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THE PROCESS OF ACCUMULATION OF GERMANIUM IN THE COAL OF UKRAINE

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УМОВИ НАКОПИЧЕННЯ ГЕРМАНІЮ У ВУГІЛЛІ УКРАЇНИ

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УСЛОВИЯ НАКОПЛЕНИЯ ГЕРМАНИЯ В УГЛЯХ УКРАИНЫ

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Abstract. This summer, the state program "Critical and Strategic Mineral Resources of Ukraine in the Context of Globalization and Climate Change" was formulated. A significant group of minerals is classified as a critical raw material, including copper, lithium, cadmium, magnesium, nickel, graphite, aluminum, germanium and other metallic and non-metallic elements. If we look at the raw material base of germanium in the world in general and in our country, in particular, it can be noted that at the present stage one of the important sources for the extraction of germanium is coal, from which this element was additionally extracted in the form of metal earlier at the coking stage. The high geochemical mobility of germanium salts and the ability to concentrate at different stages and substages of lithogenesis have become the reason for the appearance of accompanying raw materials, which attracted the attention of many specialists. The task of this article is to focus on less known facts, and to determine the main regularities in the formation and transformation of accompanying germanium in coal seams at various stages and substages of lithogenesis in general and catagenesis, in particular. Since germanium, as well as other rare (small, accompanying, trace) elements are contained in this substance, when the temperature rises, it leaves the coals, along with lipids. But before leaving completely, the complex of lipids (hydrocarbons), together with rare elements, undergoes a cycle of hydrothermal transformations. As a result, we observe the enrichment of hydrocarbons with rare elements in coal seats and interlayers as they move upward. The downward movement of fats and small elements leads to their accumulation in the roof of coal seams and interlayers. Ultimately, at temperatures of about 140^0-160^0C, germanium, together with hydrocarbons and other small elements, goes into the fractured zones, where the pressure and temperatures are lower.

Keywords: germanium, coal, rare and trace elements, rock, catagenesis.

Introduction. The beginning of the third millennium was marked by the wide use of computer technology in all industries. Now it is impossible to imagine a human society without gadgets, the Internet, and mobile communications. Scientists, with the help of modern equipment, are exploring space, the resources of the ocean depths and the still untouched Antarctica. The word "resources" has become relevant for various branches of knowledge: industry, agriculture, transport and communications. Experts are considering projects for the extraction of ferromanganese nodules from the bottom of the oceans, valuable minerals from sea waters. To meet the needs of the high-tech industry, the need to extract rare, minor, dispersed, associated elements is increasing.

In this regard, this summer, the state program "Critical and Strategic Mineral Resources of Ukraine in the Context of Globalization and Climate Change" was formulated, which has good ground for our country.

From 15th to 18th of November of this year, the 8th International Conference on Critical Raw Materials was held on this topic, with a center in Brussels, to which a large group of specialists from different countries of the World was connected online.

It is very important to divide the countries of the World into several main domains, each of which strives for relative raw material independence and most of the reports, questions and discussions were devoted to this. By this time, the countries of Africa, Latin America, Canada and Ukraine, as well as some countries of the Middle East and Asia, joined the domain of the European Union.

A significant group of minerals is classified as a critical raw material, including copper, lithium, cadmium, magnesium, nickel, graphite, aluminum, germanium and other metallic and non-metallic elements. There is a significant demand for this raw material, since they are used for the transition of the countries of the World to green energy, which has no alternative. The European Union plans to switch to renewable energy by 2050.

Currently, the processing of secondary raw materials, especially batteries, accumulators, containers, has been widely developed in the countries of the European Union. Extensive research is underway to replace some packaging materials, such as plastics, with other materials that degrade more easily and quickly without posing a threat to the environment. Environmental problems, especially for developing countries, the problem of drinking water supply are also relevant. But the problem of raw materials, its production in different countries, has now become significantly aggravated. Therefore, the creation of the specified domain from different countries under the auspices of the European Union is a kind of response to the existing challenges facing the modern generation.

If we look at the raw material base of germanium in the world in general and in our country, in particular, it can be noted that at the present stage one of the important sources for the extraction of germanium is coal, from which this element was additionally extracted in the form of metal earlier at the coking stage [1-7].

Germanium belongs to trace elements, accompanying or small elements, the clarke of which does not exceed 0.1 %. In the coals of Ukraine, the average high content (g/t) has the following microelements: Ge - 100; Pb - 125; Be - 12; Mo - 7.7; Zr - 418; V - 381; Ni - 132; Cu - 146; Zn - 216; W - 46; Yb - 6.

Earlier [1, 3] for trace elements in modern peatlands, the dependence of their composition on the composition of the demolished area was established, which was also proved for coal deposits: for ultrabasic rocks V, Cr, Co, Ni, Zn, Cu, Se are typical; for alkaline rocks Zr, V, Yb, La, Nb are typical; for acidic rocks Be, Ga, Mo, Pb, Sn, Ge are typical.

The fact that germanium and the group of the aforementioned trace elements are associated with acidic parent rocks is known and established. In addition to felsic rocks, various authors have established a relationship between the increased content of germanium and volcanic rocks.

Germanium as a chemical element was prognosed by D.M. Mendeleev back in 1871 and named it ecosilicon. This is an important detail, because the properties of this element are quite close to silicon dioxide [4]. It is also important that the forms of germanium mono- and dioxide are amphoteric, dissolves well in an alkaline medium with the formation of germanites and germanates. Germanium has numerous compounds with halogens and sulfur, forms sulfogermanates, which are readily soluble in aqueous solution. Most oxide compounds of germanium are structural analogs of silicon compounds. Therefore, this element is found as impurities in silicon minerals, to a lesser extent in iron and zinc minerals. Own minerals germanium are rare and of no practical value. Germanium accumulates in hydrothermal and sedimentary rocks, where it is possible to separate it from silicon. It is found in increased quantities in iron ores (magnetite), in brown and bituminous coals.

The question why the associated resources and reserves of germanium are associated with the coal of Donbass is not difficult. It was noted above that such element as Be, Ga, Mo, Pb, Sn, Ge, and others are associated with felsic rocks and demolished areas. The rocks of the Ukrainian Crystalline Shield are mainly acidic. Sediments containing Donbass coal were washed away from the shield (its southwestern part). Up to 60-70 % of the volume of demolished rocks (sandstones and siltstones) are fragments of quartz, in which, as noted earlier, germanium is found in increased quantities as an impurity.

Hypergenesis and upward tectonic movements on the shield area over the past 1.5-2 billion years have led to the formation of significant volumes of sediments of sandy and siltstone fractions, which were carried away by river, flood and glacial processes into the Dnieper-Donetsk depression (DDD). The average thickness of Carboniferous deposits reaches 5-10 kilometers and is represented, to a large extent, by the destroyed remains of crystalline rocks of precisely persilicic rock. The high geochemical mobility of germanium salts and the ability to concentrate at different stages and substages of lithogenesis have become the reason for the appearance of accompanying raw materials, which attracted the attention of many specialists.

It is interesting that from the beginning to the middle of the last century more attention was paid not to the coal itself, but to the products of its combustion – coal ash.

A special report on this topic, published in Washington in 1953, provides free access to interesting materials on the content of germanium in coal ash from various coal deposits of the United States, the Soviet Union, and its republics. The works of 47 authors, including well-known geochemists, geologists, who were involved in the problem of determining the possibility of extracting germanium from the coal ash. Left after burning coal of different ranks and degree of coalification, are presented. Scientific papers and even unpublished scientific reports from 1919 to 1952 were analyzed.

In the post-war years, when metallurgy and the technological industry, modern mechanical engineering were gaining momentum, new materials began to be in significant demand. The leading states spared no expense on geological surveys and scientific experiments. Many different publications, reports, scientific developments, inventions, etc. were published. The main results of these works – information about where the specified element is found in increased quantities and how to extract it, are given in the fundamental works of scientists [1-7].

Proceeding from the problem of the need to provide industry with germanium raw materials, the task of this article is to focus on less known facts, and to determine the main regularities in the formation and transformation of accompanying germanium in coal seams at various stages and substages of lithogenesis in general and catagenesis, in particular.

In schematic form, a coal deposit or coal-bearing basin is formed in several stages. At the first stage – sedimentogenesis – precipitation is formed in negative land areas or coastal areas. Demolition of terrigenous material occurs from positive regions. The thickness of these deposits is up to several meters, less often – up to several tens of meters. Under favorable conditions (temperature, humidity), wet sediments are covered with vegetation, which, over time, forms peat bogs.

With the progressive course of lithogenesis and the subsidence of this area to a certain depth, the bog is covered with a layer of newly demolished continental material, and the contents of the bog – peat bog, pass to the next stage of lithogenesis – diagenesis. At this stage, significant geochemical changes take place. Sediments are transformed into rocks; peat is transformed into brown coal, and later into coal. Usually, all these processes occur in an aqueous medium, which simplifies the release of germanium from finely destroyed quartz material, its transfer and accumulation in organic materials, moreover, mainly in lipids. This connection is well traced during coking, when the supra-resin waters released during the thermal treatment carry with them germanium, which is relatively easily utilized.

The stage of diagenesis turns into catagenesis under certain conditions. The temperature of this transition is about 60-70^{0}C, the depth can vary significantly, from several hundred meters to 2.5-3 km.

The early catagenesis substage includes coals of grades subA**,** hvAb**;** the temperature is in the range of 70-110^{0}C. Coal grade hvAb is the boundary zone between early and middle catagenesis. If we present everything in a schematic form, then the early catagenesis is separated from the middle one, by the boiling point. In general, grades of coal have comparable conditions for the transition from one stable condition to another (or from a grade to a grade). The gradient of these transitions is 20^{0}C. In other words, grade subA (hvCb hvBb) coals are formed at a temperature of about 80°C, grade hvAb coals about 100^{0}C, and mvb grade coals about 120^{0}C (but this is already the middle substage of catagenesis). The indicated temperatures were obtained without the involvement of organic matter, the methods of obtaining them are described and patented in the prescribed manner [9-10].

The middle substage of catagenesis, these are coals of grades subA (hvCb hvBb), mvb , lvb , sa . Grades subA and sa are borderline between early and middle (subA) and between middle and late catagenesis (sa). The temperature at this substage varies from 100^{0}C to 160^{0}C. This substage is characterized by the presence of heavy hydrocarbons (HH), which are no longer present at the late substage of catagenesis. By the end of this substage, sapropelite, the oil source rock, “disappears”. It leaves along with lipids (fatty constituents). We can talk about the evaporation of lipids from coal matter, primarily vitrinite, in which structureless lipids are stored.

Since germanium, as well as other rare (small, accompanying) elements are contained in this substance, when the temperature rises, it leaves the coals, along with lipids. But before leaving completely, the complex of lipids (hydrocarbons), together with rare elements, undergoes a cycle of hydrothermal transformations.

All coals pass through this cycle at the middle stage of catagenesis. This does not happen in some kind of jump at a fixed temperature, as you know, water boils at 100^0C, and fats, paraffins, hydrocarbons have higher boiling points. Therefore, this cycle or process occurs rather slowly, but for a long time according to the following scenario.

The first, naturally, water boils, turning into steam and moving up to the level of condensation. After cooling, moving down again, under the influence of gravity and boiling, the cycle for water is repeated. Lipids or fats at temperatures above 100^0C melt and, in accordance with the same law of gravity, move downward, until they sublimate or boil, after which they also move upward with steam. If for water such cycles or "swing" occur without any special consequences, then for hydrocarbons carrying rare and scattered elements, there are consequences. They consist in the movement of these elements in organic matter with a significant specific surface area. Coal seams and interlayers act as a kind of filters that trap rare elements, most likely with lipids. As a result, we observe the enrichment of hydrocarbons with rare elements in coal seats and interlayers as they move upward. The downward movement of fats and small elements leads to their accumulation in the roof of coal seams and interlayers.

Thus, germanium isolated from quartz fragments (together with other small elements) accumulates in the structureless substance of the organic mass - lipids. During the transition of coals to the sub-stage of medium catagenesis in a temperature range of about 100^0-160^0C, together with the released hydrocarbons, it participates in vertical movements (swings), enriching the organic matter of the seat and roof. Ultimately, at temperatures of about 150^0-160^0C, germanium, together with hydrocarbons and other small elements, goes into the fractured zones, where the pressure and temperatures are lower.

Subvertical fractured zones combine layers and stratigraphic horizons, therefore, due to the mixing of parameters of different layers, conditions are created in them that differ from those in the rock layers. According to our calculations, large fractured zones, which are usually the boundaries of mine fields or areas, at depths of about 2-3 km have increased concentrations of gas-condensate hydrocarbons and increased contents of rare and scattered elements.

Hydrocarbons do not reach the substage of late catagenesis. The accompanying elements go there in very limited quantities. In other words, under certain conditions (temperature, pressure), there is a differentiation of organic matter, small and scattered elements, hydrocarbons. Each of the listed types of substance occupies the most convenient niche as long as these conditions persist. If the existing conditions change, new displacements are possible, which can be predicted, to a certain extent.

If we recall the coke-chemical process, the mechanism of melting fats from coals (lipids, hydrocarbons) together with germanium, which chemists called over-resin waters, and from which the necessary germanium was extracted, becomes quite clear. When funding is resumed, this process can be recommenced, but it is logical to carry out preliminary studies and find out the entire composition of the elements included in the over-resin waters, so that over time not to look for cadmium, beryllium or any other rare accompanying element that was not extracted at one time in a convenient location.

Conclusions. The natural chain or conception of formation and transformation of germanium clusters under different conditions is considered and presented, which includes:

- destruction of the carrier of acidic rocks of the Ukrainian crystalline shield during hypergenesis;
- transfer and accumulation of clastic material in the Dnieper-Donetsk depression during sedimentogenesis;
- separation of germanium from clastic material and its transition to organometallic compounds in early catagenesis;
- redistribution of germanium compounds in coal seams and interlayers during vertical movement in early and middle catagenesis;
- isolation of germanium compounds together with hydrocarbons and their transition to fractured zones at depths of 2-3 km at the end of the middle catagenesis.

These changes occur under the influence of constantly changing conditions and for this reason the compounds of germanium and other small, rare and scattered elements do not have significant accumulations in coals at the substage of late catagenesis. For the complex extraction of these elements, improved enrichment technologies and their subsequent production are needed not only from the products of coal combustion, at coke plants, but also from fractured zones. For these purposes, it is necessary to consider the existing technological capabilities and, if necessary, improve them or offer new technologies, which is one of the areas of work of specialists from the Institute of Geotechnical Mechanics of the NAS of Ukraine.

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Анотація. Влітку цього року було сформульовано державну програму «Критичні та стратегічні мінеральні ресурси України в умовах глобалізації та зміни клімату». До критичної сировини віднесено значну групу корисних копалин, серед яких: мідь, літій, кадмій, магній, нікель, графіт, алюміній, германій та інші металеві та неметалеві елементи. Якщо подивитись на сировинну базу германію у світі загалом і в нашій країні зокрема, то можна відзначити, що на сучасному етапі одним із важливих джерел вилучення германію є вугілля, з якого цей елемент додатково витягувався у вигляді металу раніше на стадії коксування. Висока геохімічна рухливість солей германію та здатність концентруватись на різних стадіях та підстадіях літогенезу стала причиною виникнення супутньої сировини, яка привернула увагу багатьох фахівців. Завдання даної статті – зосередитись на менш відомих фактах, та визначити основні закономірності формування та трансформації супутнього германію у вугільних пластах на різних стадіях та підстадіях літогенезу взагалі та катагенезу, зокрема. Оскільки германій, як і інші рідкісні (малі, супутні, розсіяні) елементи міститься у цій речовині, у разі підвищення температури він йде з вугілля, разом із ліпідами. Але перед тим, як піти остаточно, комплекс ліпідів (вуглеводнів) разом із рідкісними елементами проходить цикл гідротермотрансформацій. У результаті, спостерігається збагачення вуглеводнями з рідкісними елементами ґрунту вугільних пластів та пропластків, коли вони переміщуються вгору. Переміщення вниз жирів і малих елементів призводить до накопичення в покрівлі вугільних пластів і пропластків.

Ключові слова: германій, вугілля, рідкісні та розсіяні елементи, породи, катагенез.

Аннотация. Летом этого года была сформулирована государственная программа «Критические и стратегические минеральные ресурсы Украины в условиях глобализации и изменения климата». К критическому сырью отнесена значительная группа полезных ископаемых, среди которых: медь, литий, кадмий, магний, никель, графит, алюминий, германий и другие металлические и неметаллические элементы. Если посмотреть на сырьевую базу германия в мире в целом и в нашей стране, то можно отметить, что на современном этапе одним из важных источников извлечения германия является уголь, из которого этот элемент дополнительно извлекался в виде металла раньше на стадии коксования. Высокая геохимическая подвижность солей германия и способность концентрироваться на разных стадиях и подстадиях литогенеза стала причиной возникновения сопутствующего сырья, привлекшего внимание многих специалистов. Задача данной статьи – сосредоточиться на менее известных фактах, определить основные закономерности формирования и трансформации сопутствующего германия в угольных пластах на разных стадиях и подстадиях литогенеза вообще и катагенеза, в частности. Поскольку германий, как и другие редкие (малые, сопутствующие, рассеянные) элементы содержится в этом веществе, при повышении температуры он уходит из угля, вместе с липидами. Но перед тем как уйти окончательно, комплекс липидов (углеводородов) вместе с редкими элементами проходит цикл гидротермотрансформаций. В результате мы наблюдаем обогащение углеводородами с редкими элементами почвы угольных пластов и пропластков, когда они перемещаются вверх. Перемещение вниз жиров и малых частиц приводит к скоплению в кровле угольных пластов и пропластков.

Ключевые слова: германий, уголь, редкие и рассеянные элементы, породы, катагенез.

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