

Optimization of Hydrogen Utilization and Process Efficiency in the Direct Reduction of Iron Oxide Pellets: A Comprehensive Analysis of Processing Parameters and Pellet Composition

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The article deals with the H₂ consumption for different processing conditions and the composition of the processed pellets during the direct reduction process. The experiments are carried out at 600–1300 °C, with gas pressures of 1–5 bar, gas flow rates of 1–5 L min⁻¹, and basicity indices of 0 to 2.15. Pellets with different compositions of TiO₂, Al₂O₃, CaO, and SiO₂ are analyzed. The gas flow rate is crucial, with 0–10 L min⁻¹ leading to an H₂ consumption of 0–5.1 kg H₂/kg pellet. The gas pressure (0–10 bar) increases the H₂ consumption from 0 to 5.1 kg H₂/kg pellet. Higher temperatures (600–1300 °C) reduce H₂ consumption from 5.1 to 0 kg H₂/kg pellet, most efficiently at 950–1050 °C, where it decreases from 0.22 to 0.10 kg H₂/kg pellet. An increase in TiO₂ content from 0% to 0.92% lowers H₂ consumption from 0.22 to 0.10 kg H₂/kg pellet, while a higher Fe content (61–67.5%) also reduces it. An increase in SiO₂ content from 0% to 3% increases H₂ consumption from 0 to 5.1 kg H₂/kg pellet. Porosity structure influences H₂ consumption, with the average pore size decreasing from 2.83 to 0.436 mm with increasing TiO₂ content, suggesting that micropores increase H₂ consumption and macropores decrease it.

direct relevance to the efficiency and cost-effectiveness of iron production, as well as its potential impact on environmental sustainability. Steel industries are spending large efforts toward the energy and greenhouse gases reductions from the overall production route. However, there are still some challenges in hydrogen-based direct reduction that require further research and refinement. It is documented in the literature that 54.0 kg of H₂ are required stoichiometrically to completely reduce one ton of iron ore (Fe₂O₃).^[7,8] In addition, the quality of the iron ore has a strong influence on H₂ consumption during hydrogen-based direct reduction, so that the use of low-grade iron ore drastically increases consumption.^[9,10]


It is important to distinguish the role of H₂ in steel production in the different stages of production. While the electric arc furnace (EAF) primarily uses electricity

and can use hydrogen for enhanced reduction, direct reduction reactors, which often use hydrogen as a reducing agent, operate on different principles and under different conditions. The integration of H₂ has a significant impact on both the processes in terms of efficiency and emissions. In shaft reduction reactors, which typically involve the reduction of iron oxide pellets, H₂ serves as a reducing agent. As a matter of fact, H₂ interacts directly with Fe₂O₃ to produce Fe and H₂O, according to the following reaction (Equation (1)). This process is highly

1. Introduction

Solid state direct reduction represents a key process for the modern ironmaking that is crucial to meeting the growing global demand for these important materials.^[1–4] Understanding and optimizing the processing parameters involved in hydrogen-based direct reduction is critical to increasing efficiency, reducing environmental impact, and ensuring the economic viability of the steel industry.^[4–6] This importance is underlined by its

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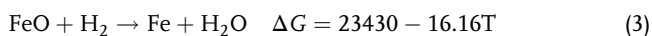
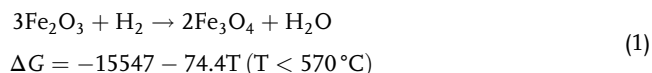
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endothermic and requires significant amounts of H₂ to maintain the reaction temperatures required for efficient reduction. The H₂ consumption in this context is directly influenced by the reaction kinetics and thermodynamics, which depend on the composition of the raw materials and the employed process parameters.^[11] In the EAF process, however, H₂ plays a different role. Although EAFs primarily use electrical energy to melt scrap or direct reduced iron, the introduction of H₂ affects the thermal dynamics within the furnace. H₂ used in burners or as part of the injectants contributes to the heat balance by providing additional heat through its combustion, even if it complicates the overall energy management due to the endothermic nature of its reactions with the residual oxides present in the feedstocks.^[12] In addition, the presence of H₂ can affect slag chemistry and the reduction of residual iron oxides, which indirectly affects the energy consumption and efficiency of EAF operation. By understanding these different roles of H₂ in both shaft reduction reactors and electric steel plants, we can better assess how optimizing H₂ consumption not only improves the energy efficiency of each process, but also contributes to the broader goal of reducing the carbon footprint in steel production. Our study focuses on optimizing the parameters in the direct reduction process to ensure efficient use of H₂. This has downstream effects on subsequent processes, such as those in the electric steel plant, thus underlining the interconnectedness of modern steel production.

It is known that the reactions in the hydrogen-based direct reduction of iron oxide can proceed in two or three stages, depending on the furnace temperature.^[13] When the temperature is below 570 °C, direct reduction of Fe₂O₃ → Fe₃O₄ → metallic iron (Fe) takes place, regardless of the type of reducing gas. At temperatures above 570 °C, Fe₃O₄ → FeO → metallic Fe. In both temperature ranges, the end product is Fe sponge with a high proportion of metallic Fe and a low proportion of FeO. The reduction of iron oxides in the presence of H₂ can be based on the following reactions:



Although H₂ is more expensive than carbon, it is a green remedy for iron oxides and outperforms CO in terms of utilization efficiency.^[14] Reducing the impact of processing costs due to hydrogen consumption, it is employed in mixing with other gases.^[15,16] However, this leads to a reduction in the reducibility of the H₂ atoms, a longer reduction time and therefore higher overall costs for the end products.

Numerous studies have investigated the influence of basicity index, gas pressure and gas temperature, as well as gas flowing on H₂ consumption during the reducing reactions.^[4,6,17–20] The results highlight the importance of maintaining an optimal basicity index for efficient reduction. In addition, when dealing with the steel production process, it is important to consider not only the efficiency of H₂ consumption, but also the basicity requirements in the subsequent EAF operations. The basicity index in the EAF plays a crucial role in the quality of the steel

produced, as it has a directly impact on the slag flowability, impurity removal efficiency, and overall energy consumption.^[1,21] While optimizing H₂ consumption is critical in reducing environmental impact and operating costs in the reduction process, ensuring adequate basicity in the electric furnace is equally important to obtain high-quality steel. High basicity enables better slag formation, which is essential for effective desulfurization and the removal of other impurities. Therefore, a holistic approach that simultaneously optimizes both H₂ consumption in the direct reduction stages and basicity in the electric steel plant is crucial. Such a solution largely improves the sustainability of the production and ensures the production of high-quality steel that complies with environmental and industry standards. Future research and process adjustments should therefore focus on developing strategies that maintain an optimal balance between these critical factors and leverage advances in process control and materials science to optimize both the upstream and downstream processes of steelmaking.

Several studies have investigated the relationship between the basicity index and H₂ consumption, but ultimately no comprehensive consensus has yet been reached on the impact of the basicity index. Some have argued that a higher baseline leads to higher H₂ consumption, while others have argued the opposite. As the direct reduction of iron oxide progresses, the interaction between gas pressure and H₂ consumption becomes more pronounced. Knowing that the basicity index is a key factor influencing the dynamic equilibrium between reactants and products. In the beginning, its influence may be small, but as the reaction progresses, the basicity index takes on a more important role and determines the course of the reduction process.^[21] At the same time, the gas pressure becomes a decisive determinant for the course of the H₂ consumption and the reaction kinetics in the direct reduction of iron oxide. The gas pressure not only determines the availability and transport of the reactants but also plays a key role in influencing the thermodynamics of the reduction process. The synergy between the basicity index and the gas pressure becomes particularly clear when the reduction is continued. The basicity index with its evolving effect and the gas pressure with its dynamic role in regulating the reaction media interact to determine the efficiency and selectivity of the direct reduction process. It has also been reported that higher gas pressure generally leads to lower H₂ consumption during the DR process. However, the discussion about the optimal pressure that leads to maximum reduction is still very hot. However, too high a gas pressure can produce inverse effects on the swelling behavior of the pellets.

The effects of gas flow rate on H₂ consumption in the hydrogen-based direct reduction of iron oxide pellets have been documented in various research results. Some studies suggest that increased gas flow rate can reduce H₂ consumption, while other studies present opposite results and indicate higher H₂ consumption at higher gas flow rates. A major factor contributing to these different observations is carbon deposition, which can significantly affect H₂ efficiency in the reduction process. At high gas flow rates, there is a risk of insufficient contact time between H₂ and the iron oxides, leading to suboptimal reduction conditions and carbon deposition.^[22] This deposition usually occurs when the CO present in mixed gas scenarios interacts insufficiently with the iron oxide, leaving unreacted CO that can be deposited as carbon on the surface of the pellets.^[19,20]

While our discussion focuses on H_2 as the primary reductant, the carbon deposition phenomena provide important insights into the complexity of mixed gas reduction processes utilizing both CO and H_2 . Furthermore, unintentional carbon deposition can act similarly to the intentional carburization that is often targeted in the cooling zones of shaft reactors. However, in the context of our study, such deposition is undesirable as it creates a barrier that hinders the access of H_2 to the surface of the iron ore, increasing overall H_2 consumption and decreasing process efficiency. Furthermore, operation at lower temperatures can exacerbate this problem as the reaction kinetics slow down and it becomes more difficult for H_2 to overcome the activation energy barrier required for effective iron oxide reduction, further increasing H_2 demand.^[22] To overcome these challenges, optimization of gas flow rates and careful control of operating temperatures are critical. Such optimizations can minimize unintended carbon deposition and increase the overall efficiency of the H_2 reduction process, ensuring better use of resources and improving the environmental sustainability of iron production.

Various studies have investigated different pellet compositions, including variation in iron oxide content, noniron oxides, etc.^[23–26] Experimental observations have shown that the presence of impurities such as nonferrous oxides significantly improves the reduction kinetics, which can directly affect the amount of H_2 consumption during the direct reduction process.^[26,27] It is important to point out that the obvious discrepancy arises from the different roles played by the quality of the iron ore and certain impurities in the reduction process. Low-grade iron ores usually have higher contents of impurities such as SiO_2 , Al_2O_3 , and phosphorus, which do not actively participate in the reduction reaction and can increase the overall H_2 consumption due to their diluting effect on the reactive iron oxide content.^[9,10] This increase in H_2 consumption is primarily due to the fact that more energy (in the form of H_2) is required to reduce the same amount of iron from a larger mass of ore in which the Fe content is lower due to these impurities.^[26,28,29] On the contrary, it has been observed that certain specific nonferrous oxides, which may be present as impurities in the ore, catalyze the reduction process.^[26] In contrast to SiO_2 or Al_2O_3 , these oxides such as TiO_2 (in a certain content^[5,30,31]) can facilitate the reduction kinetics by opening up alternative pathways or increasing the reactivity of the iron oxides. This can lead to a reduction in the amount of H_2 required per unit of reduced iron as the reaction proceeds more efficiently. Furthermore, the efficiency of H_2 utilization is closely correlated with the kinetics of the reduction reaction.^[27] Indeed, the faster reduction kinetics due to the presence of nonferrous oxides has a significant impact on the potential for more efficient utilization of H_2 in the hydrogen-based direct reduction. Studies have shown that higher gas temperatures generally lead to lower H_2 consumption.^[1,14] The high-temperature conditions in the H_2 reduction process must be carefully managed to prevent sintering and possible reoxidation of the iron pellets. The main problem at high temperatures is not the oxidation of the iron oxide, but the reoxidation of the reduced iron, especially if there is insufficient H_2 supply or if oxidizing agents such as steam or oxygen are accidentally added.^[23,32] This reoxidation can occur if the protective H_2 atmosphere is impaired or if the H_2 flow is insufficient to counteract the penetration of air or other oxidizing agents.^[23] In addition, high temperatures can lead to

sintering of the pellets, which reduces porosity and compromises mechanical integrity and the reactive surface area available for reduction.^[33,34] Both sintering and reoxidation can significantly affect the quality of the final product. In addition, Qiu et al.^[1] recently developed a nonlinear programming model for a H_2 direct reduction (HyDR) furnace based on mathematical programming to study gas utilization and consumption. The basic route optimized with this solution showed that efficiency was improved by 26.7%, hydrogen utilization was reduced by 906.34 $m^3/t-DRI$, and exergy balance was reduced by 8.8 GJ/t-DRI. However, the lack of consideration of reaction kinetics and gas sources was recognized as a certain knowledge gap for their research work.

According to the authors' findings,^[4,6,20,24,25,28,35,36] the relationships between the basicity index, the gas flow, the gas pressure, the gas temperature, and the pellet composition are very complex due to the influence of various parameters on each other and can significantly influence the H_2 consumption during the direct reduction process. This in turn contributes significantly to the energy consumption and overall costs of the direct reduction process. Since there is no comprehensive and common understanding of the individual contributions of these parameters, developing effective strategies to minimize H_2 consumption and maximize the efficiency of the reduction process is a major challenge. Understanding how processing parameters and pellet composition affect H_2 consumption will not only help to control H_2 consumption as the main limiting parameter of hydrogen-based direct reduction technology, but also the ability to control other by-products, especially carbon dioxide production, in line with international agreements is of interest.

To solve this dilemma, the present work aims to comprehensively investigate the effects of the main processing parameters, namely basicity index, gas flow, gas pressure, and gas temperature, as well as the composition of iron oxide pellets, on H_2 consumption in the direct reduction of iron oxide pellets. To this end, the following three main objectives are pursued in this article: 1) Investigation of the influence of the basicity index on H_2 consumption in the H-DRI. 2) Analysis of the influence of process parameters such as gas flow rates, gas pressure, and gas temperature on H_2 consumption and reduction performance. 3) Investigation of the correlation between the composition of iron oxide pellets and H_2 consumption.

This manuscript presents a comprehensive investigation of the interaction between different processing parameters and the composition of raw materials on H_2 consumption during DRI processing. In contrast to previous studies, which often focused on isolated parameters, this work systematically investigates the combined effects of gas flow rate, gas pressure, temperature and pellet composition, including TiO_2 , Al_2O_3 , CaO, and SiO_2 . Furthermore, quantitative insights into H_2 consumption over a wide temperature range (600–1300 °C) as well as a detailed analysis of pore structure influences are provided. This holistic approach not only provides a deeper understanding of the reduction process but also suggests practical strategies to optimize H_2 utilization, thus contributing to both energy efficiency and environmental sustainability in iron and steel production. The knowledge gained from this study can pave the way for the development of advanced process control strategies and the design of customized iron oxide pellets, thus contributing to sustainable and environmentally friendly iron and steel production.

2. Experimental Section

Vale (Brazil) provided the source material. The material was produced following the procedure indicated in.^[23] The chemical composition of the pellets was obtained from the average taken over twenty measurements; the results are summarized in Table 1. More precisely, each row in Table 1 corresponds to the average composition of 20 pellets from the same preparation batch. The selected pellets were spherically shaped; the mean diameter was in the range 1–2 cm (Figure 1a), density range between 3600 and 5200 Kg m⁻³ and specific surface ranging of 1500–1600 cm² g⁻¹. At this point, it should be noted that the number of pellets shown in Figure 1a is a random number and only the number of pellets shows their geometry and appearance. The average pellet density was derived from seven different measurements. The average diameter was obtained and the weight of each individual pellet was subsequently measured, obtaining the most precise result possible. The direct reductions were carried out in an experimental reactor developed in our laboratories (Figure 1). Noting this point is necessary that the pellets examined here have an almost spherical shape, as can be seen in the tomographic images (Figure 1a). While the influence of composition, temperature, and structural changes on H₂ consumption during H₂ direct reduction is the focus of our investigation, the geometry of these pellets is crucial for understanding the heat transfer dynamics within the furnace. In vertical shaft furnaces, the pellets are arranged in layers and form a bed through which the gasses flow during the reduction process. Variations in pellet packing and density can lead to irregularities in the heat distribution in the bed, affecting local temperature gradients and the subsequent reaction kinetics. Controlling these dynamics is considered essential for optimizing process efficiency and warrants further investigation into the thermal behavior of pellet beds in industry.

The pellets were reduced in the temperature range of 600–1300 °C. This wide temperature range of 600–1300 °C was chosen to comprehensively investigate the effects of temperature on H₂ consumption during the direct reduction process. While it is known that temperatures below 900 °C are usually sufficient

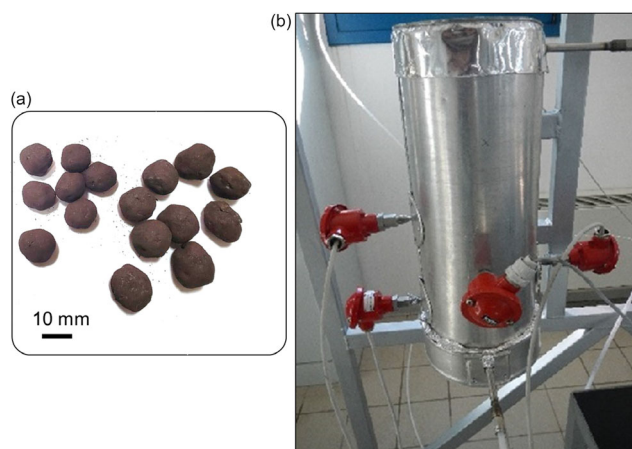


Figure 1. a) Pellets employed in the present study, b) self-designed shaft furnace.

for hydrogen reduction, the inclusion of higher temperatures was intentional. Higher temperatures can improve the reaction kinetics and potentially shorten the overall reduction time. In addition, operating at a wider range of temperatures allows the thermal stability and mechanical properties of the pellets to be investigated under different conditions. This comprehensive approach ensures that the study covers the full range of operating conditions that may be encountered in the industry. This will provide a more solid understanding of the reduction process and enable the optimization of parameters for maximum efficiency. The gas composition was 100% H₂, 50% H₂ + 50% N₂ with pressures 1–5 bar. The flow of the reducing agent was varied in the range 1–5 L min⁻¹; the basicity index of the reduced pellets fell within the range of 0.2–1.5. Three tests were carried out for each condition to ensure the reproducibility of the result.

The pore structure before and after direct reduction was analyzed by micro tomography using the instrument Phoenix v/tome/x s (General Electric).^[23,37,38] The XCT analyzes were performed with a voxel size of 10 μm, which was set based on a trade-off between image resolution and scan time. This setting allowed the detection of features down to about 20 to 30 μm, considering that the minimum detectable pore size is generally about 2 to 3 times the voxel size. These specifications are critical for accurately quantifying and analyzing the porosity and structural changes within the iron ore pellets under different experimental conditions. Understanding these limitations is fundamental to the interpretation of the XCT data, particularly in evaluating the effectiveness of the reduction process and the effects of different gas compositions and basicity indices on pellet structure. Pore segmentation was performed with the help of free software FIJI/ImageJ. A lower limit was visually determined where some pores were not selected, and an upper limit, where pores that have not been previously filled can be selected. The threshold (maximum or minimum) can be fixed for all sample layers. Determining the threshold is important, because it has a great impact on obtaining the porosity percentage of iron ore pellets.^[23] The reduction curves (percentage of reduction versus time to reduction) were used to calculate the kinetic constants and reduction rates as described in the next section. The role

Table 1. Composition of charging pellets, wt%.

Fe ₂ O ₃	Total Fe	CaO	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	Basicity (CaO/SiO ₂) index
89.5	62.5	2.6	0.7	1.2	5.7	0	0.4
96.6	67.2	1	0.0	0.5	1.7	0.0	0.5
95.3	68.2	0.2	0.3	0.3	3.6	0	0.0
100	70	0	0	0	0	0	0
97.2	67.5	1.6	0.0	0.3	0.7	0.0	2.1
96	61	1	1	0	2	0	0.5
96.6	67.5	0.1	0.1	0.2	2.6	0	0.0
97.6	68.5	0.4	0.1	0.0	1.7	0	0.2
97.0	68	0.7	0.5	0.4	1.0	0.1	0.6
96.8	67.5	0	0	0.7	1.5	0.9	0
98.1	68.1	0.0	0.0	0.4	1.2	0.0	0.0
96	67.2	1.0	0.6	0.3	1.9	0	0.5

of hydrogen in enhancing reaction kinetics has been specifically highlighted.^[24] The reduction kinetics are influenced by the pellet composition and porosity.^[23] As a matter of fact, initially, reduction rate is controlled by temperature and subsequently by pellet physical properties.^[25,39]

The H₂ consumption in this study refers to the amount of hydrogen gas required to reduce various iron oxides to metallic iron in the direct reduction process. H₂ consumption is measured in kilograms (kg) of hydrogen per ton of reduced iron ore (kg H₂/ton-Fe) to provide a standardized unit for comparison and optimization. To illustrate this, a hypothetical scenario is considered in which 500 kg of iron ore (initially in the form of Fe₂O₃) is to be reduced in a reactor. The stoichiometric calculations based on the sequential reduction reactions as shown in Equation (1)–(3). These reactions represent the stepwise reduction of iron from its highest oxide state namely Fe₂O₃, to Fe, each of which requires hydrogen and produces water as a by-product. To completely reduce one ton of Fe₂O₃ to Fe via the intermediate oxides Fe₃O₄ and FeO, 54 kg of H₂ are required. The H₂ consumption for 500 kg Fe₂O₃ would therefore be calculated as follows:

$$\text{H}_2 \text{ consumption} = \left(\frac{54 \text{ kg H}_2}{1000 \text{ kg Fe}_2\text{O}_3} \right) = 27 \text{ kg H}_2 \quad (4)$$

However, the actual H₂ consumption could be higher due to process inefficiencies such as incomplete reactions or thermal losses, which are typical in industrial scenarios.^[40]

All experimental results were processed using multiobjective optimization software in such a way as to identify the effect and weight of each process variable on a given final output.^[23,24,41,42]

Physical and mathematical functions are introduced here that represent the reduction process. The data flow contains all input parameters namely apparent density, basicity index, gas flow, gas pressure, gas temperature, total Fe (TFe), Al₂O₃, CaO, MgO, SiO₂, and TiO₂ content, that were experimentally optimized through the employment of a commercial multiobjective optimization tool (modeFrontier). These were used to define the so-called scatter matrix, in which the weight of each input on the variation of a given output is immediately defined numerically between -1 and +1. If the correlation factor is -1, this means that the input and output are perfectly inversely proportional. On the contrary, if the correlation factor is +1, the input and output are directly proportional.

The contour plots presented in this manuscript were created using OriginPro software. In particular, three columns of experimental data were used for each plot. The contour plots were created using the “contour-color-fill” type via the plot menu in the OriginPro software. This methodology ensures a comprehensive representation of the experimental data and facilitates the visual interpretation of the dependencies between the different variables.

3. Results and Discussion

3.1. Overview of H₂ Consumption and Efficiency

In the present study, the terms H₂ consumption, H₂ consumption rate, and efficiency of the reduction process were used to evaluate the interaction of processing parameters and pellet

composition on H₂ consumption. The term H₂ consumption refers to the total quantity of H₂ gas utilized during the direct reduction process of iron oxide pellets, and it is reported as the specific consumption, that is, the amount of H₂ used per unit of pellet. In the other words, in this study, the overall quantity of H₂ required for the complete reduction of the pellets. The H₂ consumption rate is defined as the rate at which the H₂ gas is consumed, which indicates the efficiency and kinetics. The efficiency of the reduction process is the effectiveness of converting iron oxide into metallic iron while minimizing H₂ gas consumption. To achieve this efficiency, temperature, basicity index, pellet composition, and density must be taken into account. The aim is to find optimal conditions that maximize efficiency while minimizing the consumption of H₂ gas in order to contribute to the development of advanced process control strategies in the iron and steel industry.

The need for H₂ in the production of DRI is related to the chemical equilibrium of oxygen and hydrogen. However, in order to achieve the required reduction temperatures, the hydrogen must be partially combusted, which increases the total demand for H₂. This partial combustion is necessary to maintain the endothermic reaction conditions. Furthermore, it is difficult to achieve 100% gas utilization due to practical limitations of the reduction process. Therefore, it is crucial to consider the efficiency of gas utilization when evaluating H₂ consumption. Our results show that the gas utilization efficiency is generally between 70% and 85%, depending on the specific operating conditions and the composition of the pellets. This efficiency range implies that additional H₂ is needed beyond the stoichiometric equilibrium to ensure adequate reduction. In this context, a key strategy to optimize H₂ utilization is the reuse of top gas.^[43–45] By reintroducing a portion of the top gas into the reduction process, the efficiency of H₂ utilization should be maximized. This recycling approach serves a dual purpose. First, it helps to maintain a favorable environment for the reduction reaction and ensures that unconverted H₂ is used effectively in subsequent reduction cycles. Secondly, it reduces potential losses and thus increases the overall yield of the reduction process.

There is a complex relationship between the different processing conditions and the composition of the iron oxide pellets in influencing H₂ consumption. As can be seen from the scatter plots in **Figure 2** and **3**, the results obtained give an overview of the complex interaction between these factors and the effects of each one.

3.2. Influence of Processing Parameters on H₂ Consumption

From the point of view of the influence of the processing parameters, it can be seen that the H₂ consumption is mainly influenced by the gas pressure, the basicity index, and the density (directly correlated) or the temperature of the reduction process (inversely correlated). The influence of non-oxidizing oxides on H₂ consumption is mainly affected by TiO₂, Al₂O₃, then CaO (direct correlation) and MgO (indirect correlation). Moreover, H₂ consumption is mainly affected by gas temperature and total iron content in the pellet (with inverse proportionality), as shown in **Figure 4**. Obviously, H₂ consumption is strongly dependent on density and temperature, so that it increases with increasing

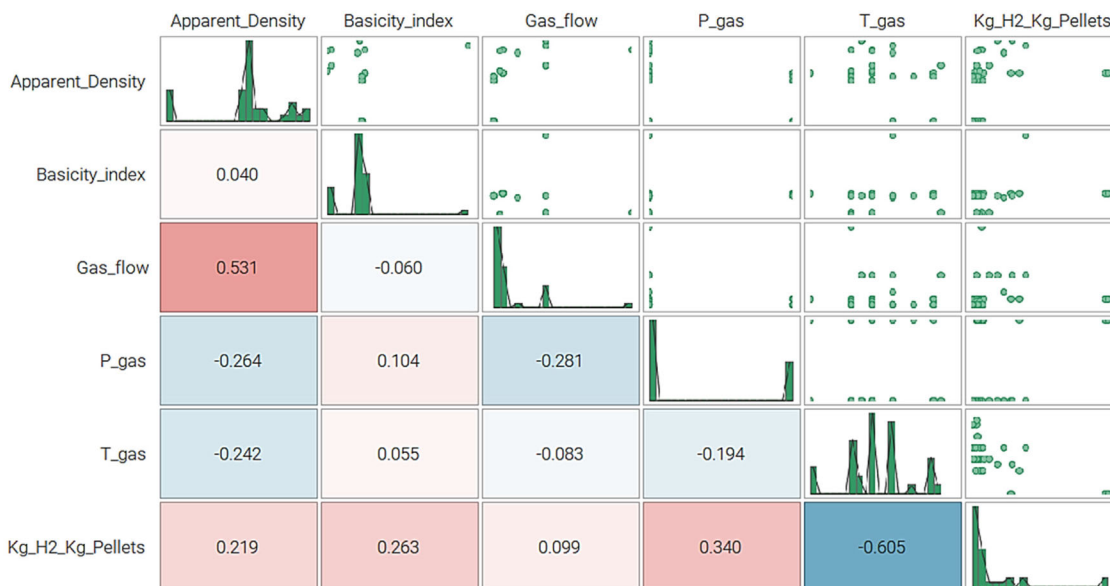


Figure 2. Scatter matrix relative to the H₂ consumption under different processing conditions.



Figure 3. Scatter matrix relative to the H₂ consumption under different non-iron oxides.

density and decreasing temperature. Pellets with higher density can reduce the gas diffusion rate and thus impair the reduction process. In particular, high-density pellets could slow down the penetration of H₂ into the pellet, resulting in slower reduction kinetics and potentially higher total H₂ consumption due to a longer process duration. The high density of the pellets means that the mass transfer of the reducing gas is restricted, which changes the reduction mechanism. The presence of layers with different phases as a result of the presence of nonferrous oxides in the industrial pellets indicates that the progress of the reaction is controlled by both the internal diffusion of H₂ and the chemical reaction. From a thermodynamic point of view, the contribution of the reducing gas and its permeability depend on the

temperature and also on the degree of porosity. From an energetic point of view, the H₂ consumption is therefore expected to depend significantly on temperature and density. Higher temperatures generally increase the reaction rate, which can lead to faster reduction and higher prompt H₂ consumption. However, a faster reaction rate could also mean a shorter overall process duration, which could lead to a lower overall H₂ consumption.

The graph in Figure 5 shows the H₂ consumption as a function of pressure and temperature. The use of H₂ as a reducing gas influences the H₂ consumption, which largely depends on its purity and pressure. It can be seen that H₂ consumption increases with increasing pressure, suggesting a direct

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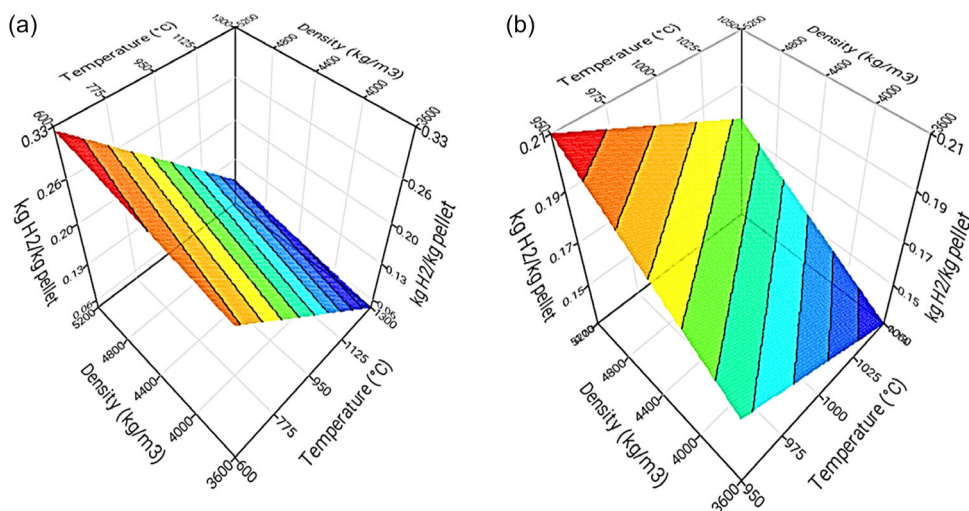


Figure 4. H₂ consumption as a function of density of the pellets and reduction temperature in H₂ atmosphere, a) at temperature range 600–1300 °C, b) 950–1050 °C.

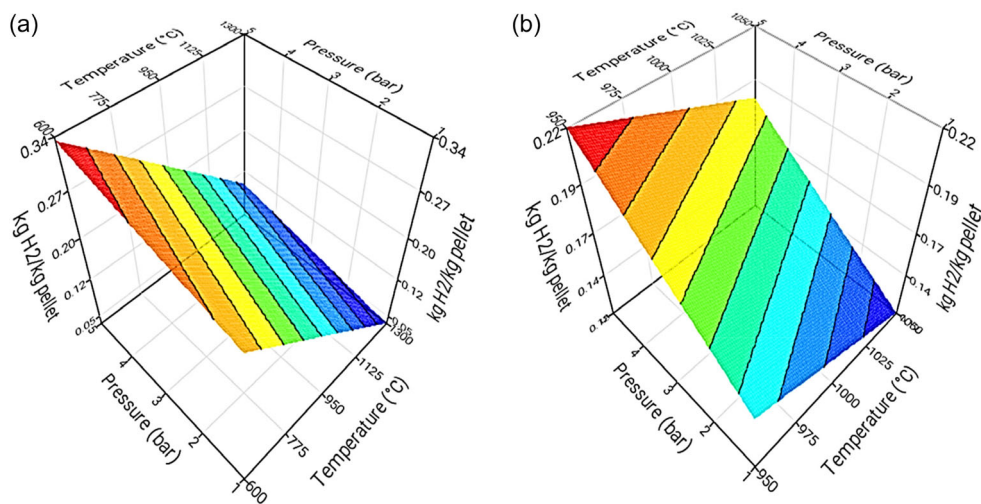


Figure 5. H₂ consumption as a function of pressure and reduction temperature in H₂ atmosphere, a) at a temperature range of 600–1300 °C, b) 950–1050 °C.

relationship between pressure and reaction rate in this particular context. A high-purity H₂ atmosphere could improve the reduction process and possibly reduce the total H₂ consumption. In direct reduction with H₂ as the reducing gas, pressure can significantly affect the rate and efficiency of the reaction. At higher pressure, the gas molecules are forced closer together, which can increase the frequency of collisions between H₂ and iron oxides.^[46,47] This can lead to a higher reaction rate and potentially higher H₂ consumption. However, high pressure can also increase the risk of harmful high-temperature reactions such as sintering or even explosion.

3.3. Effect of Non-Iron Oxides on H₂ Consumption

The plot given in **Figure 6** shows the H₂ consumption as a function of the gas flow and the reduction temperature in an H₂

atmosphere. In general, as the flow rate of H₂ gas increases, the availability of H₂ at the reaction site also increases.^[48] While a higher flow rate increases the reaction rate due to the availability of more hydrogen, it is important to balance this with the actual reduction demand. This helps to avoid excess hydrogen flow, which does not contribute to the reduction but is counted toward the total H₂ consumption. At lower flow rates, mass transfer is more likely to limit the availability of H₂ at the reaction sites, decreasing the reduction rate and consequently the H₂ consumption. Our results have shown that there is a saturation point at which a further increase in flow rate does not lead to a significant increase in H₂ consumption, as the reaction is limited by factors other than gas availability, such as reaction kinetics or heat transfer. Furthermore, at high temperatures a lower flow rate may be sufficient to maintain high reaction rates, while at lower temperatures a higher flow rate may be required to

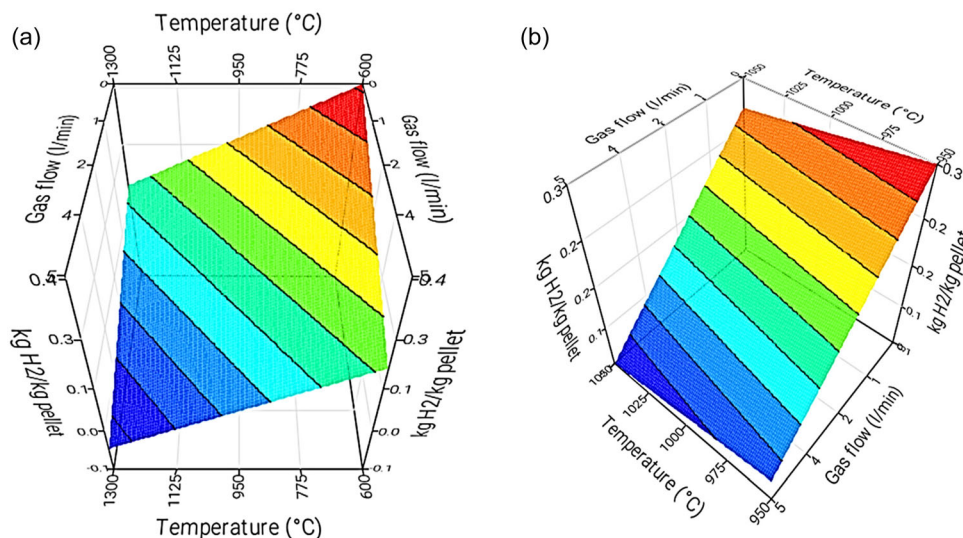


Figure 6. H₂ consumption as a function of gas flow and reduction temperature in H₂ atmosphere, a) at temperature range of 600–1300 °C, b) 950–1050 °C.

achieve similar H₂ consumption. Thus, there is an optimal range of gas flow and temperature that maximizes the efficiency of H₂ consumption.

3.4. Temperature and Basicity Index

The relationship between the basicity index, temperature, and H₂ consumption is an important factor in various industrial processes. In **Figure 7**, the contour plot illustrates the different H₂ consumption at different temperatures and basicity indices during the HyDR process. The color gradient from blue to red represents a scale with increasing H₂ consumption. The plot shows different colored areas, each representing a specific range of H₂ consumption, with the red area indicating high H₂ consumption and the blue area indicating low consumption. As a matter of fact, it is noteworthy that a lower H₂ consumption

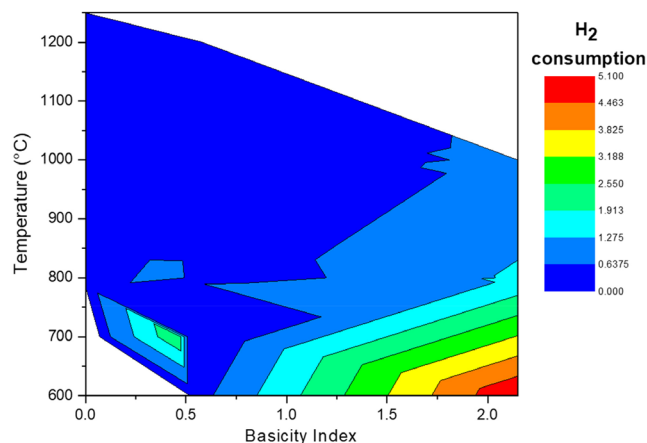


Figure 7. Contour plot of H₂ consumption as a function of basicity Index, and temperature during HyDR process. The unit of H₂ consumption is kg H₂/kg pellet.

is observed especially at lower temperatures in a wide range of basicity indices. However, a local increase in consumption can be observed especially at medium temperatures (700–800 °C) and higher basicity indices (around 1.5 to 2.0). The graph highlights critical regions where adjustments in temperature and basicity could optimize H₂ consumption. Also, the results show that for a 100% H₂, an increase in temperature leads to a decrease in H₂ consumption. In other words, there seems to be a certain temperature or temperature range at which H₂ consumption, and therefore theoretical energy consumption, can be reduced and energy saving targets achieved. In this context, Cavaliere et al.^[21] have emphasized that temperature is a key factor, with higher temperatures leading to faster reductions. At high temperatures, the kinetic energy of the molecules increases, leading to more collisions between the reacting particles. This increased frequency of collisions significantly breaks the chemical bonds in the iron oxide and enables a faster reduction process. Furthermore, the clear demarcation between the colors shows that there are certain conditions in the combination of basicity index and temperature where the H₂ consumption changes significantly. From this, it can be deduced that in a certain temperature range, a variation of the basicity index could lead to a more efficient reduction process where less H₂ is consumed. While higher temperatures generally lead to higher reaction rates, the basicity index can also change the overall reduction kinetics and efficiency.^[21,23,30,49,50] Reported results have shown that in some cases an optimal basicity index can reduce H₂ consumption during the HyDR process. This is probably due to facilitating and improving the separation of impurities. However, too high or too low basicity can have negative effects on H₂ consumption and the reduction process.^[50,51]

The H₂ consumption is mainly influenced by the gas temperature and basicity index, as shown in **Figure 8**. As shown in **Figure 8** the interplay between basicity index and reduction temperature can significantly affect H₂ consumption. For instance, under high temperatures, a too high basicity index led to

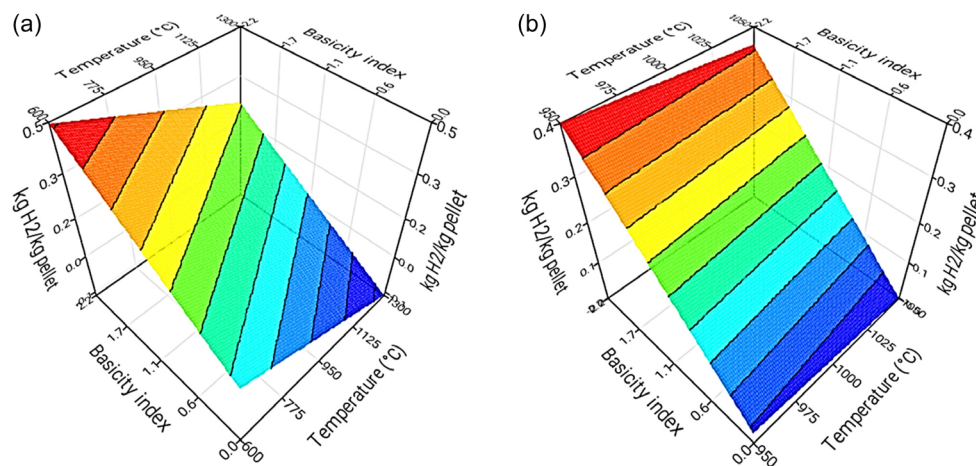


Figure 8. H₂ consumption as a function of basicity index and reduction temperature in H₂ atmosphere, a) at temperature range 600–1300 °C, b) 950–1050 °C.

sintering or fusion of materials, which could negatively impact the reaction kinetics and thus H₂ consumption. Therefore, finding the optimal combination of basicity index and reduction temperature is critical to maximize the efficiency of the reduction process and minimize H₂ consumption. In the context of the role of the basicity index in the direct reduction process, it is essential to consider its multiple effects not only on the separation of impurities but also on the initial and evolving porosity of the pellets as well as their swelling behavior.^[4,20] Indeed, the basicity index influences the initial pore structure by influencing the sintering and melting behavior during pellet formation, which in turn determines the gas permeability and reduction kinetics during the reduction process.^[4] In addition, the stabilization of the slag-forming compounds by suitable basicity can attenuate the swelling of the pellets and facilitate the physical separation of impurities within the mostly solid-phase matrix.^[52,53] These impurities form slag-like phases that either migrate to the grain boundaries or remain embedded in the pellet matrix and thus impair both the chemical purity and the physical integrity of the pellets. The optimization of basicity is therefore not only about improving the removal of impurities, but also about obtaining structural properties that enable efficient reduction and minimal H₂ consumption. Therefore, it is necessary to pay attention to the trade-off between the increased kinetics at higher temperatures and the effect of basicity on the separation of impurities, whereby a reduction in H₂ consumption and optimization of the direct reduction process can be achieved.

3.5. Impact of CaO Content and Pellet Temperature

Figure 9 shows different levels of H₂ consumption for various combinations of CaO content and temperature during the HyDR process. The image shows how changing the temperature and the amount of CaO in iron oxide pellets can affect how much H₂ gas is used when these pellets are reduced to produce iron. From one side, as the CaO content increases, it's expected that the basicity of the iron oxide pellets would also increase. As a matter of fact, the presence of CaO in iron oxide pellets can

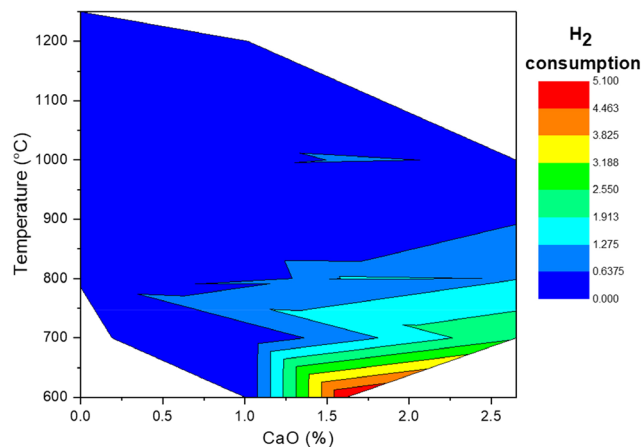


Figure 9. Contour plot of H₂ consumption as a function of CaO percentage, and temperature during HyDR process. The unit of H₂ consumption is kg H₂/kg pellet.

enhance the reduction process, potentially leading to less H₂ consumption. This is due to the fluxing properties of CaO, which can reduce the melting point of the material and thus the energy required for reduction. However, the optimal CaO content for this enhancement may be about 1 wt%, that is in line of findings in.^[54,55] However, it is important to note that if the temperature is too high, it can lead to sintering or melting of the pellets, which can be detrimental to the process.^[55] Again, it can be acknowledged that there is probably a certain range of CaO content and temperature where H₂ consumption is minimal. In addition, in the context of the fluxing effects of CaO on H₂ consumption in Figure 9, it is important to clarify the temperature conditions under which significant liquid phase formation, such as fayalite, occurs. While CaO can lower the overall melting point of the iron-silica system, temperatures of at least 1050 °C are typically required for significant liquid phase formation, including fayalite, which is above the standard operating range of many direct reduction furnaces. Although CaO

improves the reduction process and can potentially lead to lower H_2 consumption by altering slag chemistry and pellet integrity, the specific effects attributed to liquid phase formation at lower temperatures should be interpreted with caution. The contour plot in Figure 9 primarily illustrates the theoretical effect of varying CaO content and temperature on H_2 consumption without implying the formation of an extensive liquid phase within the typical temperature range of these furnaces.

3.6. Density of Reduced Pellets and Temperature

Figure 10 shows a contour plot of H_2 consumption with changes in temperature and density of the reduced pellets during the HyDR process. The density data is missing in the black zones. The correlation between these variables is complex. In general, high temperatures and porous pellet densities lead to higher H_2 consumption because the available reaction area is larger and the reaction rate increases.^[56] Conversely, lower temperatures and high density pellets tend to result in lower H_2 consumption as the reaction rate is slower and there are fewer reaction sites. More specifically, increasing the density of the pellets can have different effects on the reaction rate.^[7,57] At certain densities, an increase can increase the reaction rate as more iron oxide particles are available for the reaction. This can lead to a more efficient reduction of iron oxide to metallic iron and thus optimize H_2 utilization. However, beyond a certain density threshold, the reaction rate may decrease due to limited gas diffusion through the pellet, resulting in higher H_2 consumption.^[23,25] It can be concluded that both temperature and pellet density significantly influence H_2 consumption. The efficiency of H_2 -based reduction of iron oxide is closely linked to the interaction of these factors. High temperatures generally improve the reduction process, which can lead to lower H_2 consumption if handled efficiently. In contrast, high density pellets require careful optimization to effectively balance the reaction rate and H_2 consumption. It is crucial to consider both the temperature and density of the pellets to optimize the overall H_2 consumption during the reduction process.

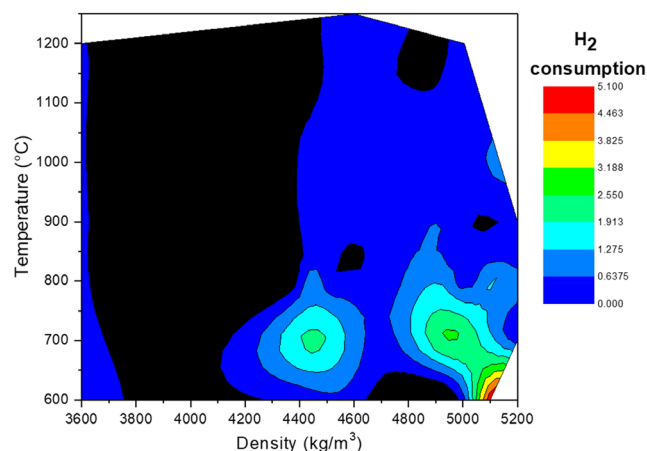


Figure 10. Contour plot of H_2 consumption as a function of density of the reduced pellets, and temperature during HyDR process. The unit of H_2 consumption is $kg H_2/kg$ pellet.

3.7. Gas Flow and Basicity Index

Figure 11 shows a contour plot of H_2 consumption as a function of gas flow and basicity index during the HyDR process. The density data are missing in the black zones. The contour plot shows areas of high and low H_2 consumption indicated by different colors. An important observation is that H_2 consumption initially increases with gas flow rate, but starts to decrease after reaching a certain threshold. This indicates that while higher gas flow rates initially provide more H_2 for the reduction reaction,^[58] too high flow rates can reduce the residence time of the gas, leading to incomplete reactions and thus lower overall H_2 consumption. The basicity index also plays an important role in H_2 consumption. In general, increasing the basicity index, that is, more basic oxides, can improve the efficiency of the reduction process and thus reduce H_2 consumption. However, beyond a certain point, a higher basicity index may no longer be beneficial and lead to increased H_2 consumption due to inefficiencies in the reaction dynamics. It can therefore be seen that both the gas flow rate and the basicity index are critical parameters for the direct H_2 reduction process. Optimizing these parameters is important to balance the efficient use of H_2 and achieve lower H_2 consumption during the HyDR process. Careful monitoring and adjustment of gas flow rates and the basicity index are necessary to ensure optimal reduction conditions and efficient H_2 utilization.^[59]

3.8. Effect of Pressure on H_2 Consumption

Figure 12 shows a graphical representation of H_2 consumption as a function of pressure in the context of the HyDR process. Typically, an increase in gas flow can lead to higher H_2 consumption as more H_2 is available for the reaction. The higher the gas flow, the more H_2 is introduced into the reaction zone. Pressure also plays a decisive role in the HyDR process. As the pressure increases, the adsorption of H_2 onto reactant particles increases. In this context, it has been reported that increased pressure leads to higher reaction rates, which could shorten the duration of

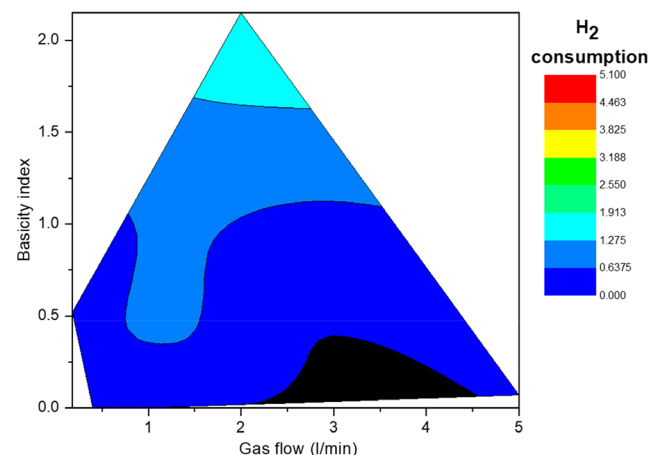


Figure 11. Contour plot of H_2 consumption as a function of gas flow and basicity index during HyDR process. The unit of H_2 consumption is $kg H_2/kg$ pellet.

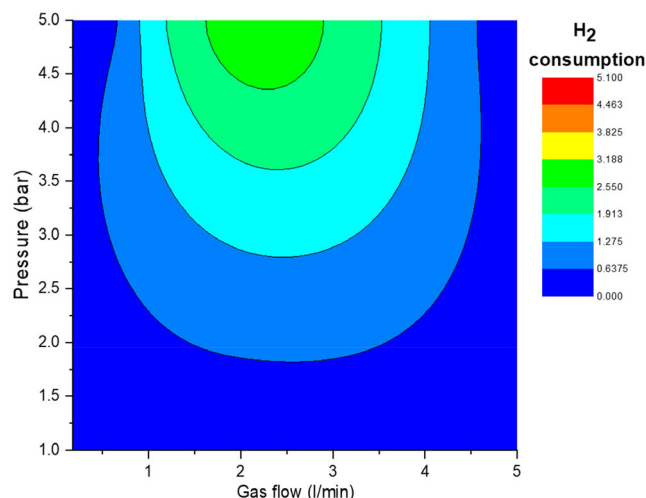


Figure 12. H₂ consumption as a function of the gas flow and pressure during the HyDR process. The unit of H₂ consumption is kg H₂/kg pellet.

hydrogen exposure required for complete reduction, which could reduce overall H₂ consumption if handled efficiently.^[60,61] However, beyond a certain threshold, the gas flow rate may be too high, leading to incomplete reactions due to insufficient residence time and thus lower H₂ consumption during the HyDR process. Lower pressure may hinder the effective adsorption of H₂ to the reactant particles, resulting in lower H₂ consumption and overall efficiency of the reduction reactions. In fact, higher pressure can shorten the time needed for complete reduction by increasing reaction rates. However, care must be taken as this can also increase the instantaneous flow rate of hydrogen, which affects the calculation of total consumption, while conversely, lower pressure could slow down the reaction rate and lead to lower H₂ consumption.

3.9. Influence of Temperature on H₂ Consumption

Figure 13 shows a graphical representation of H₂ consumption as a function of temperature during the HyDR process. The

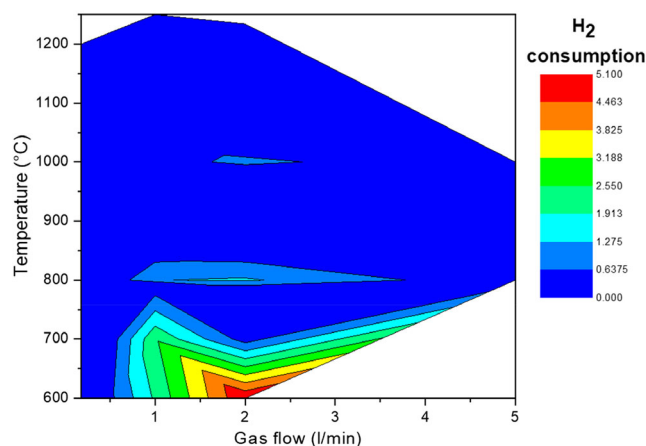


Figure 13. H₂ consumption as a function of the gas flow and temperature during the HyDR process. The unit of H₂ consumption is kg H₂/kg pellet.

observed trends indicate a complex interplay between gas flow, temperature, and H₂ consumption. When gas flow increases, H₂ consumption may also increase due to the higher availability of H₂ for the reaction. In turn, above a certain threshold, the gas flow rate might be too high, leading to incomplete reactions due to insufficient residence time and thus to a decrease in H₂ consumption per unit of reduced iron oxide. In fact, the reduction reactions at lower temperatures are chemically kinetically controlled and diffusion limitations are negligible.^[62] Overall, these results suggest that although increased pressure can improve the adsorption of H₂ and increase the reaction rate, the specific conditions and mechanisms of the reduction process are more dependent on temperature.

3.10. Effect of TiO₂ Content on Pellet Morphology and H₂ Consumption

Figure 14 shows the H₂ consumption as a function of the TiO₂ content in the pellets and the reduction temperature in an H₂ atmosphere. Obviously, both the percentage of TiO₂ in the pellets and the reduction temperature play an important role in determining the amount of H₂ consumed during the reduction process in an H₂ atmosphere. It can be observed that the influence of TiO₂ on the increase in H₂ consumption is much more pronounced when the reduction temperature is low. TiO₂ in the iron oxide pellets can influence the chemical reactions that take place during the reduction process. It is worth noting that TiO₂ can either hinder or promote H₂ consumption depending on the specific reaction mechanisms. In this context, the presence of TiO₂ can alter the physical properties of the pellets, such as their porosity or density, which in turn can affect the diffusion of H₂ and the reaction kinetics. In fact, the presence of TiO₂ more probably influenced the material swelling behavior, causing particle agglomeration, clusters formation, and a decrease in the gas permeability.^[63] Since the presence of TiO₂ probably induces swelling in the material, it could impact the available surface area for the reduction reaction.^[64] Occurring swelling create a more porous structure, potentially increasing the accessibility of iron oxide to H₂ gas. This, in turn, could affect the rate of H₂ consumption. To calculate the swelling percentage during the direct reduction of iron oxide pellets by changing the volume, the following formula can be used

$$\text{Swelling} = \frac{V_f - V_i}{V_i} \times 100 \quad (5)$$

where V_i is the initial volume of the iron oxide pellet, and V_f is the final volume of the iron oxide pellet after direct reduction. The swelling value calculated in terms of the volume changing compared to the pellet with composition TiO₂ = 0.92, Al₂O₃ = 0.7, TFe = 67.5. In order to calculate the volumes of the pellets in **Figure 15a–c**, the average diameters are first determined on three cross-sectional planes (X, Y and Z). Assuming that the pellets are spherical (based on the images where the pellets have an approximately spherical shape), the volume of each pellet is then calculated after reduction at 950 °C. The volumes given are the average values of 20 pellets under similar conditions and with similar composition. The images of the cross-sectional areas after the direct reduction process in

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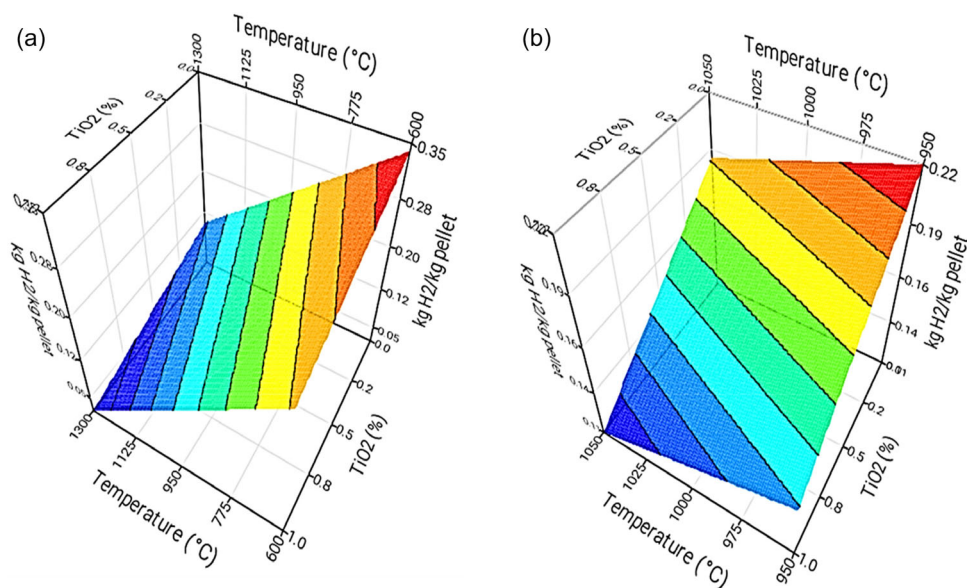


Figure 14. H₂ consumption as a function of TiO₂ percentage in the pellets and reduction temperature in H₂ atmosphere, a) at temperature range 600–1300 °C, b) 950–1050 °C.

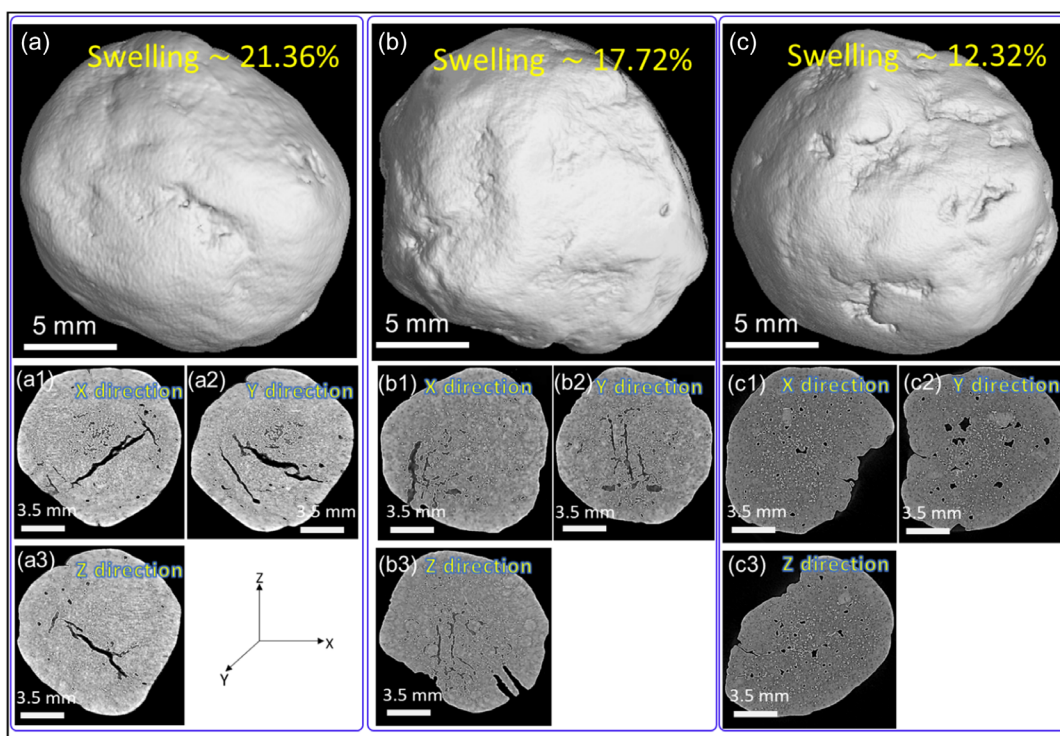


Figure 15. Tomography aspect of the studied pellets after reduction at 950 °C, with composition (wt%); a,a1,a2,a3) TiO₂ = Al₂O₃ = 0, TFe = 61; b,b1,b2,b3) TiO₂ = 0.09, Al₂O₃ = 0.53, TFe = 67.24; c,c1,c2,c3) TiO₂ = 0.92, Al₂O₃ = 0.7, TFe = 67.5.

Figure 15a1–a3, b1–b3, c1–c3 show that as the TiO₂ content is reduced, not only the pore volume increase, but the percentage of swelling also increases significantly (about 21% for the composition TiO₂ = Al₂O₃ = 0, TFe = 61). This in turn leads to the coalescence of the pores and the formation of long and large

tunnels. It is worth noting that the porosity of the pellets was in the range of 15–39%, with pore sizes varying between 9 and 20 μm. Swelling value calculated in the current study was lower than the swelling value reported by Yi et al.^[64] It is more likely that this can be explained by the dependence of reduction

on temperature and reducing gas, so that weakened swelling is likely during the HyDR process. This is consistent with the result reported in.^[64] The observed increase in pore volume and swelling with decreasing TiO₂ content, as shown in the cross-sectional images after the direct reduction process, has a direct impact on H₂ consumption. Larger pores and increased swelling contribute to changes in the structure of the material that affect gas diffusion and interaction with the iron oxide. These changes in pore properties can affect the efficiency of H₂ utilization during the reduction process, with larger pores potentially facilitating gas transport and altering the overall kinetics of the reaction. As highlighted in our study, understanding these morphological changes is critical for optimizing H₂ consumption and ensuring the effectiveness of the direct reduction process.

In addition, it is reported that TiO₂ can have catalytic properties that may either increase the efficiency of H₂ usage or alter the reaction pathway,^[63] thereby changing the H₂ consumption rate. As a result of the presence of TiO₂ in the iron oxide pellets, the agglomeration of particles and cluster formation may happen,^[65,66] which in turn, leads to a nonuniform distribution of iron oxide within the pellet. This nonuniform distribution could affect the contact between H₂ and iron oxide and thus influence the overall efficiency of the reduction process. In areas of higher particle concentration, higher H₂ consumption could occur, while in other regions reactivity could be limited. In addition, the decrease in gas permeability results in H₂ encountering more resistance when permeating the material. This decreased permeability could slow down the diffusion of H₂ into the pellet, which

affects the overall H₂ consumption during the reduction of iron oxide. It can be deduced that there is a combination of TiO₂ content and temperature that leads to the highest H₂ consumption, indicating the most active reaction conditions.

3.11. Impact of Oxides (Al₂O₃, CaO, SiO₂) on H₂ Consumption

Oxides such as Al₂O₃ and TiO₂ help to form microporosities with decreasing radius by increasing their concentration as seen from **Figure 16**. As it can see, as the total concentration of TiO₂ and Al₂O₃ increases from 0 to 0.62 and then to 1.62% (by wt%), the average pore size tends to decrease from 2.63 mm to 1.42 mm and then to 0.36 mm. In fact, the pore trend shows a decreasing tendency from the macro level to the micro level. This is consistent with the results reported in^[67] that some TiO₂ and Al₂O₃ could effectively influence the evolution of porosity during H₂-based direct reduction. The reason for this is probably the considerable solubility of these materials in Fe₃O₄ and FeO and the partial solubility limit in FeO.^[67,68]

Figure 17 shows the H₂ consumption as a function of the percentage of TiO₂, Fe, CaO, SiO₂, and Al₂O₃ in the pellets in an H₂ atmosphere. As the plotted diagrams confirm, oxides of aluminum oxide, silicon dioxide, magnesium oxide, and calcium oxide have clear and significant effects on H₂ consumption during the direct reduction process. Thus, it tends to hinder H₂ availability, possibly leading to increased consumption as a result of reduced available pathways. In contrast, CaO contributes to the formation

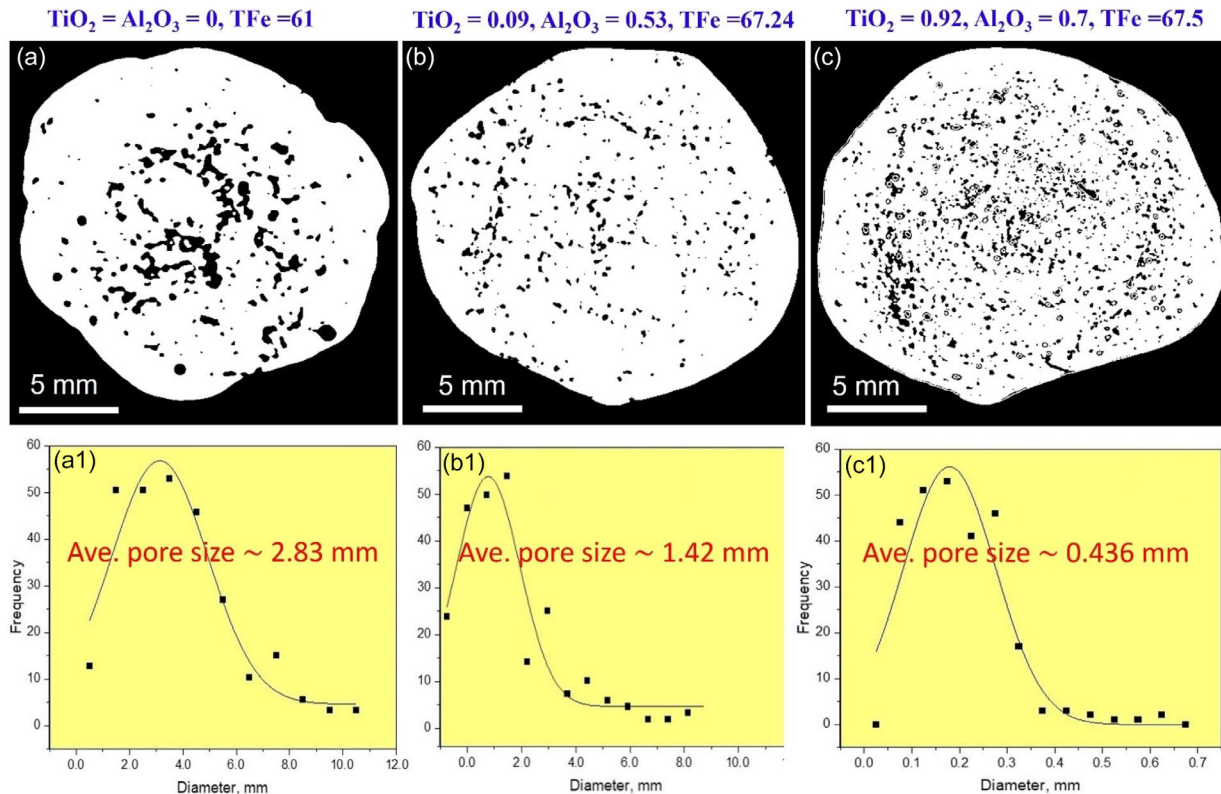


Figure 16. Cross sections of reduced pellets with composition (wt%); a,a1) TiO₂ = Al₂O₃ = 0, TFe = 61; b,b1) TiO₂ = 0.09, Al₂O₃ = 0.53, TFe = 67.24; c,c1) TiO₂ = 0.92, Al₂O₃ = 0.7, TFe = 67.5; The pore trend shows a decreasing tendency from the macro level to the micro level.

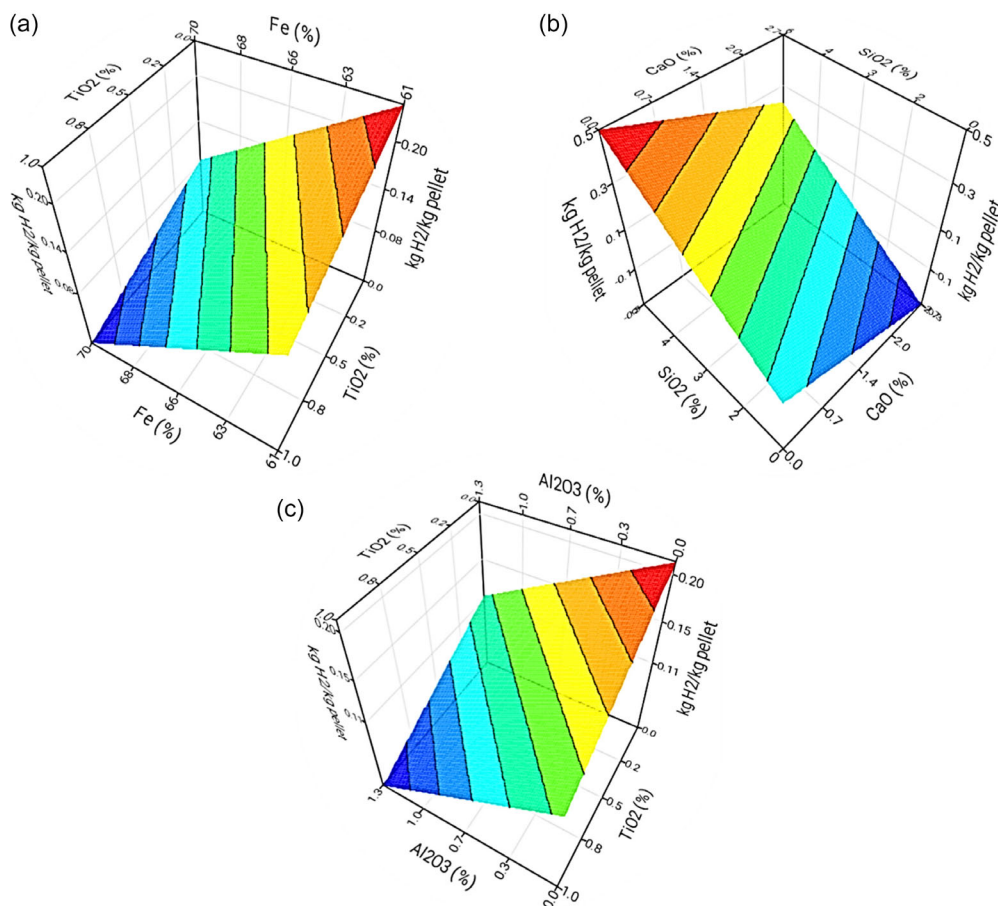


Figure 17. H₂ consumption as a function of the percentage of a) TiO₂ and Fe, b) CaO and SiO₂, and c) TiO₂ and Al₂O₃ in the pellets in a H₂ atmosphere.

of expansive porosity characterized by a gradual increase in size, indicating its potential role in enhancing gas transport. As a result, the larger porosity structure created by CaO may significantly affect H₂ consumption, as the enlarged pathways could affect the efficiency and rate of gas diffusion during the direct reduction process. In addition, SiO₂ are almost insoluble in any iron oxide and do not affect the porosity radius.^[25,67,69] This suggests that these oxides could have a negligible effect on H₂ consumption during the direct reduction process. This point is important because the purity of the pellets is directly related to the amount of H₂ consumed in the reduction process. The presence of impurities can lead to the formation of intermediate phases during the reduction process.^[70] These intermediate phases may have different thermodynamic properties, so more H₂ may be required for their reduction. Consequently, the total H₂ consumption is not only affected by the iron oxide reduction, but also by the conversion or reduction of these secondary compounds. In addition, certain compounds can act as catalysts or inhibitors from a kinetic point of view and influence the reaction rate of H₂ with iron oxide. In turn, changes in reaction kinetics can alter the overall H₂ consumption during the reduction process. In addition, impurities can change the physical and structural properties of the iron oxide pellets such that the available surface area, porosity or permeability of the pellets changes, which ultimately affects the availability of H₂ to the iron oxide.

The presence of TiO₂ in iron oxide pellets has a significant impact on the reduction kinetics and hydrogen consumption, mainly due to its influence on the microstructure of the pellet. As the TiO₂ content increases, the porosity of the pellets decreases significantly, which limits the diffusion of hydrogen gas and leads to a lower reduction efficiency. The XCT results confirm that TiO₂ leads to densification, which reduces the pore size and consequently impairs the gas permeability required for efficient hydrogen utilization. This phenomenon could be related to the formation of slag phases involving TiO₂, SiO₂ and Al₂O₃, considering the phase diagrams for the TiO₂-SiO₂ and TiO₂-SiO₂-Al₂O₃ systems.^[71,72] These phase diagrams show that TiO₂ can react with SiO₂ and Al₂O₃ at high temperatures to form stable slag compounds such as titanates and aluminosilicates, which contribute to the observed densification. The formation of such phases not only reduces porosity but also affects the overall reduction process by forming a physical barrier that slows down hydrogen diffusion and ultimately increases hydrogen consumption.

3.12. Temperature and SiO₂ Content Influence on H₂ Consumption

Figure 18 shows that the amount of SiO₂ in the pellets and the temperature at which the reduction process takes place can

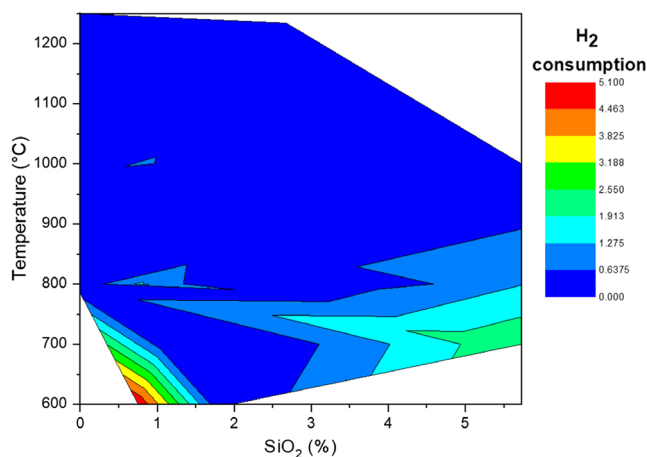


Figure 18. H₂ consumption as a function of the SiO₂ percentage and temperature during the HyDR process.

influence the amount of H₂ gas used. The contour plot reveals the complex relationship between the SiO₂ content, the temperature, and the H₂ consumption. Each contour line corresponds to a certain level of H₂ consumption. The closer these lines are to each other, the steeper the change in H₂ consumption as a function of SiO₂ content and temperature. In general, the basicity of the iron oxide pellets decreases with increasing SiO₂ content, which can slow down the reduction process and lead to higher H₂ consumption. Conversely, a reduction in the SiO₂ content can increase the reduction process and thus reduce H₂ consumption. SiO₂ could not only react with certain species and thus influence the balance of reactions involved in iron oxide reduction, but also act as a catalyst that enhances or possibly inhibits the reduction process. As the SiO₂ content increases, the basicity of the pellets decreases, which can slow down the reduction process and increase H₂ consumption.^[73] This is due to the formation of compounds such as Fe₂SiO₄, which hinder further reduction. However, the addition of SiO₂ can also enhance the direct reduction process, depending on the specific conditions and the presence of other metallic species. This could be related to the catalytic properties of SiO₂.^[74]

The role of SiO₂ in the reduction kinetics of iron oxide pellets seems to go beyond its presence as an impurity. SiO₂ is known to play a catalytic role in the reduction process, probably due to its interaction with other oxides, particularly TiO₂ and Al₂O₃, in slag formation. One of the key aspects influencing this catalytic effect is the surface tension of SiO₂ in slags. SiO₂ tends to reduce the surface tension in molten systems, which could facilitate the formation of more reactive surfaces at the pellet-gas interface. As a matter of fact, this reduction in surface tension allows for better wetting of the iron oxide by the reducing gas, namely H₂, which improves the reaction kinetics by increasing the contact between the gas and the solid phases. Moreover, the catalytic behavior of SiO₂ during slag formation can promote the separation of non-ferrous oxides from the iron oxide matrix, thus facilitating the reduction process. Consequently, the catalytic role of SiO₂ combined with its surface tension properties could be an important factor in optimizing hydrogen utilization during the reduction of iron oxide pellets.

Based on the discussed results, the H₂ consumption during the HyDR process is strongly influenced by the reduction temperature and the physical properties of the pellets. The optimization of these factors is crucial as they significantly influence the rate at which H₂ is consumed. Our results show that the reduction kinetics, which represents the overall reaction rate, is primarily influenced by the density of the pellets. This demonstrates the importance of controlling pellet density to ensure efficient H₂ utilization throughout the reduction process. Furthermore, the persistent influence of the reduction temperature emphasizes its crucial role in shaping the dynamics of H₂ consumption.

4. Conclusion

To summarize, our study investigates the critical factors affecting H₂ consumption during the direct reduction process of iron oxide pellets. Key parameters such as gas flow rate and pressure are found to be crucial and show higher consumption at higher flow rates and pressures. The following conclusions can be summarized as follows: 1) The composition of the pellets, especially the presence of non-iron oxides, has a significant effect on the porosity structure, leading to nuanced effects on H₂ consumption. 2) Micropores associated with certain oxides increase consumption, while expansive porosities, such as those associated with CaO, decrease it. 3) The interplay between basicity and temperature proves to be crucial and requires a delicate balance for efficiency and minimized H₂ consumption. a) The complex relationship between pellet density and temperature shows that higher density can lead to higher consumption despite improved reaction rates. b) The interaction of TiO₂ with SiO₂ and Al₂O₃ forms slag phases such as titanates and aluminosilicates, which reduce the porosity of the pellets and the gas permeability. This restricts hydrogen diffusion, which leads to a lower reduction rate and higher hydrogen consumption for pellets with a high TiO₂ content. Controlling the TiO₂ content is essential for optimizing hydrogen consumption in reduction processes.

The study highlights the different effects of TiO₂, Al₂O₃, and CaO on H₂ consumption and provides valuable insights for the optimization of reaction kinetics and porosity. Overall, these results emphasize the importance of a comprehensive understanding of processing parameters and pellet composition for the development of advanced control strategies aimed at improving energy efficiency and sustainability in iron and steel production.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Behzad Sadeghi: Writing—original draft, Validation, Project administration, Investigation, Funding acquisition, Visualization, Conceptualization, Data curation, Formal analysis, Conceptualization, Writing—review & editing; **Pasquale Cavaliere:** Writing—review & editing, Project administration, Funding acquisition, Validation, Conceptualization, Data curation; **Aleksandra Laskab:** Visualization, Data curation, **Angelo Perrone:** Visualization; **Leandro Dijon:** Funding acquisition, Conceptualization, Resources.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

direct reduction, H₂, optimization, pellets composition, porosity

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- [1] Z. Qiu, Q. Yue, T. Yan, Q. Wang, J. Sun, Y. Yuan, Z. Che, Y. Wang, T. Du, *Energy* **2023**, 263, 125847.
- [2] J. Zhang, J. Liu, J. Li, Y. Gao, C. Zhao, *Sustainability* **2021**, 13, 510.
- [3] F. Rosner, D. D. Papadias, K. P. Brooks, K. O. Yoro, R. K. Ahluwalia, T. S. Autrey, H. M. Breunig, *Energy Environ. Sci.* **2023**, 16, 4121.
- [4] P. Cavaliere, B. Sadeghi, L. Dijon, A. Laska, D. Koszelow, *Miner. Eng.* **2024**, 213, 108746.
- [5] P. Cavaliere, B. Sadeghi, A. Laska, D. Koszelow, *Metall. Mater. Trans. B* **2024**, 55, 3431.
- [6] B. Sadeghi, M. Najafzaheh, P. Cavaliere, A. Shabani, M. Aminaei, *Powder Technol.* **2024**, 444, 120061.
- [7] M. Shahabuddin, G. Brooks, M. A. Rhamdhani, *J. Clean. Prod.* **2023**, 395, 136391.
- [8] C. Kuhn, A. Düll, P. Rohlf, S. Tischer, M. Börnhorst, O. Deutschmann, *Appl. Energy Combust. Sci.* **2022**, 12, 100096.
- [9] M. Yellishetty, T. T. Werner, Z. Weng, in *Iron Ore*, 2nd ed., (Ed: L. Lu), Woodhead Publishing, Cambridge **2022**, pp. 711–750.
- [10] S. Li, H. Zhang, J. Nie, R. Dewil, J. Baeyens, Y. Deng, *Sustainability*, **2021**, 13, 8866.
- [11] A. Krüger, J. Andersson, S. Grönkvist, A. Cornell, *Int. J. Hydrogen Energy* **2020**, 45, 29966.
- [12] A. Bhaskar, M. Assadi, H. Nikpey Somehsaraei, *Energies* **2020**, 13, 758.
- [13] J. Oh, D. Noh, *Fuel* **2017**, 196, 144.
- [14] S. K. Kuila, R. Chatterjee, D. Ghosh, *Int. J. Hydrogen Energy* **2016**, 41, 9256.
- [15] A. Bonalde, A. Henriquez, M. Manrique, *ISIJ Int.* **2005**, 45, 1255.
- [16] P. Li, Y. Li, J. Yu, P. Gao, Y. Han, *Int. J. Hydrogen Energy* **2022**, 47, 31140.
- [17] K. Piotrowski, K. Mondal, H. Lorethova, L. Stonawski, T. Szyma, T. Wiltowski, *Int. J. Hydrogen Energy* **2005**, 30, 1543.
- [18] H. Na, J. Sun, Z. Qiu, Y. Yuan, T. Du, *Energy* **2022**, 257, 124822.
- [19] Z. Qiu, T. Du, Q. Yue, H. Na, J. Sun, Y. Yuan, Z. Che, Y. Wang, Y. Li, *Energy* **2023**, 281, 128279.
- [20] B. Sadeghi, P. Cavaliere, M. Bayat, N. Ebrahimzadeh Esfahani, A. Laska, D. Koszelow, *Int. J. Hydrogen Energy* **2024**, 69, 586.
- [21] P. D. Cavaliere, A. Perrone, D. Marsano, V. Primavera, *Steel Res. Int.* **2023**, 94, 2200791.
- [22] M. Kazemi, B. Glaser, D. Sichen, *Steel Res. Int.* **2014**, 85, 718.
- [23] P. Cavaliere, L. Dijon, A. Laska, D. Koszelow, *Int. J. Hydrogen Energy* **2024**, 49, 1235.
- [24] P. Cavaliere, A. Perrone, D. Marsano, *Powder Technol.* **2023**, 426, 118650.
- [25] P. Cavaliere, A. Perrone, L. Dijon, A. Laska, D. Koszelow, *Int. J. Hydrogen Energy* **2024**, 49, 1444.
- [26] A. Zakeri, K. S. Coley, L. Tafaghodi, *Sustainability* **2023**, 15, 13047.
- [27] Y. Iguchi, M. Inouye, *Trans. Iron Steel Inst. Jpn* **1982**, 22, 678.
- [28] G. Sun, B. Li, W.-S. Yang, J. Guo, H.-J. Guo, *Energies* **2020**, 13, 1986.
- [29] A. Heidari, N. Niknahad, M. Iljana, T. Fabritius, (Notes: MDPI stays neutral with regard to jurisdictional claims in published ...: **2021**).
- [30] J. T. Ju, Q.-D. Li, X. Xing, X. Jiang, G.-Q. Zhao, F. Lu, *Metall. Res. Technol.* **2023**, 120, 306.
- [31] R. Hu, Q.-D. Li, J.-T. Ju, X.-Y. Li, X.-R. Xiang, X.-M. Yang, *Can. Metall. Q.* **2023**, 1. <https://doi.org/10.1080/00084433.2023.2245207>.
- [32] B. Sadeghi, M. Najafzadeh, P. Cavaliere, A. Shabani, M. Aminaei, *Powder Technol.* **2024**, 444, 120061.
- [33] N. Shigematsu, H. Iwai, *Tetsu-to-Hagané* **1993**, 79, 920.
- [34] P. Metolina, T. R. Ribeiro, R. Guardani, *Int. J. Miner. Metall. Mater.* **2022**, 29, 1908.
- [35] M. Hosseinzadeh, N. Kasiri, M. Rezaei, M. A. M. Mirzaei, *Steel Res. Int.* **2023**, 94, 2300085.
- [36] B. Sadeghi, G. Fan, Z. Tan, Z. Li, A. Kondo, M. Naito, *KONA Powder Part. J.* **2022** 39, 2022004.
- [37] E. Hjortsberg, F. Forsberg, G. Gustafsson, E. Rutqvist, *Ironmaking Steelmaking* **2013**, 40, 399.
- [38] L. C. Bam, J. A. Miller, M. Becker, I. J. Basson, *Miner. Eng.* **2019**, 131, 206.
- [39] P. Cavaliere, A. Perrone, D. Marsano, *Ironmaking Steelmaking* **2023**, 50, 1045.
- [40] M. Shahabuddin, A. Rahbari, S. Sabah, G. A. Brooks, J. Pye, M. A. Rhamdhani, *Ironmaking Steelmaking: Process. Prod. Appl.* **2024**, <https://doi.org/10.1177/03019233241265179>.
- [41] P. Cavaliere, A. Perrone, A. Silvello, *J. Manuf. Process.* **2015**, 17, 9.
- [42] P. Cavaliere, A. Perrone, *Ironmaking Steelmaking* **2013**, 40, 9.
- [43] N. Hallale, F. Liu, *Adv. Environ. Res.* **2001**, 6, 81.
- [44] D. Hairston, *Chem. Eng.* **2001**, 108, 29.
- [45] X. Guo, S. Wu, J. P. Xu, K. Du, *Procedia Eng.* **2011**, 15, 4702.
- [46] Y. Nakano, M. Ishida, T. Akehata, T. Shirai, *Metall. Trans. B* **1975**, 6, 429.
- [47] N. Thüns, B. M. Krooss, Q. Zhang, H. Stanjek, *Int. J. Hydrogen Energy* **2019**, 44, 27615.
- [48] M. L. D. Vries, I. E. Grey, *Metall. Mater. Trans. B* **2006**, 37, 199.
- [49] R. K. Dishwar, O. P. Sinha, *Fuel* **2021**, 296, 120640.
- [50] D. Ernst, M. A. Zarl, J. Cejka, J. Schenk, *Materials* **2022**, 15, 4767.
- [51] I. Sohn, S. Jung, *Steel Res. Int.* **2011**, 82, 1345.
- [52] A. Heidari, V. Isteri, P. Tanskanen, T. Fabritius, *Hydrogen Reduction of LD (BOF) Slag*, Springer Nature Switzerland, Cham **2023**, pp. 855–861.
- [53] M. Naseri Seftejani, J. Schenk, D. Spreitzer, M. Andreas Zarl, *Materials* **2020**, 13, 935.
- [54] H.-B. Zuo, C.-C. Wang, J. Dong, K. Jiao, R. Xu, *Int. J. Miner. Metall. Mater.* **2015**, 22, 688.
- [55] X. Yang, Y. Xie, D. Wang, D. Huang, L. Kong, T. Yang, *J. Iron Steel Res. Int.*, **2000**, 7, 1.
- [56] W. Wang, Z.-L. Ouyang, R. Xu, X. Li, X. D. Huang, Z. Xue, *Ironmaking Steelmaking* **2018**, 45, 309.
- [57] X. Mao, P. Garg, X. Hu, Y. Li, S. Nag, S. Kundu, J. Zhang, *Int. J. Miner. Metall. Mater.* **2022**, 29, 1882.
- [58] K. V. Dobrego, N. N. Gnezdilov, S. Lee, H.-K. Choi, *Int. J. Hydrogen Energy* **2008**, 33, 5501.

- [59] P. Nikolaidis, A. Poullikkas, *Renewable Sustainable Energy Rev.* **2017**, 67, 597.
- [60] R. Takahashi, Y. Koyabu, M. Ishii, M. Ishigaki, Y. Takahashi, *Tetsu to Hagane: J. Iron Steel Inst. Jpn* **1980**, 66, 1985.
- [61] H. Y. Sohn, P. Chaubal, *ISIJ Int.* **1984**, 24, 387.
- [62] A. J. Fortini, D. D. Perlmutter, *AIChE J.* **1989**, 35, 1245.
- [63] P. E. D. Leobardo Chapa, HYL technology from HYL SAMEX, CVRD seminar, **2001**.
- [64] L. Yi, Z. Huang, T. Jiang, L. Wang, T. Qi, *Powder Technol.* **2015**, 269, 290.
- [65] T. Paananen, K. Kinnunen, *Steel Res. Int.* **2009**, 80, 408.
- [66] H. Pimenta, V. Seshadri, *Ironmaking Steelmaking* **2002**, 29, 175.
- [67] Y. Iguchi, M. Iida, M. Inoue, *Iron Steel* **1979**, 65, 24.
- [68] M. H. Jeong, D. H. Lee, J. W. Bae, *Int. J. Hydrogen Energy* **2015**, 40, 2613.
- [69] J. Yu, N. Hu, H. Xiao, P. Gao, Y. Sun, *Powder Technol.* **2021**, 385, 83.
- [70] S.-H. Kim, X. Zhang, Y. Ma, I. R. Souza Filho, K. Schweinar, K. Angenendt, D. Vogel, L. T. Stephenson, A. A. El-Zoka, J. R. Mianroodi, M. Rohwerder, B. Gault, D. Raabe, *Acta Mater.* **2021**, 212, 116933.
- [71] S. Martin-Treceno, T. Hughes, N. Weaver, A. T. Marshall, M. J. Watson, C. M. Bishop, *J. Electrochem. Soc.* **2021**, 168, 062502.
- [72] P. Wu, *Optimization and Calculation of Thermodynamic Properties and Phase Diagrams of Multi-Component Oxide Systems*, Ecole polytechnique de Montreal, Montreal **1992**.
- [73] R. Zeng, N. Wang, W. Li, *Powder Technol.* **2021**, 393, 550.
- [74] F. Ding, A. Zhang, M. Liu, X. Guo, C. H. Song, *RSC Adv.* **2014**, 4, 8930.