Petroleum and Coal

Review **Open Access**

The Rational Use of Coke Breeze: A Review

Darina Sagalay [1], *Denis Miroshnichenko* [2]

[1] *State university of economics and technology Technological institute, 50006, Stepana Tilhy str. 5, Kryvyi Rih, Ukraine*
[2] *National Technical University «Kharkiv Polytechnic Institute», 61002, Kirpychova str. 2, Kharkiv, Ukraine*

Received November 2, 2020; Accepted January 15, 2021

Abstract

The article provides an analytical review of the results of modern, rational methods of recycling and disposal of coke breeze (dust) of coke production. Directions for briquetting, granulation, use of coke breeze as carbon sorbents are considered. The methods of thermo chemical activation of coke dust have been investigated. It is proposed to use coke dust as a raw material for obtaining adsorption-active materials. The results of a study of the effect of sulfuric acid heat treatment on the adsorption capacity of carbon materials and further heat treatment to achieve the effect of thermal expansion are presented.

Keywords*: Coke breeze; Briquetting; Agglomeration; Thermo chemical activation, Carbon sorbents.*

1. The formation and quality indicators of coke breeze

Metallurgical enterprises are inextricably linked with the production of coke. One of the main products of the coking process is coke breeze (dust). It is formed in the course of any technological operations (sorting of bulk coke, dry quenching of coke, overloading of coke, etc.). It is a valuable fuel with a high carbon content. Due to the complexity of unloading and transportation, coke dust is usually returned to the charge in an amount of 1% by weight of the charge (which reduces the volume of the payload of the coal charge) or is processed «on site» by using different compaction and packing methods (very rarely, no technology). Such features of coke dust as fine dispersion and hydrophobicity make it difficult to store and use it in pure form [1–4].

According to the Ukrainian scientific manufacturing association UKRKOKS, in 2019, Ukraine produced ~10 million tons of bulk coke, with a yield of coke breeze about 4 % [5]. In the process of coke sorting, coke is divided into size classes. According to TU U 322-00190443-011 – Technical characteristics of coke breeze [3], depending on the ash content, coke breeze is divided into three grades, conventionally designated: CB 1, CB 2, CB 3. Technical characteristics of coke breeze are presented in Table 1. The physicochemical properties of blast-furnace coke, coke nut and coke breeze are presented in Table 2. Dust from a dust-free coke dispenser is formed when dispersed coke particles are captured from the air during the dispensing of a coke oven.

During the coking of coal, a significant amount of dust is formed, which until now have not been effectively used. In addition, the tightening of environmental requirements for the production of coke-chemical products dictates the need to find solutions for its utilization and use. During dry quenching of coke, the formation of fine coke dust is inevitable. It is formed when unloading coke from the oven into a coke-carriage, when loading the dry coke quenching unit chamber, when lowering the mass of coke in the chamber (due to the friction of the pieces against each other), when unloading coke from the quenching chamber onto the conveyor, as well as on drops from the conveyor to the conveyor [2].

Tab.1. Technical characteristics of coke breeze –TU U 322-00190443-011

Indicators name	Unit	Production name		
		Coke breeze, grade CB 1	Coke breeze, grade CB 2	Coke breeze, grade CB 3
Ash content (A^d), no more	%	13.0	16.0	18.0
Mass fraction of total moisture (W^r_t,) no more	%	22.0	22.0	24.0
Mass fraction of pieces larger than 10 mm, no more	%	8.0	8.0	6.0
Pieces size	mm	0-10; 0-8	0-10; 0-8	0-8

Table 2. Physical and chemical properties of blast furnace coke, coke nut and coke breeze [4]

Name of quality indicators	Unit	The value of a physical quantity with limit deviations
Main components	%	C–95.0-98.0; H–0.5-1.3; O-0.5-1.1; N-1.0-1.5; S–0.6-2.5
Melting temperature,	˚C	Not less than 1250
Ignition temperature,	˚C	from 600 to 700
Autoignition temperature,	˚C	800
Density	g/cm^3	True – 1.7-2.0; Apparent – 0.8-0.9
Solubility		Insoluble in water, organic solvents and fats
Reactivity of coke	cm^3/g· sec	0.2-0.4 (for blast furnace coke)
Prevailing form of air presence	mg/m^3	Aerosol of coke dust, predominantly fibrogenic, MPC = 6.0
Coke electrical conductivity	ohm· m/mm^2	200-450
Coke fracture, degree of fracture	T gen.	0.194-0.241

To capture dust in various places of dust formation in the technology of dry quenching of coke, effective aspiration systems are provided [5]. Large dust particles, which have the greatest erosive effect on the pipes of the waste heat boiler and the blades of the smoke exhauster, pumping the circulating gas into the quenching chamber of the dry coke quenching unit, are captured in the dust collecting bin. In the cyclones of the dry coke quenching unit, finer dust is captured, and at the final stage of cleaning - in bag filters with different cleaning surfaces – the smallest dust particles are captured. All these dust sediments are fed by pneumatic transport into a common dust collector from which they are periodically unloaded [2].

2. Techniques and methods of use of coke breeze

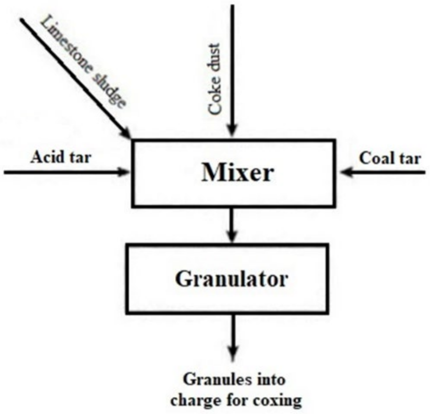

Fig. 1. Schematic diagram of the preparation of the charge from the wastes of coking plants coke production

At present, the raw material base of coking has changed significantly, and the replacement of coking coal grades with weakly sintering grades requires changes in the technology of charge preparation (Fig. 1.), including with the involvement of coke dust [6]. Coke dust requires special preparation for recycling. One of the preparation methods is blocking. Today there are three main ways of agglomeration of coke dust:

Briquetting– the process of obtaining pieces (briquettes) with and without the addition of binders, followed by pressing the mixture into briquettes of the desired size and shape.

Granulation– the process of processing material into pieces of geometrically regular, uniform shape and equal mass, called granules.

Agglomeration – the formation by sintering of relatively large porous lumps of fine ore or pulverized materials. During agglomeration, the low-melting part of the material solidifies and binds together solid particles.

Using these methods, dust can be added to the charge for coking or used as a material for foaming steel-making slag [7]. The problem of utilization of coke dust for coke chemists is very urgent. It is advisable to return the dust-like waste generated in the process of dry quenching and dispensing of coke to the cycle of coke production with the use of compaction of the charge. Moreover, it is necessary to study the effect of such additives on the ramming capacity of the charge.

The procedure for introducing dust into the charge during the experiments was as follows. First, the dust was moistened to the value of the moisture content of the charge, then it was added to the latter in the calculated amount, thoroughly mixed, and placed in a sealed container. The ramming capacity of the charge was determined using well-known methods [2] with some changes: two hits by a falling weight instead of three, the weight of the sample was 0.75 kg (instead of 1.1 kg). At the same time, the specific work of ramming did not change and amounted to–500 J/kg, which corresponds to the work of ramming in an industrial ramming-loading-ejection machine.

The ramming ability was assessed by the shear strength of the rammed sample (σ_s) and by the sample density (γ). Samples of dust of various sizes were taken for research (Table 3). The smallest size is the dust from the bag filter, the largest - from the dust collection bunker.

The results of testing the charge for ramming at different mass content of these additives in it are presented in Table 4. The ramming capacity of the initial charge at a moisture content of 11.5 % and at a grinding level of 91.0 % of the class < 3.15 mm was characterized by the following values of indicators: σ_s = 0.68 N/cm^2, γ = 1.146 g/cm^3.

Table 3. Granulometric composition of dry coke quenching unit and dust-free coke dispenser

Dust collection point	Content of size class (mm) %							
	>5	5-3.15	3.15-0.5	0.5-0.25	0.25-0.125	0.125	<0.5	<3.15
Dust bunker	5.1	7.0	53.8	23.9	7.8	2.4	34.1	87.9
Bag filter BFPR 650	–	–	–	23.0	14.4	83.3	100.0	100.0
Dust collector dry coke quenching unit (total dust)	0.4	15	4.1	20.6	38.5	34.9	94.0	98.1
Dust-free coke dispenser (total dust)	–	–	2.2	10.8	34.9	52.1	97.8	100.0

Table 4. Influence of coke dust from dry coke quenching unit and dust-free coke dispensing unit on ramming capacity of coal charge

Dust collection point	Indicators of ramming capacity of the charge (σ_s, γ) with the content of coke dust, %									
	σ_s N/cm^2	γ, g/cm^3	σ_s N/cm^2	γ, g/cm^3	σ_s N/cm^2	γ, g/cm^3	σ_s N/cm^2	γ, g/cm^3	σ_s N/cm^2	γ, g/cm^3
Dust bunker	0.68	1.144	0.67	1.141	0.65	1.138	0.61	1.131	0.53	1.114
Bag filter BFPR 650	0.72	1.154	0.78	1.161	0.82	1.167	0.83	1.171	0.80	1.171
Dust collector dry coke quenching unit (total dust)	0.70	1.149	0.73	1.152	0.76	1.161	0.76	1.159	0.74	1.154
Dust-free coke dispensing unit (total dust)	0.72	1.152	0.77	1.159	0.80	1.163	0.81	1.165	0.79	1.161

The data obtained show that the highest ramming capacity is characteristic of the charge with the addition of the most dispersed dust, which is captured by the bag filter. The maximum strength of the rammed samples is observed when the content of this dust is 3-5 %. The excess of σ_s in comparison with the same indicator of the initial charge is 0.14-0.15 N/cm^2.

The addition to the charge of dust from the dust-settling hopper of the dust dry coke quenching unit, which is characterized by a high size (higher than the size of the charge for compaction), leads to a decrease in the strength and density of the compacted sample – especially when adding > 3 % additive.

The total dust of the dry coke quenching unit, including dust from cyclones, dust collection hopper and bag filters, has a positive effect on both strength and density of the charge. The maximum values of these indicators are observed with a dust content in the range of 3-5 %. The increase in the density of the sample is 1.2 %.

A further increase in the addition of dust (up to 7 %) leads to a decrease in the values of both indicators, although they remain higher than for the initial charge. Thus, the introduction of the total dust of the dry coke quenching unit and dust-free coke dispensing unit into the charge for compaction can significantly increase the strength of the compacted cake, as well as increase the one-time charge of the charge into the coking chamber by 1.2 %. For a more complete assessment of the efficiency of feeding the dust of the dry coke quenching unit and dust-free coke dispensing unit into the charge, it is advisable to study their effect on the mechanical strength of coke and its output from the charge [2].

According to the authors of [8], the addition of finely ground coke breeze and anthracite increases the strength of coke and the yield of its large classes due to a decrease in shrinkage. When loading a wet batch in a furnace in bulk, the addition of coke breeze allows an increase in M_{40} and the yield of large grades of coke without deteriorating M_{10}. Therefore, it may be of practical interest to improve these characteristics or to reduce the cost of the charge. However, it is impossible to reduce the share of coke oven coal, because such a reduction would lead to an increase in M_{10}, which is not compensated by the addition of coke breeze. The use of coke breeze under these conditions is only of theoretical interest and cannot be recommended to industrial workers.

Another conclusion can be reached when the attrition strength of the coke is given a lower value. This applies to the practice of producing foundry coke, which must be larger and remain so, despite the mechanical stress that it undergoes. In these cases, the addition of coke breeze is recommended. When loading the rammed charge, the addition of coke breeze becomes absolutely mandatory, since in this process the goal is to obtain M_{40} of about 80. Tamping effectively improves M_{10}, but not M_{40}. From this it follows that cokes from the rammed charge have both high abrasion strength (and this allows the introduction of a significant amount of lean additives) and a low M_{40} index, which can be improved by adding coke breeze [8-9] or coke dust [10].

In works [11], studies were carried out on the effect of various leaning additives on the indicators of sintering capacity and sintering capacity of coals. The authors proposed a sequential series of fillers in descending order of caking capacity and sintering ability: dry coke quenching unit dust → coke breeze → dust-free coke dispenser.

Higher indicators of sintering capacity and sintering ability for coals with the addition of dry coke quenching unit dust and crushed coke breeze in comparison with dust-free coke dispenser dust are most likely explained by the anisotropic and rather porous structure of the particle surface: the plastic mass penetrates into pores and irregularities, its so-called «jamming», which in turn leads to a stronger contact.

The introduction of additives in certain quantities (in most cases – up to 1% of the charge weight) allows to influence the processes occurring at the stage of the plastic state, to improve the strength properties of coke and increase the yield of its large classes, which is especially important in the production of foundry coke.

Solodov *et al.* [1] to developed and substantiated the scientific and technological foundations of the process of utilization of coke dust in the form of briquettes and granules of increased strength. The studies were carried out with medium ash coke dust, the proximate analysis of which is presented in Table 5.

Table 5. Proximate analysis of the original coke dust

	W^a, %	A^d, %	V^{daf}, %	S^d_t, %	Q_s, MJ/kg
Coke dust	4.8	6.6	3.3	0.4	37.6812

A number of laboratory studies were carried out on the method of oil agglomeration with various types of binders: waste engine oil from the exhausters of the turbine hall of coke-chemical industries, carbamide, polymers, bitumen, paraffin. Urea, copolymers, bitumen and paraffin, before being introduced into the concentrate, were heated to a temperature: up to 100°C – carbamide, bitumen and paraffin, more than 200 copolymers. Binders were added in an amount of 1-2 % by weight of the concentrate. The pressing took place in steps: at first, the load was 5 atm, with a holding time of 3 minutes, and then up to 15 atm with exposure at maximum load 5 min. The step load was applied based on the experience of briquetting described in the world literature. In this case, an optimal interaction of the components in the mixture is achieved, with the formation of a briquette structure.

Briquettes made with the help of copolymers had the highest strength. Briquettes with the use of urea as a binder have the best characteristics. These briquettes had the best characteristics and, accordingly, are applicable in any technology for using briquettes [1].

Kravtsov and Papin [12] studied the agglomeration of coke dust using the technology of briquetting and thermal briquetting. The research stand consisted of a stamp press, a mold for pressing, a muffle furnace, where the briquette was heat treated. As a binder, fossil fuses of coal tar were used, since they are also a waste of coke production, obtained in quantities sufficient for the implementation of the process directly at the enterprise.

Briquettes prepared with the use of coal fossils that have not undergone thermal preparation are not smokeless, therefore, as a fuel, they are suitable only for large enterprises with a powerful chimney cleaning system. Small businesses and private consumers need smokeless briquettes, so in the future it is necessary to achieve smokeless briquettes. For this purpose, thermal briquetting and heat treatment of briquettes were used. It was found that with a lack of binder, the briquette loses its shape when removed from the mold for pressing, and with an excessive amount of the briquette, it can burn at the stage of its heat treatment or thermo briquetting during calcination. The selection of the optimal pressing pressure was also carried out, which amounted to 150 kPa. At this pressure, the briquette did not lose its shape when removed from the pressing mold (it did not collapse). The temperature regime of briquette calcination was selected - 250-300°C, at a heating rate of 25°C per minute. The optimal ratio of the mass of coke dust and the binder component was chosen, it is equal to 92:8 %. This confirms the dependence of professor Elishevich, according to which the addition of a binder of more than 10 % of the mass of the test substance is economically and technologically unprofitable. The briquettes obtained by thermal briquetting had better characteristics than the briquettes obtained by thermal treatment. However, the process of thermal briquetting is much more energy-intensive than thermal treatment, this is due to the heating of the mold and heat loss.

Livenets [13] also noted that low-smoke briquettes for technological purposes with high mechanical strength and heat resistance can be obtained by using finely dispersed materials with a low volatile matter (for example, coke or semi-coke dust) as a carbon filler. Lignosulfonate concentrate can be recommended as a binder in obtaining such briquettes using the proposed technology, and in the case of increased requirements for the sulfur content of briquettes, its mixture (in the form of emulsions) with bitumen, soft pitch, molasses (sugar production waste) [14]. Using the proposed technology at the pilot plant of JSC Talmenka-Holding-ZhBI (Altai Territory), pilot batches of briquettes from crushed coke breeze of JSC Koks (Kemerovo) with the addition of 10 % lignosulfonate concentrate were obtained. These briquettes have been successfully tested as partial substitutes for coke in cupola smelting of cast iron at

OJSC Universal (Novokuznetsk) and at a number of other enterprises. The work was carried out under the guidance of Nikishanin and Grigorkin (JSC «Talmenka-Holding-concrete goods») [15-16]. When obtaining briquettes for fuel and technological purposes from finely dispersed carbon-containing materials and wastes, a developed low-operational technology was used, which (in contrast to the classical one) makes it possible to practically exclude the most energy-intensive and ecologically most unfavorable stage - thermal drying of the initial finely dispersed raw materials [15-16]. Tests for assessing the strength of briquettes were carried out according to the standard crushing and dropping procedures given in [14] (Table 6).

Table 6. Characteristics of briquettes for technological purposes based on coke and semi-coke breeze and dust

Mix composition, %	Binder consumption, %	Pressing pressure, MPa	Briquette parameters		Strength of dried briquettes		Heat resistance, %
			diameter, mm	mass, g	for dropping, %	for compression, MPa	
Dust dry coke quenching unit - 100	8	25.0	50	80	96.10	8.73	97.2
Dust dry coke quenching unit	8	100.0	50	80	98.50	11.42	99.8
Crushed coke breeze – 100	10	37.5	80	275	98.40	8.74	96.9
Crushed coke breeze – 85; Anthracite - 15	10	37.5	80	275	97.40	8.50	95.0
Crushed semi-coke screenings- 100	8	25.0	50	50	97.10	7.08	86.7
Crushed semi-coke screenings- 100	8	100.0	50	50	98.10	8.07	90.9

This technology makes it possible to obtain briquettes and coke briquettes for technological needs on the basis of coke and semi-coke breeze and dust, as well as durable and heat-resistant fuel briquettes. By granulation on a disk granulator using water glass and lignosulfonate concentrate as binding aqueous solutions, coal-mineral compositions were obtained from pulverized waste from furnaces for the production of ferrosilicon (which are based on silica) and finely dispersed carbonaceous materials (screenings of coke and lignite semi-coke).

Dried granules (with a content ratio $C_{act}/SiO_2 = 0.55$) were proposed to be used to obtain silicon alloys and metallurgical silicon carbide, the method of production of which involves calcining the dried granules in an oven at 1800°C [16]. Granules, for which lignosulfonate or liquid glass are used as a binder, have high strength. When the mixtures are lumped on water (without a binder), weaker and relatively small granules are obtained, which are quite acceptable for use, for example, in the production of silicon carbide.

When briquetting and granulating various dusty waste (including carbon waste), not only the issue of their utilization is solved quite competently, which has a positive effect on the economy of the main technological processes, but also the damage to the environment is reduced [14].

There is a method for producing coke briquettes, including mixing coke breeze with liquid petroleum bitumen, to which 4-6 % of coke dust is preliminarily added, and then mixed with a concentrate of sulfite-alcohol stillage, modified with 10-20 % of carbamide powder by weight [11,15]. Briquetting of the mixture is carried out on a roller press with external pressure applied for 20-30 minutes. Use coke breeze with a particle size, mm: >0.05 – 10 %; 0.025 -0.05 – 25 %; 0.01-0.025 – 35 % and – 0.025 – 30 %.

The disadvantage of this method is associated with the difficulty of realizing in practice the exact ratio of the specified particle sizes of coke dust. There is one more way to obtain coke briquettes, which includes mixing fines with a particle size, mm: 0.55-3 – 20 %; 0.2-0.55 – 30-35 % and – 0.2 – 50-75 % with a binder based on a sulfonic acid derivative (liquid or powdery ammonium or calcium lignosulfonate) in an amount of 3-10 % by weight [17]. The mixture is briquetted at a pressure of 100-200 MPa, followed by heat treatment of the briquettes at 200-700 °C for 10-120 minutes.

The disadvantage of this method is the significant capital costs associated with the installation of presses that develop high pressure, which entails additional energy costs and reduces the productivity of the installation. Also, over consolidation of the briquette leads to a significant decrease in its reactivity

In 1995 Luriy proposed a method for producing coke briquettes, calling it «KOKSBRIK» [18]. Briquettes obtained by this method are proposed to be used as an energy carrier and a reducing agent for electro thermal production of phosphorus, cast iron, steel, ferroalloys, refractory products, sugar, as well as fuel in household and industrial furnaces. The proposed method [18] includes mixing coke breeze with 3-10 % by weight of a binder based on a sulfonic acid derivative, briquetting the mixture and subsequent heat treatment at 200-700 °C for 10-120 minutes. For mixing, coke breeze is used with a particle size in the following ratio: 6-2.5 mm - 15-25 %, < 1 mm - up to 100 %. Briquetting is carried out under a pressure of 5-90 MPa. Lignosulfonate or sodium salt of methylene naphthalene sulfonic acid is used as a binder. Which can be modified by 10-30% by mass of the distillation residues of tall oil rectification.

Kuznichenko *et al.* in their work [19] propose the introduction of coke breeze with a particle size of < 10 mm into the charge for coking since coke dust is several times cheaper than blast furnace, and even more so - foundry coke, it is advisable to turn it into expensive lumpy (metallurgical coke) with a certain preparation. In addition, coke breeze could partially compensate for the deficiency of lean caking coals, the presence of which in the charge is necessary. At the Kharkiv Coke Plant, the charge loaded in bulk from Donetsk coals with the addition of 5 % coke breeze (over the charge, i.e. from the total weight of the charge) and without the addition were coked. Coke breeze was crushed to 100 % content of class ≤ 2 mm. The results of coking are shown in Table 7. Coking conditions: coking period - 14 hours, temperature in the control vertical from the coke side - 1350°C.

Table 7. The quality of coke from experimental mixtures

Charge characteristics									Coke quality			
Grade composition, %					Proximate analysis, %				Class content size, %		Drum strength Sudgren, kg	
G	Zh	C	OS	Coke breeze	W^r_t	A^d	V^{daf}	St^d	>80	1.3	rest	<10 mm
10	45	25	20	-	9.1	6.8	25.4	2.11	18.6	59.0	345.2	20.5
10	58	25	7	5	8.9	7.2	27.4	2.17	32.7	68.2	338.3	28.4

In [20], studies on the preparation of petroleum coke briquettes from coke breeze obtained at a delayed coking unit for heavy oil residues and oxidized bitumen obtained by oxidation of tar, heavy pyrolysis resin or an extract from selective oil purification are presented.

The softening temperature of the used bitumen is 55-65°C. The listed components are mixed at a temperature of 180-200°C. The amount of binder is 7-15 % of the total mass. The binder is preliminarily subjected to thermal oxidative treatment at a temperature of 230-250 °C until a predetermined softening temperature is reached. The resulting mass is removed from the mixer and subjected to pressing under a pressure of 25 MPa.

The State Enterprise «UKHIN» developed technical conditions TU U 10.1-00190443-069-2002 for coke-coal briquettes [11]. These technical conditions apply to briquettes obtained by briquetting coke breeze, hard and brown coal, anthracites and their processing products (coal mines, slimes) and other organic products, as well as their mixtures, with the addition of a binder, a stabilizer, filler and water repellent.

Depending on the feedstock (coke breeze, coal products and their mixture), briquettes are divided into three types: coke briquettes; coal briquettes and coal-coke briquettes, respectively.

Cement, water, glass, lignin, lignosulfonates, molasses, starch-containing products, their mixtures or their processing products are used as a binder (3-10 %) for coke-coal briquettes.

Environmentally friendly substances. Chalk, lime, hydroxides and oxides of magnesium, manganese, etc. are used as a stabilizer (up to 2 %). It is allowed to use a filler (up to 60 %). It is a fine fraction and dust of products of metallurgical and other industries. Products of paraffinic and silicone nature are used as a water repellent, in an amount of up to 2 %.

The main consumers of such briquettes are domestic and foreign enterprises of the metallurgical, sugar industry, and the household sector [21]. Technological regulations have been developed for obtaining briquettes for the conditions of several Ukrainian enterprises.

The advantages of briquetted fuel have already been appreciated in Europe. In England, Germany, Czech Republic, Poland, Turkey, as well as the USA, Australia and other countries, briquettes based on fine coal are produced in large volumes using various technologies [11]. Based on the above studies, it was concluded that agglomeration of finely dispersed carbon-containing materials is currently a relevant process in modern production, the processes of agglomeration and granulation remain poorly studied. Foreign researchers [22-23] propose to use xylene as a binder to obtain briquettes from coke breeze.

In addition to briquetting coke breeze and dust, other methods have been proposed to improve the consumer properties of these materials.

Recently, more and more often began to investigate coke dust as industrial sorbents by the method of thermo chemical activation. Proceeding from the fact that coke dust contains 88-98 % carbon, it can also be suitable for thermo chemical treatment as a raw material for the production of adsorption-active carbon materials. Carbon sorbents are used in various forms: in the form of a powder with a particle size of up to 0.8 mm, large granules, blocks of various shapes and sizes, films, tissue fibers. The most common are powdered sorbents, which are quite easy to obtain from crushed raw materials (in this case, coke fine is considered).

The role of carbon sorbents based on coke and coke breeze in solving environmental problems is constantly increasing: the purification of drinking water, effluents, waste gases of industrial and energy enterprises. Their advantage is low ash content, although their sorption capacity is lower than that of sorbents based on activated carbons.

The characteristics of some sorbents used for broad purposes: for water purification, atmospheric air are given in Table 8 [24]. As can be seen from Table 8, there is a fairly large assortment of means for cleaning environmental objects from organic and inorganic toxicants.

Table 8. Characteristics of carbon sorbents

Sorbent type	Variety	Specific surface, m^2/g	The volume of the sorption space, cm^3/g
1. Carbon adsorbents	1.1. Granular UA:		
	a) spherical shape of granules	1000	0.9
	b) the cylindrical shape of the granules	1100-1250	0.8-0.9
	c) crushed nut ADB -13	800-900	1.2
	1.2 UA CARB (based on metal carbides)	120	0.4-1.2
	1.3 UAS (carbon black based)	300	0.3-1.2
	1.4 Activated carbon fiber materials	1000	0.9
	1.5 cellulose hydrate AUVM with a chemically modified surface	1100-1200	0.9
	1.6 Fiber PAN and other active carbon felt materials	1000-1100	0.8
	1.7 Activated carbon fabrics and materials based on them	1100	0.9
	1.8 Medical and dosage forms of carbon adsorbents, enterosorbents	1000-1200	0.4-1.2
	1.9 Dispersed carbon materials for medical use	1000	0.7
	1.10 Carbolen (powder, tablets)	200-450	0.2-0.3

In [25], studies were carried out to remove resinous substances from excess water of coke production. The following materials were used as sorbents in the studies: activated carbon,

carbon sorbents based on coke, and layered double hydroxides. Carbon sorbents (initial raw material - coke breeze of the Mariupol coke plant) were obtained as follows: the samples were dried, dispersed with the collection of fractions of 1-5 mm, carbonized at a temperature of 300 to 800°C, and then activated at a temperature of 800°C superheated steam in the presence of 1 % oxygen. To obtain various samples of activated carbon materials, the time and temperature of carbonization and oxidizing agents were varied, as well as the conditions for the action of oxidizers on carbon materials. HNO_3, H_2SO_4, $K_2Cr_2O_7$, H_2O_2, as well as solutions of various concentrations were used as oxidants; the oxidation was carried out, as a rule, at the boiling point of the solution. Carbon sorbents have a structure consisting of aromatic rings (the same as in resinous compounds - petroleum products), and can have a high adsorption capacity [25].

Therefore, various carbon sorbents based on coke were studied, obtained by heat treatment and additional oxidation with various oxidants - the most common of them are concentrated sulfuric acid, nitric acid, a mixture of sulfuric acid and potassium bichromate. The data obtained are shown in Fig. 2.

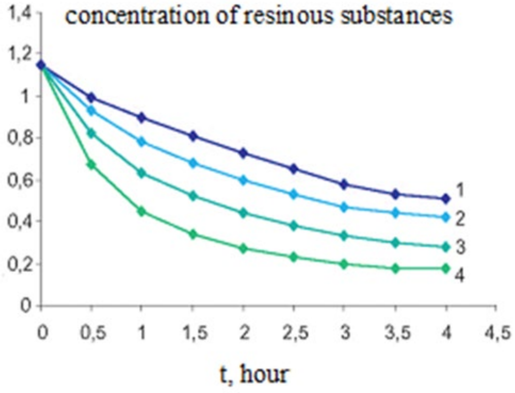

Fig. 2. Absorption of resinous substances by carbon sorbents treated with different oxidants for different times
1 – H_2SO_4; 2 – $K_2Cr_2O_7$; 3 – HNO_3; 4 – H_2SO_4 + $K_2Cr_2O_7$

Studies of adsorbents based on coke, obtained by heat treatment and additional oxidation with various oxidizers, have shown that sorbents obtained by treatment with a mixture of sulfuric acid and potassium dichromate have the highest activity (this mixture has a high oxidizing capacity, which leads to a high concentration of active oxygen centers on the internal surface of carbon material). Sorbents based on coke and coke breeze can be successfully used for the removal of resinous substances due to their low cost in comparison with activated carbon [25].

Researchers [26] subjected coke dust to activation with sulfuric acid and potassium hydroxide with further heat treatment to develop porosity and impart sorption properties [27-28]. A schematic flow diagram of methods for obtaining carbon sorbents by methods of thermo chemical activation of coke dust is shown in Fig. 3.

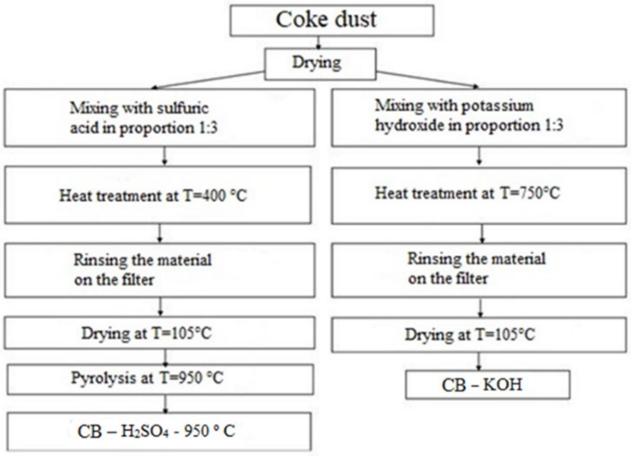

Fig. 3. Basic technological scheme of methods for obtaining carbon sorbents

On the basis of the obtained data, a method is proposed for increasing the grade of commercial toluene by sorption of impurities obtained by an adsorption-active material. When implementing the above technology, several types of relatively cheap sorbents with adsorption and structural characteristics similar to those of some industrial activated carbons were obtained from the by-product coke production waste [29-30]: material of high-temperature sulfuric acid treatment, allowing to increase the interlayer space (sample CB – H_2SO_4 - 950ºC); alkaline treatment material with selectivity to certain classes of hydrocarbons (sample CB – KOH). In addition, for the obtained materials, after their use, a utilization system can be developed, rather than regeneration.

The authors propose the use of these materials within the framework of a by-product coke plant as sorbents, selective to impurities of saturated hydrocarbons in commercial toluene for the subsequent increase in its grade. The initial stage of research on the study of the selectivity of the obtained materials was determined by the adsorption of heptane from its solutions in toluene by the refractometric method.

The sorption isotherm was constructed by the finite volume method, changing the concentration of solutions in the range of 10–90 wt. %. Based on the results of the above experiment, the carbon materials CB – H_2SO_4 - 950°C and CB – KOH were recommended as sorbents selective to saturated hydrocarbons [26].

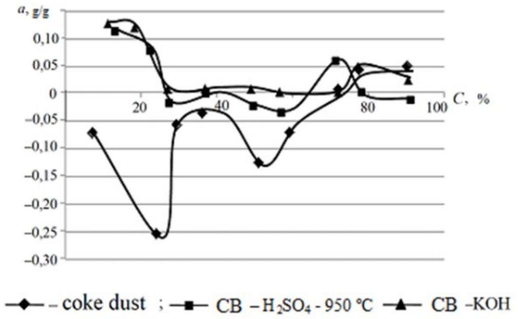

Fig. 4. Adsorption isotherms in the toluene-heptane system

To study the selectivity of samples of carbon materials CB – H_2SO_4 - 950 ºC and CB – KOH to saturated hydrocarbons using the example of adsorption of heptane from its solutions in toluene, a sorption isotherm was constructed by the finite volume method, changing the concentration of solutions in the range of 10-90 % (Fig. 4).

The isotherms indicate that carbon sorbents mainly adsorb heptane in the initial concentration range, which confirms their selectivity towards saturated hydrocarbons in dilute solutions. Thermo chemical treatment makes it possible to increase the selectivity to the investigated substances by changing the nature of the surface and acquiring additional porosity by the materials. The original coke dust sorbs mainly toluene.

Despite the high adsorption characteristics of the CB – KOH sample, the isotherm for the CB – H_2SO_4 sample - 950ºC is proportional to the amount of sorbent and has an upward character, which indicates the advantage of physical sorption (Fig. 5, 6) [24].

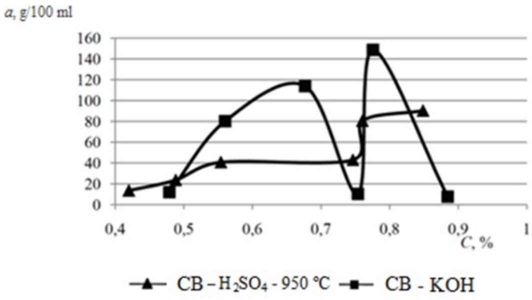

Fig. 5. Isotherms of adsorption of saturated hydrocarbons from commercial toluene by samples of carbon sorbents

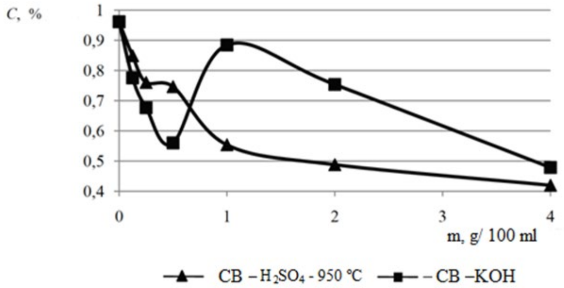

Fig. 6. Change in the content of saturated hydrocarbons depending on the amount of carbon sorbents

Also in the works of Andriyantseva and Bondarenko [31] investigated the methods of thermo chemical activation of coke dust, determined the adsorption properties of the obtained material. A full factorial experiment was carried out on the plan matrix of the second-order composite rotatable uniform planning to determine the optimal conditions for sulfuric acid treatment to obtain an oxidized intermediate product. The surface morphology of the samples was investigated using atomic force microscopy.

The authors of [29] present the results of a study of the effect of sulfuric acid heat treatment on the adsorption capacity of carbon materials and further heat treatment to achieve the effect of thermal expansion. In the technology of obtaining thermally expanded carbon material, there are two stages:

1) activation at 400ºC in the presence of sulfuric acid;
2) heat treatment at 950ºC [32].

To reveal the influence of activation methods, the equilibrium static activity for benzene, the lightening ability for methylene blue and the activity for iodine were determined. To determine the surface morphology of the samples, the surface of their particles was examined using atomic force microscopy (AFM). Based on the results obtained, the use of the obtained sorbents in the proposed method for increasing the grade of commercial toluene was proposed. To determine the optimal conditions for sulfuric acid heat treatment, a full factorial experiment was carried out according to the plan-matrix of the second-order compositional rotatable uniform planning 23 [33]. The temperature of the heat treatment and the concentration of the oxidant were chosen as independent variables.

The properties of the obtained material were evaluated according to the following parameters: product yield; humidity; volatile matter; ash content; sulfur content; adsorption capacity for benzene; iodine number; brightening ability for methylene blue; true density; porosity. Second-order equations were investigated for an extremum (maximum) as a multidimensional problem in the considered range of values of variables, which made it possible to determine the optimal process conditions for each parameter. The optimal values of the change in the concentration of sulfuric acid are in the range of 40÷67.95 %, the upper limit of the change in the range is taken to be optimal C = 68 % of the mass. The optimum heat treatment temperature was 415°C. The efficiency of the subsequent heat treatment of the adsorption-active material (AAM) was investigated to achieve the effect of thermal expansion based on the technology of obtaining graphite.

To reveal the influence of activation methods, the equilibrium static activity with respect to benzene, the clarifying ability for methylene blue, reflecting adsorption in mesopores, and the activity with respect to iodine, characterizing microporosity, were determined [34]. The results are shown in Table 9.

Table 9. Characteristics of the adsorption parameters of the carbon sorbent

Sample	Equilibrium static activity according to S_vH_v (g), g/100 g	Brightening power for methylene blue, %	Iodine activity
Initial C. D.	0.55	29	8
CB-H_2SO_4 – 415°C	1.36	37	31
CB-H_2SO_4 – 950°C	4.96	150	42

The research results showed that thermal oxidation insignificantly affects the transitional porosity and does not affect the microporosity of the material; subsequent heat treatment significantly affects the appearance of micropores and increases the transitional porosity by a factor of 5. Therefore, this material can be used as an adsorbent in the range of initial values of the relative pressure of organic compounds. To study the selectivity of the material, solutions of heptane in toluene of various concentrations were prepared, to which a certain amount of AAM was added.

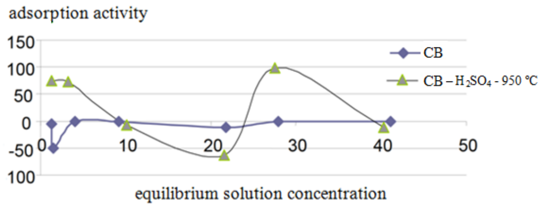

Fig. 7. Isotherms of adsorption of heptane from its solution in toluene

The adsorption capacity of materials in a heptane-toluene solution is shown in Fig. 7. The obtained isotherms showed that in the initial concentration range, the activated sample adsorbs predominantly heptane. According to the graph, it can be assumed that the lower the concentration of heptane in toluene, the greater the selectivity to it in CB-H_2SO_4 is 950°C. The original coke dust adsorbs mainly toluene. The adsorption-active material CB-H_2SO_4 -950°C can be recommended for the purification of commercial toluene impurities. To determine the purification efficiency, 25 mL of toluene were poured into flasks with a capacity of 50 mL and a weighed portion of the sorbent was added (the weighed portion was varied in the range of 0.5 g/100 mg of toluene). A day later, samples were taken.

Analysis on the chromatograph «Crystal 2000M». Based on the results of chromatographic analysis, the concentrations of equilibrium solutions were determined, the dependence of the residual concentration of saturated hydrocarbons on the sorbent mass (Fig. 8) and the sorption isotherm of saturated hydrocarbons from commercial toluene at 200°C (Fig. 9) were plotted.

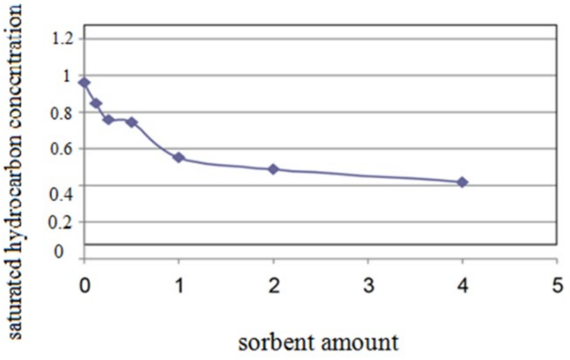

Fig. 8. Change in the content of saturated hydrocarbons depending on the amount of sorbent

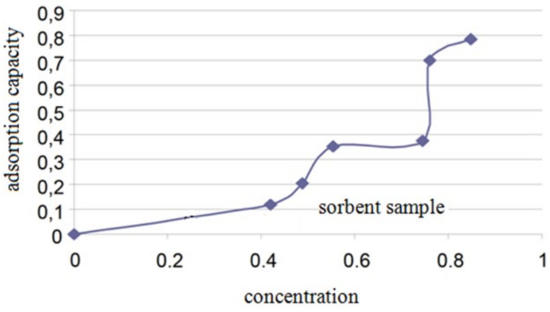

Fig. 9. Isotherms of adsorption of saturated hydrocarbons from commercial toluene by the CB-H_2SO_4 sample at - 950°C

It can be seen from the graphs that in addition to the high adsorption capacity, the isotherm of the CB-H_2SO_4 sample is 950°C. It is proportional to the amount of sorbent and has an ascending character, which indicates the advantage of physical sorption [30]. To absorb saturated hydrocarbons, a sorbent addition should be used at the rate of 0.5 g per 100 mL of toluene, i.e., 0.5 kg per 100 liters of toluene. This amount of sorbent can be added directly to toluene storage tanks. The selection of commercial toluene should be done through a filtering baffle [31].

3. Conclusions

During the coking of bituminous coals, a significant amount of coke breeze and dust is formed, which until now have not found effective qualified use;

One of the methods of using coke breeze is briquetting, which is largely due to an increase in the density of the coal charge in the furnace chambers. At the same time, an increase in density not only serves as a means of increasing the productivity of furnaces, but also improves the conditions for sintering the products of destruction of coal grains of various sizes and degrees of metamorphism, and, consequently, the mechanical strength of coke;

The most promising and economically justified is the production of carbon sorbents on the basis of coke breeze (dust). The porous structure of coke breeze used as a sorbent can be used for the purification of chemical products, etc.

Further research should be aimed at the development of new effective methods and ways of using and utilizing coke dust in coke production.

Symbols

CB	*coke breeze;*	H_2O_2	*hydrogen peroxide;*
M_{10}	*abrasion index;*	$K_2Cr_2O_7$	*potassium dichromate;*
M_{40}	*strength index;*	*AFM*	*atomic force microscopy;*
γ	*sample density;*	W^a	*analytical sample moisture;*
σ_s	*the rammed sample;*	A^d	*ash content on dry basis;*
AAM	*adsorption-active material;*	V^{daf}	*volatile matter;*
C_{act}	*active carbon;*	S^d_t	*content of total sulfur;*
SiO_2	*silicium dioxide;*	Q_s	*gross calorific value.*

References

[1] Solodov VS. Development of technology for utilization of coke dust from coke-chemical plants in the form of briquettes of increased strength. Polzunovskiy Vestnik, 2011; 4: 159–164.
[2] Kuznichenko VM. Influence of dust collector dry coke quenching unit and dust-free coke dispenser dust on charge ramming. Coal Chemistry Journal, 2011; 5: 39–42.
[3] TU U 322-00190443-011 – technical characteristics of coke breeze.
[4] Handbook of coke chemist. In 6 volumes. Volume 2. Production of coke. Kharkiv: Publishing house «Inzhek», 2014.
[5] Ukrainian scientific and production association «Ukrkoks»- http://ukrkoks.com/news/tpost/4hsup04vy6-ukrainskie-koksohimicheskie-zavodi-sokra.
[6] Pozhidaev YA. Effective methods of extinguishing coke. Vestnik MGTU G.I. Nosov, 2015; 3: 34–38.
[7] Leeder WR, Todoschuk T, Howey C, Giroux L, Ng KW, MacPhee T. Predictive model for blending coking coals to produce high strength coke. METEC & 2nd ESTAD. 2015: 1–9.
[8] Tiwari HP, Banerjee PK, Saxena VK. A novel technique for assessing the coking potential of coals / coal blends for non-recovery coke making process. Fuel, 2013; 107: 615–622.
[9] Lech K, Jursova S, Kobel P, Pustejovska P, Bilik J, Figiel A, Romański L. The relation between CRI, CSR indexes, chemical composition and physical parameters of commercial metallurgical cokes. Iron making and Steelmaking, 2018: 46: 124–132.
[10] Kuznichenko VM. Influence of dry coke quenching unit and dust-free coke dispenser dust on charge ramming. Coal Chemistry Journal, 2011; 5-6: 39-42.
[11] Shulga IV, Zelensky OI. Analysis of methods of improving consumer properties of coke breeze and dust. Coal Chemistry Journal, 2016; 5: 3–8.
[12] Kravtsov VL, Papin AV. The relevance of coke dust briquetting technology. Bulletin of Kuzbass State Technical University, 2012; 4: 112–113.
[13] Livenets VI. Briquettes and granules obtained from fine carbon materials and other waste for technological purposes. Bulletin of the Kuzbass State Technical University, 2014; 3: 71–72.
[14] Zhong Q, Yang Y, Jiang T, Li Q, Xu B. Xylene activation of coal tar pitch binding characteristics for production of metallurgical quality briquettes from coke breeze. Fuel Processing Technology, 2016; 148: 12–18.
[15] Dinelt VM, Livenets VI, Nikishan MS, Grigorkin EG. Low-operating technology for producing briquettes from fine carbonaceous materials and waste, Izv. university. Ferrous metallurgy, 2007; 6: 61–63.
[16] Huang ZC, Yi LY, Jiang T. Mechanisms of strength decrease in the initial reduction of iron ore oxide pellets. Powder Technol., 2012; 221: 284–291.
[17] Solodov VS., Papin AV., Kosintsev VI., Sechin AI. Technological aspects of briquetting finely dispersed solid carbon-containing materials, Bulletin of the Kuzbass State Technical University, 2013; 3: 110–113.
[18] Luriy VT, Kuznetsov YN, Terentyev YI. Results of research of agglomeration of coal, coke breeze and sludge. Mining information and analytical bulletin, 1995; 4: 96–97.
[19] Kuznichenko VM, Malko NI, Kubrak SS. Influence of coke breeze on strength and yield of coke in bulk and rammed loading. Uglekhim. Zh., 2013; 3-4: 16–21.
[20] Huseynova AR, Salimova NA. Development of a technology for producing fuel briquettes using coke breeze. Casting and metallurgy, 2012; 3 (67): 325–327.
[21] Evstifeev EN, Popov EM, Rassikhin GI. Processing of anthracite slimes and mines into fuel briquettes. Modern science-intensive technologies, 2014; 10: 118–120.
[22] Barroso-Bogeat A, Alexandre-Franco M, Fernandez-Gonzalez C, Gomez-Serrano V. FT-IR analysis of pyrone and chromene structures in activated. Energy Fuel, 2014; 28: 40–41.
[23] Gupta A, Dhakate SR, Petal P. Effect of graphitization temperature on structure and electrical conductivity of poly-acrylonitrile based carbon fibers. Diam Relat Mater, 2017; 78: 31–38.
[24] Abuova GB, Davydova EV. General characteristics of sorbents used to improve the operation of treatment facilities. Prospects for the development of the building complex: materials of the IX International Scientific and Practical Conference. October 27-29, 2015/under total. ed. V.A. Gutman, D.P. Anufrieva. - Astrakhat: GAOU JSC VPO AISI, 2015.
[25] Butenko EO, Kapustin AE. Adsorption purification of polluted waters with modified sorbents. Ecology and Industry, 2009; 3: 45–48.
[26] Andriyantseva SA, Bondarenko AV. Increasing the grade of commercial toluene with the use of sorbents from by-product waste. Bulletin of TSTU, 2012; 1: 159–165.

[27] Yamamoto K., Sassa Y. Effect of Coke Breeze Addition Timing on Sintering Operation. ISIJ International, 2013; 53: 1523–1528.

[28] Kienle H., Bader E., Active coals and their industrial application. trans. with him. L.: Chemistry, 1984; 2: 216.

[29] Mukhin VM, Tarasov AV, Klushin VN. Active coals of Russia. – M.: Metallurgy, 2000.

[30] Mikhalenko II. Sorption activity of carbon sorbents modified with silver and gold , Sorbents as a factor in the quality of life and health: collection of articles. Art. based on the materials of the III Intern. Scientific. Conf./Belgorod, 2008.

[31] Andriyantseva SA, Bondarenko AV. Synthesis and properties of adsorption-active materials obtained on the basis of coke. Scientific statements, 2011; 9 (104): 96–102.

[32] Wang PF, Jin LJ, Liu JH, Zhu SW, Hu HQ. Analysis of coal tar derived from pyrolysis at different atmospheres. Fuel, 2013; 104: 14–21.

[33] Andriyantseva SA, Rogatnev RG, Bondarenko AV. Thermal oxidation of coke dust as a way to increase sorption activity. Ecology of the Central Black Earth Region of the Russian Federation, 2009; 1 (22): 9–14.

To whom correspondence should be addressed: Dr. Darina Sagalay, State University of Economics and Technology Technological Institute, 50006, Stepana Tilhy str. 5, Kryvyi Rih, Ukraine, E-mail: darinasagalay@gmail.com