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GEOCHEMICAL PECULIARITIES OF GERMANIUM, ARSENIC, MERCURY, BERYLLIUM, FLUORINE AND TOTAL SULFUR IN THE C8H COAL SEAM OF THE DNIPROVSKA MINE FIELD

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Abstract. In the article, the authors establish and analyze the relationship between the contents of germanium, toxic elements and the total sulfur content of the coal seam of the Dniprovska Mine field. In the process of the research, in order to achieve the purpose set in the work, correlation and regression analysis was carried out using methods that are implemented in one of the most popular professional mining and geological information systems for 3D modeling of deposits, statistical processing of mining and geological data and construction of actual mine workings and planning of mining operations – Micromine, and their analysis in geological concepts was performed. It is proved that the distribution of germanium, toxic elements and total sulfur content in the coal seam $c_8^н$ of the Dniprovska Mine field differ from the Gauss-Laplace and lognormal distributions. It is established that analyzes of graphs of polynomial pair regression models of the relationship between the normalized concentrations of germanium and the contents of toxic elements make it possible to identify different areas of their concentrations, which differ significantly in their nature. It is substantiated that the minimum contents of arsenic, germanium and total sulfur in the coal seam $c_8^н$ of the Dniprovska Mine were jointly accumulated at the syngenetic stage of its formation. A decrease in the concentrations of germanium with an increase in the content of fluorine, mercury, arsenic, and total sulfur is associated with epigenetic processes, which in this particular case lead to the outcrop of germanium. The synchronous increase in the contents of germanium and beryllium in the area of their low and abnormally low concentrations is due to the compatible accumulation of these elements at the syngenetic stage of formation of the coal seam, and their increase in the area of maximum contents is caused by the manifestation of the empirical regularity of the "Zilbermints law". It was established that there is a very low correlation between the concentrations of germanium and toxic elements and total sulfur, therefore, the extraction of germanium from the coal seam will not be accompanied by their significant accumulation during technological processes. It is proven that for a more realistic assessment of the central tendency of the content of germanium, toxic elements and total sulfur, it is necessary to use the median values instead of the median values. The influence of syngenetic and epigenetic processes on the nature of the relationship between germanium concentrations, toxic elements and total sulfur content in the coal seam $c_8^н$ of the Dniprovska Mine was revealed.

Key words: germanium, toxic elements, total sulfur content, coal seam, cluster analysis, normal and lognormal distribution law.

1. Introduction

The relevance of researching the content of germanium in coal seams is due to the possibility of its industrial extraction as a valuable accompanying component for further commercial use. [1–3]. According to our estimate, the average monthly prices per kilogram of germanium dioxide on the world market from 1992 to 2011 ranged from 380 US dollars to 1460 US dollars. The world production of refined germanium is 130 tons, 2/3 of which is accounted for by China. The US industry annually (from 2019 to 2022) uses (the authors' estimate) about 30 tons of germanium. Today, the most important global end users of this element are the production of fiber optic systems (30%), infrared optics (25%), components for polymerization catalysis (25%), electronics and photovoltaic cells for solar energy (15%), phosphorus, metallurgical and pharmaceutical industry (total 5%). A significant amount of germanium is contained in fly ash, which is formed during the combustion of some grades of thermal coal. This element accumulates in hydrothermal and sedimentary processes, where the possibility of its separation from Si is realized. The process of natural concentration leads to its high content in some coal seams, first discovered by Victor Moritz Goldschmidt [4]. The highest concentration of germanium ever recorded in coal deposits was observed in coal ash from the Hartley deposit with a germanium content of 1.6%. Currently, coal is the main estimated source of germanium in Ukraine, China, Uzbekistan, as well as in Russia. Germanium coal deposits are developed in England, Canada, the USA, Ukraine, Russia, etc.

The research carried out is particularly relevant to the decision of the National Security and Defense Council of Ukraine dated July 16, 2021 "About stimulating the search, extraction and enrichment of minerals which are strategically important for sustainable development and defense capability of the state" and Decree of the President of Ukraine No. 306/2021, which introduces this decision in effect. In these documents, germanium ores are included in the list of strategic importance for the sustainable development and defense capability of the state.

According to the regulatory documents of the State Commission of Mineral Reserves of Ukraine , toxic and potentially toxic elements in coal include arsenic, beryllium, mercury, fluorine (toxic elements) and cobalt, manganese, nickel, lead, chromium, vanadium (potentially toxic elements). According to the "Instructions for the study of toxic components during the exploration of coal and shale deposits", the assessment of toxic elements in coal is carried out at all stages of geological exploration works, the data obtained according to the "Instructions on the content, design and procedure of submission to the State Commission of Mineral Reserves of Ukraine of Ukraine of materials on the geological and economic assessment of coal reserves and oil shale" are sent to this Commission.

Analysis of previous studies. Previously, the peculiarities of the distribution of "small elements" that belong to the group of "toxic and potentially toxic elements" in the coal seams of some mines and geological and industrial areas of Donbas were investigated [5–27]. The methods of natural typification of coal deposits by the content of accompanying elements and oil deposits of the Dnipro-Donetsk depression by the content of metals are substantiated [28–33]. In works [34–38], the main regularities of germanium distribution over the area and in the section of some coal seams of the Pavlohrad - Petropavlivka geological and industrial area of Donbas were considered.

The purpose of the research. This article is devoted to the establishment and analysis of the relationship between the concentrations of germanium and toxic elements and the total sulfur content in the coal seam of the Dniprovska Mine. It should be noted that such studies have not been carried out before.

2. Methods

The factual basis of the work was the results of 370 analyzes of germanium, beryllium, fluorine, mercury and arsenic and total sulfur performed in the central certified laboratories of production geological exploration organizations of Ukraine since 1981 from the material of reservoir samples obtained by production and scientific research enterprises and organizations and measurements of seam thickness. In a number of cases, they were added by analyzes of reservoir samples taken by the furrow method from duplicate cores and mine workings with the participation of the authors and employees of the geological service of the coal mining enterprise and production geological exploration organizations in the period from 1981 to 2017. Before taking samples from the mine workings, measurements of coal packs and rock strata were carried out, based on the results of which, the most representative areas of sampling were determined. The volume of the control test was 7% of the total volume of samples. Germanium content was determined by quantitative emission spectral analysis. Seven percent of duplicate samples were sent to internal laboratory control. Ten percent of duplicate samples were subjected to external laboratory control. The quality of the results of the analyses (correctness and reproducibility) was evaluated as the significance of the mean systematic error, which was tested using the Student's criterion, and the significance of the mean random error, which was tested using the Fisher criterion. Since the indicated errors at the significance level of 0.95 are not significant, the quality of the analyses is recognized as satisfactory.

At the initial stage of primary geochemical information processing, statistical programs were used to calculate the values of the main descriptive statistical indicators (sample arithmetic average, its standard error, median, kurtosis, mode, standard deviation, sample variance, minimum and maximum content values, coefficient of variation, sample asymmetry), the construction of frequency histograms of Ge content and reservoir thickness was carried out, and the features of the distribution of these parameters were established.

When constructing frequency cumulative histograms, the number of intervals was calculated according to Herbert Sturges' formula:

$$n = 1 + \left[log_2 N \right],$$

where n – number of intervals, $\log_2$ is the logarithm based on 2, N – number of analyses, [x] – denotes the whole part of the number x.

In the process of the research, in order to achieve the goal set in the work, correlation and regression analysis was carried out using methods that are implemented in one of the most popular professional mining and geological information systems for 3D modeling of deposits, statistical processing of mining and geological data and construction of actual mine workings and planning of mining operations - Micromine (license MM5123); and their analysis in geological concepts was performed.

3. Results and discussion

According to the data of 370 analyses, concentration of germanium in the coal of the $c_8^н$ seam in the field of the Dniprovska Mine varies from 0.14 g/t to 23.63 g/t, with an average value of 8.34 ± 0.26 g/t, a median of 6 .79 g/t, mode 7.69 g/t, standard deviation 5.04, sample variance 25.38, sample kurtosis 0.23, sample asymmetry 0.97.

The content of beryllium at the sampling sites varies from 2.05 g/t to 5.83 g/t, the average value is 4.43 ± 0.04 g/t, the median is 4.44 g/t, the standard deviation is 0.73, variance 0.54, kurtosis -0.26, asymmetry - 0.30.

The concentration of fluorine varies in the range from 63.15 g/t to 170.88 g/t, with an average value of 90.98 ± 0.92 g/t, median 88.45 g/t, standard deviation 16.49, variance 272 .21, kurtosis 2.52, asymmetry 1.17.

The content of mercury in the coal of the $c_8^н$ seam varies from 0.34 g/t to 0.03 g/t, the average value is 0.14 ± 0.003 g/t, the median is 0.14 g/t, the standard deviation is 0.06, the variance is 0.004, kurtosis -0.77, asymmetry 0.15.

The concentration of arsenic within the mine plastic varies from 4.32 g/t to 41.14 g/t, the average value is 12.49 ± 0.25 g/t, the median is 11.74 g/t, the standard deviation is 4.38, the variance 19.16, kurtosis 11.98, asymmetry 2.72.

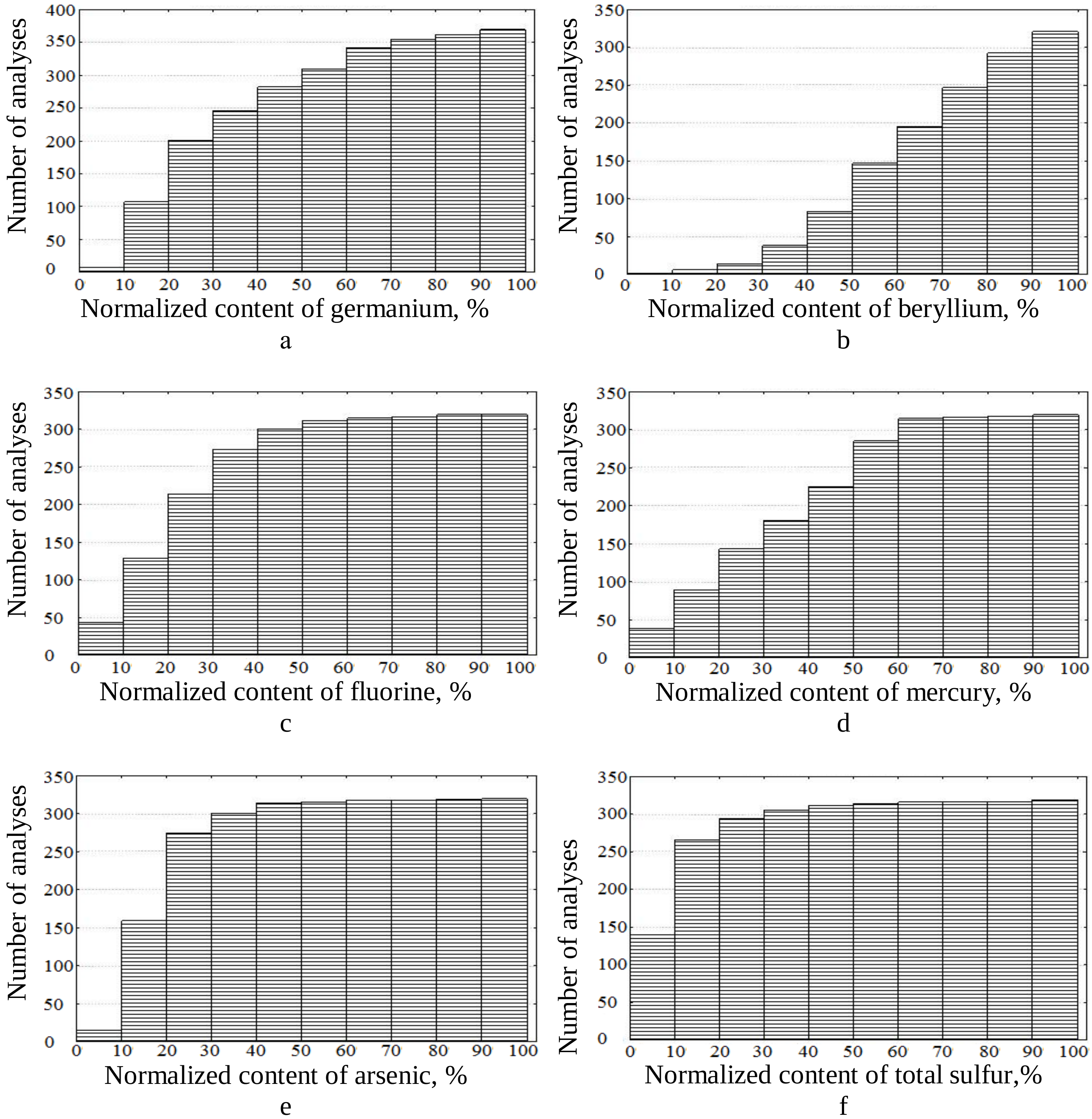
The content of total sulfur in the selected samples varies from 0.6% to 9.3%, the average value is 1.83 ± 0.06%, median 1.6%, standard deviation 1.10, variance 1.21, kurtosis 14.15, asymmetry 3.14.

In order to visualize the density distribution of concentrations of germanium, toxic elements and total sulfur, which were installed at the sampling sites, there were cumulative histograms (Fig. 1).

Visual analysis of the given histograms shows: 1) non-compliance of all samples with the normal or lognormal law of distribution; 2) in all cases, the polymodality of the distribution of indicators is fixed; 3) only in the case of the distribution of Be concentrations, a shift of the kernel of the distribution density to the right is observed, on all other histograms of the distribution, the kernel of the distribution density is shifted to the left. In addition, analytical calculations of the correspondence of the empirical distributions of the studied parameters to the Gaussian distribution were performed. For this purpose, the Kolmogorov-Smirnov, Shapiro-Wilk, Lilliefors and Pearson chi-square agreement tests were calculated. In all cases, the results of the calculations confirmed the non-compliance of the studied samples with the normal or lognormal distribution law. Thus, for a more realistic assessment of the central tendency of the content of Ge and toxic elements and total sulfur, it is necessary to use the median values instead of the median values. All these conclusions are well visualized with the help of the "box diagram with whiskers" shown in Fig. 2.

According to the results of analyzes on the Chedok scale, taking into account the data of correlation (linear Pearson correlation coefficients 0.1 and non-parametric: Spearman 0.05, Kendel 0.03 and gamma 0.03) and regression analyzes the relationship between the content of germanium and the concentration of beryllium in a coal seam is straight and very weak. The graph of the result of the regression analysis of modeling the polynomial relationship between the concentration of germanium and the content of beryllium is shown in Fig. 3. The regression equation for this model is: $Ge = 0,0068 + 1,9284 \cdot Be – 3,5156 \cdot Be^2 + 2,0249 \cdot Be^3$.

An analysis of the graph of the regression model makes it possible to identify three regions of beryllium concentrations with different nature of the relationship of this element with the contents of germanium. The first area corresponding to the normalized values of beryllium concentrations in the range from 0 to 0.4 is characterized by a significant increase in the content of germanium. The second area of beryllium concentrations, which is in the range of normalized beryllium concentrations from 0.4 to 0.8, is characterized by the absence of a relationship between this element and the germanium content. The third area of beryllium concentrations, corresponding to its anomalously high contents, is again characterized by a slight increase in the concentration of germanium. This suggests that at least the mechanisms of accumulation of these elements in the coal seam $c_8^{н}$ of the Dniprovska Mine in the areas corresponding to abnormally low, low and abnormally high beryllium contents were identical or close.



a – Ge, b – Be, c – F, d – Hg, e – As, f – total sulfur

Figure 1 – Cumulative histograms of normalized content values

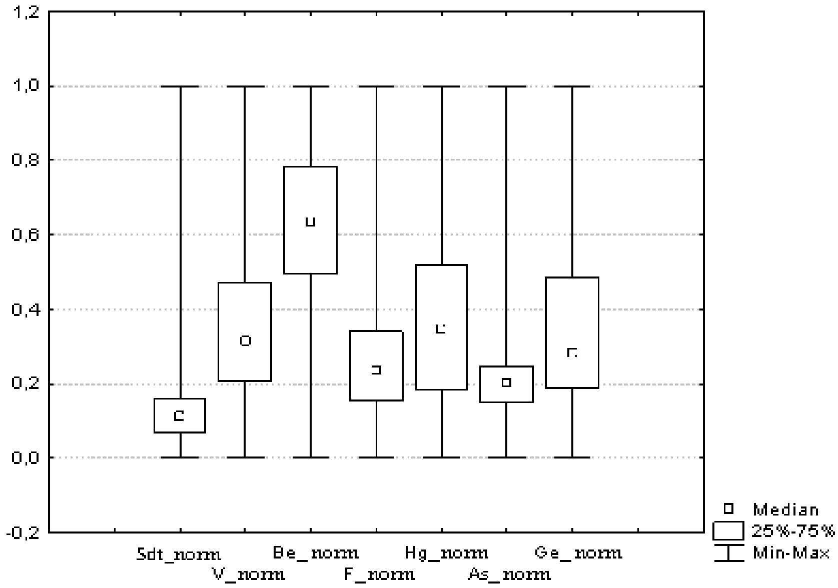


Figure 2 – "Box diagram with whiskers" of the main features of the distribution of normalized values of the studied indicators

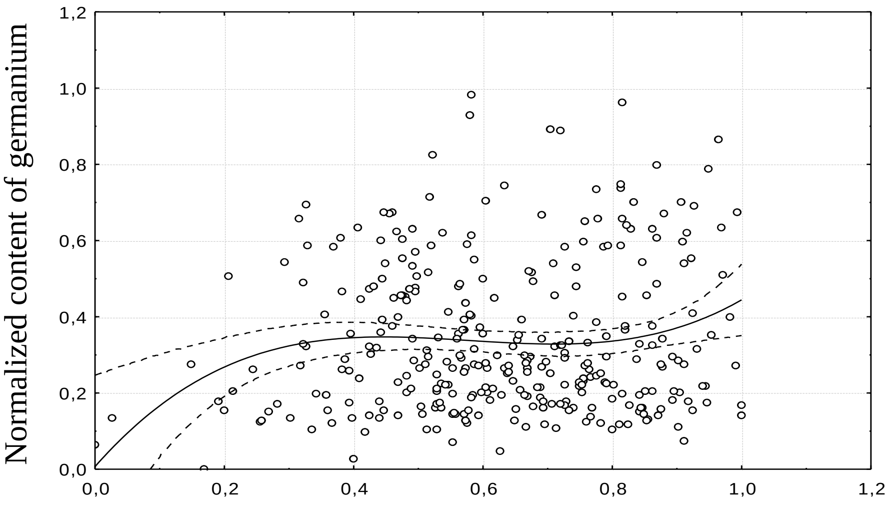


Figure 3 – The result of the regression analysis of modeling the polynomial relationship between the normalized content of germanium and the normalized content of beryllium

According to the Chedok scale, the relationship between the concentrations of germanium and fluorine in the considered coal seam, taking into account the correlation data (linear Pearson correlation coefficients -0.09 and non-parametric ones: Spearman -0.07, Kendel -0.04 and gamma -0.04) and regression analysis is inverse and very weak. The graph of the result of the regression analysis of modeling the polynomial relationship between the concentration of germanium and the content of fluorine is shown in fig. 4. The regression equation for this model is: $Ge = 0{,}368 - 0{,}2416 \cdot F + 0{,}7627 \cdot F^2 - 0{,}8651 \cdot F^3$.

Analysis of the graph of the regression model makes it possible to identify two areas of fluorine concentrations with different nature of the relationship of this element with the contents of germanium. The first area, corresponding to the normalized values of fluorine concentrations in the range from 0 to 0.6, is characterized by the absence of a relationship between this element and the germanium content. The second area of fluorine concentrations, corresponding to its high and anomalously high contents, is characterized by a significant decrease in the concentration of germanium. Thus, there is every reason to believe that the accumulation of fluorine in high and abnormally high concentrations was accompanied by the removal of germanium from the coal seam $c_8^н$ of the Dniprovska Mine.

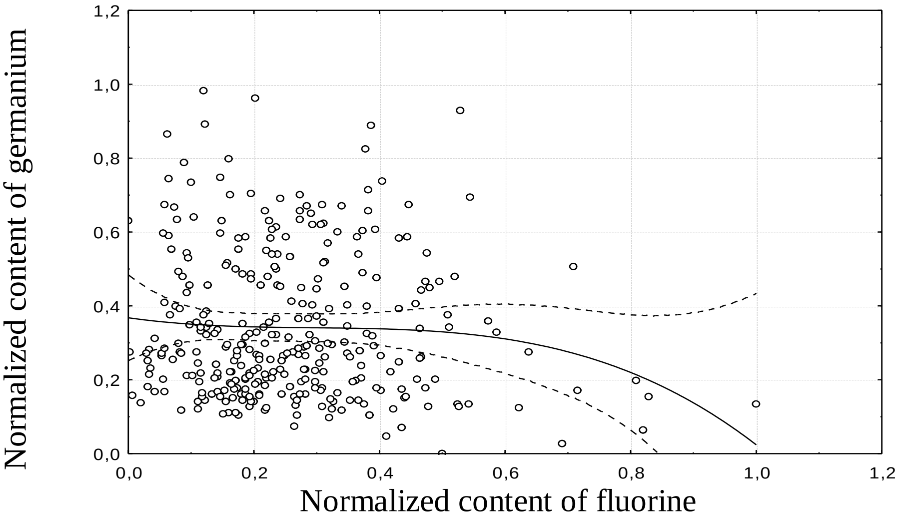


Figure 4 – The result of the regression analysis of modeling the polynomial relationship between the normalized germanium content and the normalized fluorine content

According to the Chedok scale based on the results of correlation (linear Pearson correlation coefficient -0.03, and non-parametric: Spearman -0.04, Kendel -0.03 and gamma -0.03) and regression analyzes the relationship between germanium concentration and mercury content is inverse and very weak. The graph of the result of the regression analysis of modeling the polynomial relationship between the content of germanium and the concentration of mercury is shown in fig. 5. Regression equation for the polynomial model is: $Ge = 0{,}3517 - 0{,}064 \cdot Hg + 0{,}2865 \cdot Hg^2 - 0{,}3575 \cdot Hg^3$.

Analysis of the graph of the regression model makes it possible to identify two areas of mercury concentrations with different nature of the relationship of this element with the contents of germanium. In this case, there is almost complete agreement, both between the location of these regions and in the nature of the relationship between the normalized values of the concentrations of germanium and mercury within them with the above features of the nature of the relationship between the contents of germanium and fluorine. The only difference is the weaker inverse relationship between these elements in the area corresponding to elevated and abnormally high concentrations of mercury. Summarizing the results of this analysis of the regression model and comparing it with the above analysis of the regression model of the relationship between the concentrations of germanium and fluorine, it is reasonable to note a common character for them. Therefore, it can be assumed that in this case, the accumulation of mercury in high and anomalously high concentrations was accompanied by the removal of germanium from the coal seam $c_8^н$ of the Dniprovska Mine.

According to the results of analyzes on the Chedok scale, taking into account the correlation data (linear Pearson correlation coefficient -0.04, and non-parametric: Spearman -0.01, Kendel -0.01 and gamma -0.01) and regression analyzes the relationship between the content of germanium and the concentration of arsenic in the coal seam is inverse and very weak. The graph of the result of the regression analysis of modeling the polynomial relationship between the concentration of germanium and the content of arsenic is shown in fig. 6. The regression equation for this model is: $Ge = 0,3094 + 0,296 \cdot As - 0,4691 \cdot As^2 - 0,0297 \cdot As^3$.

Analysis of the graph of the regression model makes it possible, as in the previous case, to identify two areas of arsenic concentrations with a different nature of the relationship of this element with the contents of germanium. The first area corresponding to the normalized values of arsenic concentrations in the range from 0 to 0.25 is characterized by a slight increase in the content of both elements. The second area of arsenic concentrations, on the contrary, is characterized by a slight decrease in the content of germanium. The performed analysis suggests that at least the mechanisms of accumulation of these elements in the coal seam $c_8^н$ of the Dniprovska Mine in areas corresponding to abnormally low arsenic contents were identical or similar. This gives grounds to identify this range of germanium and arsenic concentrations as due to syngenetic processes and possibly related to the content of these elements in plant remains, waters feeding the paleopeat accumulation basin, and allothigenic mineral matter brought into it by permanent and temporary water flows. At the same time, a further increase in the content of arsenic in the coal seam $c_8^н$ of the Dniprovska Mine, apparently due to epigenetic processes, is accompanied by a decrease in the concentration of germanium.

According to the Chedok scale, the relationship between the concentrations of germanium and total sulfur in the $c_8^н$ coal seam, taking into account the data of correlation (linear Pearson correlation coefficients 0.01 and non-parametric: Spearman 0.09, Kendel 0.06 and gamma 0.06) and regression analyzes is straight and very weak. In fig. 7 shows the graph of the result of the regression analysis of the modeling of the polynomial cubic relationship between the concentration of germanium and the content of total sulfur. Regression equation for this model is: $Ge = 0,2946 + 0,5893 \cdot S_{total.} - 1,1613 \cdot S_{total.}^2 - 0,3987 \cdot S_{total.}^3$.

An analysis of the graph of this regression model makes it possible to identify two areas of total sulfur concentrations with a different nature of the relationship between this indicator and the germanium content. In this case, there is an almost complete coincidence, both between the location of these areas, and in the nature of the relationship between the normalized values of the concentrations of germanium and total sulfur within them with the above features of the nature of the relationship between the contents of germanium and arsenic. The only difference is a stronger direct relationship between these elements in the area corresponding to low and abnormally low total sulfur contents. It is logical to assume that the reason for such features in changing the nature of the relationship between the indicators under consideration are the most probable mechanisms noted by us earlier that determine the nature of the relationship between germanium and arsenic. It should be noted that high and abnormally high contents of fluorine, mercury, arsenic, and total sulfur were previously found to be associated with zones of increased permeability that correspond to areas of increased fracturing, small- and low-amplitude faults [29].

In order to interpret the obtained results in geological terms, it is necessary to briefly analyze the possible forms of germanium and toxic elements in the coal seam. As it is known, the main empirical regularity due to the high organophilicity of germanium is the sharp dominance of organically bound germanium in all coals - the germanium organic form. Indications for this can be found in hundreds of works on the geochemistry of coal - practically in any work where germanium was determined, starting with Goldschmidt's first studies in 1930 and ending with ecologically oriented research of the 21st century. However, by recognizing the predominance of the germanium organic fraction, a more difficult problem is hidden - the identification of the specific chemical form of this fraction, as well as the calculation of the "balance of forms" of germanium in coal, that is, the ratio between its separate organic and mineral forms of occurrence.

A review of the results of identifying the forms of germanium in coal from various deposits by various methods of coal petrography and coal chemistry, which included correlation analysis [39, 40], microscopic studies [41], fractionation by density [40], electrodialysis of coal [42, 43], soft and hard chemical fractionation [44, 45], successive selective extraction [46, 47] showed that germanium can be contained in coal in the following forms:

1) physically sorbed on organic and mineral matter;

2) associated with humic and fulvic acids in the form of simple humates and fulvates;

3) associated with humic acids in the form of complex humates (chelates);

4) in the form of organogermanium compounds;

5) in rock-forming minerals (silica germanates and sulfides).

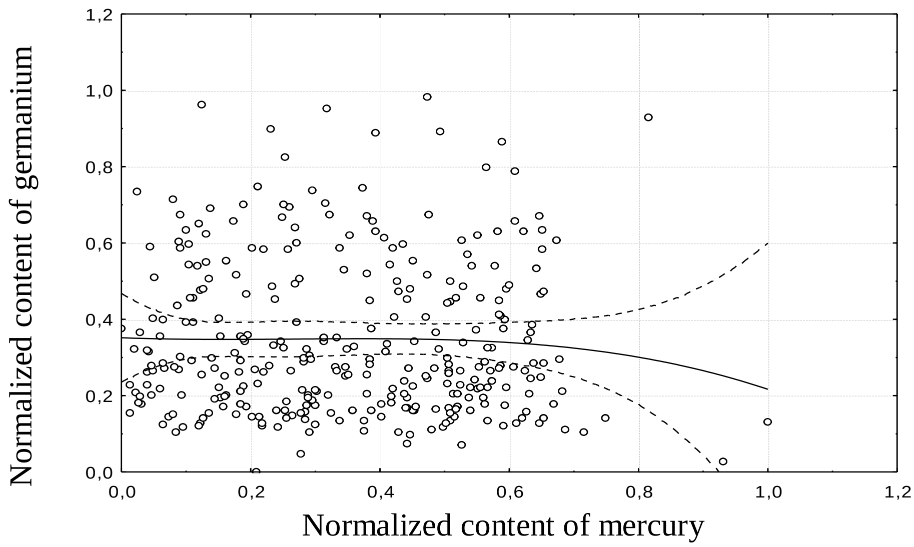


Figure 5 – The result of the regression analysis of the modeling of the polynomial relationship of the normalized content of germanium with the normalized content of mercury

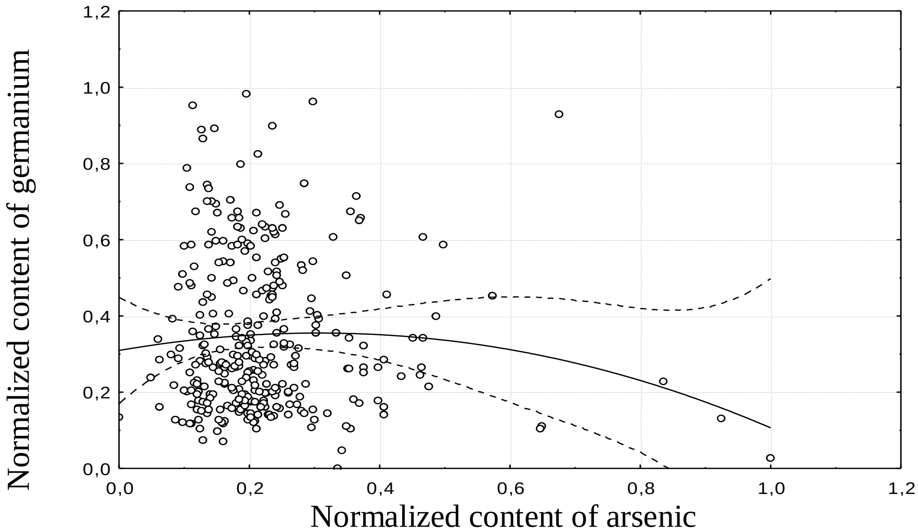


Figure 6 – The result of the regression analysis modeling the linear relationship between the normalized germanium content and the normalized arsenic content

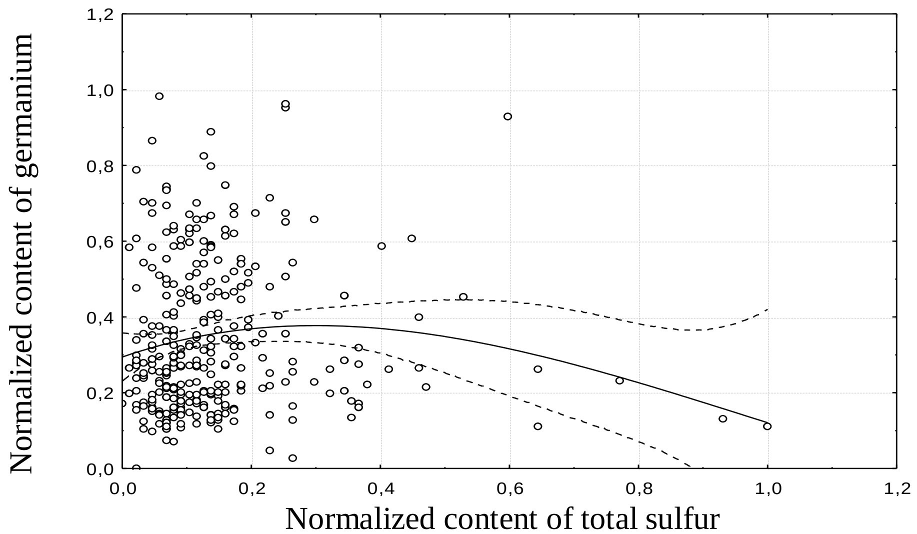


Figure 7 – The result of the regression analysis of modeling the polynomial relationship between the normalized content of germanium and the normalized content of total sulfur

A detailed analysis of the review conducted and the methods used to determine the forms of germanium in coal allows us to consider them significantly uneven, and the results obtained with their help are of a probabilistic nature. At the same time, the issue of connection of germanium with one or another component of an organic or mineral component, and even more so with the technological indicators of coal, is complicated by the possibility of its different nature (genetic or paragenetic). For example, on the basis of analyzes of 75 sectional samples from 20 profiles for the famous Upper Freeport reservoir in Pennsylvania, a significant positive correlation in the "S-Ge" coordinates was established [48]. However, in our opinion, it is unlikely that such a correlation reflects the presence of only the Ge_{sulf}. form. It is more likely that there is also a paragenetic relationship between the germanium form and the pyrite content. Unfortunately, direct microscopic studies using modern microprobe technology have so far yielded nothing, since germanium is finely distributed in coal organic matter without forming its own minerals. However, with the help of the combined SEM+EDS technique, R. Finkelman discovered the presence of germanium in kaolinite filling the pores of inertinite in the Pennsylvanian Sewell formation (in West Virginia). "Obviously, this is an authigenic formation associated, apparently, with the coprecipitation of Si and Ge from seeping solutions" [41]. At the same time, it cannot be ruled out that germanium got into these solutions from coal, according to the $Ge_{sorb.} \rightarrow Ge_{solution.} \rightarrow Ge_{min.}$, or $Ge_{opg.} \rightarrow Ge_{solution.} \rightarrow Ge_{min.}$.

A similar review was carried out based on the results of studies of the forms of presence of the above-mentioned toxic elements in coal. Thus, it was established that beryllium can be contained in coal in the following forms:

1) physically sorbed on organic and mineral matter,

2) associated with humic and fulvic acids in the form of simple humates and fulvates,

3) associated with humic acids in the form of complex humates (chelates),

4) in the form of organoberyllium compounds,

5) in rock-forming minerals (for example, in the composition of kaolinite).

Mercury can be found in coal in the following forms:

1) physically sorbed on organic (especially humus) and mineral matter (especially iron hydroxides and clay minerals),

2) associated with humic and fulvic acids in the form of humic and fulvic acid derivatives - methylmercury and hydromethylmercury,

3) associated with humic acids in the form of very stable complexes,

4) that make up the mineral fraction (for example, in the composition of kaolinite, sulfides of iron, lead, zinc and mercury, lead selenide - claustalite, carbonates and native mercury).

The presence of arsenic in coal is likely in the following forms:

1) physically sorbed on organic and mineral matter,

2) associated with humic acids in the form of complex humates (chelates),

3) in the form of organoarsenic compounds,

4) in the mineral phase (for example, in the composition of clay minerals, sulfides of iron, lead and zinc, arsenates, phosphates, sulfates, carbonates and oxides and hydroxides of iron).

The probable presence of fluoride can be associated with forms:

1) physically sorbed on organic and mineral matter,

2) in the mineral fraction (for example, in the composition of silicates - clay minerals, hydromicas, accessory amphiboles, phosphates and fluorite).

Thus, despite the significant difference in the forms of finding the elements considered in the work, it is necessary to note some commonality inherent in them, so all of them can be accumulated in coal in the following forms:

1) physically sorbed on organic and mineral matter,

2) in various mineral phases.

4. Conclusions

The conducted research allows us to formulate the following main conclusions:

1. The general diverse form of their presence in coal inherent to the considered impurity elements allows us to treat the regularities established with the help of correlation and regression analysis as a kind of trend of dependencies between them, which was realized in the specific geological conditions of the $c_8^н$ layer of the Dniprovska Mine.

2. It is proved that the distribution of germanium content, toxic elements and total sulfur in the coal seam $c_8^н$ of the Dniprovska Mine differ from the Gauss-Laplace distribution and the lognormal one.

3. It is established that analyzes of graphs of polynomial pair regression models of the relationship between the normalized concentrations of germanium and the contents of toxic elements make it possible to identify different areas of their concentrations that differ significantly in their nature.

4. It is substantiated that the minimum contents of arsenic, germanium and total sulfur in the coal seam $c_8^н$ of the Dniprovska Mine accumulated together at the syngenetic stage of its formation.

5. A decrease in germanium concentrations with an increase in the content of fluorine, mercury, arsenic and total sulfur is associated with epigenetic processes, which in this particular case lead to the removal of germanium.

6. The synchronous increase in the contents of germanium and beryllium in the area of their low and anomalously low concentrations is due to the compatible accumulation of these elements at the syngenetic stage of formation of the coal seam, and their increase in the area of maximum contents is caused by the manifestation of the empirical regularity of the "Zilbermints law".

7. Despite the insufficient study, it can be assumed that the forms of finding of the studied elements and their ratio in coal with near-Clarke concentrations and in coal with increased contents of these elements differ significantly.

The practical significance of the research results is that:

1) it is established that there is a very low correlation between the concentrations of germanium and toxic elements and total sulfur, therefore, the extraction of germanium from the coal seam will not be accompanied by their significant accumulation during technological processes

2) it has been proven that for a more realistic assessment of the central tendency of the content of germanium and toxic elements and total sulfur, it is necessary to use median values instead of median values;

The main scientific novelty of the obtained results is in establishing the non-compliance of the samples of all considered elements with the normal or lognormal distribution law, while in all cases the polymodality of the distribution of indicators is recorded, which is confirmed by analytical calculations of the correspondence of the empirical distributions of the studied parameters of the Gaussian distribution using the Kolmogorov-Smirnov, Shapiro- Wilk, Lilliefors and Pearson chi-squared agreement. It is proved that the forms of finding of the investigated elements in coal with their concentrations around Clark and in coal with increased contents differ significantly.

The influence of syngenetic and epigenetic processes on the nature of the relationship between germanium concentrations, toxic elements and total sulfur content in the coal seam $c_8^н$ of the Dniprovska Mine was revealed.

Notes: $c_8^н$ – The eighth coal seam of the lower coal pack (Lower Carboniferous).

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ГЕОХІМІЧНІ ОСОБЛИВОСТІ ГЕРМАНІЮ, АРСЕНУ, МЕРКУРІЮ, БЕРИЛІЮ, ФТОРУ ТА СІРКИ ЗАГАЛЬНОЇ У ВУГІЛЬНОМУ ПЛАСТІ С8Н ПОЛЯ ШАХТИ «ДНІПРОВСЬКА»

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Анотація. У статті встановлено та проаналізовано зв'язок між концентраціями германію, токсичними елементами і вмістом сірки загальної вугільного пласта $c_8^н$ поля шахти «Дніпровська». Для досягнення поставленої в роботі мети у процесі досліджень було здійснено кореляційний та регресійний аналіз методами, які реалізовані у одній з найпопулярніших професійних гірничо-геологічних інформаційних системах для 3D моделювання родовищ, статистичної обробки гірничо-геологічних даних та побудови фактичних гірничих виробок і планування гірничих робіт – Micromine та виконано їх аналіз у геологічних поняттях. Доведено, що розподіл значень вмісту германію, токсичних елементів та сірки загальної у вугільному пласті $c_8^н$ шахти «Дніпровська» відрізняються від розподілу Гауса – Лапласа та логнормального. Встановлено, що аналізи графіків поліноміальних парних регресійних моделей зв'язку нормованих концентрацій германію із вмістом токсичних елементів дозволяють виявити різні сфери їх концентрацій, що істотно відрізняються за її характером. Обґрунтовано, що мінімальні вмісти миш'яку, германію та сірки загальної у вугільному пласті $c_8^н$ шахти «Дніпровська» спільно акумулювалися на сингенетичному етапі його формування. Зменшення концентрацій германію при зростанні вмісту фтору, ртуті, миш'яку та сірки загальної пов'язане з епігенетичних процесів, які в даному конкретному випадку призводять до винесення германію. Синхронне збільшення вмісту германію і берилію в області їх низьких та аномально низьких концентрацій обумовлено сумісним накопиченням цих елементів на сингенетичному етапі формування вугільного пласта, а їх збільшення в області максимальних змістів викликано проявом емпіричної закономірності «закону Зільбермінця». Встановлено, наявність дуже низького кореляційного зв'язку між концентраціями германію і токсичними елементами та сіркою загальною, отже, вилучення германію із вугілля пласта не супроводжуватиметься їх суттєвим накопиченням у ході технологічних процесів. Доведено, що для більш реалістичної оцінки центральної тенденції вмісту германію та токсичних елементів і сірки загальної замість значень середнього арифметичного необхідно використовувати медіанні значення. Виявлено вплив сингенетичних та епігенетичних процесів на характер зв'язку між концентраціями германію, токсичними елементами та вмістом сірки загальної у вугільному пласті $c_8^н$ шахти «Дніпровська»

Ключові слова: германій, токсичні елементи, вміст сірки загальної, вугільний пласт, кластерний аналіз, нормальний і логнормальний закон розподілу.