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ANALYSIS OF TECHNOLOGIES FOR DESULFURIZATION OF COKING FEEDSTOCK AND PETROLEUM COKE

КОКСТЕУ ШИКІЗАТЫ МЕН МҰНАЙ КОКСЫН КҮКІРТСІЗДЕНДІРУ ТЕХНОЛОГИЯЛАРЫН ТАЛДАУ

АНАЛИЗ ТЕХНОЛОГИЙ ОБЕССЕРИВАНИЯ СЫРЬЯ КОКСОВАНИЯ И НЕФТЯНОГО КОКСА

Abstract. *In this article, the authors provide an overview of the properties of petroleum coke produced by «POCR» LLP, as well as calcined coke from «UPNK-PV» LLP, and the properties of coke required by the aluminum industry. Based on the presented data, an analysis of desulfurization technologies for petroleum coke and coking feedstock with maximum sulfur removal is conducted. Petroleum coke production is one of the directions for deepening oil refining. Currently, there is a trend toward declining oil quality, particularly with an increase in sulfur content. The elevated sulfur content in coking feedstock worsens the quality of petroleum coke and limits its use in electrode production. The burning of high-sulfur coke in furnaces leads to equipment corrosion and the release of sulfur gases into the atmosphere, resulting in environmental problems. In one of the primary applications of petroleum coke in the aluminum industry, the sulfur content requirement is 1.5 %, whereas petroleum coke from «POCR» LLP contains 2.5-3.5 % sulfur. To improve the quality of raw petroleum coke, «POCR» LLP utilizes calcination at «UPNK-PV» LLP, which enhances the structural and mechanical properties of the coke but only slightly reduces the sulfur content. The article discusses various methods for desulfurizing coking feedstock and petroleum coke, including calcination, hydrotreating, extraction, oxidative desulfurization, microbial desulfurization, and provides a comparative analysis of these methods. The most effective desulfurization method is also proposed based on the review.*

Keywords: *coking feedstock, desulfurization of heavy oil, petroleum coke desulfurization, desulfurization methods, oxidative desulfurization.*

Аңдатпа. *Бұл мақалада авторлар «ПМХЗ» ЖШС-нің мұнай коксы мен «УПНК-ПВ» ЖШС-нің күйдірілген коксының қасиеттеріне, сондай-ақ алюминий өнеркәсібінің коксқе қоятын талаптарына шолуды ұсынады. Ұсынылған деректерді ескере отырып, күкіртті мүмкіндігінше көп мөлшерде кетіру арқылы мұнай коксын және кокс өндіруге арналған шикізатты күкіртсіздендіру технологиялары талданды. Мұнай коксын өндіру мұнайды терең өңдеудің бір бағыты болып табылады. Қазіргі уақытта мұнай сапасының нашарлауы күкірттің мөлшерінің артуымен байланысты болады. Кокстеу шикізатындағы күкірттің жоғары мөлшері мұнай коксының сапасын нашарлатып, оны электродтар өндіруде пайдалануды шектейді, ал жоғарыкүкіртті коксты* *пештерде жағу жабдықтаудың коррозиясына және атмосфераға күкіртті газдардың бөлінуіне әкеліп, экологиялық проблемалар тудырады. Мұнай коксының негізгі қолдану салаларының бірі болатын алюминий өнеркәсібіндегі күкірттің құрамына қойылатын талап 1,5 % құрайды, ал «ПМХЗ» ЖШС кәсіпорнында өндірілетін мұнай коксында күкірттің мөлшері 2,5-3,5 % қамтиды. «ПМХЗ» ЖШС шикі мұнай коксының сапасын жақсарту үшін «УПНК-ПВ» ЖШС-да koksты күйдіру көзделген, бұл мұнай коксының құрылымдық-механикалық қасиеттерін жақсартады, бірақ күкірттің мөлшерін азайту шамалы. Мақалада коксsucceeded шикізаты мен мұнай коксын күкіртсіздендірудің әртүрлі әдістері, соның ішінде күйдіру, гидротазарту, экстракция, күкіртсіздендірудің тотықтыру әдістері, микробтық десульфуризация қарастырылып, олардың салыстырмалы сипаттамасы жасалған; сондай-ақ күкіртсіздендірудің қарастырылған әдістерінің небары тиімді әдісі ұсынылған.*

Түйін сөздер: *коксстеу шикізаты, гудронды десульфуризациялау, мұнай коксын десульфуризациялау, десульфуризация әдістері, тотықтырғыш десульфуризация.*

Аннотация. *В данной статье авторы представляют обзор свойств нефтяного кокса ТОО «ПНХЗ», а также прокаленного кокса ТОО «УПНК-ПВ» и свойств кокса, предъявляемых алюминиевой промышленностью. С учетом представленных данных проведен анализ технологий обессеривания нефтяного кокса и сырья коксования с максимальным удалением серы. Производство нефтяного кокса является одним из направлений углубления переработки нефти. В настоящее время наблюдается ухудшение качества нефти в сторону увеличения содержания серы. Повышенное содержание серы в сырье коксования ухудшает качество нефтяного кокса и ограничивает использование его в производстве электродов; сжигание высокосернистого кокса в печах приводит к коррозии оборудования и выделению сернистых газов в атмосферу, что влечет за собой экологические проблемы. В одной из основных областей применения нефтяного кокса в алюминиевой промышленности требование по содержанию серы 1,5 %, тогда как нефтяной кокс ТОО «ПНХЗ» содержит 2,5-3,5 % серы. Для улучшения качества сырого нефтяного кокса ТОО «ПНХЗ» предусмотрена прокалка на предприятии ТОО «УПНК-ПВ» которая улучшает структурно-механические свойства нефтяного кокса, но содержание серы значительно не понижает. В статье рассмотрены различные методы обессеривания сырья коксования и нефтяного кокса такие как прокалка, гидроочистка, экстракция, окислительные методы обессеривания, микробная десульфуризация и выполнена их сравнительная характеристика; также предложен наиболее эффективный из рассмотренных метод обессеривания.*

Ключевые слова*: сырьё коксования, обессеривание гудрона, обессеривание нефтяного кокса, методы обессеривания, окислительная десульфуризация.*

Introduction. One of the directions of deepening oil refining is coking of heavy oil residues, but recently there has been a deterioration in the quality of crude oil and heavy oil feedstock, which increasingly contains high molecular weight hydrocarbons and heteroatomic compounds. As the content of heteroatomic compounds increases, the sulfur content increases.

Heavy oil residues are used as raw materials to make petroleum coke. They contain an increasing amount of sulfur due to the degradation of the quality of the oil feedstock, which, along with the coking feedstock, causes the coking unit to be delayed and produces low-quality petroleum coke. Petroleum coke should have a sulfur concentration of no more than 1.5% in order to be used in the electrode sector. Given that the Pavlodar region does not produce petroleum coke with such a high sulfur content, the majority of petroleum coke produced there is not suitable for use as a carbon source in metallurgy. Despite having a high specific heat of combustion, high-sulfur petroleum coke poses environmental issues when used as a fuel in the energy sector. It is worth noting that the sulfur content in petroleum coke increases during the coking process, so it is necessary to pay attention to desulfurization not only of petroleum coke, but also of coking raw materials (Sashitskaya, 2024; GOST 22898-78).

There are several methods for desulfurization of petroleum coke and coking feedstock: calcination, hydrotreating, extraction, adsorption, oxidative desulfurization.

This article aims to evaluate the desulphurization processes of coking raw materials and petroleum coke, along with their comparative characteristics. The aims of this work are:

1. To examine the qualitative attributes of coking raw materials and petroleum coke;

2. Comparative analysis of requirements to petroleum coke with regard to sulfur content from aluminium industry and quality of petroleum coke after installation of «UPNK »LLP;

3 Study of methods of desulfurization of coking raw materials and their comparative characterisation;

4 Study of methods of desulfurization of petroleum coke and their comparative characterisation.

Materials and methods. Studying the regulations of the enterprise «POCR» LLP, it was revealed that the sulfur content in the coking feedstock is not regulated. This fact leads to the fact that the raw material after the secondary processes of oil refining comes to the delayed coking unit with uncontrolled sulfur content, which negatively affects the quality of petroleum coke. Petroleum coke derived from high sulfur coking feedstock is rendered inappropriate for electrode manufacturing in the aluminium sector (Sashitskaya, 2024). Crude petroleum coke produced at the delayed coking plant undergoes calcination, enhancing its structural and mechanical characteristics while reducing moisture content and chemical impurities, including sulfur, albeit not substantially. Table 1 delineates the sulfur concentration in the crude petroleum coke of «POCR» LLP, the calcined petroleum coke of «UPNK» LLP, and the sulfur content requirements for petroleum coke in the aluminium sector (GOST 22898-78; ST TOO 001140000362-04-014-2018; Kunichanskaya, 2018).

Table 1. Information on sulfur content in crude petroleum coke of PNHZ LLP, calcined petroleum coke of UPPC LLP and sulfur content requirement from aluminium industry

Name of organisation	Sulphur content in petroleum coke
Crude coke «POCR» LLP	2,5-3,5
Purified petroleum coke «UPNK» LLP	3-3,5
Sulphur content requirement for petroleum coke from aluminium industry	1,2-1,5
Note – compiled by the authors	

Based on this table we can see that the local petroleum coke does not meet the requirement for petroleum coke from the aluminium industry, therefore, it is necessary to search for methods of desulfurization of coking raw materials and petroleum coke.

According to the data, the sulfur content in petroleum coke becomes higher compared to the coking feedstock. So, for example, if the sulfur content in coking raw material was 0.25 %, then in coke it becomes twice as much, and when coking raw material with 5 % sulfur content in coke remains the same. Consequently, to reduce the sulfur content in petroleum coke it is advisable to desulfurise the coking feedstock before entering the delayed coking unit (Sashitskaya, Nesmeyanova 2024)

To reduce sulfur content in coking feedstock there are the following methods: hydrotreating, absorption, extraction, biological desufurization, oxidative desulfurization methods.

Currently, the most common method of desulfurization is hydrotreating, where sulfur-containing compounds react with hydrogen to convert them into volatile compounds. It should be noted that heavy organosulfur compounds such as alkylbenzthiophenes or dibenzthiophenes are more difficult to hydrodesulfurise as they are less reactive. To date, the efficiency of hydrogenation desulfurization methods is about 90 %. For more complete removal of sulfur it is necessary to search for the most effective methods (Fajzutdinov, 2022).

Other desulfurization methods used for desulfurization include extraction methods using diethylene glycol, sulfolane and hydrogen fluoride as extractants, sorption methods using silica gels, aluminium oxide and clay as sorbents, and biodesulfurization using microorganisms. It is worth noting the low efficiency of desulfurization with respect to such compounds as benzthiophenes and dibenzthiophenes due to their chemical stability (Stavickaya, 2015).

Oxidative desulfurization techniques involve the alteration of functional groups in sulfur compounds through the use of ozone, hydrogen peroxide, formic acid, and similar oxidative agents.

To remove sulfur from petroleum coke, calcination is currently used at local enterprises. The calcination of petroleum coke can slightly reduce the sulfur content from 3.23 to 3.14 % (Kunichanskaya, 2018).

Petroleum coke as well as tar can be desulphurised using different desulfurization methods. Table 2 shows a comparative characteristic of methods of desulfurization of petroleum coke (Askari, Khorasheh, Soltanali & Tayyedi, 2019; Chen, Ma, Wei & Wu &Li & Zhang, 2017; Gang, Qiuyun, Wei, Zhou & Qifan, 2022; Huang, Cao, Han, Lian & Zhu, 2020; Huang, Song, Yu, Ding, Zhang, Cai & Ma, 2023; Zhu, Yao, Wang, 2020).

Table 2. Comparative Characteristics of Methods for Desulfurization of Petroleum Coke

Method	Desulfurization Conditions				Desulfurization Degree, %
	Reagents	T, ^0C	The mass ratio of the agent and coke	Time, h	
Desulfurization with solvent extraction	o-Chlorophenol	160	10:1	2	19
	Tetrachloroethylene	s.c.	17:1	2	35
	o-Chlorophenol	s.c.	17:1	4	28,5
High-temperature desulfurization by calcination	-	1200-1400	-	4	76,4
Desulfurization with Alkali Metal Compounds	Alkali Metal Compounds	550	4:1	2	99,5
	NaOH	500	2:1	2	98,1
	NaOH	1600	2:1	2	98,5
	KOH	600	1,5:1	2	84,3
Hydrodesulfurization	Hydrogen and Catalyst	760	-	2	87,0
Microbial Desulfurization	Thiobacillus ferrooxidans	19-22	-	24	38,3
Oxidative desulfurization	H_2O_2 and Carboxylic Acid	60	30	12	75
Intensified desulfurization	Using Ultrasound	-	-	-	93,6
Note – compiled by (Hung, 2023)					

Based on this table we can see that the most efficient method of desulfurization is desulfurization using alkali and alkali metals, but its disadvantages are the use of high temperatures and aggressiveness of compounds, as well as the need to dispose of reagents. The use of hydrodesulfurisation also involves the use of high temperatures and pressures in the process, as well as the need for expensive catalysts and hydrogen.

At the same time, the method of oxidative desulfurization allows to remove 75 % of sulfur-containing compounds, at low temperature and harmlessness of components, as the by-product is water and sulfons dissolved in it. It is worth noting that sulphones can be used in the chemical and pharmaceutical industries and thus oxidative desulfurization methods produce by-products that can be profitable for the company. The best results of desulfurization of petroleum coke can be achieved by grinding it. To intensify desulfurization, it is possible to apply ultrasonic exposure, which increases the desulfurization efficiency up to 93.6 %. As described above, it can be successfully used in the methods of oxidative desulfurization, and the use of ultrasound in desulphurization does not deteriorate the environment and is a promising method.

Studies of efficiency of oxidative methods of desulfurization were carried out in China and Russia. The method of oxidative desulfurization of vacuum gasoil has been tested at Novokuibyshevsk refinery showing high level of its performance (Huang, Song, Yu, Ding, Zhang, Cai & Ma, 2023; Stavickaya, 2015; Kazakov, 2018).

Table 3 shows the advantages and disadvantages of petroleum coke desulfurization methods.

Table 3. Comparative characteristics of petroleum coke desulfurization methods

Method	Disadvantages	Advantages
Desulfurization with solvent extraction	Low desulfurization efficiency, the need for constant solvent regeneration, environmental concerns when using toxic and aggressive solvents, and the difficulty of selecting a solvent with selectivity for all sulfur components.	Mild impact on the microstructure of petroleum coke, selectivity in the extraction of sulfur compounds.
Microbial desulfurization	Low desulfurization efficiency, unstable system stability, and long desulfurization time	Environmental friendliness, does not require high temperatures, does not affect the structure of petroleum coke, simplicity of design
High-temperature desulfurization by calcination	Low desulfurization efficiency, requirement for high temperatures	Improved electrical conductivity and strength, reduction of metallic impurities and voltage compounds, simplicity of design enhancement of the microstructure of petroleum coke
Hydrodesulfurization	The need for elevated temperatures and pressures, a catalyst, and a large amount of hudrogen-containing gas.	High desulfurization efficiency, removal of heteroatomic compounds, does not affect the microstructure of petroleum coke.
Desulfurization with Alkali Metal Compounds	The need for high temperatures and pressures, lack of environmental friendliness, the aggressive of the reagents	High desulfurization efficiency, minimal impact on the structure of petroleum coke
Oxidative desulfurization	The need oxidizing agents, high energy consumption middle aggressive of the reagents.	High desulfurization efficiency, doesn’t require elevated temperatures and pressures, minimal impact on the structure of petroleum coke
Note – compiled by author		

The table provides a comparison of the desulfurization methods discussed. Selecting the optimal method requires a compromise solution. For example, extractive desulfurization requires a suitable solvent for the removal of sulfur compounds and constant solvent regeneration; it also exhibits low desulfurization efficiency, which reduces the economic feasibility of the method. However, this approach can be effective for the extraction of certain sulfur compounds.

Microbial desulfurization, on the one hand, is highly environmentally friendly and can be conducted at low temperatures (approximately 20-80 ^{0}C). On the other hand, it is characterized by long processing times and low desulfurization efficiency, which make the method economically unviable.

A notable advantage of high-temperature desulfurization is the improvement of the petroleum coke structure, although the process requires high temperatures, which increases energy consumption.

Hydrodesulfurization achieves a high degree of sulfur removal but requires elevated temperatures and pressures, as well as catalysts and hydrogen-containing gas, thereby demanding significant capital investment.

Desulfurization using alkalis and alkali metals demonstrates excellent sulfur removal performance but requires high temperatures and involves the use of aggressive reagents, which must be regenerated or disposed. This reduces the environmental and economic efficiency of the method.

Oxidative desulfurization also provides a high desulfurization degree, but it employs less aggressive reagents (e.g., hydrogen peroxide instead of sodium hydroxide), improving the method's environmental friendliness.

By intensifying oxidative desulfurization with ultrasound, sulfur removal levels comparable to those achieved by alkali and alkali metal methods can be reached. Importantly, oxidative desulfurization does not require high temperatures or catalysts, which significantly simplifies the process compared to hydrodesulfurization and reduces associated economic costs.

Therefore, oxidative desulfurization appears to be a promising method not only for petroleum coke but also for petroleum fuels, for which successful studies have already been conducted (Казаков, 2018, Ставицкая 2015, Huang, Song, Yu, Ding, Zhang, Cai & Ma, 2023). However, for effective application, it is necessary to determine the optimal oxidant concentration and, in the case of ultrasound-assisted methods, the appropriate intensity level that ensures effective desulfurization without negatively impacting on the environment.

Results and their discussion. Based on the search, the most effective method for desulfurization of coking raw materials and petroleum coke is oxidative desulfurization methods. This article outlines the oxidative desulfurization of tar with oxidising chemicals such glycerine and hydrogen peroxide, enhanced by ultrasonic desulfurization intensification. Method 1 involves the liquid phase oxidation of alcohols (glycerol) with oxygen, resulting in the production of hydrogen peroxide. It is assumed that during this process, a portion of hydrogen peroxide decomposes, releasing atomic oxygen, which aids in the oxidation of undesirable tar components (Stavickaya, 2015)

Oxidation of the mixture of tar and glycerol was carried out in a column type reactor shown in Figure 1.

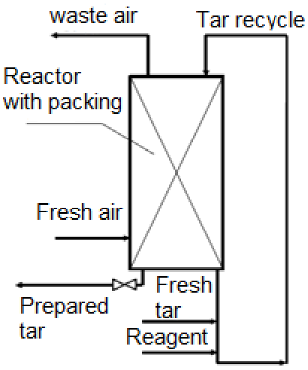


Figure 1. Installation of oxidative preparation of tar for coking process
Note – compiled by (Stavickaya, 2015)

A mixture of tar and glycerol heated to 80 ^{0}C with a volume ratio of 70:30 was fed into the heated and insulated from the outside column-type reactor equipped with nozzles (Raschig rings). The reaction was carried out in a stream of atmospheric air, which was fed from the bottom of the column in countercurrent mode. The maximum temperature in the reactor was 200 ^{0}C. The tar after the first oxidation cycle was fed back to the reactor to circulate in the system for 1 hour. The presence of glycerol favoured the removal of sulfur from the tar in the form of its volatile and gaseous organic compounds: when heated to a temperature of 200 ^{0}C, the resulting gases were carried away from the reactor with the air flow and emitted into the atmosphere (Stavickaya, 2015).

According to the second method, hydrogen peroxide was used as an oxidising agent and ultrasound was used to intensify the oxidation process. The tar samples were heated to 80 ^{0}C and mixed with 15-40 % aqueous hydrogen peroxide solution in a volume ratio of 1:1. Also, ultrasound in combination with a stirrer can be used to intensify desulfurization. The operating purity of the ultrasound is approximately 22 kHz. The source of ultrasound was a wave mixer UZS-22-4-MS of the company «Technomash» Ltd. After desulfurization, the mixture was sent to the extractor for extraction of hydrocarbon phase with the help of water at a temperature of 50-60 ^{0}C, followed by carbonization (Stavickaya, 2015).

To compare the two methods of heavy oil feedstock desulfurization described above and to reveal the dependence of the effect of ultrasound and hydrogen peroxide concentration, the results of preoxidised tar coking are presented in Table 4 (Stavickaya, 2015).

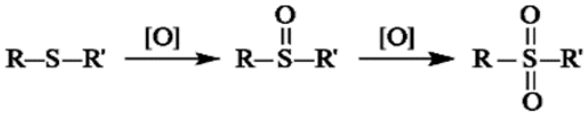
Table 4. Results of preoxidised tar coking

Indicators	Samples of tar					
Raw material quality:	0	1	2	3	4	5
Sulphur content, %	4,39	3,41	3,22	2,80	2,39	2,28
Ash content, %	0,038	0,038	0,035	0,033	0,034	0,021
Coking capacity, %	20,2	19,0	19,3	20,3	21,2	18,4
	Raw coke quality					
Sulphur content, %	4,88	3,74	3,42	2,48	2,50	2,36
Volatile matter yield, %	5,7	6,2	7,6	8,6	7,3	8,7
Ash content, %	0,725	0,622	0,56	0,534	0,548	0,431
Note – compiled by (Stavickaya, 2015)						

In this table, the samples are the following substances: sample 0 is the original tar; sample 1 is tar obtained by method 1; samples 2-5 are obtained by method 2; sample 2 is obtained by adding 15% hydrogen peroxide solution to tar after heating it to 80 ^{0}C and stirring it mechanically for 1 hour; sample 3 is obtained by adding 15 % hydrogen peroxide solution to tar after heating it to 80 ^{0}C and stirring it with ultrasound for 30 minutes; sample 4 - obtained by adding to the tar after its heating to 80 ^{0}C 30 % of hydrogen peroxide solution and stirring with ultrasound for 30 minutes; sample 5 - obtained by adding to the tar after its heating to 80 ^{0}C 40 % of hydrogen peroxide solution and stirring with ultrasound for 30 minutes (Stavickaya, 2015).

Based on Table 4 it can be concluded that the use of hydrogen peroxide as an oxidising agent provides the most complete desulfurization of tar, and the use of ultrasound significantly improves desulfurization.

Oxidation proceeds through the formation of sulfoxides, which are then oxidised to sulfones by reaction 1:



(1)

Sulfide Sulfoxide Sulfone

As a result of these reactions, sulfoxides and then sulfones are formed, which are useful products for use. Sulfoxides serve as highly effective extractants for metal salts, organic and inorganic acids, phenols, flotation agents for polymetallic ores, and plasticisers for polymeric materials. Sulfones are formulations utilised for the treatment of fungal infections in animals and serve as potent repellents. Sulfolane is a superior selective solvent and extractant, facilitating the extraction of aromatic chemicals from oil fractions and the purification of industrial gases. A method for the oxidative desulfurization of petroleum coke involves its treatment with hydrogen peroxide, acids, and alkalis (Samatov, 2007). In the article Yahia Masri, Syrian petroleum coke underwent treatment with acidic agents (hydrochloric acid, sulfuric acid, nitric acid) and alkalis (sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate), regulating the desulfurization rate to identify the most effective treatment method for reducing sulfur content. The best results were obtained with KOH and HNO_3, as the treatment of petroleum coke with potassium hydroxide for 120 minutes reduced the sulfur content from 8.4 % to 6.2 %, and the treatment of petroleum coke with HNO_3, also for 120 minutes, reduced the sulfur content from 8.4 % to 4.1 %. However, it should be noted that this is not an environmentally friendly method of desulfurization, as it involves the use of acids and alkalis in the process, which subsequently need to be disposed of, but this method shows the effectiveness of oxidative methods of desulfurization (Masri, 2020).

In the work of (Stavickaya, 2015), ozone was chosen as an oxidising agent for desulfurization of crude coke. It should also be noted that the use of ozone in oil refining is currently undeservedly ignored. There are known works, where ozonation was applied for cleaning of petrol and diesel fractions, for example, the work of Kazakov A.A. «Development of technology of refining of high-sulfur gas condensate fuel oil», where the technology of ozone cleaning of diesel fraction was successfully shown.

In the work of (Stavickaya, 2015), the method of desulfurization of petroleum coke with ozone was investigated. The advantage of this method of desulfurization is low-temperature process (0-20 ^{0}C) and carrying out the process without catalysts and pressures. The method simultaneously enhances the porous structure of coke. Also, a positive point of this method is the possibility of reducing the temperature of coke calcination from 1000-1200 ^{0}C to 500 ^{0}C. This method consists in carrying out barbotage in aqueous dispersion of ground coke. The scheme of the laboratory installation for ozonisation of oils and petroleum coke is presented in Figure 2.

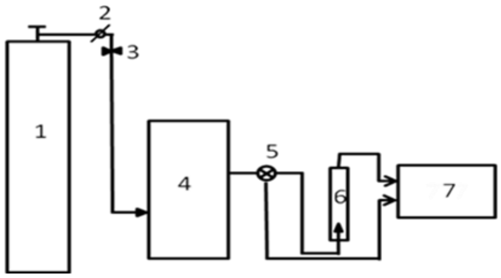


Figure 2. Schematic diagram of the laboratory installation for ozonisation with a barbotage reactor: 1 – oxygen cylinder; 2 – rotameter; 3 – fine adjustment valve; 4 – ozone generator; 5 – tap; 6 – barbotage reactor; 7 – colourimeter with UV-detector

Note – compiled by (Stavickaya, 2015)

Oxygen from the cylinder 1 through the rotameter 2 and fine control valve 3 enters the laboratory ozone generator 4. Then the ozone-oxygen mixture is partially directed through valve 5 to the lower part of the barbotage reactor 6 equipped with a dispersant. The ozone-oxygen mixture traverses the layer of the treated raw material or its solution in diverse solvents (Stavickaya, 2015) To regulate the concentration of ozone in the exhaust gas, specifically the extent of ozone absorption, the ozone-oxygen mixture extracted from the reactor and a portion of the ozone-oxygen mixture exiting the ozone generator via tap 5 were directed to the colorimeter equipped with UV detector 7, which operates on the principle of ozone's absorption of radiation at a wavelength of 300 nm. The starting ozone concentration was contrasted with the ozone concentration at the reactor outlet, and the disparity was utilised to ascertain the quantity of reacted ozone. Ozonation of coke for the purpose of its desulfurization was carried out in aqueous dispersion in a mini reactor with the amount of coke taken 2 g at 0-20 ^{0}C. The ozone concentration was 30 mg/l and the flow rate of ozone-oxygen mixture was 100 ml/min. In order to run the process efficiently, it is necessary to recirculate ozone into the barbotage reactor to prevent ozone entrainment. Reduction of sulfur content in pre-oxidised coking feedstock and coke is achieved by reducing the dissociation energy of C-S bond during oxidation of sulfur atom. Table 5 shows a comparison of the results of the experiment on ozonation of petroleum coke, using aqueous solutions of various oxidising agents under conditions of barbotage of ozone-oxygen mixture (Stavickaya, 2015).

Table 5. Results of Ozonation of Petroleum Coke

№	Experiment Conditions	Reaction Time, min	Sulfur Content, %	
			In Initial Industrial Coke	After Treatment
1	Ozone + Water	60	5,2	4,0
2	Ozone + Aqueous Solution of HNO_3			3,9
3	Ozone + Aqueous Solution of Glycerol			4,0
4	Ozone + Aqueous Solution of Isopropyl Alcohol			4,1
5	Ozone + Water (Industrial Grinding)			2,8
Note – compiled by (Stavickaya, 2015)				

Experiments 1-4 were conducted under the condition of manual grinding of coke in a granite mortar to an average particle size of 0.5 mm. Experiment 5 was carried out under the condition of coke grinding in a ball mill to powdery state and average particle size of 200 microns (Stavickaya, 2015). Thus, in the process of desulfurization of petroleum coke, the dispersion of coke is important. Thus, reduction of particle size allows to increase the degree of desulfurization by 20 %, the maximum degree of sulfur removal from coke with particle size 200 μm was 46 %. At the same time, the use of additional oxidising agents in combination with ozone did not give a significant desulfurization effect, which makes it possible to conclude about the effectiveness of ozone as an independent oxidising agent, which does not require the use of agents, catalysts and temperature, since desulfurization was carried out at a temperature of 0-20 ^{0}C (Stavickaya, 2015).

Conclusion. The purpose of this article was to analyse the methods of desulfurization of coking raw materials and petroleum coke. The study examined the quality standards for coking raw materials and petroleum coke, revealing that «POCR» LLP does not impose any requirements for coking raw materials. Nonetheless, it was observed that the quality of petroleum coke is contingent upon this parameter: the sulfur level during the coking process escalates 2-3 times in crude petroleum coke relative to the sulfur content in the coking feedstock. For instance, when the sulfur component in coking feed is 0.25 %, its concentration in petroleum coke escalates thrice. However, if the sulfur content in heavy oil feedstock is 5 % or above, it remains constant during the coking process. Consequently, emphasis must be placed on the desulfurization of heavy oil feedstock, rather than only on petroleum coke. The sulfur quality specifications for petroleum coke designated for electrode manufacturing in the aluminium sector, as well as the quality of crude petroleum coke from «POCR» LLP, were examined and evaluated. The permissible sulfur content for petroleum coke in the electrode business must not surpass 1.5 %, while the sulfur percentage in crude petroleum coke exceeds 2.5 %. Crude petroleum coke calcination at «UPNK» LLP increases structural and mechanical properties, but does not allow to remove sulfur to the level necessary for its application in aluminium industry, reducing the sulfur content from 3.23 % to 3.14 %. In the course of the study, a comparative analysis of methods of desulfurization of coking raw materials and petroleum coke was carried out. Thus, comparing different methods of desulfurization, it was found that oxidative methods of desulfurization are the most effective. The use of ultrasound should be particularly emphasised as it significantly increases the degree of desulfurization. For example, in tar desulfurization the sulfur content decreased from 4.39 % to 3.22 % using hydrogen peroxide, while using ultrasound the sulfur content decreased to 2.28 %.

A comparative analysis of methods of desulfurization of petroleum coke was also carried out. Among the considered methods at first glance, it seems that the method of desulfurization by alkali metal compounds is the most effective, but this method involves the use of high temperatures and harmful and aggressive compounds, as well as the need to dispose of reagents. Desulphurisation of petroleum coke via oxidation methods can achieve a desulfurization degree of 75 %. When enhanced by ultrasound, this degree can reach 93.6 %, without the necessity of high temperatures or aggressive agents. The decomposition of hydrogen peroxide yields water and oxygen, while the byproducts of the oxidation reaction, such as sulphoxides and sulphones, have applications in medicine and industry.

Conflict of interest. The authors declare that there is no conflict of interest.

«Notification of the use of generative AI and technologies using it in the process of writing the manuscript». The authors did not use tools of artificial intelligence services in the preparation of this paper.

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