

**INVESTIGATION OF DEPARTMENT OF CHALCOPHILIC HEAVY METALS
IN THE WASTE ROCK OF CENTRAL COAL ENRICHMENT PLANT
"CHERVONOHRADSKA" FOR THE PURPOSES OF ENVIRONMENTAL SAFETY
OF LVIV-VOLYN COAL BASIN**

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Abstract. Mining areas are centres of increased environmental danger. This is due to the development and operation of mines and subsequent beneficiation of coal, as well as the storage of significant volumes of empty waste rock in landfills. An important component of ensuring environmental safety is the investigation of the factors and ways of the impact of rock dumps on the state of the environment. In this regard, the article examines the forms of heavy metals found in the rock of the waste heap of the central coal enrichment plant "Chervonohradaska" of the Lviv-Volyn coal basin. The environmental hazard factors caused by the distribution of various forms of lead, cadmium, zinc, and copper, based on establishing the migration capabilities of these elements in the technogenesis zone, are analyzed. It was determined that the gross content of lead reaches 16.32 mg/kg, cadmium – 5.84 mg/kg (exceeding clarke up to 29.2 times in siliceous siltstone and siltstone), zinc – 421 mg/kg (exceeding clarke up to 5.26 times in sandstone, siltstone and siliceous siltstone), copper – 112.89 mg/kg (exceeding clarke by 2 times in siltstone). The concentration coefficients of heavy metals in the samples were determined in relation to the gross form. The results of the research give a reason to evaluate the rocks of the waste dump in terms of the distribution of various forms of Pb, Cd, Zn and Cu as dangerous for the environment and unsuitable for use because in all the samples an excess content was observed in one form or another.

Keywords: coal mining, department of heavy metals, environmental safety, waste dumps, coal beneficiation waste.

1. Introduction

The anthropogenic impact of coal mining in the Chervonohrad Mining and Industrial District (ChMID), which is located within the Lviv-Volyn coal basin, occurs due to the concentration of man-made coal objects – mining infrastructure, mines, a beneficiation factory, waste from coal mining and coal beneficiation, as well as waste heaps on relatively an insignificant area of 180 km², which stimulates changes and degradation in the environment. The waste rocks formed in the waste heaps are piled up right next to the mines. On the territory of the ChMID there are 14 waste dumps of coal mining mines: "Chervonohradaska", "Chervonohradaska #1", "Stepova", "Lisova", "Vidrodzhennya", "Velykomostivska", "Velykomostivska #3", "Velykomostivska #4", "Zarichna", "Mezhyrichanska", "Vizeyska", "Nadia", "Velykomostivska No. 6", "Bendyuska" – and the

dump of PJSC “Lviv Coal Company” occupying different areas – from 0.09–0.1 to 0.29–0.30 km² (Bryk et al., 2019), however, the largest waste heap of the mining district with an area of 0.85 km² was formed as a result of the activities of the central coal enrichment plant “Chervonohradska” (CCEP “Chervonohradska”), which occupies an area of 0.63 km².

CCEP “Chervonohradska” was put into operation in 1979. It enriches poor coal from all mines of the coal basin, the waste generated as a result of the technological process belongs to the 4th class of hazard. The main waste dump of the CCEP “Chervonohradska” reaches a height of 68 m. By the mineralogical composition, the rock of the dump, according to various data, contains on average: argillite – 70–97 %, siltstone – 8–28 %, sandstone – 1–20 %, coal – 1–7 %, pyrite – 1 %, humidity – 6–7 %, ash content of rocks is 54–94 %. The chemical composition of the rock (average of 4 types) is as follows: SiO₂ – 56.2 %, Al₂O₃ – 23.71 %, Fe₂SO₄ – 10.18 %, K₂O – 2.44 %, TiO₂ – 1.09 %, CaO – 0.99 %, MgO – 0.73 %, Na₂O – 0.5 % (Baranov, Knysh, 2007; Baranov, 2008).

The aim of the research is to assess the factors of ecological danger of the environment in the zone of influence of the waste dump of the CCEP “Chervonohradska” caused by the distribution of mobile forms of chalcophilic heavy metals. According to the geochemical classification of the Norwegian geochemist V. M. Goldschmidt (early 20th century), metals of the chalcophilic group are chemical elements that naturally form stable sulfide compounds. The article examines the gross, bioavailable, and soluble forms of such representatives of the chalcophilic group of chemical elements as Pb, Cd, Zn, and Cu in the zone of influence of the waste heap of the CCEP “Chervonohradska”.

2. Materials and Methods

The objects of the investigation were waste rock samples from the CCEP “Chervonohradska” waste heap, namely argillites, siltstones, sandstones, and siliceous siltstone. The selection of rock samples was carried out in different parts of the tericon from a depth of 0.2–0.3 m. All samples were dried, crushed and divided into fractions, and extractions from the rocks were made from the combined samples. The preparation of solution extracts from rocks was carried out as follows: the gross form of lead was determined after the destruction of the rock by 1 n. HNO₃ in the

presence of H₂O₂; mobile forms – from acetate-ammonium buffer solution (AABS) with pH 4.8, and water extraction using distilled water (Kuznetsov et al., 1992). AABS extracts chemical elements in ion-exchange form, which are the most available to plants and are also called bioavailable. In the vast majority of scientific reports and standards of Ukraine (DSTU 4770.1:2007-4770.9:2007), the amounts of metals extracted with an acetate-ammonium buffer solution are equated with mobile forms of metals, at the same time, metals extracted by water are mobile as well. To get each of the extracts, separate native samples were used, which were in a certain solution for a day. The “rock-solution” mass ratio of 1:10 was maintained. The determination of heavy metal content in each of the extracts was carried out by the atomic absorption method using the AAS-115-M-1 spectrometer.

Gross forms of heavy metals were compared with their clarkes in rocks. The tables contain information on the values of MAC in soils not for direct comparison but as additional information considering that the studied rocks are located on the day surface and are the parent rock for technozems which are formed very quickly together with specific phytogenic fields (Popovych, 2021).

3. Results and Discussion

3.1. Variability of the content of total forms of heavy metals

The gross content of heavy metals should be used to estimate their total content in waste rocks and determine the potential danger to the environment. The results of gross content determination in the waste rock of the CCEP “Chervonohradska” are presented in Table 1. There is also a brief description and comparative characteristics of the content of the studied heavy metals content in soils, coal deposits and waste dumps of coal mining.

The average content of lead in the Earth's crust ranges from $1.25 \cdot 10^{-3}$ to $2 \cdot 10^{-3}$ wt. % (Holland, Turekian, 2011), clarkes in brown coal – 6.7 ± 0.4 g/t (coal), 39 ± 2 g/t (ash), in hard coal – 9.0 ± 0.9 g/t (coal), 56 ± 7 g/t (ash) (Yudovich, Ketris, 2005), the average Pb content in coal of the Lviv-Volyn coal basin is 9.5 g/t, clarkes in sedimentary rocks (clays, argillites) – 20 g/t (Knysh, Karabyn, 2010). It is known that the average content of Pb in soils is 10 (2–200) mg/kg (Kyrylchuk, Bonishko, 2011).

Table 1

The gross content of heavy metals in the waste rock of the CCEP “Chervonohradska”

Metal	Class of hazard	Clarke, g/s	MAC for soils, mg/kg (Nakaz MOZ, 2020; Ryzhuka et al., 2003)	Heavy metals content (gross content) in the rock, mg/kg			
				Argillite	Siltstone	Sandstone	Siliceous siltstone
Pb	1	20	32.0	14.11	16.12	16.32	16.0
Cd	1	0,2	1.5	1.31	5.84	1.02	1.7
Zn	1	80	100.0	9.47	148.17	97.92	421.0
Cu	2	57	55.0	4.63	112.89	12.24	14.0

The content of gross forms of Pb in the waste rock of coal mines of the Lviv-Volyn coal basin in a mixture of rocks ranges from 19.1 to 41.4 mg/kg (Knysh, 2008; Knysh, Karabyn, 2010; Knysh, Karabyn, 2014), and in the waste dump of the Vizeyska mine, which borders the object of the research, this indicator is in the range of 4.72–16.97 mg/kg. As for waste mine rocks of Western Donbas, the gross lead content is 18.3 (15–20) mg/kg (Kroik et al, 2010).

As the research shows (Table 1), there is a slight variability in the content of gross forms of lead in rocks and it increases in the range of argillite – siliceous siltstone – siltstone – sandstone. Clarke of gross content was not exceeded in the studied samples. According to data (Beshlei, 2016), the gross content of Pb in the unburnt rock of the CCEP “Chervonohradska” waste heap is 10.4 mg/kg, in burned-out rock, it is 7.8 mg/kg, according to P. Bosak's research (Bosak et al., 2020), its content in the rocks of mine No 9 “Novovolynska” ranges from 5 to 14 mg/kg.

The content of cadmium in the earth's crust ranges from $1.3 \cdot 10^{-5}$ to $5 \cdot 10^{-4}$ wt. % (Holland, Turekian, 2011), clarke in brown coal – 0.24 ± 0.03 g/t (coal), 1.0 ± 0.14 g/t (ash), and in hard coal – 0.20 ± 0.05 g/t (coal), 1.5 ± 0.3 g/t (ash), the background content of cadmium in the coal of the former USSR is estimated at 0.5 g/t (Yudovich, Ketris, 2005). The prevalence of Cd in igneous and sedimentary rocks does not exceed 0.3 mg/kg, the average content in soils is between 0.07 and 1.1 mg/kg, and according to M. B. Kirkham 0.5 (0.01–0, 7) mg/kg, while background levels of Cd in soils do not exceed 0.5 mg/kg (Kyrylchuk, Bonishko, 2011; Kabata-Pendias, Pendias 2001).

According to the conducted research (Table 1), the concentration of gross forms of cadmium in rocks increases in the range of sandstone - argillite - siliceous siltstone – siltstone, and a significant excess of Clarke for rocks (0.2 g/t) is observed from 6 times in sandstone to 29 times in siltstone. According to data (Beshlei, 2016), the gross content of Cd in the unburned rock of the CCEP “Chervonohradska” waste

dump is 0.28 mg/kg, in unburnt rock – 0.38 mg/kg, which is significantly different from our data. However, the wide variability of concentrations is characteristic of chemical elements with low content in the Earth's crust.

It is known that the content of zinc in the earth's crust ranges from 0.004 to 0.02 wt. % (Holland, Turekian, 2011), the zinc content in brown coal is 18 ± 1 g/t (coal), 110 ± 10 g/t (ash); in hard coal – 29 ± 2 g/t (coal), 170 ± 10 g/t (ash), background content in the coal of the former USSR – on average 30 g/t (Yudovich, Ketris, 2005), average Zn content in the coal of the Lviv-Volyn coal basin is 24 g/t, clarke in sedimentary rocks (clays, argillites) – 80 g/t (Knysh, Karabyn, 2010). Zinc is present in rocks mainly in simple sulfide ZnS, and also replaces Mg^{2+} in silicates. Regional zinc levels for Ukraine (mg/kg soil) are as follows: Polissya Livoberezhne (left-bank) – 48 (10–96), Pravoberezhne (right-bank – 37 (9–57), Zahidne (western) – 38 (8–61); Forest Steppe – 52 (20–90); Step – 62 (33–100); Donbas – 55 (34–80); the Carpathians: Precarpathia – 85 (60–145), Transcarpathia – 89 (45–237), mountainous part – 67 (45–98). The background content of zinc in the soils of cities adjacent to landfills in the Lviv region varies from 12.63 to 26.90 g/t (Voitsikhovska, 2013). Clarke Zn according to Vinogradov and its average content in soils is 50 (10–300) mg/kg (Kyrylchuk, Bonishko, 2011; Fatieiev, Pashchenko, 2003).

The results of research (Table 1) show that the content of gross forms of zinc in rocks increases in the range of argillite – sandstone – siltstone – siliceous siltstone, and changes in a wide range from 9.49 to 421.0 mg/kg. The excess of the MAC (for soil) in siltstone is 1.48 times, and in siliceous siltstone, it is 4.21 times. The zinc content in sandstone is 1.22 times, in siltstone – 1.85 times, and in siliceous siltstone – 5.26 times higher than that of Clarke in sedimentary rocks. For comparison, the gross content of Zn in the unburned rock of the CCEP “Chervonohradska” waste dump (Beshlei, 2016) is 27.5 mg/kg, and in burned

rock, it is 26.8 mg/kg. According to (Bosak et al., 2020), its content in the rocks of Mine No 9 “Novovolynska” ranges from 13 to 19 mg/kg. The average zinc content in the waste rock of the Vizeyska mine is 46.14 g/t (Knysh, 2008), the average gross Zn content in the waste mine rocks of Western Donbas is 75 (30–100) mg/kg (Kroik et al., 2010).

The average content of copper in the earth's crust ranges from 0.0047 to 0.1 wt. % (Holland, Turekian, 2011), copper content in sedimentary rocks (clays, argillites) is 57 mg/kg, and the average copper content in soils is 20 (2–100) mg/kg (Knysh, Karabyn, 2010; Kyrylchuk, Bonishko, 2011), in city soils of the Lviv region adjacent to landfills varies from 3.1 to 14.7 g/t (Voitsikhovska, 2012). The average concentration in coal is somewhat lower than in sedimentary rocks and soils. In hard coal, the clark of copper is 17 ± 1 g/t and 110 ± 10 g/t in ash (Yudovich, Ketris, 2005).

According to the conducted research (Table 1), there are significant changes in the gross content of copper in the range of argillite – sandstone – siliceous siltstone – siltstone from 4.63 to 112 mg/kg, and there is a 2.05-fold excess of the MAC (for soil) in the gross form in siltstone. According to (Beshlei, 2016), the gross content of Cu in the unburnt rock of the CCEP “Chervonohradska” waste dump is 191.4 mg/kg; in burnt rock, it is 128.6 mg/kg. According to (Bosak et al., 2020), its content in the rocks mine No. 9 “Novovolynska” ranges from 7 to 39.5 mg/kg. For comparison, the concentration of copper in the tailings of the Viseyska mine ranges from 8.04 to 65.89 mg/kg,

and the content of gross forms of Cu in the tailings of coal mines of the Lviv-Volyn coal basin in the mixture of rocks ranges from 6.5 to 65.53 mg/kg, more detailed information is presented in (Karabyn, Kochmar, 2017). The average copper content in the waste mine rocks of Western Donbas is 38.3 (20–50) mg/kg, in the rock of the mines of the Krasnodon Coal Mine is 30 mg/kg (Kroik et al., 2010; Bohach, 2013).

3.2. Variability of heavy metals content in ammonium acetate extract and water-soluble form

As already mentioned above, the gross content of heavy metals shows their total amount in the rocks, therefore, this indicator is insufficient to assess the impact of coal beneficiation waste dumps on the environment. From the point of view of environmental safety, the peculiarities and migration routes of heavy metals in man-made landscapes are of great interest. The investigation of the migration capabilities of heavy metals is mainly carried out in acetate-ammonium and water extracts, which makes it possible to determine their mobility and bioavailability. It is known that such elements as Zn, Cu, Pb and Cd will be mobile and weakly mobile in an oxidizing and clay environment, and they will be inert in a reducing hydrogen sulfide environment (Kyrylchuk, Bonishko, 2011). The results of the determination of heavy metals content in acetate-ammonium and water extracts from the waste heap of the CCEP “Chervonohradska” are presented in Table 2.

Table 2

The content of mobile forms of heavy metals in waste rock of the CCEP “Chervonohradska”

Metal	MAC in soils, mg/kg (Nakaz MOZ, 2020)	Metals content in the waste rocks, mg/kg			
		Argillite	Siltstone	Sandstone	Siliceous siltstone
Pb*	6.0	4.49	2.69	7.6	6.29
Cd*	–	0.349	0.39	0.02	0.19
Zn*	23	3.99	6.39	11.0	19.49
Cu*	3.0	0.59	1.69	1.7	1.09
Pb**	–	0.22	0.23	0.15	0.26
Zn**	–	0.51	0.09	0.1	0.07

* AABS pH 4.8;

** water extract.

The lead content in siliceous siltstone and sandstone exceeded MAC by 1.04 and 1.26 times, respectively (Table 2). In terrestrial landscapes, Pb is mainly characterized as a low or medium barrier element: the limit of its absorption by vegetation is close to the biogeochemical background, which

explains the high toxicity of Pb for plants (Yudovich, Ketris, 2005). It is known that the content of mobile forms of lead in soils is 4.4 (0.05–46) mg/kg (Kyrylchuk, Bonishko, 2011).

The concentration of water-soluble lead is in the range of 0.15–0.26 mg/kg (Table 2). For comparison,

the concentration of Pb in the waste rock of the Vizeyska mine in the acetate-ammonium buffer solution is within the range of 0.99–1.5 mg/kg, and in the water extract, it is 0.48–1.25 mg/kg. According to (Kroik et. al, 2010), the average content of water-soluble forms of Pb in waste mine rocks of Western Donbas is 0.77 mg/kg.

The content of bioavailable cadmium determined using an ammonium-acetate extract with a pH of 4.8, increases in the range of sandstone - siliceous siltstone – argillite – siltstone and range from 0.02 to 0.39 mg/kg (Table 2), determination of water-soluble forms was not carried out. It is known that the average content of the mobile form of Cd for soils is 0.06 (0.01–0.5) mg/kg (Kyrylchuk, Bonishko, 2011).

It is generally assumed that zinc is a more inherent element of soils than other heavy metals, its characteristic feature is its biophilicity, therefore it is present in significant quantities in all plants, the average content of the mobile form of Zn in soils is 9.6 (0.01–200) mg /kg (Yudovich, Ketris, 2005; Kyrylchuk, Bonishko, 2011; Kabata-Pendias, Pendias 2001). According to the research, its content in the acetate-ammonium buffer solution (Table 2) increases in the range of argillite – siltstone – sandstone – siliceous siltstone and ranges from 3.99 to 19.49 mg/kg without exceeding the established MAC in soils. In water extract the content of zinc is in the range from 0.07 mg/kg in argillite to 0.51 mg/kg in siltstone. For comparison, the content of water-soluble forms of Zn in waste mine rocks of Western Donbass is 1.24 (0.2–3.0) mg/kg (Kroik et al., 2010).

The content of copper in the waste rock of the CCEP “Chervonohradska” ranges from 0.59 mg/kg in argillite to 1.7 mg/kg in sandstone and it does not exceed the established MAC for soils in acetate-ammonium extraction (Table 2). For comparison, in the waste rock of the Vizeyska mine, it reaches 0.5–5.49 mg/kg (Karabyn, Kochmar, 2017). The determination of the content of water-soluble forms in waste rocks of the CCEP “Chervonohradska” was not carried out. The average content of mobile forms of copper in soils is 2.9 (0.02–19.2) mg/kg (Kyrylchuk, Bonishko, 2011).

It should be noted that the assessment of the environmental impact of mobile forms of heavy metals is negatively affected and complicated by the absence of their MAC in waste rock, both for gross and bioavailable/water-soluble forms, which does not allow for a full assessment of their hazard to the environment.

3.3. The regularities of change of content coefficient of mobile forms of heavy metals with regard to their gross form

The investigation of the gross and bioavailable forms of heavy metals in the waste rock of the CCEP “Chervonohradska” makes it possible to determine the ratio between the content of chemical elements in different forms and to predict the possibility of migration of mobile forms of elements in the environment. The content (transition) coefficients were calculated as the ratio of the content of the element in acetate-ammonium and water extracts to their content in gross form.

The rocks of the CCEP “Chervonohradska” waste dump are characterized by very variable coefficients of transitions between different forms of heavy metals (Fig. 1, Fig. 2). Relatively to the gross form, the Pb concentration coefficients in the acetate-ammonium extract change as follows: siltstone – 0.1667, argillite – 0.3181, siliceous siltstone – 0.3931, sandstone – 0.4656; in water extract: siliceous siltstone – 0.0093, siltstone – 0.0137, sandstone – 0.0142, argillite – 0.0184.

Relatively to the gross form, the Cd content coefficients in the acetate-ammonium extract are: sandstone – 0.0196, siltstone – 0.0666, siliceous siltstone – 0.1117, argillite – 0.2671.

Relatively to the gross form, the Zn content coefficients in the acetate-ammonium extract are: siltstone – 0.0431, siliceous siltstone – 0.0462, sandstone – 0.1123, argillite – 0.4208; in water extraction: siliceous siltstone – 0.0002, sandstone – 0.0010, siltstone – 0.0034, argillite – 0.0078. These data are comparable to zinc content coefficients in soils adjacent to landfills in the Lviv region. Content coefficients in the ammonium acetate extract relative to the gross form range from 0.099 (soils near the Lviv landfill) to 0.1976 (soils near the Truskavetsky landfill), in the water extract – from 0.0018 to 0.0264 (Voitsikhovska, 2013).

Relatively to the gross form, the Cu content coefficients in the acetate-ammonium extract are as follows: siltstone – 0.0149, siliceous siltstone – 0.0778, argillite – 0.1194, sandstone – 0.1388. According to data (Karabyn, 2012), the copper concentration coefficients in the acetate-ammonium extract compared to the gross form in the soils adjacent to the Lviv landfills vary from 0.0789 (soils near the Lviv landfill) to 0.1773 (soils near the Drohobyt'sky landfill).

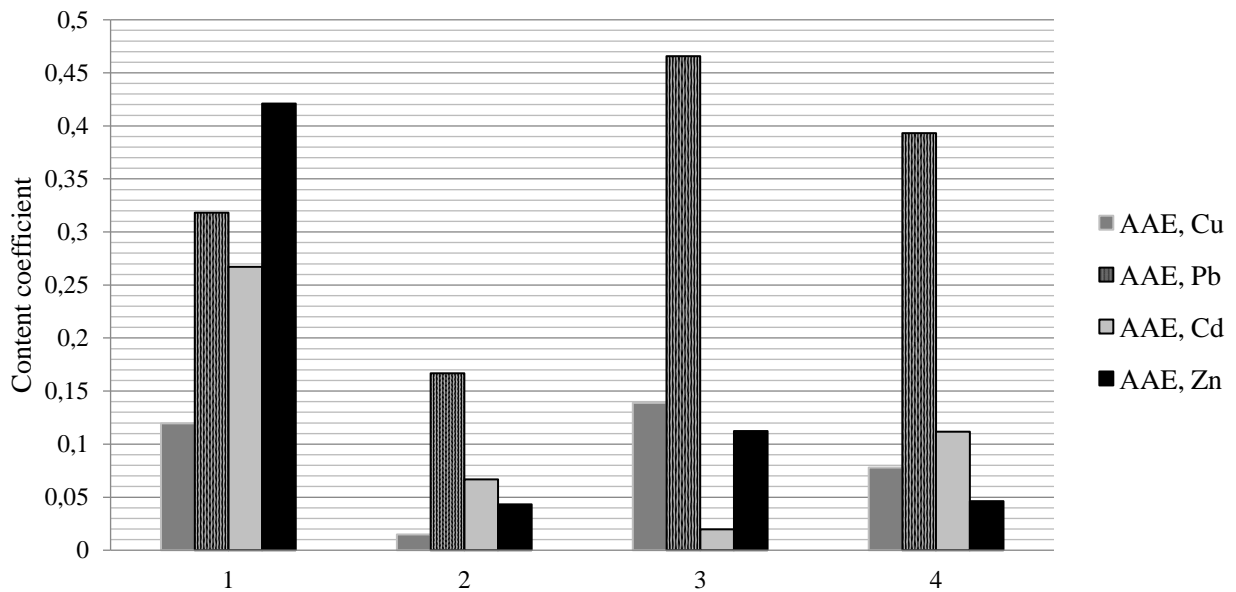


Fig. 1. Content coefficients of heavy metals in acetate-ammonium extract (AAE) relative to the gross form: 1 – argillite, 2 – siltstone, 3 – sandstone, 4 – siliceous siltstone

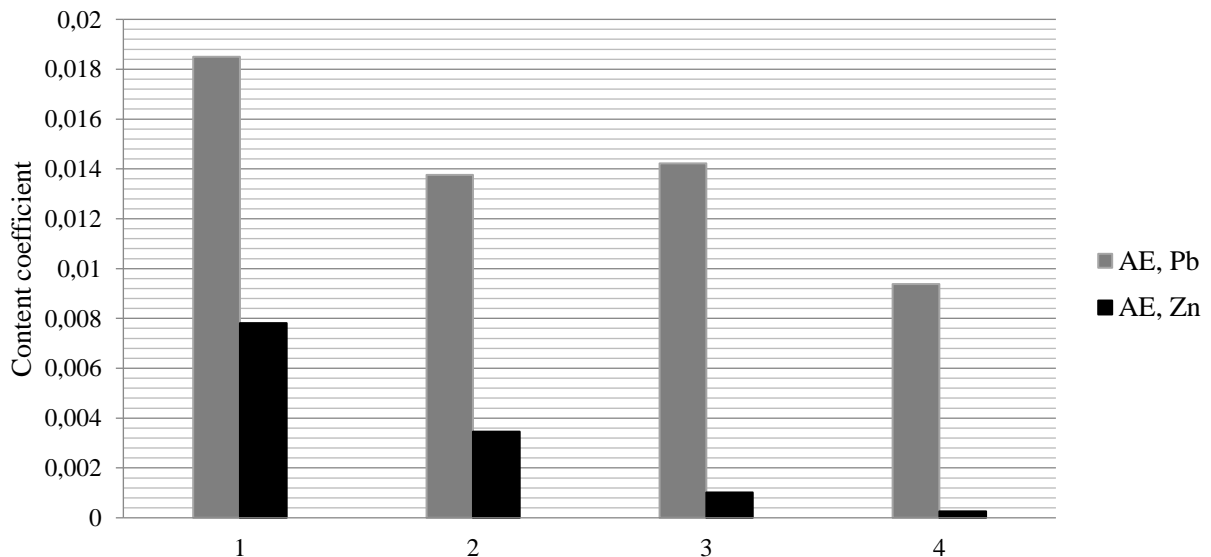


Fig. 2. Content coefficients of heavy metals in the aqueous extract (AE) relative to the gross form: 1 – argillite, 2 – siltstone, 3 – sandstone, 4 – siliceous siltstone

According to the obtained data, it can be concluded that copper is characterized by the smallest content coefficient of transition to the acetate-ammonium extract relative to the gross form – the average value is 0.0877, cadmium is 0.1163, zinc is 0.1556, and lead is the largest – 0.3359. As for the coefficients of the transition to the water extract relative to the gross form, the obtained results show that the lowest indicators are characterized by zinc 0.0031, the largest by lead 0.0139. From Fig. 1, it follows that in the vast majority of cases, argillite, sandstone and siliceous siltstone are characterized by the largest content coefficients of mobile forms (AAE) of heavy metals in relation to

gross metals forms, siltstone is the smallest, and argillite is characterized by the largest content coefficients of mobile forms (BV) of heavy metals in relation to gross metals content, smaller - siltstone and sandstone, the smallest is siliceous siltstone.

4. Conclusion

1. The CCEP “Chervonohradska” carries out enrichment of poor coal from all mines of the Lviv-Volyn coal basin, the rocks of its waste heap are represented mainly by argillite – 70–97 %, siltstone – 8–28 %, sandstone – 1–20 %, etc.

2. A comprehensive study of the heavy metals department in the waste rocks was conducted, it should be noted that a number of investigations on the determination of mobile forms for this object were conducted for the first time. Excess of MAC (in soils) in gross forms in the following heavy metals was found: cadmium in siliceous siltstone – 1.7 mg/kg and siltstone – 5.84 mg/kg; zinc in siltstone – 148.17 mg/kg and siliceous siltstone – 421.0 mg/kg; copper in siltstone – 112.89 mg/kg. Also, as a result of our research, excess of the MAC of mobile forms (acetate-ammonium buffer solution with pH 4.8) was established for lead in siliceous siltstone – 6.29 mg/kg and sandstone – 7.6 mg/kg.

3. Relative to the gross form, the content coefficients of heavy metals in the acetate-ammonium extract vary in a wide range, the smallest for copper is an average value of 0.0877, and characterizes it as a slow-moving heavy metal, and the largest for lead is 0.3359, which refers to 1st class of hazard. Heavy metals concentrated in waste rocks are immobile in water extraction.

4. Waste rocks of the CCEP "Chervonohradska" are hazardous to the environment in terms of the distribution of various forms of heavy metals of the chalcophilic group in rocks.

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