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Lead Speciation in the Technogenesis Zone of Coal Mining Sites (Case of Vizeyska Mine of Chervonohrad Mining Area, Lviv Region, Ukraine)

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Abstract

Total forms and "mobile" fractions of lead in dump rocks and adjacent territories of the impact zone of the Vizeyska mine of the Lviv-Volyn coal basin have been investigated. Environmental hazard caused by distribution of various forms of lead is analyzed basing on establishment of regularities of lead distribution in technogenesis zone. The concentration of lead in total form and acid-soluble, acetate-ammonium and water-soluble extracts have been detected in argillites, siltstones, sandstones, coal from waste heaps, as well as in the soil at a distance of 50 m and 200 m from the foot of the heap. The content of total forms of lead in the waste heaps ranges from 4.72 mg/kg to 16.97 mg/kg. The concentration of lead in the acid-soluble extract is the highest in unburned coal - 3.39 mg/kg, the lowest in unburned siltstone 1.88 mg/kg. The reduction of lead content in ammonium acetate extract is somewhat different - from 1.5 mg/kg in unburned siltstone and burnt siltstone to 0.99 mg/kg in burnt sandstone. The lead content in the aqueous extract ranges from 1.25 mg/kg in unburned coal to 0.48 mg/kg in unburned argillite. The coefficients of lead concentration in the samples were determined by relation to the total form. The coefficients of lead concentration in the rocks species were determined by relation to the clarke. Due to the results of the research the waste heap rocks of the Vizeyska mine can be regarded as safe for the environment and suitable for use in terms of the distribution of various forms of lead in rocks and soils.

Keywords: *Coal mining; Forms of heavy metals; Environmental safety; Heaps; Geochemistry of lead.*

1. Introduction

Waste heaps of coal mines cause a significant anthropogenic impact on natural areas and pose a risk to components of the environment. Heavy metals, concentrated in coal mining waste, are able to migrate (leach) into soils, surface and groundwater, accumulate in plants; rocks are blown away as a dust, making danger to the whole ecosystem. Lead is one of the heavy metals that poses a potential hazard and attracts much attention as one of the main components of chemical pollution. This element is toxic to plants and hazardous to humans.

Clarke of lead by weight is 17 mg/kg in the upper crust and 18.5 in sedimentary rocks [1].There are more than 180 lead minerals, in nature its main form is galena PbS (86.6% Pb), jamesonite $Pb_4FeSb_6S_{14}$ (40.16%), boulangerite $Pb_5Sb_4S_{11}$ (55.42%), etc. [2-3].

Lead minerals are poorly soluble in natural waters, among heavy metals Pb is the least mobile. During weathering Pb sulfides are slowly oxidized, lead can also form carbonates, may occur in clay minerals, Fe and Mn oxides, as well as bind to organic matter [3]. Typical background concentrations of lead are 100 mg/kg in soil and 5 µg/l in fresh and sea waters [4].

Natural concentration of Pb in the upper horizons of different soils ranges from 3 to 189 mg/kg. The average value by soil types are 10 - 67 mg/kg (total average - 32 mg/kg) [3].

The lead content in the soils of Ukraine is mainly 8-12 mg/kg, in the soils of Poland the average is 18 mg/kg, in the soils of Belarus - 12 mg/kg [5-7]. The background content of lead in the European part of Russia is 15-50 mg/kg [8]. Regional lead clarke for soils of Ukraine are: Polissya - 6-26 mg/kg of soil, Forest-steppe - 8-15 mg/kg of soil, Steppe - 10-15 mg/kg of soil. The highest lead content is characterized by the soils of the Carpathian zone: Precarpathian - 32-168 mg/kg of soil, Carpathians - 39-230 mg/kg of soil and Transcarpathia - 23-141 mg/kg of soil [5].

Although the Pb forms in different soil types can differ significantly, it is known that Pb is associated mainly with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. However, in some soils Pb may be concentrated in calcium carbonate particles or in phosphate nodules. The accumulation of Pb in the soil surface layer. exposed to contamination from various sources, has already led in some places to content of up to 2% on dry basis. Some soil and plant factors (for example, low soil pH, the presence of organic ligands) contribute to Pb absorption by roots or its migration into the herbs. The accumulation of Pb in the soil surface layer is of great ecological concern, because this element strongly affects the biological activity of soils [3].

In terrestrial landscapes Pb is a low or medium barrier element: its absorption barrier by vegetation is close to the biogeochemical background, which explains the high toxicity of Pb to plants [9].

The maximum allowable concentration (MAC) of lead in the soils of European countries: Russia - 30 mg/kg, Germany, Denmark, Sweden - 50 mg/kg, the Netherlands - 85 mg/kg, Poland - 100 mg/kg [10].

MAC of the total lead content in the soil is 32 mg/kg, MAC of mobile lead fractions, extracted with acetate-ammonium buffer solution with pH 4.8, in the soil is 6.0 mg/kg with relation to background content [5, 11].

The aim of the work is to assess the environmental hazards in the impact zone of waste heaps of coal mines caused by the distribution of various forms of lead (case of the Vizeyska mine of Lviv-Volyn coal basin). The object of research is lead in the heap rocks and soils in the impact zone of the Vizeyska mine of the Chervonohrad Mining Area of the Lviv-Volyn Coal Basin (LVCB). SPC Mine "Vizeiska" (until 2001 Mine No 8 "Velykomostivska"), located in Silets, Sokal district, Lviv region, was put into operation in 1960 and closed in 2009.

The investigated area covers two interconnected dumps - eastern and western with an area of 0.36 km^2, the structure of the heap is heterogeneous. The base area of the waste heap of the Viseyska mine is around 225,000 m^2, the height of the heap reaches 10–40 m, 5.1 million m^3 of rock has accumulated in the heap. The western part of the heap consists mainly of burnt rocks in the form of a truncated cone, the eastern - unburned, formed into a flat heap [12]. The waste heap of the Vizeyska mine borders on the heap of the Chervonohrad Central Concentration Factory (Fig. 1).

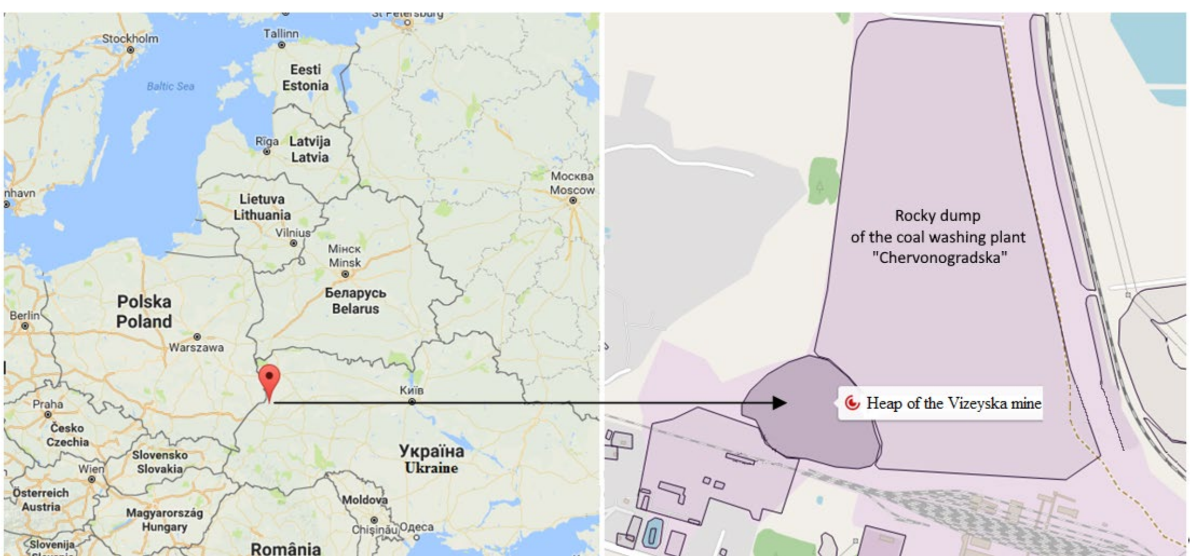

Fig. 1. Location of Vizeyska mine [13]

2. Experimental

2.1. Research methodology

20 samples of rocks were taken from different parts of the heap. Also, 10 soil samples were taken at a distance of 50 and 200 m from the foot of the heap. All samples were dried, crushed and divided into fractions. Extracts from the rocks were made from composite samples. Samples of unburned and burnt argillites, unburned and unburned siltstones, burnt sandstones, unburned coal, soils at distances of 50 and 200 m from the heap were combined.

Preparation of solutions of extracts from rocks and soil was carried out as follows: the total of lead was determined after the destruction of the rock by 1 N HNO_3 in the presence of H_2O_2; the acid-soluble form of lead was determined in the extract of 0.1 N HCl solution; mobile forms - from acetate-ammonium buffer solution (AABS) with a pH of 4.8, and an aqueous extract using distilled water. For each of the extracts separate native samples were used. The samples were left in a certain solution for 24 hours. The mass ratio "rock-solution" was 1:10.

The lead concentration in the extracts was determined by the atomic absorption method using an AAS-115-M-1 spectrometer.

The acid-soluble form of heavy metals is considered to be the main man-made component heavy metals reserve in the soil. Ammonium acetate buffer solution (AABS) extracts primarily chemical elements in ion exchange form, which are most available to plants, therefore the amounts of metals that are removed by AABS are called bioavailable. It should be noted that AABS in addition to the extraction of metabolic forms promotes the extraction of certain amounts of metals from organic matter, oxides, hydroxides [14].

There is no terminological certainty regarding the evaluation of metals extracted by acetate-ammonium and aqueous extracts. In the vast majority of scientific papers [15] and standards of Ukraine (DSTU 4770.1: 2007-4770.9: 2007), the quantities of metals that are extracted with acetate-ammonium buffer solution are identified with mobile forms of metals. In [16], the quantities of metals extracted from AABS soil and hydrochloric acid extract (1 N HCl) are classified as mobile forms. At the same time, of course, metals extracted by water extraction are mobile. To prevent misunderstandings, we omit using the term "mobile form" in this article, and will use the terms "ammonium acetate extract" and "water extract".

3. Results and discussion

3.1. Lithological and mineral composition of rocks

The rocks of the Vizeyska mine heap are represented by burnt and unburned argillites, siltstones, sandstones, and coal in the ratio of 55: 25: 15: 2. Lithological description of rocks is given in [12]. The ash content of the heap mixture varies from 41 to 98% (variance 187) and averages 72%, which is slightly lower than on other heap basins (75–79%). The ash content of the rock mixture increases with increasing burning degree of the heap rocks, the number of siltstones and partially argillites [12].

3.2. Variability of the content of total forms of lead

Lead in solid fuels is not part of the organic components, but is almost completely associated with the mineral part. Lead clarke in coal is as follows: brown coal 6.7 ± 0.4 mg/kg (coal) and 39 ± 2 mg/kg (ash); coal 9.0 ± 0.9 mg/kg (coal) and 56 ± 7 mg/kg (ash) [9].

The concentration of lead in the Donbass coal averages 76 - 90 mg/kg, in the ash 500 mg/kg. In the carbonaceous coal of Chelm in the Lublin Basin (Poland), which borders on Lviv-Volyn coal basin, the average lead content in coal is 27 mg/kg (from 2 to 270 mg/kg), in the ash 193 mg/kg (from 20 to 1620 mg/kg) [9]. As for the coal of the Vizeyska mine, the lead content in it is 12.9 mg/kg, and the average value in the coal of the Lviv-Volyn coal basin is 9.5 mg/kg [12].

According to [17], the minimum hazardous concentration of Pb is 50 mg/kg of coal, there is also evidence that the dangerous concentration of Pb differs for different coals and ranges from 8.4 mg/kg to 740 mg/kg [18].

The total lead content at the Bogdanka coal mine in the vicinity of Lublin (Poland) in different years varies from 8 to 71 mg/kg [19], while in the Sersha mine heap in Trzebinia (Poland) the concentration of lead at a depth of 0.2 - 0.3 m varies from 67.0 to 240.7 mg/kg, an average of 170 mg/kg; at a depth of 0.4 - 0.7 m is from 43.1 to 209.0 mg/kg, an average of 107.9 mg/kg [20].

The total lead content in the dump mine rocks of the Western Donbass ranges from 15.0 mg/kg to 20.0 mg/kg, the average value is 18.3 mg/kg. Indices of lead toxicity in dump mine rocks of the Western Donbass by total content is 0.57 [21]. In the rocks of Krasnodonuhol mines (Luhansk region) the lead content is 15 mg/kg, while the geochemical background is 13.7 mg/kg [22].

According to [23], the lead content in the waste heaps of the Novovolynsk mining area in the burnt rock is 3.7 mg/kg, in the unburned rock 2.4 mg/kg, in the sandstones 2 mg/kg. The lead content in plants and their various parts ranges from 1.8 to 3 mg/kg. The concentration of lead in the waste heaps of CCF CJSC "Lvivsistemenergo" ranges from 7.64 mg/kg to 273.24 mg/kg, the average value of 35.66 mg/kg [24]. The total content of Pb in the rock of the dump of the Central concentrator "Chervonohradska" in the unburned rock is 10.4 mg/kg, in the burnt rock – 7.8 mg/kg [25].

According to recent investigations [26], the distribution of Pb within the waste heap of the Stepova mine of the Chervonohrad mining area ranges from 0 to 12 mg/kg, the average values – 4.7-5 mg/kg, for the waste heap of the mine Mezhyrichanska Pb content in the rocks of the waste heap varies from 0 to 25 mg/kg, the average content is 10-11 mg/kg. In unburned rocks the Pb content is from 0 to 20 g/t, in burnt rocks – at the level of 10-15 mg/kg and decreases to 0-3 mg/kg.

The rocks of the Vizeyska mine heap have higher values of lead concentration compared to Clarke – the concentration coefficient is 1.46, the content of lead exceeds the corresponding Clarke by 23% of the area of the heap [12].

The waste heaps of the Lviv-Volyn coal basin contain lead in concentrations from 4.9 mg/kg to 41.4 mg/kg. There are very few published data on the distribution of lead in different types of coal formation of the LVCB rocks. Information on the concentrations of metals in the mixture of rocks is less suitable for predicting geochemical and environmental changes.

The content of total forms of lead in the rocks of the heaps of coal mines of the Lviv-Volyn coal basin is as follows: Vizeyska mine – argillite - 40.64 mg/kg, siltstone - 26.22 mg/kg, sandstone - 6.9 mg/kg, a mixture of rocks 18.3 mg/kg [12]; Mezhyrichanska mine – argillite - 25.0 mg/kg, siltstone - 9.2 mg/kg, sandstone - 4.9 mg/kg, rock mixture 34.1 mg/kg [27]; Chervonohradska mine – argillite - 7.74 mg/kg, siltstone - 29.8 mg/kg, sandstone - 8.3 mg/kg, rock mixture - 41.4 mg/kg [28]; mines Novovolynska 1-6 and 8 in a mixture of rocks concentration varies from 16.0 mg/kg to 29.0 mg/kg [29].

The above data indicate the variability of the lead content in the waste heaps of the mines of the Chervonohrad Mining Area of the LVCB. The most variable is the concentration of lead in argillite: 7.74 - 40.64 mg/kg. It should be noted that there is no single scheme of lead accumulation in rocks of different lithological composition, namely, the concentration of lead increases in a following order: sandstone - siltstone - argillite in the heap of Vizeiska and Mezhyrichanska mines and in a set of sandstone - argillite - siltstone in the heap of Chervonohradska mine. The concentration of lead in argillite on the Vizeyska mine heap exceeds its content in sandstone by almost 6 times.

According to the results of research (Table 1), the highest lead content was found in unburned argillite, the lowest in sandstones. The coefficients of lead concentration in the investigated species of rocks relative to clarke in sedimentary rocks are as follows: argillite (0.6) - siltstone (0.5) - coal (0.4) - sandstone (0.2).

According to our data, the content of total forms of lead in the soils samples taken in the impact zone of the waste heap of the Vizeyska mine is 4.59 mg/kg at a distance of 50 m and 4.51 mg/kg at a distance of 200 m from the heap. For comparison, in [27] at the footwall of the waste heap of the Mezhyrichanska mine the Pb content reaches - 25 mg/kg, this is the transition area from heap rocks to quaternary sandstones, in sandstones and underlying Upper

Cretaceous marls the Pb content is constant - 10 mg/kg. According to [30], the ecological state of soils in the territories adjacent to dumps of Duvanna, Knyahininska and Matroska mines (Luhansk region) ranges from 30 to 50 mg/kg of total lead content in waste heaps.

Table 1. Distribution of different lead forms in the rocks of the Vizeyska mine heap and adjacent soils

Rocks		Pb content in the extract, mg/kg			
		Total form	Hydrochloric acid extracts	Ammonium acetate extracts	Aqueous extract
1	Unburned argillite	16.97	1.89	1.25	0.48
2	Burnt argillite	9.89	2.38	1.1	0.85
3	Unburned siltstone	8.19	1.88	1.5	0.85
4	Burnt siltstone	12.49	2.87	1.5	0.95
5	Burnt sandstone	4.72	1.92	0.99	0.7
6	Unburned coal	8.58	3.39	1.0	1.25
7	Soil, 50 m from the heap	4.59	3.87	1.62	0.48
8	Soil, 200 m from the heap	4.51	3.16	1.58	0.44

3.3. Variability of lead content in hydrochloric acid and ammonium acetate extracts

There are only few results of research on the distribution of various forms of lead in the zone of mine heaps technogenesis. This is primarily due to the high complexity of research, but this information is essential for assessing the bioavailability of heavy metals, environmental safety of territories and migration forecasting.

In the rocks of the Vizeyska mine heap the highest concentration of lead in acid-soluble form was found in unburned coal (3.39 mg/kg) and the lowest in siltstone (1.88 mg/kg). The reduction of lead content in acetate-ammonium extract occurs in a following order: unburned and burnt siltstone (1.5 mg/kg) - unburned argillite (1.25 mg/kg) - burnt argillite (1.1 mg/kg) - unburned coal 1.0 mg/kg) - burnt sandstone (0.99 mg/kg) (Table 1).

According to our research data, in the soils of impact zone of the Vizeyska mine waste heap the lead content in hydrochloric acid extract at a distance of 50 m from the dump is 3.87 mg/kg, at a distance of 200 m - 3.16 mg/kg, in acetate ammonium extract - 1.62 mg/kg and 1.58 mg/kg, respectively (table 1).

For comparison, in [31] the concentration of mobile forms of lead (determined using a buffer ammonium acetate extract with a pH of 4.8) is as follows: in the rocks of the dumps of the closed mines of the Donetsk coal basin ranges from 3.9 to 4.36 mg/kg, in the soil at the foot of the dump 3.21-3.67 mg/kg, in the soil 100 m from the dump 2.12 - 3.56 mg/kg.

3.4. Variability of water-soluble forms of lead

Water-soluble forms of heavy metals are directly involved in the water cycle and therefore the control of their distribution is very important for assessing the environmental safety of the territory. Unfortunately, we did not find any reference on this matter in analyzed literature, which confirms the importance of this research. In the rocks of the Vizeyska mine heap we found lead in all water extracts, the highest concentration in the rocks was found in unburned coal – 1.25 mg/kg, the lowest in unburned argillite – 0.48 mg/kg. Soils at a distance of 50 and 200 m from the foot of the heap contain lead in the amount of 0.48 and 0.44 mg/kg respectively.

The content of water-soluble forms of lead in the dump rocks of the Western Donbass ranges from 0 to 2.5 mg/kg, the average value of 0.77 mg/kg. The index of lead toxicity in waste heaps rocks of the Western Donbass by water-soluble forms is 0.39 [21]. Instead, the content of water-soluble forms of lead in the rocks of the heap of the Sersha mine at a depth of 0.2-0.3 m averages 0.011 mg/kg, at a depth of 0.4-0.7 m – 0.017 mg/kg [20].

In the waters of the wells in Sokal district, where the Vizeyska mine is located, the authors [32] found lead in the amount of 0.03 mg/dm^3 (MAC 0.03 mg/dm^3). According to other data [33], the lead content exceeded the MAC from 1.2 to 2.9 times in 7 wells in Silets village.

As mentioned above, the level of environmental hazard in terms of threats of heavy metal pollution is determined primarily by the concentration of dissolved forms of these elements, as they are bioavailable and having a high migration capacity may cause water pollution. Most of the data on the heavy metals content in rocks and soils relate to the total forms of heavy metals. That's why, it is important to find out the correlation between the concentrations of chemical elements in different forms, which will give an opportunity to predict the concentrations of mobile forms of elements by their concentrations in total form.

The rocks of the Vizeyska mine waste heap are characterized by variable transition coefficients between different forms of lead. With regard to the total form, the fraction of lead in hydrochloric acid extract varies from 0.11 to 0.41 in rocks and from 0.7 to 0.84 in soils; in ammonium acetate – from 0.07 to 0.21 in rocks and 0.35 in soils; in water – from 0.03 to 0.15 in rocks and from 0.097 to 0.1 in soils (Fig. 2).

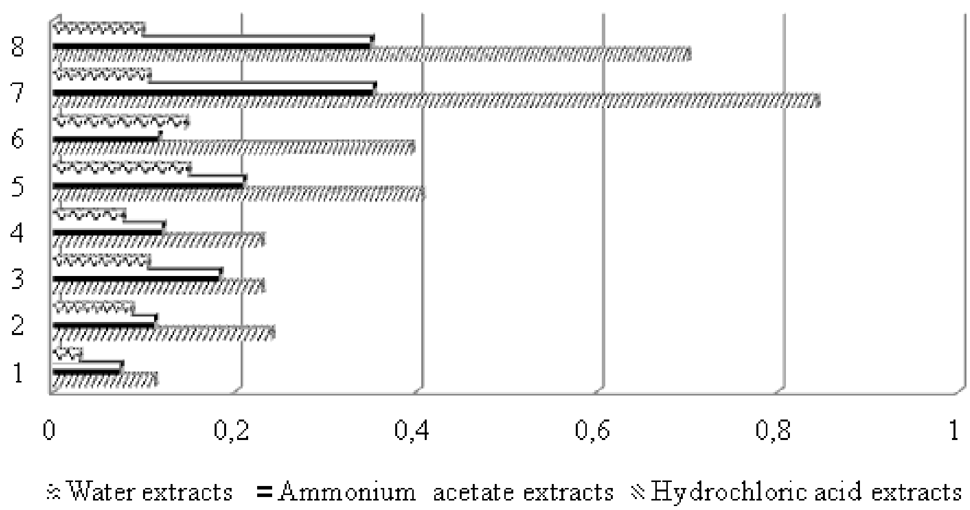

Fig. 2. The content of lead in hydrochloric acid, ammonium acetate and water extracts relative to the total form: 1 – unburned argillite, 2 – burnt argillite, 3 – unburned siltstone, 4 – burnt siltstone, 5 – burnt sandstone, 6 – unburned coal, 7 – soil at a distance of 50 m from the heap, 8 – soil at a distance of 200 m from the heap

The highest transition fractions of lead from native samples to hydrochloric acid extract is inherent to the soils (0.84 and 0.7), the lower – to sandstone (0.4) and unburned coal (0.39), the lowest – to argillites (0.24 and 0.11) and siltstones (0.23). The highest fraction of lead in the acetate-ammonium extract passes from soils (0.35), less from burnt sandstone (0.21) and unburned siltstone (0.18), the lowest from burnt siltstone (0.12), unburned coal (0, 11), burnt and unburned argillites (0.11 and 0.07). Regarding the proportion of lead leached into the water extract, the series can be represented as follows: burnt sandstone (0.15) – unburned coal (0.14) – soil at a distance of 50 m from the heap and unburned siltstone (0.1) – soil at a distance of 200 m from the heap (0.097) – burnt argillite (0.08) – burnt siltstone (0.07) – unburned argillite (0.03).

It should be noted that with increasing distance from the base of the heap, the fraction of total and acid-soluble forms decrease; this is also applicable to water extract.

3.5. Regularities of lead concentration changes due to thermal effects (weathering) on rocks

According to [12], the burnt rocks of the Vizeyska mine, in comparison with the unburned ones, concentrate lead in total form with a coefficient of 0.81. The burnt rocks of Mezhyrichanska mine concentrate lead with a coefficient of 0.5, i.e. burning of rocks led to a decrease in metal concentration [27].

Basing on the results of our research the siltstone combustion causes the decrease of Pb (all forms) content except bioavailable (ammonium acetate extract), which indicates its association in siltstone primarily with organic matter and partly with carbonates, which are partially destroyed at high temperatures. In the gross form of argillite Pb content increases during combustion, and in hydrochloric and water-soluble extracts – decreases. In the acetate-ammonium extract lead content is almost constant in burnt and unburned rocks. It is assumed that lead in the gross form of argillite is primarily concentrated in the mineral part of the rock. After combustion of the organic part of argillite, its mass decreases, which leads to an increase in Pb content. Hydrochloric acid and aqueous extracts do not dissolve the mentioned minerals, and therefore the decrease in Pb content after combustion indicates the presence of lead in organic and carbonate compounds (Fig. 3).

The obtained data and regularities are important elements for the development of the theory of chemical elements migration in the zone of hypergenesis and have practical applications for the construction of safe mining technologies [34-35] and purification technologies of polluted environment components.

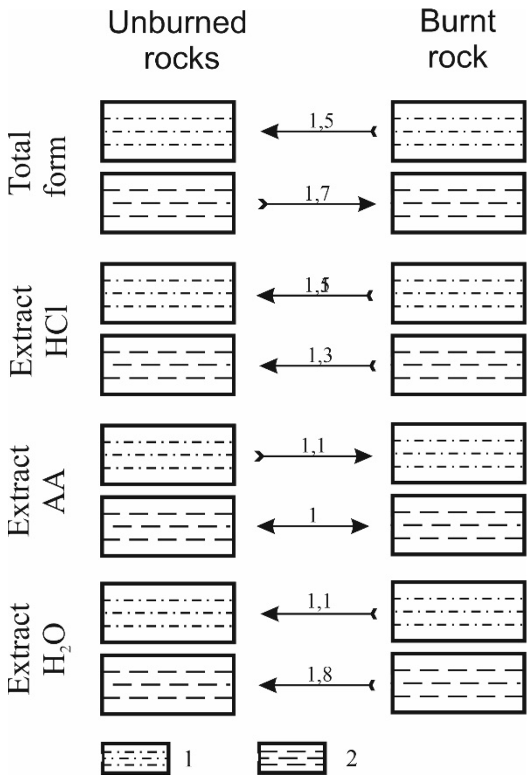

Fig. 3. Characteristics of changes in the concentration of lead in unburned and burnt rocks of Vizeyska mine: 1 – siltstone, 2 – argillite, arrows show the direction of concentration increase, numbers – the fraction of the transition

4. Conclusions

The content of total forms of Pb in the rocks of the Vizeyska mine waste heaps varies from 4.72 mg/kg to 16.97 mg/kg. The highest Pb content was found in argillites, the lowest in sandstones. The coefficients of lead content relative to clarke in sedimentary rocks are as follows: argillite (0.6) - siltstone (0.5) - coal (0.4) - sandstone (0.2). In soils of waste heap impact area the content of total forms of lead is 4.59 mg/ kg at a distance of 50 m and 4.51 mg/kg at a distance of 200 m from the heap.

In the acid-soluble extract the concentration of lead varies from 1.88 mg/kg to 3.39 mg/kg. The lead content in the acetate-ammonium extract decreases in a following order: unburned and burnt siltstone - unburned argillite - burnt argillite - unburned coal - burnt sandstone.

During burning of the rocks the lead content varies depending on its presence in mineral or organic forms. The results of analysis of changes in the lead content in unburned and burnt rocks may indirectly indicate its presence in various components of the rock.

The obtained data and regularities are important elements for the development of the theory of chemical elements migration in the zone of hypergenesis and have practical applications for the construction of safe mining technologies and purification technologies of polluted environment components.

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