Hydrogen production by natural gas pyrolysis with thermal plasma – An alternative approach of CO_2-free hydrogen supply for the steel industry

O. Daghagheleh*[1], J. Schenk[1,2], M. Zarl[2], M. Farkas[2], H. Zheng[1]

Oday Daghagheleh (Corresponding Author, [1] *Chair of Ferrous Metallurgy, Montanuniversitaet Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria; oday.daghagheleh@unileoben.ac.at)*
Johannes Schenk ([1] *Chair of Ferrous Metallurgy, Montanuniversitaet Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria;* [2] *K1-MET GmbH, Stahlstraße 14, 4020 Linz Austria; johannes.schenk@unileoben.ac.at*)
Michael Andreas Zarl ([2] *K1-MET GmbH, Stahlstraße 14, 4020 Linz Austria; Michael.zarl@k1-met.com*)
Manuel Farkas ([2] *K1-MET GmbH, Stahlstraße 14, 4020 Linz Austria; manuel.farkas@k1-met.com)*
Heng Zheng ([1] *Chair of Ferrous Metallurgy, Montanuniversitaet Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria; heng.zheng@stud.unileoben.ac.at)*

Summary

Alternatives to fossil fuels are worth developing to shift to carbon-free iron making. Accordingly, replacing coal, coke, and natural gas with hydrogen is the current trend. H_2 is mainly produced through steam methane reforming (SMR) and partial oxidation, which are not carbon neutral. The paper proposes using plasma technology to decompose natural gas, also known as pyrolysis, to produce hydrogen. The current study aims at the vision of using thermal plasma pyrolysis in combination with hydrogen-based iron-making that can lead to an enormous decrease in CO_2 emissions in the steel industry. The methane pyrolysis is tested on a laboratory scale using a DC-transferred plasma arc system with a maximum power of 16 kW, providing a voltage range of 20-100 V and a maximum current of 150 A. The arc is initiated between a hollow graphite cathode and the graphite pin anode. The plasma gas (3 l/min Ar) and methane (2 l/min CH_4) are introduced to the reaction zone through the cathode. The off-gas could flow out for further analysis, and the arc could be seen through the openings at the top. The results demonstrate a hydrogen yield of about 50%. The produced carbon black has a high purity with a fluffy and fine structure. The paper concludes that further optimization and development of the process are necessary to achieve stable continuous operation with high utilization degree and reduce carbon emissions in the steel industry.

Keywords: Natural gas pyrolysis, Methane pyrolysis, Hydrogen production, Sustainability, Sustainable steelmaking, Thermal plasma, Black carbon

1. Introduction

The frontal challenge of the steel industry in the European Union is to reach the goal of net-zero CO_2 emission by 2050. Various alternatives are being taken in order to achieve that aim. For instance, different processes are being studied and implanted in steelmaking to increase the use of hydrogen gas (H_2) as a reductant. However, the ambitious goal requires quick measures for a steeper reduction in CO_2 emission [1–6]. H_2 has emerged as a promising alternative to fossil fuels and is gaining significant interest. Its potential applications as both an energy resource and a reductant in steelmaking make it a compelling choice for reducing the industry's carbon footprint by replacing traditional materials such as coal, coke, and natural gas. One of the critical advantages of H_2 is the variety of methods available for its production. However, the conventional steam methane reforming (SMR) techniques and partial oxidation used to produce H_2 are not entirely emission-free. Figure 1 provides a graphical representation of the production share of H_2 using various methods [7].

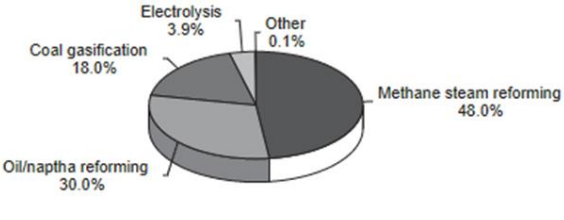

Fig 1. H_2 production shares of various methods [7].

These findings highlight the importance of exploring alternative methods of H_2 production that are more sustainable and eco-friendly. Electrolysis is a renewable method of generating hydrogen gas by passing a direct current through two electrodes immersed in a water solution, resulting in the breakdown of water bonds and the production of hydrogen and oxygen gas. Despite its potential as a sustainable source of hydrogen, electrolysis has limitations in terms of its high energy demand and relatively low efficiency, which currently limits its contribution to only 4% of the total hydrogen supply [8]. Natural gas decomposition, also known as pyrolysis, is a potential solution to produce H_2 with zero CO_2 emissions and higher efficiency. This reaction is endothermic and requires a significant amount of energy input. Figure 2 illustrates the thermodynamic aspects of CH_4 pyrolysis under normal conditions, calculated using the Factsage 8.2 software. For each mole of CH_4 gas, 2 moles of H_2 gas and 1 mol of solid carbon are produced. The full decomposition seems to occur at temperatures higher than 1200 °C.

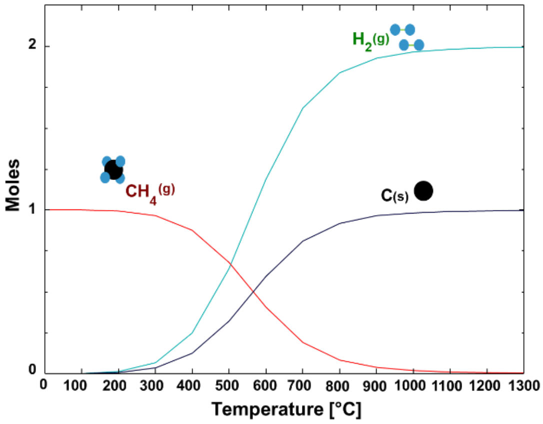

Fig 2. Thermodynamics of pyrolysis of 1 mol CH_4 with increasing temperature.

The pyrolysis process of natural gas (NG) can receive energy input from multiple sources. These include partial combustion of NG, which generates hydrogen that can fuel the reaction, as well as combustion of the carbon produced. Additionally, electric heating, solar furnaces, and plasma generation through electricity can also provide energy for the process [9]. If the required energy for pyrolysis is provided from a renewable source, such as green electricity, the zero CO_2 emission goal can be realized. This approach offers a promising path towards more sustainable and eco-friendly methods of H_2 production that align with the global efforts to reduce carbon emissions and mitigate climate change.

The pyrolysis process can be classified based on its operating temperature. At temperatures below 1000 °C, methane conversion may not be complete, thus requiring a catalyst. These types of processes are listed under the category of catalytic CH_4 decomposition and are typically carried out using electrical furnaces such as fixed and fluidized bed reactors or microwave ovens. The catalysts used for this purpose are typically based on nickel, carbon, cobalt, or iron, depending on the temperature range required. However, catalysts pose a significant challenge as they become deactivated by the deposition of carbon, making regeneration difficult and leading to potential emissions. Processes that operate at temperatures above 1200 °C fall under the category of non-catalytic decomposition methods. Thermal plasma torches are an example of this method. [10–13].

Thermal plasma is a process that converts electrical power into thermochemical energy, generating temperatures of up to 9727 °C (10000 K). One of its potential applications is in the pyrolysis of methane (CH_4), which occurs thermodynamically at temperatures higher than 1200 °C. Unlike traditional catalytic methods, thermal plasma does not require a catalytic effect for the decomposition reaction. This highlights the potential of thermal plasma as a promising and effective approach for producing hydrogen gas with zero carbon emissions through the pyrolysis of natural gas.

In addition to its effectiveness in producing hydrogen gas with zero carbon emissions, thermal plasma technology offers several advantages, such as its relatively small and simple design, high-efficiency rate, and low energy demands. An economic analysis comparing various alternatives for H_2 production has rated plasma pyrolysis as the second-highest efficiency after steam reforming, considering its advantageous [8]. Furthermore, thermal plasma enables the production of high-grade carbon black (CB) as a valuable byproduct in addition to the enriched H_2 gas. The CB product has various applications in several industries, such as mobility, plastics, and agriculture. Figure 3 shows the application share of the CB products in different sectors, highlighting the diverse potential uses for this valuable byproduct [14]. As demonstrated, most of the produced CB finds its application in the tire and rubber industry.

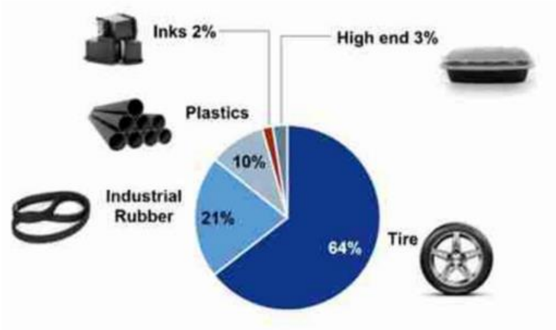

Fig 3. Application of CB in various industries [14].

The initial application of plasma pyrolysis technology focused on disposing of hazardous waste, including medical remains [15,16]. The first reported use of a plasma torch for the pyrolysis of natural gas was by the Norwegian company Kvaerner in the 1990s, which was patented. The focus of their research was on the production of carbon black using natural gas as the feed gas. In 1997, they established a production plant in Canada with an annual output of 20,000 tonnes of carbon black. However, the process was shut down in 2003 due to the unsatisfying quality of the produced carbon [12]. Despite this setback, recent advancements in plasma technology and the increasing demand for sustainable energy solutions have renewed interest in the potential of thermal plasma pyrolysis for producing hydrogen gas with zero carbon emissions and high-quality carbon black byproducts. In 2012, the US company Monolith Materials began a project to produce carbon black as the main product using plasma pyrolysis. However, the plant was dismantled in 2018 for unknown reasons. In 2020, the company commissioned a new commercial plant to produce carbon black, which continues to operate today. Monolith Materials plans to expand the plant's operations to include the production of green hydrogen and ammonia in addition to carbon black, demonstrating the potential for plasma pyrolysis to contribute to a sustainable future [17]. Except for some patents, detailed information and data on the mentioned process concepts and their progress are unavailable and difficult to track.

Different methods for plasma pyrolysis of NG are currently being studied and developed, as it offers a significant competitive advantage in producing high-quality carbon materials. These methods involve modifying various parameters such as electrode geometry and materials, flow rate, the characteristics of applied current, and different plasma gases [9].

In light of the current developments in plasma technology, it is necessary to develop a process concept that can provide scientific explanations for the effects of various process parameters on the results of methane pyrolysis. This would help to fill the existing knowledge gap and advance our understanding of the potential of plasma pyrolysis as a sustainable method for producing hydrogen and carbon.

2. Feasibility of thermal plasma pyrolysis for H_2 production

This study aims to evaluate the efficiency and feasibility of the pyrolysis process using thermal plasma technology. The primary focus is to achieve the maximum yield of H_2. To achieve this, preliminary tests were performed using a thermal plasma facility in the Chair of Ferrous Metallurgy laboratory at Montanuniversitaet Leoben. This facility is primarily used for steelmaking via hydrogen gas using plasma technics. Several works were published describing the use of this facility [18–20]. However, the facility is slightly modified for the intended pyrolysis tests. The used facility and its specifications are discussed in detail in the following section.

2.1. Methodology

The present study employs a DC-transferred arc thermal plasma laboratory facility to investigate the pyrolysis process. The facility can introduce different gas components, including Ar, H_2, CH_4, and N_2, to the reactor via the hollow cathode. The electric discharge takes place between the graphite cathode and the anode pin. The flexible arc distance from 10 to 60 mm enables a power supply range of 3.5 to 16 kW. The experimental setup is illustrated in Figure 4. A photograph of the reactor's installation is shown and described in Figure 5. The procedure of a pyrolysis test is described further:

1. Purging the entire reactor with Ar gas.Shifting the cathode to the arc ignition position – short circuit.
2. Igniting the arc using Ar as plasma gas.
3. Immediate shifting back of the cathode to a stable arc distance position.
4. Monitoring the stable arc through the camera installed on the top window of the lid.
5. Introducing CH_4 to the transferred arc by switching the gas from pure Ar to a mixture of Ar and CH_4.

6. Monitoring the reaction by the gas analysis device installed on the off-gas pipeline.
7. Stopping the CH_4 flow and the arc when the intended test is finished and switching to 100% Ar purging gas.

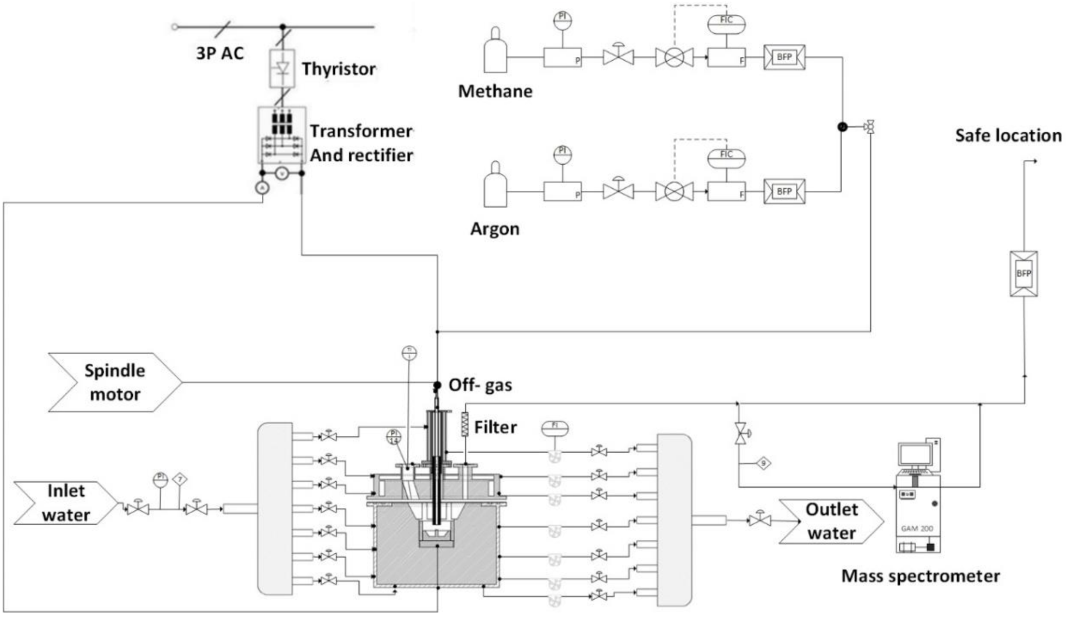

Fig 4. Process layout with different units of the thermal plasma facility.

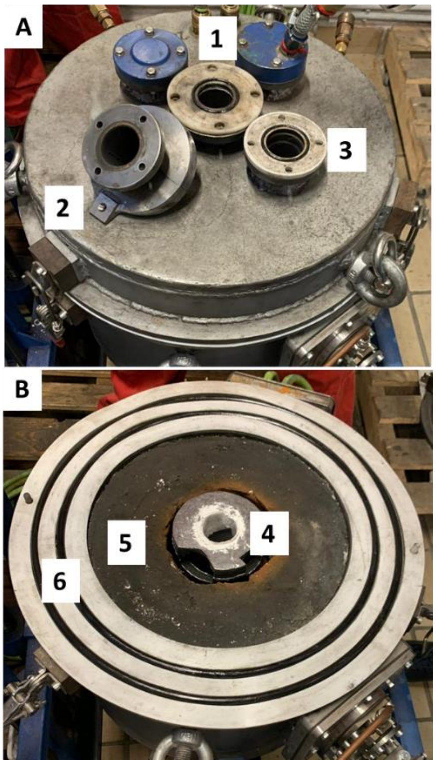

Fig 5. Reactor's installation consisting A. The lid with three openings: 1. Cathode inlet, 2. Camera window, 3. Off-gas outlet. And B. The reactor: 4. The graphite reaction chamber, 5. The lining, 6. The sealings.

The analysis of the experimental results depends on the off-gas composition, which was measured and recorded by a gas mass spectrometer of the type GAM 200, manufactured by InProcess Instruments Gesellschaft für Prozessanalytik mbH. By determining the volume of H_2 in the off-gas and adjusting the CH_4 input flow, it is possible to calculate the hydrogen yield using the following equation [21]:

$$H_2\ Yield = \frac{V_{H_2}}{2 * V_{CH_{4-in}}} * 100$$

2.2. Results

It is necessary to consider various parameters such as reactor geometry, shape, arc length, and plasma gas mixture to achieve a stable plasma arc. In this study, tests were carried out using a gas mixture with a total flow rate of 5 Nl/min, consisting of 40% CH_4 and the remainder Ar, as well as pure Ar, as a comparison. The results of the tests are shown in Figure 6, which plots the current versus voltage values. It can be observed that higher voltage fluctuations result in a less stable arc. The graph also shows the trends of a stable arc with different gas compositions and arc lengths. The blue line represents the case where the plasma gas consists of 100% Ar with a 25 mm arc length, while the remaining lines depict the results obtained using a gas mixture of 60% Ar and 40% CH_4 with two different arc lengths of 20 and 30 mm. The current of the plasma arc can be controlled through the power supply unit. A decrease in current while using 100% Ar gas composition results in nearly unchanged voltage, thus providing a stable arc with low energy input.

On the other hand, adding CH_4 to the gas mixture reduces the stability field and increases voltage fluctuations, leading to an unstable arc. CH_4 negatively affects arc stability and enhances voltage fluctuations as the arc length increases. The transition of a gas molecule to the excited form demands energy for breaking the bonds between the atoms and the ionization process. It can be concluded that CH_4 requires higher energy input to establish a plasma state compared to one monatomic Ar gas [18,22].

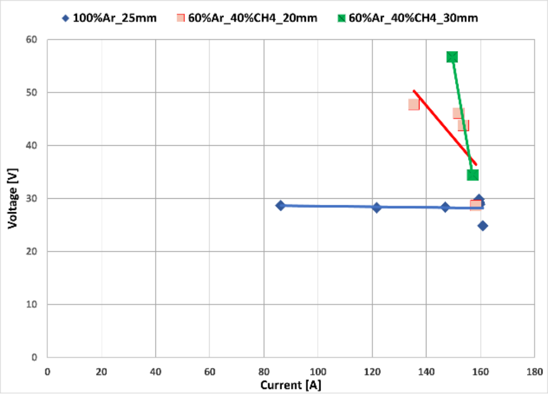

Fig 6. Arc stability field of 100% Ar gas and an Ar-CH_4 gas mixture with different arc distances.

The project's primary objective is to attain the highest H_2 yield possible. Thus, a test was conducted with the maximum possible CH_4 content, 40%, while considering the arc stability. The higher content of CH_4 in the conducted gas led to failure in igniting the plasma arc. Figure 7 depicts the H_2 yield obtained during a pyrolysis test with a total gas flow rate of 5 Nl/min, composed of 60% Ar and 40% CH_4. However, the recorded H_2 yield is subject to fluctuations due to varying arc conditions during the pyrolysis, resulting in a turbulent heated region and an unstable reaction zone.

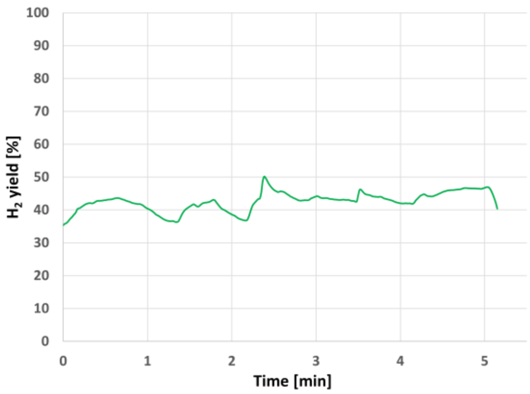

Fig 7. Calculated H_2 yield of the pyrolysis test.

The collected carbon samples were investigated using morphological and chemical analysis via scanning electron microscope (SEM) and energy dispersive X-Ray (EDX) analysis. Figure 8 shows the reaction chamber after the test. The carbon particles are attached and grown on the inner surface of that.

Fig 8. The reaction chamber after the pyrolysis test and the deposited CB on the inner surface.

The SEM images in Figure 9 show the dendritic morphology of the carbon agglomerates. These agglomerates consist of many smaller primary particles and aggregates. The EDX analysis detects highly pure carbon samples, as shown in figure 10.

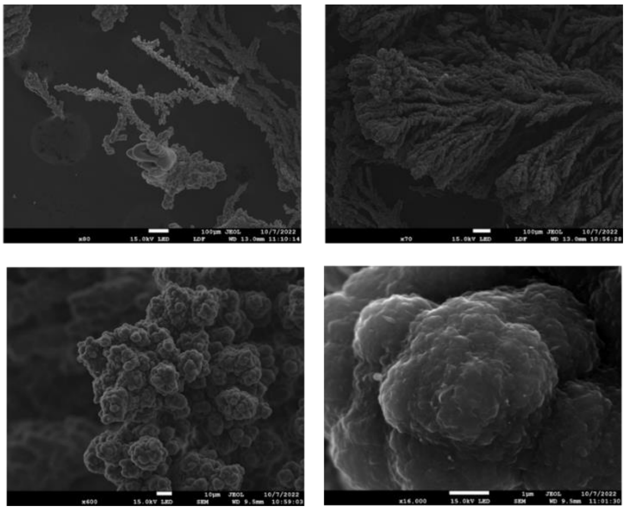

Fig 9. SEM images of the CB samples produced during the pyrolysis test.

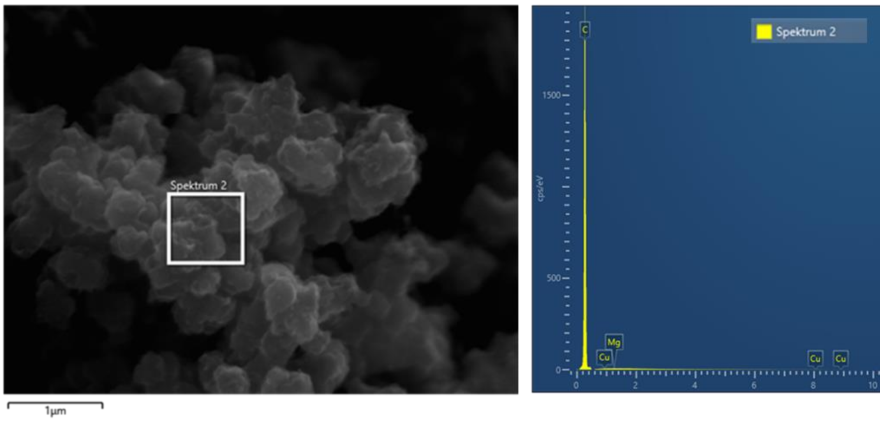

Fig 10. EDX analysis of the CB samples produced during the pyrolysis test.

3. Discussion

The technical feasibility study on methane plasma pyrolysis was satisfyingly conducted. The process seems beneficial for H_2 production, while CB as a high-value byproduct was identified. Further development, detailed experimental studies, and engineering are necessary to increase the process stability and hydrogen yield. The following challenges were defined, which can be listed:

1. The horizontal design of the reactor: in the limited reaction spot, carbon is deposited and collected within the reaction chamber. This accumulates and hinders further reaction by disturbing the plasma arc.
2. Low stability field: Additionally to the solid carbon that interrupted the arc, the power unit could not provide higher voltage ranges, causing a limited stability field of the plasma arc.
3. Refractory and contamination: refractory materials of the reactor linings and the isolation coatings can contaminate the produced solid carbon and impact its quality.
4. Erosion of the electrodes: Both cathode and anode are consumed during the test, avoiding a continuous process. Furthermore, the hollow cathode is damaged, the tip is partly cut off, or carbon is deposited in the opening leading to blockage of the gas flow.

4. Conclusion and outlook

The experimental study shows that methane plasma pyrolysis is technically feasible. However, detailed study and process screening is necessary to identify and track the influencing process parameters. It is essential to enhance the understanding of the process for further development. For instance, it is widely known and approved through the experimental study that CH_4 impacts plasma arc stability. The first trials have shown that a mixture of 60 % Ar and 40 % CH_4 is a suitable compromise between a stable process and productivity. However, the H_2 yield is limited to 50%, which should be improved. Higher power input with more comprehensive voltage ranges can help to stabilize the arc, providing a continuous process. A vertical reactor design and the reaction zone's expansion promote the process stability for a constant discharge of solid carbon, providing more room and a clean area for the reaction and the plasma arc. If the CH_4 introduce to the plasma arc from an extra separated nozzle, the electrode erosion will minimize [23]. An improved design should be adapted to facilitate the process. A combination of this technology together with H_2-based steelmaking can offer a new sustainable route for green steelmaking.

References

[1] O. Daghagheleh, J. Schenk, H. Zheng, B. Taferner, A. Forstner, G. Rosenfellner, *steel research int.* **2023**, *94*, 2200535.

[2] H. Zheng, J. Schenk, O. Daghagheleh, B. Taferner, *Metals* **2023**, *13*, 339.

[3] T. Wolfinger, D. Spreitzer, J. Schenk, *Materials (Basel, Switzerland)* **2022**, *15*.

[4] T. Wolfinger, D. Spreitzer, J. Schenk, *Materials (Basel, Switzerland)* **2022**, *15*.

[5] W. Eder, *Berg Huettenmaenn Monatsh* **2017**, *162*, 494–497.

[6] D. Spreitzer, J. Schenk, *steel research int.* **2019**, *90*, 1900108.

[7] T. Da Silva Veras, T. S. Mozer, D. Da Costa Rubim Messeder dos Santos, A. Da Silva César, *International Journal of Hydrogen Energy* **2017**, *42*, 2018–2033.

[8] C. M. Kalamaras, A. M. Efstathiou, *Conference Papers in Energy* **2013**, *2013*, 1–9.

[9] A. R. Da Costa Labanca, *International Journal of Hydrogen Energy* **2020**, *45*, 25698–25707.

[10] T. Keipi, K. E. Tolvanen, H. Tolvanen, J. Konttinen, *Energy Conversion and Management* **2016**, *126*, 923–934.

[11] D. Scheiblehner, D. Neuschitzer, S. Wibner, A. Sprung, H. Antrekowitsch, *International Journal of Hydrogen Energy* **2023**, *48*, 6233–6243.

[12] S. Schneider, S. Bajohr, F. Graf, T. Kolb, *Chemie Ingenieur Technik* **2020**, *92*, 1023–1032.

[13] Dagle, R,. et al., *An Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products*, U.S. Department of Energy Fuel Cell Technologies Office **2017**.

[14] L. Fulcheri, V.-J. Rohani, E. Wyse, N. Hardman, E. Dames, *International Journal of Hydrogen Energy* **2022**.

[15] H. Karimi, M. R. Khani, M. Gharibi, H. Mahdikia, B. Shokri, *J Mater Cycles Waste Manag* **2020**, *22*, 2059–2070.

[16] [Cannot display the reference "O P Solonenko", because the template "Bibliography - Journal Article - (Default template)" contains only fields that are empty in this reference.]

[17] Monolith materials, INC., *Monolith™ Headquarters: Corporate-Brochure-2022*, https://monolith-corp.com.

[18] M. Naseri Seftejani, J. Schenk, M. A. Zarl, *Materials (Basel, Switzerland)* **2019**, *12*.

[19] M. A. Zarl, D. Ernst, J. Cejka, J. Schenk, *Materials (Basel, Switzerland)* **2022**, *15*.

[20] M. A. Zarl, M. A. Farkas, J. Schenk, *Metals* **2020**, *10*, 1394.

[21] T. Li, C. Rehmet, Y. Cheng, Y. Jin, Y. Cheng, *Plasma Chem Plasma Process* **2017**, *37*, 1033–1049.

[22] Paul M. Bellan, *Fundamentals ofPlasma Physics* **2004**.

[23] Y. Cheng, B. Yan, T. Li, Y. Cheng, X. Li, C. Y. Guo, *Plasma Chem Plasma Process* **2015**, *35*, 401–413.