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HEAVY METALS DISTRIBUTION IN THE WASTE PILE ROCKS OF CHERVONOGRADSKA MINE OF THE LVIV-VOLYN COAL BASIN (UKRAINE)

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ABSTRACT

Chervonogradska mine of the Lviv-Volyn coal basin (Ukraine) has been producing humic coal from four beds of Namurian carbon formation since 1971. The waste pile (2.9 mln m^3 of the rock) has been formed as a result of the mine activity. The authors of this article state that the waste pile rocks contain argillite (83.8%), aleurolite (8.4%), sandstone (4.8%) and coal. The ash content of the rocks ranges from 47 to 98% and on average makes up 67.9%. The waste pile rocks have been compared with clark in siltage (clay, argillite) enriched with Cobalt (Cc 5.4), Lead (Cc 2.1), Manganese (Cc 1.9), Yttrium (Cc 1.7), Copper (Cc 1.2), Terbium and Beryllium (Cc 1.1). The waste pile rocks have Titanium(Cc 1.0), Vanadium (Cc 0.9), Zirconium (Cc 0.8) in quantities close to clark for sedimentary rocks. On the basis of middle, median content of chemical element, the distribution area of the chemical elements high content and their toxicity, we think that the most dangerous for environment are Lead, Manganese, Cobalt and Copper. It has been substantiated that Lead, Manganese, Copper and Cobalt can get into the rocks of aeration zone adjacent to the waste pile and into the water of the Solokiya river in excessively high background quantities. To prevent possible pollution of rocks adjacent to waste pile and the water of the Solokiya, the Western Buh, and the Visla with the above mentioned chemical elements we have proposed to create geochemical artificial barriers along the perimeter of the waste pile.

KEY WORDS : Chervonogradska coal mine, Waste pile, Coal, Heavy metals, The Solokiya.

INTRODUCTION

Development of coal deposits involves taking out large volumes of rocks, water and gas. Mining one ton of coal by drilling takes out to the surface nearly 100 m^3 of rock, 3 m^3 of mine water, 13 m^3 of methane, 8 m^3 of dioxide carbon (Aleksandrov, 1979).

Substances which are taken out from earth in the process of coal mining are often toxic (Baba and Türkman, 2001; Kim *et al*., 2003; Knysh and Karabyn, 2003; Knysh and Karabyn, 2010; Zheng *et al*., 2007). It leads to the formation of specific man-caused geochemical systems in upper horizons of lithosphere and on its surface, in particular, waste pile – ground - underground water, or mine water - superficial water – ground.

In Ukraine the development of coal is concentrated in three basins: Donetsk and the Lviv – Volyn coal basins and Dnipro lignite basin. The Lviv – Volyn coal basin is located in Western Ukraine close to the boundary with Poland. The coal is produced in 11 mines. Waste pile rocks of one of them, namely Chervonogradska is the object of our research (Fig. 1).

The Buh (in Ukraine – The Western Buh) flows to the north on the territory of coal basin and has numerous influxes, from which the Rata and the Solokiya are basic. In Ukraine and Poland the water from the Buh is used for drinking and economic purpose. The Rata and the Solokiya rivers are left influxes of the Buh and flow through the coal mine fields, in particular, the Solokiya flows through the field of Chervonogradska mine.

It is known that wastes of the coal mining often

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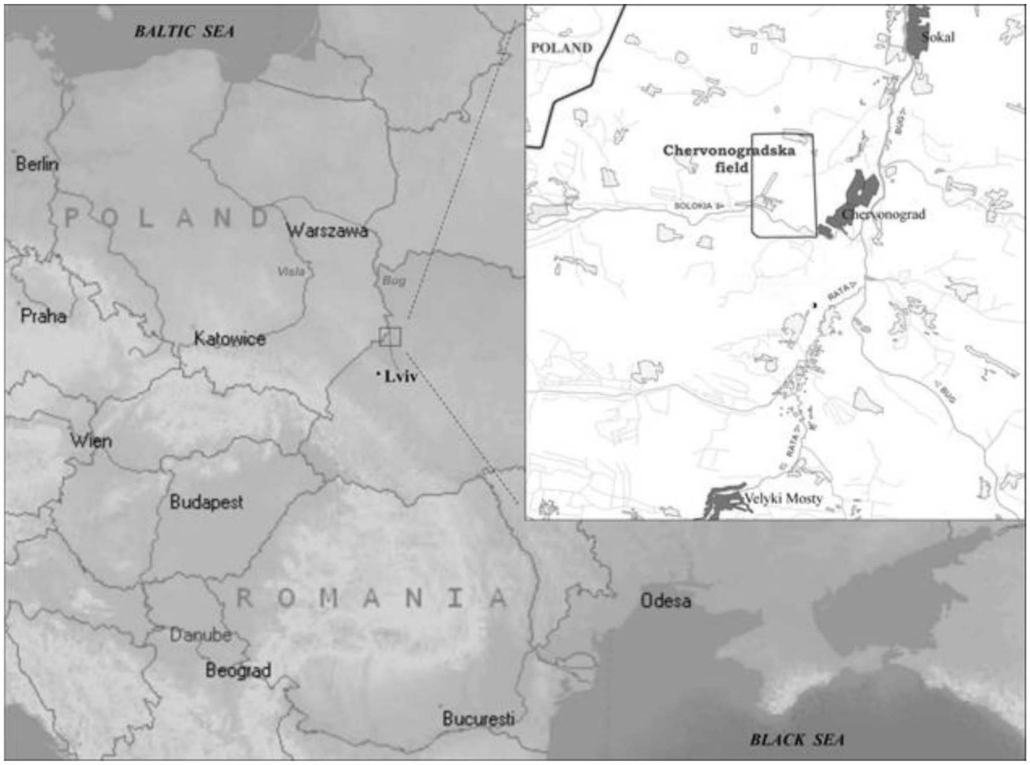

Fig. 1. Generalized map of the research territory

contain dangerous chemical elements for the environment, in particular, heavy metals. So, the location of these potential contamination sources such as waste piles of coal mines in the transnational river basin increases the topicality of this research.

The purpose of the research is to study geochemistry of microelements in the waste pile rocks of Chervonogradska mine.

Main tasks of the research

1. To study composition and morphometric characteristics of the waste pile;
2. To calculate lithological and chemical composition of waste pile rocks;
3. To estimate the contamination risk of adjoining territories by microelements, in particular the water of the Solokiya river and to offer the ways to reduce this risk.

MATERIALS AND METHODS

The ecological and geological research of the waste pile of Chervonogradska mine was done by Ivan Knysh together with the workers of Velykomostivska geological – prospecting subsidiary enterprise "Zakhidukrgeologiya". Sampling has been done on the area of 100 × 100 m and 70 samples of waste pile rocks have been selected. We have studied lithological and mineral composition of rocks and their chemical elements content. Litological description of rocks gives the percentage of argillites, aleurolites, sandstones and coal in waste pile rocks.

Using the visual microscopy method we have found a row of minerals, but in the final table intended for mathematical calculations we have used only those minerals and their content which were often detected, in particular pyrite, chalcopyrite and siderite. We have studied the degree of burnt (in %), weathering rocks (in points) and thickness of clay loam layer (in meters). Ash level of every rock sample has been determined. The content of P, Sr, Mn, Ni, Ba, Pb, V, Cu, Zr, Sn, Ga, Cr, Mo, Ti, Y, Yb, Zn, Ge, Co in mixture of waste pile rocks (argillites, aleurolites, sandstones) has been found by spectral analysis in the Central Laboratory of Lviv Prospecting Expedition of SE "Zakhidukrgeologiya".

All the research figures of the selected samples are grouped and worked out by mathematical methods.

RESULTS

To develop the main topic of the research in more details we have included a short review of geological structure and coal content of the explored territory.

Geological structure and coal content of the explored territory: Geological environment of the explored territory has been examined as a part of the Volyno-Podil plate of Western European platform, where the Paleo-Meso-Cenozoic complex of terrigenous-carbonate and fluvio-glacial sediments of the Lviv-Volyn coal basin lies on plicate epi - Hercynian basis.

The coal beds are traced along the whole profile of coal deposits, except for its lower part which belongs to the Tournaisian stage. The profile of Visean stage is characterized by reduced coal content, and the deposits of Namurian stage have higher industrial coal content including up to 50 coal beds. In lower part of Bashkir stage there are about 12 coal beds from which four beds have industrial power (Struev *et al.,* 1984).

The description of 'Chervonogradska' coal mine

The Visean - Namurian carboniferous deposits are coal-bearing in the field of Chervonogradska mine. In these deposits there are 37 coal beds (the Visean deposits – 17, Namurian deposits – 20).

Within the mine field there are four sub-horizontal coal beds n8V, n8, n7V, n7N. The thickness of the beds ranges from 0.55 to 1.40 m at the average thickness 0.85 m. The depth of bedding is 345 - 415 m.

Chervonogradska mine has been functioning since 1971. The industrial reserves make up 22 mln. tons of coal for 1.01.2012. The annual productive capacity of the mine is 0.65 mln. tons of coal and the industrial production in 2011 was 0.31 mln. tons of coal per year.

Coal production causes significant accumulation of carboniferous rocks on the surface. They are placed forming the waste pile, which is located 550 m to the north of the mine. The waste pile is located on the lessive loams of the Volyn hill, on the slope of 205 - 210 m. The rainfall from the waste pile gets into the streams and soil-reclamation canals of the Buh and Solokiya rivers. The waste pile is artificially formed group of rocks with isometrically oblong shape in profile. The waste pile basis area of Chervonograds'ka mine is 142 000 m².

The height of the waste pile is 10 – 33 m. The slope angle of rocks is 25-37 °. The waste pile has 2.9 mln. m³ of rock. Every year it gets fresh rock in the quantity of 40 000 m³.

The waste pile is heterogeneous by its structure. Some fragments are made of rocks which differ in their composition, leaching and degree of burnout. The unburned rocks prevail on the surface of waste pile.

The waste pile is partly reclamated on the slopes formed by sand and loams 0.5 - 0.7 m of thickness and they have overgrown with grass.

Lithologic and mineral composition of rocks : It has been studied that the waste pile rocks of Chervonogradska mine are presented by mainly argillites (83.8%) and less aleurolites (8.4%), sandstones (4.8%) and coal (2.1%). Moreover, carboniferous material is presented as coal in argillites and sometimes in siltstones. The waste pile rocks have grain structure and contain fragments (30 - 160 mm).

Argillites have from grey to black color, depending on the amount of coal, that saturates them. The structure of argillites is pelitic. There are more grains with 0.01 mm. Most argillites have clay minerals: hidromica, kaolin and partly chlorite.

Aleurolites have grey and dark grey colors. Sometimes they acquire greenish or brown shade. The stratification of argillites is poorly expressed. Their structure is often heterogeneous with the size of grains more than 0.07 mm. Quartz prevails in their composition (to 70%) in the form of angular grains, which are often broken and replaced with carbonates. Aleurolite contains pyrite (to 170 grains for 0.01 g of rock with 0.1-0.01 mm of faction), hydrogetite-limonite (180 grains for 0.01 g of rock). The amount of feldspar does not exceed 8-10%, mica (biotite, muscovite) – 3-6%, coal – 2%. In one third of samples we can observe chlorite in the amount of 1 grain for 0.03 gr of rock with 0.1 - 0.01mm of faction. Rarely we can find leucocsen, garnet (1 grain for 0.005 gr of rock), zircon.

Sandstones are light grey, grey with greenish or brown shade. Mainly these are strong, massive, anisomerous rocks of psammitic structure. The size of grains is ≥ 1 mm. The structure is fine grained and the texture is stratified coarse.

The main rock forming minerals contains quartz (50 - 60%), feldspars (1 - 10%), mica (to 10%).

Quartz is present as parts of grains which are often broken and replaced with carbonates. Feldspars are mainly changed by the process of pelitezation, or replaced with carbonates and siliceous matters. Mica is presented mainly by muscovite, and sometimes by biotite in the form of 0.05 - 0.35 mm scales. All grains are cemented by argillaceous and siliceous cement containing feldspars fragments.

Sandstone contains pyrite (maximum 350 grains for 0.01 g of rock with 0.25 - 0.1 of faction), hydrogetite - limonite (225 grains for 0.01 g of rock), coal (28 broken pieces for 0.01 g of rock). In one third of samples we can find chlorite and leucocsene in the amount of 1 grain for 0.02 g of rock. Tourmaline, garnet, ilmenite, staurolite, volcanic glass have been found in one or two researched samples. Coal of all beds, except for the upper part of the bed n8 of Chervonohradska mine is humic by its origin, consisting of clarain and durain. Coal includes the following main minerals: clay material, pyrite, calcite and quartz. On the whole, the amount of pyrite does not exceed 2.6% in the mixture of rocks.

Ash level of rocks of the waste pile, which have been selected by us, rates from 47 to 98% (dispersion 162) and on average it makes up 67.9%, which is slightly less than in other waste piles of the basin (70 - 79%). Ash level of rocks mixture rises with the increase of the degree of waste pile burntout rocks, the amount of aleurolite and partly argillite.

Chemical composition of rocks. Chemical composition of the waste pile rocks is close to the composition of similar carboniferous rocks in Lviv-Volyn basin.

The results of chemical analysis of waste pile rocks are given in Table 1.

We have studied that with the increase of organic matters content and decrease of grains size we observe the decrease of SiO_2 and Al_2O_3 and the increase of iron oxide.

The carbon content of the coal from Chervonogrdaska mine rates from 78.0 to 85.8%. Sulphur content in the coal rates from 1.1 to 9.4%, at the average rate - 2.25%. The average sulphur content in waste piles rocks is 0.8%.

Ash level of rocks is very important technological and ecological factor of coal quality. Ash level of coal from Chervonogradska mine rates from 3.1 to 34.5%, at average production – 30.5%.

This relatively high indicator is negative for nature protection. The ash of coal contains 37.4% SiO_2, 20.3% Fe_2O_3, 22.1% Al_2O_3, 8.1% CaO, 2.3%, MgO and 3.2% Na_2O+K_2O. Titanium oxide which is ecologically harmful is present in the ash of coal in the quantity – 0.71%. Pyrite has from 58.6 to 73.0% of sulphur. Sulphur is present in sulphate and organic compounds. The content of sulphur rates from 0.83% to 2.4%. Its average highest content has been found in coal bed n8. Sulphur in organic compounds rates from 26.6% to 35.6%. Its average highest content has been found in beds n8v and n7v. Sulfur combustion has a negative influence on soil and water in the large area (Li *et al*., 2006).

Division of microelements in coal. Coal from Chervonogradska mine accumulates molybdenum, copper, beryllium compared to clark in the earth's crust and molybdenum, copper, beryllium, scandium compared to clark in pelitic siltages (argillite, clays) (table 2).

Distribution of metals in the waste pile rocks. The establishment of geochemical specialization of the coal mining wastes is very important task, as it enables us to estimate the waste pile's industrial, agricultural and chemistry value, to develop preventive measures against possible contamination of the environment, to optimize operating and reclamation works.

The waste pile rocks of Chervonogradska mine in comparison to clark in the earth's crust accumulate ytterbium (coefficient of concentration (Cc) 10.8), cobalt (Cc 3.9), plumbum (Cc 3.3), stannum (Cc 2.5), yttrium (Cc 1.6), manganese (Cc 1.3).

The table of chemical elements content in

Table 1. The results of waste pile rocks chemical analysis of Chervonogradska mine

Name of rock	SiO_2	Al_2O_3	TiO_2	FeO**	CaO	MgO	K_2O+ Na_2O	H_2O*	SO_3	P_2O_5
Sand-stone	75-85.2	5.7-9.7	0.2-0.6	2.7-4.0	0.1-0.5	0.4-1.3	0.9-1.5	1.8-4.0	0.1-0.2	0-0.1
Argillite	49.0-58.0	9.6-22.5	0.4-1.0	8.8-9.9	0.7-3.5	1.2-2.0	1.2-3.0	1.9-4.5	0.2-6.5	0.2-2.0
Aleuro-lite	49.8-70.5	16.2-23.0	0.8-1.5	1.2-1.5	0.7-1.4	0.8-1.4	1.5-3.9	0.5-1.5	0-0.3	0.1-0.5
Burntout rock	60.0	22.7	1.0	8.0	0.8	1.5	2.5	2.5	0.95	0.1
leached rock	38.0	16.5	0.8	10.5	0.8	1.9	2.2	27.9	0.55	0.6
Fresh rock	38.5	17.4	0.7	12.0	0.8	1.5	2.3	24.8	0.35	0.2

Notes: * a loss is during decrepitation.
** Fe_2O_3+FeO.
*** by well testing

different rocks is resulted in table 3.

However, as pelitic rocks prevail in the waste pile rocks, it is more useful to compare their microelement composition to the average content of clays and argillites (Vinogradov, 1962). Compared to clark the waste pile rocks are enriched with: cobalt (Cc 5.4), plumbum (Cc 2.1), manganese (Cc 1.9), yttrium (Cc 1.7), cuprum (Cc 1.2), ytterbium, scandium and beryllium (Cc 1.1).

Titanium (Cc 1.0), Vanadium (Cc 0.9), Zirconium (Cc 0.8) are present in the waste pile rocks in close quantities to clark in siltages. The waste pile rocks have the lowest quantity of Strontium (Cc 0.2), Barium, Zinc (Cc 0.4), Tin, Gallium, Nickel (Cc 0.5).

The chemical elements can be divided into three groups according to changeability of microelements content in the researched samples of rocks. As shown in Fig. 2 the first group of elements (Ba, Mo, Ga, Sc) is characterized by low changeability of the content. The second group of chemical elements (Yb, Be, Y, Zr) is characterized by subdivision according to which half content is in narrow range but separate extreme points are quite remote from the Median content and, as a result the dispersion of these elements content is large. The third group of chemical elements (Sn, Pb, Cr, Ni, Cu) is characterized by high and wide changeability of the content even on the interval 25% from the Median content.

Manganese content exceeds clark in siltages in 89% of samples, Cobalt – 88%, Yttrium – 85%, Plumbum – 62%, Copper – 59%, Ytterbium – 52%, Beryllium – 45%, Scandium – 41%, Titanium – 36%, Vanadium – 31%, Scandium, Zirconium, Phosphorus, Chromium,Molybdenum, Tin, Gallium, Nickel – less than 20%. None of the samples of waste pile rocks has Barium, Strontium, Nickel in more quantities than clark in siltages. Taking into account the average and Median contents of chemical elements, the distribution of high content of chemical elements and their toxicity, we think that the most dangerous for the environment are Plumbum, Cobalt, Manganese and Copper.

Table 2. The table of metal content in coal of Chervonogradska mine compared to other objects.

	Table of content, g/t					
The chemical element	Coal from Chervono-gradska mine	Average content in the coal from Lviv-Volyn basin (Lelyk, 1991)	Ash in the anthracite coal of the world (Saet *et al.*, 1990)	Range of content in coal of the world (Radenovic, 2006)	Clark in the earth's crust (Taylor, 1964)	Clark in siltages (Vinogradov, 1962)
1	2	3	4	5	6	7
Ba	344.3	399	930	20-1000	425	800
Be	3.23	3.3	21	0.1-15	2.8	3
Co	5.76	62	34	0.5-30	25	18
Cr	26.63	16	86	0.5-60	100	100
Cu	64.5	64	80	0.5-50	55	57
Ga	2.36	6.7	51	1-20	15	30
Mn	109	164	460	5-300	950	670
Mo	6.73	4.2	25	0.1-10	1.5	2
Ni	21.1	18	90	0.5-50	75	95
P	448.4	597	10-3000	1050	770	
Pb	4.46	9.5	170	2-80	12.5	20
Sc	10.6	11	20	1-10	22	10
Sn	0.8	0.8	7.5	0.2-4	2	10
Sr	373.66	248	460	15-500	375	450
Ti	756	939	4600	10-2000	5700	4500
V	53.43	37	180	2-100	135	130
Y	28.4	24	47	–	33	30
Yb	2.4	2.9	7	–	0.3	3
Zn	4.46	24	150	5-300	70	80
Zr	45.53	50	250	5-200	165	200

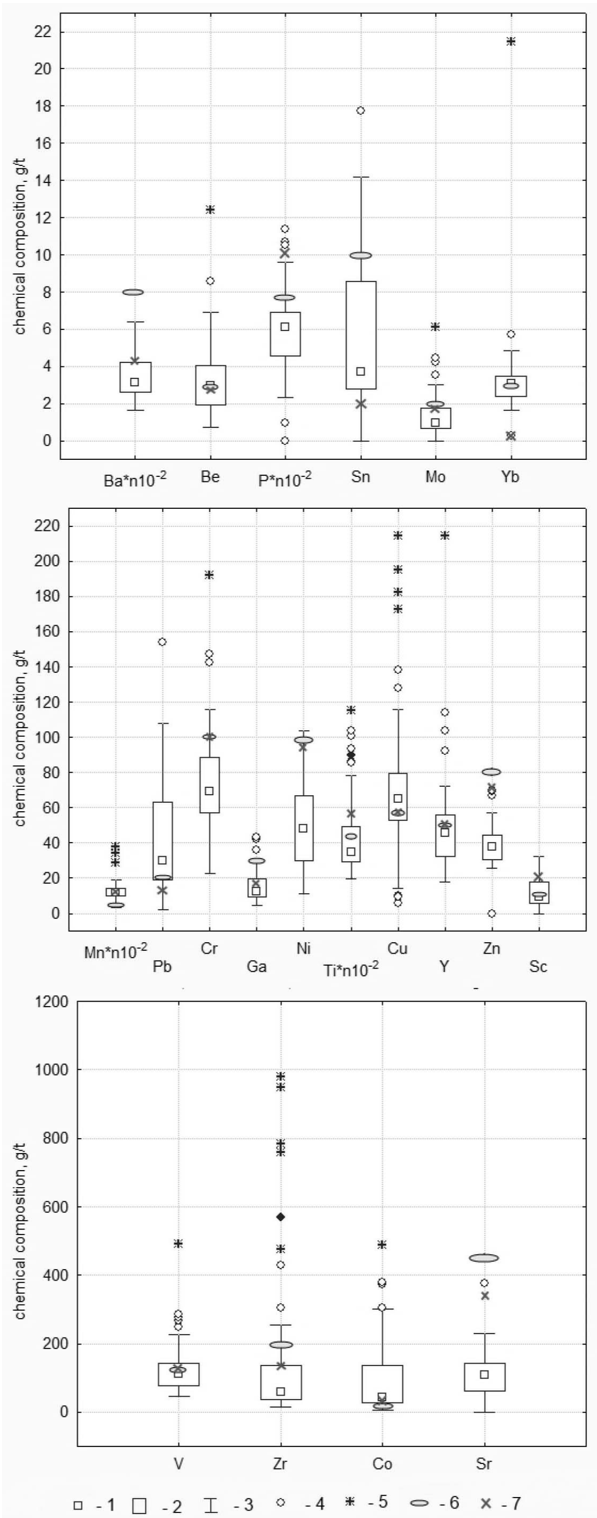

Fig. 2. 2D Box diagram of Distribution of microelements in the waste pile rocks of Chervonogradska mine in comparison to clark in siltages and argillite by Vinogradov

1 – Median, 2 – 25% - 75%, 3 – Non-Outlier Range, 4 – Outlier, 5 – Extremes, 6 – Clark in siltages (Vinogradov, 1962), 7 – Clark in the Eath's (Taylor, 1964).

DISCUSSION

Some geochemical properties of the most dangerous metals in waste pile rocks

Plumbum. The Pb content in the earth's crust is 16 g/t, in the soil 10 g/t (Vinogradov, 1957; Lukashev, 1964). The average Pb content in soil of Lviv-Volyn basin southern part is 22 g/t. Plumbum is easier leached in the soil from organic substance than from mineral (Vinogradov, 1957). In water solutions plumbum can be present in the form of free cation Pb^{2+} but it tends to form complex compounds and cations with iodine, bromine, chlorine, hydrogen, sulphate- ion with the charge +2 and +4 (Krajnov and Shvets, 1992). Ecological limit content of Pb concentration in water is 0.03 mL/dm^3 and in soil 20 g/t (Bespamjatnov and Krotov, 1985). If there is 25 g/t plumbum in soil we don't observe the Pb increase in the crop. If there is 50 g/t plumbum in the soil, the vegetation can be harmful for people due to Pb content (Grigoreva, 1980).

Cobalt. The amount of Cobalt in the earth's crust is 50 g/t, in soil – 8 g/t. With organic substances Co^{3+} it can form complex compounds. Cobalt can be leached from waste piles and soil in the form of hydrates $Co(OH)_2$ and other readily soluble compounds $Co(HCO_3)_2$, $CoSO_4$ which is facilitated by the pH solution decrease (Vinogradov, 1957; Lukashev, 1964). This metal precipitates on hydrogen sulphide and oxidated geochemical barriers.

Copper. The amount of copper in the earth's crust is 100 g/t, and in the soil – 20 g/t.

Univalent copper is present in hardly soluble minerals (sulphide and copper oxide - CuO_2), Two-valent copper forms both unsoluble –sulphide CuS, $CuFeS_2$, and readily soluble compounds with ions SO_4^-, CO_3^-, PO_4^{2-}, and H_2S. Three-valent copper with alkali forms unstable cuprite $M[Cu(OH)_4]$. One of the main properties of copper is its ability to form colloidal solution and colloidal minerals in alkaline medium. (malachite, chrysocolla, molar mass and others) (Vinogradov, 1957; Lukashev, 1964). Copper migrates the best in acid without sulphide medium and it is inactive in quickly restored alkaline medium Copper is easily adsorbed by negatively charged non-organic colloids of alumina, silica, humus, psilomelane (Lukashev, 1964). The buffering ability of soils to copper contamination is tightly related to the content of carbonates and the content of exchangeable forms of calcium and magnesium (Díez *et al.*, 2009).

Table 3. A table of chemical elements content in the waste pile rocks of Chervonogradska mine (as a result of spectral analysis), g/t

The chemical element	Waste pile rocks (average content)	Argillite	Aleurolite	Sandstone	Carboniferous rocks of LVB (Struev *et al.*, 1984)
1	2	3	4	5	6
Ba	327.7	257.4	278.3	253.9	351
Be	3.2	2.73	3.05	2.73	7.2
Co	96.7	23.2	34.3	8.2	14
Cr	68.4	50.1	43.7	26.4	108
Cu	67.5	75.4	139.3	17.1	27
Ga	15.7	32.3	29.8	26.3	15.5
Mn	1270.0	1631.8	1751.0	2036.9	620
Mo	1.3	1.01	0.49	1.05	2.2
Ni	47.6	41.6	84.4	36.2	30
P	542.6	739.7	641.9	698.1	563
Pb	41.4	7.74	29.8	8.3	21
Sc	10.8	14.00	5.45	12.2	25
Sn	5.1	–	–	–	2.8
Sr	100.2	86.7	99.2	4.95	177
Ti	4432.7	2360.7	1548.9	988.2	3777
V	122.0	124.2	113.4	115.5	85
Y	51.5	13.15	7.8	33.0	17
Yb	3.2	10.5	14.7	10.9	1.9
Zn	34.8	40.9	45.2	32.7	93
Zr	164.1	213.65	80.2	312.5	165

Manganese. The amount of Manganese in the earth's crust is 900 gr/t, in soils 850 gr/t.

In the zone of hypergenesis Manganese is mostly present in two, three and four valence forms. The compounds of two-valent manganese are unstable, they are easily oxidizable and transfer into oxides of higher valence (Vinogradov, 1957; Lukashev, 1964). The migration of manganese takes place in the form of real solutions, colloids, suspensions.

Manganese precipitation from solution can take place mechanically with clay and more coarse bits, Mn^{2+} – is concentrated on carbonate and hydrogen sulphide geochemical barriers.

Recommendations and ways of nature protection

The authors think that some heavy metals can enter the adjacent to the waste pile rocks of aeration zone and the Solokiya river in quantities higher than their background content. This supposition has been substantiated by a number of facts and hypothesis. First, Pb content on certain waste pile areas is 7 times higher than clark in siltages and it exceeds the limit content for soil. The average Co content in waste pile rocks is 5.4 times higher than clark in siltages, twice higher than Pb, 1.9 than Mn and 1.2 than Cu. Second, on the waste pile areas the percentage of movable forms of the above mentioned heavy metals can reach 45% of the total content. Third, the waste pile is located on highly permeable alluvial deposits of the Solokiya river 700 metres from its stream canal, which causes the migration of heavy metals in the Solokiya water and in the rivers Western Buh and Visla.

The contamination distribution mechanism from the waste pile to the river has difficult character. Due to the processes of deposition and sorption, pollutants which act in ionic and colloid forms (sulfates, aluminium, iron, heavy metals) can transform into hard phase, and migrate mechanically. Pollutants, which get into the river in a hard phase, due to elimination, desorption, chemical transformation are partly transformed into the liquid phase, migrate, settle again and are carried mechanically. These processes can repeat many times and facilitate the area of contamination downstream the river.

To prevent possible pollution of adjoining rocks to the waste piles in the aeration zone and the Solokiya river by these heavy metals we should dig a ditch around the waste pile and fill it with sorbent.

To protect the environment the most optimal methods are those which are based on accelerating natural transformation of contaminating substances in safe forms or their purposeful concentration on separate areas of lithosphere, that is the creation of artificial geochemical barriers (alkaline, sulfate, oxygen, adsorption, biogeochemical).

To create barriers depending on pollutants composition, natural formations should be used (soils, mountain rocks etc.) or other substances, for example, production wastes . Working experience, gained in the last few years shows high efficiency of geochemical barriers use at different situations.

For example, in Russian Kizelovsk basin it has been offered to use the barium compounds and crashed carbonate rocks which should be put in a trench within waste pile flow to normalize the superficial, and ground water content and soil quality in the waste pile areas as a reagent for pollution decrease (Maksymovych and Blinov, 2000). The research has proved the efficiency of these nature protection measures.

Another effective nature protection measure is slopes and waste pile surface reclamation. Blocking the waste pile rocks by screening layer of lessive loam twice reduces the migration of Cu, Zn, Pb, Cd, Co (Kroyik, 2004).

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