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Abstract

Iron Oxide Reduction by Hydrogen from Liquid Slag †

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1. Introduction

Steel is the second most common man-made material after concrete (annual global steel production is approximately 2 billion tons [1]). Steel is a material that enables the implementation of green energy technologies. Steel is infinitely recyclable, and its residues and waste can become valuable resources, thus contributing to a sustainable and circular EU economy. In an era when the directives and policy of the European Union and the Paris Agreement [2] aim to achieve climate neutrality by 2050, the European Green Deal [3] (the "Clean Planet for All" strategy) and thus the development of technologies aimed at almost completely eliminating CO_2 emissions (reducing CO_2 emissions from steel production by half by 2030 and by 80–95% by 2050) are initiatives for which new, carbon-free technologies for reducing iron oxides must be developed.

During steel production, the total CO_2 emission rate is 1.8 Mg CO_2/Mg steel. Steel production accounts for approximately 8% of global carbon dioxide emissions [1]. The price of CO_2 emissions in the European Union is rising along with the demand for energy: in June 2022, the price of emissions per Mg of CO_2 was approximately EUR 83/Mg [1].

The steel industry in Poland currently emits approximately 8–9 million Mg of CO_2 annually. Among the iron and steel installations, the most harmful are the raw material departments (coking plants, sinter plants, blast furnaces) located in integrated steelworks. Authors in Figure 1 presented CO_2 emission [1] from particular, selected steelmaking processes.

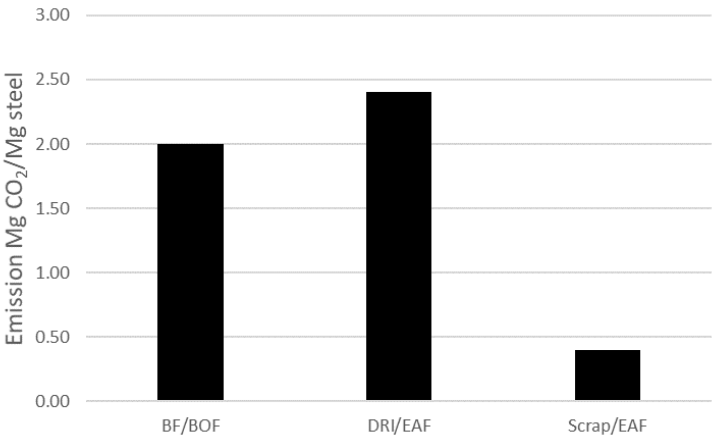


Figure 1. CO_2 emission level in the steelmaking process.

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The Clean Steel Partnership [4] proposes a three-step approach to research, development and innovation to accelerate the reduction in carbon emissions in the steel industry:

- Stage 1 concerns projects that generate "immediate" CO_2 reduction opportunities [4];
- Stage 2 focuses on those projects that may not be implemented "right away" in the installed base, but allow for rapid evolution toward improved processes [4];
- Stage 3 looks at those projects that have the potential to "revolutionise" the steel industry through disruptive development and require significant capital investment in new processes [4].

Currently, steel is mainly produced using one of two production lines: an integrated one consisting of a blast furnace and an oxygen converter, or an electric arc furnace.

The blast furnace uses iron ore, coke and limestone to produce pig iron, which is then converted into steel in an oxygen converter. In turn, the input to the electric arc furnace is steel scrap. Due to the amount of scrap available, approximately 30% of the world's steel is produced in arc furnaces. Steel, regardless of the production process (blast furnace, electric arc furnace), is "improved" in the post-furnace refining process in order to obtain the assumed properties, including the appropriate chemical composition (different steel is needed to produce sheet metal for roofs, to produce cutlery, etc.). The last stage of the steelmaking process is casting the steel and further processing it in plastic-forming processes (forging, rolling). In the classic pig iron production process, coal plays two roles: as a reducer of iron oxides from the ore and as a fuel generating the thermal energy needed to run the process.

An alternative steel production technology is the processing of materials from the so-called direct reduction of iron ore: DRI (Direct Reduction Iron).

Direct reduction involves the reduction of iron oxides to metallic iron in the solid state, occurring at temperatures below the melting point of iron, in the presence of reducing synthesis gas, most often natural gas. Modern solutions aim to replace natural gas with hydrogen gas to reduce CO_2 emissions from the process. Currently, approximately 6–7% of pig iron in the world is produced using DRI technology. A significant problem with the use of hydrogen in direct reduction technology is its very low specific gravity (4 times lighter than that of CO). Therefore, the flow of hydrogen from bottom to top in the DRI reactor takes place in 1–2 s, significantly reducing the reduction reaction's efficiency.

Moreover, DRI technology is a two-phase process. The first phase is the reduction of iron oxides below the melting point of iron using natural gas/hydrogen. The product is sponge iron—a type of iron with a purity of 90–97%, containing only small amounts of carbon and other impurities. In the second phase, sponge iron is smelted in an arc furnace using electricity. The product is steel. Figure 2 shows a schematic diagram of existing steel production technologies.

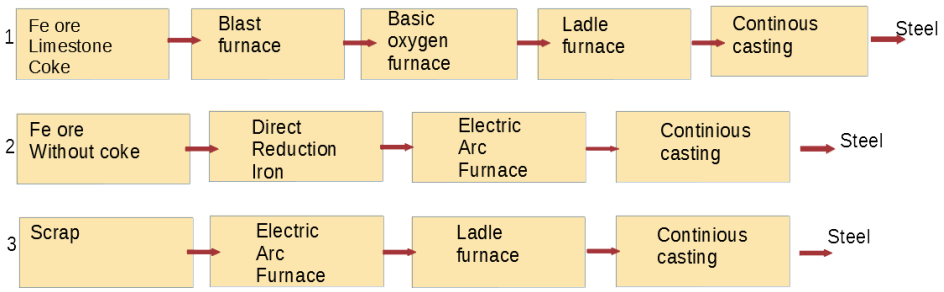


Figure 2. A schematic presentation of the technological lines used in steel production: 1. The so-called integrated technological line, where pig iron is produced from iron ore and processed into steel in an oxygen converter. 2. A technological line in which iron is produced from iron ore by direct reduction and processed into steel in an electric arc furnace. 3. A technological line in which steel is produced from circulating scrap in an electric arc furnace.

Standard iron and steel metallurgy technologies based on carbon are undergoing a significant civilizational change, replacing coal as a reducing agent with hydrogen [5].

2. Subject of Research and Research Methodology

This article deals with the reduction of iron oxides in liquid systems. The liquid slag system was based on the waste material (sludge) originating from classic metallurgical processes that was deposited in a landfill [6]. The chemical and phase compositions of the sludge were characterized by XRF and XRD techniques. The induction furnace shown in Figure 3 was the metallurgical unit used in the research to melt the solid charge and carry out the reduction process.

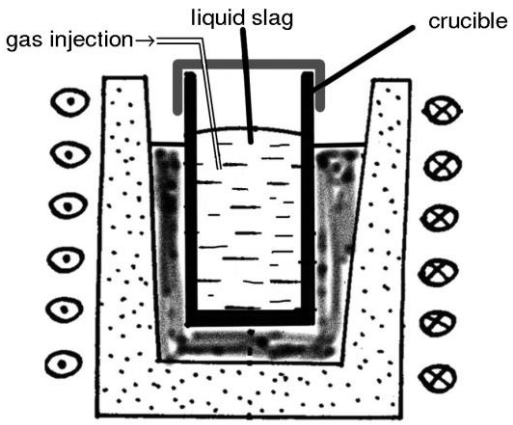


Figure 3. Induction furnace.

Iron oxides in a liquid state were reduced using a hydrogen/nitrogen gas mixture [7] and a solid hydrogen carrier. The values of hydrogen carriers used during the experiments are as follows: for the gas mixture, the flow rate was up to 4 L/min for injection times of 10–30 min; for the solid hydrogen carrier, the mass of the carrier varied in the range of 40–160 g.

3. Preliminary Results and Discussion

After the reduction processed samples were cooled down in a furnace (in Ar protection atmosphere), the samples (one example in Figure 4) were divided for SEM/EDS and XRD analyses, and in sequences, one part was milled and the second was polished.



Figure 4. Slag sample after gas hydrogen reduction.

The slag morphology was successively identified after the tests using XRD and SEM/EDS techniques for each sample. The efficiency of the reduction process was determined for various conditions of the hydrogen reduction process. The efficiency of the iron oxide reduction process was observed, along with an increase in the concentration of wustite in the samples. However, pure metallic iron was not obtained under the conditions described.

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References

1. Available online: https://worldsteel.org/ (accessed on 25 June 2024).
2. Available online: https://unfccc.int/process-and-meetings/the-paris-agreement (accessed on 25 June 2024).
3. *The European Green Deal*; EC: Brussels, Belgium, 2012.
4. *Clean Steel Partnership*; ESTEP: Brussels, Belgium, 2021.
5. Peng, H.; Forsberg, K. Advances in Process Metallurgy, The Minerals, Metals & Materials Society. *JOM* **2021**, *73*, 1629–1630. [CrossRef]
6. Bernasowski, M.; Migas, P.; Ślęzak, M.; Gondek, Ł.; Cieniek, Ł. Utilization of High-Zn Content Ferrous Landfill Sludge with the Use of Hydrogen. *Materials* **2023**, *16*, 7676. [CrossRef] [PubMed]
7. Naseri Seftejani, M.; Schenk, J. Thermodynamic of Liquid Iron Ore Reduction by Hydrogen Thermal Plasma. *Metals* **2018**, *8*, 1051. [CrossRef]

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