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Determination of Sulfur Content in Mineral Mass for Prediction of Hazardous Properties of Coal Mine Seams

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Abstract

Introduction. Sulfur is found in the organic and mineral parts of all types of solid fuels, and its concentration determines the extent of the hazardous characteristics of mine seams. Therefore, research on the determination of sulfur content in fossil fuels has not lost its relevance. The total sulfur content and its varieties has been studied in most cases in terms of the efficiency of fuel processing processes, the quality and environmental safety of coal products. Less attention was paid to the hazardous properties of mine seams, forecasting and developing preventive measures for endogenous fires in coal mines. This work aims to develop an engineering method to calculate the elemental sulfur content in the mineral mass of coal to predict the hazardous properties of mine seams.

Materials and Methods. According to the results of the correlation analysis, we established how the sulfur content in the combustible part of the fuel depended on the total sulfur. We analyzed data on coals from almost all mine seams of the Donetsk and Lviv-Volyn coal basins. We presented the ash ratios for the formation and basin samples, as well as the information about the total sulfur and sulfur content in the combustible part. This allowed us to estimate the sulfur content in mineral impurities by calculation. The initial data for developing the method were taken from reference and regulatory documents.

Results. Seven aggregates were considered, which included from 149 to 1827 mine seams. For each, reference and calculation data were summarized:

- sulfur content — total (S_t^d) and in the combustible part of the fuel ($S_г$);
- conditional points for adjusting the indicators to avoid obtaining negative average values;
- empirical equations that describe the calculated and corrected dependencies based on the ratio of S_t^d and $S_г$;
- correlation of these indicators;
- ranges of change in ash yield.

All this information was presented for clean and raw coals, for ash yields of more and less than 10%. In one case, satisfactory results were noted for determining the calculated sulfur content in a conditionally non-combustible mass. This was an aggregate of 149 mine layers. For 13 of them, the difference in indicators (S_t^d – $S_г$) was greater than or equal to zero. For 136 — less than zero. For 81, the sulfur content in the conditionally non-combustible part of the fuel $S_н$ was less than zero. At the same time, there was a sufficient level of correlation (0.79) and a limited range of changes in ash yield (2.4–10). The empirical equation corresponding to this aggregate was recommended for predicting the hazardous properties of mine seams with an ash yield of less than 10%.

Discussion and Conclusion. The results of this study can be used to improve regulations for the safe conduct of mining activities, taking into account sulfur content in organic matter and in mineral impurities of fossil coal.

Keywords: sulfur in fossil coal, engineering method for determining sulfur in the mineral mass of coal, prevention of endogenous fires in coal mines

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Научная статья

Определение содержания серы в минеральной массе для прогноза опасных свойств угольных шахтопластов

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Аннотация

Введение. Сера присутствует в органической и минеральной части всех видов твердого топлива, причем от ее содержания зависит проявление опасных свойств шахтопластов. В связи с этим не теряют актуальность научные изыскания, связанные с определением количества серы в ископаемом топливе. Содержание общей серы и ее разновидностей изучалось в большинстве случаев с позиций эффективности процессов переработки топлива, качества и экологической безопасности угольной продукции. Меньше внимания уделяли проявлению опасных свойств шахтопластов, прогнозированию и разработке профилактических мероприятий по предотвращению эндогенных пожаров в угольных шахтах. Цель представленной работы — создание инженерного метода расчетного определения элементного содержания серы в минеральной массе углей для прогноза опасных свойств шахтопластов.

Материалы и методы. По результатам корреляционного анализа установили, каким образом содержание серы в горючей части топлива зависит от общей серы. Рассмотрели данные по углям практически всех шахтопластов Донецкого и Львовско-Волынского бассейнов. Представили соотношения зольности пластовых и обогащенных проб, а также сведения о содержании общей серы и серы в горючей части. Это позволило расчетным путем оценить содержание серы в минеральных примесях. Исходные данные для разработки метода взяли из справочно-нормативных документов.

Результаты исследования. Рассмотрены семь совокупностей, которые включали от 149 до 1827 шахтопластов. По каждой обобщили справочные и расчетные данные:

– содержание серы — общей (S_t^d) и в горючей части топлива ($S_г$);
– условные точки для корректировки показателей во избежание получения отрицательных усредненных значений;
– эмпирические уравнения, которые описывают расчетные и скорректированные зависимости по соотношению S_t^d и $S_г$;
– корреляцию этих показателей;
– диапазоны изменения выхода золы.

Все эти сведения представлены для обогащенных и не обогащенных углей, для выхода золы более и менее 10 %. В одном случае отмечены удовлетворительные результаты определения расчетного содержания серы в условно негорючей массе. Это совокупность из 149 шахтопластов. Для 13 из них разность показателей ($S_t^d – S_г$) больше или равна нулю. Для 136 — меньше нуля. Для 81 содержание серы в условно негорючей части топлива $S_н$ меньше нуля. При этом отмечается достаточный уровень корреляции (0,79) и ограниченный диапазон изменения выхода золы (2,4–10). Соответствующее этой совокупности эмпирическое уравнение рекомендуется для прогноза опасных свойств шахтопластов с выходом золы менее 10 %.

Обсуждение и заключение. Полученные результаты можно использовать для совершенствования нормативных документов по безопасному ведению горных работ с учетом содержания серы, как в органической массе, так и в минеральных примесях ископаемого угля.

Ключевые слова: сера в ископаемом угле, инженерный метод определения серы в минеральной массе угля, предотвращение эндогенных пожаров в угольных шахтах

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Introduction. Sulfur is an element of compounds found in the organic and mineral parts of various fuels. In the mineral mass of coals, sulfur is found as a rule in the form of sulfates (mainly calcium and iron) and iron disulfides FeS_2 (pyrite and marcasite). In the organic mass, sulfur is found in the form of organic compounds.

There are several basic forms of sulfur in coals. These are parts of the total sulfur:

- sulfate S_{SO_4} — is a part of the inorganic mass of coal in the form of metal sulfates;
- pyrite S_p — is a part of the inorganic mass of coal in the form of metal disulfides (pyrite and marcasite);
- organic S_o — is a part of organic compounds.

Total sulfur and its varieties, unlike ash sulfur, are conditionally converted to elemental sulfur [1]:

$$S_t = S_{SO_4} + S_p + S_o \,. \tag{1}$$

Sulfur content in ash is usually calculated in the form of sulfur trioxide (SO_3). Sulfur is an undesirable and harmful part of fuel. When burning coal, sulfur is released as SO_2. It pollutes the environment, causes corrosion of metal surfaces, and reduces the heat of combustion of fuel. During coking, sulfur turns into coke, deteriorating its properties and the quality of the metal. For these reasons, the content of total sulfur and its varieties has been studied in most cases from the standpoint of the efficiency of fuel processing processes, the quality and environmental safety of coal products. Good results have been obtained in this direction, which is confirmed by the development and successful use of modern industrial classification of coals according to genetic and technological parameters. To a large extent, it is based on data from reference books, in which, based on the results of experiments, information was summarized on the quality of hard coals and anthracites [2], as well as on their processing [3].

The successes in forecasting and developing preventive measures to prevent endogenous fires during work in coal mines are less significant. Thus, for twenty years (from 1994 to 2015), more than two hundred endogenous fires occurred in the mines of Ukraine [4]. According to open data, similar accidents occur in many coal-mining countries. Thus, the problem that has been relevant since the 19th century has not been solved. At first, it was associated with spontaneous combustion of coal in warehouses and during transportation. Then accidents began to occur in coal mines caused by endogenous fires [5].

Sulfur content in coal not only determines its consumer qualities, but also significantly affects the manifestation of hazardous properties of coal seams during mining operations [6]. In particular, with an increase in the total sulfur content in coal by 1–6%, the probability of endogenous fire increases by more than three times [7]. There have been attempts to figure out how dangerous properties of mine seams can be identified by mineral impurities [8]. However, even now it is almost unknown how the studied risks depend on the type and form of sulfur in fossil coal. As a result, in regulatory documents[1, 2] the probability of endogenous fires in coal seams was determined only by the content of total sulfur[3].

Studies [5] have shown that spontaneous combustion is largely due to the nature of not only coal, but also the associated rocks[4]. It is extremely important to establish the component of the fuel, on which the probability of spontaneous combustion depends. Without this, laboratory research methods do not provide acceptable answers to the questions posed. Along with laboratory studies of coal matter, it was assumed to take into account the presence of carbonaceous rock from mineral interlayers, as well as from cover and soil rocks in fossil fuels. To do this, it is necessary to additionally consider the ash yield and the content of all types of sulfur [5].

Guidelines for the prevention and extinguishing of endogenous fires[5], as well as other regulatory documents on safe conduct of mining operations, do not take into account the presence of mineral impurities. These issues are not addressed in dust control measures in coal mines, predictions of gas emissions[6] and sudden emissions[7] or in general, in regulatory documents governing mining activities.

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[1] *Rukovodstvo po preduprezhdeniyu i tusheniyu endogennykh pozharov na ugol'nykh shakhtakh Ukrainy.* KD 12.01.402-2000 from 18.12.2000. Donetsk: Nauchno-issledovatel'skii institut gornospasatel'nogo dela; 2000. 216 p. (In Russ.).

[2] *Katalog uglei SSSR, sklonnykh k samovozgoraniyu.* Moscow: Nedra; 1982. 416 p. (In Russ.).

[3] *Rukovodstvo po preduprezhdeniyu i tusheniyu endogennykh pozharov na ugol'nykh shakhtakh Ukrainy.* KD 12.01.402-2000. Donetsk: NIIGD; 2000. 216 p. (In Russ.).

[4] GOST 25543-2013. *Brown coals, hard coals and anthracites. Classification according to genetic and technological parameters.* URL: https://files.stroyinf.ru/Data2/1/4293772/4293772639.pdf (accessed: 11.01.2023). (In Russ.).

[5] *Rukovodstvo po preduprezhdeniyu i tusheniyu endogennykh pozharov na ugol'nykh shakhtakh Ukrainy.* KD 12.01.402-2000 from 18.12.2000. Donetsk: Nauchno-issledovatel'skii institut gornospasatel'nogo dela; 2000. 216 p. (In Russ.).

[6] *Rukovodstvo po proektirovaniyu ventilyatsii ugol'nykh shakht.* Kyiv: Osnova; 1994. 311 p. (In Russ.).

[7] *Pravyla vedennya hirnychyx robit na plastax, sxyl"nyx do hazodynamichnyx yavyshh. Standart Minvuhlepromu Ukrayiny* No. SOU 10.1.00174088.011-2005. Kyiv: Ministerstvo ugol'noi promyshlennosti Ukrainy; 2005. 224 p. (In Ukr.).

Content of mineral impurities, judging by the ash yield from coal seam samples [2] and [3], can significantly exceed 40%. This undoubtedly affects the reliability of the forecast of hazardous properties of coal seams in mining operations and indicates the relevance of improving the regulatory framework. To do this, it is necessary to develop an engineering method for determining sulfur in the mineral mass of coals.

The aim of the presented work is to prove the fundamental and practically the only possibility of calculating the elemental sulfur content in the mineral mass of coals for predicting the hazardous properties of coal seams during mining operations. It should be noted that when implementing this approach, some standard indicators are used, which are recorded in the reference and regulatory documentation on the consumer qualities of fuel for each coal seam. We are referring to experimental data on sulfur content — common and in the combustible part of the fuel. Due to this information, it is possible to establish the relationship between the sulfur content in the organic mass and mineral impurities. According to ash yield, it is possible to determine the ratio between the organic mass and mineral impurities for clean coal samples. The ratio of ash content of bed and clean samples allows us to estimate sulfur content in the removed treatment products.

Materials and Methods. The research methodology is based on a close correlation ($r = 0.93$) of sulfur content in the combustible part of fuel ($S_{\mathrm{г}}$) and total sulfur (S_t^d) for coals of almost all mine seams of the Donetsk and Lviv-Volyn basins (Fig. 1)

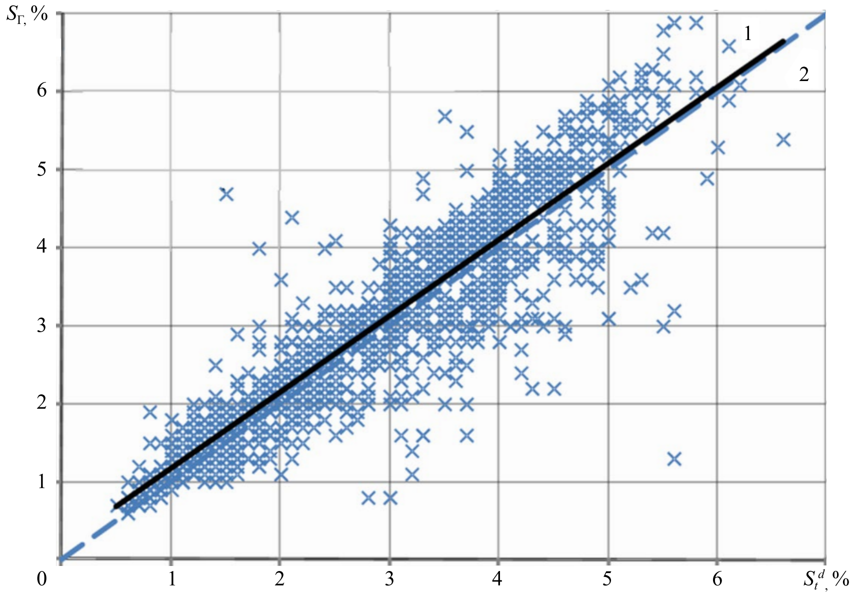


Fig. 1. Dependence of sulfur content in the combustible part of fuel ($S_{\mathrm{г}}$) on total sulfur (S_t^d) according to the statistical processing of experimental data: 1 — averaging line; 2 — bisector of the coordinate grid (the authors' figure based on [2] and 3])

Statistical processing of dependence $S_{\mathrm{г}}$ on S_t^d was performed for 1827 mine seams, for which the sulfur content was known — total and in the combustible part of fuel.

Reference normative document [3] provides general information on the consumer qualities of coal for 734 mine seams, and reference [2] provides it for 1379 mine seams.

The proximity of averaging line 1 and bisector 2 of the coordinate grid (Fig. 1) shows that, in general, the sulfur content in the combustible part of fuel ($S_{\mathrm{г}}$) can be higher or lower than total sulfur value (S_t^d). Difference between S_t^d and $S_{\mathrm{г}}$ ($S_t^d - S_{\mathrm{г}}$) in the first approximation can be a criterion for the ratio of the elemental sulfur content in the combustible mass and in the conditionally non-combustible part of the fuel. Indicator ($S_t^d - S_{\mathrm{г}}$) for 1315 coal seams was negative, which indicated a predominant sulfur content in the combustible part of the mass. For 429 coal seams, this indicator had positive values, which indicated the predominant presence of sulfur in the conditionally non-combustible part of the fuel. Zero difference ($S_t^d - S_{\mathrm{г}}$) for 83 mine seams meant that the sulfur content in the combustible and conditionally non-combustible parts of the coals was the same for the entire aggregate of mine seams considered in the article.

Information is available for 2113 coal seams. For some of them, the data in different documents match, and this is an argument in favor of the reliability of the information. The values of ash yield from bed samples are not given for four mine seams (Table 1). For this reason, it is possible to analyze the experimental data on ash yield for 2109 mine seams. Of these, processing was carried out for 1,622 mine seams, and for 487 it was not carried out.

Table 1

Information on mine seams for which data on ash yield from bed samples is not provided

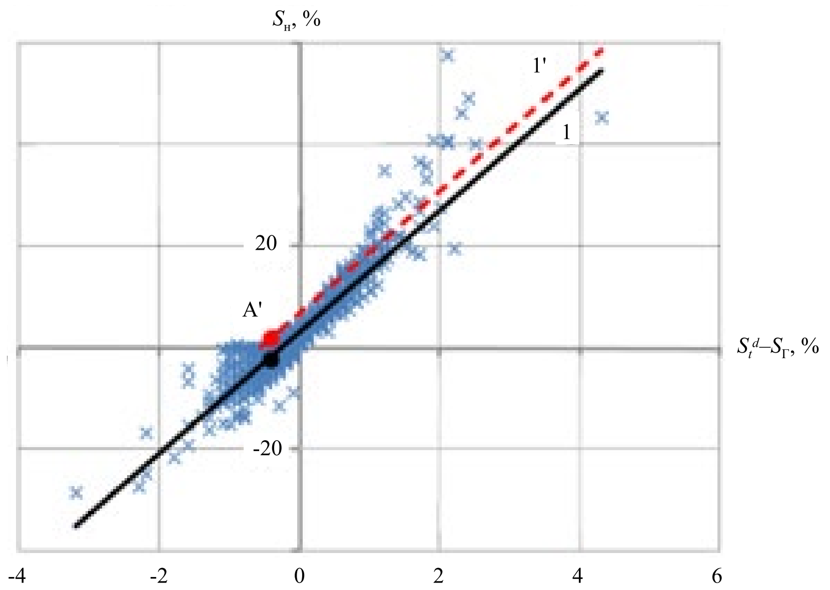
Source	Source page	Mine	Formation index	Ash content, %		Sulfur content, %	
				bed sample, $A_п^c$	clean sample, $A_о^c$	total, S_t^d	in the combustible part, $S_Г$
[3]	74	№ 144	l_1	–	6.3	6.3	1.9
			k_8	–	6.1	2.8	3.0
		10-bis	m_3	–	7.0	3.2	3.5
[4]	106	named after Voykov	l_2	–	–	–	–

Results. The indicators from [2] and [3] made it possible to calculate sulfur content in the conditionally non-combustible part of fuel $S_н$ for 827 mine seams:

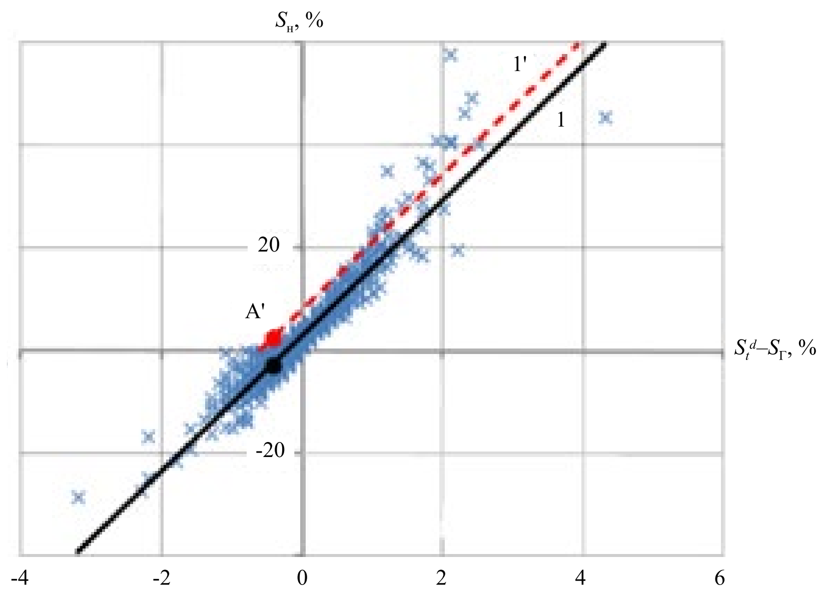
$$S_н = \frac{100 \cdot S_t^d - \left(100 - A_o^c\right) \cdot S_Г}{A_o^c}, \% \quad (2)$$

where $A_о^c$ — ash yield from clean samples, %.

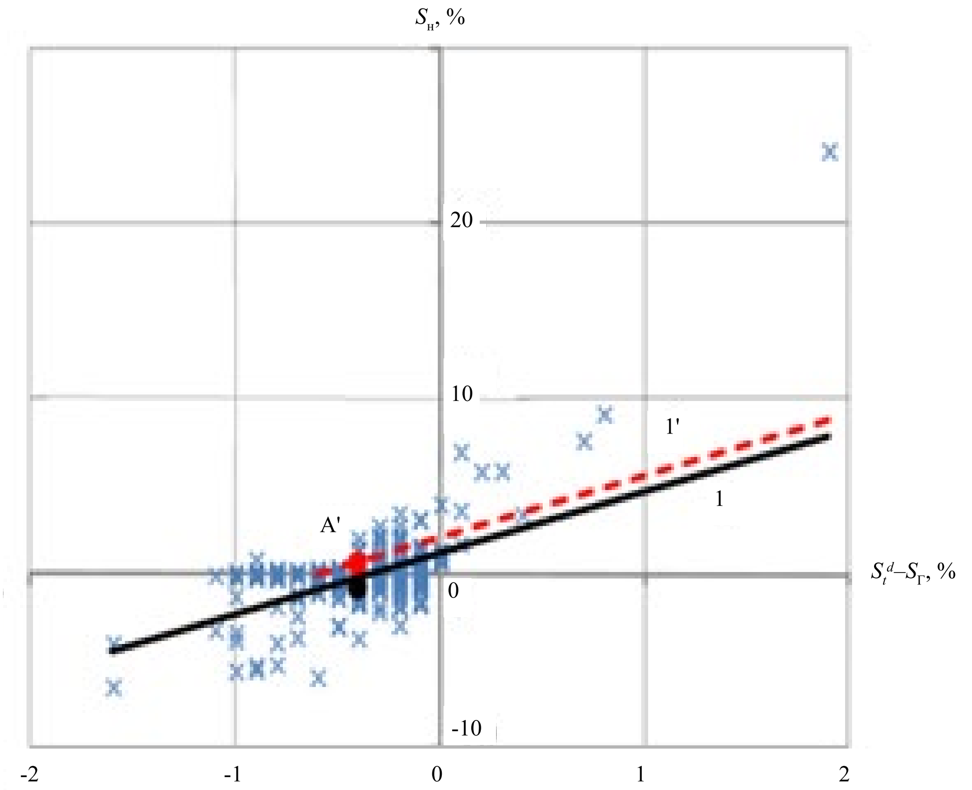
Calculated values $S_н$ were related to indicator (S_t^d–$S_Г$) by a close directly proportional correlation (r = 0.91, Fig. 2 *a*).



a)



b)



c)

Fig. 2. Dependence on criterion (S_t^d – $S_г$) of calculated values of sulfur content ($S_н$) according to equation (2) in the conditionally non-combustible part of fuel: *a* — for the entire aggregate of 1827 mine seams; *b* — for 1352 mine seams, the coals of which were pre-cleaned; *c* — for 475 mine seams with raw coals; 1 — averaging lines; 1' — adjusted positions of averaging lines; A' — conditional position of a point to correct the location of line 1' and exclude negative ("wild") averaged values *Sн*; × — calculated values *Sн* according to equation (2) [3, 4]

At the same time, we got a significant number of negative calculated values $S_н$ for 802 mine seams. Close correlation of the indicators and the presence of "wild" (negative) results indicated possible influence of systematic errors in determining the difference between total sulfur content (S_t^d) and in the combustible part of the fuel ($S_г$). The presence of negative calculated values $S_н$ could indicate that systematic errors in the determination of criterion (S_t^d – $S_г$) were due to both an underestimation of the experimental values of total sulfur and an overestimation in the combustible part of fuel.

In order to understand the origin of "wild" calculated values of sulfur content in the conditionally non-combustible part of fuel according to equation (2), methods for determining the indicators from this dependence were considered.

Several approaches to the determination of total sulfur in coals are known — from the classical gravimetric Eschka method to modern types of instrumental analysis [1]. The Eschka method, proposed in 1874, is still widely used in world practice. It is regulated by GOST[8]. Coal sample is burned by sintering with a mixture of magnesium oxide and anhydrous sodium carbonate (ratio 2:1 by weight) in an oxidizing atmosphere at a temperature of (800 ± 250) °C. The organic mass of fuel is burned, and sulfur is converted into sodium and magnesium sulfates. They are transferred to a solution. The sulfate ion is quantitatively precipitated in a hydrochloric acid medium with barium chloride in the form of barium sulfate $BaSO_4$. The total sulfur content is calculated by the mass of $BaSO_4$. The disadvantages of this approach are high time costs (at least 6–7 hours) and the possibility of losing part of the organic sulfur during sintering with a mixture [1]. In most cases, the method is used in case of disagreement. The total sulfur in standard fuel samples for calibration of analyzers is determined only by the Eschka method.

For practical purposes, an accelerated standard method for determining total sulfur, regulated by GOST[9] is recommended. The fuel sample is burned in a stream of oxygen or air in a tube furnace at 1350°C. Ash residue and gaseous combustion products are formed, which include sulfur oxides (mostly SO_2) and chlorine oxides. The analysis is

[8] *Pravyla vedennya hirnychyx robit na plastax, sxyl"nyx do hazodynamichnyx yavyshh. Standart Minvuhlepromu Ukrayiny* No. SOU 10.1.00174088.011-2005. Kyiv: Ministerstvo ugol'noi promyshlennosti Ukrainy; 2005. 224 p. (In Ukr.).

[9] GOST 2059-95 (ISO 351-96). *Solid mineral fuel. Determination of total sulfur.High temperature combustion method.* Moscow: Stansartinform; 2008. 14 p. URL: https://files.stroyinf.ru/Data2/1/4294832/4294832840.pdf (accessed: 11.11.2023). (In Russ.).

carried out in 40–60 minutes. This method was used in determining total sulfur content to establish the consumer qualities of coals. Experimental values are given in reference and regulatory documents [2, 3]. An accelerated method for determining total sulfur is recommended for monitoring the sulfur content in low-ash fuels. It is undesirable to use it in the analysis of high-ash fuels with a significant content of calcium compounds. Due to the variety of the composition of the mineral mass and sulfur compounds, it is impossible to be completely sure that some of the sulfur will not remain in the ash in the form of $CaSO_4$. As a result, the results are underestimated [1].

For most coal seams, after coal cleaning, the ash yield is less than 10%, but this indicator can also be much higher (Fig. 3).

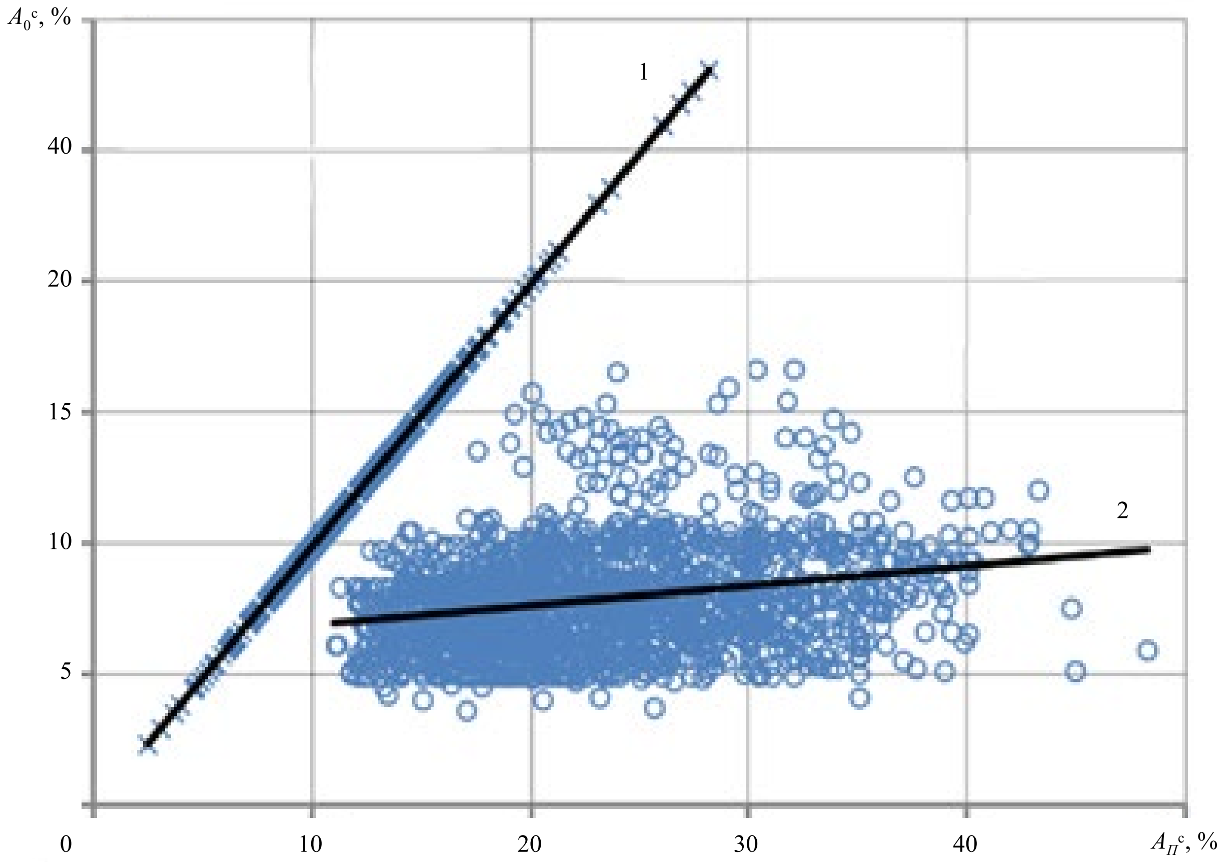


Fig. 3. Dependence of ash yield from clean coal samples ($A_о^c$) on ash yield from bed samples ($A_п^c$) according to experimental data [2, 3]

For this reason, even after cleaning a significant part of the samples, there was no reason to consider all coals low-ash. According to data [2, 3], no cleaning was carried out for 487 mine seams and the ash yield in many cases exceeded 10%, which also did not allow the coals of this aggregate of mine seams to be classified as low-ash.

Calcium compounds are present in the mineral impurities of the coals of all mine seams. This is evidenced by the typification of the composition of the ash (Table 2), according to which the CaO content can generally reach 40%.

Table 2

Typification of coal ash composition according to [2] and [3]

Types of coal ash	Composition fluctuation limits, %			
	Al_2O_3	SiO_2	Fe_2O_3	CaO
Siliceous	8–30	40–70	to 20	to 20
Alumina	30–45	40–55	to 20	to 20
Ferriferous	10–20	30–55	> 20	to 20
Lime	5–20	15–40	5–20	20–40

One of the reasons for obtaining "wild" calculated values $S_{н}$ according to equation (2) is an underestimation S_t^d when determined by the accelerated method. This conclusion is justified by:

- the analysis of ash yield from clean and bed samples;
- the possible content of calcium compounds in all types of ash.

The second factor in obtaining negative calculated values $S_н$ is an overestimation of the proportion of the combustible part of fuel using $(100–A_о^c)$ as a multiplier in equation (2). Total sulfur content S_t^d refers to both organic part and mineral mass (MM) of the fuel. For this reason, it would be more logical to use MM values in equation (2) instead of ash yield $A_о^c$ which have not been experimentally determined for the considered mine seams. According to known empirical dependencies, the MM values always exceed the ash yield to the dry state. Accounting for such an excess requires additional (missing) information about hydrate moisture, carbon dioxide released during complete decomposition of carbonates, pyrite and sulfate sulfur. For an approximate estimate of the mineral mass content, ratio $MM \approx 1.1\ A_о^c$ is sometimes used [1].

The analysis showed the reasons for the systematic underestimation of product $100 \cdot S_t^d$ and overestimation of difference $(100–A_о^c)\ S_г$ in determining the calculated values $S_н$ according to equation (2).

The presence of negative values $S_н$ for an aggregate of 802 mine seams (Fig. 2 *a*) makes it possible to estimate the average underestimation of criterion $\overline{S_t^d - S_г}$, at which "wild" results were obtained

$$\overline{S_t^d - S_г} = \frac{\sum_i^n \left(S_t^d - S_г\right)_i}{n} = \frac{-336.3}{802} = -0.42, \% \tag{3}$$

Here $n = 802$ — number of mine seams for which negative values $S_н$ were obtained; $\Sigma\left(S_t^d - S_г\right)_i$ — sum of negative values $S_t^d – S_г$ for the aggregate of $n = 802$ mine seams.

Average negative value $\overline{S_t^d - S_г} = -\ 0.42\%$ corresponds to average negative value $\overline{S_н}$:

$$\overline{S_н} = \frac{\sum_i^n S_{нi}}{n} = \frac{-1682.18}{802} = -2.10, \%, \tag{4}$$

where $\sum_i^n S_{нi}$ — sum of negative calculated values $S_н$ for the aggregate of $n = 802$ mine seams.

To exclude negative averaged values $S_н$, it is necessary to adjust the position of line 1 (Fig. 2*a*) taking into account coordinates $\overline{S_t^d - S_г} = -0.42\%$ and $\overline{S_н} = -2.10\%$. Adjusted line 1' should pass at least below point A' with coordinates $\overline{S_t^d - S_г} = -0.42\%$ and $\overline{S_н} = -2.10\%$. Directly proportional dependence $S_н$ on $(S_t^d – S_г)$ ($r = 0.91$) indicates the fact that the true position of corrected line 1' will be close to its parallelism with line 1. The use of values $S_н'$ in engineering calculations, determined by equation 1' (Fig. 2 *a*), guarantees, at least, the absence of their negative averaged values.

Empirical equation 1' was obtained based on the experimental data for 1827 mine seams. Of these, pre-cleaning was performed for coal samples from 1.352 mine seams. Ash yield from the bed samples of coals of the remaining 475 mine seams was slightly lower, therefore, cleaning was not applied to them.

Preliminary cleaning significantly affected the ash yield compared to raw samples (Fig. 3). It was necessary to find out how the accuracy of the calculated determination of sulfur according to equation (2) in the conditionally non-combustible part of the fuel depended on cleaning. To do this, we considered individual characteristic sets of mine seams. One aggregate of 1.352 variants included mine seams, the coals of which were subjected to preliminary cleaning (Fig. 2 *b*). Before cleaning, the ash yield from bed samples was 11.0–48.2%, and after — 3.7–16.7% (Fig. 3).

In the second aggregate of 475 mine seams, the option was considered for mine seams, the coals of which were not previously cleaned (Fig. 2 *c*), since they were conditionally classified as low-ash. The yield of ash from the untreated coals of this aggregate of mine seams ranged from 2.4% to 28.1% (Fig. 3).

The ash yield for both considered aggregates of mine seams in many cases significantly exceeded 10%. The yield ranges were 3.7–16.7% and 2.4–28.1%, respectively. This indicated the absence in some cases for both aggregates of a reasonable application of an alternative accelerated standard method for determining total sulfur S_t^d [9]. As a result, calculated values S_t^d were underestimated for most of the considered mine seams. As a consequence, the "wild" values calculated according to equation (2) were obtained for 558 and 244 mine seams of both (second and third) aggregates, respectively (Table 3).

Table 3

Summary results of determination of calculated values $S_н$ according to statistical processing of experimental data for different aggregates of mine seams

No.	Number of mine seams				Coordinates of points A', %		Empirical equations	Correlation		Range of ash yield change, %	Explanation
	total	$S_t^d - S_г \geq 0$	$S_t^d - S_г < 0$	$S_н < 0$	$\overline{S_t^d - S_г}$	$\overline{S_н}$		σ, %	r		
1	1827	512	1315	802	–0.42	2.1	$S_н^{*} = 11.97\left(S_t^d - S_г\right) + 3.34$	0.91	2.67	2.4–48.2	Whole aggregate of mine seams with clean and raw coals
							$S_н'^{**} = 11.97\left(S_t^d - S_г\right) + 7.12$	–	–		
2	1352	491	861	558	–0.42	2.69	$S_н = 13.15\left(S_t^d - S_г\right) + 3.11$	0.94	2.43	3.7–16.7	Cleaning was carried out
							$S_н' = 13.50\left(S_t^d - S_г\right) + 8.21$	–	–		
3	475	21	454	244	–0.41	0.71	$S_н = 3.50\left(S_t^d - S_г\right) + 1.24$	0.56	1.5	2.4–28.1	Mine seams with presumably low-ash coals
							$S_н' = 3.50\left(S_t^d - S_г\right) + 2.15$	–	–		
4	1181	452	729	487	–0.41	2.88	$S_н = 13.84\left(S_t^d - S_г\right) + 3.00$	0.95	2.28	3.7–10	Clean coals with an ash yield of less than 10%
							$S_н' = 13.84\left(S_t^d - S_г\right) + 8.55$	–	–		
5	171	39	132	71	–0.50	1.36	$S_н = 7.50\left(S_t^d - S_г\right) + 2.84$	0.92	1.47	10.1–16.7	Ash yield after cleaning of more than 10%
							$S_н' = 7.50\left(S_t^d - S_г\right) + 5.11$	–	–		
6	149	13	136	81	–0.26	1.13	$S_н = 8.27\left(S_t^d - S_г\right) + 1.57$	0.79	1.61	2.4–10	Ash yield from raw samples of less than 10%
							$S_н' = 8.27\left(S_t^d - S_г\right) + 3.28$	–	–		
7	326	8	318	163	–0.48	0.5	$S_н = 2.53\left(S_t^d - S_г\right) + 1.13$	0.56	1.04	10.1–28.1	Ash yield from bed raw samples of more than 10%
							$S_н' = 2.53\left(S_t^d - S_г\right) + 1.71$	–	–		

Notes. In the first column, No. — number of the bed aggregate; * — dependencies according to calculated values $S_н$ according to equation (2) and experimental data of criterion ($S_t^d - S_г$); ** — adjusted dependencies $S_н'$; σ — standard deviation.

Average negative values $\overline{S_t^d - S_Г}$ of the second and third aggregates were calculated using equation (3). They were –0.42% and –0.41%, respectively. This indicated that the average errors of underestimation of the calculated total sulfur content by an alternative accelerated method for both aggregates were almost identical when calculating $S_н$ according to equation (2). Due to these circumstances, the accelerated method for determining total sulfur and possible underestimations of its true values did not relate to the differences between the second and third aggregates of mine seams.

Logic of equation (2) shows that different calculated values $S_н$ of the second and third aggregates can be obtained only taking into account the different ash yield from clean and bed samples of coals. For the convenience of analyzing the potential impact of ash yield from clean and raw coal samples, equation (2) was presented in the form of terms.

For clean samples (aggregate 2):

$$S_н^o = \frac{100}{A_с^o} \cdot S_t^d - \frac{100}{A_с^o} \cdot S_г^o + S_г^o, \%. \quad (5)$$

For raw bed samples (aggregate 3):

$$S_н^п = \frac{100}{A_п^с} \cdot S_t^d - \frac{100}{A_п^с} \cdot S_г^п + S_г^п, \%. \quad (6)$$

Comparing the terms of equations (5) and (6), we determined the direction of their influence on the calculated values $S_н$. The first term $\left(100/A_с^o\right) \cdot S_t^d$ of equation (5) was obviously larger than the corresponding term $\left(100/A_п^с\right) \cdot S_t^d$ of equation (6). This was determined by the undeniable excess of ash yield from bed samples compared with ash yield from raw samples ($A_п^с > A_о^с$). The inequality suggested that the values of total sulfur determined by the accelerated alternative method would be more underestimated for bed samples. For this reason, S_t^d values of equation (5), were at least not less than in (6).

The second terms with a minus sign of equations (5) and (6) $\left(\left(100/A_о^с\right) \cdot S_г^о \text{ and } \left(100/A_п^с\right) \cdot S_г^п\right)$ characterize an increase in the proportion of sulfur content in the combustible part of fuel after coal cleaning compared with the content in bed samples before cleaning. Under the influence of cleaning processes, the ash yield is reduced several times ($A_о^c < A_п^c$, Fig. 3). As a result, the proportion of the combustible part of fuel of clean coals increases $\left(100/A_с^o\right)$ compared with its share in bed samples $\left(100/A_п^с\right)$. This, as well as the stability of sulfur compounds, cause an increase in the relative (percentage) content of sulfur $S_г^о$ in the combustible part of fuel after cleaning. These values always exceed the percentage of sulfur in the bed raw samples, i.e. the inequality $S_г > S_г^п$ is observed. Negative terms of equations (5) and (6) $\left(\left(100/A_о^с\right) \cdot S_г^о \text{ and } \left(100/A_п^с\right) \cdot S_г^п\right)$ in any ratio, make up only a certain part of the sulfur content in the combustible mass. As a result, the total values of the second and third terms of equations (5) and (6) will be positive.

Let us consider the inequality of terms in (5) and (6): $S_г^о > S_г^п$ and $\left(100/A_о^с\right) \cdot S_t^d$ and $\left(100/A_п^с\right) \cdot S_t^d$. This suggests that cleaning leads to a percentage increase in the sulfur content in the non-combustible part of fuel ($S_н$) and its close, almost functional dependence ($r = 0.94$) on criterion $S_t^d – S_г$ (Fig. 2 *b*). Strong correlation $S_н$ and $S_t^d – S_г$ for clean coal of the second aggregate is due to a significant forced reduction in the content of conditionally non-combustible (mineral) impurities. This is evidenced by a reduction in the range of ash yield from bed raw samples from 11.0–48.2% to 3.7–16.7% after cleaning. For the considered aggregate of mine seams, in most cases (about 90%), the ash yield was less than 10%, which indicates an insignificant proportion of mineral impurities in coals after cleaning. Cleaning is largely explained by the approximation of mass fraction of combustible part of fuel to the organic mass. Correlation dependence 1 (Fig. 2 *b*) refers to an insignificant proportion (less than 10%) of mineral (conditionally nonflammable) impurities preserved after cleaning. The relatively high regression coefficient of equation 1 (13.15) indicates a disparity in the indicators:

- reduction of ash yield after coal cleaning;
- sulfur content in the preserved part of conditionally nonflammable (mineral) impurities [10].

As it can be seen from equation (5), high correlation dependence of $S_н$ on indicator $S_t^d – S_г$ for mine seams of the second aggregate was ensured by a relative consistency of ash yield $A_о^с$ for most mine seams in the range of 3.7–10.0%. This effectively eliminates the significant influence of unpredictable fluctuations in the proportion of conditionally non-combustible (mineral) impurities in wider ranges. Values $S_н^о$ for the second aggregate of mine seams, calculated according to equation (5), are determined by experimental data from S_t^d and $S_г^о$. This was confirmed by the results of statistical processing (Fig. 2 *b*). Influence of fluctuations in ash yield $A_о^с$ after coal cleaning was minimized, and calculated values $S_н^о$ were more dependent on two indicators — S_t^d and $S_г^о$.

Such a stable relationship between $S_н$ and ($S_t^d – S_г$) is not observed in the absence of cleaning processes (Fig. 2 *c*). This resulted in a lower correlation coefficient ($r = 0.56$) and a decrease in regression coefficients of empirical equations 1 from 13.15 (Fig. 2 *b*) to 3.50 (Fig. 2 *c*).

When calculating $S_н^п$ according to equation (6) for the third aggregate of mine seams, the range of unpredictable fluctuations in values $A_п^с$ of ash yield expanded to 2.4%–28.1%. This is significantly more than with a stable ash yield from clean coal samples of the second aggregate. We note the increased influence of an additional factor associated with significant fluctuations in the ash yield from bed samples in wider intervals. This led to a weakening of correlation dependence 1 to value $r = 0.56$ (Fig. 2 *c*).

The vast majority of coals of the third aggregate of coal seams according to criterion $S_t^d – S_г < 0$ should be classified as low-ash. Out of 475 coal seams of the entire aggregate under consideration, 454 (i.e., 95.6%) criterion values were negative. According to negative values of $S_t^d – S_г$ criterion, the main percentage of sulfur had to be conditionally attributed to the combustible mass of the coals of these mine seams. Determination of $S_н$ according to equation (6) for 244 mine seams gave "wild" values. For the remaining 231 mine seams, calculated values $S_н$ were positive (210 variants) or equal to zero (21 variants). The study revealed an approximately equal number of near-zero calculated values $S_н$. This confirms the presence of systematic errors of experimentally determined parameters included in (6). The proof is also the approximate equality in absolute magnitude of the average negative (–0.71%) and average positive (+0.80%) calculated values $S_н$. This makes it possible to reasonably make quantitative adjustments to the calculations in order to exclude "wild" results.

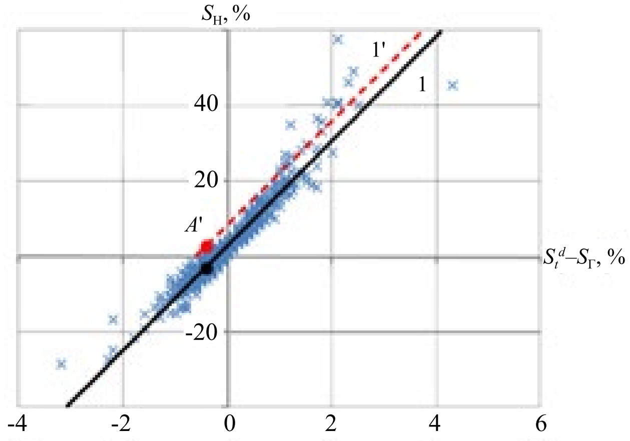
Comparison of calculated values of sulfur content in the non-combustible part of fuel for the second and third aggregates demonstrates a significant difference in the initial parameters of the indicators that were used to determine $S_н$ and $S_н^п$ according to equations (5) and (6), respectively. The main difference was due to the preliminary cleaning of coals of the second aggregate. Cleaning changed disproportionately the ratio of ash yield and sulfur content in the combustible part of fuel. The initial ratios were formed in natural conditions and were associated with the individual geological history of the formation of each mine seam, namely:

- consistent accumulation of precipitation;
- immersion and transformation of the initial substance at the stages of peat formation and diagenesis preceding metamorphism.

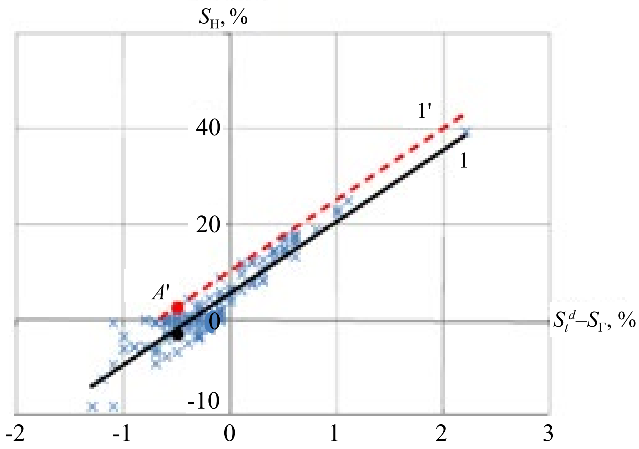
In coals of the third aggregate of mine seams, the initial established natural ratios between the ash yield from bed samples, the content of total sulfur and some of its part in the combustible mass of fuel have been preserved.

Cleaning of coals of the second aggregate of mine seams and the reduction of ash yield (in most cases below 10%) predetermined the artificial proximity of the entire aggregate in terms of the content of mineral (conditionally non-combustible) impurities. As a result of actual elimination of the influence of ash yield from clean samples for most of the mine seams according to equation (5), calculated values $S_н^п$ were obtained, which were largely directly related to criterion ($S_t^d – S_г$). This predetermined their high correlation interdependence (Fig. 2 *b*).

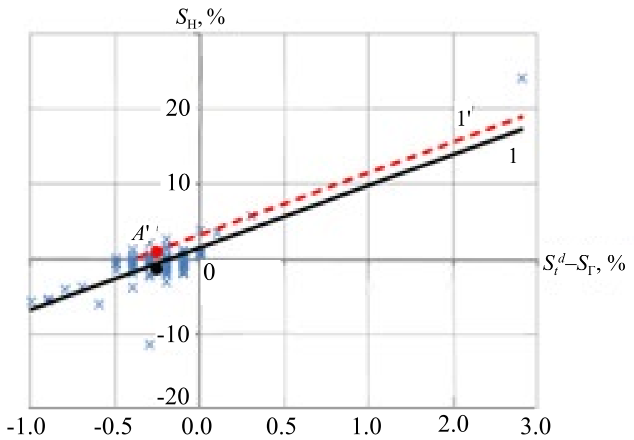
The main difference between the coals of the second and third mine seam aggregates is the values of ash yield from clean and bed samples of coals. For a detailed understanding of the effect of ash yield from clean and raw coal samples on calculated values $S_н$ four aggregates of mine seams of varying degrees of cleaning were additionally considered (Fig. 4).



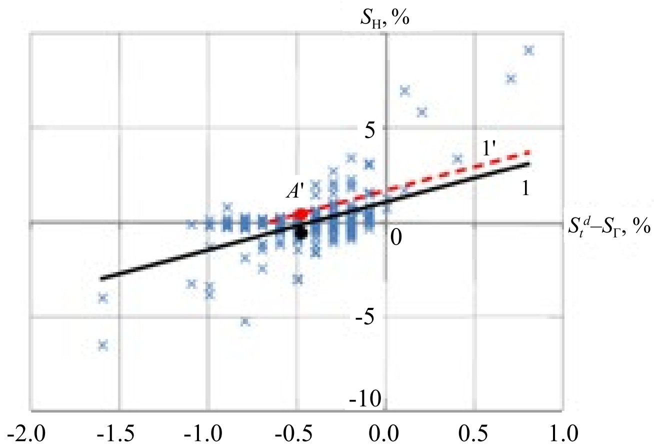
a)



b)



c)



d)

Fig. 4. Dependence of calculated values of sulfur content ($S_Н$) in conditionally non-combustible part of fuel on criterion ($S_t^d – S_Г$) [2, 3]

According to the ash yield from clean samples, mine seams were divided into two groups: less than 10% and more than 10% (Fig. 3). The corresponding aggregates were considered — fourth (Fig. 4 *a*) and fifth (Fig. 4 *b*).

The majority of mine seams (1181% or 87.4%), according to the ash yield of less than 10% of clean samples, were attributed to the fourth aggregate. In the fifth aggregate of mine seams with an ash yield of more than 10%, calculated values $S_Н$ for 171 mine seams were considered, which amounted to 12.6% of the total number of mine seams (1352), the coals of which were cleaned.

Close directly proportional correlation dependencies of calculated values $S_Н$ on $S_t^d – S_Г$ criterion were obtained for both aggregates of mine seams after processing. The correlation coefficients are 0.95 and 0.92, respectively. The regression coefficients of these dependencies (Fig. 4 *a, b*) were 13.84 and 7.50, respectively. The almost twofold difference between the empirical regression coefficients indicates significant differences between the coals of the fourth and fifth aggregates. It can be explained by:

– quantitative and qualitative composition of mineral impurities in bed samples;

– different processing efficiency.

The influence of these factors requires a separate detailed study [11].

Similar aggregates of mine seams were formed by the ash yield from bed (raw) samples of less than and more than 10%. For the sixth aggregate of 149 mine seams, the dependence of $S_н$ on $S_t^d – S_г$ criterion was established when ash yield from raw (bed) samples was less than 10% (Fig. 4 *c*). In the seventh aggregate of 326 mine seams, similar dependencies of calculated values of $S_н$ on ($S_t^d – S_г$) criterion at an ash yield of more than 10% were considered (Fig. 4 *d*).

The obtained directly proportional empirical dependences for the sixth and seventh aggregates of mine seams with different ash yields from raw (bed) samples differ significantly. The differences are due to both the closeness of correlations and the regression coefficients of empirical equations.

The ash yield of less than 10% from raw (bed) samples indicates a low ash content of coals of the sixth aggregate of mine seams. In this case, the correlation is quite high (r = 0.79). For the more ashy coals of the seventh aggregate of mine seams, the correlation is much weaker (r = 0.56).

The regression coefficients of the empirical equations of the sixth and seventh aggregates of mine seams differ by more than three times. They are respectively equal to 8.27 (Fig. 4 *c*) and 2.53 (Fig. 4 *d*).

The revealed significant differences between the empirical dependencies of the sixth and seventh aggregates of mine seams in terms of the closeness of correlations and regression coefficients indicate different features of the conditions for accumulation of sulfur in the mineral (conditionally non-combustible) part of fuel for coals with different ash yield levels.

Low ash yield (less than 10%) indicates an insignificant content of mineral impurities. A fairly high correlation coefficient (r = 0.79) is recorded between the calculated sulfur content in the conditionally non-combustible part and criterion ($S_t^d – S_г$) (Fig. 4 *c*). This means that sulfur was formed simultaneously in mineral impurities and in organic matter at different stages of coal formation. The absence of such a close correlation for high-ash coals indicates different conditions for the formation of sulfur content in mineral impurities and in the organic mass of the seventh aggregate of mine seams (Fig. 4 *d*).

Discussion and Conclusion. According to empirical equations (Fig. 4), the aggregates of mine seams were considered in pairs, which, other things being equal, differed in two factors (Table 3):

− whether or not the coals were cleaned;

− ash yield from cleaned or raw coals was less than or more than 10%.

Processing significantly changes the relationship between:

− organic matter and mineral impurities;

− combustible and conditionally non-combustible parts of the fuel.

For this reason, the first, second, fourth and fifth aggregates of mine seams and the corresponding empirical equations do not reflect the true natural sulfur content in non-combustible parts of fossil coals. They should not be used to predict the hazardous properties of mine seams during mining operations.

Sulfur content in conditionally non-combustible mass of raw samples for the third and seventh aggregates is underestimated due to the presence of a high ash yield and the use of an alternative standard method for determining the total sulfur content. The scope of application of the empirical equations corresponding to these aggregates is limited to coal mines with low-ash coals and an insignificant content of calcium compounds in mineral impurities.

The most reliable results of determining the calculated sulfur content in a conditionally non-combustible mass were obtained for the sixth aggregate of mine seams. Practical application of the corresponding empirical equation is recommended when predicting the hazardous properties of mine seams with an ash yield of less than 10%.

It is possible to improve the proposed method for determining sulfur in mineral impurities and expand its scope of application. To do this, it is necessary to establish the following ratios:

− sulfur content in organic and combustible mass of coals;

− mineral impurities and ash yield (with the determination of its chemical composition).

The results of such studies can be used to improve standards for safe mining operations, taking into account the sulfur content in both organic matter and mineral impurities of fossil coals.

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NV Pronskaya, EN Filatieva: formulation of the basic concept, goals and objectives of the study.
MV Filatiev: academic advising, analysis of the research results, formulation of the conclusions.
NV Shashlo: calculations, preparation of the text and design of the article.

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