GEOLOGY, MINERALOGY AND SOIL SCIENCE

Ishkov Valerii Valeriiovych
Candidate of Geological and Mineralogical Sciences, Associate Professor,
Department of Geology and Mineral Prospecting,
Dnipro University of Technology, Ukraine;
Senior Research Fellow, Laboratory of Studies of Structural Changes Rocks,
M.S. Polyakov Institute of Geotechnical Mechanics of the NAS of Ukraine, Ukraine

Kozii Yevhen Serhiiovych
Candidate of Geological Sciences, Director of Educational
and Scientific Center for Training of Foreign Citizens,
Dnipro University of Technology, Ukraine

Chernobuk Oleksandr Ivanovych
Deputy Director of Department of Strategic Production Planning,
Georgian Manganese, Georgia

Kozar Mykola Antonovych
Senior Research Fellow, Candidate of Geological Sciences,
M.P. Semenenko Institute of Geochemistry,
Mineralogy and Ore Formation of the NAS of Ukraine, Ukraine

Pashchenko Pavlo Serhiiovych
Candidate of Geological Sciences, Senior Research Fellow,
Laboratory of Studies of Structural Changes Rocks,
M.S. Polyakov Institute of Geotechnical Mechanics of the NAS of Ukraine, Ukraine

Diachkov Pavlo Anatoliiovych
Senior Lecturer, Department of Transport Systems and Technology,
Dnipro University of Technology, Ukraine

Vladyk Danyil Volodymyrovych
student, Department of Geology and Mineral Prospecting,
Dnipro University of Technology, Ukraine

MANIFESTATION OF THE PHENOMENON OF COAL ENRICHMENT WITH GERMANIUM OF LOW-POWERED AREAS OF THE SEAMS OF THE DNIPROVSKA MINE (UKRAINE) AND THE «ZYLBERMINTS LAW»

Abstract. *The study of the germanium distribution over the area and in the cross-section of coal seams* $c_8^н$, $c_8^в$, $c_{10}^в$ *of the "Dniprovska" mine made it possible to establish the presence of a very high inverse correlation between the thickness of the seams and their germanium content; the presence of zones of Ge enrichment with a thickness of 10–30 cm at the contacts of the layers. This made it possible to explain in geochemical terms the joint manifestation of the phenomenon of germanium enrichment in low-powered areas and the "Zilberminets law" in the seams of the Dniprovska mine.*

Keywords: *germanium, cross-section, coal seams, enrichment zones.*

Introduction. The relevance of studying the germanium content in coal seams is due to the possibility of its industrial extraction and use as a valuable accompanying component. For an objective geological and economic assessment of the possibility of simultaneous extraction of Ge from coal, waste and products of its processing and planning of the most effective organizational and technical measures in this regard, it is first of all necessary to have information about the nature of the distribution and the level of concentration of this element in coal. In order to obtain such information, the authors carried out detailed studies of the germanium distribution over the area and in the section of coal seams $c_8^н$, $c_8^в$, $c_{10}^в$ of the Dniprovska mine.

Recent achievements. 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-industrial areas of Donbas were investigated, it was established that there is a close inverse correlation between the thickness of the seam and the contents of Ge and some other impurity elements [1-48]. At the same time, the establishment of a relationship between the content of germanium and the thickness of the coal seams of the Dniprovska mine and its analysis had not been carried out before.

Purpose: establishment of a relationship between the content of germanium and the thickness of the coal seams of the Dniprovska mine.

Materials and Methods. The factual basis of the work was the results of 370 Ge analyzes performed after 1981 in the central certified laboratories of production geological exploration organizations of Ukraine from the material of reservoir samples obtained by production and scientific research enterprises and organizations and measurements of reservoir capacity. Germanium content was determined by quantitative emission spectral analysis. The quality of the results of the analyzes was evaluated as the significance of the average systematic error, which is tested using the Student criterion, and the significance of the average random error, which is tested using the Fisher criterion. Since the above-mentioned errors at the significance level of 0.95 are not significant, the quality of the analyzes is recognized as satisfactory.

Findings and Discussion. The relationship between the germanium content and the thickness of the coal seam $c_8^н$, $c_8^в$, $c_{10}^в$ according to the results of the analyzes of the general sample according to the Chedok scale, taking into account the data of the correlation analysis for all seams, is inverse and very high, with a confidence interval of 0.99 it is statistically significant. The calculated corresponding correlation coefficients are –0.94, –0.91 and –0.96. Analysis of the results of sectional testing of the formations showed the presence of Ge enrichment zones with a thickness of up to 0.30 m, located in the roof and soil.

For the first time, such zonality of Ge distribution in the section of coal seams was described as early as 1936 in the work of V. A. Zilberminets and his colleagues on the coals of the Donets Basin [49]. Later, in 1966 A.V. Pavlov proposed to call this empirical regularity "Zilbermints law" [50]. During the research of the South Yakutsk coal basin [51] variants of Ge distribution in the section of the coal seam were noted: a) enrichment near the soil and roof (seams of a simple structure); b) at the roof, soil and interlayers (seams of complex structure); c) only at the roof; d) only near the soil; e) uniform distribution over the seam, with a general increased content (usually these are seams with a thickness of less than 0.5 m).

According to the results of sectional testing of 12 coal deposits in Japan, it became obvious that Ge is concentrated in the contact zones, although such enrichment is always asymmetric. For example, at the Hiraga deposit, mainly near-soil sections are enriched, while at the Mino deposit, near-top sections are enriched. This situation is interpreted by Japanese geologists as evidence of the diagenetic migration of Ge from outside [52].

The low-ash and low-sulfur seam Blue Gem in southeastern Kentucky, 0.7 m thickness, was sampled in five sections. Published analyzes [53] shows that the Ge content in ash and coal does not correlate with the ash content, but abrupt enrichment of edge sections with germanium is observed.

Almost simultaneously with the discovery of contact enrichment, another empirical pattern was established: the inverse relationship between the germanium content of coals and the thickness of coal seams. For example, as noted by V.R. Kler [54], in the Donbas, within one coal seam of variable thickness, "the Ge content behind the operating thickness contour is usually 2 times or more higher than within the industrial contour."

In the vast majority of cases, all other things being equal (in particular, within the same coal-bearing basin or deposit), the thicker the coal seam, the lower the average content of Ge in it. Thin non-industrial coal seams and interlayers are almost always germanium-bearing, while thick industrial seams contain 10–100 times less Ge. Various researchers at different times attempted to explain this phenomenon in terms of the facies of coal-forming peatlands or in terms of the rate of peat accumulation.

For example, Zodrow, who studied the coals of the Sydney Basin (Canada), noted that some elements, in particular V and Ni, enrich thin seams. He associated this with slower peat accumulation during their formation [55].

In our opinion, "syngenetic" interpretations of the phenomenon of enrichment of thin seams with germanium seem untenable. The fact is that the thickness of the zones of contact enrichment of seams with Ge and other impurity elements does not depend on the thickness of the seams; it is approximately the same everywhere and varies within narrow limits from 10 to 30 cm. Therefore, a thin coal seam geochemically differs from a thick seam only in the increased contribution of contact zones.

For example, if in a seam 2 m thick the share of two contact zones 10 cm thick is only 10% by volume, then with the same thickness of contact zones in a thin seam 0.4 m thick, they will already amount to 50%. If we have a thin coal interlayer with a thickness of only 10 cm, then it can be considered as two merged (superimposed) contact zones - upper and lower. Such seam should be richer in germanium than each of the contact zones of a thick seam separately.

Thus, in our opinion, the inverse dependence of Ge content in coal seams on their thickness can be easily interpreted.

The similarity of thin seams with contact zones is also manifested in the fact that, probably, the composition of host rocks is far from being indifferent to the enrichment of thin layers. If the sample of coal seams under study is dominated by thin seams, the host rock factor can have a significant impact.

Conclusions:

The study of the distribution of Ge over the area and in the cross-section of coal seams $c_8^н$, $c_8^в$, $c_{10}^в$ of the "Dniprovska" mine made it possible to establish: 1) the presence of a very high inverse correlation between the thickness of the seams and their Ge content; 2) the presence of zones of Ge enrichment with a thickness of 10–30 cm at the contacts of the seams. This made it possible to explain in geochemical terms the joint manifestation of the phenomenon of germanium enrichment in low-power areas and the "Zilbermints law" in the seams of the Dniprovska mine.

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Крупко Галина Дмитрівна
кандидат сільськогосподарських наук, головний інженер-ґрунтознавець
Рівненська філія державної установи «Інститут охорони ґрунтів України», Україна

ДИНАМІКА КИСЛОТНОСТІ ҐРУНТІВ РІВНЕНСЬКОЇ ОБЛАСТІ

Ґрунтовий покрив Рівненської області неоднорідний і відзначається значною різноманітністю ґрунтів і за генезисом, гранулометричним складом, водно-фізичними властивостями, і за родючістю.

Реакція ґрунтового розчину відіграє важливу роль у розвитку рослин і ґрунтових мікроорганізмів, впливає на швидкість і напрямок перебігу в ньому хімічних і біохімічних процесів. Засвоєння рослинами елементів живлення, інтенсивність мікробіологічної життєдіяльності, мінералізація органічної речовини, розкладення ґрунтових мінералів і розчинення різноманітних важкорозчинних сполук, коагуляція і пептизація колоїдів та інші фізико-хімічні процеси великою мірою визначають реакцію ґрунту [1–8].

Кисла реакція ґрунту відноситься до числа несприятливих екологічних факторів, що стримують ріст і розвиток більшості видів сільськогосподарських культур. Кисла реакція властива дерново-підзолистим і болотним ґрунтам, нейтральна – чорноземам. Всі сільськогосподарські культури по різному відносяться до ступеня кислотності ґрунту, тому певна культура має свій інтервал pH, при якому вона добре росте і розвивається.

Агрохімічну паспортизацію земель сільськогосподарського призначення проводили згідно керівного нормативного документа [9, 10]. Визначення pH проводилося згідно ДСТУ ISO 10390:2007 іонометричним методом визначення pH сольової витяжки в ґрунтах.

Результатами досліджень встановлено, що за кислотністю згідно даних XI туру (2015–2020 роки) обстеження ґрунти області розподілилися на такі