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SCIENTIFIC, TECHNICAL AND ECOLOGICAL ASPECTS OF EXPANDING THE FUEL BASE OF ENERGY AND CEMENT PRODUCTION DUE TO PETROLEUM COKE

Purpose. Generalization of experience in the fuel use of petroleum coke using various combustion technologies and development of scientific foundations for its use for rotary kilns in the production of Portland cement clinker in compliance with environmental requirements.

Methodology. Determination of the efficiency of sulfur capturing in a rotary kiln and in a decarbonizer based on the material balance of sulfur in raw materials, fuel and clinker. Determination of the permissible content of petroleum coke in fuel based on the calculating of the level of sulfur dioxide emissions using the found sulfur binding coefficient.

Findings. It is shown that petroleum coke is equivalent to high-sulfur lean coal as a fuel. The experience of using petroleum coke in power plants with circulating fluidized bed (CFB) and pulverized combustion, in particular, in the boiler of the 800 MW power unit of the Slovianska TPP, is analyzed. The technology of “dry” cement production is considered. It is proven that the conditions of petcoke combustion in a rotary kiln for clinker calcination, calcium carbonate decomposition in a decarbonizer, and calcium oxide contact with sulfur dioxide coincide with the optimal conditions for sulfur capturing in the technology of coal CFB. The efficiency of sulfur capturing in a rotary kiln and in a decarbonizer is determined based on the material balance of sulfur in raw materials, fuel, and clinker. The permissible content of petroleum coke in fuel for pulverized combustion and for rotary kilns is determined based on the calculation of the level of sulfur dioxide emissions using the found sulfur binding coefficient. Recommendations for the use of petroleum coke in cement production to expand its fuel base while complying with environmental requirements are provided.

Originality. The efficiency of sulfur binding of solid fuel in a rotary kiln and in a decarbonizer is determined. It is proven that in the technology of “dry” cement production with a higher proportion of petroleum coke in the fuel, sulfur dioxide emissions are 11 times lower than in pulverized combustion. A methodology for assessing the permissible content of petroleum coke in fuel for a rotary kiln is developed.

Practical value. The advantages of using petroleum coke as fuel for rotary kilns in clinker production are proven. The permissible content of petroleum coke in fuel is determined while meeting EU environmental requirements. Recommendations are provided for the use of petroleum coke in cement production to expand its fuel base.

Keywords: *petroleum coke, hard coal, Portland cement clinker, rotary kiln, decarbonizer*

Introduction. Despite the global course towards carbon-free energy, hydrocarbon motor fuels are still indispensable. Accordingly, the task of utilizing petroleum coke, a solid by-product of the coking of petroleum hydrocarbons, which is formed during oil refining and is characterized by a combination of high energy value and high sulfur content, remains relevant.

In Europe, coal preparation sludge and petroleum coke have been used in the cement industry for many decades as a fuel for clinker firing cheaper in energy equivalent than coal, with the emissions from combustion fully integrated into the product. A reference document on best available technologies and management practices (BAT) for the production of cement, lime and magnesium oxide [1] (pursuant to Directive 2010/75/EU [2]),

which defines petroleum coke as a traditional fuel for the cement industry, is available on the website of the Ministry of Environmental Protection and Natural Resources. However, the current “Technological Standards for Permissible Emissions of Pollutants from Equipment (Plant) for the Production of Portland Cement Clinker in Rotary Kilns” [3] does not mention petroleum coke at all. The reason for this is that petroleum coke is still considered in Ukraine an undesirable fuel for use in both power plants and cement production due to its high sulfur content, which causes the risk of high sulfur dioxide emissions. Accordingly, there are no domestic publications on the physicochemical properties of petcoke as a solid fuel, comparison of its behavior in different combustion technologies, features, optimal process conditions and efficiency of petcoke sulfur binding in Portland cement clinker firing technologies, experience and recommendations

for the use of petroleum coke in cement production in compliance with environmental requirements.

The purpose of the study is to summarize the experience of fuel use of petroleum coke using various combustion technologies and to develop scientific bases for its use for rotary kilns in the production of Portland cement clinker in compliance with environmental requirements.

Literature review. Petroleum coke is a product of the coking of petroleum hydrocarbons, a carbon-rich solid by-product formed in the process of deep oil refining. During coking at a temperature of 400–500 °C, the following transformations of the main components of heavy oil residues (oils, resins, asphaltenes) occur [4]:

- the paraffinic part of oils is cracked (split) into liquid and gaseous products. Due to the presence of naphthenic cycles with mobile hydrogen atoms in the molecules and hydrogen redistribution, some molecules are converted into saturated hydrocarbons and cracked, while the other part becomes more aromatic and replenishes the solid phase of asphaltenes;

- tars are partially cracked to gaseous and liquid products. The main part of the tar components is dealkylated and loses oxygen-containing functional groups. As a result, the degree of aromaticity increases, and tars are converted to asphaltenes;

- asphaltenes decompose at temperatures above 300 °C to form gas, liquid products and coke with a high degree of aromaticity.

So, in terms of the chemical composition of the organic part, petroleum coke, like coal, is mainly polymerized aromatic compounds consisting of carbon and hydrogen, with a small content of oxygen, nitrogen and sulfur. The only difference is that the polyaromatic structure of coal was formed as a result of slow long-term carbonization, while petroleum coke was formed as a result of rapid processes of oil cracking and coking of heavy residues [5]. The relatively low content of volatile substances in petroleum coke (up to 15 %) and the low reactivity of the solid residue correspond to lean coal (according to the Ukrainian classification DSTU 3472:2015 “Lignite, hard coal and anthracite. Classification”). The general difference between petroleum coke and coal is low ash content due to the lack of contact of the petcoke organic part with the host rocks, which is inevitable in the process of coal carbonization, and often high sulfur content [6].

Technological properties and applications of petroleum coke depend on the sulfur content of oil feedstock and coking technology [7]. More expensive heat-treated (so-called calcined or roasted) low-sulfur needle, sponge and flexi-coke are used in graphite production, as adsorbents and for other technological needs. Unrefined, so-called “green” petroleum cokes with a sulfur content of 1.5–8.0 %, are used as fuel, with volatile yield and reactivity similar to lean coal, but with low ash content (less than 3 %) and high caloric value (over 7,400 kcal/kg).

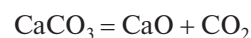
For many decades, the cost of petroleum coke as a by-product has been lower than coal, with a higher heat value. Although in 2024, European prices for fuel oil coke (\$140–180 per ton in 2024) even outpaced coal (\$145–155 per ton), it is still cheaper in terms of energy equivalent. Therefore, fuel oil coke has been and is widely used in the energy sector as an equivalent of thermal coal. However, at the same time the problem of re-

ducing sulfur dioxide emissions with a high sulfur content must be addressed.

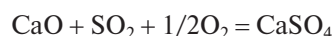
In the energy sector, petroleum coke is most traditionally used as part of fuel mixtures based on hard coal [8]. Back in 2000, the US energy sector consumed more than 1.5 million tons of petroleum coke in the form of mixtures. Its use in the mixtures made it possible to increase the calorific value of fuel for pulverized combustion without applying additional measures for desulphurization [9]; maintaining sulfur dioxide emissions below the permissible level was ensured by adding low-sulfur coal and/or wood waste that contains almost no sulfur to the mixture. However, this was only possible before the introduction of modern, more stringent environmental standards.

The most thorough experience of using petroleum coke at Ukrainian TPPs was obtained in 2018–2019 at the pulverized-coal anthracite boiler TPP-200-1 of the 800 MW power unit of Slovianska TPP with scientific and technical support from Thermal Energy Technology Institute of the National Academy of Sciences of Ukraine [10]. At that time, low-sulfur anthracite with high ash content ($W_t^r = 8.8 \%$, $A^d = 28.1 \%$, $V^{daf} = 6.3 \%$, $S_t^d = 1.3 \%$, $Q_i^r = 5,096$ kcal/kg) was burned in a boiler with molten slag removal designed to fuel calorific value of over 5400 kcal/kg. From time to time there happened slag solidification in the outlets due to a decrease in the flame temperature. During the tests, petroleum coke ($W_t^r = 5.2 \%$, $A^d = 1.4 \%$, $V^{daf} = 9.7 \%$, $S_t^d = 5.8 \%$, $Q_i^r = 7,670$ kcal/kg) was added to the fuel at the rate of up to 15 % by weight. To ensure the homogeneity of the mixture, the blending of the raw fuel was performed when it was fed to the production using the “one conveyor – two feeders” technology [11]. By reducing the ash content and increasing the caloric value to more than 5,400 kcal/kg, the combustion modes of the mixture and the flow of molten slag were significantly improved compared to anthracite. At the same time, the content of SO₂ in flue gases did not exceed 4,440 mg/nm³ (in terms of 6 % O₂) [12]. In other words, sulfur dioxide emissions were lower than the permissible value according to the current Ukrainian technological standard for lean coal of 4,500 mg/Nm³ [13] and the environmental permit for Slovianska TPP of 4,482 mg/Nm³. However, this level no longer meets the requirements for gross SO₂ emissions according to the National Plan for Reducing Emissions from Large Combustion Plants [14]. This stipulates that pulverized petroleum coke combustion is possible only if expensive systems for deep desulphurization of waste gases are installed.

Another area of fuel use of petroleum coke is combustion in a fluidized bed (FB) and circulating fluidized bed (CFB) (Fig. 1), which allows for in-furnace sulfur binding with limestone, which is fed into the furnace in crushed form along with the fuel [15]. Limestone consists mainly of calcium carbonate CaCO₃. The latter is thermally decomposed in the furnace to calcium oxide



which reacts with sulfur dioxide to form gypsum, which, together with the remaining unreacted oxides, is removed from the furnace as bottom ash and fly ash



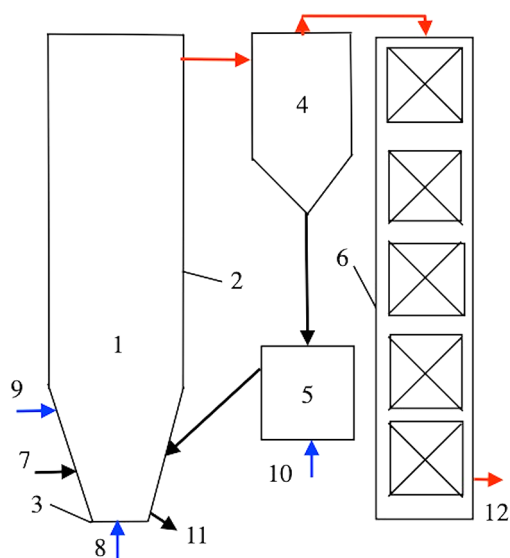


Fig. 1. Generalized technological scheme of coal combustion in a circulating fluidized bed:

1 – furnace; 2 – furnace screens; 3 – grate; 4 – cyclone; 5 – fluidized bed valve; 6 – convective pass; 7 – fuel and limestone; 8 – primary air; 9 – secondary air; 10 – fluidizing air; 11 – bottom ash outlet; 12 – flue gases

The rate of thermal decomposition of limestone (in general, calcium and magnesium carbonates) becomes noticeable starting from 750–800 °C. The completeness of the processes of thermal decomposition of limestone and sulfur binding by alkaline earth metal oxides is ensured by their significant residence time in the furnace due to the circulation of the solid phase captured by the cyclone and the conditions of intensive mixing in the fluidized bed. On the other hand, the reaction of SO₂ interaction with calcium oxide is reversible, and at temperatures above 950–1,000 °C it begins to shift towards the thermal decomposition of gypsum, i.e., the equilibrium pressure of SO₂ increases to a level that exceeds its permissible content in flue gases [16]. The optimal temperature range of 850–920 °C is realized in the FB and CFB furnaces, in which limestone decomposes intensively, but gypsum does not yet undergo thermal decomposition, and the last contact of flue gases with calcium and/or magnesium oxide occurs in the cyclone at a temperature not exceeding 800 °C [17]. This range of combustion temperatures also ensures low generation of thermal nitrogen oxides [15–17].

The efficiency of sulfur binding in this process with an excess of calcium with a molar Ca/S ratio of 1.6–2.0 (CFB) to 2.0–2.5 (FB) reaches 90–96 %. The main problem here is the chemical activity of the ash, which contains residual oxides of alkaline earth metals and gypsum, and requires either rather expensive measures for its disposal or integration with the technological process of its utilization, for example, in the production of building materials. In Ukraine, such integration is not developed, and the only existing CFB boiler unit of the 215 MW of Starobeshevska TPP [17] remained on the temporarily occupied territory.

The main types of raw materials for cement production are limestone, chalk, marl, shale, and clay, with additional raw materials such as bauxite, iron ore, slag from blast furnaces, fuel combustion ash, or molding

sand. The cement production process begins with the thermal decomposition at a temperature of 880–900 °C of calcium carbonate, which is part of limestone, chalk, and marl, with the loss of CO₂ and the formation of calcium oxide (this process is called calcination or decarbonization). In the subsequent clinker formation process in a rotary kiln, calcium oxide reacts at high temperatures (1,500–2,000 °C) with silica, alumina, and iron oxides to form calcium silicates, aluminates, and ferrites, which make up clinker. Magnesium compounds, which are much less in the raw material, behave similarly to calcium compounds in these processes. The fired clinker is milled together with gypsum and other additives to form cement [1].

The known technological methods of cement production are wet, semi-wet, semi-dry and dry. In the wet process, the raw material components are ground in water to form a slurry that can be pumped by a pump. The slurry is then fed first to a dryer or directly to a rotary kiln. In the dry process, the raw material components are ground and dried to form the raw meal in the form of a loose powder and fed into the rotary kiln. The semi-wet and semi-dry processes differ in that the dewatered sludge or moistened ground raw meal are used to form pellets suitable for firing in cheaper, though less efficient, grate kilns. In Europe, more than 90 % of production is based on dry technologies, which do not use additional fuel energy to dry components [1, 18].

Based on economic considerations and the possibility of integrating ash into clinker, solid fuels such as coal, coal preparation sludge, RDF, peat, and petroleum coke are predominantly used in cement production. Given the different temperature levels required in the rotary kiln and decarbonizer, the former is usually fed with high-calorific fuels, which may include low-reactivity petroleum coke, and the latter with low-calorific fuels.

In dry technologies (Fig. 2), raw materials from bunker 1 are fed to mill 2, after grinding they are accumulated in the raw mixture silo 3. High- and low-calorific fuel from bunkers 4, 7 are fed to mills 5, 8, and the finished pulverized fuel is accumulated in bunkers 6, 9. The raw meal passes through a multi-stage cyclone heater 10 and the combustion chamber 11 of the decarbonizer, and after thermal decomposition, it passes through a rotary kiln for firing Portland cement clinker 12. The clinker is cooled in a refrigerator 13, and after adding gypsum 14 and the necessary mineral admixtures 15, it is finally ground in a cement mill 16. The finished cement is stored in a silo 16. To heat the rotary kiln, high-calorific pulverized fuel is fed along with air to meet the clinker movement. Hot combustion products from the rotary kiln and additionally low-calorific pulverized fuel are fed with air into the combustion chamber of the decarbonizer are used to heat the decarbonizer to compensate for the thermal effect of endothermic reactions of limestone decomposition. The conditions of intensive mixing of the solid phase and its contact with gases in the rotary kiln are ensured by pouring the material during the rotational movement of the kiln, in the decarbonizer – by multi-stage recirculation of the material captured in the cyclones.

After passing through the decarbonizer, the flue gases, which have released heat for the thermal decomposition of limestone and cooled to 350–400 °C, are fed to

tion technology has not been established and requires experimental determination.

In order to determine the efficiency of sulfur binding in cement production, this study developed a methodology based on the material balance of sulfur in the solid phase: the incoming part – with raw materials and fuel, the outgoing part – with the finished clinker. The sulfur consumption in each component $G_{S(i)}$, t, is determined by the formula

$$G_{S(i)} = G_i \cdot S_{r(i)}^r / 100, \quad (4)$$

where G_i is the consumption of the component for the selected period, tons.

The above analysis of the composition of raw materials and the technological process suggests that the sulfur of raw materials is bound by exchange reactions with compounds of their own alkali metals in the solid phase and completely remains in the clinker. Instead, fuel sulfur is transferred to the gas phase during combustion and is only partially bound by calcium and magnesium oxides formed in the decarbonizer. Thus, the efficiency of fuel sulfur binding is determined by the ratio of the difference between the consumption of clinker and raw materials sulfur and the consumption of fuel sulfur for the selected period.

Results and discussion. Determination of sulfur binding efficiency. To calculate the material balance for sulfur, we used data from one of the domestic enterprises producing Portland cement using dry technology for two continuous periods of approximately 3 weeks each, when the fuel composition included only coal (in the first period) and coal and petroleum coke (in the second period), and no alternative fuels were used. The primary mixing of fuels took place when raw fuel was fed from to the bunkers using the “one conveyor – two feeders” technology, and the final mixing took place when the fuel mixtures were milled.

According to the current standards of Ukraine, the content of total sulfur in solid fuels is determined directly (Eschka method – burning a sample with the capture of sulfur oxides with magnesium oxide and sodium carbonate, DSTU 3528-97). When determining the chemical composition of the mineral part (DSTU 9045:2020), the sample is first fused with sodium carbonate, then dissolved, and the sulfur trioxide content SO_3 is determined by the gravimetric method based on the precipi-

Table 1

Characteristics of fuels for sulfur balancing periods

Fuel	Moisture W_i^r , %	Ash content A^r , %	Total sulfur S_i^r , %	Q_i^r , kcal/kg
Balance period 1				
To the rotary kiln	1.16	14.2	1.53	6,732
To the decarbonizer	1.11	14.8	1.52	6,682
Balance period 2				
To the rotary kiln:				
- coal	0.99	16.95	1.04	6,587
- petroleum coke	1.01	0.4	4.90	7,600
- mixture, total	0.99	15.30	1.43	6,688
To the decarbonizer	1.68	39.9	1.40	4,400

tation of sulfate ions in the form of barium sulfate. To convert the SO_3 content to sulfur content, it is enough to multiply it by the ratio of the molecular weights of sulfur and sulfur trioxide $32/80 = 0.4$.

Table 1 shows the characteristics of the fuels (after drying), and Table 2 shows the results of the analysis of the chemical composition of raw materials and fired clinker (without CO_2 carbonates) on average for the balance sheet periods.

Table 3 shows the results of calculating the material balance of sulfur in the solid phase and the efficiency of fuel sulfur binding during the two balance periods. They show that at a mass fraction of petroleum coke in the rotary kiln fuel of 10 %, the contribution of petroleum coke sulfur is the smallest among other components. It should be noted that the sulfur content in a low-ash mixture of coal and petroleum coke may be lower than in a higher-ash coal for a decarbonizer due to the contribution of pyrite sulfur from the mineral part of the coal. In general, sulfur contributions from fuel and raw materials are comparable.

The results shown in Table 3 demonstrate that the fuel sulfur binding efficiency is about 93 % and does not depend on the proportion of total sulfur and the presence of petroleum coke in the fuel. This value lies in the middle of the above range of sulfur binding efficiency of

Table 2

Chemical composition of raw materials and fired clinker for the periods of sulfur balancing

Substance	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Balance period 1								
Limestone	1.53	0.60	0.15	53.82	0.25	0.05	0.10	0.00
Marl	23.23	6.28	4.78	36.27	1.28	0.55	1.16	0.04
Raw material mixture	12.35	3.43	3.46	43.97	0.76	0.30	0.63	0.02
Clinker	20.79	5.24	4.00	66.28	0.83	0.92	0.96	0.09
Balance period 2								
Limestone	0.90	0.21	0.11	54.61	0.35	0.05	0.10	0.00
Marl	22.72	6.28	2.31	34.60	1.04	0.43	1.35	0.04
Raw material mix	11.79	3.24	2.21	44.53	0.69	0.24	0.63	0.02
Clinker	20.58	5.23	4.04	66.36	0.92	0.83	1.23	0.09

Table 3

Results of the material balance calculating of sulfur in the solid phase for the balance sheet periods

Component	Weight, t	S, %	S, t
Balance period 1			
Input:			
Raw materials	287,633.5	0.120	345.16
Coal to the rotary kiln	10,647.9	1.53	162.91
Coal to the decarbonizer	12,614.1	1.52	191.73
Total	–	–	699.81
Output:	–	–	–
Clinker	183,439.7	0.368	675.06
Fuel sulfur consumption, total	–	–	354.65
Difference in sulfur consumption in clinker and raw materials	–	–	329.90
Sulfur binding efficiency	–	–	0.93
Balance period 2			
Input:			
Raw materials	330,574.0	0.096	317.35
Coal to the rotary kiln	11,802.6	1.04	122.75
Petroleum coke to the rotary kiln	1,311.4	4.90	64.26
Coal to the decarbonizer	16,029.0	1.40	224.41
The total of	–	–	728.76
Exit:	–	–	–
Clinker	210,825.0	0.332	699.94
Fuel sulfur consumption, total	–	–	411.42
Difference in sulfur consumption in clinker and raw materials	–	–	382.59
Sulfur binding efficiency	–	–	0.93

limestone during combustion in the CFB, which confirms the identity of the binding mechanism in these technologies. It is advisable to use it when calculating the expected level of sulfur dioxide emissions in cement production with a known sulfur content in the fuel (using formulas (1, 3)), or vice versa – when calculating the maximum allowable sulfur content in the fuel at a given maximum allowable level of sulfur dioxide emissions.

Calculation of the permissible sulfur content in fuel for different combustion technologies. Table 4 shows the results of calculating the permissible sulfur content in fuel for two combustion technologies based on the permissible sulfur dioxide emissions in pulverized coal boilers and cement production according to the methodology [19]:

- an example of pulverized coal combustion is a mixture of 85 % anthracite ($W_i^r = 8.8 \%$, $A^d = 28.1 \%$, $S_i^d = 1.3 \%$, $Q_i^r = 5,096$ kcal/kg) with 15 % petroleum coke ($W_i^r = 6.5 \%$, $A^d = 0.3 \%$, $S_i^d = 6.0 \%$, $Q_i^r = 7,800$ kcal/kg), $\eta_f = 0.05$;

- an example of combustion in cement production is a mixture of 35 % high-calorific bituminous coal ($W_i^r = 11.0 \%$, $A^d = 15.0 \%$, $S_i^d = 1.4 \%$, $Q_i^r = 5,870$ kcal/kg), 40 % of low-calorific bituminous coal ($W_i^r = 6.0 \%$, $A^d = 35.0 \%$, $S_i^d = 1.7 \%$, $Q_i^r = 4,500$ kcal/kg) and 25 % of petroleum coke of the above composition, $\eta_f = 0.93$.

The different values of sulfur content in coal chosen in this case are due to the known tendency to decrease the sulfur content with an increase in the degree of coal metamorphism [20], as well as the fact that the sulfur content of coal from one deposit increases with an increase in ash content due to the contribution of pyrite sulfur contained in the mineral part of the fuel [21].

The presented results correlate with the actual levels of sulfur dioxide emissions in pulverized-coal boilers and in cement production and prove the advantages of using petroleum coke as an additional fuel for rotary kilns in the production of Portland cement clinker. Due to the peculiarities of the process, with a higher proportion of petroleum coke in the fuel and a higher sulfur content in coal, SO₂ emissions are 11 times lower than in pulverized coal combustion.

Based on these data, it is possible to estimate the permissible share of petroleum coke in the fuel for cement production depending on the calorific content and sulfur content of the main fuel – hard coal.

Calculation of the permissible share of petroleum coke in fuel for cement production. The complexity of this calculation is that, as shown above, we should consider a mixture of not two, but three components – petroleum coke, high-calorific coal (for the rotary kiln) and low-calorific coal (for the decarbonizer). Changing the proportion of petroleum coke in the fuel will change the proportion of high-calorific coal, as well as the elemental composition of the average fuel, which makes such calculations based on the regulatory methodology [19] cumbersome and practically inapplicable.

The calculation can be simplified based on the findings of [22], which shows that the concentration of sulfur dioxide in flue gases is directly proportional to the content of total sulfur for the fuel operating condition S_i^r and inversely proportional to the specific volume of dry flue gases, which, in turn, is directly proportional to the lower calorific value for the fuel operating condition Q_i^r . Therefore, it seems expedient to use the value of reduced sulfur S_i^r/Q_i^r , % kg/Mcal, as the main criterion for the predictive assessment of the sulfur dioxide concentration. In [22], it was proved that the dependence of the sulfur dioxide concentration on the reduced sulfur is linear with an approximation factor of 0.99

$$c_{\text{SO}_2} = (S_i^r/Q_i^r) \cdot 12,115 + 197.44.$$

Substitution of the values S_i^r and Q_i^r from Table 4 for the case of pulverized coal combustion in (5) gives $c_{(\text{SO}_2)} = 4,436$ mg/nm³, which practically coincides with the result obtained by calculation according to [19]. Substituting the values of S_i^r and Q_i^r from Table 4 for the case of cement production formally gives $c_{\text{SO}_2} = 5,357$ mg/nm³. To bring this value to the conditions of cement production, it should be divided by

Table 4

Results of calculating the sulfur content in fuel at the maximum permissible concentration of sulfur dioxide in the exhaust gases for two combustion technologies

Calculation option	Pulverized fuel combustion	Cement production
Mixture composition per unit of as-received fuel:		
$W_i^r, \%$	8.41	7.88
$A^r, \%$	21.86	17.90
$C^r, \%$	64.67	61.37
$H^r, \%$	1.80	3.79
$O^r, \%$	0.71	5.56
$N^r, \%$	0.63	1.02
$S^r, \%$	1.92	2.48
$Q_i^r, \text{ kcal/kg}$	5,488	5,823
Degree of fuel carbon oxidation ε_c in a power plant	0.949	0.999
Mass content of combustible carbon C, %, per unit of as-received fuel	61.381	61.305
Specific volume of oxygen required for stoichiometric oxidation reactions, nm^3/kg	1.254	1.333
Specific volume of air nitrogen required for fuel combustion, nm^3/kg	4.717	5.016
Specific volume of dry flue gases $V_{fg}^o, \text{ nm}^3/\text{kg}$ (in the absence of oxygen)	5.881	6.185
Specific gravity of dry flue gases $m_{fg}^o, \text{ kg/kg}$	8.190	8.575
Density of dry flue gases $\rho_{fg}^o, \text{ kg/nm}^3$	1.393	1.386
Specific volume of dry flue gases reduced to 6 % $O_{(2)}$ in flue gases $v_{fg}, \text{ nm}^3/\text{kg}$	8.234	8.660
Sulfur binding efficiency	0.05	0.93
SO_2 emission factor $k_j, \text{ g/GJ}$	1,590.2	142.3
Concentration of SO_2 in dry flue gases $c_j, \text{ mg/nm}^3$	4,437.4	400.6
Maximum permissible concentration of $SO_2, \text{ mg/nm}^3$	4,500 [4]	400 [4]

(1 – 0.05) and multiplied by (1 – 0.93), where 0.05 and 0.93 are the values of η_l for pulverized combustion, for which the empirical relationship (5) was obtained, and for cement production, respectively. Then $c_{(SO_2)} = 395 \text{ mg/nm}^3$, which differs from the result obtained by calculation according to [19] by less than 1.5 %. This accuracy seems suitable for a preliminary assessment.

Let us take the consumption of low-calorie coal in the decarbonizer G_{coal2} as 1 and denote G_{coal1} and G_{pc} as the reduced consumption of high-calorie coal and pe-

troleum coke (PC) fed to the rotary kiln. For simplicity, the total sulfur content for high and low calorific coal is assumed to be the same, which is true for all fuels

$$S_i^r = ((G_{coal1} + 1)S_{i(coal)}^r + G_{PC}S_{i(PC)}^r) / (G_{coal1} + G_{PC} + 1); \quad (6)$$

$$Q_i^r = (G_{coal1} \cdot Q_{i(coal1)}^r + G_{PC} \cdot Q_{i(PC)}^r + 1 \cdot Q_{i(coal2)}^r) / (G_{coal1} + G_{PC} + 1); \quad (7)$$

$$S_i^r / Q_i^r = ((G_{coal1} + 1) \cdot S_{i(coal)}^r + G_{PC} \cdot S_{i(PC)}^r) / (G_{coal1} \cdot Q_{i(coal1)}^r + G_{PC} \cdot Q_{i(PC)}^r + 1 \cdot Q_{i(coal2)}^r). \quad (8)$$

According to Tables 1, 3, the values of fuel heat input to the rotary kiln and decarbonizer in the first balance sheet period are 0.85:1, in the second – 1.24:1. For simplicity, as a first approximation, this ratio can be assumed to be 1:1 and can be fixed, regardless of the proportion of petroleum coke. For an approximate estimate, the lower heating value “as received” of high-calorific, low-calorific coal and petroleum coke it is advisable to take as the characteristic values of the production of Portland cement clinker. They can be taken from Table 1, accounting the moisture content of the raw fuel, namely 6.0, 4.2 and 7.5 Mcal/kg, respectively. Then

$$S_i^r / Q_i^r = ((G_{coal1} + 1) \cdot S_{i(coal)}^r + G_{PC} \cdot S_{i(PC)}^r) / 8.4; \quad (9)$$

$$G_{coal1} = (G_{PC} \cdot 7.5 - 4.2) / 6; \quad (10)$$

$$c_{SO_2} = ((S_i^r / Q_i^r) \cdot 12,115 + 197.44) \cdot 0.07 / 0.95. \quad (11)$$

Table 5 shows the results of calculating the permissible share of petroleum coke in high-calorific fuel for the rotary kiln and in all fuel at different sulfur content in petroleum coke and coal (the consumption of low-calorific coal for the decarbonizer is taken as 1).

The results indicate a significant potential for replacing high-calorific coal with petroleum coke in cement production. Thus, with a sulfur content of 1.6 % per working weight of coal and 6 % of petroleum coke, the permissible share of petroleum coke in the total fuel is 13.8 %, and in high-calorie fuel for a rotary kiln – 32.3 %. With a sulfur content of 5 % per working weight of petroleum coke, its permissible shares in all and high-calorific fuel are 19 and 43 %, respectively. At the same time, due to the higher calorific content of petroleum coke, the share of high-calorific coal it replaces is 40 and 54 %, respectively. These indicators should be considered as preliminary recommendations for the use of petroleum coke in cement production to expand its fuel base. In specific cases they should be specified according to the methodology presented, taking into account the specific values of the lower calorific value and sulfur content of coal for the rotary kiln and decarbonizer at a given production facility.

Conclusions. The paper considers the physicochemical properties of petroleum coke and proves that it is equivalent to lean coal as a fuel, which differs from it only in low ash and high sulfur content. The experience of using petroleum coke as a cheaper solid fuel along with coal or as a substitute for coal in power plants with circulating fluidized bed and pulverized combustion, in

Table 5

Allowable share of petroleum coke (PC) in high-calorie fuel for the rotary kiln and in the total fuel

$S_{i(\text{coal})}^r, \%$	Consumption of PC	Consumption of high-calorific coal	Share of PC in all fuel	Share of PC in high-calorific fuel	Share of high-calorific coal substituted by PC
$S_{i(\text{PC})}^r = 6 \%$					
1.2	0.352	0.260	0.218	0.503	0.63
1.4	0.293	0.334	0.180	0.419	0.52
1.6	0.226	0.418	0.138	0.323	0.40
1.8	0.150	0.513	0.090	0.214	0.27
2.0	0.064	0.620	0.038	0.091	0.11
$S_{i(\text{PC})}^r = 5 \%$					
1.2	0.453	0.134	0.29	0.647	0.81
1.4	0.383	0.221	0.24	0.547	0.68
1.6	0.301	0.324	0.19	0.430	0.54
1.8	0.205	0.444	0.12	0.293	0.37
2.0	0.090	0.588	0.05	0.129	0.16

particular, in the pulverized coal boiler of the 800 MW power unit of Slovianska TPP, is analyzed. The technology of “dry” cement production is considered. It is proved that the conditions of petroleum coke combustion in a rotary clinker kiln, decomposition of calcium carbonate in a decarbonizer, and contact of calcium oxide with sulfur dioxide generated during solid fuel combustion correspond to the optimal conditions for in-furnace sulfur binding by limestone in the technology of coal combustion in a pulverized coal combustion plant. This correspondence ensures effective desulfurization of the flue gases. The efficiency of solid fuel sulfur binding by calcium and magnesium oxides in a rotary kiln and in a decarbonizer was determined on the basis of the developed method of material balance of sulfur in raw materials, fuel, and clinker; for the studied case, it is 0.93, that is, approximately in the middle of the known range of sulfur binding efficiency by limestone during CFB combustion and does not depend on the proportion of total sulfur and on the presence of petroleum coke in the fuel.

The permissible content of petroleum coke in the fuel for pulverized coal combustion and for rotary kilns for clinker firing was determined on the basis of the regulatory method for calculating the level of sulfur dioxide emissions using the current standards for the permissible sulfur content in flue gases in Ukraine and Europe and the found sulfur binding coefficient. It is shown that, due to the peculiarities of the dry cement production process, with a higher proportion of petroleum coke in the fuel and a higher sulfur content in coal, SO₂ emissions are 11 times lower than in pulverized coal combustion.

A methodology for estimating the permissible content of petroleum coke in the fuel for a rotary kiln has been developed. The permissible share of petroleum

coke in high-calorific fuel for a rotary kiln and in all fuel at different sulfur content in petroleum coke and coal was calculated. It is shown that at a sulfur content of 1.6 % per working weight of coal and 6 % of petroleum coke, the permissible share of petroleum coke in the entire fuel is 13.8 %, in high-calorific fuel for a rotary kiln – 32.3 %, and at a sulfur content of 5 % of petroleum coke – 19 and 43 %, respectively. At the same time, due to the higher calorific content of petroleum coke, the share of high-calorific coal that it replaces is 40 and 54 %, respectively. The significant potential of replacing high-calorific coal with petroleum coke in cement production has been proved and recommendations for the use of petroleum coke in cement production to expand its fuel base in compliance with environmental requirements have been provided.

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Науково-технічні й екологічні аспекти розширення паливної бази енергетики та цементного виробництва за рахунок нафтового коксу

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Мета. Узагальнення досвіду паливного використання нафтового коксу за різними технологіями спалювання й розроблення наукових основ його використання у виробництві портландцементного клінкеру із дотриманням екологічних вимог.

Методика. Визначення ефективності зв'язування сірки в обертовій печі та в декарбонізаторі на

основі матеріального балансу сірки в сировині, паливі й клінкері. Визначення допустимого вмісту нафтового коксу в паливі на основі розрахунку рівня викидів сірчистого ангідриду із використанням знайденого коефіцієнту зв'язування сірки.

Результати. Показано, що в якості палива нафтовий кокс еквівалентний до високосірчистого пісного вугілля. Проаналізовано досвід використання нафтококсу в енергоустановках зі спалюванням у циркулюючому киплячому шарі (ЦКШ) і з пиловидним спалюванням, зокрема, у котлі енергоблоку 800 МВт Слов'янської ТЕС. Розглянута технологія «сухого» виробництва цементу. Доведено, що умови спалювання нафтококсу в обертовій печі обпалу клінкеру, розкладу карбонату кальцію в декарбонізаторі й контакту оксиду кальцію з сірчистим ангідридом співпадають з оптимальними умовами зв'язування сірки в технології спалювання вугілля у ЦКШ. Визначена ефективність зв'язування сірки в обертовій печі та у декарбонізаторі на основі матеріального балансу сірки в сировині, паливі й клінкері. Визначено допустимий вміст нафтового коксу в паливі для пиловидного спалювання й для обертових печей на основі розрахунку рівня викидів сірчистого ангідриду із використанням знайденого коефіцієнту зв'язування сірки. Надані рекомендації із використання нафтового коксу у цементному виробництві для розширення його паливної бази із дотриманням екологічних вимог.

Наукова новизна. Визначена ефективність зв'язування сірки твердого палива в обертовій печі та у декарбонізаторі. Доведено, що у технології «сухого» виробництва цементу при більшій частці нафтококсу в паливі забезпечуються викиди діоксиду сірки в 11 разів менші, ніж при пиловидному спалюванні. Розроблена методика оцінки допустимого вмісту нафтококсу в паливі для обертової печі.

Практична значимість. Доведені переваги використання нафтового коксу як палива для обертових печей у виробництві клінкеру. Визначено допустимий вміст нафтококсу в паливі із виконанням екологічних вимог ЄС. Надані рекомендації із використання нафтового коксу у цементному виробництві для розширення його паливної бази.

Ключові слова: нафтовий кокс, кам'яне вугілля, портландцементний клінкер, обертова піч, декарбонізатор

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