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ECOLOGICAL AND GEOCHEMICAL ASPECTS OF THERMAL EFFECTS ON ARGILLITES OF THE LVIV-VOLYN COAL BASIN SPOIL TIPS

Purpose. Determination of the thermal effect (combustion) on the geochemical characteristics of waste rock argillite, and on the leachability of pollutants for establishing the potential of these compounds as a source of drainage and groundwater pollution.

Methodology. The article describes the investigation of argillite, the main component of the basin's waste heaps, the analysis of pollutant leaching from unburned and burned argillite using a washing plant, their X-ray fluorescence analysis, the surface morphology of different types of argillite by scanning electron microscopy (SEM), the qualitative and quantitative composition of samples using energy dispersive X-ray spectroscopy (EDS) and the content of water-soluble heavy metals by atomic absorption.

Findings. As a result of thermal effects on argillite, the salt content in the washing water increases by 2.5 times and reaches 185 ppm in water from unburned rock and 462 ppm from burned rock, the sulfur content in the burned rock after washing decreased by 21.3 times. The variability of changes in the content of water-soluble compounds in the studied samples is also noted, since the amount of Mn, Pb, Cu and Co leached out is up to 15.5 times higher in unburned argillite, but the amount of Fe and Zn leached out after combustion increases up to 17.4 times compared to unburned rock.

Originality. The series of changes in the content of chemical elements and compounds as a result of combustion and rock washing have been established, which are important for assessing and predicting the migration potential of chemical elements from coal dump rocks to soils and waters within coal spoil tips.

Practical value. The conducted research characterises the ecological state of spoil tips and can be used for reclamation or remediation works in these areas, taking into account the degree of rock metamorphism.

Keywords: coal mining waste, leaching, metals, waste heap, environmental safety

Introduction. Coal mining is followed by changes in the geomechanical state of rocks [1, 2], landscape transformation, surface subsidence [3], which creates risks of flooding [4], contamination of soil [5], surface and groundwater [6], waste generation, which has a significant impact on the environment. Their storage in spoil tips (terricones) of various sizes has a high probability of long-term environmental hazards [7, 8]. Specific phytogenic fields are formed in the area of coal mining and coal preparation [9]. The safe disposal and storage of large amounts of waste that accumulate as a result of hard coal mining and preparation, including waste rock, tailings, etc. is an important issue for the mining industry worldwide [10].

Literature review. Weathering, water erosion, and leaching are the main processes that cause pollutants from waste heaps within mining complexes to enter the soil environment, which creates a risk of contamination of groundwater in open aquifers and surface water in the areas of waste heaps [11, 12]. Waste rock dumps often differ in terms of component composition, the level of the thermal impact, structure, organic matter content, and size, which affects the rate of pollutant release [13]. There is also considerable interest in studying the variability and intensity of leaching of various elements from mine waste in the laboratory, since the potential environmental hazards posed by pollutants contained in waste rocks with varying degrees of thermal exposure can be characterized by toxicity, bioavailability, and different geochemical behavior [14, 15].

A particular problem is that coal mining and coal preparation wastes contain sulphide minerals, such as pyrite (FeS_2), chalcopyrite (CuFeS_2), and pyrrhotite (Fe_7S_8) [12]. Sulphide minerals can oxidize when exposed to the air and form dilute sulfuric acid, resulting in a decrease in the pH of waste rock and soil and causing increased migration of metals such as Fe, Al, Mg, Na, K, Co, Ni, Zn, Cu and other elements from waste rock located around mines and entering aquifers. Acidic drainage solutions occur in both active and

decommissioned waste heaps, and therefore acidic components spread over significant distances beyond the mining area, contributing to the pollution of both surface and groundwater with sulfate ions [16].

Self-heating of coal waste is a significant problem in countries where coal mining is carried out. It is known that self-heating depends on many factors, such as the properties of organic matter (mineral composition and species), moisture and pyrite content, climate impact, and storage conditions (form of dumping or compaction of coal waste) [17]. Moreover, oxidation can lead to self-heating with a total temperature of more than 1000 °C, and the process of burning the waste heap can last up to 20 years. During these self-heating processes, both organic and mineral substances undergo oxidative and thermal changes [18].

Joana Ribeiro and others [19] assessed a mixture of coal waste rocks obtained as a result of coal mining. The study found a decrease in the concentration of As, Cd, Co, Mn, Pb, Sb, Sn and Zn in the burnt material, which the authors attribute to the partial evaporation of these elements at high combustion temperatures. The authors believe the presence of metals such as As, Co, Cr, Cu, Mo, Ni, Pb and U in coal spoil tips is an environmental problem.

Unsolved aspects of the problem. The results of the investigations described above were mostly obtained for a mixture of coal mine spoil tips. Such results are valuable, but it is difficult to extend them to other coal basins, as the rocks of different coal basins differ petrographically and geochemically. To obtain more universal information, it is reasonable to conduct more detailed studies of individual coal dump rocks, such as argillites, siltstones, and sandstones, which dominate the composition of the spoil tips. Since argillites make up more than 70 % of the dump rocks in the Lviv-Volyn basin, we focused on their detailed investigation.

In addition, the researchers studied the thermal effect on rocks by analyzing burnt and unburnt mixtures of rocks simultaneously taken from coal spoil tips. However, such samples could have been different in geochemical terms before they

were thermally transformed. Therefore, it is important to study identical rock samples by subjecting them to thermal effects in the laboratory.

Purpose and objectives of the article. The object of the research was the samples of argillite taken from the spoil tip of the Chervonohradska Central Processing Plant (CPP), Lviv region, Ukraine.

The research aims to investigate the thermal effect on the geochemical characteristics of coal-bearing argillite by analyzing its geochemical changes during thermal exposure under laboratory conditions, and the leaching ability of pollutants in order to determine the potential of these compounds as a source of drainage and groundwater pollution.

Research methodology. As mentioned above, the object of the study was samples of argillite from the waste rock of the Chervonohradska CPP spoil tip. Rock samples (10 samples) were taken from different parts of the waste heap to a depth of 0.2–0.3 m. The rock samples were combined, then dried, crushed and separated into fractions. We used two samples of mudstone to achieve our goals: 1 – unburned rock; 2 – rock that has been thermally affected (burned in a muffle furnace for 4 hours at a temperature of up to 600 °C (Fig. 1.) After that, the two samples of argillite were alternately washed with distilled water (8.5 l) for 24 hours (Fig. 2), for which 100 g of the test sample was placed in the column and deionized water was passed through it with an average flow rate of 300 ml/min.

The elemental analysis of the argillite before and after

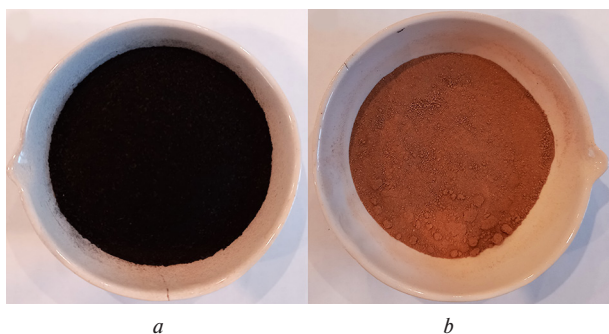


Fig. 1. Argillite:
a – unburned rock; b – burned rock at a temperature of 600 °C

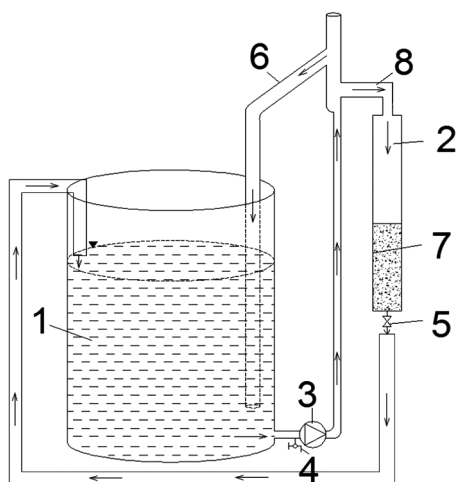


Fig. 2. Experimental stand scheme:
1 – tank for deionized water; 2 – filtration column; 3 – feed pump; 4 – sampling point (before filtration); 5 – filtrate supply point; 6 – overflow pipe; 7 – filter material (argillite); 8 – deionized water distribution pipe to the column (the idea of the stand was derived from [20])

washing was performed using an ElvaX Light SDD X-ray fluorescence analyzer, which is highly sensitive (0.01 %) in a wide range of chemical elements: from ^{11}Na to ^{92}U .

The surface morphology of unburned and unburned washed argillite, as well as burned and burned washed argillite, was studied by scanning electron microscopy (SEM). The qualitative and quantitative composition of the samples was determined using energy dispersive X-ray spectroscopy (EDS) on a Tescan Vega3 LMU electron microscope with an Oxford Instruments Aztec ONE system (CCD Si drift detector X-MaxN20). Before the study, the sample powders were applied to an electrically conductive film. The study was performed at a W-cathode voltage of 15 kV and a vacuum of 10^{-3} Pa. The SE-detector characterizes the surface morphology and details its irregularities, while the BSE-detector demonstrates the contrast of phases with different elemental content.

The concentration of metals in the filtrate after washing unburned and burned argillite was determined by the atomic absorption method using the AAS-115-C spectrometer. Nitrates (NO_3^-) and nitrites (NO_2^-) were determined by the photocolometric method, namely: the content of nitrates – by interaction with a solution of sodium salicylate in a sulfuric acid solution; nitrites – with the Griess reagent. Only soluble forms of ions were determined. The content of chlorides (Cl^-) and bicarbonates (HCO_3^-) was determined by titration, and sulfates (SO_4^{2-}) were determined by mass analysis.

The main findings and conclusions of scientific research.

X-ray fluorescence analysis. The average chemical composition of the mixture of rocks of the Chervonohradska CPP is as follows: SiO_2 – 56.2 %, Fe_2SO_4 – 10.18 %, Al_2O_3 – 23.71 %, CaO – 0.99 %, MgO – 0.73 %, K_2O – 2.44 %, Na_2O – 0.5 %, SO_3 – 7.55 %, TiO_2 – 1.09 %, for a more detailed and in-depth study of the main component of the dump – argillite, the content of which reaches up to 70 %, its chemical composition was analyzed (Tables 1, 2). Analyzing the data on the elemental content of the studied samples, a set of chemical elements, the content of which decreases in the burned material compared to unburned samples, was compiled: Ni (1.3) – Cu, Al (1.2) – Fe, Mn (1.1) – Pb, Cd, Cr, Si, Mg (1.0) – Ti, Co (0.9) – K, P Ca, Na, S, Zr, Zn, Sr, Y, Rb (0.8). The increase in the chemical element content due to combustion (Ni, Cu, Al, Fe, Mn) is probably caused by a decrease in the total mass of the sample. The decrease in chemical element content due to combustion (K, P Ca, Na, S, Zr, Zn, Sr, Y, Rb) may be attributed to the presence of these metals in carbonate and other compounds unstable to thermal effects.

For long-term environmental monitoring and forecasting purposes, it is also important to establish a series of changes in the chemical element content depending on the impact of rainfall. For this purpose, the rock samples were washed using the installation described above. Thus, as a result of washing of unburned argillite, the content of chemical elements decreases in a series: Zn, Ni (1.8) – Mg (1.3) – Pb, Fe, Co, Rb, Mn, Ca (1.2) – Zr, Na, Cr, Ti (1.1) – Cd, Sr, Y, P (1.0) – K, Al, Si, S (0.9) – Cu (0.5). As a result of washing of burnt argillite, the following series of chemical components decrease was obtained: Zn (1.6) – Y (1.3) – Mg (1.2) – Mn, Ca, Fe, Co (1.1) – Na, Ti, Ni, Rb, Zr, Cd, Cu, Al, Si (1.0) – Sr, Cr, P, K (0.9) – Pb (0.8).

The obtained series are important for assessing and predicting the migration potential of chemical elements from the coal dump rocks to the soil and water. The most hazardous and mobile elements in unburnt rocks are Cu, Cd, Sr and in burnt rocks – Pb, Sr, Cr, Cd, Cu, Ni.

According to the results of X-ray fluorescence analysis (Table 2), silicon, aluminum, calcium, iron, and magnesium oxides in unburned argillite contain almost 95.5 % of the mineral component of the sample. Secondary elements

Table 1

Content of chemical elements in argillites of Chervonohradaska CPP based on the results of investigations of native and thermally modified samples under laboratory conditions

Chemical element	Chemical elements content, % wt.			
	Unburnt argillite	Unburned argillite washed for 24 hours	Burnt argillite 600 °C	Burnt argillite 600 °C, washed for 24 hours
Na	<0.242	<0.258	<0.200	<0.208
Mg	4.481 ± 0.271	5.629 ± 0.280	4.278 ± 0.234	5.287 ± 0.233
Al	9.894 ± 0.135	8.988 ± 0.135	11.510 ± 0.124	11.158 ± 0.127
Si	19.968 ± 0.125	17.805 ± 0.122	19.755 ± 0.108	18.941 ± 0.115
P	<0.077	<0.076	<0.064	<0.059
S	1.323 ± 0.014	1.177 ± 0.014	1.086 ± 0.011	0.051 ± 0.005
K	1.476 ± 0.231	1.401 ± 0.240	1.254 ± 0.172	1.140 ± 0.172
Ca	11.989 ± 0.174	13.850 ± 0.184	9.959 ± 0.134	10.701 ± 0.139
Ti	0.454 ± 0.050	0.477 ± 0.054	0.414 ± 0.038	0.423 ± 0.038
Cr	0.016 ± 0.012	0.017 ± 0.014	0.016 ± 0.009	0.015 ± 0.009
Mn	0.416 ± 0.014	0.482 ± 0.016	0.441 ± 0.012	0.498 ± 0.012
Fe	6.901 ± 0.046	8.249 ± 0.055	7.694 ± 0.043	8.235 ± 0.047
Co	<0.018	<0.021	<0.016	<0.017
Ni	0.006 ± 0.003	0.011 ± 0.004	0.008 ± 0.003	0.008 ± 0.003
Cu	0.006 ± 0.002	<0.003	0.007 ± 0.001	0.007 ± 0.001
Zn	0.009 ± 0.001	0.017 ± 0.002	0.007 ± 0.001	0.011 ± 0.001
Rb	0.012 ± 0.000	0.014 ± 0.001	0.009 ± 0.000	0.009 ± 0.000
Sr	0.022 ± 0.001	0.022 ± 0.001	0.017 ± 0.000	0.016 ± 0.000
Y	0.004 ± 0.000	0.004 ± 0.000	0.003 ± 0.000	0.004 ± 0.000
Zr	0.015 ± 0.001	0.017 ± 0.001	0.012 ± 0.000	0.012 ± 0.000
Cd	<0.001	0.001 ± 0.002	<0.001	0.001 ± 0.001
Pb	0.005 ± 0.001	0.006 ± 0.001	0.005 ± 0.001	0.004 ± 0.001

Table 2

The content of chemical compounds in argillites of Chervonohradaska CPP according to the results of X-ray fluorescence analysis

Compound name	Content of the compound (oxide form, % wt.)			
	Unburnt argillite	Unburned argillite washed for 24 hours	Burnt argillite 600 °C	Burnt argillite 600 °C, washed for 24 hours
Na	<0.242	<0.258	<0.200	<0.208
MgO	7.431 ± 0.271	9.335 ± 0.280	7.094 ± 0.234	8.767 ± 0.233
Al ₂ O ₃	18.695 ± 0.135	16.983 ± 0.135	21.747 ± 0.124	21.083 ± 0.127
SiO ₂	42.718 ± 0.125	38.090 ± 0.122	42.262 ± 0.108	40.520 ± 0.115
P ₂ O ₅	<0.077	<0.076	<0.064	<0.059
S	1.323 ± 0.014	1.177 ± 0.014	1.086 ± 0.011	0.051 ± 0.005
K ₂ O	1.778 ± 0.231	1.687 ± 0.240	1.510 ± 0.172	1.374 ± 0.172
CaO	16.775 ± 0.174	19.379 ± 0.184	13.934 ± 0.134	14.972 ± 0.139
TiO ₂	0.758 ± 0.050	0.795 ± 0.054	0.690 ± 0.038	0.706 ± 0.038
Cr ₂ O ₃	0.023 ± 0.012	0.025 ± 0.014	0.024 ± 0.009	0.022 ± 0.009
MnO	0.537 ± 0.014	0.622 ± 0.016	0.569 ± 0.012	0.644 ± 0.012
Fe ₂ O ₃	9.866 ± 0.046	11.793 ± 0.055	11.000 ± 0.043	11.773 ± 0.047
Co ₃ O ₄	<0.018	<0.021	<0.016	<0.017
NiO	0.008 ± 0.003	0.014 ± 0.004	0.010 ± 0.003	0.010 ± 0.003
CuO	0.008 ± 0.002	< 0.003	0.009 ± 0.001	0.009 ± 0.001
ZnO	0.011 ± 0.001	0.022 ± 0.002	0.009 ± 0.001	0.014 ± 0.001
Rb ₂ O	0.013 ± 0.000	0.016 ± 0.001	0.010 ± 0.000	0.010 ± 0.000
SrO	0.025 ± 0.001	0.026 ± 0.001	0.020 ± 0.000	0.019 ± 0.000
Y ₂ O ₃	0.005 ± 0.000	0.006 ± 0.000	0.004 ± 0.000	0.005 ± 0.000
ZrO ₂	0.020 ± 0.001	0.023 ± 0.001	0.016 ± 0.000	0.016 ± 0.000
CdO	<0.001	0.001 ± 0.002	<0.001	0.001 ± 0.001
PbO	0.005 ± 0.001	0.007 ± 0.001	0.005 ± 0.001	0.005 ± 0.001

including potassium, manganese, titanium and sulfur oxides make up approximately 4.4 % of the mineral composition. At the same time, oxides of trace elements: chromium, nickel, copper, zinc, rubidium, strontium, yttrium, zirconium and lead make up about 0.12 %. In the burnt argillite, oxides of silicon, aluminum, calcium, iron, and magnesium contain almost 96 % of the mineral component of the sample, minor elements make up about 3.85 % of the mineral composition, accordingly, the amount of trace element oxides is about 0.1 %.

It should be noted that after burning of argillite, the content of MgO in the rock practically does not change, but after washing, its content increases by an average of 1.24 times in both samples. Rock combustion increases the relative content of Al₂O₃ in the sample by 1.16 times, but has virtually no effect on the amount of this oxide after washing. As for the main component SiO₂, its content in the unburnt rock after washing decreases by 1.12 times, the S content also decreases by 1.12 times, but the amount of CaO increases by 1.15 times, MnO – by 1.16 times.

Upon thermal exposure of argillite, the S content in the rock decreases by 1.21 times, and after washing its content in the burnt rock decreases by 21.3 times, which indicates the effect of burning on its ability to leach. The content of CaO and K₂O decreases in the burnt argillite by 1.2 times, TiO₂ – by 1.1 times, but the content of Fe₂O₃ increases by 1.11 times. It should be noted that the burning of rocks has virtually no effect on the amount of potassium, calcium, manganese, and iron oxides, because, as in the case of unburnt rock, after washing, they increase by about 1.1 times.

The range of decrease in oxides content due to the burning of argillite is as follows: NiO (1.3) – Al₂O₃ (1.2) – CuO, Fe₂O₃, MnO (1.1) – Cr₂O₃, PbO, CdO, SiO₂, MgO (1.0) – TiO₂, Co₃O₄ (0.9) – K₂O, P₂O₅, CaO, ZnO, ZrO₂, Y₂O₃, SrO, Rb₂O (0.8). The decrease in oxide content due to washing of unburnt mudstone is as follows: ZnO (2.0) – NiO (1.8) – PbO (1.4) – MgO (1.3) – Rb₂O, Y₂O₃, Fe₂O₃, Co₃O₄,

MnO, CaO, ZrO₂ (1.2) – Cr₂O₃ (1.1) – TiO₂, SrO, CdO, P₂O₅ (1.0) – K₂O, Al₂O₃, SiO₂ (0.9) – CuO, (0.4). As a result of washing of burnt argillite, we obtain the following series of oxide content reduction: ZnO (1.6) – Y₂O₃ (1.3) – MgO (1.2) – MnO, CaO, Fe₂O₃, Co₃O₄ (1.1) – TiO₂, NiO, PbO, Rb₂O, ZrO₂, CdO, CuO, Al₂O₃, SiO₂, SrO (1.0) – P₂O₅, Cr₂O₃, K₂O (0.9).

SEM of the studied argillite. Fig. 3 shows the surface morphology of the powder samples of the studied argillite.

As can be seen from Fig. 3, the surface area of the grains increased significantly due to heat treatment and washing of the argillite material. The porosity of microcrystallites at the annealing stage increases due to the release of low molecular weight products (H₂O, CO₂, SO₂, H₂S, NH₃, etc.). Washing ensures the leaching of soluble and poorly soluble salts from the argillite matrix, but due to the consolidation (Figs. 3, c, d) of small grains <1–3 μm into aggregates up to 15–20 μm, leaching occurs mainly from the surface layer. This explains the tendency to decrease the leaching of such elements as Mn, Pb, Cu, and Co due to the generation of hardly soluble forms (oxides, phosphates, carbonates, etc.) and due to the blocking of channels and voids in the structure of the matrix. The increase in Fe and Zn content leached from the matrix can be explained by their amphotericity: during annealing, chemical interaction of the components with alkaline and alkaline earth components occurs, resulting in the formation of intermediate compounds that have the ability to leach, probably due to hydrolysis with a shift in the acid-base equilibrium. The elemental distribution shows the homogeneity of the aluminosilicate phase in the argillite matrix and the dynamics of changes in the concentration of leachable components.

Fig. 4 shows the elemental distribution on the sample surface. The ratio of elements for the original sample (unburnt argillite) is O/Mg/Al/Si/S/K/Ca/Ti/Mn/Fe 69.74/2.24/6.40/14.13/0.90/1.06/2.60/0.20/0.11/2.05, the ratio of elements of unburnt, washed argillite is O/Na/Mg/Al/Si/S/K/Ca/Ti/

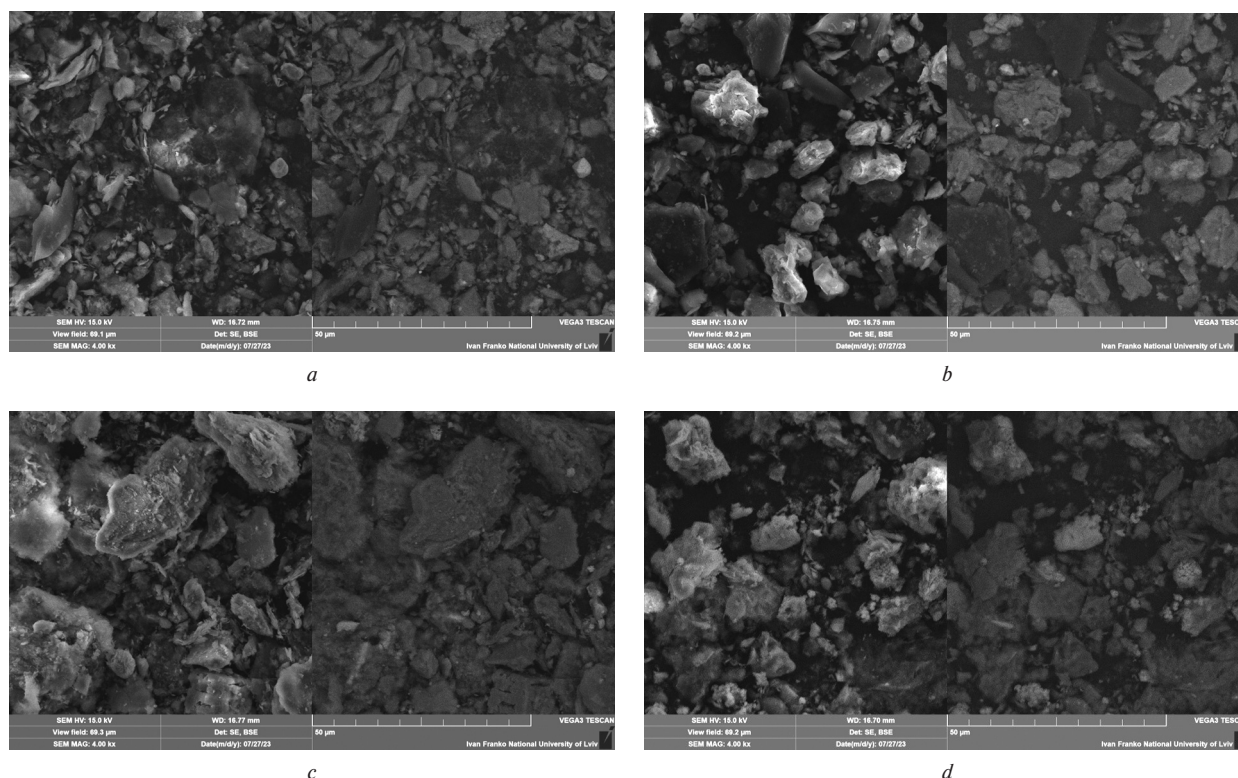


Fig. 3. SEM images of argillite (SE-detector on the left, BSE-detector on the right):

a – unburnt argillite (original sample); b – unburnt argillite, washed for 24 hours; c – argillite burned at 600 °C; d – argillite burned at 600 °C, washed for 24 hours

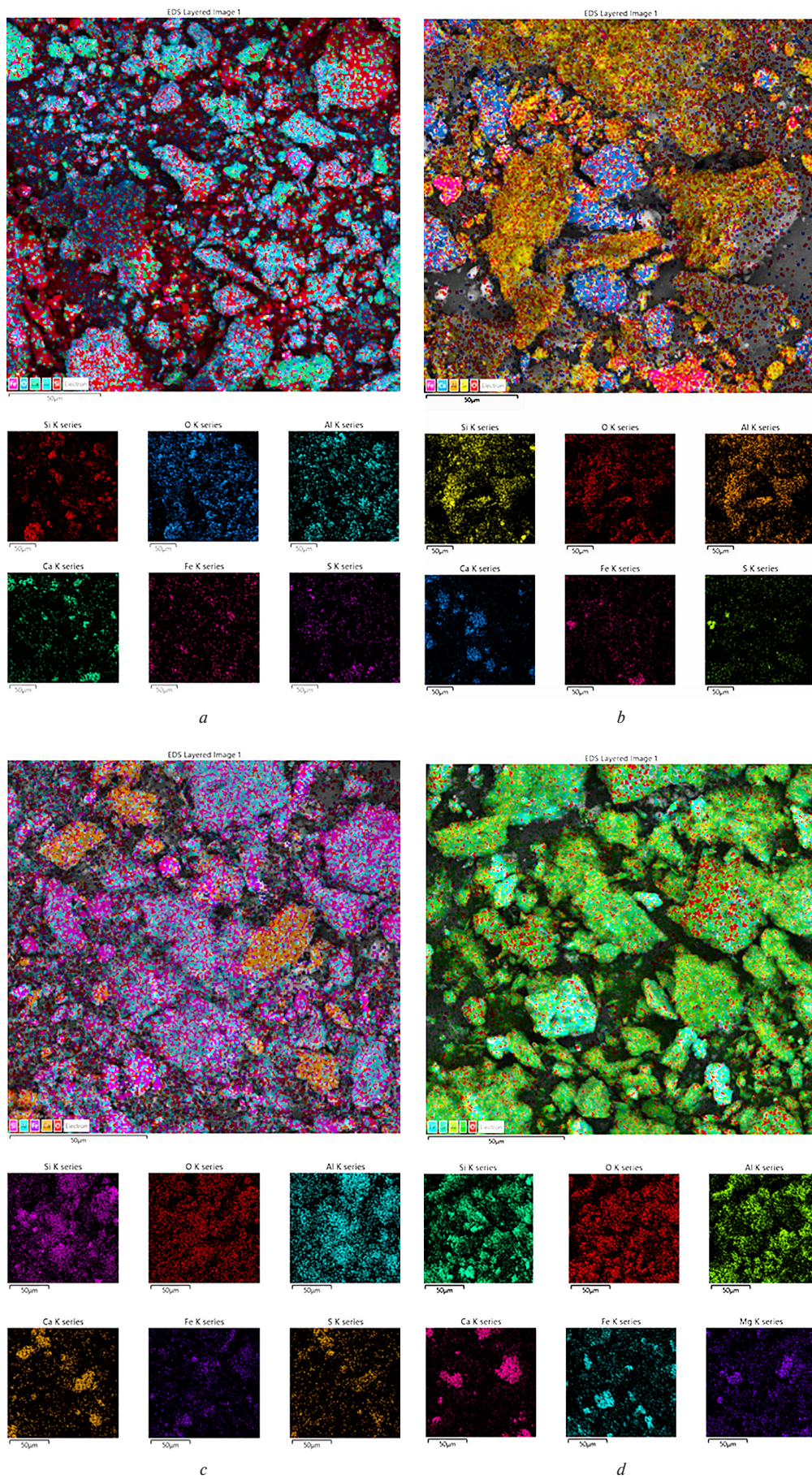


Fig. 4. Elemental distribution on the argillite surface:

a – unburned argillite (original sample); b – unburned argillite, washed for 24 hours; c – argillite burned at 600 °C; d – argillite burned at 600 °C, washed for 24 hours

Mn/Fe 68.20/0.33/2.48/8.29/12.17/1.18/0.77/3.58/0.22/0.11/2.28. The ratio of elemental composition for the sample calcined in a muffle furnace and the calcined washed sample is O/Na/Mg/Al/Si/S/K/Ca/Ti/Mn/Fe 70.35/0.17/1.92/8.49/12.29/0.97/0.81/1.88/0.23/0.11/2.60 and O/Na/Mg/Al/Si/S/K/Ca/Ti/Mn/Fe 70.33/0.12/2.50/8.05/12.03/0.02/0.66/0.23/0.18/3.59 respectively.

Leaching of pollutants. Our results (Table 3) clearly show that the thermal effect due to the burning of waste rock – argillite contributes to an increase in the salt content in the washing water by 3.66 times during the first 2 hours of the experiment and by 2.5 times after the leaching is completed and reaches 185 ppm in unburned rock and 462 ppm in burned rock, the same situation is observed with electrical conductivity, which confirms the data [14] about the increase in mobility of minerals that have been oxidized due to their solubility in water and at the same time increases the leaching of minerals into groundwater.

Table 3

Changes in the mineralization of washing water (filtrate) as a result of laboratory studies of thermal effects on argillite

Duration of the experiment, hours	Mineralization, ppm	
	Unburnt argillite	Burnt argillite
2	50	183
4	97	338
8	120	362
12	144	383
16	156	399
20	162	437
24	185	462

Table 4

The content of potentially hazardous elements (substances) in the filtrate

Index	Filtrate from unburned argillite	Filtrate from burned argillite
Total hardness, mmol/dm ³	2.1	7.56
pH, units	5.96	6.07
Electrical conductivity	370	924
Nitrite (NO ₂ ⁻), mg/l	0.01	0.004
Nitrates (NO ₃ ⁻), mg/l	1.6	1.4
Hydrocarbonates (HCO ₃ ⁻), mg/l	25.6	44.8
Sulphates (SO ₄ ²⁻), mg/l	141.5	318.0
Chlorides (Cl ⁻), mg/l	≤5.0	9.1
Sodium (Na ⁺), mg/l	10.5	7.8
Calcium (Ca ²⁺), mg/l	5.7	10.4
Potassium (K ⁺), mg/l	1.7	5.3
Magnesium (Mg ²⁺), mg/l	4.0	7.8
Ammonium (NH ₄ ⁺), mg/l	1.7	<0.5
Iron, mg/l	0.0022	0.037
Copper, mg/l	0.005	0.006
Zinc, mg/l	0.06	0.02
Lead, mg/l	0.005	0.001
Manganese, mg/l	0.14	0.008
Chromium (Cr ³⁺), mg/l	<0.025	<0.025
Cobalt, mg/l	0.05	0.04

Also, in order to assess the thermal effect on the leaching of potentially hazardous elements, the leachates from unburned and burned argillite were studied (Table 4).

The total hardness in the leachate from the burnt rock is 3.6 times higher than in the leachate from the unburned rock, and the pH of the extracts is slightly acidic. The content of nitrite and nitrate in the leachate from unburned argillite is 2.5 and 1.14 times higher than in the burned one. The amount of Na⁺ in the leachate from the burnt rock decreases by 1.35 times, and ammonium is not detected in the leachate from the burnt rock. The opposite trend is found with SO₄²⁻, its content increases in the filtrate from the burnt rock by 2.24 times, HCO₃⁻ – by 1.75 times, K⁺ – by 3.1 times, Mg²⁺ – by 1.95 times and Ca²⁺ – by 1.82 times, chlorides are found only in the filtrate from the burnt argillite. It can be assumed that Ca²⁺ and Mg²⁺ are interrelated and may come from a related source, such as carbonate minerals.

The content of metals in water-soluble compounds in the studied samples is shown in Fig. 5. It shows that the amount of Mn is 17.5 times higher, Pb 5.25 times higher, Cu 3 times higher, Co 1.25 times higher in unburned clay, but the content of Fe in clay washed out after burning increases by 17.4 times and Zn by 1.2 times.

The results are important for predicting the migration capacity of pollutants and designing environmental protection measures.

Conclusions and prospects for further development in this area. According to the results of X-ray fluorescence analysis, silicon, aluminum, calcium, iron, and magnesium oxides contain almost 95.5 % in the unburned argillite and 96 % in the burned argillite of the mineral component of the sample. Secondary elements, including potassium, manganese, titanium, and sulfur oxides, make up about 4.4 % of the mineral composition of unburned argillite and 3.85 % of burned argillite, and trace element oxides make up about 0.12 % in unburned and 0.1 % in burned argillite.

The series of changes in the content of chemical elements and compounds as a result of combustion and washing were established, which are important for assessing and predicting the migration potential of chemical elements from coal dump rocks to the soil and water. A decrease in the content of chemical elements in the burned material compared to unburned samples was detected in the following range: Ni (1.3) – Cu, Al (1.2) – Fe, Mn (1.1) – Pb, Cd, Cr, Si, Mg (1.0) – Ti, Co (0.9) – K, P Ca, Na, S, Zr, Zn, Sr, Y, Rb (0.8). As a result of washing of unburned argillite, the content of chemical elements decreases in the following series: Zn, Ni (1.8) – Mg (1.3) – Pb, Fe, Co, Rb, Mn, Ca (1.2) – Zr, Na, Cr, Ti (1.1) – Cd, Sr, Y, P (1.0) – K, Al, Si, S (0.9) – Cu (0.5). As a result of washing of burnt argillite, the following series of chemical ele-

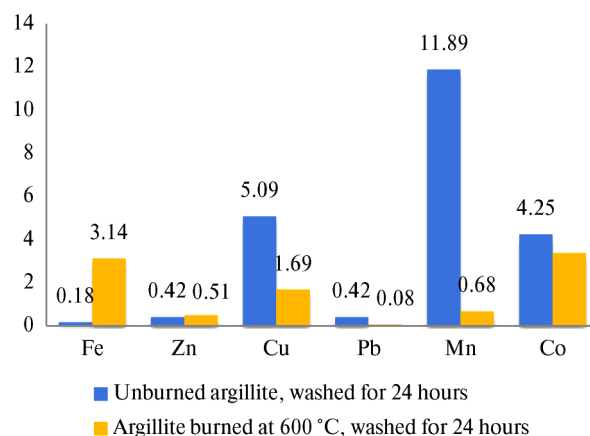


Fig. 5. The content of water-soluble metals in the studied samples, mg/kg

ments decrease was obtained: Zn (1.6) – Y (1.3) – Mg (1.2) – Mn, Ca, Fe, Co (1.1) – Na, Ti, Ni, Rb, Zr, Cd, Cu, Al, Si (1.0) – Sr, Cr, P, K (0.9) – Pb (0.8). Therefore, the most hazardous to the environment and the most mobile elements in unburned rocks are Cu, Cd, Sr, and in burned rocks – Pb, Sr, Cr, Cd, Cu, Ni.

A significant effect on the possibility of sulfur leaching after the burning of argillite was found, which indicates the influence of combustion on its ability to leach and poses a potential threat to water resources. The leaching of potentially hazardous elements, namely sulphates, nitrites and nitrates, and ammonium, is higher in unburned argillite, while the opposite trend was found for potassium, magnesium, and calcium. As for the water-soluble manganese, lead, copper and cobalt, their higher content was found in the leachate from the unburned rock, and iron and zinc in the leachate from the burned argillite, indicating the importance of thermal effects on the water solubility of these elements. Removed by water from the argillite formed during self-heating, such compounds should be considered a serious threat to the environment. The research results provide information on the environmental condition of spoil tips and can be used for recultivation or reclamation work in these areas. Burnt waste heaps are more likely to produce acidic water than unburnt spoil heaps due to the presence of water-soluble sulfates, which are highly susceptible to leaching and oxidation.

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Еколого-геохімічні аспекти термічного впливу на аргіліти відвалів Львівсько-Волинського кам'яновугільного басейну

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Мета. Встановлення термічного впливу (горіння) на геохімічні характеристики аргіліту відвальних порід, а також на здатність вимивання забруднюючих речовин для встановлення потенціалу цих сполук виступати в ролі джерела забруднення дренажних і підземних вод.

Методика. У статті досліджено аргіліт – основну складову породних відвалів Львівсько-Волинського вугільного басейну, проаналізоване вилуговування забруднюючих речовин із негорілого й горілого аргіліту з використанням промивної установки, здійснено їх рентгенофлуорисцентний аналіз, досліджена морфологія поверхні різних видів аргіліту методом скануючої електронної мікроскопії (SEM), визначено якісний і кількісний склад зразків за допомогою енергодисперсійної рентгенівської спектроскопії (ЕДРС) і вміст водорозчинних важких металів атомно-абсорбційним методом.

Результати. Унаслідок термічного впливу на аргіліт збільшується солевміст у промивній воді у 2,5 рази, та сягає 185 ppm у воді з негорілої породи та 462 ppm – з горілої. Вміст сірки у горілій породі після промивання зменшився у 21,3 рази, також спостерігається мінливість зміни вмісту водорозчинних сполук металів у досліджуваних зразках, адже кількість Mn, Pb, Cu і Co, що

вимивається, до 15,5 раз більший у негорілому аргіліті, проте вміст Fe та Zn, що вимивається після горіння, збільшується до 17,4 раз у порівнянні з негорілою породою.

Наукова новизна. Установлені ряди зміни вмісту хімічних елементів і сполук унаслідок горіння та промивання породи, що є важливими для оцінювання та прогнозування міграційного потенціалу хімічних елементів із порід вугільного відвалу у ґрунті й воді в межах вугільних відвалів.

Практична значимість. Проведені дослідження характеризують екологічний стан породних відвалів і можуть бути використані для проведення рекультивації чи меліоративних робіт на даних територіях з урахуванням ступеню метаморфізму порід.

Ключові слова: *відходи вуглевидобутку, вилуговування, важкі метали, терикон, екологічна безпека*

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