To the Question of the Production of Silicon Carbide

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Abstract. The issue of qualified use of the whole granulomeres composition of petroleum coke is considered. The possibility of using petrochemical fines for the production of silicon carbide is shown. Various technologies for upgrading petro-coke fines are presented and their advantages and disadvantages are revealed. An optimal variant of the preparation of petrochemical fines, in which the main driver for the production of silicon carbide is proposed. The possibility of a significant increase in the reactivity and specific surface area of oil reducing agents due to precision sifting by refined petrochemical fines and removal of excess moisture from petrochemical fines is shown. Due to the evaporation of moisture and the action of water vapor on the carbonaceous material, a positive effect can be created, consisting in the vapor activation of the reducing agent, accompanied by an increase in its reactivity and resistivity. It has been established that the increased humidity of the reducing agent degrades the heat balance of the electric smelting because of the heat costs for evaporation and, in part, the dissociation of water, and also causes an increased consumption of the reducing agent due to its active oxidation with water vapor and water dissociation products.

1. Introduction

In recent years, silicon carbide has firmly won a place among semiconductor materials. Already long established applications of polycrystalline silicon carbide that use its semiconductor properties based on it produce ignitron arsonists, heaters, electrical furnaces, various types of nonlinear resistors, etc.

Silicon carbide is a material that has an extremely wide range of useful properties: electrical, anti-corrosion, strength. Due to this, it is increasingly being introduced into the technology. High hardness allows using it as an abrasive, and heat resistance and chemical inertness determine its application as a refractory structural and protective material in metallurgy, mechanical engineering, chemical building [1].

Silicon carbide is a physical and chemical compound of carbon with silicon: Si₂C (Si=C=Si). Grains of silicon carbide, thanks to the solid and crystalline structure with high cutting capacity, are suitable for the processing of varnish, paint, putty, glass, ceramics, stone, cast iron, titanium, rubber and various polymers.

Production of silicon carbide is carried out according to the formula:

\[ \text{SiO}_2 + 3 \text{C} = \text{SiC} + 2 \text{CO} \ (1600-2500 \degree C) \]

As carbon, the petrocoke trifle is applied. We have presented the use of the total grain size composition of petroleum coke refers to the problem of refining coke. The difficulty of calcining small fractions of coke due to their intensive combustion requires the development of alternative ways of
involving this product in further production or giving coke fines such properties that would meet the requirements of a certain range of consumers. The petrocoke trifle turns out when cutting coke "pie" the hydro cutting torch [2].

We have studied dependence of formation of a petrocoke trifle by production of crude coke as reducer by production of carbide of silicon; it is presented in the figure 1.

Figure 1. Granulometric composition of total petroleum coke.

The graph shows the grain size composition of the Angarsk refinery's oil coke breeze, which shows that the content of the fraction of the oil coke breeze (0-8 mm.) is 50% of the total volume of the oil coke.

Also conducted a separate study of the granulometric composition of the fraction of 0-8 mm. With the purpose of studying the individual properties of things (the content of inner moisture, the volume of the open pores, porosity, specific surface). The graph shows the grain size composition of the Angarsk refinery's oil coke breeze, which shows that the content of the fraction of the oil coke breeze (0-8 mm.) is 50% of the total volume of the oil coke.

Figure 2. Granulometric composition of the fraction of 0-8 mm.

A dashed line in Fig. 2 draws the total line of all measurements. The graph shows that, 70% of the fines is a fraction of 0-3 mm. studies have shown that this fraction contains the largest number of
internal moisture (15 %), therefore, the release of this moisture will increase the volume of open pores and the specific surface area.

The fineness of carbon reducing agent is of great importance for the production of silicon carbide, the smaller the better. The lower limit is determined by the conditions of removal of particles from the upper layer of the ore-thermal furnace by the core gases, the upper technical and economic considerations (class yield, quantity and feasibility of small items, etc.)

Research of oil-box trifle has shown that the content of internal moisture does not allow using a trifle in the form in which it is made on installation.

The moisture of the reducing agent is harmful for the production of silicon carbide for a number of reasons. It is a source of hydrogen, makes it difficult, and with a high content makes it impossible to process the screening and obtaining an unconstrained reducing agent. Fluctuations in the humidity of the reducing agent make it difficult for it to accurately dose and comply with the given excess carbon.

Due to the evaporation of moisture and the impact of water vapor on the carbon material, a positive effect can be created, consisting in the vapor activation of the reducing agent, accompanied by an increase in its reactivity and resistivity. The recovery rate depends on the surface available to the oxidizer, carbon activity, reaction mechanism and conditions of their course.

The moisture content of oil cokes at the ultrasonic cooling system is due to the specifics of their discharge from the coking reactors by water jets. In this case, the discharged coke is moistened by both contact with water and transport of water through pore channels, and by "drawing" water into the pores of the coke because of condensation of vapors and reducing the volume of gases in the pores during cooling of coke [3].

The presence of large (up to 15 %) amounts of moisture in coke creates considerable difficulties when it inside the installation processing for ultrasonic testing (low efficiency of screening on the roar of freezing in winter in the bunkers), transportation (freezing in winter in cars), unloading and consumption. Transportation of coke with high moisture content - ballast-leads to irrational use of railway transport. In addition, during the calcination of dried coke, its fumes are reduced and fuel consumption is increased by 10-20% the productivity of the calcining plants [4].

The porosity of coke when using high-pressure water jets in the process of its unloading from the reactors causes the presence of moisture in it both internal, filling the pores, and external, located in the inter-inlet space.

Kinetics of dehydration of the total coke in the at-reactor spent fuel area (storage of coke, combined with the filter sump) shows that is safe against freezing, the total moisture of coke (FR. 0-250 mm) 8% is achieved after 15-16 hours. It should be noted that increasing the performance of existing ultrasonic inspection by reducing the coking cycle to 24 h or less, the coke with at-reactor spent fuel site in the bunker warehouse ships in 4-5 h with a moisture content of 12-15%, but if no delay, with a moisture content of 15-25%. That is, natural dehydration of total coke does not reach the required level – 7 - 8%.

These circumstances cause the need to address the question of whether the forced removal of moisture from the coke directly to UT. It is experimentally established that oil coke in the pores can hold more than 30% of moisture, which is 97% free, i.e. able to move under the influence of gravity.
The calculations have shown that the most effective installation for drying petrocoke trifle breeze is a drum type dryer, in the work carried out its calculations, for the cost of capital investments and energy. When using a drum dryer, humidity is reduced to 3-4 % at a capacity of 20 t/hour. The drum has a diameter D = 2 m, and a length L= 12 m. the residence time of the material in the drum 20 minutes.

Advantages of drum dryer:
* Intensity and uniformity of drying due to the close contact of the material and the drying agent;
* Relative simplicity and compactness of the device;
* Great performance;
* Large voltage of the drum with moisture;

It should be noted that the thermal drying of coke on the narrow is quite a costly process. The estimated cost of manufacturing the main process equipment of the drying plant with a capacity of 20 t / h in Russia will be 50 thousand dollars. In addition, when using a coke drying plant on the narrow, it is necessary to have intermediate bins of large capacity to ensure the continuity of its operation.

The main indicators of the quality of oil-coke fines affecting the process of silicon carbide recovery are the reactivity and specific surface area. Learning these indicators allows us to draw a conclusion about the possibility and method of ennobling (activation) of oil-box trifles.

Physic-chemical properties of reducing agents have a complex effect on the efficiency of slag-free processes. Currently, however, there was no model, which would reflect the contribution of each of the properties and in interaction with others. It is only known that with the increase of the surface, reactivity and resistivity, the efficiency of the use of reducing agents increases. Therefore, when talking about requirements, there is no need to limit the upper limit of indicators. It will be determined by the efficiency in production and in use. The establishment of the permissible lower value of the physical and chemical properties of the reducing agent is necessary, but it is a complex and responsible task. For reducing agents for siliceous alloys, such indicators are ECP = 7 m2 / h, PC=0.8 ml (g-s), EPP=3 Ohms-cm [5].

In the process of drying petroleum, coke to temperatures 470 – 490 C is steam activation of oil coke breeze increases the surface and porosity due to the release of capelar water, in this connection increases the reactivity of the fines. The reactivity of a carbon reducing agent characterizes its ability to react with carbon dioxide (CO2). The results of the research allow us to conclude that the PC MIND is determined by their molecular and crystal structure, degree and nature of porosity. Moreover, the PC of petroleum coke (NK) depends on the influence of various factors:
* Quality and preliminary preparation of raw materials;
* Coking technologies;
* Heat treatment temperature;
The properties of oil-box fines, including the reactivity can be regulated by pre-heat treatment of the coke itself [6]. Properties of a petrocoke trifle, including reactionary ability can be regulated preliminary heat treatment of coke [6].

![Figure 4. The dependence of the reactivity of the moisture of coke.](image)

From Fig. 4 shows that the reactivity drained petrocoke trifle higher than the little things with the moisture content (10-15 %).

The specific surface area of the particles significantly affects the behavior of powders during molding and sintering. It is very important for reactions taking place on the surface of materials. The specific surface area is the sum of the outer surfaces of all particles present in a unit of its volume or mass. It depends on the size, shape and microstructure of carbon particles. Determination of the specific surface area was carried out on a multifunctional device PSH-12, designed to measure the gas permeability of porous samples, the specific surface area and the average particle size of powders. The measurement results of the device PSH-12 (SP) meet the standards: European (DIN, ISO), American (ASTM).

![Figure 5. Dependence of a specific surface on humidity of coke.](image)

From Fig. 5 it can be seen that the specific surface of the drained oil-coke fines is much higher than the fines with a moisture content (10-15 %).

Pilot tests on the furnace with a capacity of 1000 kW of the Irkutsk aluminum plant have shown the principal possibility of using the oil-coke trifle of the Angarsk refinery as a component of the carbon part of the charge in the production of silicon carbide [7].
2. Conclusion
Thus, it was found that the increased humidity of the reducing agent worsens the heat balance of the electric furnace due to the heat costs for evaporation and, partially, water dissociation, as well as causes an increased consumption of the reducing agent due to its active oxidation by water vapor and water dissociation products. In addition, when using a wet reducing agent, there are difficulties with its sieving on vibrating screens, especially in the process of separating the FR trifles. 0-8 mm. However, the greatest negative impact in general is not so much the absolute moisture content as the instability of this indicator, which causes a decrease in the accuracy of furnace charge by carbon.

It is shown that the increase in the reactivity and specific surface area of the oil-box trifle entails the improvement of the technology of silicon carbide production and a reduction (by 15-20%) of material and capital costs for its production

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