Refractory issues related to the use of hydrogen as an alternative fuel

By James G. Hemrick

With the increased interest in using hydrogen as an alternative fuel to reduce carbon dioxide emissions, this article looks at some of the effects on refractory ceramic lining systems when industrial furnaces are fired on hydrogen in place of or in addition to traditional fuels.

The United States Department of Energy (DOE) has devoted significant interest and resources to the use of hydrogen as an alternative industrial fuel source because it is known to create only water when combusted and, depending on its production method, generates little or no carbon dioxide.

Yet while much attention is being given to the economics and feasibility of the supply and utilization of hydrogen as an alternative fuel, less consideration is currently aimed at the effects such fuel changes may have on industrial processes where they are implemented.

Industrial processes are currently based largely on the use of fossil fuels, which are responsible for a major portion of industrial emissions. According to a 2019 report by Freidlingstein et al., industrial emissions accounted for 22% of global carbon dioxide emissions, with fuel used for process heating accounting for 42% of industrial emissions globally and 58% in the United States.[1]

Yet, the industrial sector may be more reticent than other sectors (such as electric power or transportation) to invest in alternative fuels that may reduce emissions due to the high capital investments required and long operating lifetimes of equipment, the inability to pass on price premiums to consumers, and the specific technical requirements that limit the options for substituting alternative fuel streams.[2] Such aspects of industrial heating that may be relevant include the absolute temperature, heat flux, heat availability, and heat reliability supplied by the fuel source. All these aspects can be issues when considering using hydrogen as an alternative energy source.

While some work can be found on changes in burner design and implementation when firing hydrogen, less work is available on possible refractory ceramic issues that may occur in furnace lining systems when furnace atmospheres and temperature characteristics are changed by the firing of hydrogen in place of traditional fuels such as natural gas. It is the hypothesis of the author that such changes will influence refractory selection and performance, and the extent of this effect is what will be proposed in the discussion to follow. Although the examples and studies cited in this article are not exhaustive, it is hoped that the issues and experiences summarized will further the discussion of possible issues that may be encountered and whether greater consideration of this topic is warranted.

Effects of the use of hydrogen on burner design

Most relevant work in the literature deals with burner design and alterations needed when burning hydrogen in combination with traditional fuels. These issues are well summarized by Baukal et al.[3] and are described in general below. Some of these effects were also found to be prevalent in applications where hydrogen was used as an alternative fuel in industrial applications, and they will be discussed in greater detail in the section to follow.

Because hydrogen is a light molecule, it has a high heating value on a mass basis and low heating value on a volume basis, leading to higher volumetric flow rates (higher fuel pressures) being required compared to other common fuels. Hydrogen also exhibits a high flame speed and relatively high adiabatic flame temperature compared to other fuels, which can lead to increased NO_x levels during combustion with air and more extreme conditions for burner components. A comparison of hydrogen and other common fuels is given in Figure 1.[4]

Radiation heat transfer from the flame (a function of the fourth power of the absolute temperature) will also be higher with hydrogen, and the combustion product volume flow rate will be reduced compared to more traditional fuels. Additionally, hydrogen produces more water when combusted compared to other hydrocarbon fuels, which may result in water vapor being present in the furnace atmosphere.

Examples of and challenges with using hydrogen as an alternative fuel

As far back as 2013, efforts were made to burn hydrogen-rich tail gases in place of fuel oil to reduce energy consumption and emissions in industrial furnaces.[5] In the study by Hsu et al. (2014), two industrial heating furnaces (11.4 m × 5 m × 10 m) each employing 14 burners (single center nozzle to burn oil and the surrounding nozzles to burn gas) were used. It was found that with the increased use of hydrogen, the volume of resulting flue gas was decreased, reducing the internal furnace pressure. This reduced pressure led to reduced residence time of hot gases in the furnace radiation zone, inefficient heat exchange, and excess heat in the furnace convection zone. Additionally, increased NO_x levels were noted.

Similarly, for the past 10 years, a pulp and paper mill used industrially vented hydrogen from an adjacent chemical process to supplement lime kilns traditionally fired on natural gas and other waste gas.[6] The hydrogen gas was not burned at a constant rate but was used for spot power for several hours a day and up to several weeks as the waste gas was available and based on availability and pricing of primary fuels.

Issues regarding the use of hydrogen in place of traditional fuels have included its higher heat release rate, which can lead to more heat at the front end of the kiln requiring changes to the process air and other parameters. Accelerated wear was also noted in select sections of the kiln due to firing of the hydrogen (seven-foot sections located in regions 50–60 feet and 80–85 feet along the length of the kiln), but it was not clear whether this wear was primarily due to the alternative fuel use or stop/start of the kiln to facilitate fuel changes. Also, discoloration of the refractory lining surface after the use of hydrogen, compared to the firing of traditional fuels, was noted (greenish tinge discoloration). Due to the chemical process resulting in the production of the hydrogen waste gas, it was found to contain chlorides, which are attributed to causing this noted discoloration. Burner issues were also encountered during the initial transition to hydrogen firing.

Heating value

Gas	Btu/lb	Btu/scf
Methane (CH_4)	21,495	912
Propane (C_3H_8)	19,937	2,385
n-Butane (C_4H_{10})	19,679	3,113
n-Pentane (C5H12)	19,507	3,714
Ethylene (C_2H_4)	20,275	1,512
Propylene (C_3H_6)	19,687	2,185
Hydrogen (H_2)	51,625	274.6
Carbon Monoxide (CO)	4,347	321.9

Flame speed (laminar burning velocity)

Gas	ft/s	cm/s
Methane (CH_4)	1.37	44.8
Propane (C_3H_8)	1.41	46.2
n-Butane (C_4H_{10})	1.37	44.9
n-Pentane (C5H12)	1.31	43.0
Ethylene (C_2H_4)	2.24	73.5
Propylene (C_3H_6)	1.56	51.2
Hydrogen (H_2)	9.91	325
Carbon Monoxide (CO)	1.58	52.0

Adiabatic flame temperature

Gas	°F	°C
Methane (CH_4)	3542	1950
Propane (C_3H_8)	3610	1988
n-Butane (C_4H_{10})	3583	1973
Ethylene (C_2H_4)	3790	2088
Propylene (C_3H_6)	3742	2061
Hydrogen (H_2)	3807	2097
Carbon Monoxide (CO)	3826	2108

Credit: Fuels, C. Baukal

Figure 1. Properties of hydrogen compared to other common fuels.[4]

Simplification of the burner design was undertaken, along with modifications to accommodate flow rates and fuel properties of the hydrogen waste gas. Currently, a nearby petrochemical plant is being built as well to be exclusively fired on the waste hydrogen fuel and to also use hydrogen produced from new methanol plants being constructed.

Work in Germany in 2018 looked at the hypothetical effects of mixing hydrogen with natural gas for combustion in industrial applications.[7] Issues con-

The H2@Scale initiative at DOE

The H2@Scale initiative at the United States Department of Energy was created to "bring together stakeholders to advance affordable hydrogen production, transport, storage, and utilization to enable decarbonization and revenue opportunities across multiple sectors."[8]

Under this initiative, in October 2021, the DOE announced nearly $8 million in cooperative projects at U.S. national laboratories to support DOE's Hydrogen Shot goal to drive down the cost of clean hydrogen by 80% within the decade.[9] Projects funded under this initiative will be carried out under cooperative research and development agreements (CRADAs) and will leverage the Advanced Research on Intergraded Energy Systems (ARIES) platform to enable the integration of hydrogen technologies in future energy systems, including energy storage and a specific focus on safety and risk mitigation.

A list of funded projects can be found at:

https://www.energy.gov/eere/articles/doe-announces-nearly-8-million-national-laboratory-h2scale-projects-help-reach

Additional information on the H2@Scale initiative and the Hydrogen Shot goal can be found at:

https://www.energy.gov/eere/fuelcells/h2scale

https://www.energy.gov/eere/fuelcells/hydrogen-shot ■

sidered when directly introducing hydrogen into the current industrial gas streams include product quality, process efficiency, and pollutant emissions (NO_x). Both computer simulations (computational fluid dynamics, CFD) and actual experiments were performed using "off-the-shelf" industrial burner systems in a semi-industrial burner rig, with the effects of hydrogen contents of up to 50% by volume considered regarding process efficiency, heat transfer, and pollutant emissions. Three different burner systems were considered: a modular nonpremixed jet burner, a forced-draught burner, and a flameless oxidation burner (firing rates for all burners in the range of 100 kW and air excess ratios of 1.05).

Increased NO_x emissions were noted in the burner testing due to increased local combustion temperatures, but these emissions could be controlled to some degree by adjusting the settings of the individual burners (especially for the flameless oxidation burner). Changes in flame length (decreased with increasing hydrogen content) and shape were also seen in CFD modeling of the burners. Additionally, modeling showed that higher hydrogen concentrations in the fuel impacts the energy balance of the furnace, which could lead to insufficient heat released inside the furnace.

To evaluate changes in furnace efficiency and heat balance, a heat transfer impact factor (HTIF) was developed (Equation 1),[7] where $\dot{Q}_{Load}$ is the heat flux into the furnace load (product), $\dot{Q}_{Load,Reference}$ is the reference case heat flux into the furnace load (product), $\dot{Q}_{Wall}$ is the heat flux into the furnace wall, and $\dot{Q}_{Wall,Reference}$ is the reference case heat flux into the furnace wall.

$$\mathrm{HTIF}=\dot{Q}_{Load}/\dot{Q}_{Load,Reference}=\dot{Q}_{Wall}/\dot{Q}_{Wall,Reference}) \qquad (1)$$

Using this factor, heat flux within a hypothetical furnace was evaluated using CFD simulations to estimate the heat flux into the product being processed or directly into the furnace walls for various hydrogen concentration levels. An analysis for 20% by volume of hydrogen in natural gas showed reductions of 5–13% in HTIF compared to pure natural gas firing. This finding indicates that more heat is going into the refractory walls of the furnace than into the product when firing hydrogen, thus raising the operating temperatures of the refractory, which accelerate corrosion and wear and require more energy input into the process.

A similar computer simulation analysis was carried out for a regenerative glass melting furnace (for pure natural gas, 10% hydrogen substitution, and 50% hydrogen substitution).[7] Flue gas temperatures were seen to decrease with the introduction of hydrogen, while maximum furnace temperatures within the model tended to increase with hydrogen concentration. This situation resulted in reduced heat transfer to the glass melt and increased heat transfer to the furnace walls, as seen in the earlier simulation described above. Additionally, drastic increases in NO_x emissions were noted. Finally, questions regarding whether hydrogen will chemically interact with the metal and glass products being processed were raised, as well as a need was identified to determine the possible interactions of the hydrogen with the refractory lining materials of the furnace, which could lead to reduced furnace lifetimes and increased maintenance requirements.

A more recent area where hydrogen was considered as an alternative fuel is in industrial boilers.[10] To reduce carbon monoxide and carbon dioxide emissions, along with plant fuel costs, users of industrial boilers are considering alternative fuel sources that they have available to them, such as residual hydrogen left over from reforming and refining processes. Such hydrogen (which is often flared or released) can be injected into a fuel gas stream to supplement normal fuels. However, as noted by users and previously highlighted, the use of this hydrogen can lead to higher flame speeds and firing temperatures, requiring changes in burner construction materials and burner types to facilitate the incorporation of hydrogen into the fuel stream. Additionally, it was noted that some steels used in traditional burner construction could undergo hydrogen embrittlement and attack at elevated temperatures, which can lead to premature failure of the burner.

Due to the burner modifications noted above, impact is also seen in burner emissions and performance.[10] The high flame propagation speed of hydrogen causes the combustion process to occur more rapidly than for natural gas, leading to localized heating near the flame and increased NO_x emission rates. (Field and test facility data have shown that standard low-NO_x burners firing hydrogen typically exhibit an increase in NO_x emission rates by up to a factor of 3.) These phenomena are confirmed in earlier efforts by the petroleum industry to use hydrogen in the firing of process heaters, where a stainless steel burner deflector temperature was seen to increase from 480°F when firing natural gas to 1,300°F when firing 95% hydrogen and NO_x levels increased from just over 40 ppm to nearly 70 ppm, respectively.[11]

These issues were shown to result in higher temperatures, longer heating resident times, and different heat distributions seen by refractory lining materials in service. Additionally, hydrogen produces more water compared to other hydrocarbon fuels and may result in water vapor being present in the furnace atmosphere, which can lead to increased refractory corrosion for certain refractory compositions. All these factors are known to have possibly deleterious effect on refractory materials depending on the compositions employed.[12]

It also has been noted that changes may be seen within the boiler regarding where and how heat transfer occurs, along with increased furnace gas exit temperatures due to the higher flame temperatures. Such changes in boiler performance may require alternative strategies for type and location of refractory materials used.

Hydrogen has been used in combination with natural gas for industrial heat treatment furnaces as well.[13] Natural gas/hydrogen blends were used as alternative fuel due to economic potential for decreasing carbon dioxide emissions. As noted previously, alterations were required to the heating system to account for the differing thermophysical properties of the fuel blends and the corresponding changes to the flue gases (thermodynamic and chemical). In particular, increased NO_x emissions were noted (increases of 10% for air-staged combustion and about 100% for flameless combustion were measured at a 40% hydrogen content in comparison to pure natural gas firing). Again, refractory issues were not noted, but similar issues to those highlighted above are expected with the change in furnace conditions.

In China, hydrogen-rich fuel was injected into a steel blast furnace in place of part of the coke loading to reduce carbon dioxide emissions and energy usage.[14] The effect on refractory performance was not discussed, but the increased hydrogen content of the furnace atmosphere was found to change the thermodynamic and kinetic conditions of the furnace due to altered temperatures (increased flame temperatures) and gas flow (lower gas flow rates). The existence of more water in the furnace was also noted. All these factors lead to reduced efficiency of the blast furnace and would be expected to alter the performance of the furnace lining system. Additionally, the effects of using hydrogen in place of coal will be compounded because the coal not only provides heat but also carbon monoxide and physical structure for the reactions occurring within the blast furnace.[4]

Also for steel production, Tenova S.p.A. introduced a new burner system (TSX Smartburner) for use in steel reheat furnaces in 2020.[15] This megawatt-size flameless combustion system is capable of burning any mixture of natural gas and hydrogen (up to 100% hydrogen) using Tenova's integrated advanced digital control solutions. NO_x emissions are controlled by the flameless combustion technology (releasing < 80 mg/Nm^3 @ 5% of oxygen with furnace at 1,250°C). It also boasts optimal heat transfer uniformity within the furnace with full adaptation of the fuel mixture to balance the available hydrogen stream through the burner control logic. This design is expected to address some of the problems noted previously regarding uneven furnace heating leading to hot spots and to be flexible to varying hydrogen availability, therefore possibly reducing these effects on refractory performance.

Additionally, in Germany, multinational steel producer ArcelorMittal received state funding to implement its plans to invest in a demonstration steel plant using hydrogen produced from renewable electricity.[16] The proposed plant will be a direct reduced iron plant using green hydrogen to reduce iron ore in a carbon-free steelmaking process. Starting in 2025, they plan to produce all "green" steel using clean direct reduced iron (up to 100,000 tons) from a 50 MW electrolyser and melted scrap in a green powered electric arc furnace. The direct reduced iron process is much more amenable to the use of hydrogen as an alternative fuel because it traditionally uses natural gas and generally not coal, as is the case for blast furnaces. Still, changes to the chemistry and thermodynamics of the furnace atmosphere are expected and therefore refractory issues should be a consideration.

The use of hydrogen was also explored in glass melting. Since 1991, numerous container glass furnaces were converted from air-fuel to oxy-fuel firing, where pure oxygen is substituted for part of or all the air mixed with the combustion fuel. Recent advances in this technology have looked at substituting hydrogen in place of oxygen.[17] Such a substitution is hoped to further reduce fuel requirements and emissions while also improving glass quality. It is noted that some batch modification to optimize the glass fining chemistry and control glass foaming may be required, along with further burner improvement. It is therefore expected that reevaluation of the furnace refractory structure may also be required, as was the case when the move to oxy-fuel firing was first undertaken.[18]

Relatedly, in September 2021, NSG Group announced that they successfully manufactured architectural glass at their Greengate location in the United Kingdom using hydrogen in place of natural gas for all power production at the site.[19,20] This demonstration was part of their "HyNet Industrial Fuel Switching" project to prove that hydrogen was as capable as natural gas in achieving excellent melting performance while also reducing carbon emissions by replacing natural gas in the float glass furnace, which accounts for most of the company's overall carbon emissions. Although extended furnace performance was not monitored and therefore the effects on the refractory lining were not evaluated, in this initial short-term three-week trial, a "seamless transition" between fuels was noted.

Examples of the use of hydrogen in cement production were not found, but it is estimated that 30% of high-temperature industrial heat is used in the cement industry and hydrogen should be well suited for use as an alternative fuel.[4] Due to the large carbon footprint of this industry, decarbonization of the fuel source should be attractive. Refractory lined vessels that would be affected include preheating and calcination towers, clinker production kilns, and cooling sections. Additionally, examples of the use of hydrogen in aluminum production were not found, but hydrogen may be a suitable alternative to natural gas used in secondary aluminum production furnaces, which accounts for more than 80% of U.S. aluminum production.[4] Issues concerning mechanical abuse, thermal shock, and metal penetration/reaction already exist in many aluminum reverberatory furnaces, and these issues are expected to be compounded by changes in furnace atmosphere and temperature profiles if hydrogen is introduced.

Conclusions

Significant resources and attention are being devoted to the use of hydrogen as an alternative fuel source to fossil fuels. By doing so, significant reductions in carbon dioxide emissions are possible, but modifications to burner technology and furnace operating procedures will be necessary.

Although much effort has been documented regarding burner design and implementation, less information is available regarding the effects of hydrogen firing on processes and process vessels. In addition, almost no information is available regarding the effects on refractory ceramic materials when hydrogen is used as a part or all of the fuel stream.

Many of the issues associated with the firing of hydrogen in place of traditional fuels such as natural gas result from the properties of the gas itself. Hydrogen is a light molecule with a high heating value on a mass basis but low heating value on a volume basis. This fact leads to higher volumetric flow rates (higher fuel pressures) being required compared to other common fuels. Additionally, hydrogen exhibits high flame speeds and relatively high adiabatic flame temperatures compared to other fuels, leading to higher radiation of heat transfer from the flame and reduced combustion product volume flow rates. This process has been shown in many cases to result in higher temperatures, longer heating resident times, increased NO_x levels, and different heat distributions within furnaces, causing more extreme conditions for burner and correspondingly furnace components.

Examples of hydrogen being used in industrial processes date back over a decade and often involve mixing hydrogen with other traditional fuel sources such as natural gas. Many of these efforts rely on hydrogen from tail gases, vented from chemical processes, or recovered from other processes, while more recent efforts use “blue” or “green” hydrogen production. Regardless of the source, several common issues are prevalent when hydrogen is used as an alternative fuel.

As mentioned above, with increased hydrogen use, the volume and temperature of the furnace flue gas can be decreased, therefore reducing the internal furnace pressure. This reduced pressure leads to reduced residence time of hot gases in the furnace and inefficient heat exchange/transfer, along with excess heat in the furnace convection zone or increased overall furnace temperatures requiring changes to furnace operating parameters. Additionally, increased local combustion temperatures and changes in flame length, speed, and shape can occur, affecting the energy balance of the furnace. Also noted in all cases where hydrogen was used was a significant to extreme increase in NO_x emissions and increased presence of water in the furnace. With the decrease in flue gas temperature and the increase in water content within the furnace, there may also be concern about aqueous condensation and dissolution of NO_x to form an acid compound.

These issues can all have deleterious effects on refractory ceramic lining material performance. Such effects can include accelerated wear, chemical attack, and overheating. For example, it was shown that reactions occur between reducing gas (such as hydrogen) and stable oxides like silica, alumina, and zirconia that make up many refractory ceramic lining materials.[21] This reaction produces gaseous suboxides and water vapor that can be carried downstream to interact with furnace components and the product being processed. Additionally, such reduction of these oxides was shown to accelerate refractory corrosion and deceased refractory strength.[22] Thus, alternative refractory selection may be necessary, or the use of novel lining strategies or configurations may be required to maintain current furnace lifetimes and maintenance schedules.

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