UDC 550.42:553.98 DOI: https://doi.org/10.15407/geotm2022.162.164

THE RELATIONSHIP OF GERMANIUM CONCENTRATIONS AND THE THICKNESS OF THE C8H COAL SEAM OF THE DNIPROVSKA COAL MINE

[1]Ishkov V.V., [2,3]Kozii Ye.S., [4]Chernobuk O. I., [1]Pashchenko P.S.

[1]Institute of Geotechnical Mechanics named by N. Poliakov of National Academy of Sciences of Ukraine, [2]Dnipro University of Technology, [3]State Agrarian and Economic University, [4]Georgian Manganese, Department of Strategic Production Planning

Abstract. The research devoted to the study and analysis of the influence of the thickness for the c_8^H coal seam of the Dniprovska coal mine on the content of germanium and elaboration of an objective (natural) typifying of the coal seam areas of different thickness according to the element's concentration. The study is based on the data set of 370 samples of germanium and other impurity elements (so called "small elements") as well as measurements of seam thickness, ash content and sulfur content of coal performed in the central certified laboratories of geological production and exploration enterprises of Ukraine derived from the matter of formation samples obtained by production and research enterprises and companies. In order to bring the samples to the same scale, the raw data were normalized. In order to achieve the purpose of the study laboratory and statistical methods of research were applied, taking into account and interpreting the obtained results in terms of geological concept. During the research, the clustering of seam sections of different thickness according to germanium content was carried out using the weighted centroid median method, which was implemented in the statistical software platforms that provided the analysis of the clustering results. The implementation of the approach outlined in the article makes it possible to propose a natural typifying of areas based on the thickness of the coal seam according to the germanium content. The analysis of the modeling results shows that they comply with so-called "Zilbermints' law", i.e. an empirical regularity that describes enrichment of some elements (predominant germanium enrichment) in the near-contact zones of coal seams. The thickness of such layers usually does not exceed 0.2 - 0.3 m. The novelty of the study is determining of the relationships for the differential influence of the coal seam thickness of the Dniprovska coal mine on the content of germanium as well as development of a natural typifying for areas with different thickness of the seam of the Dniprovska mine according to the concentration of the elements. The practical approach implies method and an algorithm of actions that allow to distinguish between natural seams, seams with similar germanium content as well as genetically related areas, which provides the possibility of the most efficient planning of operational and technological measures and the implementation of their most probable geological and economic assessment, which aimed at extracting germanium from coal.

Keywords: germanium, coal seam, regression analysis, cluster analysis, distribution histogram, normalized content.

1. Introduction

The relevance of the study for the content of germanium in coal seams is due to the possibility of its industrial extraction and utilization as a valuable co-product [1-5]. According to our estimation, the average monthly prices for a kilogram of germanium dioxide on the world market from 1992 to 2011 ranged from US$380 to US$1460. The world's production of refined germanium is about 130 tons, 2/3 of which is produced by China. US industry annually (from 2019 to 2022) uses (authors' estimation) about 30 tons of germanium. As of today the most important global end consumers of this element are the following: the fiber optic systems production (30%), infrared optics production (25%), production of components for polymerization catalysis (25%), electronics and photovoltaic cells for solar energy (15%), phosphorus, metallurgical and pharmaceutical industry (total consumption 5%). A significant amount of germanium is contained in fly ash, which is formed during the combustion of some types of thermal coal. Germanium is accumulated in products hydrothermal and sedimentary processes where the possibility of its separation from silicon is provided. Unconventional process of natural enrichment leads to high germanium content in some coal seams discovered by Victor Moritz

Goldschmidt during an extensive survey of germanium deposits [6] The highest value of germanium concentration was found in the coal ash of the Hartley coal deposit with a germanium content of 1.6%. China's coal deposits near Xilinhaote, Inner Mongolia, contain about 1600 tons of germanium.

Currently, coal is the main well-estimated source of germanium in Ukraine, China, Uzbekistan as well as Russia. Germanium-coal deposits are being developed in England, Canada, USA, Ukraine, Russia etc. An interesting fact that is directly related to the topic of the study: in the USSR back in the 1980s, about 4.5 t/year of germanium was obtained exclusively at the coke plants of Ukraine. As of 2021 this amount of germanium for average price US$1200 costs US$5400000. The research carried out is particularly relevant taking into account the decision of the National Security and Defense Council of Ukraine dated July 16, 2021 "About the promotion of the search, extraction and enrichment of minerals of strategic importance for the sustainable development and defense capability of the state" and Decree of the President of Ukraine No. 306/2021, which sets this decision up. In these documents, germanium ores are included in the list of materials for strategic importance for the sustainable development and defense capability of the state.

Analysis of previous studies. For the first time, the phenomenon of zonal distribution of germanium along the cross-section of coal seams with its accumulation within contact zones (underground and roof package as well as packages near rock's intra-layer layers - partings) was established in 1936 in Zilbermints' study carried out with co-authors for the coal of Western Donbas [7]. Back in 1966, Pavlov suggested to designate such an empirical regularity the "Zilbermints' law" [8].

Purpose. This work is devoted to the study of the influence of the $c_8^н$ coal seam thickness of the Dniprovska coal mine on the content of germanium and the development of an objective (natural) typifying of the coal seam areas of different thickness according to the concentrations of the element.

It should be noted that such studies have not been carried out ever before. Thus, the development of a natural typification for coal seam areas of different thickness according to germanium concentration is an urgent problem, which creates an opportunity to determine their geochemical features as well as ecological and economic consequences of deposits' use.

2. Methods

The study is based on the data set of 370 samples of germanium and other impurity elements (so called "small elements") as well as measurements of seam thickness, ash content and sulfur content of coal performed since 1983 in the central certified laboratories of geological production and exploration enterprises of Ukraine derived from the matter of formation samples obtained by production and research enterprises and companies. In some cases, they were supplemented by seam samples' testing taken by the furrow method [9] from duplicate cores and mine workings from 1983 until 2017.

Before sample taking from the mine workings, measurements of coal packages and rock seams were carried out. Based on the measurement results, the most representative areas of sampling were determined. The volume of the control testing comprises 7% of the total sample volume.

The concentration of germanium was determined according to [10]. The content of Hg was determined by atomic absorption analysis. The content of As was determined according to [11]. The content of other elements was determined by quantitative emission spectral analysis [12]. Six percent of duplicate samples were sent for internal laboratory control treatment, while 10% of duplicate samples were subjected to external laboratory control. The quality of the testing results s (correctness and reproducibility) was evaluated as the significance of the mean systematic error, which is tested by means of the Student's t-distribution and the significance of the mean random error, which is tested by means of the Fisher's criterion. Since the abovementioned errors for the confidence level of 0.95 are not significant, the quality of the testing is satisfactory.

At the initial stage of primary geochemical information processing, the values of the main descriptive statistical indicators were calculated by means of statistical software (sample arithmetic mean, its standard error, median, kurtosis, mode, standard deviation, sample variance, minimum and maximum content values, coefficient of variation, sample asymmetry), frequency histograms plotting for Ge content as well as seam thickness and determining of features for the distribution of these parameters were carried out.

The number of intervals was calculated according to Sturges' rule while plotting frequency histograms:

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

where n – number of intervals, $\log_2$ – logarithm to base 2, N – samples number, [x] – denotes the whole part of a number x.

It is well known that the typifying (classifying) procedure is the systematization of objects according to preliminary specified features. The objective reason for the practical importance of typification process is the complex problems of storage, search and operation of large empirical data sets. There is a need to reduce the amount of data and at the same time not to lose too much information data contains. Cluster analysis, taxonomy, pattern recognition, and factor analysis are usually used for this purpose.

One of the most efficient procedures for simplifying and minimizing the array of data in order to facilitate its meaningful interpretation is clustering. The term "cluster analysis", introduced by Tryon back in 1939, currently includes more than 100 different algorithms [13]. Despite the fact that cluster analysis has been known for a long time, this group of methods became widespread much later than other multivariate methods of statistical analysis. The book by R. Sokal and P. Sneath "Numerical Taxonomy: The Principles and Practice of Numerical Classification" published back in 1973 causes growth of studies performed by means of this method

[14]. Currently, clustering methods are widely used in biology (for the selection of spatial and temporal groups of organisms in homogeneous conditions as well as aggregating similar genomic sequences, for determining genotypes, etc.). The same methods are used in medicine (for antibiotics classification according to the type of antibacterial activity, for automatic selection of different types of tissues in a three-dimensional image of positron emission tomography, etc.), in marketing (for data processing of various surveys, selection of distinguished groups of buyers, market dividing for creating private offers, etc.). Clustering methods are used in computer sciences (for determining population niches formed during the evolutionary algorithms processing, in image segmentation for determining boundaries and object recognition, etc.) Nevertheless, rare case studies with successful application of cluster analysis are known in geological research to date, despite its exceptional simplicity and visual transparency. At the same time, cluster analysis not only solves the problem of systematization of objects in much more simple and transparent way, but also has an undeniable advantage, because the result of its applying prevents loss of incoming information about the objects difference or correlation of features.

It is important that, unlike other methods used in solving typification problems, cluster analysis does not require preliminary assumptions about the data set, which does not impose restrictions on the presentation of the studied objects, allows analyzing natural indicators of various data types (interval data, frequency arrays, binary data, etc.) The use of cluster analysis for typification has a number of advantages, since it allows to divide a large number of the studied objects and features into groups or clusters that are homogeneous in the appropriate sense, as well as reveal the internal structure (at different hierarchical levels) of the sampled population. At the same time, like any other method, cluster analysis has certain flaws. In particular, the composition and number of clusters depends on the selected grouping criteria ("classification strategies"), and the application of different methods corresponding to different conceptual approaches to the selection of taxa to the same samples can lead to drastically different results [13]. Thus, a distinctive feature of the cluster analysis, unlike other methods of multivariate statistics, is the strong dependence of the obtained results on the preliminary assumptions of the study at the substantive level. In our case, preliminary assumptions are as follows: the absence of hypotheses regarding the number of clusters, their structure and shape; achieving maximum level of visualization for the deposits division by classes at different scale levels; determining a clustering method (algorithm) for the most stable division of the entire array of seam’s sections being considered.

In the cluster analysis, the features assumed as follows: a) selected parameters basically allow the desired division into clusters; b) units of measurement (scale) are chosen correctly.

Thus, the choice of scale in typifying methods is of great importance. In order to bring the raw data to the same scale, as a rule, they got normalized in one way or another. Since the content of germanium in the considered areas of the coal seam quite uniformly fills in entire interval of values, without significant deviations that exceed conventional distribution, normalization of the initial values of the germanium content and thickness of the seam was carried out according to the relationship:

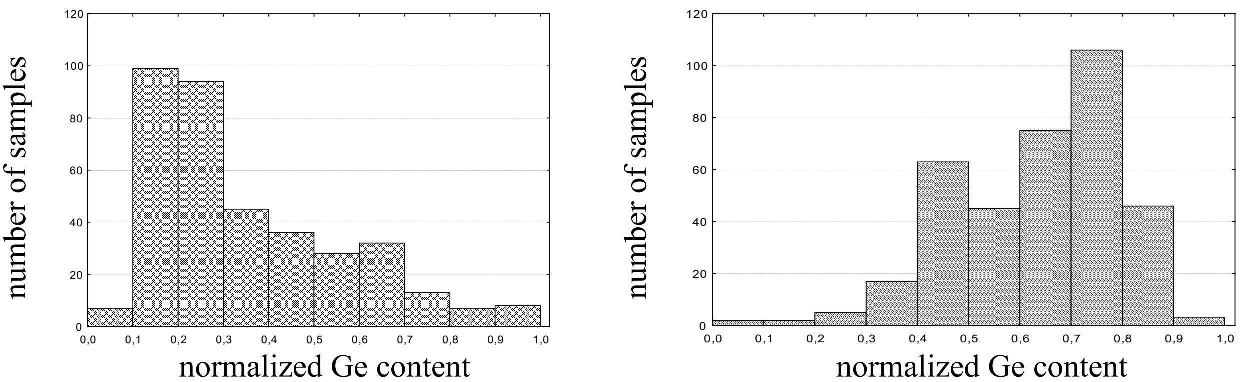
$$X_{i\ norm.} = (X_i - X_{i\ min}) / (X_{i\ max} - X_{i\ min}),$$

where $X_{i\ norm.}$ - single normalized value of germanium content, X_i - single value of germanium content, $X_{i\ max.}$ - maximum value of germanium content in coal, $X_{i\ min.}$ - minimum value of germanium content in coal.

In order to achieve the purpose of the study, clustering process was applied for the seam areas of different thickness according to germanium content by means of weighted centroid median method, which was implemented in the statistical software platforms. Further, the analysis of clustering results was performed.

3. Results and discussion

Research results and their discussion. For the deposits of the Dniprovska coal mine, the concentration of germanium in the coal of the $c_8^{н}$ seam according to the data obtained from 370 samples varies between 0.14 g/t and 23.63 g/t, while an average value is 8.34 ± 0.26 g/t, a median is 6.79 g/t, mode is 7.69 g/t, standard deviation is 5.04, sample variance is 25.38, sample kurtosis is 0.23, sample asymmetry is 0.97. The thickness of the seam at the sampling sites varies between 0.06 m and 1.00 m, the average value is 0.66 ± 0.01 m, the median is 0.7 m, the mode value is 0.7 m, standard deviation is 0.16, the variance is 0.02, kurtosis is 0.55, asymmetry – 0.69. In order to visualize density distribution of germanium concentrations and thickness of the seam related to the sampling sites, histograms were plotted (Fig. 1).



a b

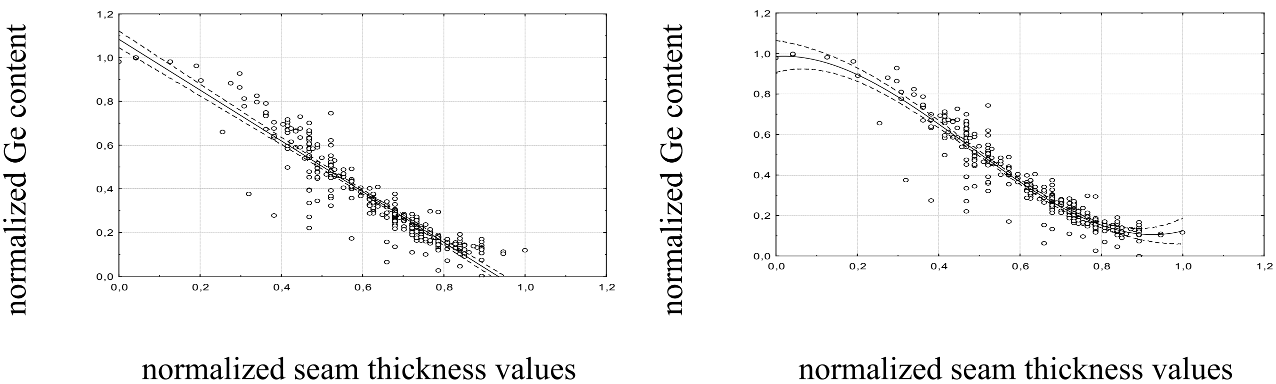
a – normalized Ge content, b – normalized values of seam thickness

Figure 1 – Histograms

Visual analysis of the given histograms shows the following: 1) non-compliance of both samples with the normal or lognormal distribution law; 2) in both cases, the bimodality of the distribution indicators is clearly noticed; 3) in the case of the distribution for germanium concentration, a shift of the distribution density kernel to the left is observed, while in histogram of the seam thickness distribution, the distribution density kernel is shifted to the right.

Despite the convincing visual analysis of the distribution histograms (Fig. 1), the authors have performed calculations to prove the correspondence of the empirical distributions for the studied parameters with the Gaussian distribution. For this purpose, Shapiro-Wilk test, Pearson's chi-square test, Kolmogorov-Smirnov test as well as Lilliefors test were were performed. In all cases, the results of the calculations have confirmed the non-compliance of both samples with the normal or lognormal distribution law. Thus, for a more realistic assessment of the central tendency for germanium content and seam thickness, instead of the arithmetic mean values, it is necessary to use the median values of both indicators.

The relationship between the content of germanium and the thickness of a coal seam according to the analysis of the general sample regarding to the Chaddock scale, taking into account the data of correlation (for linear Pearson's correlation this value is 0.94, non-parametric Spearman –0.95, Kendel –0.84 and gamma –0.86) and regression of data is inverse and very tight. For a confidence level of 0.99 it is statistically significant. Figure 2a shows the the results of the regression analysis for the modeling of the linear relationship between the germanium content and the coal seam thickness. The regression equation for this model is the following: Ge = 1.0835 – 1.1614·m, but in our opinion, the cubic polynomial is more suitable for interpretation of the results in geological terms. Its curve is shown in Fig. 2b, while the obtained regression equation is the following: $Ge = 0.987 + 0.1291 \cdot m - 3.3477 \cdot m^2 + 2.357 \cdot m^3$. When analyzing this regression model taking into consideration initial data for both germanium content and seam thickness as well as the results of previous studies [15-20], it is possible to make preliminary conclusions regarding the relationship between these indicators.



a b

a - linear relationship between germanium content and coal seam thickness, b - cubic polynomial relationship between germanium content and coal seam thickness

Figure 2 – The results of the regression analysis

It is obvious that Ge is distributed extremely non-uniformly within the vertical profile of the coal seam. The main influence on the germanium content of the seam thickness is a consequence of the manifestation of the so-called "Zilbermints' law", i.e. empirical regularity that describes enrichment of some elements (predominant germanium enrichment) in the near-contact zones of coal seams. The thickness of such layers usually does not exceed 0.2-0.3 m. It should be noted that manifestations of the "Zilbermints' law" are registered in every coal basin of the world. These manifestations find a rather satisfactory interpretation within the framework of the concept for post-sedimentary diagenetic accumulation of germanium in the contact zone by means of diffusion process and, partly, by means of filtration mechanisms during the period of turf accumulation [21-23]. Thus, with other conditions being equal, decreasing of the seam thickness as a whole leads to an increase in the contribution of germanium-enriched areas within the total content of this metal in the seam. At the same time, in some cases, these enriched layers will merge and the entire coal seam will represent a continuous zone of enrichment. This feature can explain a bond of almost all abnormally high values of germanium content with the areas of the formation with a seam thickness that does not exceed 0.45 m.

In order to develop a methodology for selection of the most efficient method of creation an objective (natural) typification for coal seam sections of different thickness according to germanium concentration, the general sample, taking into account the number of samples, was divided into 10 partial samples, which main parameters are shown in Table 1.

Table 1 – Main parameters of partial samples for germanium content

Number of partial sample	1	2	3	4	5	6	7	8	9	10
Thickness interval, m	≤ 0.45	0.45 – 0.50	0.50 – 0.55	055 – 0.60	0.60 – 0.65	0.65 – 0.70	0.70 – 0.75	0.75 – 0.80	0.80 – 0.85	≥ 0.85
Number of samples	35	40	35	19	26	44	58	47	27	22
Median values of germanium content normalized for the total number of samples	0.73	0.60	0.48	0.44	0.34	0.28	0.22	0.18	0.14	0.12
Dispersion values	0.023	0.012	0.007	0.006	0.001	0.002	0.001	0.002	0.001	0.001

In order to visualize the statistical features of all the partial samples, a box diagram (Fig. 3) was plotted.

The box diagram (Fig. 3) shows five most important consolidated parameters (minimum value, median value, first and third quartile, maximum value), as well as values that were qualified by means of the interquartile range criterion as outliers and their variants - extreme outliers. For distinguished manifestation of the central tendency variability for private samples, their median values are connected with a straight line. Formal analysis of the diagram allows to outline the following: 1) the minimum interquartile range is observed in 9-th partial sample, while the maximum interquartile range is observed in the first partial sample; 2) all partial samples, except the fifth one, show the presence of outliers. Their number varies between one (for samples 1, 4, 7 and 10) and four (for samples 2 and 6). In most cases, outliers are below the values of the interquartile range (for samples 1, 2, 4, 7, 9 and 10), while their number is rarely the same for the samples 3, 6 and 8; 3) extreme single outliers observed in all paired partial samples (2, 4, 6, 8 and 10) show abnormally low values of germanium concentration; 4) the variability of the inclination for the line connecting the median values of partial samples reflects the general variability of this indicator.

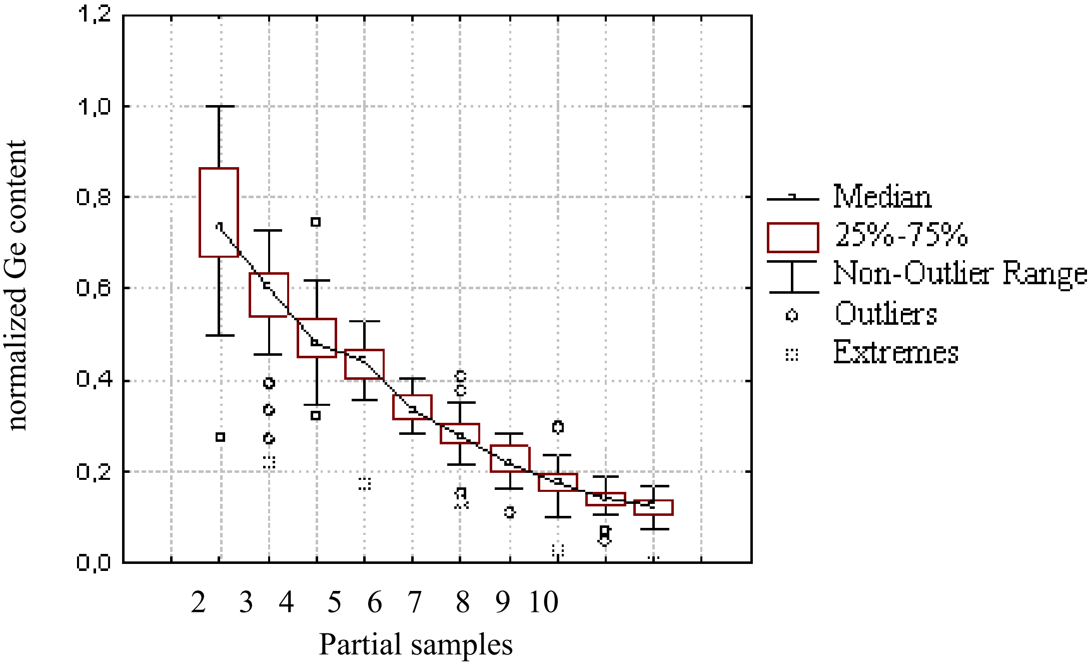
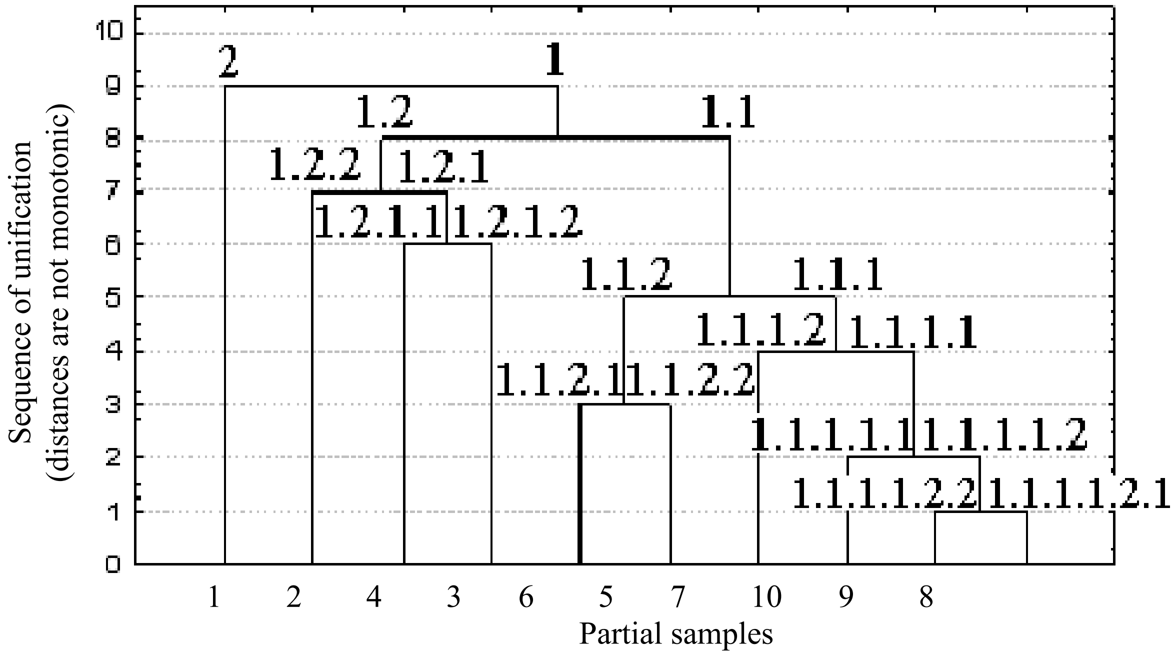


Figure 3 – Box diagram of germanium concentration in partial samples

In studies [24-40], the use of one of the methods for cluster analysis, i.e. the weighted centroid median method for the development of natural classification (typification) of oil deposits and coal seams by the content of impurity elements, as well as areas of coal seams by germanium concentration was substantiated. As a result of the cluster analysis using the specified method, a clustering dendrogram was plotted (Fig. 4).

Analysis of the dendrogram of the clustering results allows, using qualitative estimations, to divide all the main clusters for germanium concentration into 7 types: 1) cluster 1.1.1.1. consists of the areas with abnormally low germanium content values with a seam thickness that exceeds 0.75 m. Partial samples 8, 9, 10 pertain to this cluster. The median value of normalized germanium concentration is 0.15, which corresponds to 3.67 g/t; 2) cluster 1.1.1.2 with low germanium concentration values contains only 7 partial samples, aggregating sections of the coal seam with a thickness that varies between 0.70m and 0.75 m. The median value of normalized germanium concentration is 0.22, which corresponds to 5.25 g/t; 3) cluster 1.1.2 with germanium content values below the average value includes two subclusters 1.1.2.1



Legend: 1, 2, 1.1, 1.2, 1.1.1, 1.1.2, 1.1.1.1, 1.1.1.2, 1.2.1, 1.2.2, 1.2.1.1, 1.1.2.1, 1.1.2.2, 1.1.1.1.1, 1.1.1.1.2, 1.2.1.2, 1.1.1.1.2.1, 1.1.1.1.2.2 – clusters

Figure 4 – Dendrogram of clustering results obtained by means of weighted centroid median method by germanium content

and 1.1.2.2, that consist of the sections of the layer with a thickness of 0.60 - 0.65m and 0.65 - 0.70m respectively. Thus, on the average, the median value of normalized germanium concentration per cluster is 0.30, which corresponds to 7.11 g/t; 4) cluster 1.2.1.1 consists of only 4 partial samples, aggregating sections of the seam with a thickness that varies between 0.55m and 0.60 m. For average values of germaniume content indicators, its median value of normalized germanium concentration is 0.44, which corresponds to 10.37 g/ t; 5) cluster 1.2.1.2 is composed of 3 partial samples of seam sections with a thickness that varies between 0.50m and 0.55 m with an above-average germanium content. The median normalized value of this element for this cluster is 0.48, which corresponds to 11.41 g/t; 6) high values of germanium content are found in the 0.45-0.50 m layer sections of cluster 1.1.2, which pertain to partial sample 2. The median value of the normalized germanium concentration for the sample is 0.60, which corresponds to 14.25 g/t; 7) cluster 2 is consists of the areas of layer 1 of the sample with an abnormally high germanium content. The thickness of the seam in the sections is less than 0.45 m. The median value of normalized concentration is 0.73, which corresponds to 17.36 g/t.

4. Conclusions

The conducted studies allow to outline the following conclusions:

1. For the deposits of the Dniprovska coal mine, the concentration of germanium in the coal for the $c_8^н$ seam according to the data of 370 samples varies between 0.14 g/t and 23.63 g/t, with an average value of 8.34 ± 0.26 g/t, median value is 6.79 g/t, mode value is 7.69 g/t, standard deviation value is 5.04, sample variance value is 25.38, sample kurtosis value is 0.23, sample asymmetry value is 0.97.

2. The thickness of the seam at the sampling sites varies between 0.06 m and 1.00 m, the average value is 0.66 ± 0.01 m, the median value is 0.7 m, the mode value is 0.7 m, the standard deviation value is 0.16, variance value is 0.02, kurtosis value is 0.55, asymmetry value is 0.69.

3. The overall distribution of samples for both germanium content and seam thickness is bimodal and asymmetric relative to each other. The relationship between the concentration of germanium and the coal seam thickness according to the analysis of the samples related to the Chaddock scale, taking into account the data of correlation and regression analysis is inverse and extremely tight, with a confidence level of 0.99 it is statistically significant.

4. The result of the regression analysis on the relationship between the germanium content and the coal seam thickness shows that the cubic polynomial model is the most relevant.

5. The analysis of the regression analysis as well as box diagram plotting show the manifestation of the so-called "Zilbermints' law", i.e. the empirical regularity of the enrichment of some elements (predominant germanium enrichment) in the near-contact zones of coal seams for this case. The thickness of such layers usually does not exceed 0.2-0.3 m.

6. Based on the results of the cluster analysis, the sample mean values of germanium concentration, which differ significantly between individual samples of areas by the thickness of the coal seam, could be interpreted in terms of qualitative assessment as follows: abnormally low; low; below average; average; above average; high; abnormally high values. The implementation of this approach, in turn, makes it possible to propose a natural typification of areas by the thickness of the coal seam according to the germanium content shown in Table 2.

Table 2 – Natural typification of areas with different seam thickness for the $c_8^н$ coal seam of the Dniprovska coal mine by germanium content

№	Parameters of germanium content (qualitative assessment of content; content range; median value of content), g/t	Coal seam thickness, m
1	abnormally low values; 0.14/7.12; 3.67	≥ 0.0 – 0.75
2	low values; 2.72/6.82; 5.25	0.70 – 0.75
3	values below average; 1.65/9.68; 7.11	0.60 – 0.70
4	average value; 4.17/12.57; 10.37	0.55 – 0.60
5	values above average; 7.69/17.62; 11.41	0.50 – 0.55
6	high value; 5.32/17.26; 14.25	0.45 – 0.50
7	abnormally high values; 6.62/23.63; 17.36	≤ 0.45

The practical approach implies method and an algorithm of actions that allow to distinguish between natural seams, seams with similar germanium content as well as genetically related areas, which provides the possibility of the most efficient planning of operational and technological measures and the implementation of their most probable geological and economic assessment, which aimed at extracting germanium from coal.

The novelty of the study is determining of the relationships for the differential influence of the coal seam thickness of the Dniprovska coal mine on the content of germanium as well as development of a natural typifying for areas with different thickness of the $c_8^н$ seam of the Dniprovska mine according to the concentration of the elements.

REFERENCES

1. Naumov, A.V. (2007), "The world market of germanium and its prospects", Izv. vuzov. Tsv. Metallurgiya, no. 4, pp. 32-40. https://doi.org/10.3103/S1067821207040049

2. Naumov, A.V. (2007), "World market of germanium and its prospects". *Russian Journal of Non-Ferrous Metals*, vol. 48, no. 4, pp. 265-272. https://doi.org/10.3103/S1067821207040049

3. Ishkov, V.V., Kozii, Ye.S., Klymenko, A.G. (2021), "Peculiarities of germanium distribution in coal seam c_1 of the "Dniprovska" mine", *Proceedings of the 4th International Scientific and Technical Conference* "Problems of development of mining and industrial areas", DonNTU", Pokrovsk, pp. 42-50.

4. Ishkov, V.V., Kozii, Ye.S., Slyvnyi, S.O. (2021), "About distribution of germanium in the $c_8^в$ coal seam of the "Zakhidno-Donbaska" mine field", *Proceedings of the XIX International Conference of Young Scientists "Geotechnical problems of mining of mineral deposits",* IGTM by name M.S. Polyakov NAS of Ukraine, Dnipro, pp. 27-32.

5. Ishkov, V.V., Kozii, Ye.S., Chernobuk, O.I., Lozovyi, A.L. (2022), "Results of dispersion and spatial analysis of the germanium distribution in coal seam $c_8^в$ of Zahidno-Donbaska mine field (Ukraine)", Proceedings of the XXVIII International Scientific and Practical Conference "Science and practice, actual problems, innovations", Milan, Italy, pp. 66-73. https://doi.org/10.46299/ISG.2022.1.28

6. Goldshmidt, V.M. (1930), "On the occurrence of germanium in hard coal and hard coal products", *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, Mathematisch-Physikalische Klasse, pp. 141-167.

7. Zilbermints, V.A., Rusanov, A.K., Kostrykin, V.M. (1936), "On the question of the distribution of germanium in fossil coals", *Academician V.I. Vernadsky on the fiftieth anniversary of scientific activity*, M.: AN SSSR, vol. 1, pp. 169-190.

8. Pavlov, A.V. (1966), "Material composition of coal ash in some areas of Western Spitsbergen", *Uch. zap. NIIGA. Regionaln. geol.* no. 8, pp. 128-136.

9. All-Union State Standard (1975), 9815-75: Ugli buryie, kamennyie, antratsit i goryuchie slantsyi. Metod otbora plastovyih prob. M: Izd-vo standartov. 6 p.

10. All-Union State Standard (1975), 10175-75: Ugli buryie, kamennyie, antratsityi, argillityi i alevrolityi. Metodyi opredeleniya soderzhaniya germaniya. M: Izd-vo standartov. 14 p.

11. All-Union State Standard (1993), 10478-93: Toplivo tverdoe. Metodyi opredeleniya myishyaka. M: Izd-vo standartov. 13 p.

12. All-Union State Standard (1991), 28974-91: Ugli buryie, kamennyie i antratsityi. Metodyi opredeleniya berilliya, bora, margantsa, bariya, hrom, nikelya, kobalta, svintsa, galliya, vanadiya, medi, tsinka, molibdena, ittriya i lantana. M: Izd-vo standartov. 8 p.

13. Ishkov, V.V., Kozii, Ye.S. (2014), "About classification of coal seams by the content of toxic elements using cluster analysis", *Zbirnyk naukovykh prats Natsionalnoho hirnychoho universytetu*, no. 45, pp. 209 -221.

14. Koziy E.S. (2017), "Peculiarities of distribution of toxic and potentially toxic elements in the coal of the layer $c_{10}^в$ in the Stashkov mine of Pavlograd-Petropavlovsk geological and industrial district", *Geotekhnichna Mekhanika [Geo-Technical Mechanics]*, no. 132, pp. 157-172.

15. Ishkov V.V., Koziy E.S. (2017), "About peculiarities of distribution of toxic and potentially toxic elements in the coal of the layer $c_{10}^в$ of the Dneprovskaya mine of Pavlogradsko-Petropavlovskiy geological and industrial district of Donbass", *Geotekhnichna Mekhanika [Geo-Technical Mechanics]*, no. 133, pp. 213-227.

16. Koziy, E.S. (2018), "Arsenic, beryllium, fluorine and mercury in the coal of the layer $c_8^в$ of the "Dniprovska" mine of Pavlogradsko-Petropavlovskiy geological and industrial district", *Visnyk Dnipropetrovskoho universytetu. Heolohiia-Heohrafiia*, no. 26(1), pp. 113-120. https://doi.org/10.15421/111812

17. Kozii, Ye.S. (2021), "Toxic elements in the c_1 coal seam of the Blahodatna mine of Pavlohrad-Petropavlivka geological and industrial area of Donbas", *Geo-Technical Mechanics*, no. 158. pp. 103-116. https://doi.org/10.15407/geotm2021.158.103

18. Kozii, Ye.S. (2021), "Arsenic, mercury, fluorine and beryllium in the c_1 coal seam of the Blahodatna mine of Pavlohrad-Petropavlivka geological and industrial area of western Donbas", *Geotekhnichna Mekhanika* [Geo-Technical Mechanics], no 159. pp. 58-68. https://doi.org/10.15407/geotm2021.159.058

19. Ishkov, V.V., Koziy, E.S. (2017), "Distribution of toxic and potentially toxic elements in the coal of the layer c7 н of the "Pavlogradskaya" mine of Pavlogradsko-Petropavlovskiy geological and industrial district", *Visnyk Kyivskoho natsionalnoho universytetu. Heolohiia*, no. 79(4), pp. 59-66. https://doi.org/10.17721/1728-2713.79.09

20. Ishkov, V.V. (1999), "Problems of geochemistry of small and toxic elements in the coal of Ukraine", *Nauk. visnyk NHA Ukrainy*. no. 1. pp. 128-132.

21. Yudovych, Ya.E. (1978), *Heokhymyia yskopaemyikh uhlei* [Geochemistry of fossil coals], L.: Nauka, 262 p.

22. Yudovich, Ya.E. (1965), *Raspredelenie elementov v vertikalnom profile ugolnyih plastov* [Distribution of elements in the vertical profile of coal seams], L.: Nedra, no. 7, p. 134-142.

23. Yudovich, Ya.E., Ketris, M.P. (2005), *Selen v uglyah* [Selenium in coals], Geoprint, Syktyvkar, 68 p.

24. Koziy, E.S., Ishkov, V.V. (2017), "Coal classification of main working seams of Pavlohrad-Petropavlivka geological and industrial district on content of toxic and potentially toxic elements", *Geotekhnichna Mekhanika [Geo-Technical Mechanics]*, no. 136, pp. 74-86.

25. Ishkov, V.V., Serdyuk, E.A., Slipenkiy E.V. (2003), "Features of using of cluster analysis methods for the classification of coal seams according to the content of toxic and potentially toxic elements (on the example of the Krasnoarmiiskiy geological and industrial district area)", *Sb. nauch. tr. NGU,* Vol.1., No. 19, pp. 5-16.

26. Kozar, M.A., Ishkov, V.V., Kozii, E.S., Strielnyk, Yu.V. (2021), "Toxic elements of mineral and organic composition of lower carbon coal Western Donbas", *Abstracts of Scientific Conference "Geological science in independent Ukraine"*, NAS of Ukraine, M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, Kyiv, pp. 55-58.

27. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S., Bartashevskiy, S.Ye. (2021), "Research of clusterization methods of oil deposits in the Dnipro-Donetsk depression with the purpose of creating their classification by metal content (on the vanadium example)", *Scientific Papers of Donntu Series: "The Mining and Geology"*, No. 1-25-2-26, pp. 83-93. https://doi.org/10.31474/2073-9575-2021-1(25)-2(26)-83-93

28. Kozii, Ye. (2020), Coal height of coal seam k_5 of "Kapitalna" mine, *Proceedings of the International Forum for Students and Young Researchers "Widening Our Horizons",* pp. 399-401.

29. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S., Bartashevskiy, S.Ye. (2021), "Geochemical features of nickel in the oils of the Dnipro-Donetsk basin", *Geotekhnichna Mekhanika [Geo-Technical Mechanics]*, no. 160, pp. 17-30. https://doi.org/10.15407/geotm2022.160.005

30. Ishkov, V., Kozii, Ye. (2020), "Distribution of mercury in coal seam $c_7{}^H$ of Pavlohradska mine field", *Scientific Papers of DONNTU Series: "The Mining and Geology"*, no. 1(23)-2(24), pp. 26-33. https://doi.org/10.31474/2073-9575-2020-3(23)-4(24)-26-33

31. Kozii, Ye. (2021), Chromium in the coal seams of the Chervonoarmiiskyi geological and industrial area of Donbas, *Proceedings of the International Forum for Students and Young Researchers "Widening Our Horizons",* pp. 453-455.

32. Ishkov, V.V., Kozii, Ye.S. (2021), "Distribution of arsene and mercury in the coal seam k_5 of the Kapitalna mine, Donbas", *Mineralogical Journal,* no. 43(4), pp. 73-86. https://doi.org/10.15407/mineraljournal.43.04.073

33. Ishkov, V.V., Kozii, Ye.S. (2020), "Some features of beryllium distribution in the k_5 coal seam of the "Kapitalna" mine of the Krasnoarmiiskyi geological and industrial district of Donbas", *Odesa National University Herald. Geography and Geology*, vol. 25, no. 1(36), pp. 214-227. https://doi.org/10.18524/2303-9914.2020.1(36).205180

34. Ishkov, V.V., Kozii, Ye.S. (2020), "Peculiarities of lead distribution in coal seams of Donetsk-Makiivka geological and industrial area of Donbas", *Tectonics and Stratigraphy*, no. 47, pp. 77-90. https://doi.org/10.30836/igs.0375-7773.2020.216155

35. Mametova, L.F., Mirek, A., Kozii, Ye.S. (2020), "Pyritization of the Middle Carboniferous Sandstones of the Donbas". *Mineral. Journ. (Ukraine)*, vol. 42, no. 2, pp. 14-19. https://doi.org/10.15407/mineraljournal.42.02.014

36. Kozar, M.A., Ishkov, V.V., Kozii, Ye.S., Pashchenko P.S. (2020), "New data about the distribution of nickel, lead and chromium in the coal seams of the Donetsk-Makiivka geological and industrial district of the Donbas", *Journ. Geol. Geograph. Geoecology*, no. 29(4), pp. 722-730. https://doi.org/10.15421/112065

37. Ishkov V.V., Kozii Ye.S. (2019), "Analysis of the distribution of chrome and mercury in the main coals of the Krasnoarmiiskyi geological and industrial area", *Tectonics and Stratigraphy*, no. 46, pp. 96-104. https://doi.org/10.30836/igs.0375-7773.2019.208881

38. Nesterovskyi, V.A, Ishkov, V.V, Kozii Ye.S. (2020), "Toxic and potentially toxic elements in the coal of the seam $c_8{}^H$ of the "Blagodatna" mine of Pavlohrad-Petropavlivka geological and industrial area", *Visnyk Of Taras Shevchenko National University Of Kyiv: Geology*, no. 88(1), pp. 17-24. http://doi.org/10.17721/1728-2713.88.03

39. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), "Influence of main geological and technical indicators of Kachalivskyi, Kulychykhinskyi, Matlakhovskyi, Malosorochynskyi and Sofiivskyi deposits on vanadium content in the oil", Papers of International Scientific and Technical Conference "Ukrainian Mining Forum", NTU DP, Dnipro, pp. 177-185.

40. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), "Peculiarities of influence of main geological-technological indicators of oil deposits of Ukraine on vanadium content", *Proceedings of the II International Scientific Conference "* Modern problems of mining geology and geoecology", pp. 115-120.

About authors

Ishkov Valerii Valeriiovych, Candidate of Geological and Mineralogical Sciences (Ph.D.), Senior Research in Laboratory of Studies of Structural Changes Rocks, Institute of Geotechnical Mechanics named by N. Poljakov of the National Academy of Sciences of Ukraine (IGTM of NAS of Ukraine), Dnipro, Ukraine, ishwishw37@gmail.com

Kozii Yevhen Serhiiovych, Candidate of Geological Sciences (Ph.D.), Director of Educational and Scientific Center for Training of Foreign Citizens, Dnipro University of Technology (NTU "DP"), Dnipro, Ukraine, Associate Professor of the Department of Civil Engineering, Construction Technologies and Environmental Protection, Dnipro State Agrarian and Economic University, Dnipro, Ukraine, koziy.es@gmail.com

Chernobuk Oleksandr Ivanovych, Deputy Director of Department of Strategic Production Planning, Georgian Manganese, Tbilisi, Georgia, o.chernobuk@gm.ge

Pashchenko Pavlo Serhiiovych, Candidate of Geological Sciences (Ph.D.), Senior Research in Laboratory of Studies of Structural Changes of Rocks, Institute of Geotechnical Mechanics named by N. Poliakov of National Academy of Sciences of Ukraine (IGTM NAS of Ukraine), Dnipro, Ukraine, pavelsp123@gmail.com

ЗВ'ЯЗОК КОНЦЕНТРАЦІЙ ГЕРМАНІЮ І ПОТУЖНОСТІ ВУГІЛЬНОГО ПЛАСТА С8Н ПОЛЯ ШАХТИ ДНІПРОВСЬКА

Ішков В.В., Козій Є.С., Чернобук О.І., Пащенко П.С.

Анотація. У статті досліджено та проаналізовано вплив потужності вугільного пласта $c_8^н$ шахти Дніпровська на вміст германію та розроблено об'єктивну (природну) типізацію ділянок вугільного пласта різної потужності за концентраціями цього елемента. Фактологічною основою роботи були результати 370 аналізів германію та інших елементів-домішок (їх ще називають «малими елементами»), вимірювань потужності пласту, зольності та сірчистості вугілля виконаних в центральних сертифікованих лабораторіях виробничих геологорозвідувальних організацій України з матеріалу пластових проб отриманих виробничими і науково-дослідницькими підприємствами і організаціями. Для приведення вибірок до одного масштабу вихідні дані нормувались. Для досягнення поставленої мети у роботі використано лабораторні та статистичні методи наукових досліджень з урахуванням та інтерпретації отриманих результатів в геологічних поняттях. У процесі досліджень було здійснено кластеризацію ділянок пласта різної потужності за вмістом Ge зваженим центроїдним медіанним методом, який був реалізований у найпопулярніших професійних статистичних програмних платформах «STATISTICA» та «SPSS» й виконано аналіз результатів кластеризації. Реалізація підходу, який викладений в статті, дає можливість запропонувати природну типізацію ділянок за потужністю вугільного пласта по вмісту германію. Аналіз отриманих результатів моделювання свідчить про прояв так званого «закону Зільбермінця» – емпіричної закономірності збагачення деякими елементами (насамперед – германію) приконтактових зон вугільних пластів. Потужність таких шарів звичайно не перевищує 0,2 – 0,3 м. Полягає у встановленні чисельних характеристик диференційного впливу потужності вугільного пласта $c_8^н$ шахти «Дніпровська» на вміст Ge та розробці природної типізації ділянок із різною потужністю пласта $c_8^н$ шахти Дніпровська за концентрацією цього елемента. Полягає у тому, що запропоновано методичний підхід та алгоритм дій для поділу вугільних пластів на природні, близькі за вмістом Ge і генетично споріднені ділянки, що надає можливість найбільш ефективного планування організаційно-технологічних заходів та виконання їх максимально вірогідної геолого-економічної оцінки, яка спрямована на видобуток Ge з вугілля.

Ключові слова: германій, вугільний пласт, регресійний аналіз, кластерний аналіз, гістограма розподілу, нормований вміст.

The manuscript was submitted 28.09.2022