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Comparative analysis of modern trends in the use of industrial wastes of coke chemistry

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Abstract. Modern methods of using industrial wastes of by-product-coking industry are analyzed. The paper contains the review of the main types of coke production waste. The environmental aspects of waste disposal and utilization are considered. The analysis of the use of liquid and solid wastes in technological processes is carried out.

1. Introduction

The use of wastes from by-product-coking industry is an important issue widely discussed in the literature [1 - 23]. When coking coal a significant amount of waste is formed, which until now do not find any effective use. In addition, the toughening of environmental requirements for the production of coke-chemical products dictates the need to find solutions for the recycling and use of various types of waste. One of the pressing problems of the coke-chemical industry is the problem of expanding the raw material base of coking by using low-quality coal in the coke to replace the better quality one.

The purpose of this work is a comparative analysis of current trends in the use of industrial wastes of coke chemistry.

Among the wastes of by-product coke production are liquid wastes (heavy coal-tar products, acid tar, polymers, etc.) and solid wastes (coke dust).

2. Resinous wastes

Tar sludges – heavy residues of coal tar, containing 40-50% of coal and coke dust, carried by coke oven gas. They settle on the bottom of mechanical sedimentation tanks and clarifiers and represent a heavy viscous mass [1].

Tar sludges are used as a fuel or as part of a charge for coking and gasification. They are mixed and pelleted with basic components and other types of combustible waste. In many factories, due to the lack of equipment, a significant mass of tar sludges is not used and is sent to storage tanks.

The second area of application of tar sludges is the construction industry. On the basis of tar sludges, materials are made for protective coatings of concrete, reinforced concrete and metal products. Such compositions are obtained by dissolving tar sludges in white alcohol and other solvents with the addition of polyvinyl chloride resin and subsequent settling. Coatings have a stable hydrophobicity, high strength and water resistance.

Acid tar – residues of condensation of light tar from coke oven gas and polymerization products of unsaturated compounds present in coke oven gas under the influence of sulfuric acid during the process of gas purification from ammonia.

Acid tar is added to the coke during coking and used in the production of bitumen of different grades, for the production of sulfur dioxide followed by processing it into sulfuric acid [2].

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The tar is also used as an additive to cement clinker for intensification of grinding and activation of cement hardening, as swelling additives to the charge in the production of expanded clay. After neutralization, it can be used for the production of road tar oils. Neutralization is carried out with alkaline waste and reagents. It is possible to use sour resin instead of joiner's glue.

Thus, the resinous waste of by-product-coking industry is used in the construction industry and can be returned to the main cycle as part of the charge for coking.

3. Coke dust

Coke dust is trapped from dry quenching plants when blowing with inert gases of unloaded coke, as well as from installations for dustless coke discharge from coke-oven battery. It is almost not used due to the complexity of unloading and transportation, therefore it is usually returned to the charge of coking in the amount of 1% of the charge mass or processed "in situ" using various methods of compaction and packing, or packed into containers (sacks). In general, due to the finely dispersed state and high ash content, the coke dust is not suitable for direct use [11, 12].

The volumes of coke dust are very high, on average, about 18-20 thousand tonnes of coke dust per year is generated at one coke plant. Traditionally, dust accumulated in storages (which are already filled) or added to the charge without prior technological preparation. Other ways of wastes disposal (burial, burning, biodegradation) were also ineffective.

At present, the raw material base for coking and the replacement of coking coal grades with low-caking grades have changed significantly, and there are changes in the technology of charge preparation, including with the use of coke dust.

The modern coal raw material base is very unstable in terms of its grades composition and technological properties, coal is unevenly supplied to the plants, and the charge for coking is multicomponent. Fluctuations in the quality of the charge can not be eliminated only through organizational measures in the coal industry. It seems that the problem of obtaining blast-furnace coke from the charge of modern grades composition can be solved by introducing new efficient technological processes for the preparation of this charge with an increase in the loading density [11, 12].

The effectiveness of all new methods of preparation of coal charge before coking, including briquetting, is largely due to the increase in the density of coal charge in the furnace chambers. Moreover, the increase in density not only serves for increase in the productivity of the furnaces, but also improves the conditions for sintering the products of the destruction of coal grains of various sizes and degrees of metamorphism, and, consequently, the mechanical strength of coke.

To expand the coking feedstock base, different methods are used to prepare the coal charge for coking, in particular, compaction of coal charge with the addition of fluid waste of by-product-coking production. A number of authors propose to use such wastes as a binder for partial briquetting of coal charge for coking, which will allow not only the amount of low-caking coal grades to be increased, but also the production wastes to be disposed. The increase in the charge density is 800-870 kg/m^3, which leads to an increase in the strength of coke [13, 14].

Briquetting of coke dust, including mixing of the crushed solid fuel with a binder component, is considered in the sources [13, 14]. As a pulverized solid fuel, pre-enriched coke dust is used for the oil agglomeration, and the preheated carbamide is used as a binder component. It is also possible to use tar as additives (after neutralization) to the charge for coking (gasification), formed as a waste during interaction of tar products of coke oven gas with sulfuric acid in the process of ammonium sulfate production.

Thus, the possibility of using coke dust together with other production wastes in the charge for coking coal is shown in figure 1.

The use of highly dispersed materials of technogenic origin, that have no value and have large amounts of accumulation, as raw materials is a relatively new, promising and energy-saving direction in electrothermal processes, in particular, silicon carbide technology [15, 16].

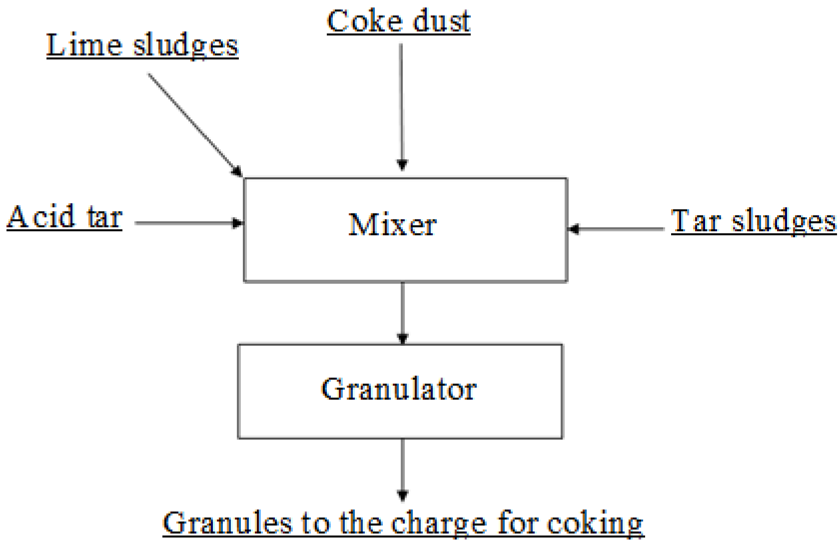

Figure 1. Schematic diagram of charge preparation from wastes of by-product-coking production.

According to the existing thermodynamic concepts, the process of carbon thermal reduction of silica proceeds with the active participation of gaseous silicon oxides. The size effect, arising in the one-component system "gas-dispersed crystalline phase", consists in changing the saturated vapour pressure above the surface of crystalline particles, depending on the degree of dispersion of the solid phase. It is supposed that the interaction rate can be increased by increasing the evaporation surface of SiO_2 and using a carbonaceous reductant with a high adsorption capacity and a developed surface [17]. Coke dust may be proposed as such reducing agent.

To realize the electrothermal process on the basis of microsilica and coke dust, the technology of furnace synthesis of highly dispersed silicon carbide has been developed, which makes it possible to obtain a product with a specific surface of 3000-4000 m/kg and a carbide content of 90-92 wt% [16].

Thus, the coke dust together with other wastes of by-product-coking production can be successfully applied in the composition of coke charge and in some electrothermal processes.

4. Wastewaters of by-product-coking production

By-product-coking production is the source of a significant number of highly toxic secondary products (wastes). The greatest part of them (about 99%) is phenolic wastewater generated in the process of coking coal charges; the share of other wastes (acid tar, tar sludges, oil, etc.), formed in the shops for the trapping and processing of coking products, is about 1%. Wastewater contain various oils, suspended solids and other impurities of organic and inorganic origin, most of which are harmful, making it difficult to use wastewater in production.

The amount of wastewater and the concentration of impurities in them depend on the quality of the coked coals, operating conditions and the state of the chemical equipment and is usually 0.25-0.3 m^3/h per 1 ton of coke charge, the absolute amount is up to 150-170 m^3/h [18-21] .

Phenolic waters disrupt the natural processes of self-purification. Surface water reservoirs, especially small ones, are converted into sewage ditches without animal and plant world. They can not be used for cultural, recreational and household needs. In addition, surface water reservoirs contaminated with phenolic wastewater contribute to the deterioration of the quality of underground water sources.

Currently, there is a number of environmentally-friendly technical solutions that can significantly reduce the harmful impact of wastes from by-product-coking production on the environment, taking into account the specificity of their physical and chemical properties. Reduction is carried out by means of mechanical, extraction and biochemical methods [22].

Purified and neutralized wastewater from the by-product-coking production is used in its circulating cycles and in related industries. Scientists [3] write about the possibility of using supramolecular water as an inhibitor of carbonate salt deposition, while observing optimal concentrations.

5. Coke oven gas

Coke oven gas is formed during the coking of coal as a result of thermal decomposition and is a by-product in the production of coke. Approximate composition of coke oven gas, % vol.: CO_2 1.6 – 3%, O_2 0.4 – 0.8%, N_2 2 – 3.5%, C_mH_n 2 – 2.5%, CO 5 – 6.5%, CH_4 24.5 – 26.5%, H_2 58 – 62% [3].

Direct coke oven gas undergoes compulsory treatment, during which vapours of resins and water condense, and ammonia and benzene hydrocarbons are trapped. After such treatment the gas is called the inverse and it is used mainly for combustion as a fuel alone or in the mixture with a blast furnace one.

6. Conclusion

The review of main types of waste from by-product-coking production on the basis of modern literature is presented. It is established that one of the most urgent environmental problems is the need to recycle industrial waste. Modern ways of using by-product-coking productio wastes, including as charge materials of electrothermal processes (silicon carbide production) are analyzed.

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