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metal, and chemical industries in the CIS



# **Petroleum Coke (green and calcined) Production, Market and Forecast in the CIS**

**19<sup>th</sup> Edition**

Sample PDF

Moscow  
October, 2016

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## CONTENTS:

<b>Annotation</b> .....	12
<b>Introduction</b> .....	14
<b>I. Technology of the petroleum coke production, and resources used in the industry</b> .....	16
I.1. Raw materials for obtaining petroleum coke .....	16
I.2. Methods of obtaining green and calcined petroleum coke.....	19
I.3. Classification of green coke, produced in the CIS, by its quality, standards on coke, accepted in the CIS.....	25
<b>II. Production of petroleum coke (green and calcined) in the CIS</b> .....	29
II.1. Production of petroleum coke in the former USSR (until 1991) and in the CIS in 1996-2015 .....	29
II.2. The state of main enterprises producing petroleum coke in Russia .....	37
II.2.1. Branch of PAO ANK Bashneft – Ufaneftekhim (Ufa, Republic of Bashkortostan).....	38
II.2.2. Branch of PAO ANK Bashneft – Novoil (Ufa, Republic of Bashkortostan)..	42
II.2.3. OOO Lukoil-Volgogradneftepererabotka (Volgograd).....	46
II.2.4. OOO Lukoil-Permnefteorgsintez (Perm).....	52
II.2.5. OAO Rosneft-Novokuibyshevsk oil refinery (Novokuibyshevsk, Samara region).....	56
II.2.6. OAO Gazpromneft-Omsk oil refinery (Omsk).....	60
II.2.7. OAO Rosneft - Angarsk petrochemical company (Angarsk, Irkutsk region)	64
II.2.8. OOO Rosneft-Komsomolsk oil refinery (Komsomolsk-on-Amur, Khabarovsk Territory).....	67
II.2.9. OAO Plant Slantsy (Slantsy, Leningrad region) .....	69
II.3. Producers of petroleum coke in other CIS countries .....	74
II.3.1. Kazakhstan.....	74
TOO Pavlodar Petrochemical Plant (Pavlodar).....	77
TOO Atyrau oil refinery (Atyrau).....	82
II.3.2. Azerbaijan.....	86
Baku oil refinery named after G. Aliyev (Baku).....	86
II.3.3. Turkmenistan .....	90
Turkmenbashi Complex of oil refineries.....	90
II.3.4. Uzbekistan.....	95
SE Fergana oil refinery (Fergana).....	95
II.3.5. Ukraine .....	97
II.3.6. Belarus .....	100

<b>III. Export-import of petroleum coke in the CIS</b> .....	101
III.1. Export-import of petroleum coke in Russia in 1996-2016.....	101
III.1.1. Volumes of export-import.....	101
III.1.2. Main directions of export-import supplies.....	105
Exports.....	105
Imports.....	109
III.2. Export-import of petroleum coke in Ukraine in 1999-2016.....	117
III.3. Export-import of petroleum coke in other CIS countries in 1997-2015 ....	122
<b>IV. Review of prices of petroleum coke</b> .....	123
IV.1. Domestic prices of petroleum coke in RF in 2002-2016.....	123
IV.2. Dynamics of export-import prices in Russia in 1999-2016.....	126
IV.3. Forecast of export-import prices in RF until 2025.....	133
IV.4. Dynamics of export-import prices in Ukraine in 2003-2016.....	135
<b>V. Consumption of petroleum coke (green and calcined) in the CIS</b> .....	140
V.1. Balance of consumption of petroleum coke in RF in 1996-2015.....	140
V.2. Structure of consumption of petroleum coke in RF.....	143
V.3. Main areas of use of petroleum coke in RF.....	146
V.3.1. Production of the anode mass and anodes.....	146
V.3.2. Production of graphite electrodes.....	150
V.3.3. Other areas of application.....	155
V.4. Balance of consumption of petroleum coke in Ukraine in 1999-2015.....	156
V.5 Main enterprisers-consumers of petroleum coke in the CIS, their projects .	159
V.5.1. Aluminum enterprises of the CIS.....	160
OAO RUSAL-Krasnoyarsk (Krasnoyarsk).....	163
OAO RUSAL-Bratsk (Bratsk, Irkutsk region).....	166
OAO RUSAL-Sayanogorsk (Sayanogorsk, Republic of Khakassia).....	169
OAO RUSAL-Novokuznetsk (Novokuznetsk, Kemerovo region).....	172
OAO Volgograd aluminum plant (Volgograd).....	175
SUE Tajik Aluminum Company (Talco) (Tursunzade, Tajikistan).....	179
V.5.2. Electrode plants of Russia and Ukraine.....	184
OAO Enegroprom-Novocherkassk electrode plant (EPM-NEZ, Novocherkassk, Rostov region).....	185
ZAO Enegroprom-Novosibirsk electrode plant (EPM-NovEZ, Linevo, Novosibirsk region).....	189
OAO Enegroprom-Chelyabinsk Electrode Plant (EPM-ChEZ, Chelyabinsk).....	193
OAO Chelyabinsk electrometallurgical combine (ChEMK, Chelyabinsk).....	197
PAO Ukrainian graphite (Zaporozhye, Ukraine).....	200
<b>VI. Development prospects of the market of petroleum coke in Russia and the CIS countries until 2025</b> .....	204
VI.1. Forecast of production of petroleum coke (green and calcined) in Russia and the CIS until 2025.....	204
VI.2. Forecast of consumption of petroleum coke (green and calcined) in Russia until 2025.....	208

VI.3. Balance of production and consumption of petroleum coke (green and calcined) in Russia up to 2025 ..... 210

**Appendix 1:** Address directory of producers of petroleum coke in the CIS

**Appendix 2:** Address directory of largest consumers of petroleum coke in the CIS

## **LIST OF TABLES:**

- Table 1: Properties of green coke
- Table 2: Specifications on petroleum for oil refineries (according to GOST 9965-76)
- Table 3: Suppliers of petroleum to oil refineries of the CIS, producing coke
- Table 4: Yield of products at the delayed coking unit, mass %
- Table 5: Basic characteristics of different types of delayed coking units, used at the CIS oil refineries
- Table 6: Capacities for calcination of green petroleum at refineries of the CIS
- Table 7: Requirements imposed on quality of coke of delayed coking process (KZ-8) (according to GOST 22898-78)
- Table 8: Requirements imposed on quality of calcined needle petroleum coke (KZI) of a delayed coking process according to GOST 26132-84
- Table 9: Requirements imposed on quality of sulfur petroleum coke of delayed coking process, TU 38101525-75
- Table 10: Requirements imposed on quality of calcined petroleum coke
- Table 11: Quality indicators of petroleum coke, produced at the Russian oil refineries
- Table 12: Production of petroleum coke in the CIS by grades
- Table 13: Type and quantity of delayed coking units at enterprises-producers of petroleum coke
- Table 14: Production of petroleum coke in the CIS countries in 1996-2015, thousand tons
- Table 15: Capacities for production of petroleum coke in the CIS countries
- Table 16: Production of green petroleum coke at the CIS enterprises in 1996-2015, thousand tons
- Table 17: Production of calcined petroleum coke at the CIS enterprises in 1996-2015, thousand tons
- Table 18: Consumers of petroleum coke and the coke additive of production of OAO Ufaneftekhim in 2009-2015, thousand tons
- Table 19: Material balance of DCU at JSC "Ufaneftekhim" before and after reconstruction
- Table 20: Technical specifications on the coke additive of the production of OAO Ufaneftekhim
- Table 21: Consumers of petroleum coke of production of OAO Novoil in 2002-2015, thousand tons
- Table 22: Distribution of petroleum coke, supplied by transport companies, by consumers in Russia in 2008-2015, thousand tons
- Table 23: Consumers of petroleum coke of production of OOO Lukoil-Volgogradneftepererabotka in 2003-2015, thousand tons
- Table 24: Consumers of petroleum coke of production of OOO Lukoil-Permnefteorgsintez in 2002-2015, thousand tons
- Table 25: Consumers of petroleum coke of production OAO Novokuibyshevsk oil refinery in 2002-2015, thousand tons

- Table 26: Consumers of petroleum coke of production of OAO Gazprom neft-Omsk oil refinery in 2002-2015, thousand tons
- Table 27: Consumers of petroleum coke of production of Angarsk petrochemical company in 2002-2015, thousand tons
- Table 28: Requirements for the quality of low-sulfurous calcined cake of OAO Slantsy
- Table 29: Requirements for the quality of electrode coke, calcined in chamber furnaces of OAO Slantsy
- Table 30: Supplies of green coke to OAO Plant Slantsy in 2002-2015, thousand tons
- Table 31: Main consumers of petroleum coke of production of OAO Plant Slantsy in 2002-2015, thousand tons
- Table 32: Exports of green coke by Pavlodar Petrochemical Plant in 2002-2015, thousand tons
- Table 33: Exports of coke (green and calcined) by Atyrau oil refinery in 2002-2015, thousand tons
- Table 34: Supplies of petroleum coke of Baku oil refinery to Russian enterprises and to other countries in 2002-2015, thousand tons
- Table 35: Supplies of petroleum coke of Turkmenbashi oil refinery to enterprises of Russia and the CIS countries in 2002-2015, thousand tons
- Table 36: Share of export of PAO Neftekhimik Prikarpat'ya in the total production of coke in 1999-2011, %
- Table 37: Export-import of coke (green and calcined) in RF in 1996-2016, thousand tons
- Table 38: Russian exports of green petroleum coke by countries-recipients in 1996-2016, thousand tons
- Table 39: Export of green petroleum coke by the Russian enterprises in 2001-2016, thousand tons
- Table 40: Export of calcined petroleum coke by the Russian enterprises in 2001-2016, thousand tons
- Table 41: Russian exports of calcined petroleum coke by countries-recipients in 1998-2016, thousand tons
- Table 42: Russian imports of green petroleum coke by countries-suppliers in 1996-2016, thousand tons
- Table 43: Imports of green petroleum coke by enterprises of RF in 2002-2016, thousand tons
- Table 44: Russian imports of calcined petroleum coke by countries-suppliers in 1996-2016, thousand tons
- Table 45: Imports of calcined petroleum coke by enterprises of RF in 2002-2016, thousand tons
- Table 46: Main suppliers of green petroleum coke to RF in 2008-2016, thousand tons
- Table 47: Main suppliers of calcined petroleum coke to RF in 2008-2016, thousand tons
- Table 48: Export-import of coke in Ukraine in 1999-2016, thousand tons
- Table 49: Export of green petroleum coke from Ukraine in 1999-2011, thousand tons
- Table 50: Imports of petroleum coke to Ukraine in 1999-2016, thousand tons

- Table 51: Ukrainian consumers of imported petroleum coke in 1999-2016, thousand tons
- Table 52: Export of petroleum coke from other CIS countries in 1997-2015, thousand tons
- Table 53: Average prices for petroleum coke by Federal Districts of RF in 2012-2016, rub/ton (excluding VAT)
- Table 54: Annual average export-import prices on green and calcined petroleum coke in Russia in 1999-2016, \$/ton
- Table 55: Average annual import prices of calcined petroleum coke for main Russian consumers in 2003-2016, \$/ton
- Table 56: Average annual import prices of green petroleum coke for main Russian consumers in 2003-2016, \$/ton
- Table 57: Russian export prices on calcined petroleum coke by recipient countries in 2004-2016, \$/ton
- Table 58: Russian export prices on calcined petroleum coke by suppliers in 2004-2016, \$/ton
- Table 59: Average import prices for coke, supplied to Ukraine by various countries in 2003-2016, \$/ton
- Table 60: Average import prices of petroleum coke for Ukrainian consumers in 2003-2016, \$/ton
- Table 61: Average export prices for Ukrainian green coke for consuming countries in 2003-2011, \$/ton
- Table 62: Domestic consumption of petroleum coke (green and calcined) in Russia in 1996-2015, thousand tons
- Table 63: Structure of consumption of petroleum coke in the USSR (1990-1991), %
- Table 64: Structure of consumption of petroleum coke in Russia in 2002-2015, %
- Table 65: Requirements for the anode mass
- Table 66: Requirements for the pre-baked anode blocks
- Table 67: Deliveries of petroleum coke to aluminum plants of RF in 2011-2015, thousand tons
- Table 68: Deliveries of petroleum coke to electrode plants of RF in 2011-2015, thousand tons
- Table 69: Domestic consumption of petroleum coke in Ukraine in 1999-2015, thousand tons, %
- Table 70: Supply patterns of petroleum coke to main consumers in the CIS in 2011-2015
- Table 71: Calcination of petroleum coke at aluminum plants in Russia in 2002-2015, thousand tons
- Table 72: Supplies of petroleum coke to OAO RUSAL-Krasnoyarsk in 2002-2015, thousand tons
- Table 73: Supplies of petroleum coke to OAO RUSAL-Bratsk in 2002-2015, thousand tons
- Table 74: Supplies of calcined petroleum coke to OAO RUSAL-Sayanogorsk in 2002-2015, thousand tons



- Table 75: Supplies of calcined petroleum coke to OAO RUSAL-Novokuznetsk in 2005-2015, thousand tons
- Table 76: Supplies of calcined petroleum coke to OAO Volgograd aluminum plant in 2002-2015, thousand tons
- Table 77: Imports of petroleum coke from the CIS countries to Tajikistan in 2000-2015, thousand tons
- Table 78: Production volumes of OAO Enegroprom-NEZ in 2001-2015, thousand tons
- Table 79: Supplies of petroleum coke to OAO Enegroprom-NEZ in 2002-2015, thousand tons
- Table 80: Production volumes of of ZAO Energoprom-NovEZ in 1996-2015, thousand tons
- Table 81: Supplies of petroleum coke to ZAO EPM-NovEZ in 2002-2015, thousand tons
- Table 82: Supplies of calcined coke of production of ZAO EPM-NovEZ in 2006-2015, thousand tons
- Table 83: Production volumes at OAO EPM-ChEZ 2001-2015, thousand tons, million rub.
- Table 84: Supplies of calcined petroleum coke to OAO EPM-ChEZ in 2002-2015, thousand tons
- Table 85: Supplies of petroleum coke to ChEMK in 2003-2015, thousand tons
- Table 86: Supplies of imported coke to PAO Ukrainian graphite in 2002-2015, thousand tons
- Table 87: Russian enterprises, which plan the construction of delayed coking units
- Table 88: Forecast of consumption of petroleum coke in RF by industries for the period up to 2025

## **LIST OF FIGURES**

- Figure 1: Shares of countries of the CIS in the coke production in 2002-2015, %
- Figure 2: Dynamics of the petroleum coke production in the CIS in 1996-2015, thousand tons
- Figure 3: Dynamics of production of petroleum coke in Russia, Azerbaijan, Kazakhstan and Turkmenistan in 1996-2015, thousand tons
- Figure 4: Applications of petroleum coke and coke additive of production of OAO Ufaneftekhim
- Figure 5: Dynamics of production of petroleum coke at OAO Novoil in 1996-2015, thousand tons
- Figure 6: Dynamics of production of petroleum coke at OOO Lukoil-Volgogradneftepererabotka in 1995-2015, thousand tons
- Figure 7: Dynamics of production of petroleum coke at OOO Lukoil-Permnefteorgsintez in 1996-2015, thousand tons
- Figure 8: Dynamics of production of petroleum coke at OAO Novokuibyshevsk oil refinery in 1996-2015, thousand tons
- Figure 9: Dynamics of production of green and calcined coke at OAO Gazpromneft-Omsk oil refinery in 1998-2015, thousand tons
- Figure 10: Dynamics of production of petroleum coke at OAO Angarsk petrochemical company in 1996-2015, thousand tons
- Figure 11: Dynamics of production of calcined petroleum coke at Plant Slantsy in 1996-2015, thousand tons
- Figure 12: Dynamics of production and refining of oil in Kazakhstan in 2008-2015, million tons
- Figure 13: Dynamics of production of petroleum coke by Kazakh enterprises in 1995-2015, thousand tons
- Figure 14: Dynamics of production of petroleum coke by enterprises of Kazakhstan in 1995-2015, thousand tons
- Figure 15: Dynamics of production of petroleum coke (green and calcined) at TOO Pavlodar oil refinery in 1995-2015, thousand tons
- Figure 16: Technological scheme of the installation for calcination of petroleum coke UPNK
- Figure 17: Dynamics of production of petroleum coke (green and calcined) at OAO Atyrau oil refinery in 1995-2015, thousand tons
- Figure 18: Dynamics of production of petroleum coke at Baku oil refinery named after G. Aliyev in 1996-2015, thousand tons
- Figure 19: Dynamics of production of petroleum coke (green and calcined) at Turkmenbashi Complex of oil refineries in 1995-2015, thousand tons
- Figure 20: Production of petroleum coke by enterprises of Ukraine in 1995-2015, thousand tons
- Figure 21: Dynamics of export-import deliveries of petroleum coke in RF in 1995-2015, thousand tons
- Figure 22: Import of calcined and green petroleum coke to RF in 1996-2015, thousand tons

- Figure 23: Geographical structure of the Russian import of green coke in 2002-2016, %
- Figure 24: Dynamics of export-import deliveries of petroleum coke in Ukraine in 1999-2015, thousand tons
- Figure 25: Dynamics of the average Russian prices of petroleum coke (including shale coke) in 2002-2016, rub/ton, excluding VAT
- Figure 26: Quarterly dynamics of import prices of oil (\$/barrel) and petroleum coke (\$/ton) in RF in 2004-2016
- Figure 27: Dynamics of export-import prices in RF for green petroleum coke in 1999-2015 and forecast until 2025, \$/ton, \$/barrel
- Figure 28: Dynamics of average import prices (\$/ton) for calcined coke and its imports (thousand tons) to Ukraine in 2003-2016
- Figure 29: Dynamics of export-import prices in Ukraine on green coke in 2003-2016, \$/ton
- Figure 30: "Apparent" consumption (million tons) and growth rates of consumption (%) of petroleum coke in RF in 1997-2015
- Figure 31: Production, export-import and consumption of petroleum coke in RF in 1996-2015, thousand tons
- Figure 32: Sectoral structure of consumption of petroleum coke in RF in 2007-2015, %
- Figure 33: Dynamics of production of primary aluminum in Russia in 2000-2015, thousand tons
- Figure 34: Dynamics of release of graphite electrodes in RF in 1996-2015, thousand tons
- Figure 35: Dynamics of major indicators of the petroleum coke market in Ukraine in 1999-2015, thousand tons
- Figure 36: Sectoral structure of consumption of petroleum coke in Ukraine in 2011, 2013, and 2015, %
- Figure 37: Dynamics of supplies of petroleum coke (green and calcined) to aluminum plants of Russia in 2002-2015, thousand tons
- Figure 38: Dynamics of production of primary aluminum and pre-baked anodes at Talco in 2006-2015, thousand tons
- Figure 39: Dynamics of production of pre-baked anodes and coke deliveries to Talco in 2000-2015, thousand tons
- Figure 40: Dynamics of the electrode production at OAO ChEMK in 2001-2015, thousand tons
- Figure 41: Dynamics of production of carbon electrodes (including graphite electrodes) at PAO Ukrainian graphite in 2000-2015, thousand tons
- Figure 42: Dynamics of production of petroleum coke in RF in 1999-2015 and forecast up to 2025, thousand tons
- Figure 43: Dynamics of production of petroleum coke in other CIS countries in 1998-2015 and forecast until 2025, thousand tons
- Figure 44: Balance of production and consumption of petroleum coke in RF in 1998-2015 and forecast up to 2025, million tons

## **Annotation**

This report is the **nineteenth edition** of the study of the petroleum coke market in Russia and the CIS.

The **purpose of the study** is the analysis of the petroleum coke market in the CIS.

The **object of this study** is petroleum coke (green and calcined).

The work is a **desk study**. As **information sources**, we used the UN database (UNdata), the data of Statistical committees of the CIS countries (including the Federal State Statistics Service (Rosstat), State Statistics Service of Ukraine, the Statistics Agency of the Republic of Kazakhstan, etc.), of customs statistics of the Russian Federation and Ukraine, of the official railway statistics; of the sectoral (industrial) and regional press, annual and quarterly reports of companies- issuers of securities, as well as data from websites of companies producing and consuming petroleum coke, and the database of InfoMine.

In addition, some data were verified and refined through telephone interviews with specialists of enterprises, which are considered in this report.

All this has allowed experts to draw a picture of the petroleum coke market in the CIS and prospects of its development.

The **chronological scope of the study**: 1996-2015 and the first half of 2016; the forecast for the 2016-2025 period.

**Geography of the study**: the Russian Federation - a comprehensive detailed analysis of the market; Ukraine, Kazakhstan, Azerbaijan and other CIS countries - an overall retrospective analysis of the market.

The report is composed of 6 chapters, contains 213 pages, including 44 Figures, 88 Tables and 2 Appendices.

The **first chapter** of the report presents data on raw material resources, required for production of petroleum coke, and their characteristics. The section also describes in detail the technology of the coke production and quality parameters of the final products.

The **second chapter** is devoted to production of petroleum coke (green and calcined) in the CIS countries. This section presents statistical and estimated data on the coke production in Russia and the CIS countries. The chapter describes in detail all companies-producers of petroleum coke in Russia and the CIS, their current standing and prospects of development.

The **third chapter** of the report presents data on foreign trade operations in petroleum coke in Russia and the CIS countries.

The **fourth chapter** of the report presents data on producer's prices on various grades of coke on the Russian market. Besides, it analyses data on dynamics of export-import prices on the products in Russia and Ukraine. In addition, this section gives a forecast of the prices up to 2025.

The **fifth chapter** analyses consumption of petroleum coke. The section presents the supply-demand balance of petroleum coke in Russia and Ukraine, a sectoral structure of its consumption in Russia, describes the main consumers in Russia and the CIS, and analyzes their current standing and prospects of development.

The **sixth chapter** presents a forecast of development of the petroleum coke market in Russia until 2025.

The Appendices present contact information on producers and consumers of petroleum coke in the CIS.

**The target audience of the study:**

- Participants of the petroleum coke market - producers, consumers, traders;
- Potential investors.

The presented research claims to be the reference source for marketing services and for specialists, making management decisions on the market of petroleum coke.

## Introduction

**Petroleum coke** (carbon of petroleum origin, often abbreviated petcoke) is a porous solid, infusible and insoluble, dark gray to black mass. It is composed of high-condensed high-aromatic polycyclic hydrocarbons with a small content of hydrogen, as well as other organic compounds.

The elementary composition of green (non-calcined) petroleum coke is as follows:

C: 91-99.5  
H: 0.035-4  
S: 0.5-8  
(N+O): 1.3-3.8,  
the rest are metals

Petroleum coke is a complex disperse system, in which the disperse phase is composed of crystalline elements of various sizes and of ordering in the mutual position of molecules and pores, and the disperse medium, filling pores in a crystalline matter, is presented by a continuous gaseous or liquid phase, forming adsorption-solvate layers, or solvated complexes.

Carbon is ordered in fragments of the graphite structure. A degree of ordering depends on a raw material and a technology of its preparation. For instance, directly distilled heavy oil residues yield a low-ordered structure, whereas distilled cracking residues yield a high-ordered one. The degree of ordering governs the graphitization ability of petroleum cokes and properties of the obtained graphite.

The main indicators of quality of petroleum coke are the content of sulfur, ash, moisture and volatile compounds, a grain size, and a mechanical strength.

By the sulfur content petcokes are divided into the low-sulfurous (up to 1% S), sulfurous (up to 2%) and high-sulfurous (above 2%) varieties. According to the content of ash cokes are divided into low-ash (0.5%), medium-ash (0.5-0.8%), and high-ash (above 0.8%). By the granulometric composition - into lumps (the fraction with a particle size more than 25 mm), a "hazelnut" size (6-25 mm), and fines (less than 6 mm).

The main properties of green cokes are given in Table 1.

By method of obtaining, petroleum cokes can be divided into cokes, obtained by a delayed coking, and by coking in heated stills.

Before use, petroleum coke is usually subjected to refining (calcination) at oil refineries directly after obtaining, or by customers themselves.

Petroleum coke is used mainly in metallurgy.

**Table 1: Properties of green coke**

Indicator	low-sulfurous		sulfurous		high-sulfurous	
	> 25 mm	< 25 mm	> 25 mm	< 25 mm	> 25 mm	< 25 mm
Yield, mass %						
of fractions	41.5	58.5	35.7	64.3	45.0	55.0
of volatile components	8.7	10.2	6.8	9.3	6.8	7.2
Content, mass %						
sulfur	0.52	0.53	1.2	1.37	4.0	4.07
ash	0.43	0.50	0.27	0.34	0.46	0.49
Mechanical strength, MPa	5.7	4.0	4.6	2.8	6.0	5.3
Porosity, %	16-56					
Bulk mass, kg/m <sup>3</sup>	400-500					
Specific electric resistance, Ohm·m	(80-100)·10 <sup>6</sup>					

Source: review of the scientific and technical literature

Areas of use of petroleum coke: for obtaining the anode paste in the aluminum production, graphitized electrodes for arc furnaces in the steelmaking industry, for obtaining sulfidizing agents in the non-ferrous metallurgy (for conversion of metals or their oxides into sulfides to simplify the metals extraction from ores, for instance, in the production of Cu, Ni and Co).

Besides, in the chemical industry petroleum coke is applied as a reducer, for instance, in production of BaS<sub>2</sub> from barite, in obtaining CS<sub>2</sub>, carbides of Ca and Si.

Special grades of coke are used as a structural material in the manufacture of corrosion-resistant apparatus. In the food industry, coke is applied in the sugar production as a substitute of the blast furnace coke. A low quality sulfurous coke is used as a fuel.

## **I. Technology of the petroleum coke production, and resources used in the industry**

### **I.1. Raw materials for obtaining petroleum coke**

The quality of raw materials is a priority parameter, governing properties of the final product – petroleum coke.

Production of coke in the CIS is mainly conducted at delayed coking units (DCU). A feature of the DCU operation is that they use, as resources, various semis and wastes of the oil refining at refineries.

As raw materials, the following materials are used: heavy oil fractions, obtained by distillation (fuel oil, tar), cracking-residues of thermal cracking of fuel oil and tar, heavy gas-oil of catalytic cracking, oil production residues (asphalt, extracts of the phenol cleaning of oils, etc.).

Of all oil residues, prone to formation of various types of structures of coke, most preferred are aromatic concentrates (residues of the distillate cracking), and some other high molecular weight hydrocarbons. For this reason, raw distillates are considered promising feedstocks.

Refineries initially have different operating conditions and run on different oils. This fact is an important parameter for the production of coke of a given quality, so for each oil refinery the delayed coking units have been built with the specific conditions in mind.

Among the main parameters that determine the quality of oils, such as the density, the fractional and chemical composition of petroleum products, the most significant are the density and the sulfur content index.

*Sulfur* is one of the most undesirable impurities in the composition of crude oils and of the final product - petroleum coke. Depending on the mass fraction of sulfur, cokes, as well as oils, are classified into low-sulfurous, sulfurous, and high-sulfurous.

Sulfurous cokes possess less favorable properties as compared to low-sulfurous cokes: they cause corrosion of equipment, an increased number of cracks in the electrode products, the destruction of the refractory masonry of calcination furnaces, so that their use is restricted to certain area.

Oil coming to refineries varies in composition, particularly on the sulfur content. The former Soviet Union, and especially Russia, usually process mainly sulfurous and high-sulfurous oils.

In the territory of the ex-USSR, a large share of the Baku, Grozny, Sakhalin, Turkmen and some Ukrainian and Kazakh oils belong to the low-sulfurous oils (below 0.5%).

Sulfurous petroleum (0.5-2.5% S) is produced in the Ural-Povolzh'e (Tuimazy, Romashinskoe oil fields, etc.), and the Western Siberia oil fields (Samotlor, Nizhnevartovsk, Megion, etc.).

High-sulfurous oils (above 2.5% S) are produced in the Ural-Povolzh'e – the Arlanskoe, Radaevskoe, and Pokrovskoe oil fields.

Currently, the main raw material for the coke production in the CIS is sulfurous oil.



According to Specifications, GOST 9965-76 (Table 2), petroleum is subdivided into 3 groups depending on degree of preparation, and into 3 classes by the sulfur content. The each class is subdivided into 3 types (depending on the density at 20°C).

**Table 2: Specifications on petroleum for oil refineries  
(according to GOST 9965-76)**

<i>Depending on the mass fraction of sulfur</i>				
Low-sulfurous		up to 0.60%		
Sulfurous		from 0.61% to 1.80%		
High-sulfurous		above 1.80%		
<i>Depending on density at 20°C, kg/m<sup>3</sup></i>				
Light		Up to 850		
Medium		from 851 to 885		
Heavy		above 885		
<i>By parameters of degree of preparation</i>				
Group	Chlorides concentration, mg/dm <sup>3</sup>	Mass fraction of water, %	Mass fraction of mechanical impurities, %	Saturated vapor pressure, kPa
I	maximum 100	maximum 0.5	-	-
II	maximum 300	maximum 1.0	maximum 0.05	maximum 66.7
III	maximum 900	maximum 1.0	-	-

Source: FSUE Standartinform

Application of technologies, allowing to obtain a high-grade coke independent of the initial petroleum composition, solves many problems: provides the electrode industry with quality resources, allows to use wider ranges of oils, and to deepen the refining of petroleum at oil refineries.

To de-sulfurize a final product, the calcination of coke is applied. One more way to obtain the de-sulfurized coke from high sulfurous oils is preliminary oil cleaning of sulfur by methods of the hydro-desulfurization, hydro-cracking or de-asphaltization. This variant is considered to be more efficient, in spite of its complexity and additional expenditures.

To the Russian refineries, oil is mainly supplied by the system of main pipelines of AK Transneft, in which the West-Siberian oil of the grade Siberian Light is mixed with the more heavy and sulfurous oil of the grade Urals.

Table 3 presents the main suppliers of petroleum to oil refineries of the CIS, producing coke.

**Table 3: Suppliers of petroleum to oil refineries of the CIS, producing coke**

Oil refinery/Petroleum companies	Lukoil	Rosneft	Bashneft	Tatneft	Gazpromneft	Ukrnafta	KazMunaiGaz	MangistauMunaiGaz	Turkmenneft	Uzbekneftegaz	PetroKazakhstan	GNKAR
Novoil												
Ufaneftekhim												
Novokuibyshevsk oil refinery												
Angarsk petrochemical company												
Volgogradneftepererabotka												
Permnefteorgsintez												
Omsk oil refinery												
Komsomolsk oil refinery												
Neftekhimik Prikarpat'ya												
Pavlodar oil refinery												
Atyrau oil refinery												
Turkmenbashi Complex												
Novo-Baku oil refinery												
Uzneftepererabotka												

Source: InfoMine

In 2010, the structure of oil suppliers to enterprises belonging to PAO ANK Bashneft – OAO Novoil and OAO Ufaneftekhim - changed. If previously the raw material for these enterprises was the hydrocarbon feedstock, which almost by half consisted of the West Siberian oil (sellers Lukoil and TNK), then in 2010, the enterprises are provided fully with own raw materials (Bashneft).

## I.2. Methods of obtaining green and calcined petroleum coke

Coking of petroleum is the most hard form of the thermal cracking of petroleum residues. It is conducted at a low pressure and temperatures of 480-560°C to obtain petroleum coke, as well as hydrocarbon gases, petrol and kerosene-gas-oil fractions.

Coking breaks all components of the raw materials to obtain liquid distillate fractions and hydrocarbon gases; the destruction and cyclization of hydrocarbons with an intensive release of kerosene-gas-oil fractions; the condensation and polycondensation of hydrocarbons and a deep compression of high-molecular compounds with the formation of massive coke residues.

The industrial process of coking is conducted at units of 3 types: *the periodical coking in coke stills, the delayed coking in chambers, and the continuous coking in a pseudo-liquefied layer of a coke-carrier.*

In the CIS, petroleum coke is obtained by delayed coking and coking in coke stills.

### *Delayed coking*

The delayed (semi-continuous) coking is the most widespread method in the world. Raw materials, preliminarily heated in tube furnaces up to 350-380°C, are continuously fed to cascade dishes of the rectification column (working at an atmospheric pressure) and contacts with vapors, rising from the reaction apparatus.

As a result of the mass- and heat-exchange, a part of vapors is condensed, forming with initial raw materials so-called secondary resources, which are heated in tube furnaces up to 490-510°C and then go to coke chambers – hollow vertical cylindrical apparatus of 3-7 m in diameter and of the height of 22-30 m.

The reaction mass is continuously fed in coke chambers for 24-26 hours and is coked thanks to the accumulated heat. After filling the chamber with coke by 70-90%, the accumulated coke is removed from the chamber, usually by the water jet under a high pressure (up to 15 MPa). Coke goes to the crusher, where it is crushed into pieces of the maximum size of 150 mm, and then is screened to fractions 150-25, 25-6 and 6-0.5 mm. The chamber is heated by steam and vapors from operating coke chambers, and is filled with the coking mass again.

Volatile products of coking, being a vapor-liquid mixture, are continuously discharged from operating chambers and separated consequently in the rectification tower, the water-separator, the gas block and the evaporation column into gases, petrols and kerosene-gas-oil fractions (see Table 4).

Typical parameters of the process: the temperature in the chambers is 450-480°C, the pressure is 0.2-0.6 MPa, and the duration is up to 48 hours.

**Table 4: Yield of products at the delayed coking unit, mass %**

Product	Raw materials		
	Fuel oil (density 0.950 g/cm <sup>3</sup> )	Tar (density 0.991 g/cm <sup>3</sup> )	Cracking-residue (density 1.024 g/cm <sup>3</sup> )
Coke	14-15	23-24	34-35
Gases	4-5	6-7	7-8
Gasolines	7-8	15-16	6-7
Kerosene-gas-oil fractions	68-69	58-59	46-47

Source: InfoMine based on data of enterprises

The advantage of the delayed coking is a high yield of low-ash coke. The method yields by 1.5-1.6 times more coke than the continuous coking (from the same amount of resources).

Russian oil refineries exploit the one-block and twin-block DCUs (each block includes 2-3 reactors) of various types. DCU are designed by Institutes Giproneftezavody and VNIPIneft. DCU are classified by the yield of the final product.

Twin-block DCU are subdivided into four types.

1. **DCU of the first type (21-10/300, 21-10/600)** are equipped with reaction chambers with the inner diameter of 4.6 or 5 m and heating furnaces of the tent-shaped type. The DCU unit includes devices of absorption and stabilization of petrol, they also yield kerosene, gas-oil, furnace fuel, heat of which is used for heating. Four chambers operate in pairs, independently of each other; therefore each pair can be switched off independently for repair.

2. **DCU units of the second type 21-10/3M** have a similar design, but with reaction chambers of the inner diameter of 5.5 m. The DCU units of this type use direct distilled petroleum residues, with high-aromatic components (the aromatization of the coking resources promote an increasing yield and the quality of coke and prolongs a service-life of DCU).

3. In 1975-1990, a number of oil refineries commissioned **twin-block DCU of the type 21-10/6 (6M)**. These DCU are equipped with highly efficient equipment: reaction chambers of alloyed steel of 5.5 m in diameter and of the height of 27.6 m (operating at a pressure of up to 0.6 MPa); tube furnaces of a volume flame for heating initial resources and heat-carrier and vertical-torch furnaces (for heating secondary resources) with a bottom position of burners. Three radioactive level gauges, installed at the reactor, register level of the phase separation (coke-foam). The use of level gauges allows optimizing the utilization of a chamber space.

The increasing efficiency of the DCU operation is also reached at the expense of the use of air-cooling facilities as condensers and by a deep utilization of the exhaust heat. The decreasing temperature of the secondary resources heating and the decreased coke precipitation are reached at the expense of heating primary resources (heavy coking gas-oil) up to 515°C in a special twisted tube; it is also possible to supply the additional heat into the reactor.

The reaction furnace coils are fed with the turbulence promoter and the detergent, which increases the uptime of furnaces. In order to decrease and depress the foam formation, a special anti-foaming reagent is fed to the top zone of chambers. The coke

precipitation in slam lines of chambers is prevented by the supply of cooled gas-oil of coking. Besides, improvements were made in a scheme of catching products of the chamber heating, steaming and the coke cooling.

4. Reaction chambers **DCU 21-10/5K** have a diameter of 7 m and the height of 29.3 m. In addition to modernizations, applied at the earlier built DCUs, this unit was modified to increase the efficiency of the coke production. The unit has an axial feeding of resources into reaction chambers, coke-removing hydraulic complexes with a remote control of cutters, electric-driven valves at transfer pipelines, mechanization of labor-consuming processes, and a coke warehouse of the floor type.

The main characteristics of delayed coking units of various types, used in the CIS, are presented in Table 5.

**Table 5: Basic characteristics of different types of delayed coking units, used at the CIS oil refineries**

Indicator	Type of the unit				
	21-10/300	21-10/600	21-10/3M	21-10/6	21-10/5K
Production, thousand tons per year:					
By raw material	300	600	600	600	1500
By green coke	75	100	120	120	250
Temperature of reactor, °C					
Top	450	450	450	450	450
Bottom	475	475	475	475	475
Pressure in reactor, MPa:					
Top	0.18	0.4	0.4	0.4	0.4
Bottom	0.38	0.6	0.6	0.6	0.6
Height of reactor filling, m	18-20	16-19	17,5	17	19
Cycle duration, h	48-120	68-112	60-99	84-154	-
Inner diameter of reactor, mm	5000	4500	5500	5500	7000

Source: InfoMine, data of enterprises

In the CIS, the most widespread DCU are those of types 21-10/300, 21-10/600 and 21-10/3M. Note, that by quality the DCU coke is inferior to still coke because of the increased moisture (by 2% in average) and the content of volatile components (by 1-2%).

### ***Periodical coking***

The process is conducted in horizontal cylindrical apparatus of 2-4 m in diameter and 10-13 m long. Raw materials in a still are gradually heated from the bottom by open fire. Then distillates are separated, coke is dried and calcined (2-3 hours). Then the temperature in the furnace under the still is gradually decreased, and the still is cooled by steam and then by air. After the temperature of coke decreases to 150-200°C, the product is unloaded from the still.

Typical parameters of the process are: the temperature of the vapor phase is 360-400°C, and the pressure is the atmospheric pressure. This method yields the electrode and special high-grade types of coke with a low content of volatiles.

However, this is a low productivity method, it requires a large consumption of fuel and manual labor, and, therefore, it is practically not used in the industry. This method is not used abroad at all, and in the CIS it yields around 1% of coke, by assessment of InfoMine.

### ***Continuous coking in a fluidized bed (thermo-contact cracking)***

Raw materials, preliminarily heated in a heat exchanger, contact in a reactor with a hot inert heat-carrier and coked at its surface for 6-12 minutes. As the heat carrier, usually a powdery coke is used with a particle size of up to 0.3 mm, rarely more.

The formed coke and the heat-carrier are removed from a reaction zone and are fed to a regenerator (a coke heater). There an air flow maintains the heat-carrier in a suspended state, up to 40% of coke are burned in this flow, and the bulk is supplied to customers. The heat, generated from burning a part of coke, heats the carrier, which is returned to the reactor by a pneumo-transport by steam or by a gas flow. Distillate fractions and gases are removed from the reactor and are separated by the same way as in the delayed coking process.

Typical parameters of the process are: the temperature in the heat exchanger is 300-320°C, in the reactor - 510-540°C and in the regenerator 600-620°C, the pressure in the reactor and in the regenerator is 0.14-0.16 and 0.12-0.16 MPa, respectively, the resources/heat-carrier ratio (by mass) – (6.5-8.0):1.

Coking in a fluidized bed is used for the increasing production of light petroleum derivatives. Besides, the combination of a continuous coking with the gasification of the formed coke can be applied for obtaining diesel and boiler fuels.

### Calcination

Before the use, petroleum coke is usually subjected to refining, which includes several processes. Calcination removes volatile components and partially heteroatoms (for instance, sulfur and vanadium), and decreases the electric resistance. The graphitization transforms two-dimensional crystallites into three-dimensional formations. In general, stages of coke refining can be presented by the following scheme:

**Crystalline components** → **carbonization** (calcination at 500-1000°C) → **the two-dimension ordering of a structure** (1000-1400°C) → **pre-crystallization** (transformation of crystalline components at 1400°C and above) → **crystallization, or graphitization** (2200-2800°C).

The green coke calcination at refineries in the CIS is conducted in rotary, hearth, and chamber ovens of various productivity (Table 6).

**Table 6: Capacities for calcination of green petroleum at refineries of the CIS**

Enterprise	Type of calcination unit	# of furnaces	Rated capacity on green coke, thousand tons	Rated capacity on calcined coke, thousand tons	Calcined product
Turkmenbashi	rotary oven	1	170	140	Lumpy coke and coke breeze
Fergana	rotary oven	1	150	115	Lumpy coke and coke breeze
Omsk oil refinery	rotary oven	1	140	100	Lumpy coke and coke breeze
Volgograd	rotary oven	2	200	140	Lumpy coke and coke breeze
Atyrau	rotary oven	1	140	100	Lumpy coke and coke breeze
Plant Slantsy	chamber oven	92	350	250	Coke breeze
<b>Total</b>			<b>1150</b>	<b>845</b>	

Source: *InfoMine*

At the present time, in the CIS, there are 5 oil refineries and OAO Plant Slantsy (Zavod Slantsy), having units for the coke calcination. However, the bulk of coke is calcined by customers themselves: at aluminum smelters (11 furnaces) and electrode plants (3 furnaces).

The first unit for calcination of petroleum coke using a hearth furnace has been launched in 1977 at the Krasnovodsk oil refinery (now the Turkmenbashi Complex of refineries, Turkmenistan).

The unit was removed from service after 15 years due to a sealing of the inter-pipe space of the boiler-utilizer with ash from exhaust gases and wear. The drawback of the technology was a too high rate of the coke heating, causing its expansion with the decrease of density. In 1987-1989, oil refineries in Fergana (Uzbekistan), Krasnovodsk (Turkmenbashi, Turkmenistan) and Atyrau (Kazakhstan), launched the coke calcination units with rotary furnaces of the firm Kennedy Van Saun

after a contract with Mannesmann. The technology, on the whole, met modern requirements, except problems with some equipment.

The Institute of oil petrochemical processing of Bashkortostan (SUE INKhP) participated in implementing projects with hearth and rotary furnaces, preparing the technical order on purchase of equipment, participating in the assessment of projects, mastering the facilities, performing the analytical control of quality of coke, participating in the reconstruction with modernization of some units and equipment.

By design of SUE INKhP and with the use of the domestic equipment, in 1988, a coke calcinations unit with the capacity of 140 thousand tons per year was constructed at the Pavlodar oil refinery (Kazakhstan). In 1990, a similar facility was constructed at the Omsk oil refinery. The technological scheme of the facility and the main exploitation characteristics (the productivity of 140 thousand tons per year, the calcination temperature of 1250-1350°C) are typical for the world practice. The employed rotary furnace (60x3.5 m) and the cooler (40x3.0 m) are typical for Russia and are manufactured by JSC Uralkhimmash plant. The after-burner of the original design, developed by SUE INKhP provides a high degree of after-burning of coke dust.

In 2005, the first line of facility for coke calcination (of the capacity of 100 thousand tons per year) was launched at Volgograd oil refinery, in 2013 – the second line (the capacity increased to 140 thousand tons per year).



### I.3. Classification of green coke, produced in the CIS, by its quality, standards on coke, accepted in the CIS

In the CIS various requirements are imposed on quality of petroleum coke, depending on its purpose.

Basic requirements imposed by the *aluminum industry* are: a good electrical conductivity of the calcined coke and a low content of vanadium, titanium, chromium and manganese. The total content of these four metals should not exceed 0.01%. For the *electrode industry*, the main criterion for the quality is the homogeneity of the structure of cokes.

Petroleum cokes are subclassified *by the sulfur content*, taking into account their further application, into:

- low-sulfurous ones, up to 1% of sulfur (electrodes, structural materials);
- medium-sulfurous, up to 1.5% of sulfur (anodes for production of aluminum, carbides);
- sulfurous, up to 4% of sulfur (they can be applied, after desulfurization, as raw material for the anodes production);
- high-sulfurous, above 4% of sulfur (a reducing agent and a sulfurizing agent).

*By granulometric composition* petroleum cokes are subclassified into:

- lumpy (a fraction above 25 mm);
- coke breeze (a fraction from 6-8 mm to 25 mm);
- fines (a fraction below 8 mm).

Sorting of coke into fractions is conducted only at units of delayed coke process.

Petroleum cokes also contain various *amounts of ash components*, by content of which the following types are recognized:

- low-ash petroleum coke (the ash content up to 0.5%);
- medium-ash (0.5-0.8%);
- high-ash (above 0.8%).

When categorizing petroleum cokes, one should particularly recognize the *needle coke*, produced from a highly aromatized raw material, which does not include asphaltenes and heteroelements or their content is low. The needle coke has special properties:

- an anisometric shape of particles;
- a low content of hetero-impurities, in particular, sulfur and ash;
- a low heat expansion coefficient;
- a good graphitization;
- a high density;
- a low reactivity.

These properties make the needle coke the sole suitable raw material for manufacturing large-sized graphitized electrodes. In the CIS, the needle coke is produced in insufficient amounts that is due to both the problems of obtaining the special raw material (low-sulfurous gas oil of the catalytic cracking) and a low quality of equipment, which does not allow to obtain cracking-residues after the

thermo-cracking with a low content of light fractions.

Depending on the method of producing petroleum coke and on the basis of its classification by various properties, in the CIS, in accordance with the applicable standards, 6 types of green petroleum coke are produced (Tables 7-9).

**KZ is petroleum coke of delayed coking process** (GOST 22898-78). It combines useful properties of petroleum coke of the cracking and of the pyrolysis still types. Its structure is uneven (fibrous and point) and satisfies the main requirements, imposed on raw materials for the electrode production; it has a high strength and demonstrates a good graphitization. Depending on a granulometric composition (the content of fraction below 8 mm), two types of the KZ coke are recognized: KZ-8 (larger pieces), and KZ-0 (fines).

**Table 7: Requirements imposed on quality of coke of delayed coking process (KZ-8) (according to GOST 22898-78)**

Indicator	Category of quality	
	highest	first
Mass fraction of total moisture, %, no more than	3	3
Volatile components yield, %, no more than	7	9
Ash content, %, no more than	0.4	0.6
Mass fraction of sulphur, %, no more than	1.0	1.5
Mass fraction of fines <25 mm, %, no more than	8	10
Actual density after calcination at 1300°C (5 hours) (1300°C, 5 hours), kg/m <sup>3</sup>	2100-2130	2080-2130
Mass fraction, %, no more than		
Si	0.06	0.08
Fe	0.07	0.08
V	0.08	0.015

Source: FSUE Standartinform

**KZI is a needle petroleum coke of a delayed coking process** (GOST 26132-84). It is produced from highly aromatized raw materials, free from asphaltenes and heteroelements. This type of coke is characterized by a high anisotropy.

**Table 8: Requirements imposed on quality of calcined needle petroleum coke (KZI) of a delayed coking process according to GOST 26132-84**

Indicator	Value
Actual density kg/m <sup>3</sup> , no less than	absent
Ash content, % no more than	0.4
Mass fraction of sulfur, % no more than	0.6
Oxidizability, %, no more than	1.5
Actual density kg/m <sup>3</sup> , no less than	2110
Content of grains with piece size more than 6.0 mm, % , no less than	25

Source: FSUE Standartinform

Besides the above-listed types of coke, also in the CIS a **sulfuric petroleum coke of delayed coking process** is produced. Its quality is regulated by Specifications (TU 38101525-75); this coke is characterized by an increased sulfur content (up to 3%).

**Table 9: Requirements imposed on quality of sulfur petroleum coke of delayed coking process, TU 38101525-75**

Indicator	Category of quality	
	A (fraction 25-250)	B (fraction 8-25)
Mass fraction of total moisture, %, no more than	3	3
Volatile components yield, %, no more than	7.5	9
Ash content, % no more than	0.5	0.5
Mass fraction of sulfur, % no more than	3	3
Content of particles, % no more than:		
piece size less than 25 mm	10	-
piece size less than 8 mm	-	10

Source: FSUE Standartinform

According to the standards, valid in the CIS, two kinds of *calcined petroleum coke* are produced: the total coke (the standard TU 101698-80), and calcined coke fines (the standard TU 381097-81) (Table 10).

**Table 10: Requirements imposed on quality of calcined petroleum coke**

Indicator	Lumpy coke + coke breeze TU 101698-80	Coke breeze TU 381097-81	
		highest	first
Mass fraction of total moisture, %, no more than	0.5	absent	
Ash content, % no more than	0.7	0.8	0.7
Mass fraction of sulphur, % no more than	1	1	1
Actual density, kg/m <sup>3</sup>	no more than 2080	no more than 2080	no more than 2080
Content of grains more than 6 mm, % no less than	30	-	30

Source: FSUE Standartinform

Petroleum cokes, produced by Russian enterprises, are characterized by a low content of volatile components – 7.6-10.2% (Table 11). SUE INKHP, for several years, was developing technological solutions, aimed at obtaining the high-quality petroleum coke for the aluminum and electrode industries, with a choice of technology of a "delayed" coking: a required coefficient of recycling, and a supply of a heat carrier. The technology allows obtaining coke with a low yield of volatile components (7-9%) and a high mechanical strength.

Indicators of quality of petroleum coke produced in the Russian Federation are typical of the world practice for their use in the aluminum industry.