Review article

Using semi-coke as a reducing agent in the production of ferroalloys

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Abstract

Ferroalloys are compounds of iron with other elements that have many applications in various industries. The production of ferroalloys is usually done in electric arc furnaces and by the carbothermic process. In this method, metal oxides are reduced by different carbon materials, and the type of carbon material used can affect the way the process is carried out and the quality of the product. Among the carbon materials, we can mention coke, semi-coke, coal, and charcoal, which have various physical and chemical properties. Metallurgical coke is the most common reducing agent in the production of ferroalloys, but due to its increasing shortage, high price, and relatively high content of harmful impurities, manufacturers are looking for other options. Charcoal has less ash than other carbon materials, but due to environmental problems, its use is not common. Coal with the highest reactivity is not considered among the main options due to its high sulfur content and low compressive strength. Recently, semi-coke, which is prepared at a lower temperature than coke, has gained attention in the ferroalloys industry due to its unique characteristics (high fixed carbon, high specific resistance, high chemical activity, low ash, and low sulfur). Semi-coke improves the quality of ferroalloy and reduces energy consumption and production costs. So far, semi-coke has been used in the process of iron and ferroalloy production in a limited way, and their results show the advantages of the presence of semi-coke. Therefore, in this research, the carbon materials used in the production of ferroalloys, the advantages of semi-coke, and the production method of semi-coke are discussed.

Keywords: semi-coke, ferroalloy, carbothermic, carbon materials, reducing agent.

1. Introduction

Ferroalloys are very important for making different types of steel and alloys with special properties such as corrosion resistance, hardness, wear resistance, etc. The production of ferroalloys is carried out by carbothermic reduction processes, in which carbon materials are used as reductants in an electric arc furnace. Carbon materials are complex systems that generally have a heterogeneous nature. These materials have various physical and chemical properties. For the production of ferroalloys, different types of carbon-containing materials are used, whose chemical properties control the reduction reaction and have a great impact on the overall cost, amount of reducing agent, energy consumption, operation stability, and finally on the quality of the final product. On the other hand, the physical properties of carbon materials are effective in the productivity and efficiency of the process to achieve sustainable development [1-3].

The main material of carbon is metallurgical coke produced from coal. However, it is possible to use alternative reductants such as coal, charcoal, petroleum coke, coke, semi-coke, etc. The selection of carbon materials for the ferroalloy industry depends on their availability, properties, and cost. About 35 to 40 percent of the total cost of production is related to reducing materials. The high price of biochar and the shortage of good coking coal are forcing industries to find alternative raw materials [2, 4, 5].

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For efficient use in the ferroalloy industry, carbon materials must have specific physical and chemical properties. Low ash percentage, low volatile content, high fixed carbon, high strength, and suitable size distribution are some important properties [6, 7].

A model of the reduction of metal oxides by solid carbon materials shows that most of the oxides of ferroalloy elements (such as chromium, manganese, silicon, etc.) are converted to metal only with solid carbon. Because the ability to reduce carbon oxide gas is not enough to reduce these oxides, parameters such as reduction start temperature, reductant consumption, degree of reduction, and interaction of oxides with carbon must be considered [7].

2. Carbon materials

Different carbon materials are used in the carbothermic method of producing ferroalloys. Coal, which is mainly composed of carbon, hydrogen, nitrogen, sulfur, and inorganic materials, is used both directly and after being converted into coke or semi-coke. The selection criteria for coal are the amount of volatile matter, amount of ash, chemical properties, and reactivity with CO_2 [7, 8].

Metallurgical coke is produced by heating coal in the absence of air at 1100 °C. The most important properties of coke that are affected by coal quality include chemical properties, particle size, reactivity, and strength. Petroleum coke and bituminous coke are also used in the production of ferroalloys, which have a very high price due to the small amount of ash and volatile substances [8, 9].

Charcoal can also be used in the production of ferroalloys as biomass obtained from plants. This material has high volatility, less brittleness, and high moisture absorption [10].

In electric furnaces for the production of ferroalloys, the heat required for the reduction reaction is provided by the passage of electricity through the charging resistance of the furnace. Therefore, the physical properties of raw materials, especially carbon materials, have a significant effect on the reduction process. Carbon reagents are not only a source of carbon for a reduction but also act as a filter for the large volume of gas produced in the reaction zones at the bottom of the furnace [9].

In the ferroalloys production industry, coke is usually used as a reducing agent. In addition, coke is also used for reduction in its production in blast furnaces. Since the mid-1950s, due to the increasing scarcity of metallurgical coke, its high price, and relatively high content of harmful impurities, producers wanted to substitute cheaper carbon agents such as natural (semi-coke, lignin-based coke) or synthetic (coal, briquette coal, and lignin) [11]. These types of agents have high reactive power and low content of sulfur and phosphorus. Some analyses and properties of commonly used carbon materials are shown in Table 1. In the furnace, metal oxides and carbon materials are gradually heated and start reduction reactions. Usually, iron oxides are more easily reduced with CO gas than other metal oxides and converted to iron metal. In this case, the produced CO_2 reacts with the added carbon materials based on the following reaction, which is known as Boudward's reaction [1, 12]:

$$C + CO_2 = 2CO \quad \text{Eq.(1)}$$

Due to the endothermic nature of the Boudouard reaction, increasing the reaction of CO_2 with C leads to an increase in carbon consumption, CO content in the exhaust gas, and energy consumption. Therefore, using a carbon material with high reactivity increases the extent of the Boudouard reaction. Consequently, the ideal carbon material for most process conditions should have low reactivity with CO_2 [1].

The thermal resistance of carbon materials, as one of the influencing factors, may have a limiting effect. Carbon materials with low strength cause environmental pollution through the production of dust. It also creates

Table 1. The most important properties of carbon materials used [1, 12].

	Metallurgical coke	Industrial charcoal	Pine charcoal	Petroleum coke	Wood
Fixed carbon (%)	86-88	65-85	93.8	84-90	15-20
Volatile matter (%)	<1	15-35	3.8	9-16	80
Ash (%)	10-12	0.4-4	2.4	<1	0.1-1
CO_2 activity at 1060 °C (%C/s)	$(0.2\text{-}0.5)10^{-2}$	$(2.1\text{-}2.3)10^{-2}$	$(2.8\text{-}3.2)10^{-2}$	-	-
Electrical resistance (Ωm)	10-20	5-35	-	10-20	10^{14}

fine particles in the furnace that block the charging surface and reduce the electrical resistance in the coke bed. Generally, charcoal has less strength than metallurgical coke [1, 11].

The most important physicochemical property of carbon reducing agents in the production of ferroalloys is electrical resistance, which affects the resistance of the substrate layer and energy distribution in the working space. The specific surface area of the carbon material, which determines the chemical absorption properties of the carbon substrate and, as a result, the extent and completeness of the reduction of elements in the target alloy, affects the porosity and gas permeability of the substrate layer. These properties depend significantly on the temperature and the chemical composition of reducing agents [11].

There are various requirements for the selection of carbon agents in reduction processes: high reactivity that provides a high reduction rate and low starting temperature, porous structure, optimal ash content with low content of sulfur and phosphorus, low content of volatile substances, and being wet; Appropriate size and sufficient mechanical strength at low and high temperatures, low cost, etc. [11].

One of the parameters that can be checked is the special price based on the fixed carbon content of the carbon material. In such a way that charcoal or wood usually has a higher specific price compared to fossil reducing agents. Of course, in some countries such as Brazil, due to having large forests and rare coal reserves, the cost of using charcoal is lower [13].

Since slag can increase the amount of slag produced and change the chemical composition of slag, it is considered an ineffective component in a reducing agent. Therefore, in practice, the amount of ash should be low. Among the carbon materials, wood and charcoal have the lowest average ash and coke has the highest ash. Charcoal performs better than fossil compounds (coal and coke) regarding the average ratio of ash to fixed carbon. Accordingly, replacing coke with charcoal reduces 62.6% of ash for metallurgical operations [12, 13].

In carbothermic reduction processes, the major source of input sulfur is reducing agents. Therefore, the amount of sulfur in reducing agents should be as low as possible. Sulfur content is the highest in fossil reducing agents. Charcoal has the lowest ratio of sulfur to fixed carbon, and replacing coke with charcoal reduces sulfur by 94% for metallurgical operations [2, 13].

One of the substitutes for coke is semi-coke. Semi-coke (also called blue coke and semi-carbon coal) is a solid carbon product with the low volatile matter, which is obtained from the thermal decomposition of bituminous coal with high volatile matter content and low cracking ability at low temperature (500-650 °C) or medium (650-800 °C) [14, 15].

Semi-coke has unique characteristics such as high fixed carbon, high specific strength, high chemical activity, low ash content, low aluminum, low sulfur, low phosphorus, etc. These features have made it widely used in industries such as chemical industries, metallurgical industries, gas industries, etc. Meanwhile, semi-coke has been used to produce calcium carbide, ferroalloys, ferrosilicon, silicon carbide, silicon manganese, and calcium carbide, and in recent years in the iron production process in blast furnace. The standard specifications of semi-coke are shown in Table 2 [16].

Semi-coke has a highly branched internal structure, even more so than the original coal. During the process of use, due to the eruption of volatile substances, the coal breaks and increases its reactivity compared to semi-coke. However, the formation of a large amount of fine-reducing particles in the bed of the electric furnace during the process reduces gas permeability and disrupts the normal flow of the reduction process [7].

In reduction processes, coal is the most active. After that, semi-coke and coke can be called. But coal is crushed mechanically at a temperature of 500-700 °C under a standard load of 2 kg, while under the same conditions, the semi-coke completely maintains its shape [7].

Semi-coke even entered the urban clean fuel market in 2014 and has been recommended as an alternative raw material for coal. It is an alternative clean fuel in the process of converting coal to electricity and coal to gas [16].

Since 1978, the semi-coke industry has developed greatly for 40 years. After choosing the type of furnace on a large scale, how to cool the semi-coke with steam and also treat the process effluents, improve the technology level of semi-coke production. Gradually, the possibility of using large quantities of even low-rank coal and producing semi-coke products of high quality and low price significantly developed the semi-coke industry. Of course, the quality of semi-coke depends on the composition of coal and the operating parameters of the furnaces. In general, the advantages of semi-coke compared to metallurgical coke in ferroalloy production can be stated as follows [16]:

Table 2. Semi-coke standard specifications [16].

standard specifications	Fixed carbon (%)	Moisture (%)	Ash (%)	Volatile matter (%)	Sulfur (%)	Phosphorus (%)	Size (mm)
	min 83	max 15	max 9	max 8	max 0.4	max 0.03	6-18

- Improving the quality of ferroalloys, especially low alumina alloys ($Al_2O_3 \leq 0.1\%$)
- Significant reduction in electricity consumption (saves approximately more than 1000 kWh, i.e. 8-10%)
- Reducing the cost of raw materials because they are cheaper
- Replacing coke, petroleum coke, and charcoal with semi-coke is very simple and there is no need to upgrade the equipment.

3. Methods of semi-bake production

In most coal conversion processes, pyrolysis is the first step. In general, two processes of polymerization and condensation occur when coal is heated. Gas, water vapor, and tar are produced in polymerization processes. Next, coke or semi-coke is formed during the condensation or repolymerization process [17]:

$$\text{coal} \rightarrow \text{char (coke/semi-coke)} + \text{tar} + \text{gases (e.g. } H_2 \text{ and CO)} \quad \text{Eq.(2)}$$

Production of semi-coke from different coals has been done industrially in different companies. Figures 1 and 2 respectively show the classification of semi-coke based on different raw materials and the general flow diagram of semi-coke production factors [18].

Semi-coke is produced from raw material under high heating rates and different temperature paths by pyrolysis. Types of pyrolysis processes can be divided into normal pyrolysis, fast pyrolysis, flash pyrolysis, and low pyrolysis. Meanwhile, the pyrolysis process produces more semi-coke with a fast and low heating rate. The characteristic of the semi-coke formation process is that first drying and disposal occur at a temperature of more than 300 °C, followed by primary decomposition and polymerization with the formation of semi-coke and intermediate products of bitumen and gases. Compared to slow pyrolysis, in fast pyrolysis, there is a possibility of reducing the efficiency of bitumen formation, while the volume fraction of gases such as carbon monoxide increases and as a result, carbon dioxide decreases [18, 19].

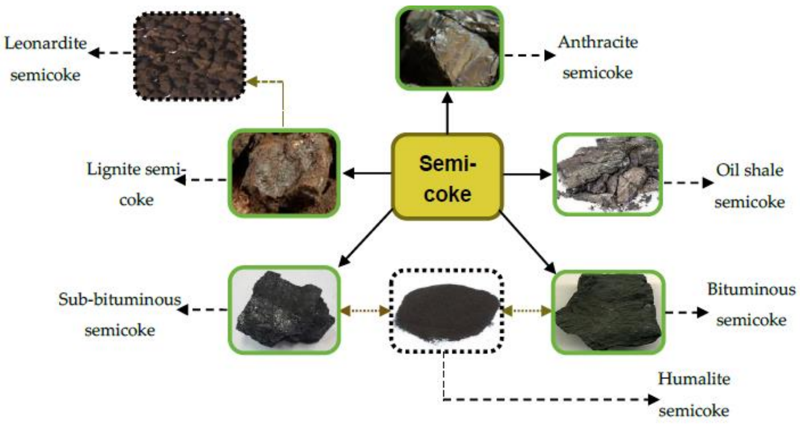


Fig. 1. Classification of types of semi-coke after processing [18].

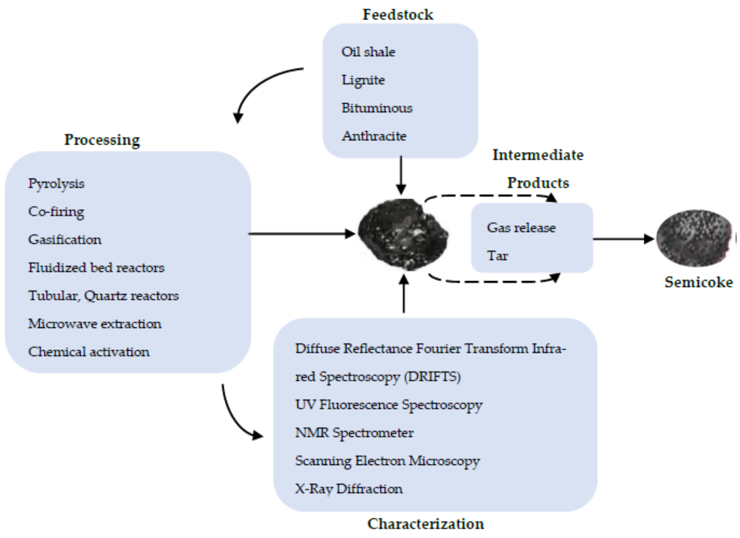


Fig. 2. Flow process of some semi-coke preparation factors [18].

Figure 3 shows a schematic of a conventional process for producing semi-coke from a low-rank coal. Due to the specific macromolecular structure of semi-coke, producing significant pores of different sizes dispersed within the particles, relatively high heat (thermal decomposition) must be provided to break the matrix. In this process, the possible slow pyrolysis phenomenon can affect the performance. Many of the surface and internal components of semi-coke are vaporized in the initial stages of pyrolysis. Of course, further heating leads to significant losses and decomposition of aromatic structures by changing the aromatic and aliphatic structures at high temperatures, which affects the process performance. These conversions are the same in the different semi-coke processing methods, despite minor differences during the initial periods of semi-coke operation and heating [18, 20].

Among the primary sources of semi-coke, coal and oil shale are difficult to burn due to their low content of organic and mineral substances. Essential parameters for semi-coke production include pyrolysis time, coal particle size, and ambient pressure, which can increase production efficiency. Recently, it has been reported that the use of fluidized bed reactors, fixed bed reactors, and drip tube reactors can reduce the rate of semi-coke produced by gasification processes [18, 21].

One of the points that are considered in the production of semi-coke is how to cool it after the conversion process. In traditional technology, the semi-coke produced is cooled by water spray. Therefore, during quenching, due to the thermal shock, micro-cracks are formed throughout the semi-coke grains. In the case, of the new method with semi-dry quench, there are no such cracks in the semi-coke, and for this reason, its crushing happens to a small extent [7].

Production of semi-coke is done through low-temperature distillation. Since the early 90s, the internal heating shaft furnace has been developed and successfully converted coal as raw material into semi-coke. This relatively simple process is used today as the main process on an industrial scale for semi-coke production due to features such as lower investment, easy control, and higher tar recovery. Of course, this process has problems such as high water consumption, more dust output, technical and economic index at a lower level, etc. (Figure 4) [22].

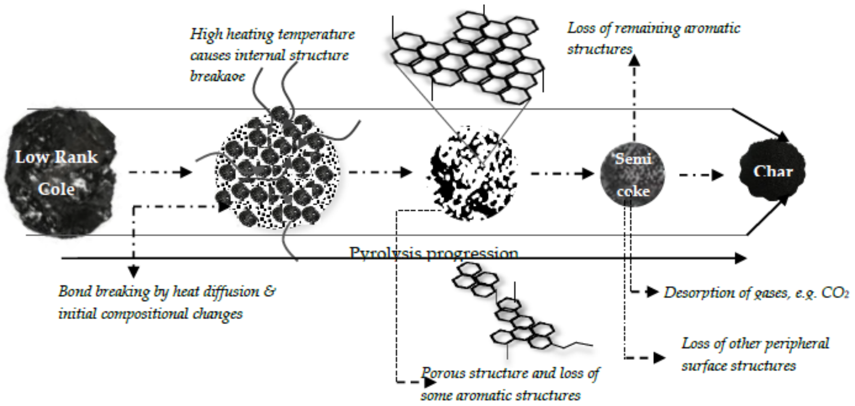
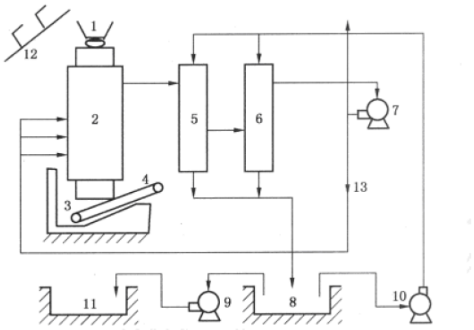


Fig. 3. Outline of the semi-coke production process [18].



1.coal adding tunnel; 2.shaft furnace; 3. coke quenching pool;
4. semi-coke discharge; 5.gas cooling tower; 6.gas,tar and water seperating tower; 7. blowing engine; 8. tar seperating pool;
9. tar pump; 10.water pump; 11. tar collection pool;
12. coal hoisting machine; 13. gas pipe

Fig. 4. Semi-coke production flow chart [22].

In addition to consuming a lot of water, cooling semi-coke traditionally also affects the quality of the product. In the semi-coke industry, in the dry quenching process of semi-coke after bitumen separation, cool neutral gas is used to cool the hot semi-coke. In this case, the heat of semi-hot coke is recovered from the neutral gas and used in the coal distillation process. By doing this, 10% of energy consumption and more than 30% of water consumption are reduced. In this condition, the moisture content of the product can be controlled by up to 5% (Figure 5). The amount of heat loss in coke production is about 330,000 cal/ton of coke, and for semi-coke, it is about 160,000 cal/ton of coke [22].

Sometimes annular furnaces can be used to produce coke or semi-coke from various solid fuels. Coal pyrolysis in these furnaces involves heating a relatively thin layer (50 to 200 mm) of coal charge on a movable furnace to a certain temperature.

Semi-coke production is also done in chamber outdoor furnaces. This method has a little environmental impact and the following operations are performed: preparing coal, crushing it, charging it into the chamber and baking it in outdoor furnaces, cooling semi-coke with water, discharging it from the furnace, crushing it, and classifying it. In this process, semi-coke baking includes the following steps [23]:

- Release of water vapor at a maximum temperature of 200 °C.
- Release of volatile substances (H_2, CH_4, CO, aromatic hydrocarbons, water bound to chemicals) in the range of 350 to 600-700 °C.
- The transformation of the solid phase into a plastic state at around 400 °C.
- Hardening of the plastic mass at 500-550 °C to form semi-coke.
- Formation of the final product at a temperature of 950-1000 °C.

Figure 6 shows the schematic of the semi-coke production process in Sary-Arka-Spetskok company, which includes the following steps: coal preparation, pyrolysis (semi-coking), cooling and discharge of semi-coke, classification, purification of the resulting gas and use from waste [24].

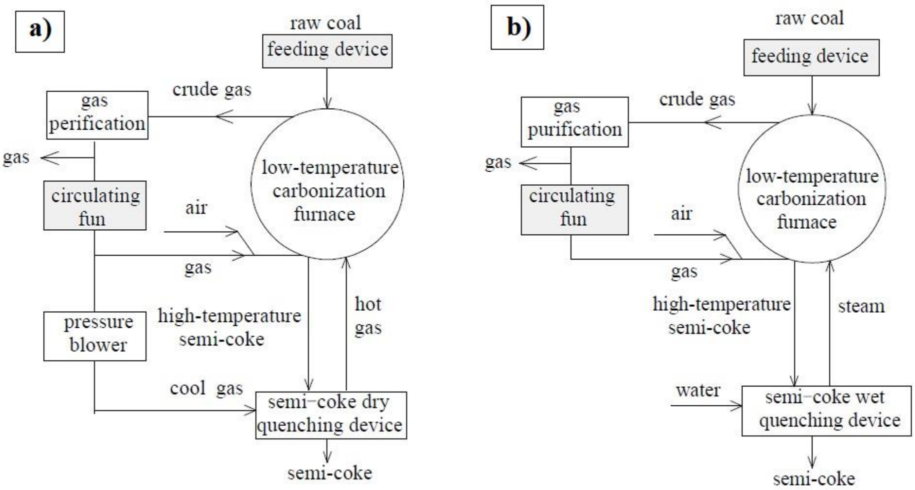


Fig. 5. Coke quenching process: a) a conventional method and b) a new method [22].

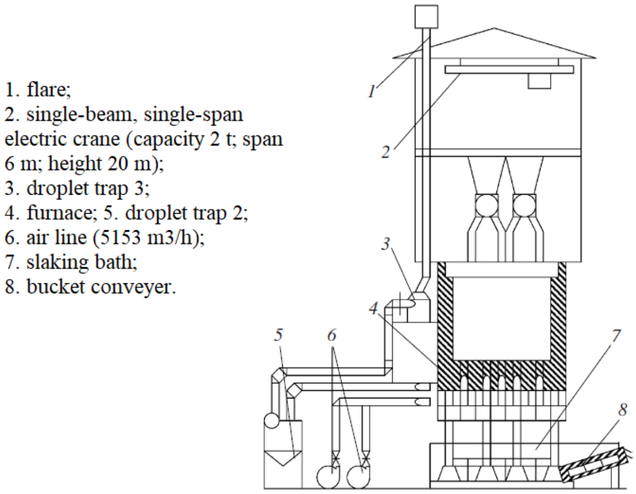


Fig. 6. Pilot unit for semi-coke production [24].

In another process, semi-coke baking is done in a low-temperature square furnace with drying, pyrolysis and cooling zones. Raw coal is in the furnace for about 6 hours. The baking temperature of semi-coke is 500-600 °C. The semi-coke is cooled by a water bath, which when exiting, the temperature of the semi-coke is 70 to 80 °C and the moisture is about 25% [24].

In the gasification unit of AO Kazakhstan INVEST KOMIR company, semi-coke is produced by the coal gasification process. This process includes the following steps: preparing coal and loading it from the top of the reactor, providing air for combustion, adjusting the temperature of the reaction zone to less than 1100 °C, cooling the semi-coke, and discharging the reactor [23].

In China's Shenmu region, semi-coke is produced in a plant equipped with vertical SJ furnaces. Coal is loaded through the tanks on the furnace. Gas is injected to heat the charge through tubes in the furnace walls. With partial combustion, the volatile components of the coal are released and the gas uniformly heats the coal load. In the baking area, the temperature reaches 750±20 °C. In the cooling zone, the temperature is above 80-100 °C. For cooling, semi-coke is charged to a water chamber [23].

4. Use of semi-coke

In addition to the use of semi-coke as a reducing agent, the production of semi-coke during coal tar by pyrolysis can be used as a solid heat carrier, which is economical. On the other hand, semi-coke provides many active surfaces due to its semi-porous structure [25]. Therefore, a good catalytic activity can be obtained from semi-coke [26]. Of course, the production of semi-coke with steam, due to the creation of a larger surface area and more metal species on its surface, causes a much better catalytic performance for tar reduction than raw [15].

To expand the range of fuel types in the iron making process, the possibility of using semi-coke as fuel injected into the blast furnace as well as alternative fuel for sintering has been comprehensively investigated. The research results showed that both basic properties and technological features (grind ability, explosiveness, fluidity, ignition temperature, calorific value, etc.) using semi-coke in these two processes have many technical and economic advantages [27-29]:

- The basic properties of semi-coke including ash, volatility, fixed carbon, and calorific value make it capable of being used as injection fuel for blast furnaces and alternative fuel for sintering machines. On the other hand, the chemical composition of semi-coke, such as low sulfur content, low zinc content, and low alkali content, will have a beneficial effect on the performance of the blast furnace and sintering machine.
- Due to the processing properties of semi-coke, it can be used for the injection process instead of anthracite as an injection fuel in the blast furnace. The use of semi-coke as an alternative fuel reduced the coal rate and the overall fuel rate of the blast furnace. In such a way the addition of semi-coke has reduced the cost of coal by 4.8 Yuan/t.
- The use of semi-coke in the sintering process improves the sintering properties (both chemical properties and physical strength). Of course, the proportion of semi-coke in the total fuel should be 30 to 40% to prevent excessive combustion while benefiting from the high reactivity and high calorific value of semi-coke.

In a study, the preparation of semi-coke from low-grade coal and the possibility of its use in ferroalloy industries with a partial replacement of coke/wood coal have been investigated [2].

Table 3. Characteristics of several coke production systems [23].

	unit	product	Notes
Arcelor Mittal Temirtau	Coke battery	Metallurgical coke	Coke oven gas is used in the factory. A by-product collection system is required.
Aksai ferroalloy plant	Movable mesh system	Semi-coke	Volatile materials burn on top of the grate system of the furnace.
Aksai ferroalloy plant	open furnace	Metallurgical coke	Coke oven gas is burned in an external oven. Purification is unnecessary.
Sary-Arka-Spetskoks	Experimental unit	Semi-coke	Semi-coke gas is burned in an open furnace. Purification is unnecessary.
Kazakhstan Invest Komir	Gasification reactor	Semi-coke	Semi-coke gas does not contain dust or tar. It is used in the metallurgy and electrical industries.

Since the fixed carbon content of semi-coke is equal to petroleum coke and even better than coal, it shows high specific resistance and good chemical reaction. Therefore, adding a certain ratio of semi-coke to the carbon reducing agent is expected to improve the SiO_2 reduction process and thus the performance of the silicon furnace. Due to the low sulfur content of semi-coke, less nitrogen oxides will be produced during the desulfurization process after replacing petroleum coke. In general, it can be concluded that adding a certain ratio of semi-coke to carbon reducing materials, while increasing resistance, and reducing the consumption of raw materials and electrodes, improves the efficiency of the silicon furnace. The presence of semi-coke in the mixture of carbon materials in the silicon furnace increases the exergy efficiency to 0.34 without recycling and to 0.44 during recycling. Therefore, semi-coke can be used for the production of industrial silicon in silicon furnaces as a reducing agent instead of petroleum coke and coal, it also reduces the cost of preparing carbon reducing agents and environmental pollution [28].

Pavlov and et al. [7] investigated the simulated reduction process of ferrochrome using coke, semi-coke, coal and graphite. They showed that semi-coke starts its reaction with chrome rock at 1200°C, while coke reaction starts at 1400°C or more. Of course, at a temperature above 1600 °C, the reaction power of all carbon agents is the same. Finally, they concluded that semi-cake, which has a low level of moisture and volatile substances, can be an efficient and effective substitute for filings cake.

In a research in Iran Ferosilis Company, Etemadi et al. [30] investigated the effect of seven different combinations of carbon materials including metallurgical coke, coal, charcoal, semi-coke and wood chips on process energy consumption and product quality. It was shown that due to the higher porosity of semi-coke compared to other carbon agents, the transfer of SiO gas becomes easier and its reactivity improves, which leads to an increase in furnace efficiency. Comparing coke with metallurgical coke, the specific electrical resistance of semi-coke is higher at all temperatures. In this research, it was shown that the presence of 30-35% of semi-coke in the composition of carbon materials reduces the energy factor per ton and increases the silicon recovery [29].

5. Conclusions

The production of ferroalloys is usually done by the carbothermic method with different carbon materials. Since carbon materials play an important role in product quality as a reducing agent, their properties were investigated in this research. The physical and chemical properties of carbon agents affect the performance and production efficiency of ferroalloys. Among the carbon materials used, semi-coke has recently attracted attention due to a series of important properties, including high fixed carbon, high specific strength, high chemical activity, low ash content, and low sulfur. Therefore, the use of semi-coke improves the quality of ferroalloy and reduces energy consumption and production costs.

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