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THE INVESTIGATION OF HEAVY METAL ION CONTENT IN ROCK AND COAL PRODUCTION

A review over the methods of heavy metals determination in coal and products of coal mining is present. Expediency of the use of microwave and declines of temperature for ash tests is educed for the exactness increase of determination and diminishing time for analysis.

The problem and its connection with scientific and practical problems. It`s know that coal contains a lot of different valuable components which include germanium, uranium, zinc, copper, titanium and others. The mineral part of coal and associated rocks are extensively used in the building materials production and building. Many investigations were made on coal construction matter and its properties. But the study of liquid and dispersed element content, forms of their connection with the coal substance, improved method developing of these element quantitative determination in coal are in the development stage. These issues include the small number of impurity element content valuation in coal. This is because there are some difficulties of their definition [1-3].

Not all coal micro components are useful. Elements such as arsenic, mercury, vanadium, chromium, cobalt with a significant content of coal can be potentially hazardous to the environment, especially in the use of raw coal for energy purposes.

Impurities content in coal varies quite significant even within a single coal seam. Moreover variety of element determining methods is observed that lead to difficulties in statistical data analysis from different authors. In this regard, the development of improved methods for impurities in coal determining are important scientific and practical problem and requires research and comparison of technology preparing samples for chemical analysis and implementation methods.

Analysis of research and publications. Trace elements can be in coal organic matter in the chemical compound form, sorbs and finely dispersed condition, as ore minerals and their composition, in the form of non-metallic mineral formations or in their warehouse.

For proper industrial evaluation of the valuable component content it is necessary to know the shapes of a coal finding, which define ways to extract this component. The simplest method for this is the fractional analysis with component content definition of any faction. Mineralogical, spectrographically, chemical and physical methods are used to research the valuable components content [1-4].

The mineral part of solid fuel chemical composition is determined by ash structure (calcined part). The ash structure characterizes both mineral components and ash-forming, which are composed of organic compounds in coal. In this regard, the coal mineral part composition may vary significantly from the ash composition. The main chemical components of the solid fuels ash are SiO2, Al2O3, Fe2O3, CaO, MgO, K2O, Na2O, TiO2. Apart from these ones in ash a number of trace elements presents, which content is below 1%. The ash composition is one of the most important factors determining of the slag and ash removal character, their removal technology and recycling opportunities.

Along with the basic ash-forming components coal concentrates rare and diffused elements, colored, precious and radioactive metals in small quantities. They are picked out codenamed "small" or microelements and are studied as useful or harmful components.

Microelements accumulation both syngenetically and epigenetically according to coal accumulation is mainly due to their concentration on the sorption and renewable barriers. In renewable barriers it is much lesser extent by nutrient concentration and deposition on the thermodynamic barrier. Accumulation on sorption barriers associated with the microelements sorption by organic substance from water coming in peat or layer, is typical for elements mainly associated with coal organic matter and, above all, for germanium, vanadium, beryllium.

Accumulation associated with a concentration on renewable barriers, is characteristic for the elements with high contrast migration in the oxidation -reduction environment (uranium, zinc, lead, rhenium, selenium, molybdenum). This is evident when the oxygen containing water comes in coal-bearing formations layers that have high renewable capacity due to the high content of organic matter.

Concentration on the thermodynamic barriers is the result of hydrothermal activity that often accompanies the formation of coal-bearing formations and post inversed tectonic processes. Mercury mineralization in Donbass coal related to this mineralization type [2].

As harmful components that have potential environment pollution danger, arsenic, mercury, lead, beryllium fluoride and radioactive elements are to be studied and evaluated its content in coal. It is necessary to have a determining method which are reliable, relatively easy to implement using modern equipment and don’t require a lot of time.

Problem statement. The purpose of this paper is the known method reviewing and developing of rock sample and coal-mining product preparing methods to determine the heavy metals ions content.

Presentation of the material and results. The use possibility evaluation of coal

with a harmful components high concentration is associated with their utilization. In some cases accompanying extraction of such components is only possible due to sanitary standards or technological reasons.

Investigation of the distribution and element content types in coal is constrained by the lack of perfected analysis methods. Mineral elements forms are poorly understood, because processing the mineral sample changes their composition. Bold microelements from coal and converting them into a form suitable for analysis leads to the destruction of their connections with organic coal matter, their complexes by the coal ashing at high temperatures and special additional conditions , which leads to losses and reduces the analysis accuracy. Currently semi-quantitative spectral analysis is used as the identifying primary method and microelements content estimating. The emission spectral analysis on secondary dispersion spectrographs with coal ash sample evaporation is the most common. Semiquantitative spectral determination sensitivity for Tl, Li, Rb, Cs, Ta, In, Cd, Ce, Hg, Th below their possible content in coal, and basic rock-forming elements identifying Si, Al, Fe, K, Na, Mg Ca hasn't sense because these elements in coal ash contain in an amount exceeding 1% and is measured by ISO methods. Sensitivity of semiquantitative methods and approximate quantitative spectral coal ash and host rocks analysis are given in Table [6].

The microelement content determined by quantitative methods (g/t of dry coal)

Element	Au	Co	Cu	Mo	As	Ni	Hg	Ag	Ti	Cr	Zn
The average content level	<0,1	1-15	1-30	1-10	<100	5-100	<1	<1	100-5000	1-100	5-300
Mass search method sensitivity	3	10	1	1	-	1	-	0,1	10	30	10
The lower level measured content	0,1	10	100	10	10	100	5	10	1000	1000	100

For the quantitative microelements determination in solid coal industrial waste, three-dimensional, atomic absorption, electrometric and other analysis methods are used. The use of various methods depends on the element concentration, the interfering element presence, required sensitivity and accuracy of the determination. Most of the tests carried out in the ash after the organic compounds decomposition by ashing, oxidation, sintering or fusing. At ashing partial or complete loss of light volatile elements is frequently occurred.

During the research it was found that the ashing temperature lowering from the

standard 850 °C to 400-500 °C is necessary for the experimental elements determination reliability. At ashing an oxygen excess should be provided, that leads to element compound transition in the less volatile oxides, and slow heating rate should be provide too. Heavy metals are bound in coal. Therefore, for a reliable determination of their number such elements should be transferred into solution as ions.

Samples for analysis conducting should have adequate preparing namely to be dried to air-dry state in the oven or on the air. Grinding tests should be conducted under conditions that avoid getting unnecessary additives. The screening is carried out on a clean sheet of glass or aluminum, may not use the sieve of bronze, brass or tinned grid. Then ashing tests are carried out in laboratory furnace. The resulting ash is mixed with a buffer mixture, dissolved and necessary elements identify is defined by polar graphic method. To determine the various elements different buffer mixtures and dissolving substances are used.

In determining the mercury content in coal or rock ash analysis is not meaningful, because about 90 % of mercury flies by ashing. For analysis of mercury content it must be catch and be put in a solution of iodine, then mercury analyzer "Julia 2" is used to determine by the atomic absorption method. For this purpose an analytical coal sample is put to a tube furnace and it slowly is heated to 800 ± 20 °C. The gases given off are passed through the absorbing vessel, containing 50-100 cm^3 of prepared in advance iodine solution. The resulting solution analysis containing heavy metals extracted from coal or solid waste is produced by the method of polar graphic analysis, which is more sophisticated method.

In conducting ashing at low temperature and the opened oven door process rate decreases. Therefore, the final destruction of chemical bonds, single action microwave is used for 10 minutes in a typical microwave. Thus there is enough light complete destruction of the natural organic coal matter and its products in the (MWF) microwave field. At using microwave ashing complete samples ashing are not achieved. This is due to only technical reasons namely for complete ashing a special container with an inert material that could withstand high temperatures and have a special device to prevent splashing and removal of dust and gaseous products is necessary to have. Therefore, the studied sample was exposed by microwave ashing up to of light smoke appearance, indicating the sample decomposition beginning. Final ashing was carried out in the thermal furnace, but overall time process significantly reduced at the analysis accuracy improving. The results of heavy metals content determination in different coal samples and sludge flotation are given below in the figure.

The data presented in the figure indicate that the decrease in coal samples ashing temperature to 450 °C and the use of microwave field lead to obtaining higher values of heavy metal content. This is due to more complete capture of heavy metal com-

pounds by reducing their losses at ashing by the standard method when the compounds part flies at high temperatures. The accuracy increasing of the heavy metals content in coal and products of its mining and processing for hazardous substances that are a danger to environmental pollution have particular importance.

In addition, the use of microwave action allows greatly increasing analytical study performance by reducing the time loss for analysis.

These data show that the heavy metals concentration in products is about 0,02-0,1%, but for the annual processing volume this figure is quite significant.

Conclusions and directions for further research. The obtained results showed that the developed technique of solid samples preparation and analyzing them for heavy metals content may be useful to detect element concentrations that are of particular interest for industrial use or dangers as harmful components.

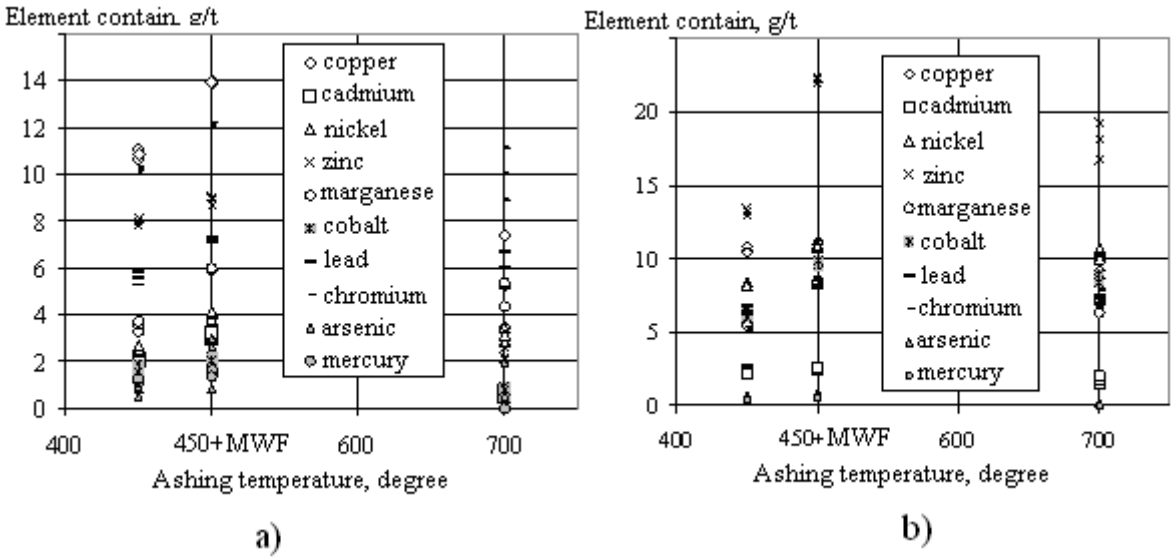

Fig.1 Heavy metals content in coal production and processing:
a - coal, b - flotation sludge

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