**Towards H2 implementation in the iron- and steelmaking industry: State of the art, requirements, and challenges for refractory materials**

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**Abstract**

The iron- and steelmaking sector accounts for 7–9% of global anthropogenic CO2 emissions. Industrywide efforts are currently underway to bring those figures down, and hydrogen has emerged as a key part of the solution. Hydrogen is projected to take over the role of reducing agent for iron oxides in direct reduction processes, and it can also be used as an alternative, more sustainable fuel in industrial furnaces. Importantly, the implementation of H2 in different installations will affect the refractory lining, but wear mechanisms are not fully understood. This review addresses this question, placing emphasis on chemical aspects – especially the effect of exposure to reducing hydrogen atmospheres, or to the water vapor that will be generated when H2 is used. The present state of knowledge, as well as the main challenges and open questions, is outlined with a view to guiding researchers and engineers in both academia and industry.

Keywords: hydrogen, iron- and steelmaking, refractories, corrosion, high temperature.

1. **Introduction**

It is widely known that CO2 emissions constitute a major driver of global warming and its associated effects, such as an increased risk of droughts and floods, threats to biodiversity, the melting of polar ice caps and glaciers, and the rise of sea levels. [1] To avert the more severe consequences of climate change, the Paris Agreement stipulates that the increase in the global average temperature must stay below 2 °C measured against pre-industrial levels, with the target of 1.5 °C [2] – which warrants that net-zero be attained by 2050. [3] Currently responsible for 2.6 Gt of annual CO2 emissions worldwide, or 7– 9% of global anthropogenic CO2 emissions, [4] the iron and steel sector will play an important role in attaining those goals. In the face of this challenge, the steel industry is going through a paradigm shift, with decarbonization efforts taking center stage in business and technology. Different strategies are being developed for this purpose, and approaches include increasing the efficiency of blast furnaces in integrated plants, carbon capture, usage and storage (CCUS) technologies, ramping up the use of scrap in the electric arc furnace (EAF), and adopting hydrogen in iron- and steelmaking processes. [5,6]

Various challenges stand to be overcome for implementing hydrogen, from production and transportation to availability and safety, [7,8] but it is going to be an important part of the solution. In fact, hydrogen has come to the fore as the main focus of CO2 abatement efforts in the steel industry in Europe. [9] H2 is going to contribute to decarbonization in two primary ways. First, the prevailing blast furnace (BF) technology will give way to direct reduction (DR) processes, and here hydrogen can be used as a reducing agent to dramatically reduce emissions. [10,11] Second, it can be deployed as a fuel for industrial furnaces, superseding fossil fuels. [12] Despite substantial efforts to develop these technologies, one factor is often overlooked: the implications for refractory materials, which are essential for the production of iron and steel. The purpose of this review is to tackle this question, drawing from research that has been published in the past decades as well as knowledge derived from industrial applications.

After briefly describing the basics of hydrogen and its use in different installations and furnaces in chapter 1, we will focus on hydrogen as a process gas and as a fuel in chapters 2 and 3, respectively. The main changes to process conditions in iron and steel production will be outlined, and a discussion concerning the effects upon refractories will follow. Each subsection will cover an important refractory ceramic oxide or oxide group. Chapter 4 closes the paper with the conclusions and the outstanding challenges for the implementation of hydrogen in iron and steel production from the refractory perspective.

* 1. **Basics of hydrogen**

Hydrogen is the lightest and most simply built atom of the periodic table as well as the most plentiful element in the universe. [13–15] On Earth, it represents one in six atoms in the Earth’s crust. It mainly occurs in the form of water (H2O) and hydrocarbons (CmHn), the main source being methane (CH4) in natural gas where each of the four hydrogen atoms shares a covalent bond with the sp3-hybridized carbon atom. Under normal conditions, hydrogen in its elemental form is a colorless and odorless gas with the formula H2. It is a widely used reactant in various key industrial processes, such as autothermal reforming or ammonia production via the Haber-Bosch process. [13,16] H2 is considered as an alternative fuel and is often compared with natural gas (NG) or other hydrocarbons (Table 1). Attention should be paid to the higher diffusivity (associated with its low molecular weight), wider flammability range and detonation limits, reduced ignition energy, higher adiabatic flame temperature, and lower density. [17]

|  |  |  |  |
| --- | --- | --- | --- |
| Energy carrier | Value | Unit | Energy in kWh/kg |
| Hydrogen | 3.00 | kWh/Nm3 | 33.33 |
| Oil | approx. 1 | toe/t | approx. 11.6 |
| Diesel | approx. 10 | kWh/l | approx. 11.9 |
| Benzine | approx. 8.8 | kWh/l | approx. 12.0 |
| Methanol | 4.44 | kWh/l | 5.47 |
| Methane | 9.97 | kWh/Nm3 | 13.9 |
| NG (82 – 93% CH4) | 8.8 – 10.4 | kWh/Nm3 | 10.6 – 3.1 |
| Propane | 25.89 | kWh/Nm3 | 12.88 |

*Table 1 – Comparison of hydrogen with other energy carriers.*

Hydrogen can be produced through a multiplicity of methods. In fact, it is *en vogue* to attribute colors to hydrogen based on its origin, side products, and other criteria such as social aspects. An overview of the most common hydrogen types and their current color codes can be found in Figure 1. Brown and black hydrogen are derived from brown (lignite) and black (bituminous) coal, respectively, and their production through gasification processes is associated with high CO2 emission levels. The prevalent H2 form, and slightly less polluting than the black or brown varieties, grey hydrogen is produced via steam reforming using NG. This process can be made less polluting if carbon is sequestrated and stored – in this case, we have blue hydrogen. It is a reasonable transition technology, together with turquoise hydrogen, which still uses NG and hence implicates depletion of our limited resources, but yields solid C as a byproduct instead of directly releasing CO2. Research and development of this technology is still ongoing.

Notably, water can also be used to generate hydrogen via electrolysis, potentially with minimal environmental impact – which depends on how the electrical power is generated. If the electricity stems from renewable sources, we have the so-called green hydrogen. Different sustainable energy alternatives can be used, such as wind or solar power, the latter case corresponding to what is often referred to as yellow hydrogen. Nuclear energy can also be employed to power electrolysis allowing to curb CO2 emissions, but on the other hand the production of nuclear waste is in disagreement with sustainability targets. Nonetheless, the development of safer and more sustainable nuclear power sources such as thorium reactors could help cope with the needed power input for electrolysis. Another H2 source is gaining attention, namely naturally occurring hydrogen, which has been termed white hydrogen. Until recently, the occurrence of hydrogen in its elemental form was thought to be scarce, but there may be profuse resources lying in underground reserves. Yet another potential technology is the production of H2  via the recycling of waste products – sometimes also called white hydrogen. [18–24]

In addition, there are also alternative methods, albeit less relevant from an industrial perspective, including biological routes using enzymes or bacteria to split hydrogen from sugars, radiolysis, thermolysis, metal oxidation with water, or new approaches towards known processes that are still under development – one example being the pyrolysis of methane in a liquid metal bath instead of plasmolysis. [25–27]

A chart of different objects

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*Figure 1 – Hydrogen production types and their current color codes.*

In the sustainability context, it is also worth mentioning that there are different possibilities to store and transport hydrogen. The most common alternatives are underground storage in rock reservoirs, the liquification of H2 under high pressures (and with considerable energy usage), gaseous hydrogen in pressurized vessels, in the form of ammonia (liquid), and via pipelines. To make green or at least CO2-reduced hydrogen widely available, immense infrastructural efforts and investments are necessary. Supply chain corridors have been defined and are constantly revised according to the political, economic, and technical boundary conditions established by the European Commission and industrial networks. There are extensive investigations available and underway that evaluate the addition of H2 to NG pipelines and the adaptations that would be needed, given the differences in density, diffusivity, and reactivity. The lower density would translate to different gas velocities and pressures, which could require changes to pipe dimensioning. Materials would have to reassessed as hydrogen can cause embrittlement in certain polymers and metals. [28,29] However, a full analysis of this topic is outside the scope of this review.

The general idea of using hydrogen for decarbonization is that (i) it can be produced in a sustainable way and (ii) its energy can also be utilized in a sustainable way. The most common underlying assumptions are that (i) hydrogen is produced from water using green energy providing a theoretically unlimited source of energy and (ii) the byproduct of hydrogen usage is water. [30] Nevertheless, approximately 95% of the currently available H2 comes from fossils fuels. Green hydrogen is still scarcely available, but technical advancements and alliances are accelerating. According to the Fuel Cells and Hydrogen 2 Joint Undertaking, hydrogen could account for up to 24% of the total energy supplied in the European Union by 2050. Most scientifically founded published scenarios that allow meeting the CO2 and in consequence climate targets rely, among other essential measures, on H2. [31] Hydrogen can also contribute to decarbonization via a sectorial coupling of solutions where it plays a central role in a complex value chain acting as an energy buffer. It is important to keep in mind that production, transport, and availability of H2 are essential puzzle pieces to reach CO2 targets.

**1. 2 Use of hydrogen in different installations/furnaces**

In general, hydrogen can be utilized in different ways to reduce the carbon footprint in iron- and steelmaking processes (Figure 2).

1. Hydrogen can be used as a process gas, namely reducing agent. In this regard, usage is mainly considered for the reduction of iron ore to iron. [11,30,32,33] The reducing agents in industrial state-of-the art processes for iron production, the blast furnace and direct reduction units that depend on coke and NG, respectively, can be partially – or in the latter case completely – substituted by H2 gas.
2. H2 could also be used to replace NG (partially or completely) as a fuel. Fuel switch to hydrogen is currently considered for preheating applications (e.g. ladles or submerged entry nozzles), reheating furnaces, or even for installations such as the EAF. [34]
3. More disruptive approaches currently under development include flash ironmaking or the use of hydrogen plasma. [35]
4. **Hydrogen as process gas**

To produce steel, naturally occurring iron ore has to be reduced to iron metal. This requires a reducing agent, and coke is the hitherto prevalent choice. In the most usual ironmaking route, coke is fed to the top of a blast furnace and reacts with oxygen to form carbon monoxide, which in turn reduces the molten ore (Equation 1). CO2 is generated as a by-product, and BFs release huge quantities of CO2 into the atmosphere. [37] The reduction step accounts for a staggering 80 – 90% of total emissions in an integrated plant. [38]

A diagram of steel making process

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*Figure 2 – Use of H2 in steelmaking targeting decarbonization.* [36]

*Equation 1*

As an alternative to the conventional route, direct reduction – where iron ore is reduced in the solid state and then further treated in the EAF – has been implemented in a few locations, using primarily NG as reducing agent. The main factor driving the expansion of DR has been the availability of natural gas in certain areas, and it has been geographically circumscribed to the regions of the world where this resource is abundant. [39] However, there is now growing interest in this route in the context of sustainability. The process run on natural gas enables a 38% decrease in emissions. Moreover, DR has the potential to operate with hydrogen as reducing agent instead, releasing water as a by-product (Equation 2). A DR process with hydrogen derived from renewable energy would allow a cutback in emissions of over 80%. [40]

*Equation 2*

Additionally, the injection of hydrogen into the blast furnace is being investigated. Albeit not at the same level of technological maturity as direct reduction, other alternative routes that make use of hydrogen are under development and could gain ground in ironmaking, such as hydrogen plasma smelting reduction and the flash technology. This section will present those processes and provide a panorama of the role hydrogen will play in the reduction of iron ore. In sequence, a discussion will be made from the perspective of refractories, exploring the potential effects that the utilization of hydrogen as a process gas may have on the refractory lining.

**2.1 Processes where hydrogen can be used**

* + 1. **Blast furnace**

Typically, most iron ores, agglomerates, and pellets are smelted in a blast furnace. The BF is a shaft furnace which operates continuously on the countercurrent principle. The charge, consisting of iron carriers, coke, and aggregates sinks from top to bottom, while the reducing gas produced by the combustion of the coke with the blast wind rises from bottom to top. The main products of the BF are pig iron (with a high content of additional elements), slag, and blast furnace gas. Blast furnaces are operated with counter-pressure to increase output. By reducing the flow velocity of the gas, counter-pressure increases the contact time between the gas and the solid, which has a positive effect on gas utilisation and heat transfer.

The injection of auxiliary fuels such as coal, oil, natural gas, and waste hydrocarbons through the tuyeres reduces the consumption of coke in the BF. This can reduce the energy cost of iron production. Improved control of the blast furnace process is another important benefit of auxiliary fuel injection. [41] The auxiliary fuels can perform some of the functions of coke, acting as reducing agents or carburisers, but they cannot replace the coke skeleton necessary for sufficient permeability in the furnace. However, since gaseous fuels are already in practice, introducing hydrogen is a possible strategy to reduce CO2 emissions in the short term using the existing infrastructure. [42] Injecting H2 into the BF results in a multitude of changes to various process parameters, which are interrelated and interdependent, so potential problems need to be identified and resolved to deliver a safe and stable process. M. Chu et al. conducted numerical simulations of a blast furnace with hydrogen-bearing material injection (such as waste hydrocarbons and natural gas). It was found that the furnace temperature level is lowered, and the reduction ratio tends towards indirect reduction compared with an all-coke process. [43] Further simulations of the blast furnace operation with increased H2 content, up to 43 mol.%, were conducted by H. Nogami et al. [44,45] A trend of lowered shaft and top gas temperatures was observed. Although the amount of coke and therefore the permeability has been reduced, an increased hydrogen content also results in a reduced pressure drop, which could be related to a lower gas velocity due to the decrease in shaft temperature and gas density. While the above simulations kept the raceway conditions similar, Liu et al. examined the effects on the raceway in their simulation, such as the temperature distribution and the behaviour of volatiles when pulverised coal and hydrogen are co-injected. [46] It was shown that, for the given model and boundary conditions, there is a tipping point from which higher hydrogen contents lead to slightly lower raceway temperatures and the increasing dominance of favourable hydrogen combustion over volatile combustion. The additional injection of hydrogen into the shaft has also been modelled and is considered a valuable approach to solving some of the thermal problems arising from the endothermic reduction of iron oxides with H2, as the combustion of hydrogen is exothermic and provides energy to the process. However, some potential inefficiencies in reducing gas utilisation were identified. The influence of shaft injection on flow and burden behaviour in the numerical approaches also showed that higher injection rates allow deeper penetration into the shaft, but not to the same extent as an increased amount of coke. [47,48] From experimental work in which a model load was exposed to varying degrees of hydrogen-enriched auxiliary fuels, Qie et al. concluded that the onset of softening happens at lower temperatures with H2 addition, while the melting temperature goes up. [49] They also found that, compared with traditional BF operation, lower amounts of primary slag were produced, the size of the cohesive zone was reduced, and the reduction rate increased. The increased permeability is attributed to a reduced amount of melt in the cohesive zone. It was also found that hydrogen enrichment results in primary slag compositions close to the final slag composition. [50] The effect of gas injection on the amount of slag has already been observed with natural gas injection; less coal is used, so less ash needs to be added to the slag, which also reduces the amount of flux required. [51] The interaction between the coke and changes in the atmosphere must also be considered. At temperatures above 1100°C, the reaction rate of H2O with coke is significantly higher than that of CO2 with coke. Also, at lower temperatures, H2O is more likely to degrade the properties of the coke than CO2 due to diffusivity and subsequent reactions. [52] Therefore, measurements must be taken to maintain the properties of the coke suitable for the process, such as improving the coke binding process with additives to reduce the porosity. [53] An obvious and prominent obstacle to the use of hydrogen as an auxiliary fuel for the blast furnace is its availability and economic viability. Further and more in-depth information can be accessed through comprehensive and recent reviews focusing on the topic of hydrogen-assisted ironmaking in blast furnaces. [54,55]

Testing in different plants across the globe is ongoing and some examples are briefly described here. In February 2018, NEDO announced the successful testing of hydrogen as reducing agent in their test blast furnace, as a part of the Japanese COURSE50 program. Industrial trials are already underway and partially concluded. [56] In November 2019, thyssenkrupp Steel Europe started to use hydrogen via one of the tuyeres in blast furnace no. 9 in Duisburg Hamborn, Germany. [57] These trials were successfully completed in February 2021. In a next step, tests are planned to include all the 28 tuyeres of the furnace. In 2021, ArcelorMittal Asturias had finalized a project to inject coke oven gas into its blast furnace b located at the Gijon plant. [58] Coke-oven gas tends to have H2 contents above 50%. Following the successful tests at NEDO's experimental blast furnace, Nippon Steel Corporation plans to start injecting hydrogen-enriched auxiliary fuels into its no. 2 blast furnace at East Nippon Works Kimitsu Area, Japan, beginning in 2026. In this case, the hydrogen will be directly supplied from within the plant. [59]

* + 1. **Direct reduction processes**

The DR-EAF route is an alternative to the traditional BF-BOF route. Provided green hydrogen is used, this technology allows a significant cutback in emissions, as the DR process can use comparatively higher amounts of hydrogen than the BF – up to 100%. Additionally, the EAF can theoretically run on green electricity. The oldest direct reduction plant still in operation dates from 1971. Although most iron is produced as pig iron from blast furnaces, production through DR has been increasing over the last thirty years, demonstrating the viability of the technology. Most of the direct reduced iron (DRI) production is achieved using MIDREX plants, while the HYL/ENERGIRON and rotary kiln processes are also of industrial importance. The product of these processes is sponge iron which, owing to its high surface area, tends to re-oxidize and self-ignite, so it must be treated accordingly. The surface area is usually reduced by compressing the iron into hot briquetted iron (HBI) or cold briquetted iron (CBI).

The MIDREX process operates at a pressure of 1.5 bar and a gas injection temperature between 750 and 900 °C. The furnace is fed from the top with iron ore, which comes into contact with the reducing gas in countercurrent. The iron ore is first heated, converted from Fe2O3 to FeO, and then reduced to metallic iron (Fe) in the hot zone of the shaft furnace at around 800 °C. After the actual reduction process, the reduced iron is cooled with a mixture of natural gas and hydrogen, further increasing the carbon content to approximately 2.3%. Another important aspect of the process is the reformer used to generate the reducing gas. In the case of MIDREX, natural gas is converted to H2 and CO on a nickel surface at temperatures around 900 °C. The reduction gas, which is about 60% hydrogen, leaves the reformer at about 930 °C and is then heated to about 980 °C by adding oxygen and natural gas. This has a positive effect on the chemical balance of the shaft furnace. For higher efficiency, water is removed as a reaction product in a scrubber and the reducing gases are returned to the process.

The second well-consolidated shaft-based DR technology is known as HYL/ENERGIRON. While HYL I was a batch retort-based system, HYL III and ENERGIRON III are continuous shaft-based processes. The main differences to the MIDREX technology are the higher pressure in the reactor, between 6 and 8 bar, and the reduction temperatures above 1050 °C. The reforming process is also different, using additional steam. This results in a higher hydrogen content in the reducing gas, of about 80%. A further development of the process is HYL ZR, now ENERGIRON ZR – a zero reformer variant where the catalytic effect of the DRI in the lower shaft is used instead of an external reformer.

Another existing DR technology is the process based on a rotary kiln. The principle is that lumpy, pelletised, or agglomerated iron ores, mixed with lumpy or fine carbon carriers, are fed into a rotary kiln and generally heated in countercurrent with hot gases, being reduced in the process. The iron is discharged while still hot with a degree of reduction of up to 98%, and then cooled in a smaller rotary kiln unit. For improved process control, the kiln can be further upgraded, for example with mantle burners.

Although direct reduction plants are already operating with fairly high levels of hydrogen, there are still a number of challenges to overcome before large-scale industrial application can be achieved. The main obstacle, as with hydrogen injection into the blast furnace, is the supply gap for green hydrogen. If carbon sources are used to produce the hydrogen, the potential to minimise CO2 emissions is reduced. From a process point of view, reduction with 100% hydrogen results in a DRI product with no carbon content. This is disadvantageous for further processing in steelmaking, as will be discussed in more detail in section 2.3.2. [60] Similar to blast furnace enrichment, the energy balance of the system is affected by the endothermic hydrogen reduction reaction. To counterbalance this, additional energy sources must be added, such as excess hydrogen that can be combusted with oxygen, higher preheating temperatures of the injected gas, or the addition of natural gas, which may also assist in the carburisation of the DRI. Changes to the process caused by the reducing gas will generate a higher gas volume, which will in turn result in a higher gas velocity, pressure drop, and gas density. As these factors will affect the gas distribution in the reactor, they must be taken into account and studied properly. They should be considered in reactor design to ensure a good contact and mixing between the load and the reducing gas. In order to increase the contact between the gas and the solid, iron carriers with a higher surface area may be of interest to increase reduction efficiency. If used, the preheating equipment and its power requirements must be evaluated as they are correlated. [11]

Aluminosilicate materials are currently used to line the shaft furnaces. A trend towards higher alumina contents in these materials is reported, as those are more resistant to wear mechanisms such as gas erosion and abrasion, alkali attack and degradation, and spalling mechanisms due to thermal cycling. [61] HYL III reactors use aluminosilicates (fireclay bricks) in the reduction zone of the shaft as well as in other areas. Similarly composed materials are used in the inlet section of the reactor. [62] In that sense, aluminosilicate refractory linings for DR shaft processes might be used, where higher alumina contents might be needed in hydrogen-heavy processes. Mullite-based refractory linings might also be considered in rotary kiln DR processes to improve energy efficiency as opposed to low cement, high alumina castable lining concepts. Refractory selection will be discussed in more detail in section 2.2.

Industrial trials to increase the hydrogen content of direct reduction plants are currently in progress, with a large number of plants being commissioned and built. As early as the 1990s, Tenova HYL carried out tests with increased hydrogen contents of more than 90 vol.%. A well-advanced project to produce steel without the use of fossil fuels is the Swedish HYBRIT project. [63] It is a cooperation between the Swedish government and companies SSAB, LKAB, and Vattenfall. The project uses ENERGIRON's DRI technology. Interestingly, they have also delivered the first fossil-free steel to customers as a demonstration, and plan to deliver on an industrial scale in 2026. [64] Salzgitter Flachstahl's SALCOS project involves the construction of a DRI reactor based on the ENERGIRON technology as part of the existing integrated steelworks. [65] Hydrogen and natural gas will be used in flexible quantities and the energy required for hydrogen production will be supplied by wind power. Thyssenkrupp is also planning to add a DRI unit to its existing integrated steel mill in Duisburg. In order to achieve carbon neutrality by 2045, the first MIDREX flex DRI plant, built and supported by MIDREX Technologies and Paul Wurth, is planned to be commissioned in 2026. Tata Steel Netherlands is working with ENERGIRON to convert its steelmaking process from the blast furnaces currently in use. [66] ArcelorMittal is conducting trials in Contrecoeur, Quebec. [67] Here, 6.8% of natural gas was replaced by hydrogen over a 24-hour period in May 2022. A DRI plant based on the ENERGIRON ZR technology is planned for Dofasco. [68] ArcelorMittal's DRI plant in Hamburg, Germany, also focuses on decarbonization. [69] In addition to the existing MIDREX plant, a new demonstrator for 100% hydrogen reduction is planned for 2023. DRI plants are planned for the two integrated steel mills in Bremen and Eisenhüttenstadt, both in Germany. [70] Posco plans to expand its existing FINEX plant by developing a HyREX facility using only hydrogen for reduction in collaboration with Primetals Technologies. [71] A demonstration plant is to be built and evaluated by 2030. The focus is on using lower grades of ore directly in the reduction plant, thereby reducing the amount of conditioning that would otherwise be required. Voestalpine has successfully tested its DRI pilot plant at the Donawitz site in April 2021. The plant was built in cooperation with Primetals Technologies and is called HYFOR. [72] The advantage of this direct reduction process is that finer ores can be used directly, omitting pre-agglomeration and conditioning.

* + 1. **Novel ironmaking concepts**

There are also new ideas for producing iron, and later steel, with hydrogen. They presently have a low technology readiness level (TRL) but could gain space in the future. Currently under development are hydrogen plasma smelting reduction (HPSR), flash ironmaking technology (FIT), and iron electrolysis. What these projects have in common is that they aim not only to reduce CO2 emissions, but also to reform the ironmaking process in such a way that large parts of the traditional infrastructure coupled with integrated plants can be avoided, such as coke ovens and ore conditioning via sintering and pelletising. As the application of HPSR and FIT technologies will also lead to challenges for the lining concept, they are briefly presented here.

What is now known as HPSR was introduced as a research topic by Prof. Hiebler at the University of Leoben in the early 1990s. [73,74] The concept is to melt iron ores and then reduce the oxide melt to liquid iron using hydrogen plasma. The main advantage of hydrogen in the plasma state is its higher reduction potential – in terms of enthalpy, the reduction potential is three to fifteen times higher than that of molecular hydrogen, potentially reducing all other oxides. To achieve these conditions, high localized temperatures are required. [73,75] In the lab-scale reactor in Leoben, the plasma is introduced via an electric arc and the gas (hydrogen mixed with argon) flows through a hollow graphite cathode with the anode at the bottom. [76–78] This set-up is only able to reduce small charges of about 50 to 200 g. In a scale-up, a pilot plant has been built and investigated in the course of the SuSteel project, a collaboration between voestalpine, K1-MET, and the University of Leoben. The pilot reactor is located at the voestalpine plant in Donawitz, with a loading potential between about 50 and 80 kg. [79] Recent studies focus on the control of the arc to make the process safe and stable. [80,81] The harsh conditions in the reactor will also affect the refractory lining. When investigating slag formation, Masab et al. found that parts of the sodium silicate-bonded refractory melted, leading to a lower slag basicity. In addition, the introduction of MgO from the lining altered the originally favourable slag composition, resulting in solid constituents at 1550 °C. It was therefore recommended that the lining be changed and high alumina and spinel-based systems be introduced. [76] Optical emission spectroscopy also showed that MgO in the lining was attacked by the arc. Damage to the refractory lining around the steel crucible was also found during an investigation of optimal charging rates. [77]

FIT is another approach to modify the ironmaking process. It was introduced in 2012 as a research project by Prof. Sohn at the University of Utah, with partners including the American Iron and Steel Institute (AISI). [78] The concept is already established for copper and nickel production, and the aim is to adapt the process for ironmaking. Iron carriers and fluxes are charged via a top feed, and a gaseous fuel is introduced and partially fired to achieve the required temperature between 1200 and 1600 °C for the reduction of iron oxide. The process is designed to work with either or both NG and H2. The idea is to enable a direct steelmaking process, so that after in-flight reduction the burden can be separated via density, and the slag and melt can be further processed. Unreacted gas would be removed, cleaned, and reused. The advantages of this technology over the conventional DR process are the use of fine ores, which means less conditioning of iron carriers, and the ability to run at higher temperatures, as melting and sticking are not expected (contrary to the case of conventional shafts). [82] Kinetics is a rather important factor for flash reactors and studies have been carried out on magnetite ore to predict feasibility. Natural gas and magnetite are in focus due to their availability in the United States, where the technology is being developed. Following successful trials with model natural gas and hydrogen in a laboratory test reactor, a pilot facility has been designed for large-scale testing. The lining of this reactor consists of a high alumina castable as the working lining, an insulating layer of lightweight crystalline silica, and finally an aluminosilicate fibre blanket. [83] The effects of flash ironmaking conditions on alumina-based refractories have also been investigated on 99.5% alumina samples. The formation of a hercynite layer was observed, and it was concluded that alumina is a suitable refractory material. [84] The pilot reactor was used to collect process parameters for an industrial scale-up, such as complete reduction of magnetite ore at 1350 °C and the required amount of hydrogen above equilibrium. [83]

* 1. **The effect of hydrogen on refractory materials**

As described above, the use of hydrogen in steelmaking poses several technological challenges. Among them, it is important to consider how it will affect the refractory lining in metallurgical vessels. Hydrogen has long been known to corrode and degrade metals, especially due to its high diffusion and permeation rates. Hydrogen embrittlement or hydrogen stress cracking is a cause of concern for metallurgists, having produced the failure of anchor rods in the San Francisco-Oakland Bay Bridge in 2013. [85–87] Another known type of steel corrosion is hydrogen-induced pitting. [87,88]

On the other hand, the effect of hydrogen on ceramics is not so well established. Considering thermodynamics, hydrogen can reduce ceramic oxides under certain conditions. Compounds that are used for refractory applications – such as silica, alumina, calcia, magnesia, and zirconia – will be reduced to form volatile products, which means hydrogen will gradually consume those materials. However, reduction is expected to occur to an appreciable extent only at very high temperatures. [89,90] Misra estimated the stability of different ceramics and proposed a maximum application temperature under hydrogen atmospheres, the upper temperature limit corresponding to a partial pressure of reduction products of 10-6 atm at equilibrium (or 1 ppm). [89] Based on this definition, the corresponding limits for ceramics that are relevant to the refractory industry were estimated using FactSage 8.1 and the FactPS database (Figure 3). It is known, however, that the range of stability can be stretched to higher temperatures if even a small amount of water is present in the atmosphere, [78,80–82] or the material is deployed in a high-pressure environment. [89,91]

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*Figure 3 – Upper temperature limit for the application of different ceramic materials in an atmosphere of 100% hydrogen at a pressure of 1 atm.*

Besides thermochemical considerations, it is also important to understand the process from a kinetic perspective. Different studies aim to elucidate the mechanism of ceramics corrosion by hydrogen and to describe the underlying kinetics. However, considering the inherent complexity of solid-gas reactions, the results are often inconsistent, and many unknowns persist. Solid-gas reactions are intricate, involving the interplay of many different phenomena – for example, mass transport from the bulk gas, pore diffusion, adsorption and desorption, and the chemical reaction itself (Figure 4). Besides, as the reaction progresses the structure of the solid changes continuously, establishing transient, complex conditions. The solid may, for example, undergo weight loss, chemical changes, sintering, and modification of the pore structure. [94]

This section of the review presents what is currently known regarding the interaction of hydrogen with refractories. The studies mentioned span over a century of research – even though hydrogen-based DR is a novel technology, this question is of import for different industrial applications, including the reformer and gasifier reactors in petrochemical processing, DR based on natural gas, nuclear reactors and propulsion systems, aircraft engines, fuel cells, and heterogeneous catalysis. Each subsection deals with an important refractory ceramic oxide or group of oxides, and studies are shown that examine from pure ceramics to commercial refractory products.

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f)

g)

*Figure 4 – Mechanism of a non-catalytic solid-gas reaction with products in the gas phase: a) mass transport of the reactant from the bulk gas to the surface of the solid; b) diffusion of the reactant through the solid pores; c) adsorption of the reactant; d) chemical reaction; e) desorption of reaction products; f) diffusion of products through the solid pores; g) mass transport of reaction products from the surface of the solid to the bulk gas.*

* + 1. **Silica**

Silica is the most common compound in the Earth’s crust and has found numerous applications as a

non-basic refractory material, whether in crystalline form (tridymite, cristobalite, or quartz) derived mainly from the firing of quartzite, or as an amorphous/vitreous material. [95,96] However, silica has been shown to be susceptible to corrosion by hydrogen, with palpable technological implications. In the hydrogen-bearing atmosphere of reformer vessels, SiO2 may volatilize in the form of SiO, conducing to premature wear of the refractory lining. The silicon monoxide is entrained with the process gas, and later solidifies upon cooling. Silica deposits thus formed have been reported to cause clogging issues, fouling of heat exchangers, decrease in the heat recovery efficiency of boilers, and product contamination. [97,98] Corrosion of silicates by hydrogen also leads to wear in coal gasification processes. [99,100] Hydrogen can also affect the stability of SiO2 scales which protect SiC ceramics in aircraft turbine engines against further oxidation. [101–103]

Thermodynamic calculations indicate two main products of silica reduction by H2. At low temperatures, silane (SiH4) is the main product – however, in the temperature range where silane predominates, the extent of reaction is extremely low (Figure 5). At high temperatures (above 900 °C), silicon monoxide is the primary product of reduction (Equation 3). [89] The thermodynamics of the reaction was experimentally investigated by Grube and Speidel, who observed the formation of a black condensate and determined it to consist of SiO. [104] Tombs and Welch likewise reported a heterogeneous deposit to have the net composition of silicon monoxide, and next to it they analyzed changes in the atmosphere of the experiment via thermal conductivity measurements. [105] Other possible reaction products have been mentioned, such as metallic Si, the gaseous suboxides Si2O2 and Si2O3, and SiH. [106–108] However, the amount of those products, if formed, would be negligible. For instance, Chen calculates the partial pressure of Si2O3 to be four to six orders of magnitude lower than that of SiO. [106] Importantly, most references on silica reduction cited on this review are exclusively concerned with the formation of silicon monoxide.

*Equation 3*

A graph of temperature and temperature

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*Figure 5 – Simulation results of the partial pressure of products of silica reduction as a function of temperature at a pressure of 1 atm (calculated using FactSage 8.1 and the FactPS database).*

Among all the oxides surveyed in the review, silica is the material for which the most extensive reduction kinetics studies have been made. Different authors draw Arrhenius plots and thereby calculate the activation energy for the reduction of silica glass. Their estimates are in close agreement, as shown in Table 2. There have also been numerous attempts to identify the rate-controlling mechanism in the hydrogen reduction of silica. Schwerdtfeger analyzed the rate of reduction of silica glass and determined convective diffusion to be the main controlling mechanism. However, there were some discrepancies in the data fit, which could be accounted for by a mixed control regime. [109] Likewise, Chen pointed out that the reduction of silica glass is controlled by diffusion through the boundary layer. [106] On the other hand, Gardner reached a different conclusion: the adjustment of thermogravimetry data to a kinetic model pointed to rate control by the reaction at the moving interface in silica glass. This result was corroborated by the observation that the reaction rate was independent of hydrogen flow. [110] Similarly, Shirai et al. observed that changing the H2 flow rate or the tube diameter did not alter the reduction rate of fused silica, and inferred that kinetics is controlled by the reaction. [111] Nevertheless, other studies show that the controlling mechanism in force depends on the full experimental conditions. Tso and Pask plotted the reaction rate of quartz glass as a function of the hydrogen flow, and observed that a linear relationship existed initially, but there was a critical point above which the reaction rate leveled off as the hydrogen flow continued to increase. [99] This suggests a switch in the rate-controlling step from mass transport through the boundary layer to the kinetics of the surface reaction. Han and Sohn, in turn, found that the mechanism is conditional on the temperature: at low temperatures, the reaction is slow-moving, and the reduction rate is controlled by the reaction kinetics; at elevated temperatures, the rate of reduction is constrained by mass transport through the boundary layer. [112]

|  |  |  |
| --- | --- | --- |
| Source | Temperature range | Activation energy (kcal/mol) |
| Gardner et al [110] | 1115 – 1630 °C | 85 |
| Tso and Pask [99] | 1200 – 1400 °C | 82 |
| Shirai et al [111] | 700 – 1200 °C | 85 |

*Table 2 – Estimation of the activation energy for the reduction of silica by hydrogen.*

Gardner et al. investigated the effect of sample shape on reaction kinetics by comparing fused quartz powder, a tube, and a rod. As expected, the powder is reduced more rapidly. Nonetheless, the effect of surface area is not very pronounced – there was no difference in reduction rate between the tube and the rod. [110] Chen also observed identical corrosion flows for a spherical and a quasi-plane sample. [106] Different studies show that the presence of steam decreases the rate of reduction of silica by hydrogen. [106,110,113] Gardner attributed this to the adsorption of -OH groups in the surface of silica glass, taking up sites that could otherwise be used for the adsorption of H2. [110] However, it can also be explained in terms of chemical equilibrium: since water is a reduction product (Equation 3), adding it to the system makes reduction less favorable. Schwerdtfeger also investigated the effect of dilution: the more diluted the hydrogen, the slower the reduction of silica. It was also determined that the diffusion media bears an effect, as dilution with argon decreased the reduction rate to a larger extent than with helium. This is probably linked to the difference in diffusivity between the two gases. [109]

In addition to volatilization, other effects of hydrogen exposure on silica have been observed. Tso and Pask noted a phase change induced by hydrogen: silica glass devitrified in temperatures from 1200 to 1400 °C, forming cristobalite. A baseline test with air did not produce the same devitrification effect. It was then observed that the phenomenon was related to impurities present in the alumina tube in the experimental set-up: Na2O and K2O were reduced to form sodium and potassium vapor, which deposited on the surface of silica to form sodium silicate glass. The glass was deemed responsible for prompting the formation of crystal nuclei. [99] Other studies observed an accelerating effect of hydrogen on the devitrification of SiO2 crucibles. In a H2-H2O atmosphere, the transformation increased with the proportion of H2. The effect was pointed out to be associated with surface modifications – a thin SiO film could form and later introduce crystallization nuclei as it decomposes. [114] On the other hand, Schwerdtfeger observed no devitrification of silica glass under hydrogen at 1500 °C. The phase transformation was only observed on trials with a CO-CO2 atmosphere, but those went on for a much longer time than the tests performed with H2. [109]

As for microstructural changes induced by hydrogen exposure, Gardner draws attention to the dome shape displayed by fused quartz grains, which is suggestive of reduction taking place preferentially at the grain boundaries. [110] Tso and Pask, in turn, observed the formation of deep holes in silica glass after hydrogen exposure. This phenomenon was attributed to the existence of a temperature gradient in silica. As the bulk of the sample is hotter than the surface, small holes that are initially formed tend to grow progressively deeper with exposure. [99] Pit-hole formation was also observed by Chen, who proposed that it could be linked to the catalytic effect of impurities. [106]

Ewles and Youell heated silica in hydrogen at 750 °C for 2 h and this led to an oxygen deficit of 0.05%, which remained after the sample was stored for six months. The H2 treatment also rendered silica luminescent. [115] Another possible outcome of the exposure of silica to hydrogen is the formation of hydroxyl [116–121] and hydride groups. [117,121,122] Formation of hydroxyl has been demonstrated at a wide temperature range, from 200 to 1500 °C. Lou showed that the diffusivity of hydrogen in silica initially increases with temperature, but unexpectedly decreases after 1000 °C due to the heightened reactivity of hydrogen with silica glass to form hydroxyl and hydride groups. [121] The development of the -OH groups depends on the existing defect structure and may lead to a decrease in the density of vitreous silica. [119,123]

Where atomic hydrogen is present, McTaggart found that dissociated hydrogen from a microwave discharge can easily reduce silica at temperatures of 815 and 900 °C, causing deep etching. [124]

In addition to the studies on pure silica, investigations have been made on refractory products. An early study showed that, at a low temperature range of 650 to 700 °C, a silica brick with lime bond changed color: it first formed green spots, and with continued exposure it became grey. [125] Grant and Williamson made interesting observations on how the phase composition of silica bricks changes with exposure to hydrogen. In a first study, the bricks (made from quartzite and silcrete) are heated in H2 for 4 h at 1200 °C, and this results in embrittlement and a substantial decrease in strength. The embrittlement effect could also be observed in the milder conditions of 1 h exposure at 1000 °C, and it was attributed to the crystallization of calcium silicate in the matrix. In a later study by the same authors, silica bricks (from different suppliers and manufactured with different raw materials, including quartzite, flint, and pebble quartz) were subjected to hydrogen atmospheres, and again became embrittled. In this case, however, reheating trials allowed to rule out the devitrification of calcium silicates as the cause behind the weakening of the material. An alternative explanation was then proposed: the bricks disintegrate because of the formation of a well-crystallized cristobalite phase, mainly from quartz and tridymite. A quartzite brick, for example, had 60% of the quartz phase converted to cristobalite after 12 h on hydrogen at 1400 °C, while the phase composition remained essentially unchanged when air was made to flow instead of hydrogen. [126,127] The authors also compare hydrogen and carbon monoxide, and observe that the attack by the former is more severe – in line with the observations for pure silica from Schwerdtfeger. [109]

Crowley demonstrates very clearly the susceptibility of silica bricks to hydrogen corrosion: after 50 h in a 100% H2 atmosphere at 1400 °C, a 95% silica brick lost over 70% of its mass. Moreover, when investigating a series of ten commercial bricks with different SiO2 contents (from the just mentioned 95% silica brick to a 90% alumina brick containing silica in the mullite phase), the weight loss was seen to increase with the silica content. It was deduced from the experiments that SiO2 starts volatilizing between 870 and 970 °C. Interestingly, it was observed that the reduction slowed down substantially when water vapor was introduced in the inlet stream, or when high pressure conditions were imposed. [128,129]

While it would be unthinkable today to use a silica brick in a high-temperature metallurgical process where hydrogen is a component in the atmosphere, silica-containing refractories in the spectrum of the alumina-silica system, such as mullite and fireclay, can be regarded as potential candidates, especially for areas under low or medium stress. They will be reviewed in sections 2.2.3 and 2.2.4.

* + 1. **Alumina**

Alumina is widely used in refractory applications, and in addition to its high refractoriness and outstanding mechanical properties, [130] it is exceptionally stable in hydrogen atmospheres. Li et al. calculated a minuscule equilibrium Al partial pressure of 9.3 x 10-22 Pa at 1200 °C, and even at 1800 °C, it is still of just 2 x 10-12 Pa. [90] Misra predicted two main chemical reactions for the reduction of aluminum oxide, forming either gaseous Al or Al2O (Figure 6). [89] It is shown, however, that Al is the main product (Equation 4), having an equilibrium partial pressure that is one order of magnitude higher than that of Al2O across a wide range of temperatures. This is in good agreement with the mass spectroscopy results obtained by Dooley et al. After striking an alumina specimen with atomic hydrogen, the authors detected only Al and H2O. Other species, such as AlO, AlH, AlOH, Al2O, and Al2OH, were not found. [131]

*Equation 4*

A graph of different colored lines

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*Figure 6 – Simulation results of the partial pressure of alumina reduction products as a function of temperature at a pressure of 1 atm (calculated using FactSage 8.1 and the FactPS database).*

In addition to its high stability in reducing atmospheres, Al2O3 has been proved to have a very low permeability by hydrogen even at temperatures above 1400 °C. In fact, alumina is regarded as an excellent material for use as a Hydrogen Permeation Barrier (HPB) in high-temperature applications, such as the prevention of tritium leakage on nuclear power plants. [132–136]

Various studies illustrate the stability of alumina in hydrogen. Lang exposed dense fired alumina to H2 flow at 260 and 538 °C and pressures of 2.58, 5.17, and 6.89 MPa, and after 144 h of exposure no changes in mechanical properties or the microstructure were detected. [137] Li et al. found a commercial brown corundum powder to be stable in hydrogen atmospheres at temperatures up to 1800 °C. Only the impurities were reduced after 8 h, leading to a decrease in the total mass and to an increase in the purity of alumina. Whilst the Fe2O3, SiO2, and MgO impurities volatilized, TiO2 formed solid suboxides, including Ti2O3, which was shown to have high stability in a hydrogen atmosphere. CaO formed a very stable hibonite phase (CaAl12O19), as demonstrated by XRD. [90] In another report, aluminum oxide rods were exposed to hydrogen flow for 2 h at temperatures up to 2000 °C, and it was only at 1900 °C that volatilization was detected. Even then, however, it could not be clearly attributed to Al2O3 reduction. Na2O, SiO2, and MgO started to volatilize earlier at 1100, 1500, and 1700 °C respectively. [138] The reduction of impurities in alumina was also reported by Ahmad. A tube with an alumina content of 99.7% was exposed to flowing hydrogen at 1320 °C, and the Na2O impurity (with an initial content of 0.2%) was reduced to metallic sodium vapor, which then cooled down and formed a white whisker deposit on the inside of the tube. [139]

Other investigations demonstrate that alumina can be reduced by hydrogen when samples are heated at sufficiently high temperatures or for long enough periods of time. Gulbransen and Andrew exposed alumina powder to dry hydrogen at 2000 °C for 30 minutes, resulting in a weight loss of 12%. The extent of reduction, however, diminished substantially when a small amount of water was introduced in the atmosphere, or when vacuum conditions were established. [113] Readey and Kuczynski heated single-crystal alumina spheres in hydrogen at temperatures from 1500 to 1900 °C for 10 h, and under those conditions alumina sublimated as a result of reacting with hydrogen. The radius of the spheres was seen to decrease with time. Kinetic data is presented for temperatures from 1750 to 1850 °C, and an analysis of the data plot suggests that the sublimation rate is controlled by gas diffusion of the reaction products, rather than by the reduction reaction. Additionally, surface etching was observed, and the spheres morphed into polygons having facets covered with fine steps. [140] Braaten et al. exposed alumina to hydrogen flow for 24 h at temperatures up to 1700 °C and observed that the sample color changed from white to grey, and at the highest temperatures dark spots were formed. Those areas showed the appearance of molten material when observed in the SEM and a strong Al signal was detected by EDS analysis, indicating that the spots consist of metallic aluminum. [141] The high-temperature reactivity of alumina with hydrogen has also been demonstrated by the synthesis of alumina whiskers via vapor deposition. Hydrogen reduced an aluminum oxide rod and the products of reduction volatilized, which was followed by deposition on cooler sections of the furnace to form the alumina whiskers. It is stated that evaporation temperatures were of up to 2000 °C, but the authors do not specify the temperature at which the reduction starts to occur. The alumina whiskers then grow in the temperature range of 1600 – 1700 °C inside the furnace. [142] It is also noted that the presence of water vapor in the hydrogen flow largely inhibits this process, as can be expected from thermodynamics. [143]

At a lower temperature than those just cited, Herbell et al exposed commercial sintered alumina to hydrogen saturated with water at 1400 °C for 100 h and observed that microstructural changes arose with the formation of what the authors call “rosettes”. It was pointed out that these structures can be attributed to phase changes in the material, but the transformations were not specified. Moreover, a decrease in flexural strength of 20% was reported, [144] notwithstanding the thermodynamic calculations which show alumina to be stable in wet hydrogen atmospheres at this temperature. However, Ignatova et al. observed the opposite effect on the mechanical properties. Exposure of granular corundum to an atmosphere of 75% H2 and 25% N2 at 1700 °C for 50 h led to a 36% increase in compressive strength, which was attributed to the sintering of the material and accompanied by a decrease in apparent density, a reduction in gas permeability, and an enlargement of the pores. Those effects were also observed, but to a lesser extent, after hydrogen treatment at 1500 °C. [145]

It has also been reported that low-temperature reduction of alumina could happen to a minor extent at the surface level. Weller and Montagna carried out experiments where hydrogen flowed over η-alumina and γ-alumina samples for two days, and at the highest temperatures investigated of 450 and 550 °C, hydrogen consumption was verified to occur at a constant rate for the entire period. [146] The authors propose that the uptake could either be described as chemisorption, corresponding to a surface coverage of less than 1% in the two days, or surface reduction, which would be consistent with the formation of nonstoichiometric alumina (with formula Al2O2.998). In a later report, Tang et al. performed a TPR (Temperature Programmed Reduction) analysis on pure alumina samples and discerned a hydrogen uptake peak around 800 °C, but could rule out the possibility that it corresponds to hydrogen adsorption. The conclusion was that the peak can be attributed to the reduction of coordinatively unsaturated Al cations found on the alumina surface. [147] In other TPR analyses of pure alumina supports, Ranga et al. heated the sample up to 900 °C, [148] and Li et al. [149] and Dimas-Rivera [150] up to 1000 °C, and in none of these studies was a reduction peak observed. On the other hand, Ratkovic et al. found a peak in hydrogen uptake by the alumina substrate at 760 °C, which is consistent with Tang’s observation. [151] However, there is no evidence so far that surface reduction and the ensuing formation of oxygen vacancies in alumina could be consequential in refractory applications.

Studies with atomic hydrogen [141] and hydrogen plasma [152–155] have also been carried out. When a beam of atomic hydrogen produced by effusion from a hot dissociation oven was directed towards an alumina target, no reaction products were detected until 1300 °C. At higher temperatures, a mass spectrometer revealed the presence of Al and H2O. [141] Braaten et al. heated a mix of alumina powder and fine-grained aluminum at 1200 °C, and observed a significant mass loss of the oxide. The authors concluded that reduction was enabled by the dissociation of the hydrogen molecule in the molten aluminum. [141] Those investigations show that atomic hydrogen can reduce alumina from temperatures of 1200 – 1300 °C. Rains and Kadlec investigate the reduction of Al2O3 to Al by an induction coupled plasma consisting of mixes of argon with hydrogen, carbon monoxide, and methane at powers corresponding to argon temperatures between 10,900 and 11,200 K. [152] The conversion under reducing atmospheres happens via reduction of Al2O3 to Al2O, followed by the decomposition of Al2O. While CO and CH4 additions double the conversion from alumina to aluminum, hydrogen only promotes a very small increase in the conversion rate compared to just argon, the total conversion being just slightly above 10%. Employing a different method for introducing the alumina, Lyubochko et al. accomplish reduction of Al2O3 to Al in a nonequilibrium hydrogen plasma at relatively low temperatures of approximately 3,000 K, attaining a conversion rate of 50-60%. [153]

In studies with corundum refractories, some weight loss is noted, but it is unclear whether the alumina component is at all affected. The weight loss percentages are extremely low and consistent with the lack of reaction for the aluminum oxide – it is likely that only the impurities or other components of the refractory are volatilized. Even with the harsh exposure conditions of 100% H2 atmosphere for 192 h at 1500 °C, a lightweight refractory brick made up of 99% alumina lost less than 1% of its weight. [91] It has been repeatedly demonstrated that in alumina-silica refractories the resistance to corrosion by hydrogen increases with the Al2O3 content. [82,116, 140,141] Besides the minor weight loss, alumina or high-alumina bricks have been reported to change color (Figure 7), in a similar fashion to silica as described above. [157,158] However, the color change was ascribed to the reduction of impurities, especially Fe2O3 and P2O5 producing Fe and P respectively, which alloyed in metal droplets. [157] Nevertheless, oxygen vacancies could also be the reason behind the color change. Additionally, Yakovlev reported the formation of regions with characteristic metallic shine and the aspect of fused material on the surface of corundum bricks kept in a hydrogen atmosphere at 1850 °C and 500 Pa. The authors suggested that the molten material could be eutectic compounds that alumina would form with impurities in the presence of hydrogen. In that case, the Al2O3-CaO eutectic has a melting point of approximately 1400 °C, and Al2O3-SiO2 of around 1595 °C. [159] An XRD analysis showed a phase transformation from β-Al2O3 to α-Al2O3, which was attributed to the volatilization of the Na2O originally present in the lattice. This led to the formation of small cracks. Furthermore, the compressive strength doubled for the two alumina bricks that were investigated. [158]

Several rectangular bricks with writing on them

Description automatically generated

*Figure 7 – Color change in a high-alumina brick: a) as original; b) after exposure to hydrogen for 200 h at 1000 °C.*

Alumina also has excellent performance in the combined presence of hydrogen and CO. In trials designed to simulate DR with a feed gas mix of hydrogen and natural gas, Bertrand et al. heated up two corundum bricks containing 95 and 99% alumina. An almost linear decrease in weight was observed in the first 240 h, but it corresponds to less than 0.1% weight loss. The authors extrapolated this to a weight loss of 1.3 and 1.9 kg respectively in 10,000 h, but more experiments would be needed to predict refractory behavior after such long exposure times. A decrease in Young’s Modulus of about 15% was measured for the bricks after 240 h, but it is unclear whether this is due to hydrogen or carbon monoxide, and whether alumina is at all involved. [160] Another study inspired by DRI examines a mix of hydrogen and natural gas, and the high-alumina refractories had the lowest weight loss. It was also noted that bricks outperformed castables for a similar alumina content. [161]

Owing to the resistance of alumina to hydrogen, high-alumina refractories are used to line the hot face of gasifiers with gas or liquid feedstock. [162–164] Coal gasification units vary widely in their operation parameters, but high-alumina refractories will usually find atmospheres of 50% H2, also containing H2O, CO, CO2, CH4, and other gases, temperatures of 800 – 1100 °C, and pressures from ambient to 100 atm. Crowley states that phosphate-bonded high alumina refractories are suitable for this application. [163] Additionally, high alumina refractories are used to line reformer vessels, including secondary reformers in ammonia plants containing gas mixtures with up to 60% hydrogen and with a typical operating temperature of 1350 °C and pressure of 35 bar. Chakraborty highlights that for such an exacting application it is important to use very pure synthetic aluminum oxide, such as white fused alumina (WFA) or white tabular alumina (WTA). [165] In this case, Al2O3 generally shows stability at temperatures even higher than those encountered at the gasifier, but it could be that reduction is precluded by the presence of water and the extremely high pressures. Nonetheless, Crowley reported that deposits have been found on the waste heat boiler in an ammonia plant comprising calcium aluminates and alumina (with additionally some silica, sodium phosphate, and sodium chloride). [129]

**2.2.3 Mullite**

With an approximate composition of 3Al2O3·2SiO2, mullite has remarkable thermal stability, mechanical strength, and corrosion resistance. [166] It also displays resistance to hydrogen atmospheres at moderately high temperatures. The stability of mullite in hydrogen depends on the reactivity of its two constituent oxides, silica and alumina. Inasmuch as SiO2 is considerably more reactive than Al2O3, it is the stability of silica that is determinant. It is, however, important to take its activity into account. If mullite is in equilibrium with silica, the activity of SiO2 is unity, and the silica in mullite will behave in a similar way to pure silica. On the other hand, if mullite is in equilibrium with Al2O3, the activity of silica in mullite is lower than unity, hence it is more stable. A comparative thermodynamic simulation showed that SiO2 in a brick comprised of 96.3% alumina and 3.7% mullite is more stable than in pure stoichiometric mullite, and SiO2 present as a minor impurity in high purity alumina is even more stable. [92]

Herbell et al. put forth a mechanism for the corrosion of mullite by hydrogen gas. The mechanism is illustrated in Figure 8. First, the glassy phase in the grain boundaries is attacked, and in sequence the mullite grains are corroded via the removal of silica from the mullite structure. This leaves behind a porous residual α-alumina phase. Correspondingly, a substantial increase in porosity is observed, accompanied by a decrease in density. [167] The formation of secondary alumina arising from the exposure of pure mullite to hydrogen was also seen to occur in other studies. [99,106]

Chen studied the reaction of synthetic mullite spheres with hydrogen at 1400 – 1500 °C and concluded that it consists of a mixed control process, governed by the reaction kinetics but also the transport of gas products through the porous alumina layer and then through a gaseous film. [106] On the other hand, Tso and Pask observed that the high porosity of the alumina strip allows hydrogen to easily land at the reaction interface, and reaction products to diffuse away from it – which controverts the previous finding by Chen that diffusion through the porous layer is rate-limiting. The activation energy for the reduction of mullite by hydrogen was calculated to be of 93 kcal/mol. This value is higher than the estimates for silica shown in Table 2, which means that it is more difficult to volatilize silica in pure mullite than in a pure silica sample. [99]

In a study where mullite was exposed to hydrogen at 1050 and 1250 °C for an extended duration of 500 h, a significant loss of strength was verified to occur. At 1050 °C, the Modulus of Rupture (MOR) had a 22% decrease after 500 h, which was attributed to the recrystallization of the glass boundary phase to form beidellite. This phase transformation depends on the presence of Ca, and did not take place when the mullite sample was free of calcium impurities. At 1250 °C, the effect of hydrogen on the strength is more pronounced. The decrease in the MOR was of 53%, which can be ascribed to the corrosion of the mullite grains and mainly the glassy phase. Those observations underscore the recommendation that mullite should present a low content of glassy phase and Ca impurities in the case of utilization under hydrogen atmospheres. [167]

A decrease in the MOR was also observed by Lang even though the set of conditions was different, with temperatures of 260 and 538 °C and pressures of 2.58, 5.17 and 6.89 MPa. The MOR decreased for all temperature and pressure combinations to an extent of 10 to 25%. As no bulk reaction can furnish an explanation for the observed degradation of strength, the author proposes it could be related to a surface process. Nevertheless, the cause remains unclear. An examination of the microstructure revealed that the mullite needles became sharper, indicating that surface etching took place. [137]

Several different types of alginate

Description automatically generated

*Figure 8 – Mechanism of corrosion of mullite by hydrogen: a) initially, mullite grains and a glass phase are present; b) the glass phase is removed; c) corrosion of mullite grains starts, leading to the formation of secondary alumina; d) mullite may be completely converted to secondary alumina with the removal of silica by hydrogen.*

When it comes to mullite refractories, Crowley also tested a mullite brick, as well as bricks containing different proportions of mullite and cristobalite, on hydrogen atmospheres. In line with the aforementioned observations for pure oxides, free silica was more easily removed than silica present in mullite or an aluminosilicate structure. A surprising observation was that the mullite-containing bricks turned bright blue after exposure to 75 or 50% H2 in N2 in the temperature range from 1100 to 1400 °C. XRD revealed no new phases that could account for this effect, and the authors believe it to be linked to modifications in the structure of mullite or in the oxidation state of Ti or Fe impurities. It was verified that refractories with mullite or aluminosilicate bonding were more severely attacked in an atmosphere with 75% H2 than in a 100% H2 atmosphere. However, no explanation was provided for this phenomenon. [129] Ignatova et al. observed extensive changes on the microstructure of dense corundum-mullite after exposure to 99.1% pure hydrogen at 1500 °C for 50 h. The reduction of silica led to the formation of SiO, and the authors claim that a part of it volatilized, and the other part constituted a new phase in the material. The presence of SiO, however, is not demonstrated in the publication, and this result is at odds with other studies which indicate that the silicon monoxide formed in reduction reactions will completely volatilize. With the removal of silica from the mullite, new corundum crystals were formed with prismatic shape and dimensions of 0.01 – 0.04 mm, and a glassy phase was observed to separate. The volatilization of SiO also produced an increase in porosity. [145] Yakovlev et al. exposed a mullite refractory to hydrogen for 45 h at 1500 °C. The authors observed a color change from light rose to grey, a slight mass reduction of 0.54%, and a decrease in compressive strength of 20%. The initially present α-cristobalite line disappeared, and silica was also removed from the mullite structure, leading to the formation of corundum crystals which the authors assumed to have a principal direction of growth. In the same study, a mullite-corundum refractory was exposed to hydrogen at 1450 °C, and only a color change (from light yellow to grey) was observed. At 1600 °C, besides the color change, the mullite-corundum brick lost 4.18% of its mass and exhibited fine cracks and a linear shrinkage of 1.27%. [158] Primachenko et al. subjected fused mullite to thermal cycling under hydrogen, each cycle being 10 hours long, and reaching a maximum temperature of 1500 °C. In the first cycle the open porosity underwent a sharp decrease from 4.2 to 1.5%, and with further cycling it presented an upward trend, attaining the value of 5.8% after 12 sets. A glass-like phase was seen to form on the surface of the mullite grains, which is consistent with the observations of Ignatova et al. The effect of grain size was demonstrated to be relevant: grains in the 3 – 0.5 mm fraction exhibited no change in chemistry, whereas for the fraction finer than 0.5 mm a decrease in the proportion of silica was verified. [145] In another study, a refractory compound containing 96.31% alumina and 3.69% mullite was exposed to 5% H2 in N2 at 1000 °C, and it lost less than 0.2% of its mass after 100 h. However, a downward trend was still visible when the trial was wound up, suggesting slow but continued weight loss. On the other hand, when 2.3% water was present in the H2-N2 atmosphere, the sample gained approximately 0.15% weight in the first few hours, and then the mass remained constant over the 250 h of duration of the trials. [92] In a more recent study, mullite-based castables were seen to lose weight and have an increase in porosity at 1500 and 1600 °C. [168]

Changes on a mullite brick similar to those that happened in pure specimens were observed by Wright and Wolff at temperatures above 1250 °C. Free silica volatilized, followed by combined silica and resulting in the formation of a porous corundum phase. Additionally, secondary mullite was seen to form via the recombination of corundum with local silica deposits. However, in this study, the refractories were submitted to the more complex atmosphere of a regenerator furnace for the pyrolysis of natural gas, and it is not possible to confirm that the described reactions can be attributed to hydrogen. It is important to note that extensive carbon deposition in the lining was observed in the trials. [169] Bertrand et al. observed a decrease in the Young’s Modulus of a mullite and a fused mullite brick of 10 and 14% respectively under hydrogen exposure conditions that sought to simulate DRI. The bricks were submitted to four thermal cycles going up to 630 °C and adding up to 240 h at a 75% H2 – 25% CO atmosphere and 2 bar absolute pressure. [170]

Mullite-fireclay bricks are presently used in DRI shaft kilns operating on natural gas, sometimes with a phosphate bond. They can be found on the gas inlet area as well as the lower part of the shaft kiln, and in pressurized vessels they are used from top to bottom. In addition, mullite-corundum bricks are deployed in the lining of the bustle port, which distributes the reducing gas to the shaft. Firing temperatures above 1700 °C might confer the bricks with higher corrosion and abrasion resistance. [171] It remains to be determined, however, whether mullite will also be suitable for DRI when the inlet gas is enriched in H2. The studies mentioned point to complex changes that may arise in mullite as a result of hydrogen exposure.

**2.2.4 Other materials in the alumina-silica system**

Following the discussion on the effect of hydrogen on mullite, this section will enumerate studies that deal with other materials in the alumina-silica system. Tso and Pask investigated two different aluminosilicate glasses, identified as L (70% SiO2 and 30% Al2O3) and S (57% SiO2, 38% Al2O3, and 5% CaO). Upon hydrogen exposure, the silica present in the glass was reduced to form volatile SiO, while the alumina was left unreacted. The reduction of silica in the aluminosilicate glass structure, however, happened at a lower rate than the reduction of silica glass. The authors postulate the following explanation: at high temperatures, the Al atom constitutes a Lewis acid site, which has strong affinity for the hydroxyl groups and water and will therefore hinder the desorption step, thereby stabilizing silica. In the study, it is also noted that the reaction with hydrogen led to the formation of two porous layers. The outer layer consisted of α-alumina, and the inner layer displayed a composition similar to that of mullite. [128]

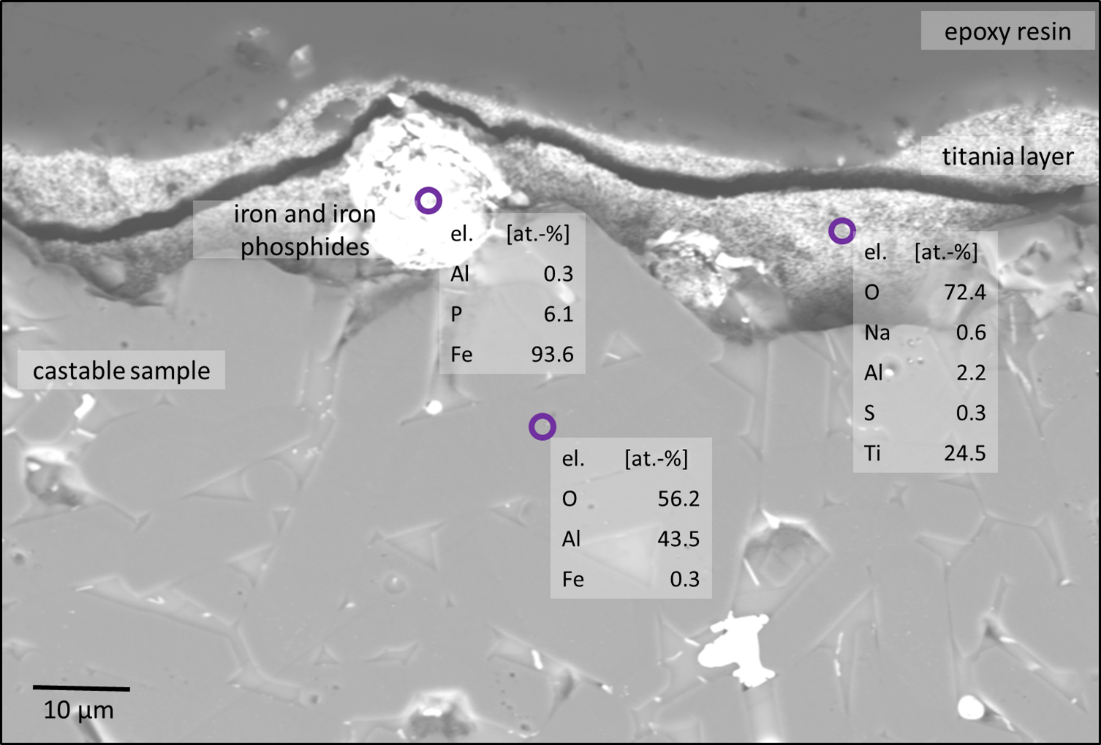
Concerning refractories, reports are found on semisilica, high duty, super duty [128,129], sillimanite [128,129,145], kaolin, chamotte [145,172], fireclay, [91,157,172] and andalusite [157]. As in the case of mullite, it is the silica that volatilizes, not the alumina; the corrosion rate increases in proportion to the silica content; free silica is more easily removed than silica bound in an aluminosilicate structure, whether amorphous or crystalline; the formation of secondary alumina can come about as a result of silica removal. [128,129,145,157,172] In a recent study by one of the authors involving a number of different alumina-silica bricks, it was determined that the formation of secondary alumina only happens provided the ratio of alumina to silica is higher than 2.6. [157] Ignatova et al further observed that hydrogen exposure enhanced the crystallization of mullite in kaolin and chamotte refractories, giving rise to a network of mullite prisms within the silicate glass. Additional sintering was seen to occur, as well as modifications in the pore structure. Those changes include an increase in the proportion of fine pores, a decrease in open porosity, and a reduction of gas permeability. Insofar as mechanical properties go, the compressive strength of the materials increased after hydrogen exposure at 1500 °C, but a creep test performed on the sillimanite and kaolin samples showed a considerable deterioration of the deformation properties of the refractories. [145]

In the past, fireclay gunning mixes and bricks have been used to line secondary reformers for ammonia production. However, in the highly reducing atmosphere containing from 30 to 60% H2, silica was seen to volatilize. In addition to the rapid corrosion of the lining, clogging issues arose with the condensation of silica when it cooled down, and the heat balance of the reformer was disturbed by the endothermic reduction reaction. [98] Nowadays, high-fired fireclay bricks are occasionally used to line the upper shaft in direct reduction kilns operated with natural gas. Even though unreacted reducing gases may still be found in this region of the kiln, the fireclay bricks show an adequate performance. A post-mortem analysis of a brick removed from the upper shaft of a DR vessel showed no signs of reduction – the chemical composition of the used brick was very close to the average values for the brand. [173] However, the ramp up of hydrogen use in DR could require a switch to other compositions with a higher alumina content, such as mullite-fireclay.

* + 1. **Bauxite**

Refractory-grade bauxite can be used as aggregate in castables as well as bricks. It provides favorable properties while having a lower cost compared with other high-alumina materials. [174,175] Some of the authors of this review investigated bauxite refractories, exposing a bauxite-based castable with calcium aluminate cement (CAC) to a gas flow of 10% H2 and 90% Ar at temperatures of 1100 and 1500 °C for up to 72 h. The samples became dark in color, but the measured weight loss was low (0.67% after 72 h at 1500 °C) and the chemical and phase composition remained largely stable. Only the impurities were reduced, in particular Fe2O3, P2O5, and TiO2. Interestingly, an EDS analysis showed that iron went from being distributed in the entire system to agglomerating on the gas-solid interfaces, either at the surface or in the pores. Hydrogen permeated through the refractory and reduced the iron, which gained a higher mobility and migrated to the surface - part of the iron was still in the metallic form, while the other part re-oxidized during the cooling step. At the highest temperature and exposure time, a layer of titania was observed in addition to the iron layer. There was a decrease in the overall phosphorous content as some of the less oxidized variants of P2O5 volatilized after reduction. Nevertheless, phosphorous was also detected in the iron agglomerates, as can be observed in Figure 9. [176] In a study involving shaped refractories, Bertrand et al. exposed a phosphate-bonded bauxite brick to a 75% H2 and 25% CO atmosphere for 240 h at 630 °C and 2 bar. In that case, a large decrease in Young’s Modulus was observed. The degradation of mechanical properties was attributed to the CO attack prompted by the presence of iron. [160]

Other authors report attempts to reduce bauxite ore with hydrogen, with the goal of reducing CO2 emissions in the iron separation step of the Pederson process for alumina production. Lazou et al. observed that diaspore and boehmite dehydrate at 505–510 °C under hydrogen atmosphere to form alumina, and that the reduction of hematite to iron commences under 560 °C – a process which is slowed down from 760 °C by the formation of a hercynite (FeAl2O4) phase. [177] Parhi et al. treated bauxite with molecular hydrogen at 650 °C, and with hydrogen plasma at 800 °C. In neither case were any of the initially present oxides reduced apart from iron oxide. [178] Skibelid et al. investigated the treatment of a bauxite residue with hydrogen, and besides the reduction of iron the authors observed that the Al-containing phases first transformed to gehlenite in sintering, and then to mayenite with hydrogen treatment at 1000 – 1200 °C. [179]



*Figure 9 – SEM micrograph of the surface of a bauxite sample after exposure to hydrogen for 72 h at 1500 °C. Iron, titanium, and phosphorous can be seen to segregate.*

**2.2.6 Magnesia**

With a melting point of 2840 °C, magnesia is distinguished by its refractoriness and resistance to basic slags. [180] However, thermodynamic simulations show that MgO could be susceptible to reduction under hydrogen atmospheres, having a level of stability close to that of silica. [89,90] The reaction of MgO with hydrogen is shown in Equation 5.

*Equation 5*

Unfortunately, there is only scarce information on the behavior of MgO under hydrogen atmospheres and in conditions that are relevant to refractories. In Ruprecht´s work, an MgO brick made with dead-burned magnesia was exposed to hydrogen at temperatures from 870 to 970 °C, and a color change was observed, with the brick turning metallic grey. However, the authors did not evaluate the physical or mechanical properties of the material. [125] Herbell et al. exposed pure magnesia bars to wet hydrogen at 1200 °C, and after 100 h the samples were essentially unchanged, except for grain coarsening. However, when the temperature was increased to 1400 °C, clear signs of attack on the MgO grains were observed. In spite of this, the room temperature strength of magnesia was not affected. [167] In other publications from the field of refractories, magnesium oxide was analyzed as an impurity in alumina. After exposing an alumina sample containing 0.25% MgO to hydrogen, Trostel detected magnesia volatilization starting between 1500 and 1700°C. [138] In a brown corundum sample which originally contained 0.17% MgO, Li et al. observed a decrease in the weight fraction of magnesia starting between 1600 and 1800 °C. [90]

An interesting phenomenon was observed by Briggs: after exposing MgO crystals to hydrogen flow at 1250 °C for 20 h, lenticular cavities with a diameter of up to 200 µm and containing high-pressure hydrogen (about 400 atm) were formed. Using hydrogen isotopes, Briggs ruled out hydrogen diffusion as the cause behind cavity formation. An underpinning mechanism was postulated which involves MgO reduction by hydrogen at the surface triggering a reaction of the hydroxyl impurities inside the crystal with production of H2 gas. Surface reduction was key for explaining the formation of cavities, which also took place when the reduction was carried out with carbon monoxide. The cavities imparted a cloudy appearance to the crystals, and their formation was observed to occur exclusively when hydroxyl impurities are present. [181,182]

From the field of heterogenous catalysis, a number of TPR profiles of pure MgO substrates can be found. In these tests, magnesia is slowly heated up under a hydrogen atmosphere and the uptake of hydrogen is measured as a function of temperature. Some authors indicated that no reduction of MgO takes place. Pudi et al. heated the magnesia substrate up to 800 °C and discerned no hydrogen consumption in this temperature range. [183] Caravaggio et al. went up to 900 °C and Parmaliana et al. to 1000 °C, and still no uptake of hydrogen was detected. [154 -155] Lower temperature peaks in the 490 – 650 °C range have been discerned, but are likely related to the reaction of hydrogen with surface -OH groups. [185–187] Moreover, some authors consistently resolve small peaks in hydrogen consumption by MgO in the range of 700 – 750 °C: Pandhare et al. at 706 °C, [185] Zigla et al. at 720 °C, [188] Chen et al. at 730 °C, [189] Boudjeema et al. at around 740° C. [190] This could potentially be due to surface reduction taking place at this temperature. In another study, Lundin et al. analyzed a MgO/MgAl2O4 support for a thin-film Pd membrane. They observed substantial reduction of MgO at 700 °C to form Mg, which alloyed with the Pd membrane and went on to segregate at the surface. This was shown to happen due to the dissociation of hydrogen as it permeates through the Pd membrane, demonstrating that MgO can be severely reduced by atomic hydrogen at this temperature. [191]

On top of being susceptible to corrosion by hydrogen, MgO is prone to hydration, and this combination makes magnesia unsuitable for the lining of vessels where H2 is used as a reductant for iron. [192]

**2.2.7 Zirconia**

Employed in especially demanding applications such as steel casting and glass furnaces, zirconia is known for its exceptional hardness and corrosion resistance. It has a very low tendency to react with other oxides, liquid metal, and molten glass. [193] The superior corrosion resistance also extends to reducing atmospheres. Thermodynamics shows zirconia to be outstandingly stable in the presence of hydrogen, even more so than alumina. [89] The reaction between zirconia and hydrogen yields ZrO as the main product (Equation 6), but ZrH2 and Zr can also be formed in lower quantities (Figure 10). Thermodynamic considerations also suggest that the use of MgO or CaO as stabilizing agents could have a detrimental effect for the stability of ZrO2; for high temperature applications, yttria-stabilized zirconia should be preferred. [89]

*Equation 6*

A graph of a temperature

Description automatically generated

*Figure 10 – Simulation results of the partial pressure of zirconia reduction products as a function of temperature at a pressure of 1 atm (calculated using FactSage 8.1 and the FactPS database).*

In a series of two consecutive reports, the stability of ZrO2 was analyzed on a static hydrogen atmosphere at extremely high temperatures, from 2200 to 2760 °C. The highest temperature at which zirconia was demonstrated to be stable was of 2230 °C, and the lowest temperature for which it was shown to react with hydrogen was of 2760 °C, with 95% pure zirconia lumps losing 27% of their mass after 1 h exposure at this temperature. A phase change was also noted. The original material exhibited the cubic and monoclinic phases, but after treatment the cubic line disappeared on XRD – possibly because of the loss of the MgO that stabilized it. The fracture resistance was lowered, and the initially yellow material acquired a metallic luster. Powdered zirconia was also investigated, and at 2560 °C it sintered into a small dark pellet. [194] In a study at 2500 °C and 150 atm hydrogen pressure, ZrO2 was not reduced. [195] Besides alumina (as described above), Trostel also investigated the effect of hydrogen on CaO-stabilized zirconia. The ZrO2 rod started losing mass below 1500 °C on account of the volatilization of the silica and titania impurities, and a slight volatilization of ZrO2 was first detected at 1900 °C. Calcium oxide only started to volatilize at 2000 °C, which demonstrates that it is suitable to stabilize zirconia even at very elevated temperatures. [138] Those studies experimentally confirm the very high stability of zirconia in hydrogen that is predicted by thermodynamics, and point to zirconia as a potential material for applications at particularly high temperatures.

Eder and Kramer reported that hydrogen can adsorb onto the zirconia surface and create oxygen vacancies according to Equation 7. [196,197] In the study, zirconia was exposed to a dry hydrogen flow at temperatures of 600 and 750 °C for 10 h. Compared with samples that were treated *in vacuo,* specimens that were exposed to hydrogen showed a much higher uptake of oxygen when later submitted to an oxygen flow*.* This demonstrates that oxygen vacancies were formed during the hydrogen treatment. Whereas vacancies were limited to the surface at the reduction temperature of 600 °C, at 750 °C bulk vacancies formed as well. The authors suggested a mechanism for vacancy formation which involves the adsorption and dissociation of hydrogen, followed by the formation of water and its desorption from the material. The number of vacancies formed increases with temperature, time, and the hydrogen flow rate, and decreases with the partial pressure of steam. The authors also noted a color change (from white to grey) and concluded that the defects affect the catalytic activity of zirconia.

*Equation 7*

Pomfret et al. exposed yttria-stabilized zirconia (YSZ) to 5% hydrogen in argon at 1000 °C for 6 h, and surface reduction of the zirconia was clearly observed. [198] Whereas Eder and Kramer suggested that bulk vacancies form at 750 °C, in this case it was demonstrated that the chemically modified region was restricted to the surface and a few nanometers underneath it. [196] Kogler et al. similarly circumscribe the reduction of both ZrO2 and YSZ by hydrogen at temperatures up to 900 °C to the surface and surface-near region. [199] In a TPR analysis, hydrogen uptake by zirconia took place in an appreciable way from around 500 °C – in agreement with Dall’Agnol et al. where hydrogen uptake also starts at around 500 °C, [200] and Hoang and Lieske where the starting temperature is of approximately 550 °C. [201] In a similar line of investigation, Sinhamahapatra et al. noted that zirconia containing a high concentration of oxygen vacancies turns black. The high vacancy concentration is attained with magnesiothermic reduction involving hydrogen gas and Mg, but reduction to a smaller extent is already observed when the sample is exposed to 5% hydrogen in argon for 4 h at 650 °C. The black zirconia shows enhanced photocatalytic activity, but it is unclear whether the change in surface state could also have implications for refractory products. [202]

As for atomic hydrogen, McTaggart stated that zirconia is not easily reducible, but observes the formation of a black or golden surface layer in zirconia when the frequency of the exciting field which produces the hydrogen atoms is high enough. The temperature of the oxide specimen was of 1200 °C. [203]

* + 1. **Zircon**

Zircon (ZrSiO4) is a silicate that can be recovered from sand or igneous rocks, and it is mainly used in refractories for steel ladles and glassmaking furnaces. It boasts high corrosion resistance, especially to acidic melts. [204,205] Only a single study on the interaction between zircon and hydrogen has been reported to the best of the authors’ knowledge, and it was published in 1975. Gardner et al. investigated the kinetics of corrosion of zircon powder by flowing hydrogen, both dry (containing 2 ppm water) and wet (water-saturated with a dew point of 24 °C), in the temperature range from 1360 to 1630 °C. [206] Mirroring mullite, the reduction of zircon entails removal of silica leaving behind a porous zirconia phase. The activation energy for the reduction by dry hydrogen was found to be of 82 kcal/mol, which is very close to reported values for silica. The value was higher for wet hydrogen, at 121 kcal/mol. The kinetic data indicates that reduction is controlled principally by the reaction interface. An interesting observation was an increase in the reaction rate at 60% completion, and it was suggested that the mechanism of reduction changed at this point due to nuclei growth and interference phenomena.

**2.2.9 Bonding systems**

The composition and properties of bonding systems are determinant for the final performance of refractory materials at high temperatures, including under hydrogen environments. Despite the relevance of the bonding systems, they have been less investigated. The most determinant compositions are described below.

**2.2.9.1 Calcium aluminate cement**

Refractories are sometimes bonded through hydraulic binding. In this process, raw materials are mixed with cements, which undergo a chemical reaction upon water addition causing the material to solidify. One of the most relevant cement compositions for the refractory industry is calcium aluminate cement, which has a higher refractoriness compared with other types, e.g. calcium silicate cement. Yakovlev et al. exposed a cement-bonded alumina brick to a hydrogen atmosphere at 1450 and 1500 °C and found that the CA6 phase decomposed to CaO and α-Al2O3. [158] In another study, a 94% alumina cement-bonded castable and a 96% alumina phosphate-bonded ramming mix were exposed to hydrogen at 260 and 538 °C and pressures of 2.58, 5.17, and 6.89 MPa for 144 h. For both materials, a decrease in the MOR was observed. In the case of the cement-bonded refractory, this was attributed to a reaction of calcium aluminates CA and C12A7 with hydrogen to form C4A3H3 – a phase which provides less bonding. [207] Crowley also investigated a concrete composed of a crushed super-duty brick with CAC. While the concrete lost up to 10% weight under hydrogen, the cement bond was preserved. The compressive strength was not affected, which shows the importance of selecting a bonding phase that is resistant to hydrogen. If it is only the aggregate that is attacked, the refractory might still retain its strength. [128]

**2.2.9.2 Phosphates**

Phosphates belong to the group of chemical binders that are mainly used for refractory mixes with an alumina content higher than 60 wt%. Aluminum phosphates and phosphoric acid are commonly utilized as phosphate binders and provide high-temperature strength. The hydrogen reduction behavior of phosphorus present as an impurity in iron ore has been investigated in the context of sintering processes. [208] In the 1960s, Crowley affirmed that phosphate-bonded alumina bricks have a good performance in hydrogen atmospheres. The phosphate was not removed in his experiments. [128] Sperber et al. investigated hydrogen-blended coke oven gas, and also pure hydrogen, in a pilot plant. They focused on the effects on gas permeability and pore size distribution. These two characteristics play an important role because the hydrogen molecules are very small compared with the other components in the furnace gas. It has been observed that hydrogen creates a path through the refractory material forming channel-like structures. The authors found that the pore area could be reduced by adding a phosphate binder. The tests showed that a minimum of 1.5wt.% P2O5 added to an 60% high-alumina brick was sufficient to obtain a higher average pore diameter, lower porosity, and higher strength. [209] However, in recent studies the reduction of phosphates was observed, with the detection of phosphorous alloyed with iron in specimens exposed to hydrogen. [157,176] Fundamental research is therefore still needed to provide an understanding of the behavior of phosphate binders under hydrogen atmospheres at different temperatures.

* + - 1. **Sol-gel**

Another possibility for binding refractory materials is the use of colloidal systems such as sol-gel. Sol-gel allows the elimination of cement and hence of unwanted calcium compounds. Advantages of sol-gel over cement include high permeability and rapid water removal, leading to faster drying. In addition, there is no dependence on water quality, as water can be dispensed with. The frequently used silica sol is the precursor for the formation of mullite, which in turn provides high-temperature resistance. [210] In a recent study, a comparison was drawn between mullite-based castables with alumina cement and silica sol bonding. The latter displayed a lower corrosion resistance due to silica volatilization. [168] Apart from this, there are hardly any scientific investigations dealing with the influence of hydrogen on sol-gel based materials. However, the resulting phases, such as mullite, Al2O3, and SiO2, have been examined separately, as described in the present paper.

* 1. **Changes to downstream processes**

As DR processes, either with hydrogen or natural gas, gain space in primary steelmaking, changes will be brought about to downstream processes as well. Those will also necessitate adaptations and new developments from the side of refractories. In the following sessions, the effect of DRI charge on the EAF will be reviewed, in general and for the more specific case of DRI produced with 100% hydrogen. Finally, an emergent alternative technology – the smelter – will be briefly discussed.

**2.3.1 EAF operation with a DRI charge**

Customarily, DRI is charged to the electric arc furnace to be converted into steel. However, the partial or total switch from scrap to DRI affects EAF operation in multiple ways. While scrap is usually charged using buckets, pellet-shaped, uniformly dense DRI is fed continuously through a hole in the roof of the EAF. To aid the melting of DRI, a higher melt volume is left in the furnace for the subsequent heat (the “hot heel”), and flat bath conditions are established. Those factors lead to a higher stability and facilitate operation and control. On the other hand, the specific energy consumption increases. While the lowering of the arc length slightly diminishes the efficiency of heat transfer in the EAF when charged with DRI, energy requirements rise due to the addition of slag formers and to the high slag volumes. [211–216] In addition, DRI typically presents a high FeO content, and the endothermic reduction of iron(II) oxide by excess carbon in the EAF expends further energy. As it is necessary to reduce the FeO and to bring the additional slag into solution, melting time, as well as tap-to-tap time, is prolonged. Owing to the high gangue content of DRI, the yield – the amount of metal that is tapped, relative to the amount that is charged – is lower. [213,215,217] The size of DRI units in integrated steel plants will increase relative to the mini-mills, and this will aggravate the issue of low melt movement. [212] Nevertheless, even if the use of DRI as a replacement for scrap could impair the process in certain ways, the adverse effects can be counteracted by adjusting operation accordingly, which will come with practice, a more thorough understanding of process changes, and optimization strategies. [213,216]

One of the main changes that result from DRI charging, and that will be now analyzed in more detail, concerns the slag make-up. Compared with scrap, DRI presents a higher SiO2 content. This will modify the slag composition in the direction of lower basicity, or lower CaO/SiO2 ratio. [211] However, maintaining the standard basicity is necessary to ensure adequate slag foaming – which plays a critical role for the stability and efficiency of the EAF. [218] In the face of this, the addition of fluxes such as lime, doloma, and dolomitic lime is needed to compensate for the high SiO2 levels in DRI. The flux input generates a high volume of FeO-rich slag, leading to an increase in FeO losses, a decrease in productivity and yield, and to a higher energy consumption. In order to minimize those issues, high-quality iron ore with a low gangue content should be used. [212,213,219] As phosphorous oxides are not reduced in DR processes, DRI also presents a relatively high content of undesirable phosphorous impurities. [220,221] On top of this, the lowering of the basicity leads to a decrease in the stability of P2O5 in the slag, which could render dephosphorization more difficult. [222] However, one study demonstrated that this does not represent an issue – the phosphorous oxides would melt early in the heat, move to the slag phase, and be directly flushed. [221]

If on the one hand the content of gangue elements is high, on the other the amount of tramp elements (such as Cu, Ni, Cr, and Sr) is low. Additionally, nitrogen content is minimal. DRI produced with coal or natural gas often presents a high carbon content, and carbon monoxide evolves as the carbon is burned in the EAF. The CO bubbles that are originated form a barrier between the steel and the surrounding atmosphere, thereby flushing out nitrogen from the melt while preventing the dissolution of N2 from the air. In this regard, the early occurrence of slag formation also has a protective effect. This makes DRI the ideal starting material for steel grades with low nitrogen contents, which boast superior mechanical properties and formability. [217,223,224]

The high silica content in DRI slags has another crucial effect: it can increase the solubility of MgO in the slag and hence exacerbate the corrosion of the basic refractory lining. [211,225] In the EAF, the hearth is usually lined with basic mixes, and MgO-C bricks are employed in the side walls. However, the attack of the lining can be delayed by the formation of a magnesiowüstite layer at the slag-refractory interface, which wards off slag penetration and refractory dissolution. To promote the formation of the layer, the MgO content in the slag should be adjusted to saturation level from the start of operation, which can be realized by adding MgO carriers as slag formers. [211,213,226] Another aggravating factor is the higher slag volume, and it should be noted that flat bath operation makes refractories in the side walls more exposed to arc radiation, which can lead to a decrease in lifetime. [215] Those stresses will necessitate changes to the refractory lining. The share of high-quality refractories, based on fused and sintered MgO (carbon- or resin-bonded), will increase, and in some cases top-quality refractories will be needed, made with the highest grades of fused magnesia. The use of recycled raw materials, on the other hand, will have to be done with caution. Additionally, specific refractory consumption will enlarge – it is projected that it will more than double, driven mainly by hearth mixes, maintenance mixes, and slag zone working linings. [212]

**2.3.2 EAF operation with 100% H2 DRI**

As discussed previously, the implementation of direct reduction with 100% H2 is currently being considered. This would bring further changes to EAF operation, primarily because the resulting sponge iron would contain no carbon in its composition. Pfeiffer et al analyzed the melting behavior of DRI with varying carbon contents, and found that carbon-free DRI has a higher liquidus temperature and takes a longer time to melt. [227] This could lead to a decrease in productivity. In addition, the carbon present in pellets produced with conventional DR technologies performs different, important roles in EAF operation, and its effects would be forsaken in the case of 100% H2 DRI. First, carbon reduces residual FeO, thereby helping to complete metallization. Second, burning the excess carbon provides chemical energy to the operation of the EAF, and allows to cut down on electricity consumption. Third, the CO that is produced when carbon is burned promotes foaming and the elimination of detrimental impurities in steel (such as N, H, S, and P). While carbon can also be directly injected in the EAF for such purposes, which is a current practice in some mini-mills, C as a component of DRI presents higher purity and combustion efficiency. On top of this, alternative sources could have an environmental impact. [228] Besides EAF operation, the use of carbon-free DRI could also affect steel quality. One study described the appearance of blisters and gangue entrapments when carbon-free DRI was used. [214] With regard to refractories, the lower C content in the melt would promote the dissolution of carbon from the lining (for example, from MgO-C bricks in the side walls). The longer melting times and higher amounts of FeO slags could also expedite wear.

**2.3.3 The smelter technology**

A limiting factor for the implementation of the DRI-EAF route is the undersupply of high-grade iron ore. The iron used in DR units has to meet stringent requirements, in particular with regard to gangue content – otherwise, as explained above, issues will be redoubled such as higher metal losses, decreased yield and productivity, increased energy consumption, and accelerated refractory wear rate. However, high-quality ores are being depleted, and the demand is projected to surpass availability. While some solutions are being developed, including the exploitation of new mines, beneficiation steps to concentrate pellets, or the use of novel pellet binders, they will likely not suffice, and the shortage of high-quality ores could put a brake on the expansion of the DR technology. [216,229,230] However, a solution is emerging that would accommodate low-grade DRI: the smelter, or submerged arc furnace. Already established in the non-ferrous industry, it could be adapted and transplanted to steel production. A future scenario is envisaged where iron ores from a wide range of qualities are reduced in DR processes, and then the high-grade products proceed to the EAF, whereas the low-grade iron is directed to the smelter. In a smelter unit, iron ore is melted and reduced, and in sequence the melt is charged into a BOF (basic oxygen furnace) converter for refining. BOFs already in operation could be used, which facilitates the implementation of this technology in integrated plants. Only minor adaptations would be needed, most notably to the blowing system, as the melt produced in the smelter has a lower carbon and silica content compared with the hot metal from the BF. [212,219,231,232] Iron smelters will also introduce new challenges to refractory engineering. Smelters are characterized by their massive dimensions, and at such scales the refractory lining must be carefully designed so as to create a thermal profile that will enable uniform expansion upon heat-up. The metal bath is very hot, and the slag is FeO-rich and markedly aggressive. Extremely tough conditions will be found at the interface between the bath, the slag, and the off-gas. In the case of open bath operation, the roof will be subjected to intense thermal and chemical stresses, and refractory selection should preclude its collapse. Another area that warrants attention is the hearth, which has to withstand high lifting forces. [212,233]

1. **Hydrogen as fuel**

Carbon-based fuels have allowed the development of humankind thanks to the huge amounts of natural sources, easy extraction, storage, and use, but this paradigm must change. The consumption of immense quantities of cheap coal, natural gas, and petroleum-derived fuels has increased our quality of life, life expectancy, and worldwide population in the last decades, but other negative effects such as global warming, political conflicts, and depletion of natural resources have arisen. [4] In view of this, carbon-based energy should be replaced with sustainable alternatives, such as green hydrogen – a fuel which releases water instead of CO2 when burned. While H2 is being considered for the powering of trucks and airplanes and for providing energy to domestic applications, it is believed that it could make a particularly significant contribution as a heating fuel in heavy industries like iron and steel. [234,235]

Owing to current hydrogen prices, it is important to consider not only the likely far future scenario of 100% H2, but also transition stages where H2 will be blended with natural gas in different ratios. There is no miscibility gap between H2 and NG, and the ratio could fluctuate in response to fuel costs and availability. In industrial furnaces, hydrogen can be used in combination with either air or oxygen for combustion, and the latter – the so-called oxyfuel technology – has gained prominence as it enables fuel savings of up to 50%. It would be especially convenient when on-site electrolysis is used, given that O2 is generated as a side product. It is also worth noting that the oxyfuel technology, especially with NG, is already widespread and could allow an easier switch to oxyfuel with hydrogen. [236]

Different applications are envisaged for hydrogen firing in steel production. For instance, it could replace natural gas in reheating furnaces used for the hot rolling of steel, [34,237–239] in ladle preheating, [240] or in the auxiliary burners of the EAF. [241] A full-scale demonstration of hydrogen firing with oxyfuel was carried out by Ovako and Linde in Sweden in a hot rolling mill. An upgraded burner was used that could operate with both H2 and liquefied petroleum gas (LPG). Preheating with hydrogen could be realized in a controlled way with uniform temperatures, and an inspection of the final steel bars showed that hydrogen firing had no negative effect on product quality compared with combustion using LPG. [239] At ArcellorMittal in Sestao, a ladle was preheated using 100% H2, the casting temperature being successfully attained with a controlled heating curve. [240] Other processes might benefit from H2 combustion, but in some cases it could be more difficult to make a full replacement. One example is the blast furnace, where solid fuels fulfill different roles. [242]

While electrification remains an option to decarbonize industrial heating, the switch from fossil fuels to hydrogen would require fewer adjustments and could be more readily implemented. However, some challenges still have to be handled, such as safety issues, modifications to burner design and feed systems, and the compatibility of sensor and control technologies. [242] As pertains to safety, hydrogen has a wide flammability range and will ignite at volume concentrations from 4 to 75% – for comparison, the range for methane is of 5 to 15%. [243] Additionally, it requires a small amount of energy to combust: its ignition energy is of 0.019 mJ, whereas the corresponding value for methane is of 0.290 mJ. [244] Nevertheless, in some ways the use of hydrogen is safer than that of other flammable fuels. Hydrogen is non-toxic, and as it is a very light gas it can easily disperse (conversely, propane and gasoline are heavier than air and their concentration can build up at ground level following a leakage). [245]

As the properties of hydrogen differ from those of NG and other fuels used for industrial heating applications, burner designs will have to be adapted for H2 combustion. Hydrogen is a very small molecule, and because of this it presents a high calorific value on mass base, and a low calorific value on volume base. As a result, H2 will have a high volumetric flow rate – at constant burner capacity, the volume flow rate of hydrogen is 3.33 times higher than that of NG. This translates to a flame speed that is up to 5 times higher at stoichiometric conditions. Such speeds increase the likelihood of flashback in burners with premix configurations (including lean premix and rapid premix), and given that flashbacks can damage burner components, those designs are unsuitable for hydrogen combustion. [246–248] In addition, the adiabatic flame temperature of hydrogen is higher than that of natural gas. This necessitates a reevaluation of the materials used in burners, both the refractories and the metals. For the metal parts, a higher grade of stainless steel or alloy should be selected, and it is also important to ensure that it is not susceptible to hydrogen embrittlement. [248] Burner design should also factor in the changes to flame shape (which will depend on burner type) and the shorter flame length, a result of the high reactivity and flammability of H2. [249,250] It is also important that the burner has a high performance and thus impedes the escape of unburned hydrogen – which could provoke H2 embrittlement and therefore affect the quality of the final steel.

Hydrogen firing could also impact furnace operation in two main ways. First, as the flue gas composition will be different, the furnace atmosphere will be affected. Second, there will be changes to heat transfer, both in the form of radiation and convection. Insofar as the furnace atmosphere goes, the combustion gas will present a high content of water vapor (up to 100% in case of stoichiometric pure combustion with O2). [246,247] It has been hypothesized that the steam could, for example, affect scale formation in the hot rolling of steel. In a laboratory test comparing the reheating of two steel grades in atmospheres corresponding to the combustion of 100% H2 and 100% NG, it was verified that the formed scale had a slightly higher thickness for the case of the H2 combustion atmosphere, as well as a different aspect. [251] However, as described previously, a full-scale demonstration showed no detriment to the quality of steel with 100% H2 firing in oxyfuel. [239] In addition, NOx formation takes place when the temperature exceeds 1371 °C, and this value can be more easily reached with hydrogen firing as adiabatic flame temperatures are higher. On top of this, the rapid burning of hydrogen and quick energy release lead to localized heating near the flame, pushing temperatures up even further. In fact, the utilization of hydrogen could lead to a threefold increase in NOx emissions. [248] In terms of heat transfer, the change in the chemical composition of the flue gas leads to a change in its thermal properties. Mayrhofer et al demonstrated that the emissivity of the flue gas in the combustion of a H2-NG blend increases with the hydrogen content, peaking at 90% H2. This means that a higher amount of radiative heat transfer from the gas to the product can be expected in this case. In addition, the thermal conductivity and the specific heat capacity of the gas will increase with hydrogen content, enhancing the heat transfer to the product even further. [252] In a simulation of the EAF, a switch from natural gas to hydrogen led to a slightly higher temperature of the liquid steel during operation. However, those changes could easily be counterweighed by slightly tweaking operation parameters. [241]

Changes to instrumentation and control systems will also be required. For combustion control, the absence of CO poses a challenge, as typical control algorithms and measurement devices focus on combined CO and O2 measurements in the off-gas. Modern in-situ measurement technology is certified for fossil-fired processes, but their applicability has not been proved for H2 combustion. In addition, burners designed to operate with NG, H2,and mixtures thereof should be equipped with sensors to monitor the varying composition of the fuel stream so that the control system can adjust the fuel-air ratio accordingly. [248] In fact, a study involving different types of burners (modular non-premixed jet, forced-draught, and flameless oxidation) demonstrated that the deployment of advanced sensing and control allows the substitution of NG by H2 to occur with no detriment to the process. By adjusting the fuel and air volume flow rates in response to the hydrogen content in the fuel, the firing rate and air excess ratio can be stabilized, and potential negative effects (related, for instance, to flame shape, heat transfer, and NOx emissions) are offset. [250]

In the past few decades, engineers, burner providers, gas producers, and distributors have worked on these issues and identified different solutions. However, refractories received little attention so far, even though the different thermal gradients and peak temperatures, gas velocities, and higher humidity could affect the specifications needed to ensure proper refractoriness, thermomechanical properties, erosion and corrosion resistance, and insulation. If we take for example the case of preheating, we can find a variety of refractory products that could be affected, including MgO-C, alumina castables, sol-bonded monolithics, non-basic bricks, porous insulation products, doloma bricks, and ISO tubes. The impact on refractory products is significant and important for regular plant operation.

**3.1 Effect of water vapor on refractories**

Using H2 as a fuel generates huge amounts of water vapor, as can be seen from the combustion reaction in Equation 8. If pure O2 is chosen as oxidizer for the combustion process, the off-gas will contain 100 vol.% H2O for an air ratio of λ =1. In general, water vapor reacts as an oxidizing gas, and it can play a critical role for the application of refractories. In the following session, we will focus on the effect of water vapor on ceramics and present the challenges per refractory product type. As various metallurgical furnaces operating in different conditions have the potential to be fired with hydrogen, the session will cover the known effects of water on ceramics for a wide range of temperatures and pressures.

*Equation 8*

**3.1.1 Silica**

As discussed above, silica volatilizes under hydrogen atmospheres. The same happens in water vapor, although in this case it is the oxidation of silica, instead of reduction, that takes place. The reactions that are considered the most plausible are presented in Equations 9-12. Different studies undertook to determine the chemical nature of the volatile species, either through thermodynamic simulations [253] or experimentally, via transpiration methods, [254,255] mass spectrometry, [256] and analyses of parametric dependencies in kinetic studies. [102,103,257] is widely acknowledged as the predominant volatile product, [102,103,253–260] and evidence has also been found for other species, such as , [102,253,255,256] SiO(OH), and . [102] While an increase in the rate of volatilization with temperature is often described, Cheng and Cutler found that this tendency reverses after reaching a certain point. The rate of the reaction initially increases with temperature and peaks at 1350 °C, with a sharp decline thereafter. [261] The weight loss also increases with the partial pressure of water vapor. [256,261] In fact, Opila et al found that oxidation has a stronger dependence on the partial pressure of steam than on the temperature. [256] It has also been demonstrated that the formation of volatile silicon hydroxide is hugely influenced by the system pressure, [253,262–265] and studies found a parametric dependence of the pressure to a power of 1.5. [102,260] The rate of recession of silica is also affected by the gas velocity. [102,260] Opila mapped the recession rate of silica scales for different pressures and gas speeds, and while volatilization is negligible when the pressure and gas speed are low, it becomes significant if the value of either, or both, is raised. [265]

*Equation 9*

*Equation 10*

*Equation 11*

*Equation 12*

It is known that silica occurring in natural waters can volatilize in steam and then deposit as a scale in boilers and associated steam pipelines, which negatively affects thermal efficiency and may compromise safety. [266–268] For this reason, industry standards set rigorous limits for silicon content in boiler feedwater. [269] Silica scales can also form through the same mechanism in steam turbine blades, restricting the steam flow and conducing to a decrease in turbine capacity and efficiency. [270,271] In oxidizing combustion atmospheres, SiC and Si3N4 form a protective SiO2 scale which impedes further oxidation (as described in section 2.2.1), but it has been demonstrated that this scale can volatilize in the presence of steam with a linear recession rate. [101,102,253,257,260,265,272,273]

From the field of refractories, investigations have been made regarding materials used in coal gasifiers [163,253,262,263,274–276] and ammonia plants [263,277,278]. During the start-up or shutdown, corrosion may happen through the dissolution of solid oxides by the condensate. [163] Silica is soluble in water to a small degree – for instance, at 104 °C the equilibrium solubility is of 58 ppm, and at 274 °C it is of 500 ppm. [279] During operation, free or combined silica may react with water vapor to form volatile silicic acids (as described in Equations 9-12). Not only does the leaching of silica cause the refractory lining to lose strength and erosion resistance, it also leads to the formation of deposits that can cause choking issues in the equipment. [97] Gac observed the removal of silica from refractory castables at the modest temperature of 199 °C and pressure of 30.6 atm. It was only the free silica (in the form of α-quartz) that reacted; the silica in mullite or in the CA2S phase went unaffected. [277] Palmer did a post-mortem analysis of an alumina-silica castable that had been used in the transfer line of an ammonia plant, under a steam-containing atmosphere, for over 10 years at high pressures and temperatures up to 950 °C. The precise initial composition was unknown. Visually, the author identified no signs of corrosion or erosion, albeit some customary cracking and spalling were present. However, a chemical analysis showed that the aggregate in the hot face contained 22.1% SiO2, and the aggregate in the center of the brick had 42.6% SiO2. As for the matrix, there was virtually no difference: a SiO2 content of 31.3% was measured in the hot face, and a weight percentage of 30.2% was verified in the center. This shows that the depletion of silica, which the author attributes to reaction with steam, is restricted to the surface area. Additionally, silica is removed from the aggregate phase, and not from the matrix. [278] Based on such observations, it has been recommended that the use of silica-containing refractories in such applications be avoided, [163,274] and the use of high-alumina refractories with only a minor silica content became widespread. [263,275,280]

However, the view that silica is unsuitable for high-temperature steam atmospheres has been contested. Sadler III and Davis describe that neither a ground super duty brick nor silica flour lost an appreciable weight after exposure to steam at 1000 °C and 6.9 MPa. Exposure time, however, was limited to 8 h. At the higher temperature of 1400 °C, weight losses for super duty and silica bricks were higher, but did not surpass 3% after 120 h. Interestingly, the weight loss halted after about 80 h, and it was not possible to correlate initial silica content with weight loss. [263] Wiederhorn et al demonstrated that a silica-containing flint clay castable refractory developed outstanding strength and erosion resistance in steam atmospheres owing to the formation of anorthite (CaAl2Si2O8). In comparison, a high-purity alumina castable underwent a sharp decrease in strength with the hydration of calcium aluminate phases. [281] Robbins and Mauer also observed the leaching of silica by steam in a CaO-Al2O3-SiO2 castable with a kaolin aggregate having 36% SiO2. In a high-pressure gasification pilot plant, silica volatilized at around 900 °C and then deposited on cooler parts of the gasifier. Nevertheless, the negative effects of silica removal were outweighed by the strong bonding provided by the formation of an anorthite phase. The phase already appears at 350 to 500 °C, and then forms very rapidly at 700 to 1000 °C, remaining stable under steam atmospheres. [276] After a 9-year study involving 60 different refractory compositions, Sadler III et al contended that the leaching of silica from refractories is not critical. They propose that silica-containing intermediate alumina refractories are preferable to high-alumina compositions. The intermediate alumina refractories gained strength upon exposure to steam, and whereas other authors attribute this to the formation of anorthite, in this case it was linked to the emergence of a structure of interlocking mullite grains. [262]

**3.1.2 Alumina**

Alumina may react with water to form aluminum hydroxides. A number of such compounds have been crystallographically described and the equilibrium has been investigated. The phase diagram (Figure 11) shows that different hydroxides are stable up to approximately 420 °C, decomposing to corundum at higher temperatures. [282–286] The formation of aluminum hydroxides has been demonstrated to affect the behavior of alumina when deployed as a tribo-material at high pressures and temperatures below 500 °C in steam or water. [284,287–289] Furthermore, aluminum hydroxides have been observed to form in refractories in experiments that reproduced the conditions at the cold face of the lining in coal gasification plants [137,281,290–294] or ammonia transfer lines [277,295]. Boehmite starts to form from around 200 °C and is no longer detected at temperatures higher than 300 °C, which indicates that it decomposes. [137,277,281,290] One study identified the formation of a gibbsite phase in an alumina refractory after exposure to high-pressure steam at 110 °C. [281]

Research findings indicate that the alumina from the cement phase can react with steam to form boehmite, with the reactivity of different cements depending on the quantity of free present. [277,281,295] Alumina in the form of aggregate is also susceptible to react, and in one case calcined alumina generated boehmite while the tabular alumina remained unaffected. [290] It was found that steam saturation plays an important role: in one study, the quantity of boehmite formed increased in proportion to the steam saturation, and the reaction was only verified to occur from a minimum of 10 – 30% saturation level (depending on temperature and pressure). [291] Boehmite formation is also favored by lower densities, high porosity levels, and the presence of CO in the atmosphere. [277,295] The reaction is accompanied by a volumetric expansion, and in some instances cracking and spalling ensued, [277] but this could also help close pores. A study showed that the MOR of a cement-bonded castable increased after exposure to steam atmospheres, and the increase in mechanical strength was proportional to the quantity of boehmite formed. [290] It has been reported, in fact, that a boehmite bonding can be created by adding reactive alumina to the recipe and then exposing the refractory to saturated steam at 200 °C, the properties of boehmite-bonded refractories being on a par with those of fired bricks with chemical bonding. [296] Conversely, other investigations showed a decrease in the MOR or the flexural strength of alumina refractories exposed to steam at 200 – 300 °C. In this case, however, it would be related to the calcium impurities. A calcium-enriched glass phase can provide additional intergranular bonding to the alumina refractories, but upon steam exposure calcium migrates to the external surface and loses its effect. [137,297] The corrosion mechanism whereby steam attacks impurities in the grain boundaries leading to a deterioration of mechanical properties has been described by other authors. Oda and Yoshio have documented the hydrothermal dissolution of and impurities in alumina, highlighting the adverse impact of this phenomenon on the fracture strength of the material. [298]

At higher temperatures, however, a different phenomenon occurs: alumina may volatilize in the presence of steam. This has been reported to be an issue for protective alumina coatings applied in components of propulsion and energy generation systems, which are exposed to steam-containing combustion atmospheres. [273,299–302] The main reaction is described in Equation 13, with being the predominant volatile product. Even though other species could potentially form, such as and calculations made by Opila and Myers based on the thermochemical data provided by Gurvich et al [303] indicate that they should only became significant after 1800 °C. [299] Experimental studies found a dependence of the corrosion rate on the water vapor partial pressure to an exponent of approximately 1.5, which is consistent with the stoichiometry of Equation 13. [299,301] Various researchers observed a small reduction in the mass of alumina within the temperature range of 1250 to 1500 °C, [273,299,301,304] and the collected data was used to estimate the recession of alumina over 10,000 h in combustion atmospheres, as shown in Table 3. [273,299,301] Other authors, however, observed no decrease in weight, [305,306] or even a small increase. [300] A hypothesis was made that this could be due to the formation of hydroxyl groups on the surface of the alumina grains, but no evidence supporting this idea was detected on an infrared spectroscopy analysis, and the diffusion of water vapor into the Al2O3 lattice was proposed as an alternative explanation. [300] In those instances, mass could still be lost due to hydroxide formation, but this effect would be offset by vapor diffusion leading to a net weight gain or the preservation of the weight.

Equation 2

*Equation 13*

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*Figure 11 – Phase diagram for the system. [282]*

The enthalpy of the reaction in Equation 13 has been estimated to be of 210 kJ/mol by Opila and Myers, [299] and the activation energy was calculated by Yuri et al to be of 240 kJ/mol [301] and by Frisch et al as 233 kJ/mol. [304] A linear decrease in weight with time was observed, which indicates that the corrosion kinetics is controlled by the surface reaction. [301,304] The recession rate was found to vary exponentially with the temperature. [299,301] While Opila and Myers determined the recession of alumina in steam to be proportional to the pressure, [299] Yuri and Hisamatsu established an inverse proportionality relation. [301] The corrosion rate was found to be proportional to the square root of the gas velocity. [299] The same corrosion rate was obtained for sapphire and polycrystalline alumina, suggesting that grain boundaries do not affect recession. [301]

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Source | Temperature (°C) | Pressure (atm) | Gas velocity (m/s) | Recession (mm) |
| Fritsch et al [304] | 1300 | 15 | 150 | 1.8 |
| Opila and Myers [299] | 1300 | 10 | 50 | 0.25 |
| Yuri and Himasatsu [301] | 1250 | 15 | 110 | 0.7 |

*Table 3 – Predicted recession rate of alumina over 10,000 h in combustion atmospheres containing steam.*

The volatilization of alumina modifies the microstructure of the material: features have been described such as ledges, pitting, [299] terrace fields, [300] and surface etching [304,305]. This indicates preferential corrosion at the grain boundaries, which can be attributed to either the concentration of impurities in this region or to a less stable bonding between atoms. Abnormal grain growth was also observed, which could be linked to the higher mobility of etched grain boundaries, or to hydrogen defects that could increase the diffusion rates for aluminum cations and oxygen anions. Tai et al observed a decline in the flexural strength at 1700 °C in a steam atmosphere, and it was proposed that the deterioration of the mechanical properties can be attributed to the combined effect of surface etching and grain growth. [305]

**3.1.3 Mullite**

As in the case of hydrogen corrosion, the attack of mullite by steam at high temperatures entails the removal of silica from the mullite structure, leading to the formation of a porous layer of secondary alumina. [304,307–310] However, in this case silica is leached as a volatile hydroxide (Equation 14). The occurrence of this reaction has been described between 1200 and 1670 °C. [304,307–309,311,312] Despite the reduction of silica, mullite gained weight in some studies after being exposed to a steam atmosphere. This is because of the presence of two competing effects: the specimens gain weight by the absorption of water molecules, while simultaneously experiencing weight loss due to the volatilization of silica. [307,308]

*Equation 14*

Using an Arrhenius plot, Fritsch et al estimated the activation energy for the oxidation of mullite to be of 78 KJ/mol at temperatures between 1300 and 1500 °C, which is considerably lower than that of alumina and in a range comparable to the activation energy for silica. The authors observed a linear kinetic profile, which is suggestive of a corrosion process controlled by the surface reaction. [304] Nevertheless, it was noted that high gas velocities – such as those found in turbines – dramatically affect the decomposition rate of mullite. [307,310] Ueno et al demonstrated that sodium impurities present in the material accelerate the water vapor corrosion of silica. The effect can be observed even for very low quantities of sodium – the precursor alumina for the synthesis of mullite had 0.001% sodium, while the precursor silica had 10 ppm sodium. It was proposed that NaO reacts with water to form NaOH, and then the hydroxide ion acts as a catalyst for the water corrosion of silica. [299,307] Another study also found that the presence of sodium accentuates corrosion, but in this case sodium likely has an extrinsic origin, coming from the alumina tube, rod, or crucible. [312] Schmüker et al drew a comparison between single crystal and polycrystalline mullite, and it was found that the polycrystalline material had a higher nucleation density of secondary alumina. [311]

Cavities have been observed to form due to the corrosion of mullite at temperatures above 1300 °C. The mullite phase was attacked at the surface and pores, whereas the bulk composition remained unchanged. [299,307] Schmüker et al remarked that the newly formed alumina crystals occur in clusters, which suggests that existing structural defects on the surface of mullite single-crystal plates may trigger the decomposition of mullite into alumina. The authors also determined the growth of the alumina grains to be anisotropic. [309] Eils et al observed changes in the microstructure and proposed a corrosion mechanism based upon it: the exposure of mullite to steam would lead to the formation of a melt phase which generates an aluminosilicate glass, and the - grains would then crystallize from this glass phase. As a result, the glass is enriched in silica, but it goes on to volatilize via formation of silicon hydroxide. In the end, the -alumina grains find themselves located in empty cavities. [312]

In just one case, recession of the mullite phase, and not only silica removal, was observed. Ueno et al report mullite recession at only 1200 °C after exposure to a high-speed steam jet simulating gas turbine conditions. [307] One study also reports changes at low temperatures, before volatilization of silica sets about. Lang and Day observed a remarkable decline in the MOR of mullite ceramics exposed to steam, especially if saturated. At 285 °C and 6.89 MPa, the MOR was reduced from 52.9 to 10.8 MPa. The deterioration of mechanical properties is probably linked to the dissolution of the glass phase, with the impurities originally present in the glass concentrating at the external surface. Additionally, a phase change was detected from sillimanite to kyanite. [137]

**3.1.4 Magnesia**

It is widely known that magnesia refractories are prone to hydration. MgO can react with moisture during storage, or with vapor when the refractory lining is dried after installation. Hydration can also occur in service (for instance, in non-ferrous smelting furnaces, where water might leak from the water-cooling equipment or condense around the cooling pipes). [313,314] Magnesia is attacked by either liquid water or steam, and significant hydration can occur even at ambient conditions. The hydration of MgO (Equation 15) leads to the formation of brucite (Mg(OH)2), which is accompanied by a volumetric expansion by a factor of 2.2. [314] Therefore, the reaction can severely damage the mechanical properties of refractories. [313–316] At the initial hydration stages, brucite can help close pores in the material leading to an increase in strength, but from a certain point the expansion can no longer be accommodated and the material cracks in the wake of the resulting tensions. [313] The mechanical properties can also be greatly impaired by the thermal decomposition of the formed brucite, which sets in at around 300 °C. [317,318] As magnesium hydroxide decomposes with the recrystallization of MgO and the release of water, the bond between the magnesia grains and the brick weakens. [315] Furthermore, complete disintegration of a refractory brick can occur, which is known as “dusting”. [314,319]

*Equation 15*

The hydration of magnesia has been shown to involve the adsorption of water molecules as a first step. [320–323] Magnesium oxide then dissolves in the water, and when supersaturation is reached magnesium hydroxide nucleates and grows on the surface of MgO (the so-called dissolution/precipitation mechanism). [323–326] Hydration happens in a different way for single crystals and polycrystalline materials. For single crystals, it starts off slowly at the surface, then accelerates with the increase in porosity, and towards the end it slows down again. In the process, a sound brucite layer grows continually. For the case of polycrystals, an interesting phenomenon is observed: as brucite forms, the volume expansion creates tensions that smash the polycrystals into smaller grains. The process continues until the material is reduced to single crystals. During the dusting stage, the hydration rate increases rapidly, and when the disintegration is completed the rate slows down. [313]

It has been noted that the rate of hydration increases with the porosity of the material. [316] The preparation and properties of the MgO grains are also determinant. The rate of reaction increases with the surface area and decreases with the grain size, [237, 238, 244, 245] and high-temperature calcination may constrain the hydration of MgO by virtue of the enhanced sintering. [320,327,328] The kinetics is also influenced by particle morphology, which is related to the choice of precursor. [329] Additionally, the concentration of surface defects greatly affects the dissolution of MgO in water as Mg(OH)2. [330] Impurities can also play a role, especially lime and silica, with the hydration rate increasing as the CaO/SiO2 ratio rises. [314] The temperature, pressure, and the partial pressure of steam also have an influence on the reaction rate. As mentioned above, it has been shown that the reaction of water vapor with MgO involves the adsorption of water particles, and sufficient adsorption is required in order for the reaction to occur to an appreciable extent. This would only be reached for water vapor pressures above a certain threshold, which is especially high for samples with low surface area. [320–322]

As magnesium oxide is the stable species from 271 °C at atmospheric pressure, [331] the formation of brucite happens at relatively low temperatures. However, at higher temperatures, MgO can react with steam to produce gaseous . Experimental data for the high-temperature volatilization of MgO in steam has been produced by Maeda et al [332] and Alexander et al. [333] However, in those cases magnesia is very resistant. In fact, the volatility of MgO in water vapor has been shown to be lower than that of SiO2, Al2O3, and CaO for a wide range of temperatures both at low [254] and high pressures. [334]

**3.1.5 Zirconia**

The low-temperature degradation of zirconia under steam atmospheres is well known. Zirconia may undergo a phase transformation from tetragonal to monoclinic, which is accompanied by a volume expansion and conduces to cracking. While this transformation can already take place in air, it is significantly amplified in the presence of water vapor. [335–343] In humid air, degradation is most rapid between 200 and 250 °C. It can be slowed down by increasing the content of stabilizer, [343] and it has been show that the use of magnesia as stabilizing agent accentuates degradation, [344] whereas ceria sets it back. [336] Cracking and degradation, however, only happen provided the grain size is higher than a critical value, and can be eschewed by having small grain sizes in the material. [335–337,345] The rationale is that the tetragonal phase presents a lower surface energy than the monoclinic phase, which renders it stable below a critical grain size. [346,347]

A number of mechanisms have been proposed to account for the promotive effect of water vapor on the low-temperature degradation of zirconia. Yoshimura et al proposed that the chemisorption of water in YSZ leads to the formation of Zr-OH and Y-OH bonds, which generates stresses. This leads to the creation of defects, which play the role of nucleation sites for monoclinic zirconia. [341] Guo et al also associate degradation to hydroxide groups, but the proposed mechanism is different. The OH- ions that are formed following the chemisorption of water would diffuse into the interior of the sample through the grain boundaries and annihilate oxygen vacancies. Those are believed to help stabilize the tetragonal phase, therefore their elimination promotes the transformation to the monoclinic polymorph. [342] Lange et al, on the other hand, suggest that yttrium reacts with water to form Y(OH)3, which results in yttrium depletion. The volume where yttrium is missing then acts as a nucleus for phase transformation. [337] Xie et al went down a different route: he proposed that water lowers the surface energy of both polymorphs, but preferentially that of the monoclinic phase, which speeds up its formation. [340] Murase and Kato also point to the surface stabilization effect, and observe that it counteracts the promotion of grain growth through enhanced surface diffusion. [338]

At higher temperatures, Fritsch et al exposed YSZ to steam in the temperature range from 1200 to 1500 °C, and no weight loss was observed after 120 h. However, it was found that the initial tetragonal/cubic phase was destabilized, leading to formation of a monoclinic phase which brought about an increase in volume and the formation of stress-induced cracks. [304] Etori et al, on the other hand, measured a decrease in the weight of zirconia exposed to steam at 1500 °C for 400 h. Curiously, the weight loss of approximately 14 g/cm2 was higher than that of alumina (8 g/cm2). However, as in the case of Al2O3, the authors affirm that the weight loss could possibly be attributed to erosion by the gas. The flow rate was of 150 m/s to emulate the conditions encountered in gas turbines. [273]

**3.1.6 Zircon**

The corrosion of zircon in steam atmospheres has been reported from 1200 to 1500 °C. It involves the removal of silica from the zircon structure and the formation of monoclinic ZrO2 with a highly porous structure. [304,348,349] Corrosion of the silica-rich amorphous phase in grain boundaries has also been described. [348] Overall, the corrosion mechanism of zircon in steam is analogous to that of mullite.

Microstructurally, attack of the amorphous phase leads the formation of pits in grain boundaries. Changes have also been noted in grain surfaces, with the formation of a sand ripple morphology. [348] Crack formation has been observed, and while Fritsch et al attributed it to the monoclinic-tetragonal transformation of zirconia, [304] other authors correlated it with the difference in coefficient of thermal expansion between zirconia and zircon. [348,349] The corrosion kinetics was found to be linear, [350] and Ueno et al reported a recession rate of in a static corrosion test at 1300 °C, which increased by a factor of ten with flowing steam at a velocity of . [348]

**3.1.7 Calcium aluminates**

One of the effects of exposing CACs to steam atmospheres is further hydration. Residual unreacted compounds can react with steam to form CAHx phases. [137,276,277,295,351] It has been reported that the formation of additional cementitious material could enhance mechanical properties. Gac observed a twofold increase in the strength of high-alumina castables exposed to an atmosphere of steam and N2 at 199 °C and 30.6 atm for 18 days, and ascribed this effect to cement hydration. [277] Robins and Mauer did an interesting in-situ study where they observed phase changes in a cement-bonded alumina castable at 7 MPa during heating up to 1000 °C in steam. A sequence of different hydrated phases were observed (Equation 16), until their disappearance at 625 °C. [276]

*Equation 16*

However, when cement-bonded refractories were exposed to a mixed atmosphere of steam and CO, a deterioration of the mechanical properties was observed. This is due to the formation of CaCO3 (aragonite) via the reaction with CO, but also Ca(HCO2)2 (calcium formate) through a reaction with steam and CO2 (Equation 17). Calcium formate, a white material with a fibrous and flaky aspect, was observed to form on the surface of the castable. Furthermore, it has been demonstrated that steam can leach calcium from the cement at 199 °C and 30.6 atm. The reaction of the bonding phase to form CaCO3 and Ca(HCO2)2, together with the leaching of calcium, conduces to a decrease in strength. The tests were carried out for a maximum period of 18 days, but it can be predicted that with continued exposure the attack of the bonding phase would severely compromise the integrity of the material. [277,295]

*Equation 17*

**3.1.8 Phosphate-bonded refractories**

Diverging results have been described in the literature regarding the effect of steam on the mechanical properties of phosphate-bonded materials. Ballard and Day carried out trials in a steam-CO atmosphere at 199 °C and 30.6 atm, and compared fired alumina having a ceramic bond with a phosphate-bonded alumina castable. Whereas the ceramic bond degraded leading to a 30% decrease in flexural strength, no reactions were detected that involved the AlPO4 bond phase. It was therefore concluded that phosphate bonding provides adequate corrosion resistance for refractories under water vapor atmospheres. [352] On the other hand, Lang observed a considerable decrease in MOR for a phosphate-bonded ramming mix exposed to pure steam or steam-hydrogen atmospheres at temperatures from 260 to 538 °C and pressures between 25.5 and 68 atm. In pure steam conditions, the MOR decreased as the total pressure went up, and saturated steam was the most damaging. However, no new phases were detected, and it is proposed that the phosphate bond could be weakened by either a dissolution or a hydration mechanism. [137]

1. **Conclusion and challenges**

Hydrogen will play a critical role in the decarbonization of the steel industry, either as a reducing agent to transform iron ore into metallic iron and later steel, or as a fuel to power the high-temperature furnaces used in steelmaking. Processes that have been in place for decades are now set to change, and refractory materials need to withstand the modified operation conditions in the long term. Various installations could be affected, including the blast furnace and direct reduction units where hydrogen can be injected (up to 100% in the latter case), steel ladles which could be preheated with H2, the EAF if it is charged with DRI or has H2 as an auxiliary fuel, and towards the end of the steelmaking process the reheating furnaces for hot rolling, which can also be fueled by hydrogen. In addition, equipment which are not yet in use or have a very limited reach could become important and bring new challenges, such as the HPSR furnace, the flash reactor, and the smelter.

Compounded with thermal and mechanical solicitations, continuous corrosion could constitute an important factor of degradation in most of the aforementioned processes. The refractory lining will be subjected to chemical stresses, originating from the surrounding or penetrating gas. In the case of hydrogen-based DRI or H2 injection in the BF, the presence of vast amounts of fast-flowing hydrogen in the vessel could bring about the volatilization of refractory compounds, and the water generated as a result of iron reduction could also affect the lining. As for the fuel application, the high efficiency of modern burners means that only minor amounts of hydrogen will escape and reach the interior of metallurgical vessels, therefore hydrogen corrosion should not constitute a significant issue. On the other hand, the combustion of hydrogen will generate large amounts of water vapor, which could degrade the refractory lining via the formation of multiple volatile hydroxides at high temperatures, or at lower temperatures by means of forming solid hydroxides or inducing phase changes.

The compiled studies unequivocally show that material selection is important for hot hydrogen applications. Refractories may volatilize under hydrogen atmospheres, and both experimental evidence and thermodynamic simulations show that refractories differ in their ability to withstand H2 corrosion. Silica may volatilize at relatively low temperatures, while alumina and zirconia will likely provide long-term stability to the refractory lining. Aluminosilicates such as fireclay and mullite could potentially be a good compromise, especially if the total silica content is kept low. Bauxite and zircon may also be contenders depending on the operating conditions, and MgO should be considered only if required for compatibility with basic slags, given its susceptibility to both reduction and hydration. Higher purity levels are desirable, as impurities may be reduced and segregate in the material – especially Fe2O3, TiO2, and P2O5. With regard to the physical properties, a better performance will be obtained with refractories of high density and low porosity, and comprising aggregates with a large grain size and low surface area. However, it remains important to better understand the reduction mechanisms, as well as the other changes that have been reported. In addition to the formation of volatile species and the accompanying weight loss, increase in porosity, decrease in density, and deterioration of mechanical properties, other effects were observed to be caused by hydrogen exposure, including phase transformations, evolution of the microstructure, impurity segregation, and the formation of oxygen vacancies. The conditions under which hydrogen-induced refractory volatilization occurs and results in adverse consequences to the lining remain unclear. In fact, it might be that under the conditions usually found in DR vessels, or in many parts of it, hydrogen will actually be innocuous. Testing temperatures in most investigations are higher than those found in actual direct reduction processes, and an increase in temperature may not only alter the rate of reaction, but also cause a switch to an altogether different corrosion mechanism, or initiate corrosion which otherwise would not take place.

Water vapor can also volatilize refractory materials at high temperatures. Those reactions, which have been found to follow linear kinetics, could potentially compromise the structural stability of the lining in the long run. However, the severity of steam corrosion is contended, as in the case of hydrogen corrosion. Even for silica, which is regarded as relatively more prone to oxidation, there is a debate as to whether prolonged exposure to steam has significant consequences. Most of the experience-based knowledge in this area has been derived from high-pressure processes, and there is a gap in knowledge for atmospheric pressures. At lower temperatures, water vapor could lead to condensation within the refractory lining, and silica has been found to have a small but non-negligible solubility in H2O. Alumina can react with water at around 200 °C to form boehmite, its mechanical properties being affected as a result. There is no consensus as to whether boehmite formation enhances or deteriorates the properties of alumina-based refractories. The hydration of MgO to form brucite at temperatures below 300 °C is well-known and severely damaging, possibly culminating in disintegration. The presence of water vapor also promotes the low-temperature tetragonal to monoclinic transformation in zirconia, leading to crack formation. Water may leach calcium from cement-bonded refractories, but could also strengthen the cement bonding by promoting further hydration.

Decades of research cast light on the heterogeneous reactions of hydrogen and water vapor with ceramics and in particular refractories. However, most of the references on this topic stem from different applications, where the set of conditions is substantially different. There is a noticeable lack of investigations concerning refractories in the context of hydrogen reduction of iron ore or H2 firing in metallurgical vessels. It is important that studies be targeted at those applications and parametrized closer to the operating conditions, as it has been demonstrated that corrosion reactions can be strongly influenced by temperature, time, pressure, flow rate, and the coexistence of other components in the gas. However, approximating the real processes in the laboratory is not straightforward – a refractory is usually expected to be in service for many years and must abide multiple simultaneous stresses. Furthermore, the chemical composition of the atmosphere should be considered in conjunction with other changes that will arise with the implementation of hydrogen, such as modified gas velocities and a different thermal profile. While available studies hint at problems that may be encountered, further investigations are required for a full understanding of the changes that refractories will undergo, the underpinning corrosion mechanisms, and the wear kinetics. Only then will it be possible to establish how refractories can reliably support the hydrogen revolution in the steel industry.

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