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INDUSTRIAL TECHNOLOGIES OF DIRECT REDUCTION OF IRON FROM ORE RAW MATERIALS AND PROSPECTS FOR THE USE OF HYDROGEN IN REDUCTION PROCESSES

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ABSTRACT

A significant reduction in carbon dioxide emissions in metallurgy can be achieved by using a mixture of carbon monoxide and hydrogen for iron reduction. Industrial technologies of direct reduction of iron from ore raw materials are considered. Reactions in reduction processes are analyzed. It is shown that at temperatures above 800 °C, hydrogen is a more effective reducing agent than carbon monoxide. Ways of improving the energy efficiency of existing technologies are demonstrated. It is shown that today the main technology of iron reduction from ore is reduction in shaft furnaces using a mixture of carbon monoxide and hydrogen. A generalized scheme of direct reduced iron production is presented. It is shown that in the production of direct reduced iron, the use of hydrogen makes it possible to halve carbon dioxide emissions compared to the use of natural gas, provided that electricity is generated from renewable sources or at nuclear power plants. It is concluded that a promising way to eliminate carbon emissions during the reduction of iron from ore or pellets is the use of plasma technologies.

KEYWORDS: direct reduced iron, hydrogen, shaft furnace, carbon dioxide emissions

INTRODUCTION

The production of pig iron and steel accounts for about 7 % of global carbon dioxide emissions due to the use of carbon for iron reduction from ore [1]. At present, the main route for obtaining steel from iron ore raw materials is iron reduction in blast furnaces with the production of pig iron, followed by its conversion into steel in basic oxygen converters. A significant reduction of carbon dioxide emissions in these processes cannot be achieved due to their technological schemes. In a blast furnace, layers of iron ore materials alternate with layers of coke, the main element of which is carbon. The coke layers ensure the gas permeability of the charge column, maintain the reducing potential of the gas phase in the upper part of the furnace, while coke carbon acts as a direct reducing agent in the lower part of the furnace and as the main source of energy for heating the charge and sustaining chemical reactions. In basic oxygen converters, the carbon in pig iron is oxidized until its concentration is reduced to the required level in steel. In this case, carbon combustion is the main source of energy for the process.

A significant reduction in carbon dioxide emissions in ferrous metallurgy can only be achieved by using a reducing agent that does not contain carbon. In terms of availability, cost, environmental friendliness, and reducing properties, the most appropriate option for iron reduction is the use of hydrogen.

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There are many methods of hydrogen production [2]. Brown or black hydrogen is obtained by coal gasification using steam, gray hydrogen by steam reforming of natural gas (if carbon emissions are captured and stored, such hydrogen is called blue), and turquoise hydrogen by pyrolysis of natural gas with the formation of solid carbon. However, in all these methods, extraction of fossil fuels is required, and as a result, in addition to hydrogen, carbon or its oxides are formed, which must be utilized. A fundamentally different approach to hydrogen production is water electrolysis. In this case, if nuclear energy is used for electrolysis, the hydrogen is called pink; if electricity of mixed origin is used — yellow; and if electricity is derived exclusively from renewable sources it is called green. Green hydrogen is the most environmentally friendly, but also the most expensive. Therefore, it is important to ensure minimal hydrogen losses in the metallurgical process. The substitution of carbon with hydrogen as a reducing agent would allow for a significant reduction in carbon dioxide emissions in metallurgy, but it is clear that in this case a different technological scheme for producing steel from iron ore raw materials should be applied. It is also important to minimize energy consumption from both environmental and economic perspectives.

PROBLEM STATEMENT

Iron obtained through direct reduction technologies is called direct reduced iron (DRI). Its share in the

total volume of pig iron and DRI production increases every year. In 2021, it amounted to 7.2 %, in 2022 — 7.9 %, and in 2023 — 8.5 % [3]. In 2023, the volume of DRI production reached 136 mln t [4]. Of this amount, about 30 % was produced using technologies based on coal. Most often these are rotary kiln processes (for example, the SL/RN process) or rotary hearth furnaces. The majority of these facilities are located in India or South Africa, due to the developed coal industry in these countries. However, the use of coal carbon as a reducing agent makes it impossible to significantly reduce carbon dioxide emissions compared to the blast furnace process.

The most widespread group of industrial technologies for DRI production are shaft furnace reduction technologies: MIDREX (about 80 % of DRI production in shaft furnaces), Hyl/Energiron (17 %), Pered (3 %), Finmet, Circored, Fior, and others [4–8]. Today, the capacity of individual shaft furnaces can reach 2.5 mln t per year, for example, Tosyali Algérie and Algerian Qatari Steel (Algeria, MIDREX), Nucor Steel Louisiana (USA, Energiron).

In a lined shaft furnace, as in a blast furnace, there is a counterflow of iron-containing charge materials (lump iron ore or iron ore pellets), which descend under the action of gravity, and the ascending reducing gases, consisting mainly of hydrogen and carbon monoxide. The temperature in the technological process is regulated in such a way as to prevent softening and sticking of the charge materials. Therefore, there is no need for coke layers in the charge column, one of whose functions in the blast furnace is to ensure the gas permeability of the charge. In such processes, various reducing gases can be used: coke oven gas, products of coal gasification, natural gas or its conversion products, hydrogen. Most of these installations have been built in the Middle East, North Africa, and the Caribbean region, i.e., in areas rich in natural gas. Accordingly, the technological processes employed in existing installations are mostly designed for the use of natural gas or its conversion products. However, developers note the possibility of adjusting the technologies for the use of various gaseous reducing agents without carbon content.

One of the advantages of using gaseous reducing agents is their purity. Unlike coke and coal, they do not introduce additional impurities into DRI, such as sulfur, phosphorus, or arsenic. Thus, the content of harmful impurities in the product depends only on the purity of the iron ore raw materials. On the other hand, all the gangue contained in the iron ore materials remains in the DRI and enters the steelmaking furnaces, which leads to an increase in the amount of slag and energy consumption. Therefore, charge ma-

terials should contain as little gangue as possible. The optimal composition of iron ore or iron ore pellets is considered to be, % [5]: Fe = 67.0; $SiO_2 + Al_2O_3 = 3.0$; S = 0.008; P = 0.03; $TiO_2 = 0.15$.

There are few deposits of such rich iron ore. In particular, in commercial ores of the Kryvyi Rih basin, the average iron content ranges from 46.9 to 65.6 % [9]. This necessitates, as in the blast furnace process, the enrichment of relatively poor iron ores. For effective enrichment, the ore is ground, and after enrichment it is agglomerated to obtain sinter for the blast furnace or pellets for the blast furnace or for DRI production. Unlike the blast furnace, the production of direct reduced iron is possible in a fluidized bed of finely ground iron ore materials [8, 10, 11]. This is achieved through the use of gaseous reducing agents and limited heating of the iron ore raw materials. At present, such technologies have not yet found wide application, probably due to the prevention of particle sticking. However, they undoubtedly have prospects due to the elimination of the costs of agglomeration, which could significantly reduce the cost of DRI.

A shaft furnace for DRI production can be divided into zones of preliminary heating of the charge materials, reduction reactions, supply of reducing gases, and discharge of the metallized product [5, 6]. The main reduction reactions are the reactions of reducing iron from higher oxides to lower oxides and further to metallic iron by carbon monoxide and hydrogen:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2; \tag{1}$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O;$$
 (2)

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2;$$
 (3)

$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O;$$
 (4)

$$FeO + CO \rightarrow Fe + CO_2;$$
 (5)

$$FeO + H_2 \rightarrow Fe + H_2O. \tag{6}$$

Reactions (1) and (2) occur relatively easily in the upper part of the furnace. Reactions (3)–(6) require a significant excess of the reducing agent. Table 1 shows the composition of equilibrium gas mixtures for the reduction reactions depending on temperature [11].

From Table 1 it can be seen that reactions (5) and (6), i.e., the reactions of obtaining metallic iron, require the greatest excess of reducing agent. With increasing temperature, the reducing ability of hydrogen increases, while that of carbon monoxide decreases in reaction (5). At temperatures above 800 °C, hydrogen is a more effective reducing agent than carbon monoxide, and from a thermodynamic point of view, iron reduction is possible solely due to hydrogen. However, in any case, less than half of the reducing agent

Reaction	Temperature, °C									
	600	700	800	900	1000	1100	1200			
(3)	55.2/44.8	64.8/35.2	71.9/28.1	77.6/22.4	82.2/17.8	85.9/14.1	88.9/11.1			
(4)	30.1/69.9	54.2/45.8	71.3/28.7	82.3/17.7	89.0/11.0	92.7/7.3	95.2/4.8			
(5)	47.2/52.8	40.0/60.0	34.7/65.3	31.5/68.5	28.4/71.6	26.2/73.8	24.3/75.7			
(6)	23.9/76.1	29.9/70.1	34.0/66.0	38.1/61.9	41.1/58.9	42.6/57.4	44.5/55.5			

Table 1. Composition of equilibrium gas mixtures for reduction reactions of H₂O/H₂ or CO₂/CO

can be used for the reduction of iron to metal under equilibrium conditions. In real industrial processes, the equilibrium is not achieved, and therefore an even greater excess of the reducing agent is required. Obviously, for the economic use of reducing agents, the off-gases from the shaft furnace must be cleaned and reused.

As a result of the reduction reactions, the degree of iron metallization in industrial technologies amounts to about 94 %.

The use of DRI is most appropriate for steelmaking in electric arc furnaces (EAF). On the one hand, the operation of an EAF does not lead to significant carbon dioxide emissions provided that electricity is generated from clean sources. On the other hand, DRI, unlike scrap metal, is characterized by a known and stable chemical composition and, given the purity of the iron ore raw materials, its use does not require significant means of steel refining.

Initially, the product of shaft furnace units consisted only of metallized pellets cooled prior to discharge — Cold Direct Reduction Iron (CDRI) [5]. However, they have a certain drawback — a tendency to oxidize and even self-ignite due to their developed surface area [11]. Therefore, for more convenient and safe transportation and storage, some plants later introduced the discharge of hot product into a roller press, where it is formed into dense pillow-shaped briquettes — Hot Briquetted Iron (HBI). In 2023, the share of HBI amounted to about 9 % of total DRI production [4].

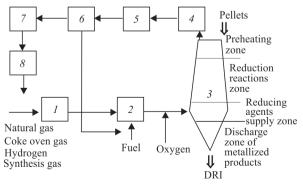


Figure 1. Technological scheme of DRI production: 1 — humidifier; 2 — heater; 3 — shaft furnace; 4 — heat exchanger; 5 — filtration system; 6 — water removal equipment; 7 — compressors; 8 — CO, removal equipment

Obviously, cooling DRI upon discharge from the shaft furnace and its subsequent reheating in the steelmaking furnace results in unnecessary energy, economic, and resource losses. Therefore, at some steel plants equipped with both shaft reduction furnaces and electric arc furnaces (EAF), the practice of discharging Hot Direct Reduction Iron (HDRI) has been implemented [5]. As a result, in addition to reducing the specific consumption of electricity, the productivity of steelmaking furnaces increases by up to 20 % [12]. This is because less energy and time are required to heat DRI to the melting temperature, thereby shortening the overall melting cycle. An empirical rule shows that electricity consumption decreases by approximately 20 kW·h/t of liquid steel for every 100 °C increase in DRI temperature. Thus, energy savings at DRI temperatures above 600 °C can reach up to 120 kW·h/t. Additional advantages, besides reduced electricity consumption, include lower electrode and EAF lining consumption and the possibility of using less powerful electrical equipment. Reduced energy consumption, in turn, leads to lower environmental pollution. In 2023, HDRI accounted for about 11 % of DRI production [4].

Depending on plant layout, different systems may be applied to transport HDRI to the steelmaking shop: conveyors (for distances up to 200 m), transport vessels (for distances above 100 m), or, if the distance is within 40 m, specialized systems such as HOTLINK [5]. The latter transfers HDRI at temperatures up to 700 °C directly into a neighboring EAF, enabled by positioning the MIDREX shaft furnace adjacent to the external wall of the steelmaking shop. HDRI is discharged hot into a storage bin and then fed directly into the EAF with minimal heat losses. HDRI transportation occurs by gravity. Due to the airtight design of the HOTLINK system, no re-oxidation of HDRI takes place. The HOTLINK system is designed to allow for the discharge of HBI or CDRI, in case the EAF does not require HDRI at a given moment, without stopping production [12].

A generalized flow diagram of DRI production is shown in the Figure 1.

Reducing gases (coke oven gas, coal gasification products, natural gas or its conversion products, hy-

Gas	100 % NG			50 % NG + 50 % H ₂			20 % NG + 80 % H ₂		
Source of electricity	Nuclear/ renewable	NG	Coal	Nuclear/ renewable	NG	Coal	Nuclear/ renewable	NG	Coal
Direct emissions during DRI production	495	-	-	287	_	-	200	_	-
Emissions associated with electricity use: in the reduction process in ${\rm H_2}$ production	2 0	50 0	84 0	2 31	45 754	75 1262	2 46	42 1114	71 1864
Total emissions	495	545	579	320	1086	1624	248	1356	2135

Table 2. CO₂ emissions depending on the composition of the reducing gas mixture and the method of electricity generation, kg CO₂ per 1 t DRI [6]

drogen) are supplied to the humidifier *I*, where steam is used for the conversion of hydrocarbons. Subsequently, in the heater *2*, the gas mixture is heated to the required temperature. The heated gases are then introduced into the shaft furnace *3* for utilization in reduction processes. Oxygen may be added to the gas mixture prior to entering the shaft furnace in order to further increase its temperature.

The gases leaving the shaft furnace first pass through the heat exchanger 4 to ensure efficient utilization of thermal energy. They are then directed to the filtration system 5, where the gases are cleaned primarily of iron ore dust. At the next stage 6, cooling leads to the removal of water. Further, part of the gases can be used as fuel for heating the reducing gas mixture, while another portion, with the aid of compressors 7, is sent to the CO_2 removal unit 8. As a result, the gas mixture, now contains in predominantly reducing gases, and is reused in the reduction processes.

The presented scheme is generalized and may vary depending on the technological features of a specific plant. In particular, when hydrogen is used as the sole reducing agent, the stages of humidification I and CO_2 removal from the off-gas δ are omitted.

As noted above, there are numerous methods for hydrogen production, with the most environmentally attractive option being the use of H₂ obtained via water electrolysis for reduction processes. However, when discussing environmental sustainability, CO, emissions associated with the production of electricity required for electrolysis must be considered. For example, the authors of study [6] estimated the approximate amount of CO₂ generated during DRI production under different natural gas (NG) to hydrogen ratios in the reducing gas mixture and under various electricity generation scenarios, making the following assumptions: the electricity consumption for producing 1 kg of hydrogen via electrolysis is 56 kW·h; CO, emissions per 1 kW·h of electricity amount to 20 g when generated from renewable sources or at nuclear power plants, 490 g when generated by natural gas combustion, and 820 g when generated by coal combustion.

The results of these investigations are presented in Table 2 [6].

Thus, the use of hydrogen as a reducing agent in shaft furnace—based DRI production allows a reduction of carbon dioxide emissions by approximately half, provided that the electricity required for hydrogen production is generated from nuclear or renewable sources — i.e., when using so-called pink or green hydrogen. On the other hand, reliance on electricity from fossil fuel—based power plants leads to a substantial increase in CO_2 emissions. It should also be emphasized that these calculations are valid for operations following the schematic process shown in the Figure 1, i.e., under the condition of reusing the gases exiting the shaft furnace.

It is evident that the reduction of CO₂ emissions in metallurgy is ensured by decreasing electricity consumption at any stage of steel production. As noted above, significant power savings can be achieved through the production of hot direct reduced iron (HDRI).

Another potential pathway for reducing CO₂ emissions in metallurgy is the application of plasma technologies. In particular, iron reduction in the molten state within plasma furnaces using reducing gases — including hydrogen [1, 13] and even the thermal decomposition of iron oxides [14] is considered feasible. The hot reducing gases discharged under such conditions from plasma furnaces could then be utilized either directly for iron reduction in shaft furnaces or for preheating the reducing gases fed into the shaft furnaces. However, these approaches still require further research, both in the field of plasma technologies proper and in the development of methods for their integration into shaft furnace—based iron reduction processes.

CONCLUSIONS

1. The primary group of technologies for direct iron reduction from ore feedstock is shaft furnace—based reduction processes. Hydrogen, as a component of reducing gases, actively participates in the reduction

reactions. From a thermodynamic perspective, even the use of pure hydrogen as an iron reducing agent is feasible in these technologies.

- 2. In DRI production, the use of hydrogen allows reducing CO₂ emissions by half compared with natural gas, provided that electricity is generated from renewable sources or at nuclear power plants.
- 3. The application of plasma-based hydrogen reduction technologies represents a promising pathway for decreasing CO₂ emissions in metallurgy. However, further research is required, both regarding the technological features of the process and the design aspects of shaft furnaces.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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