficiency increase of around 65%, surpassing recuperative furnaces. Refractory bricks arranged in a checkerboard pattern form the regenerator itself, facilitating alternating cycles of combustion air and exhaust gases. The flame arrangement varies depending on the regenerator's position. Electric furnaces with submerged electrodes, which are in demand due to environmental concerns, offer superior conductivity but are constrained by high energy costs. Molybdenum electrodes are employed to deliver energy for melting raw materials, but their indirect carbon footprint is dependent on emissions from the power plant that supplies electricity. In exceptional cases, the oxy-combustion furnaces, with a wide capacity range from 2 to 800 TPD, enhance heat transfer and reduce the carbon footprint. By the late 1990s, around 30% of glass furnaces employed oxygen-enriched air without significant furnace modifications, often to increase production. However, this option has additional costs for oxygen consumption. Hybrid options combining oxy-hydrogen combustion and electric boosting are still under investigation for industrial viability, dependent on cost optimization amidst energy transition dynamics [4, 26, 29-31, 33, 34].

Furnace design considerations also include the crown height, burner arrangement, and flue port location to maximize furnace energy efficiency. Since the 1970s, glass melting furnaces have successfully applied oxy-fuel boosting burners. It has been proven effective in glass furnaces, but it faces challenges with flame interaction. To optimize performance, researchers developed advanced burners that adjust flame properties. The oxy-boost method involves using auxiliary oxy-fuel burners to accelerate the melting process, resulting in production increases of about 10 to 30%. Quality can also be improved by placing strategically oxy-boost burners in the furnaces, allowing the reduction of superstructure temperatures, hence reducing temperature-related defects in the glass. Boost burners also have a positive impact on the convective currents in the glass mass, allowing for faster melting, greater predictability, and greater load stability. The flexibility of oxy-fuel burners allows for precise control of temperature distribution, contributing to production rate increases. However, retrofitting existing air-fired furnaces with oxy-fuel burners requires careful selection and placement to optimize heat transfer while minimizing alkali volatilization and refractory corrosion [25, 28, 35]. In a synchronized boosting system, oxy-boost burners can adjust flame properties with each regenerator reversal, thereby maximizing flame quality despite turbulence [35].

Since the 1990s, advanced oxy-fuel burners have notably reduced NOx emissions, improved heat transfer, and decreased the volatilization of alkali vapors from molten glass and batch. The design and arrangement of burners play a critical role in controlling flame size and shape. Traditional burners typically consist of two ducts or tubes, somehow associated. The first duct transports the fuel, while the second one serves as the oxidant. The design of burners depends on the type of fuel and oxidant, as changes to these variables significantly affect volumes and velocities. Preheated air, oxygen, or fuel also changes, most importantly, the volumes and flame characteristics. Burner durability is paramount in glass furnace applications due to the extended operational campaigns. Volatiles present in the atmosphere can chemically attack burners, leading to corrosion, particularly in exposed nozzles and burner blocks. High-momentum flame patterns further exacerbate gas movement into the burner, generating differential pressure around the burner that can accelerate wear. Water-cooled burners operate at relatively low temperatures, supposedly reducing wear; however, lower temperatures can facilitate the condensation of corrosive volatiles, thereby potentially exacerbating localized corrosion. Oxygen-enriched flames are typically shortened, directing high-energy flames closer to gas outlet nozzles. Combined with higher oxygen levels in the furnace, this can potentially promote rapid oxidation of metallic parts and tends to decrease burner lifetime. Recommended developments to mitigate corrosive effects on burners include eliminating water cooling, reducing gas flow velocity, and implementing self-purging systems. These practices reduce the impact of aggressive combustion chamber environments, extend burner lifetime, and technically enable the use of oxy-combustion in the glass industry. Therefore, the appropriate design and installation of burners for oxygen use are crucial for accessing the energy gains, productivity increases, and quality improvements associated with sustainable long-term

oxygen utilization [25, 28, 31, 35, 36].

Burner manufacturers have developed a wide range of oxy-combustion burner technologies over the years, aiming to maximize the benefits of oxygen by promoting efficient heat transfer, stable flame operation, and improved product quality. While these benefits are attractive, careful consideration of their impacts is essential for successful implementation. Each furnace has specific conditions, needing a tailored approach to burner development and application based on operational experience and production parameters. Despite early challenges in adapting oxygen technologies originally developed for the steel industry, innovations such as adjusting flame characteristics and pre-combustor techniques have improved the suitability of oxy-combustion burners for glass production. To increase heat transfer efficiency, sophisticated techniques are applied to the burner design to explore higher radiation from the regions of higher temperatures in the flame. The concept of staged combustion is solidly applied in oxyfuel burners and enhances combustion for glass melting through the oxygen injection into the lower region of the main flame, which increases the temperature in this part of the flame. Leveraging the fourth power law of radiation heat transfer, which states that the temperature difference between bodies exchanging heat is raised to the fourth power and directly proportional to heat transfer, it is logical to enhance this correlation strategically in the combustion chamber. Another variable directly proportional to heat transfer is the surface area of the flame, which can be manipulated by varying the shape factor. The flame profile not only increases glass coverage, but can also increase luminosity due to increased fuel cracking. Staged oxygen injection can create a highly radiant lower flame region without obstruction, while the upper flame region exhibits a slightly reducing flame and a dense soot cloud, which acts as a shield against radiation to the superstructure. This staged oxygen injection also serves to delay the reaction with fuel, decentralizing hot spots in the flame and reducing NOx emissions, a common pollutant from glass furnace combustion. Some industrial trials using oxyfuel boosting burners revealed a slight reduction in the crown average temperature. The directionality of the heat towards the glass melt is responsible for this decrease. Lower crown temperatures are desired to extend the furnace lifetime and reduce glass defects [35, 37, 38].

In previous studies, experimental tests with state-of-the-art burners were conducted using different mixtures of hydrogen and natural gas, ranging from 100% natural gas to 100% hydrogen, primarily using oxygen as an oxidizer. Minor adjustments were implemented in the burner configuration to accommodate hydrogen, followed by an examination of flame attributes such as shape and brightness. Experiments demonstrated that augmenting the hydrogen concentration in combustion diminishes flame brightness. Simultaneously, the flame morphology alters with increasing hydrogen levels, resulting in shorter flame length due to increased combustion kinetics. Nevertheless, the altered gaseous composition in the fuel did not cause any deterioration effects within the combustion chamber or localized overheating on the burner block during the experimental assessments. Further investigation is still necessary [39].

COMBUSTION ATMOSPHERES

All of the trends for more sustainable glass melting and to meet energy transition requirements by the new legislation will have an impact on the chamber's atmosphere. Three strong tendencies have been specifically changing the atmosphere compositions and temperatures: the oxy-fuel combustion, the hydrogen addition to fuel, and the oxygen and fuel preheating. The technologies, separately, already resulted in significant alterations. Moreover, the goal of minimizing direct CO_2 emissions from glass melting could potentially combine two or even three of these technologies. The addition of pure O_2 to the combustion results in changes in the thermophysical properties of flue gases, as seen in the graphic comparison in Figure 3. Even for a low level of enrichment, under 30% O_2 concentration in the comburent, these changes can significantly impact the interaction of the

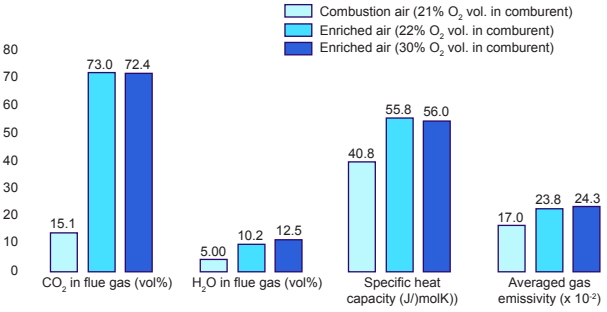

Figure 3: Thermophysical properties of flue gas under different conditions (adapted from [23]).

atmosphere and furnace or the glass [23].

Among all the flue gas modifications, an increase in water concentration is particularly concerning because it could influence system interaction between flame, atmosphere, glass, and refractory lining in the superstructure. Moreover, higher flame temperatures exponentiate reactions at interfaces, which can lead to more severe corrosion. Koohestanian [23] indicates in his oxyfuel evaluation that the average flame temperature tends to increase with an increase in O_2 concentration, but the magnitude of the flame temperature difference depends on the process conditions and type of fuel. The same for other properties highlighted in his study. Evaluating adiabatic flame conditions without considering the influence of the process environment accentuates the tendency of flame temperature increase with O_2 enrichment. That is clearly observed in the graphic representation of methane flame temperature on Figure 4. In his review of the principles for oxy-fuel combustion applied to CO_2 capture, Kirschner highlights that, in addition to the variation in flame temperatures, the use of oxygen increases flame radiation, which has a positive effect on glass melting [24].

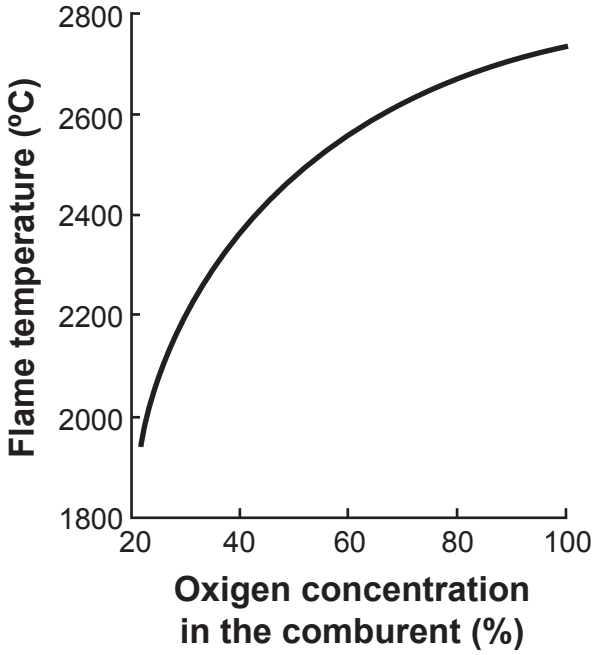

Figure 4: Effect of oxygen enrichment on methane flame temperature (adapted from [24]).

When using oxygen as comburent, the total volume of combustion gases also drastically reduces. For glass melting temperatures, the reduction in combustion gas volume can be greater than 90% when replacing the oxidant from the air with 100% oxygen. Efficiency increases, leading to a reduction in fuel consumption, yet the combustion reaction still yields the same molar proportions of CO_2 and H_2O when oxidizing a hydrocarbon. For instance, 1 mol of methane (CH_4) requires 2 moles of oxygen gas (O_2) for complete combustion. Consequently, the resulting products remain consistent: 1 mol of CO_2 and 2 moles of H_2O. However, the substantial nitrogen volume eliminated when switching air by oxygen affects the concentration of combustion products and consequently alters the furnace atmosphere. The absence of dilution in the combustion products leads to moisture concentration. It is critical to distinguish this concept, as there is no increase in water (H_2O) generation. Instead, the generation of water remains either equal to or less than that observed in combustion with air. The only impact is the higher concentration of moisture [21, 22, 24-26, 36, 40-42].

When low-carbon fuels are used, the CO_2 concentration in the combustion products is even lower. As indicated in the graphic of Figure 5, oxy-fuel combination with hydrogen addition to the fuel could reach volume levels close to 100% H_2O in the fuels. It is essential to point out that water vapor concentration impacts both glass chemistry and refractory life. For typical oxy-combustion atmospheres, same as for oxy-hydrogen combustion, the main constituent of the fumes becomes H_2O, a molecule significantly reactive at the operating temperatures of glass melting furnaces [42].

Furthermore, elevated flame temperatures can lead to increased volatilization of raw materials, particularly in environments with higher moisture concentrations, such as oxy-fuel systems and hydrogen combustion. This volatilization not only diminishes raw material yield but also alters the composition of the combustion atmosphere. Water vapor combined with other compounds in the furnace atmosphere creates corrosive gaseous substances that shorten the furnace's life by speeding up the corrosion of the silica-based refractory linings. This is one of the fundamental causes of the greater refractory corrosion that is frequently observed in furnaces under oxy-fuel combustion [25, 27, 42]. Constituents volatilized from raw material due to the high temperatures are released before glass formation. Alkaline compounds such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) can be formed in the combustion atmosphere. Soda-lime glasses primarily contain sodium as the key alkali, added in the form of sodium carbonate to serve as a silica flux. More moisture in the atmosphere during oxy-combustion and the release of alkalis from raw materials increase the formation of alkaline hydroxide [8, 30, 43, 44].

Preheating with oxygen and natural gas, along with additional technology to enhance fuel efficiency, has the potential to modify the flame profile and heat transfer from

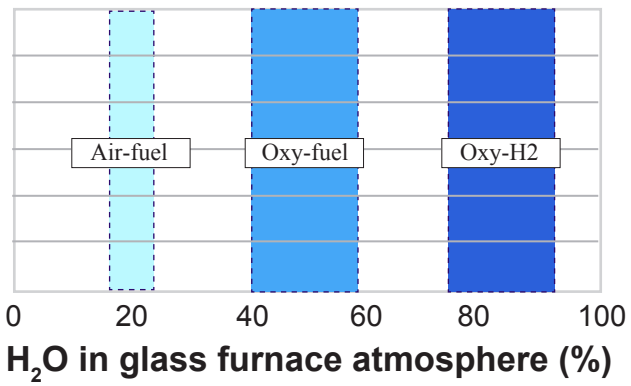

Figure 5: Moisture concentration ranges for different combustion reactants applied for glass melting (adapted from [42]).

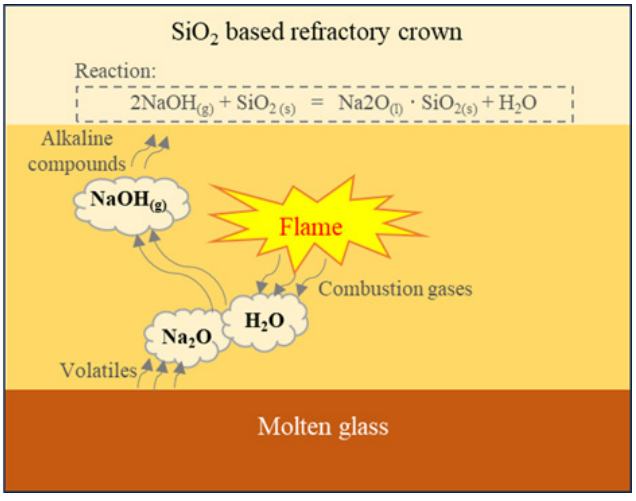

Figure 6: Diagram showing the alkaline components in the furnace atmosphere and their interactions leading to refractory corrosion (adapted from [43]).

the flame. It may result in varying energy distribution profiles within the combustion chamber, and these changes can have a significant impact on the atmosphere and refractory temperatures. Therefore, similar effects on increased raw material volatilization can be expected from the employment of energy recovery technology, although there is still a lack of industrial experience documented about the impact of such technology in real environments.

Since the 1950s, researchers have studied the impact of alkaline concentration on refractory corrosion in glass melting furnaces. By the late 1990s, the adoption of oxy-combustion technologies by glass manufacturers led to significant challenges in the durability of crown refractories and furnace superstructures, due to the consequent higher water concentration and alkaline hydroxide presence in combustion gases.

Multiple research efforts focused on recording corrosion rate measurements. Solomin, in his study, examines different refractories when exposed to low-alkali glasses. The focus of this and many other experiments was to investigate corrosion rates under laboratory conditions [45]. Spear and Allendorf went beyond when investigating the mechanisms of silica refractory corrosion in glass-melting furnaces using oxy-fuel instead of air-fuel. The focus was on the equilibrium predictions in the Na_2O-SiO_2 system to understand the formation of liquid-phase corrosion products. This research line lasted for years and provided valuable insights into the impact of furnace variables on corrosion rates, such as temperature and NaOH concentrations. Although this research led to the establishment of a thermodynamic database, the examination of corrosion mechanisms, and the creation of an analytical model to forecast corrosion rates, the studies primarily concentrated on the effects of changing the composition of the atmosphere from air-fuel to oxy-fuel. However, they did not delve deeply into the influence of refractory surface temperature on corrosion [43, 46, 47]. A few years later, Rimsza deepened the study in the chemical aspect of this phenomenon by researching the interaction of NaOH solutions with silica surfaces and observing that the oxygen present in the silica surface formed hydrogen bonds instead of the expected proton-ion exchange. This research provides a valuable understanding of the thermochemical aspects of reaction formations, although it may benefit from further consideration of industry-specific practical applications and the potential influence of surface temperature effects [48].

It has been great identifying corrosion mechanisms, characterizing furnace samples, determining refractory properties, and obtaining typical gas-phase compound temperatures and concentrations. Based on the literature and documented studies on laboratory and industrial levels, the primary cause identified for severe corrosion on oxy-fuel furnaces is the high concentration of alkali vapor. Nevertheless, corrosion rates typically increase exponentially with temperature. In practical experiences, the corrosion temperature detected varies widely. Some furnaces exhibit the most severe corrosion close to the raw material charging, while others experience more corrosion near hot spots in the furnace. Pragmatically, a relevant portion of the challenges related to higher water concentration revealed in the oxygen-fired versus air-fired atmospheres investigations were addressed through minor adjustments on burners and combustion control. A similar approach may be useful on the path for converting air-natural gas or oxy-natural gas furnaces to air-hydrogen or oxy-hydrogen combustion [28, 42, 49].

REFRACTORY LINING

High-quality refractories are indispensable for the effective operation of all components within a glass tank furnace, which acts as the nucleus of a glass manufacturing facility. Glass furnaces apply refractory materials to ensure durability over extended periods of operation, given the high temperatures required for glass melting. Thus, the performance of refractories is essential for securing a smooth operation of the glass furnace. On average, the specific consumption of refractories per ton of glass produced globally is approximately 4 kg [50].

The effectiveness of refractories within a glass tank furnace significantly influences production costs and the quality of the glass output. Given the diverse operating conditions across different areas within the furnace, various types of refractories are utilized in specific zones. Besides resisting extreme temperatures, refractory materials are intended to maintain consistent performance and physical properties throughout the furnace lifetime. The development of refractories for use in glass furnaces remains a constant evolution, and each region of the furnace requires a specific type of refractory with a varied chemical composition [50, 51].

A meticulous selection of refractories, taking into account the specific demand in each area, is critical to ensuring optimal furnace functionality. Some important considerations are the resistance and stability under high operational temperatures, including special attention to the maximum working temperature. Resistance to thermal shock and thermal expansion is particularly critical during initial heating phases from the ambient temperature until the operational temperatures to minimize exposure to thermal fatigue. Along with mechanical strength and creeping (resistance to deformation under load), thermal conductivity is a very important factor for insulating well and reducing heat loss. These are also important building characteristics for the crown and the whole superstructure. The quality of the chosen refractories will directly impact the resultant glass quality and potential defects in the glass, besides playing a considerable role in determining furnace energy consumption. Thus, the accurate and judicious selection of refractories emerges as a pilar for operational efficiency. Refractory manufacturers highlight that refractories contribute to 50% of defects observed in glass production. Burak İzmirlioğlue and his collaborators summarized the most used types of refractories applied in the construction of glass furnaces. Typical refractories are listed in the following

Table III – Refractory types and typical applied location in furnaces (adapted from [51]).

Refractory Type	Location in Furnace
Silica	Melter and working end Crown, Melter refining and working end Superstructure
Alumina	Melter superstructure (float), Awall (float), Waist crown (float), Forehearth canal/superstructure (containers, tableware)
Mulite	Regenerator walls, waist crown
Sillimanite	F/H cover block
Zircon	Isolation between alumina/silica mortar, monolithic
Fused cast AZS	Melter sideblocks, Melter tuckstones, Melter pavings, Melter superstructure
Magnesia	Regenerator walls, crowns, checkers

table. All these materials need to withstand extremely harsh environmental conditions during the glass furnace campaign, exposed to chemical, physical, and thermal stresses [30, 51].

For the regenerators, as there is a temperature gradient between the upper and lower sections reaching approximately 1500 °C at the top and 500 °C at the bottom, refractory bricks composed of magnesia, mullite ($3Al_2O_3.2SiO_2$), or zirconia (ZrO_2) are frequently utilized. Elevated temperatures, internal furnace particle carryover, and the condensation of volatiles from the raw materials all affect the upper region in the regenerators. For the glass exposure regions in the furnace, typically in the range between 1.100 and 1.500 ºC, refractories must be capable of avoiding dissolution to the molten glass, as it could generate inhomogeneity and unwanted defects. In the soda-lime glass production, casted AZS (alumina-zirconia-silicate) refractories are commonly found in contact with molten glass, just as for the side walls in the furnaces. At the interface between molten glass and atmosphere, in contact with the wall (melt line), corrosion rates are typically higher. Specific refractories with greater corrosion resistance, such as chromium oxide bricks, can be used in the metal line. Another alternative to minimize corrosion at this point is the use of air cooling on the outside of the furnace. Furnace superstructure temperatures, including the crown, can reach levels between 1550 and 1700 ºC, with the highest temperatures being found in borosilicate glass or glass-ceramic production. Refractories in this zone must resist potential chemical attacks by combustion gases and volatile components that can combine in the atmosphere. This region of the furnace hosts a variety of refractories, including sintered alumina-zirconia-silica, traditional silica, and fused alumina. For many years, silica bricks were applied to the glass furnace crowns, but with high water vapor concentrations in the atmosphere, corrosion can be observed in this material due to alkalis evaporated. Fused silica and special silica bricks with low calcium content are preferred for crown applications due to their reduced reactivity with alkali vapor species. Additionally, AZS with low glassy phase content is recommended. Pure alumina and spinel ($MgAlO_4$) demonstrate low absorption rates for alkali vapor species [25, 30, 31, 52, 53].

When selecting the appropriate refractory, not only the chemical composition of the refractory must be considered but also the microstructure, macrostructure (particle size, bonding phases), and level of impurities of the refractory. All these factors influence the costs and investment in the furnace, but they also play a crucial role in ensuring the durability and quality of the produced glass [30, 31]. Table IV summarizes the main demands and environmental conditions for the refractories exposed in each region of the furnace.

Strong convective currents exist within the glass bath on the side walls, where the molten glass reaches temperatures between 1550 and 1600 °C. Consequently, the primary causes of damage to the refractory lining are chemical corrosion from contact with molten glass and physical erosion from the moving glass stream, while thermal shock plays a negligible role due to the continuous operation of the glass tank furnace over extended periods. As previously mentioned, these refractory demands necessitate the application of fused-cast AZS along the sidewall, usually containing 33–35% ZrO_2, making it the most suitable option. AZS fusion cast refractories, which are made up of alumina, zirconia, and glass, have different amounts of ZrO_2; higher amounts make them more resistant to glass corrosion. To mitigate severe upward corrosion at horizontal joint intersections, single blocks are employed to cover the entire depth of the glass bath. Chemical segregation may occur within AZS blocks during manufacturing due to differences in phase densities and solidification temperatures, necessitating testing for variations in grain sizes and porosity before use. Exposure to combustion gases and alkali vapors at temperatures ranging from 1550 to 1600 °C primarily causes damage to refractories in various sections of the furnace, including the wall above the glass bath, port, and bridge wall, and doghouse sidewall. Combustion gases carrying the dust particles formed through evaporation from the glass bath move at high velocities within the furnace. In a cross-fired furnace, the conditions for refractories vary significantly from upstream to downstream. The doghouse experiences considerable batch carryover, with

Table IV – Refractory requirements for the different locations in the furnace [53].

Area	Conditions	Requirements
Crown (working lining)	Alkali vapors high and variable temperatures	Volume stability. Low permeability. Creep resistance Thermal shock resistance
Superstructure	Batch carryover High temperature Volatiles: alkali vapors	Thermal shock resistance Corrosion and erosion resistance
Sidewalls	High temperature Glass corrosion Machinability	Corrosion resistance Chemical compatibility
Bottom paving	Glass corrosion Machinability	High refractoriness under load Corrosion resistance
Safety layer	Glass contact	Corrosion and erosion resistance
Insulation	High thermal load	Low thermal conductivity Good mechanical strength

lower temperatures and temperature fluctuations primarily influenced by external air contact. AZS fused cast blocks are recommended for this area. However, in sections of the doghouse where temperature fluctuations are excessive, fused silica or fireclay refractories are preferred. Conversely, an end-port furnace, characterized by its relatively small size and a U-shaped flame trajectory after striking the bridge wall, exposes the entire melter to severe conditions. As a result, the severity of conditions faced by the refractories remains consistent across the entire melting area. The walls close to the charging suffer significantly from batch carryover, although the temperature in these areas is relatively low. Conversely, walls close to the center of the furnace experience high temperatures, creating a highly corrosive environment due to batch carryover. The refractory lining required for these specific application areas should exhibit several key characteristics to ensure optimal performance. Firstly, it must possess outstanding resistance to corrosion caused by alkali vapors. Additionally, it should demonstrate resilience against spalling, particularly within higher temperature ranges. Lastly, it should have minimal susceptibility to contamination from glass batch materials. These qualities are essential for maintaining the integrity and effectiveness of the refractory lining in environments subjected to intense heat and chemical exposure, ensuring prolonged and efficient operation within glass manufacturing facilities [50, 54, 55].

β-Alumina fused cast refractories are suitable for use in areas downstream where lower temperatures and minimal impact from batch carryover are experienced. Characterized as a single-phase refractory saturated with alkali, β-alumina fused-cast refractory exhibits excellent corrosion resistance to alkali vapor and imparts minimal contamination to molten glass. Fused-cast β-alumina also ensures high thermal shock resistance and stability in alkali and alkaline earth environments. However, it becomes unstable in the presence of SiO_2 at higher temperatures due to soda release during the conversion to α-alumina, resulting in refractory cracking. Corrosion resistance to batch carryover is crucial in high-temperature areas near the raw material charging. Therefore, it is recommended for use in the refining area, feeder, and forehearth. The refractory lining in the crown suffers extended periods of exposure to high temperatures and chemical corrosion from alkali vapor. This environment requires refractories that can withstand such conditions effectively. Key requirements for refractories in the crown area include excellent resistance to alkali vapor at elevated temperatures, resilience against thermal shock, superior volume stability under high temperature conditions, and strong resistance to creep deformation. These characteristics are essential for ensuring the durability and reliability of the refractory lining in the crown of glass furnaces over extended operational periods. Silica and mullite bricks are predominantly utilized in the crown of glass furnaces. Alumina fused cast refractory, consisting of 40% α-alumina and 60% β-alumina, demonstrates effective performance in this area. Silica refractory is commonly employed in regenerative and recuperative glass furnaces' crowns. The impurities and fluxing oxide content such as Al_2O_3, TiO_2, and alkalis influence significantly the silica bricks performance and properties. Analysis reveals a notable increase in liquid

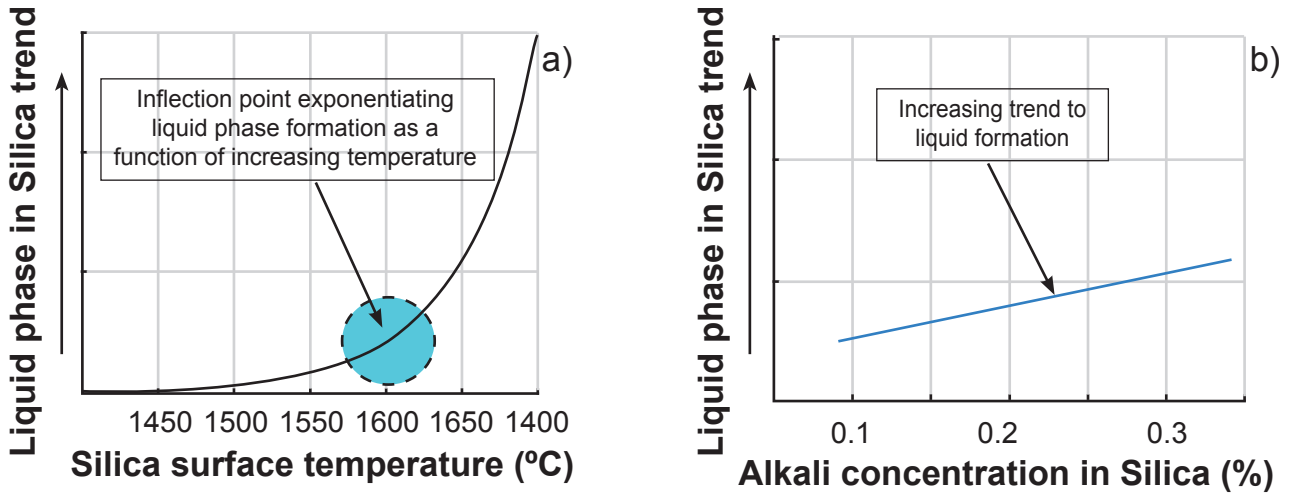

Figure 7: Liquid phase formation tendency as a function of the temperature increase in the silica refractory and the alkali concentration dissolved in silica [50, 57, 58].

content in silica refractories at high temperatures, particularly evident above 1600 °C, emphasizing the importance of limiting service temperatures to avoid detrimental effects. Research indicates the migration of fluxing oxides towards the cold face, leading to increased silica content in the hot face of silica bricks. Corrosion mechanisms involve NaOH attacking the bonding phase of traditional silica bricks, followed by silica grain dissolution, with lime-free silica refractories exhibiting superior resistance [50, 56].

Silica refractories, consisting of at least 95% SiO_2, typically contain impurities such as CaO, Fe_2O_3, and Al_2O_3, sourced from quartzite in various forms ranging from coarse crystalline to fine crystalline varieties. The suitability of quartzite for silica refractory production depends on factors like polymorphism behavior, fracture characteristics, microstructure, chemical composition, refractoriness, and porosity, with combined Al_2O_3 and TiO_2 ideally below 2% and alkali content below 0.3%, preferably below 0.1% for high-quality products. Polymorphism in quartz involves reversible and irreversible transformations at different temperatures, affecting volume changes, with specific quartzite types preferred based on their degradation rate upon heating. Manufacturing involves using milk of lime as a binder, providing CaO for mineralization,

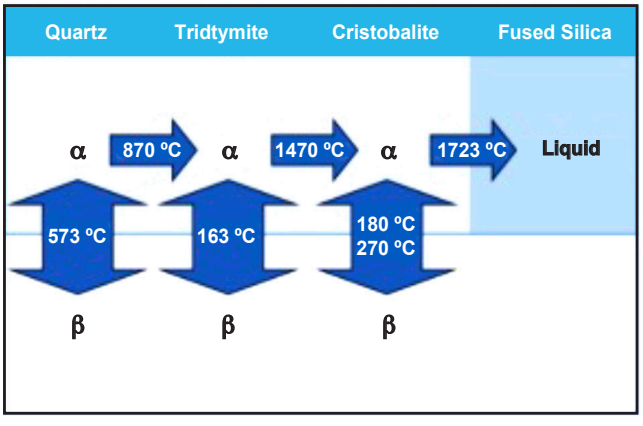

Figure 8: Polymorphic transformation of silica [50].

and facilitating desired phase conversions in quartz, while Fe_2O_3 helps to promote the desired phase transformation. The absence of CaO in modern silica refractories enhances performance under harsh operating conditions [57, 58].

Silica refractories commonly contain various crystalline forms of silica, with tridymite being the most preferred phase. However, the presence of residual or free quartz is highly undesirable due to its propensity for conversion to tridymite and cristobalite during service, causing a significant volume expansion of 14% and leading to refractory cracking. Detection of free quartz can be achieved through its characteristic thermal expansion behavior with temperature and determination of specific gravity, with an ideal silica brick having a specific gravity below 2.34. Despite these challenges, silica refractories exhibit excellent thermal shock resistance above 600 °C and exceptional thermomechanical stability at temperatures up to 1600 °C, making them widely utilized in constructing the crown and superstructure of glass tank furnaces [57, 58].

CONCLUSIONS AND FUTURE OUTLOOK

The challenges the glass industry faces in decarbonization culminate in a huge pressure to reduce the consumption of fossil fuels. To approach carbon neutrality, a few technology options, like oxy-fuel combustion, electrification, hydrogen combustion, and combinations of those, are considered. Oxy-fuel appears to be a more readily available option, largely tested and industrially implemented. Many alternative fuels are being researched and developed; the infrastructure for producing and delivering these fuels is currently the biggest limitation. Hydrogen is one of the most promising fuels or energy vectors that allows carbon footprint reduction. Both development lines, hydrogen as a fuel or oxygen as a more efficient oxidizer, result in higher temperature flames and water concentrations in the combustion gases. Soda-lime glass still exhibits a significant amount of alkali volatilization when processing its raw material composition.

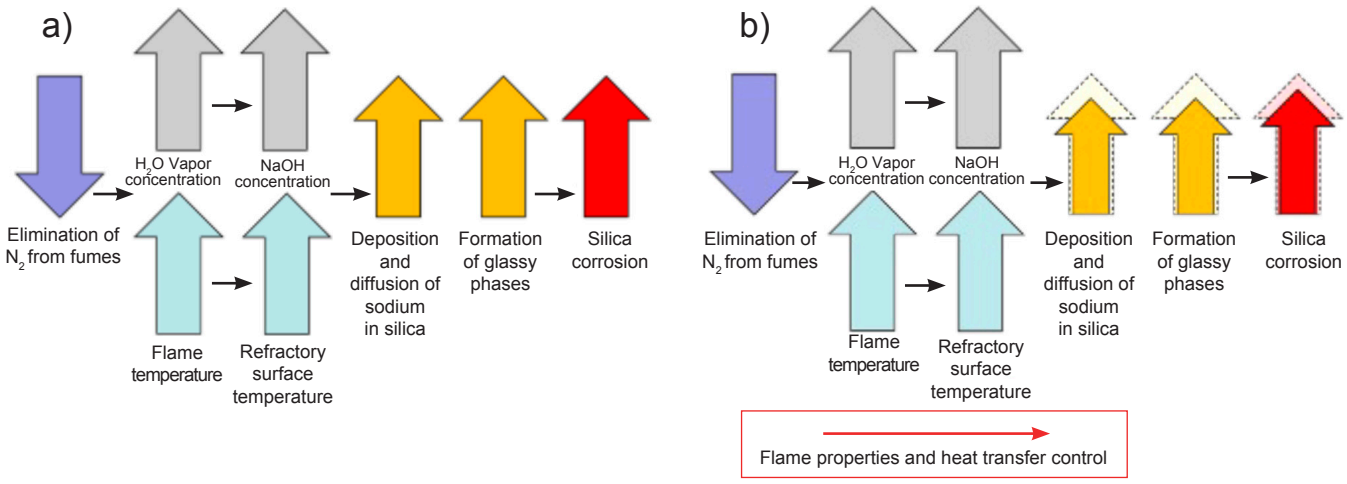

Figure 9: Conditions under oxy-fuel that can affect the interface between combustion atmosphere and refractory silica

Furthermore, peak temperatures in the furnace may result in higher volatilization if not properly controlled. Hydrogen combustion necessitates a larger fuel volume for the same energy input, which affects changes in flame velocities and particulate carryover to the atmosphere.

In the way of decarbonization, the eminent consequent combination of higher flame temperatures and higher water concentration in the combustion chamber tends to form more alkali corrodent compounds and lead to more refractory corrosion, especially to the silica-based bricks in the crown. Some burner technologies may aid in controlling flame properties and energy transfer, but their influence on the combustion products is limited, except NOx formation. The main concern remains the corrosion of the superstructure and crown, as it is critical for the long-term production campaigns and viability of glass production. As previously exposed silica is still significantly applied to the furnace crowns due to its relevant thermal mechanic properties and thermal shock resistance, nevertheless corrosion resistance under high alkali concentration atmospheres remains an important constraint for this material. The literature review on the advancement of refractory materials reveals a deficiency in information regarding mitigating measures to counteract the more aggressive conditions, which are crucial for managing the lifetime of glass furnaces. Certainly, new materials may appear to address the more severe requirements. Instead, using combustion techniques wisely and taking advantage of new burner and furnace technologies could lead to an easy and pragmatic way to lessen the inevitable effects of the combustion transformation. Figure 9 illustrates the use of flame property control as a means to mitigate refractory corrosion.

Researchers have already extensively studied the effect of the furnace's atmosphere composition on refractory corrosion. The literature also mentions and highlights the impact of surface temperature on refractory corrosion, not only for silica but also for other refractory materials. Considering that higher temperature in the flame and higher water concentration on fumes are inevitable consequences of the energy transition, a deep study on the impact of the surface temperature on corrosion for the refractory applied to the glass lining is recommended. Experimental studies on this effect are currently underway and will be published elsewhere.

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