Three-dimensional distribution of heavy metals in the areas of tailing pits of the Kryvyi Rih mining and processing objects

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It was determined the regularity of distribution of heavy metals in areas adjacent to the ore-dressing and mining objects, which have the largest impact on pollution of the environment in Kryvyi Rih. As the objects of research, soils from ravines and tailing pits located close to mining and processing objects were taken. Specification of geochemical concentrations of heavy metals was done by atomic emission spectral analysis and atomic absorption spectral analysis. The results were correlated with the maximum allowable concentrations established by the normative documents. The results of the performed studies have confirmed that the accumulation of heavy metals in the geologic environment is affected by mining and processing plants, as well as by domestic waste and municipal wastewater. As an additional factor of the distribution of heavy metals in soils, prevailing winds and ground relief have been taken into account. Also, the trend to active absorption of some part of heavy metals by vegetation has been confirmed. In combination with periodic recultivation works, it significantly reduces concentrations of heavy metals to the levels not exceeding the maximum allowable concentrations.

Key words: heavy metals, atomic emission spectral analysis, maximum allowable concentrations, atomic absorption spectral analysis, tailing pits

Introduction

One of the basic principles of the balanced management of natural resources is the development of industrial metallurgy-related objects in such a way that favourable ecological conditions for future generations will be provided. This principle began to be implemented in the system of the subsurface resources management only recently and now is not sufficiently popular. In the majority of countries with metallurgy industry, the following method of mineral recourses management is used: if there is a need in a mineral product, and if such a mineral product is available, the mineral product is mined without control. The principle above means the strict monitoring of works for mining and processing iron ore in such a way that the iron ore production volume would be sufficient for satisfying the minimum required volume at present, the remaining iron ore would be sufficient for satisfying future needs, and there would be sufficient time for the environment self-restoring. Considering this, it is arguable that the population carrying capacity of the geologic environment of the Kryvyi Rih iron-ore region is closely related to the problem of the rational use of mineral recourses in the iron-ore region.

It is evident that the situation in the studied region at present is close to environmentally unsafe. The anthropogenic impact on the geological environment exceeds the maximum level allowed for the population carrying capacity of the region. According to research (Hrin, 1980), (Korzhnev, 2000, 2003*)*, (Kurilo, 2014), (Sadovnikov, 1984*), (*Taranov, 2001) the basic hazardous substances are migrating waste products of imperfect production processes, such as gas emission products, wastewaters, and mine waters, which contain toxic substances and enter soils and water-storage reservoirs. Some analyses showed that especially technogenically loaded natural objects are sedimentary rocks of the studied area. In scientific studies (Stetsenko and Ivanchenko, 2016) it is stated that the sedimentary complex is represented by quaternary and prequaternary (Paleogene, Neogene) deposits that overlap the complex of metamorphic rocks of the Krivoy Rog series. Their power is not sustained, and, mainly, depends on the relief of the indigenous species. In the eastern regions, it is 20-25 m, in the western - it reaches 55-60m.

The city of Kryvy Rih is located in the central part of the Ukrainian crystalline massif. The geological construction of the city and its vicinity consists of the Quaternary loams (3-25m of thickness), which are bedded with Neogene clay, sand or cracked limestones (5-11m). Over the Neogene sediments, the Precambrian crystalline rocks (granites) which extend to the surface only in river valleys are lying. Common chernozems are the primary genetic group of soils in the suburban and urban areas of Kryvyi Rih. As Kryvyi Rih Region is the

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largest iron ore mining and processing region in Ukraine, these soils become the primary objects of the influence of all iron processing enterprises, such as ArcelorMittal Kryvyi Rih, Kryvbasshakhtozakryttia, Mekhanobrchermet, and Central Mining and Processing Integrated Plant. All these enterprises are located within the townsite and pollute the environment to a large extent (Fig. 1).

Fig. 1. Summarised map of the research objects.

Material and methods

To determine the three-dimensional distribution of heavy metals in Kryvyi Rih, Ukraine, some literary sources were studied (Klos, 2012; Kurbatova, 2004; Saprishkin, 1984; Voskresenskaya, 2013) and four sites for studies were chosen. These sites are the Red Ravine, which is located at a distance of 3 km from ArcelorMittal Kryvyi Rih; the Svystunov Ravine, which is virtually the containment pond of Kryvbasshakhtozakryttia; the tailing pit, used for hydro projection now, which is located between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine, and the area adjacent to No. 1 Open Pit, including the tailing pit of the Central Mining and Processing Integrated Plant. At these sites, samples were taken from soils presented by black soil, industrial silt, loam, aqua-gel, sand with the addition of oil products and bottom sediments, and mud.

Specification of geochemical concentrations of heavy metals was done by atomic emission spectral analysis and atomic absorption spectral analysis following the scientific research (Jovinskiy and Kruchenko, 2007). The results were correlated with the maximum allowable concentrations established by the normative documents.

To determine the concentrations of chemical elements in samples of soils, bottom sediments and vegetation in them, an atomic-emission spectral analysis was used, which was performed in the laboratory of the Institute of Geochemistry, Mineralogy and ore formation named after M.P Semenenko National Academy of Sciences of Ukraine on the STE-1 spectrograph of large dispersion (4.7 A0 / mm). Investigated sample, roughly 200 mesh (to powder form), are burned in a vertical arc of an alternating current of 20 A, 220 V from a coal electrode crater. The received spectra of samples are fixed on a photographic plate. After that, the interpretation of the spectra by the method of comparison of blackening of the lines with the reference samples is carried out (Fig. 2).

Fig. 2. The scheme of preparation of samples.

The density of the line of each element in the spectrum is proportional to its content in the sample and corresponds to the standard described by Rusanov (1971). Preliminary preparation of samples was carried out in the same laboratory.

For a more accurate understanding of the content of heavy metals in the selected samples, the results of atomic emission spectral analysis were compared with the results of the atomic-adsorption spectral analysis. The last one was done with the help of the ground-breaking iCE 3300 AA Spectrometer (Fig. 3) which makes even the most complicated analyses simple.

Fig. 3. Thermo Scientific iCE 3300 AA Spectrometer.

It was chosen because among its characteristics there are: high precision, exceptional optical stability and new universal titanium burner with improved solids capability increases the efficiency and accuracy of your flame analysis. The iCE 3300 has an unrivalled flame sensitivity which is achieved by high-efficiency nebulization through a fully inert impact bead, spoiler and spray chamber. The new finned universal titanium burner ensures exceptional atomization, even with the most difficult samples. The fully automatic gas box uses binary flow control for safe, reliable and repeatable analysis with all flame types. All critical parameters can be optimised automatically if required – burner height, gas flows, even optical instrument parameters. The iCE

3300 accepts the GFS33 Integrated Graphite Furnace and Auto-sampler Module which offers the best in detection limits with minimum interferences. Dynamic optical temperature feedback ensures accurate heating rates up to 3000 ºC per second regardless of cuvette age.

The GFS33 has unrivalled graphite furnace automation. Huge capacity and infinite solution preparation facilities cater for all needs. The auto-sampler remains permanently in alignment with the furnace eliminating the need to re-align the probe every time the furnace is fitted.

Results and discussion

Red Ravine

Fig. 4. Distribution of Pb along the Red Ravine depending on the relief.

Fig. 5. Distribution of Cu along the Red Ravine depending on the relief.

Fig. 6. Distribution of Zn along the Red Ravine depending on the relief

Fig. 8. Distribution of Ni along the Red Ravine depending on the relief.

As is seen from the plot of lead (Pb) (see Tab. 1 & Fig. 4) distribution at the Red Ravine, the lead content in soil is not characterised by large differences. Along the whole length of the relief, excluding several points, the lead content ranges from 30 – 32 mg/kg to 60 mg/kg. The maximum values 60 – 80 mg/kg are characteristic for the *estuary* and end of the ravine. Such lead concentration distribution is caused by the accumulation of a large amount of domestic waste in the ravine *estuary* (Fig. 9) and by the neighbourhood of ArcelorMittal Kryvyi Rih.

Fig. 9. The estuary of the Red Ravine.

The lead-containing elements are transferred to the middle part of the ravine due to water flow and east wind, which, according to archival meteorological data, is prevailing in this geographical area. At the middle part of the ravine, the gradual washout of lead-containing elements also takes place, as well as the washout due to periodical recultivation works provided by the local municipal administration. These two factors cause that the lead concentration in the middle part of the ravine only slightly exceeds the maximum allowed concentration, notwithstanding the immediate vicinity of ArcelorMittal Kryvyi Rih. The high lead concentration at the end of the ravine profile is caused by the dam located at the end of the ravine (Fig. 10), which prevents the further migration of heavy metals.

Fig. 10. The end of the Red Ravine.

According to some study works, there is an opinion that the lead distribution is caused by the washout of lead-containing elements by plants and further accumulation of the lead-containing elements in the humus layer. It is arguable that this opinion is correct due to the vicinity of the park area. Unfortunately, no experimental data are confirming this opinion.

The distribution of copper (Cu) (Tab. 1 & Fig. 5) concentration along the ravine profile is similar to the distribution of lead concentration, but with some differences. According to the study results, the copper concentration, as well as the lead concentration, is high at the *estuary* of the ravine (100 mg/kg), that is, the copper concentration is twice as large as the maximum allowable concentration in soil (55 mg/kg). Further, along with the ravine profile, the copper distribution is almost uniform, with a slight excess of the maximum allowable concentration in some areas. At the end of the ravine, the copper-containing elements do not accumulate, in contrast to the lead-containing elements. It is possible that this feature is caused by that the copper concentration depends on vegetation in a greater degree than the lead concentration. According to the results of studies (published electronically), there is a direct relationship between copper concentration in soil and copper absorption by vegetation. Copper concentration of 60 mg/kg is considered excessive. As is seen from the results of the atomic emission spectral analysis of the soil samples taken at the ravine, the average copper concentration conforms to this limit value. So, the copper-containing elements that could reach the end and accumulate at the end of the ravine are absorbed by vegetation due to the copper absorption capacity of the vegetation.

According to the effective normative documents, the approximate allowable concentration of zinc (Zn) (Tab. 1 & Fig. 6) in soil is 100 mg/kg. Relying on the results of the atomic emission spectral analysis, it is possible to state that the copper concentrations in the soils of the Red Ravine do not exceed the established limit values. However, the results of the comparative atomic emission spectral analysis with 2М HNO3 and 0,5М HCl demonstrate that this statement is not correct, as two analysis procedures have shown that the zinc concentration is from 154.87 mg/kg through 670.73 mg/kg for the majority of soil samples. The average zinc concentration is about 200 mg/kg, that is, exceeds the approximate allowable concentration two-fold. The zinc concentration at the ravine *estuary* is as high as the concentrations of the other studied heavy metals. The zinc concentration does not change along the ravine profile. The concentration does not depend on ground relief, prevailing winds, and water flows. The conclusion, which is possible on the basis of the data characterising the zinc concentration at the ravine end, is that recultivation works in combination with the absorption of migrating zinc-containing elements by vegetation have a positive impact on the reduction of zinc concentration at the ravine end, as no maximum concentration values were registered in the area adjacent to the dam.

Chromium (Cr) (Tab. 1 $\&$ Fig. 7) is somewhat distinctive among the elements analysed. The established maximum allowable chromium concentration is 100 mg/kg. According to the results of the atomic emission spectral analysis, the chromium concentrations do not exceed the maximum allowable values. The results of the atomic emission spectral analysis using 0,5М HCl confirm this conclusion and demonstrate that the chromium concentrations are relatively low. The results of the atomic emission spectral analysis with $2M HNO₃$ demonstrate that the concentrations are higher and range from 104 mg/kg through 159 mg/kg, that is, the error is relatively low as compared with the preceding data. Therefore, it is possible to state that the first analysis results are reliable.

Considering the special properties of chromium, it is possible to assume that the sources of pollution of the Red Ravine are ArcelorMittal Kryvyi Rih and sediments of residential wastewater, as the ravine begins at the town district with private houses. According to the study results (Kovda, 1985, Baiseitiva, 2014, Dobrovolskiy, 1983), chromium in soils easy forms compounds with organic substances. Chromium migrates as a colloid component of a mechanical suspension. Usually, the characteristic feature of chromium is lack of its biogenic accumulation in a humus layer, as is confirmed by the results obtained by the authors of this paper (chromium concentrations do not exceed the maximum allowable concentration). Chromium is almost evenly distributed along the ravine profile depending on humus content (to a lesser extent), on grain-size composition (to a greater extent), and, particularly, on the accumulation of silt fraction, which is present in the Red Ravine in a sufficient amount.

According to the normative documents, the approximate allowable concentration of total nickel (Ni) (Tab. 1 & Fig. 8) in soils is $20 - 80$ mg/kg. The study results demonstrate that the average nickel content in the soils of the Red Ravine does not exceed the maximum allowable value along the whole ravine profile and is 50 mg/kg and, occasionally, 60 mg/kg. It is stated (Perelman, 1984; Chertko, 2008; Drugov, 2007; Cholodov, 2006), that nickel in soils is not characterised by high mobility. Nickel basically concentrates in silt fraction. Depending on the thickness of soil covering, nickel migrates, in cationic form, in molecular solutions and compounds, although migration in mechanical suspensions is also possible. The properties above are characteristic, with sufficient accuracy, for the Red Ravine, and make it possible to explain the uniform distribution of nickel along the ravine profile. It is also possible that the low nickel concentrations at the Red Ravine are only caused by ArcelorMittal Kryvyi Rih, as there are no other plants and any enterprises where waste, oil, or gasoline might be burned. It is probable that there are other factors, specifically recultivation works, which have a positive effect of the dynamic characteristics of accumulation of heavy metals at the Red Ravine.

Ravine of Svystunova

Tab. 2. The content of heavy metals in Ravine of Svystunova.

Fig. 11. Distribution of Pb along the Ravine of Svystunova depending on the relief.

Fig. 12. Distribution of Cu along the Ravine of Svystunova depending on the relief.

Fig. 13. Distribution of Zn along the Ravine of Svystunova depending on the relief.

Fig. 14. .Distribution of Cr along the Ravine of Svystunova depending on the relief.

Fig. 15. Distribution of Ni along the Ravine of Svystunova depending on the relief.

The Ravine of Svystunova is used as a containment pond for the discharge of mine waters from four Kryvyi Rih mining plants (Fig. 16).

Fig. 16. Ravine of Svystunova.

According to the results of the ecological inspection performed in 2015, the annual volume of accumulated highly mineralised mine waters in the Svystunov Ravine is 12 million cubic meters. In the Ravine of Svystunova, mine waters are settled, additives in the mine waters are deposited, and then the cleared waters are discharged into the Ingulets River. Due to the dosed discharge of mine waters from the Svystunov Ravine according to the established limits, the concentration of heavy metals accumulated at the ravine has been significantly reduced. As is shown in Table 2, the concentration of each of the analysed elements does not exceed the maximum allowable concentration. It should be noted that there are some characteristic features of the heavy metal distribution along the ravine.

The concentrations (see Tab. 2 & Fig. 11, 14) of chromium and lead increase from the ravine *estuary* to the ravine's end, so it is possible to assume the significant impact of water and air flows on the concentrations.

The distribution of nickel (Fig. 15) along the ravine is as uniform as that at the Red Ravine, confirming the statement that nickel in soils is not characterised by high mobility. The continuous sedimentation of various impurities along the ravine promotes the formation of extensive silt deposits as basic environment for the nickel concentration. Because of this, the nickel concentration distribution along the ravine is uniform, as is shown on the plot of distribution.

The copper (Fig. 12) concentration along the ravine profile is significantly reduced in the area near the ravine end. The analysis results demonstrate the availability of fluctuations of copper concentration (8 – 20mg/kg) due to the absorption of part of nickel-containing elements by vegetation additionally to the discharge of excessive mine waters into the Ingulets River.

Tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine

Cu content (g/t)

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Fig. 17. Distribution of Pb in tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine depending on the relief.

Fig. 18. .Distribution of Cu in tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine depending on the relief.

80 78 81 76 71 71 80 83 **Height, m**

Fig. 19. Distribution of Zn in tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine depending on the relief.

Fig. 20. Distribution of Cr in tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine depending on the relief.

Fig. 21. Distribution of Ni in tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine depending on the relief.

The third study area that is the tailing pit (Fig. 22) located between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine is characterised by relatively uniform ground relief with altitude differences not more than $8 - 10$ m.

Fig. 22. Tailing pit between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine.

The location of the tailing pit is the cause of availability of various sediments and formations within the tailing pit. The samples taken within the pit are presented by various bottom deposits, products of iron-ore dressing, mud mixed with mine waste, sediments from mine water, and ordinary quartz sand.

When analysing the plot of lead (Tab. $3 \&$ Fig. 17) concentration distribution along the tailing pit perimeter, No. 26 point should be distinguished. At this point, the lead concentration is 50 mg/kg, that is, the lead concentration is one and a half the maximum allowable concentration. As compared with the other values, this maximum value is abnormal and may be considered unreliable. The other factor, which does not allow the lead concentration distribution plot to be accepted, is the low lead concentrations (lower than the concentrations determined by atomic emission spectral analysis) obtained by atomic absorption spectral analysis with 2M HNO₃ and 0,5M HCl. The difference between the results obtained by using these analysis procedures is far less as compared with the results of the atomic emission spectral analysis. The results of the atomic absorption spectral analysis are more reliable. Therefore, the lead concentration along the perimeter of the tailing pit is uniform, probably due to lack of any express factors promoting migration of lead.

According to the results (Tab. 3 & Fig. 18) of the atomic emission spectral analysis, the copper concentration distribution along the tailing pit profile is characterised by periodical changes in directions of increase and decrease. Although the lead concentrations do not exceed the maximum allowable concentration, the sampling inspection of the data by atomic emission spectral analysis has demonstrated that the data at some points should be rejected. As a result, the copper concentration distribution is more uniform and smooth and is 15 – 20mg/kg on the average. Such low copper concentrations can be caused by a large amount of vegetation, which absorbs lead-containing elements, and the vicinity of the Saksagan River. Lead-containing elements reaching the river does not have a significant impact on the ecological state of the river but contribute to the unfavourable ecological state of the environment caused by the tailing pits of the Motherland Mine located down-stream of the river.

The zinc (Tab. 3 & Fig. 19) concentrations obtained in the studied area are contradictory. According to the plot of zinc concentration distribution obtained from the results of atomic emission spectral analysis, the zinc concentrations are close to the maximum allowable concentration at the west edge of the tailing pit, which is located nearer to the South Open Pit and far away from the Saksagan River. At the other points along the perimeter of the tailing pit, the zinc concentrations are significantly lower. It is possible that this feature is caused by the transfer of settled particles of zinc-containing elements by the east wind from the higher east bank to the lower (by 10m) west bank of the tailing pit. According to the results of the sampling atomic emission spectral analysis, the zinc concentration distribution plot is not correct, so the maximum allowable concentration at the west bank of the tailing pit is not achieved, and the average zinc concentration is $20 - 60$ mg/kg. These data demonstrate that there are no active external factors affecting the process of accumulation of zinccontaining elements. According to the opinion of the authors of this paper, such factors are improbable. Because of this, the zinc concentration distribution plot obtained according to the results of the atomic emission spectral analysis is accepted.

The plot of chromium (see Tab. $3 \&$ Fig. 20) concentration distribution is also doubtful. According to the results of the atomic emission spectral analysis, the accumulation of chromium-containing elements depends on the change of the relief height along the perimeter of the tailing pit. There is the trend to the accumulation of zinc-containing elements in the higher north-east areas of the tailing pit. There is virtually no zinc concentration in the south-west areas of the tailing pit. These results were considered as doubtful. Therefore, the samples were additionally analysed by performing atomic absorption spectral analysis procedure. The analysis results obtained were absolutely different. The conclusion is that the first method and the method with atomic absorption spectral analysis procedure with 2M HNO₃ are not correct, because the first method provides underestimate concentration values, and the second method provides overestimate values. The optimal is the method with atomic absorption spectral analysis with 0,5М HCl because the results of the atomic absorption spectral analysis with 0,5M HCl correspond to the actual chromium concentration of $30 - 60$ mg/kg to the greater extent. The location of ore mining and processing plants close to the river with a water storage basin positively promotes processes of accumulation and deposition of silt fraction. From the preceding description, it is known that these processes are more characteristic for chromium accumulation as compared with hummus.

The fourth study area encompasses sufficiently ample territory (Fig. 23). For this reason, the area was divided into three parts: the tailing pit of the Central Mining and Processing Integrated Plant, which is located at the thalwegs of the Great Lozovatka and Small Lozovatka ravines; the perimeter of the tailing pit of No. 1 Open Pit, and the west edge of No. 1 Open Pit.

Fig. 23. An overview map of the northern research objects.

The results of the study of the distribution of heavy metals within the tailing pit of the Central Mining and Processing Integrated Plant by using the aforementioned methods have demonstrated the inaccuracy of the method with atomic emission spectral analysis, because both the procedures of atomic absorption spectral analysis with 2M HNO₃ and 0,5M HCl has confirmed the presence of higher concentrations of heavy metals, as compared with atomic emission spectral analysis. The results of the analysis of the distribution of heavy metals along the tailing pit profile have demonstrated only the excess of the maximum allowable concentration of chromium (the average chromium concentration is $150 - 160$ mg/kg). The concentrations of other elements fluctuate (except nickel) but do not exceed the maximum allowable values. These results confirm the conclusion that heavy metals do not have a significant impact on chemical processes possible for deposit accumulation in the current conditions.

When analysing the three-dimensional distribution of heavy metals, such as copper, lead, and nickel, within the tailing pit of No. 1 Open Pit, the trend is detected for the accumulation of heavy metals in higher concentrations if the study areas are located close to the tailing pit. The more is the distance between the study areas and the tailing pit; the lesser is the concentration of heavy metals in the area. Analysing the plot of chromium distribution (Tab. 4 $\&$ Fig. 24), the increase of chromium concentration at a distance from the tailing pit margin is caused by the effect of municipal wastewater but not the impact of No. 1 Open Pit.

Fig. 24. Distribution of Cr along the tailing pit of No. 1 Open Pit depending on the relief.

It should be noted that the concentrations of all the elements do not exceed the maximum allowable concentrations for these elements. It is possible to explain this feature by the vicinity of the significantly larger tailing pit of the Central Mining and Processing Integrated Plant, which receives the most amount of mining waste.

The last object studied is the west edge of No. 1 Open Pit (Tab. 5). This area is unique by that samples were taken directly at the mining plant.

West edge of No. 1 Open Pit

Tab. 5. Distribution of heavy metals along the edge of No. 1 Open Pit.

Fig. 25. Distribution of Pb along the edge of No. 1 Open Pit depending on the relief

Fig. 27. Distribution of Zn along the edge of No. 1 Open Pit depending on the relief

Fig. 26. Distribution of Cu along the edge of No. 1 Open Pit depending on the relief

Fig. 28. Distribution of Cr along the edge of No. 1 Open Pit depending on the relief

Fig. 29. Distribution of Ni along the edge of No. 1 Open Pit depending on the relief.

In the south-west part of the pit edge, the concentrations of all the heavy metals (see Fig. 25-29) increase and exceed the maximum allowable concentrations. The west part of the pit edge is characterised by the even distribution of heavy metals, which concentrations are close to the maximum allowable concentrations. It is possible that the accumulation of heavy metals in these areas is caused by the impact of prevailing north-east winds, which promote the transfer of deposits with accumulated heavy metals.

Conclusions

The results of the performed studies have confirmed that the accumulation of heavy metals in the geologic environment is affected by mining and processing plants, as well as by domestic waste and municipal wastewater. Additionally, prevailing winds and ground relief have been taken into account as additional factors in the distribution of heavy metals. The trend to active absorption of some part of heavy metals by vegetation has been confirmed. The absorption of heavy metals, in combination with periodic recultivation works, significantly reduces concentrations of heavy metals to the levels not exceeding the maximum allowable concentrations, excluding the concentrations of heavy metals in areas which are located close to mining sites.

In our opinion, in order to achieve more significant results, the reclamation works of the geological environment in Kryvy Rih has to be complemented by some additional measures. Regarding the objects located in the centre of the city (Red Ravine, the tailing pit, used for hydro projection now, which is located between Mekhanobrchermet, South Open Pit, and Hihant-Glyboka Mine), regular annual removal and replacement of contaminated soil would be appropriate. As follows, several goals could be achieved: the risk to human health could be significantly reduced because, despite the proximity to the metallurgical enterprise, the area along the ponds in the Red Ravine is still considered as "beach" ones. Also, the probability of intensive subsidence and failure within the tailings storage could be reduced because the regular flooding by mine water creates a constant risk in those areas. Another additional measure to remediation works may be the active use of plant adaptation possibilities. Namely, the practical use of the research results of the Orlovsky breeding institute in Kryvy Rih. In the city boundaries, the use of plant-concentrates of heavy metals may be appropriate, because, in this case, it is possible to remove their subterranean and underground masses regularly (the best would be every 2-3 years) and plant the area with new green plantations. On the outskirts of the city, it would be more appropriate to use plants that are not characterised by the accumulation of heavy metals in fruits and are relatively stable to the conditions typical for the vicinity of quarries and tailing storages. Among such plants, according to climatic and geological conditions of the Kryvyi Rih, the most suitable would be sea buckthorn, currant, raspberry and cherry.

These measures can significantly improve the efficiency of remediation works, and therefore reduce the level of anthropogenic load on the geological environment, allowing assimilation processes proceed times faster.

References

- Baiseitova, N., Sartaeva, H. (2014). Accumulation of heavy metals in plants, depending on the level of soil contamination. *Young Scientist, 2, 379-382.*
- Chertko N. (2008). Geochemistry and Ecology of Chemical Elements. *BSU Publishing Center*, *p.140*.
- Cholodov V. (2006). Geochemistry of the sedimentary process. *M. "Geos", p.608*.
- Dobrovolskiy, G., Urusevska, I. (1983). Map of soil-geographical zoning of the USSR for higher educational institutions. New types of maps and methods of their creation, *Moscow State University*, *74-85*.
- Drugov U. (2007). Analysis of contaminated soil and hazardous waste: a practical guide. *BINOM. Knowledge lab*, *p.624*.

Korzhnev M. (*2005*). Ecological geology. *Kyiv National University, p.250*.

Ecological, toxicological, hydrochenical, and agrochemical methods of analysis of fertilizers, *available online*: *http://www.novaecologia.org/voecos-1613-6.html* [*accessed on 26 April 2017*]

Effect of heavy metals on plants, *available online: http://biofile.ru/bio/36884.html* [*accessed on 23 April 2017*]

- Hrin, A., Li, S. (1980) Ingress of heavy metals in plants, depending on their content and migration capacity. *Paper presented at the Second World Conference on Migration of Polluting Substances in Soils in Certain Regions, Leningrad*, *46-48*.
- Influence of metallurgical production on the environment (2011), *available online*: *http://www.ecoproblems.org/2011/11/blog-post.html* [*accessed on 25 April 2017*]
- Jovinskiy, E., Kruchenko, N. (2007). Geochemical search methods oriented on mobile forms of chemical elements on the Ukrainian shield. *The Far East-2. Mining Information Analytical Bulletin*, *15, 213-222*.
- Klos, Y., Birke, M., Zhovinski, E., Akinfiiev, G. (2012). Regional geochemical study of Ukrainian grounds within the bounds of the international project of geochemical mapping agricultural and grazing lands of Europe (GEMAS). *Search and ecological geochemistry*, *1, 51-66*.
- Korzhnev M. (2003). Ecological-economic problems of the development of the mineral-raw material complex of Ukraine. *Ed. Geologist of Ukraine*, *2, pp. 19-23.*
- Korzhnev, M., Kurilo, M., Zahariy, N. (2014). Resource and ecological criteria for determining the assimilation potential of the geological environment by the example of the mining regions of Ukraine. *Bulletin of Tomsk State University*, *387, pp. 243-252.*
- Korzhnev, M., Mishchenko, V., Shestopalov, V., Yakovlev, E. (2000). The conceptual foundations of environmental improvement for Ukrainian mining regions, *Kiev: SOPS Ukrainy Publ., p.75*.
- Kovda V. (1985). Biogeochemistry of soil covering, *M., Nauka*.
- Krisanov O. (2008). Resource significance of the natural environment carrying capacity and its place in the system of economic relations. *Visnik SumDU. Seriya Ekonomika - The Vysnik of the SSU. Economic Sciences*, *2*.
- Kurbatova A. (2004). Ecology of the city. *M. The scientific world, p.624*.
- Orlov, D., Sadovnikova, L., Lozanivskaya, I. (2002). Ecology and protection of the biosphere in the case of chemical pollution. *Tutorial for chemical, chemical engineering and biological specialized higher education institutions; M., High School*, *p.334*.
- Perelman, A., Nirlian, N. (1984). About geochemical principles of systematics anthropogenic landscapes. *M. University Academic Press*, *44-50*.
- Rusanov A. (1971). Fundamentals of quantitative spectral analysis of ores and minerals. *M., Nedra*, p.360.
- Sadovnikov L. (1984). The influence of industrial enterprises on the environment. *Theses of reports. Monitoring the content of heavy metals in soils of natural and man-made landscapes*, *p.163*.
- Saprishkin F. (1984). Soil geochemistry and nature protection. *L., Nedra*, *p.342*.
- Stetsenko, A., Ivanchenko, V. (2016). The main sources and factors of technogenic influence on sedimentary rocks of the central part of Kryvbas. *East European Scientific Journal*, *12, part 1, 39-46*.
- Study of heavy metals in soils, *available online: http://biofile.ru/bio/35489.html* [*accessed on 25 April 2017*]
- Taranov, A., Manilo, I., Momontov, U., Usmanov, V. Assimilation potential of the region, *available online*: https://www.kazedu.kz/referat/85115 [*accessed on 10 September 2016*]
- The problem of heavy metals, *available online*: *https://medn.ru/statyi/Problematyazhelyxmetallov.html* [*accessed on 20 March 2017*]
- Thermo Scientific iCE 3300 AA Spectrometer, Elemental Analysis, *available online*: *https://www.thermofisher.com/order/catalog/product/942350033312* [*accessed on 02 May 2017*]
- Voskresenskaya, O., Voskresenskiy, V., Alyabysheva, E. (2013). Accumulation of heavy metals by soil and plants in the field of collection and temporary storage of solid waste wastes. *Modern problems of science and education*, 2.