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Hydrogen as a Zero-Emission Fuel: An Opportunity for Energy-Intensive Industries

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Abstract

The importance of hydrogen in the context of the energy transition is particularly emphasized within the framework of the European Green Deal—the European Union's strategy aimed at achieving climate neutrality by 2050 [1]. The use of hydrogen in industry can play a key role in the decarbonization of high-temperature and energy-intensive processes, such as those in metallurgy, metalworking, foundry operations, the cement industry, coke production, the glass industry, and the manufacturing of building materials, including modular and refractory materials. Its application in these sectors enables not only the reduction of CO_2 emissions but also the modernization of technological processes and an increase in the energy efficiency of industrial plants. However, the introduction of hydrogen into existing industrial processes involves a number of technical and material challenges. It becomes crucial to understand the impact of hydrogen on the course of chemical reactions, the properties of structural materials used, and the quality of the products manufactured. Of particular importance are issues related to the interaction of hydrogen with refractory linings applied in high-temperature industrial installations. Studies indicate that hydrogen can induce corrosion processes in refractory materials, the intensity of which depends on temperature, pressure, and the duration of hydrogen exposure. The literature describes examples of refractory ceramic degradation that may lead to reduced lining durability and an increased operational risk of installations in industrial plants. In order to minimize potential risks associated with the introduction of hydrogen into existing industrial installations, research at the quarter-technical and pilot scales is essential, as it allows new processes to be safely tested without the risk of production interruptions. In this way, enterprises can assess the need for installation modifications, select appropriate materials resistant to hydrogen exposure, and develop optimal technological conditions. The implementation of such research is particularly important in energy-intensive industries, where equipment failure or production limitations may result in significant financial losses.

Keywords: Hydrogen, Zero-Emission Fuel, Refractory Materials, Hydrogen Corrosion.

Introduction

Hydrogen is a gas characterized by an exceptionally wide flammability range, from 4 to 75%, which means that its mixtures with air can easily ignite over a very broad range of proportions. Once ignited, the combustion reaction of hydrogen is a self-sustaining process, further highlighting its energy potential as well as the safety requirements associated with its use. Hydrogen also has the highest calorific value among commonly used fuels, ranging from 120 to 142 MJ/kg. As a result, it is a fuel with a very high energy density on a mass basis. The product of hydrogen combustion in the presence of oxygen is exclusively water vapor, which makes it a zero-emission fuel in terms of carbon dioxide emissions. An additional advantage of hydrogen is the characteristic of its flame. The hydrogen flame has a shape and length similar to that of a methane flame, as well as a comparable heat distribution [2]. In practice, this means that hydrogen can be used in existing industrial processes with minimal modifications to heating equipment, which may facilitate its future application in energy-intensive industries. The implementation of hydrogen as a fuel in these sectors is currently a matter not only of technology, but also of the economics of its production and availability.

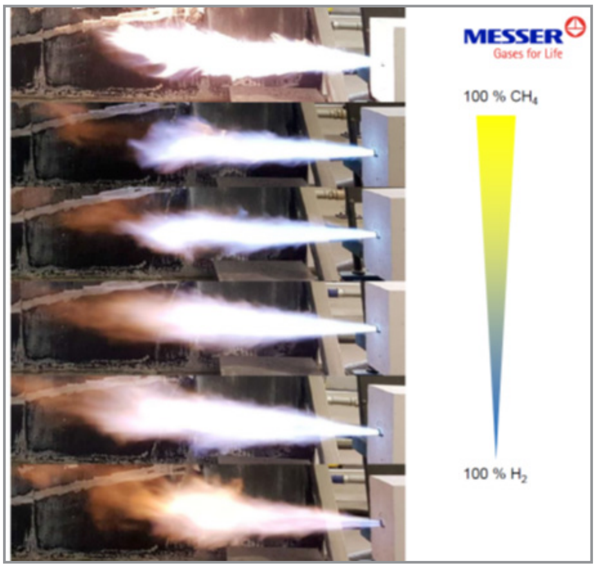

Figure 1: Flame shape and length as a function of the hydrogen content in methane [1].

In every energy-intensive industrial sector, the use of refractory materials is essential. Their primary function is to protect steel components against high temperatures, erosion, corrosion, and aggressive chemical conditions prevailing in production processes [3]. These materials make it possible to extend the service life of equipment, increase process efficiency, and ensure operational safety.

The most commonly used refractory materials in industry are aluminosilicate, high-alumina, and corundum-based materials [4]. Their main component is aluminum oxide (Al_2O_3), which provides resistance to high temperatures and mechanical strength. Each of these materials also contains silicon dioxide (SiO_2), the addition of which improves the thermal shock resistance of refractory ceramics, significantly extending their service life under extreme conditions.

However, in the context of using hydrogen as a zero-emission fuel, a significant limitation arises. In a hydrogen-containing atmosphere, the presence of silicon dioxide in refractory materials may lead to unfavorable chemical reactions, such as the reduction of SiO_2, which in turn weakens the ceramic structure and shortens its service life [5]. Therefore, the development of hydrogen-based technologies in industry requires the parallel development of new refractory materials or the modification of existing ones to ensure resistance to hydrogen exposure and high temperatures. This is currently one of the key challenges in the field of ceramic materials for the industry of the future.

The first publications on the effects of hydrogen on refractory materials at high temperatures appeared in 1966. Pioneering research in this field was conducted by, who presented a setup for studying the impact of hydrogen on ceramics. In these experiments, the author placed small samples of refractory materials in a tube furnace, which was then heated to a temperature of 2400°F (approximately 1315°C) for 50 hours in a hydrogen–nitrogen atmosphere mixed in various proportions.

As a result of the conducted studies, the author observed a significant mass loss in the tested samples, with the rate of material degradation being strongly dependent on the hydrogen concentration in the furnace atmosphere and the silicon dioxide content in the ceramics. He found that the higher the hydrogen content surrounding the samples, the greater the loss of SiO_2 in the refractory material. These results clearly indicated the reducing effect of hydrogen on silicon dioxide at high temperatures and highlighted the necessity of considering this factor when designing ceramic materials for hydrogen-utilizing industries.

In the following years, a series of studies dedicated to the corrosion of ceramics were published; however, most of them focused on the interaction of water vapor (including hydrogen) with ceramic materials and raw materials. These studies highlighted the mechanisms of chemical and thermal degradation of ceramics in the presence of moisture and high temperatures, but they did not sufficiently analyze the effect of pure hydrogen as a reducing gas on the structure of refractory materials.

Few publications directly address the interaction of hydrogen as a gas with refractory materials, indicating a significant research gap in this area. In one of the rare studies, it was noted that although the available literature describes structural and technological changes related to the design and implementation of hydrogen burners, much less information exists on the potential issues associated with the degradation of refractory ceramics in furnace lining systems [6]. These phenomena include both mass loss and changes in microstructure, thermal damage, and chemical reduction processes in the ceramic layer, which can significantly affect the durability and operational safety of the installation.

This highlights the need for systematic investigations into the interaction of hydrogen with various types of refractory ceramics, including aluminosilicate, high-alumina, and corundum-based materials, under the high-temperature conditions typical of energy-intensive industrial processes. A thorough understanding of these interactions is essential not only for optimizing the performance of refractory materials but also for the design of furnaces and heating systems capable of operating efficiently with hydrogen as a zero-emission fuel.

It is also important to note that the adoption of hydrogen as an industrial fuel affects not only energy efficiency but also significantly alters the composition of flue gases. Specifically, it leads to increased concentrations of nitrogen oxides (NOx) and water vapor in the furnace atmosphere. The presence of these components can adversely affect the properties of refractory ceramic materials, which has critical implications for the durability and safe operation of industrial installations [7].

Hydrogen negatively affects refractory materials by accelerating surface wear, intensifying chemical processes within the material, and causing local overheating of lining elements. As a reducing gas, hydrogen can react with seemingly stable oxides such as silica (SiO_2), alumina (Al_2O_3), and zirconia (ZrO_2), which are primary constituents of many industrial furnace ceramics. These reactions generate gaseous sub-oxides and additional water vapor, which can migrate with furnace gases and interact with other furnace components or the processed product. The reduction of ceramic oxides by hydrogen weakens the material chemically and accelerates corrosion, decreasing both mechanical and thermal strength [8]. Aluminosilicate materials with high SiO_2 content are particularly vulnerable, as they can be reduced to volatile silanes and other compounds, leading to mass loss and microcrack formation.

Implementing hydrogen in energy-intensive industrial processes therefore requires careful selection of refractory materials or the development of new ceramics resistant to reducing atmospheres. Strategies include using materials with lower SiO_2 content, higher concentrations of stable metal oxides (e.g., Al_2O_3, ZrO_2, MgO), and multi-component ceramics with microstructures optimized for reduction and chemical erosion resistance. Additionally, protective coatings and surface modification techniques can limit hydrogen contact with ceramics and reduce the risk of degradation.

The development and implementation of such solutions are crucial for maintaining the operational lifespan of industrial installations and ensuring process safety, while also enabling the full utilization of hydrogen's potential as a zero-emission fuel.

One of the key sectors of energy-intensive industry is metallurgy, where hydrogen has been applied as a non-oxidizing gas in direct reduction steelmaking, used in shaft furnaces. Despite extensive descriptions of the metallurgical process, the literature lacks systematic studies on the resistance of refractory materials to reduction and the mechanisms of corrosion in Al_2O_3–SiO_2 ceramics used in these installations.

Due to the limited availability of suitable research facilities that allow corrosion testing under conditions approximating the actual parameters of hydrogen-based shaft furnaces, researchers adopt a hybrid approach combining thermodynamic simulations with laboratory experiments [9]. Within these studies, authors analyze changes in mass, mechanical strength, phase composition, and microstructure of selected refractory materials before and after exposure to a hydrogen-reducing environment, often enriched with carbon monoxide (CO) to better simulate industrial conditions.

Studies have shown that the presence of hydrogen in combination with carbon monoxide significantly alters the corrosion behavior of Al_2O_3–SiO_2 materials. Hydrogen, as a reducing gas, can lead to the reduction of silicon oxide and partial deoxidation of aluminum, causing a loss of cohesion in the ceramic structure and the formation of microcracks. Carbon monoxide further affects the kinetics of the reduction reactions, accelerating degradation processes and producing gaseous by-products that can penetrate the porous ceramic structure, intensifying internal corrosion [10].

Microstructural analysis after exposure revealed changes in phase distribution, localized cracking, and the formation of new oxide forms with reduced thermal stability. These changes directly impact the mechanical properties of the material, including compressive strength, resistance to thermal shocks, and long-term operational durability. The study findings indicate that designing refractory ceramics for hydrogen-based shaft furnaces requires not only optimization of chemical composition and microstructure but also consideration of the synergistic effects of reducing gases such as H_2 and CO.

It should be emphasized that the lack of comprehensive experimental data on the effects of hydrogen on Al_2O_3–SiO_2 materials under actual industrial conditions represents a significant research gap. Therefore, the development of refractory materials resistant to reduction and corrosion in hydrogen atmospheres is a critical issue for ensuring the longevity of shaft furnaces and the efficiency of future metallurgical processes.

When hydrogen is used as a zero-emission fuel, emissions of carbon oxides (CO, CO_2) and sulfur oxides (SO_2, SO_3), which are common in processes based on the combustion of fossil fuels such as coal or petroleum, are eliminated. The absence of these pollutants results in a significant change in the chemical nature of industrial furnace atmospheres, directly affecting interactions with refractory materials. Traditional corrosion models and operational data cannot be fully applied to hydrogen atmospheres, as the mechanisms of ceramic degradation largely depend on the presence of oxidizing gases, combustion products of carbon and sulfur, and water generated from reactions with these components [11].

Consequently, a key step in the development of technologies using hydrogen as an industrial fuel has been the design and construction of pilot-scale facilities. Such installations allow controlled testing of hydrogen's effects on refractory materials under conditions approximating real industrial parameters, including temperature, pressure, and furnace atmosphere composition. Pilot-scale setups provide experimental data unavailable in small-scale laboratory tests, such as material degradation rates, microstructural changes, chemical reactions of ceramic oxides, the influence of local temperature fluctuations, and the dynamic effects of gas flow [12].

Data obtained from such installations are essential for the development of new refractory materials resistant to the reducing effects of hydrogen, as well as for the validation of simulation models predicting the durability of furnace linings under industrial conditions. Additionally, pilot-scale facilities allow the study of synergistic effects of water vapor and potential gas impurities that may form during metal reduction or other chemical processes. This enables not only a deeper understanding of the mechanisms of ceramic degradation under new operational conditions but also the development of maintenance strategies and operational optimization for hydrogen furnaces, which is critical for ensuring process safety and the longevity of industrial infrastructure.

The Łukasiewicz Research Network – Institute of Ceramics and Building Materials is currently the only facility in Europe equipped with a pilot-scale test rig enabling comprehensive studies on the effects of furnace gas atmospheres, resulting from hydrogen combustion or co-combustion, on the properties of metallic and non-metallic materials. These materials form the structural and construction basis across multiple industries, including energy, metallurgy, ceramics, and chemicals.

The research facility is equipped with a combustion chamber with a volume of 1 m^3, capable of operating at temperatures up to 1750 °C, allowing the replication of conditions close to real industrial processes. Hydrogen is used as fuel either in its pure form or in mixtures with oxygen, natural gas, and air in any percentage ratios, enabling flexible modeling of various operational scenarios. This broad configurational capability allows for the study of both pure hydrogen combustion and its co-combustion with conventional fuels, which is crucial for assessing the potential effects of introducing hydrogen into existing industrial installations.

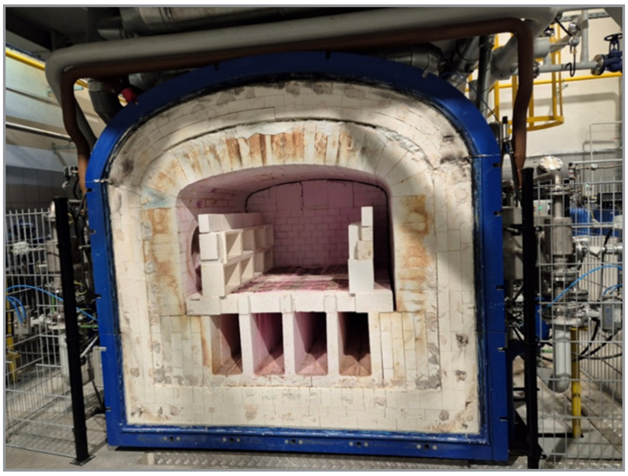

Figure 2: Photograph of a hydrogen-fired furnace at Łukasiewicz-ICiMB

Thanks to this facility, both industry professionals and researchers can obtain answers to a range of critical technical questions. In particular, it is possible to determine the impact of hydrogen as a fuel on technological processes, including the rate of chemical reactions, the thermal characteristics of furnaces, and the temperature distribution within refractory linings. Additionally, studies allow for the assessment of how hydrogen use affects the properties of produced materials and products, including their mechanical durability, chemical resistance, and microstructural stability.

The facility also enables the analysis of the effects of hydrogen use in existing installations, including the identification of hazards related to corrosion, reduction of ceramic oxides, water vapor interactions, and changes in flue gas composition. Based on the research results, it is possible to recommend necessary design and technological modifications to furnaces, refractory linings, and burners, ensuring that hydrogen can be used as a zero-emission fuel safely and efficiently.

Thanks to this position, Łukasiewicz – Institute of Ceramics and Building Materials plays a key role in the development of hydrogen technologies in Europe, enabling the conduct of scientific research and industrial projects that provide the necessary knowledge for the implementation of hydrogen in energy-intensive industries, while ensuring material durability and the safety of technological processes.

Experiments conducted at Łukasiewicz – Institute of Ceramics and Building Materials, i.e., firing multi-component concretes in a furnace using a 50:50 mixture of hydrogen and methane, clearly confirm that even small concentrations of hydrogen remaining in the exhaust gases, acting over a prolonged period under high-temperature conditions, lead to significant destruction of refractory linings containing silica (SiO_2) (Figures 3 and 4). According to literature reports, silicon oxide plays a key role in the mechanisms of hydrogen interaction with ceramic materials at temperatures typical for industrial furnaces [13].

As a result of this interaction, a reduction reaction of SiO_2 by hydrogen occurs, leading to the formation of gaseous products such as silicon monoxide (SiO) and water vapor (H_2O), which can be represented by the chemical equation [14].

$$SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$$

This process results in the loss of mass of the refractory material, which constitutes one of the first and most measurable indicators of the progress of hydrogen corrosion. The increase in mass loss correlates with the intensity of ceramic structure degradation, which directly translates into a reduction in mechanical strength and microstructural stability of the material [15].

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Microstructural analyses of samples, performed using scanning electron microscopy (SEM), allow for a detailed assessment of local changes within refractory linings. SEM enables high-resolution imaging of cross-sections of the samples, making it possible to observe, among other things, an increase in pore volume, the formation of microcracks, and changes in the morphology of ceramic phases. Increased porosity indicates a local weakening of the material's cohesion and is a direct consequence of chemical reactions between hydrogen and silica.

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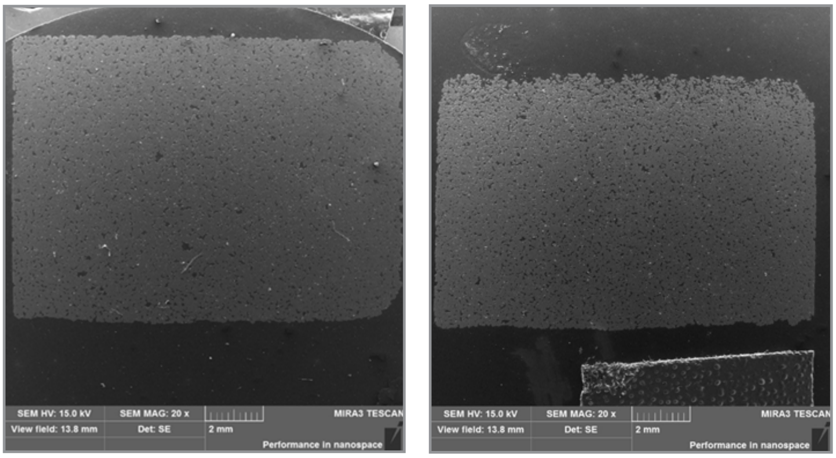

Figure 3: Micrographs, general view of a multi-component concrete sample before and after operation in a hydrogen-fired furnace, magnification 20x.

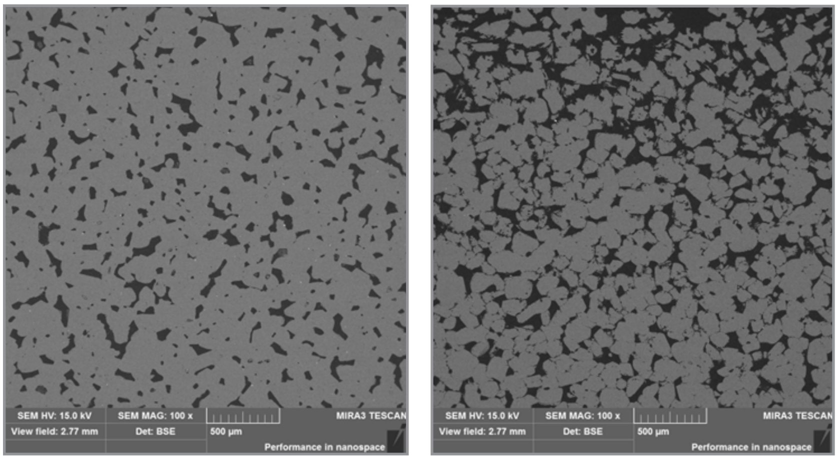

Figure 4: Micrographs from Fig. 3, magnification 100x

Mass loss and the observed microstructural changes provide clear evidence that hydrogen corrosion leads to the degradation of refractory linings, and the intensity of this process is strongly dependent on the exposure time and the hydrogen concentration in the furnace atmosphere. These results highlight the necessity of using refractory materials with a modified chemical composition, including a reduced SiO_2 content, in industrial processes that utilize hydrogen as a zero-emission fuel.

Summary

Ceramics, including refractory materials, as a class of engineering materials, generally exhibit very high chemical resistance in hydrogen environments, making them particularly attractive for applications related to hydrogen energy and high-temperature processes. The mechanism of this resistance primarily results from strong covalent or ionic-covalent atomic bonds characteristic of ceramic structures, which significantly limit the solubility and diffusion of hydrogen within the material. As a result, refractory materials can serve as effective diffusion barriers, preventing hydrogen penetration into metallic substrates and thereby protecting them against hydrogen embrittlement, which is one of the key operational hazards in systems operating in H_2 atmospheres.

Refractory materials such as aluminum oxide (Al_2O_3) or mullite ($3Al_2O_3 \cdot 2SiO_2$), as well as non-oxide ceramics including silicon carbide and silicon nitride (SiC, Si_3N_4), exhibit particularly high stability under hydrogen exposure. These materials retain their mechanical and microstructural properties over a wide temperature range, often exceeding 1000 °C, making them well-suited for applications in fuel cell structural components, high-temperature reactors, heat exchangers, and protective linings in hydrogen installations.

At the same time, it should be emphasized that not all ceramic materials exhibit the same level of resistance under extreme operating conditions. Silica-based refractory materials (SiO_2), especially in the form of glassy or poorly crystalline phases, can degrade at very high temperatures, above approximately 1200 °C. Under such conditions, mass loss, phase changes, and the development of microstructural defects, such as cracks or increased porosity, may occur. These processes can be further intensified by the presence of impurities, particularly metal oxides such as Fe_2O_3 or MgO, which can act as fluxes, lowering the softening temperature of silica and promoting the formation of liquid phases at grain boundaries.

For these reasons, the resistance of refractory materials in hydrogen environments should not be considered a universal property, but rather one that strongly depends on chemical composition, crystal structure, microstructure, and operating conditions such as temperature, hydrogen pressure, and the presence of dopants or impurities. A comprehensive assessment of these factors is essential when designing materials and ceramic coatings intended for long-term use in advanced hydrogen-based energy systems.

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