Commercial products of mining and metallurgical companies in river sediments of industrial regions

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Abstract. Modern alluvium is a complex multicomponent system that includes both natural and man-made material. In the process of research on the pollution of river sediments with industrial waste, the authors established the presence of commercial products of mining and processing enterprises in the sediments. It includes crushed granite, metallurgical slags, ores and concentrates, coal and other products. Significant volumes of inputs of these materials into the ecosystem motivate the development of special technologies aimed at additional production of mineral products through the complex processing of modern river alluvium. In addition to economic benefits, the implementation of these projects will improve the state of the environment in regions with significant technogenic load.

1. Brief description of the study region
1.1. The Kryvyi Rih iron ore basin as a complex man-made deposit

The Kryvyi Rih iron ore basin is the largest basin in Ukraine with deposits of rich iron ores, the main mining center of the country, located in the Dnipropetrovsk region.

Giant mining enterprises of the Ukrrudprom concern are concentrated in the basin: five large mining and processing plants include ten quarries with a depth of more than 300 m for the opencast mining and 17 mines with a depth of 80-1300 m for the underground iron ore mining. The largest production facilities of the metallurgical industry are OJSC ArcelorMittal Kryvyi Rih and a coke plant, as well as plants for the production of cement, raw materials for the paint and varnish industry, construction materials and other enterprises. Mining of crude iron ore and its processing into iron-containing products, as noted above, is carried out by five processing plants: “Yuzhniy GOK” Mining and Processing Plant (UGOK); Novokryvyi Rih of ArcelorMittal (NKGOK); Central GOK, Ingulets GOK and Northern GOK of Metinvest.

Currently, the average depth of Kryvbas quarries is up to 400 m (UGOK quarry), the height of heaps and dams - sludge storage - up to 100 m (heaps Hannivsky quarry, tailings Voykivske, Mykolaivske), the depth of mines - up to 1400 m (“Rodyna”, “Jubileyna”) [1]. According to V P Palienko’s calculations: the total area occupied by quarries in Kryvbas is 33.34 km², dumps - 60.0 km², tailings - 52.74 km², subsidence zones above the minefields - 34.71 km² [2] Mining complexes now occupy almost 40 thousand hectares and are an important component in the operation of the modern Kryvyi Rih landscape-technical system [3].
The volume of Kryvbas waste is estimated at 10 billion tons and accounts for more than 30\% of the total industrial waste of Ukrainian enterprises. More than 80\% of iron ore is extracted here and 20\% of Ukraine’s metal is produced. In this regard, the territory of the Kryvyi Rih basin is one of the most man-made geoecosystem in the world.

Industrial waste of the Kryvyi Rih basin is classified as a complex man-made deposits because they contain different types of waste and are studied comprehensively. The quite high complexity of Kryvyi Rih iron ore deposits is due to the peculiarities of genesis, geological conditions and the composition of ferruginous quartzites, containing, lateral and overburden. Within the deposits, the rocks discovered by quarries are represented by granites, migmatites, gneisses, amphibolites, etc. The cover is composed of various loess loams, clays, sands, limestones, talc shales and other rocks. The technogenic resources includes three main types of man-made waste that require further processing:

- Heaps of rocks. More than 2.16 billion $m^3$ of rocks have been accumulated in heaps on the territory of the Kryvbas
- Dumps of sludge waste, enrichment of ferrous quartzites from processing plants. The total amount of sludge waste in sludge storage facilities is over 2.4 billion $m^3$
- Waste slag of the metallurgical plant. The waste of the ArcelorMittal Kryvyi Rih and the Kryvyi Rih TPP of Dniproenerho OJSC is 76.2 million tons. These include:
  - smelting and blast furnace slag;
  - metallurgical sludge;
  - rolled scale;
  - ash-slag dumps [4].

1.2. Ingulets river system
There are 8 rivers at the territory of Kryvyi Rih. But only two cross the city directly - the Ingulets river and the Saksagan river. The bottom sediments of these rivers were studied by authors.

The length of the Ingulets River is 549 km. The drainage basin is 14870 thousand $km^2$. The width of the riverbed near Kryvyi Rih is 25-30 m, and the depth is up to 1.7 m. The terraces of the river valley are buried under heaps of poor rocks, the sludge storage and other industrial buildings. In the southern part of Kriviy Rih the river valley is totally changed: river banks are look like canyon due to heaps of poor ore of the processing plant of ArcelorMittal and UGOK.

Economic activity in the Ingulets river basin has a complex and diversified structure. Combination of the main directions of production with the features of the water use system functioning formed a number of other powerful natural and man-made systems. The specific water management and the river basin operation puts the Ingulets River into a list of special types of rivers in Ukraine. [5]

2. Preconditions of the research
Oursdays is the world of huge anthropogenic and industrial pressure on the natural geoecosystems.

The intensity of human activities during the last centuries causes a significant violation on the existing balance of the nature. Along with the scientific and technological progress, the scale of the impact on the environment is increasing, which leads to undesirable changes of air, water, and soil physical, chemical, and biological characteristics, and these can have adverse effects on humans, animals, and plant lives. Among serious environmental problems, the investigation of increasing pollution of the hydrosphere is particularly important. [6]

The most sensitive to different pollution is aquatic ecosystems. Pollutants are various: domestic sewage water, organic and petrochemical agents, fertilizers, microplastic pellets and the last but not least – industrial waste. Industrial sewage contains trace metals in large quantities
and organic pollutants. Huge amounts of mine tailings are accidentally (or not) spilled into rivers.

River ecosystems are under pressure from several different stressors. Among these, inorganic pollutants contribute to multiple stressor situations and the overall degradation of the ecological status of the aquatic environments. The main sources of pollution include different industrial activities, untreated effluents from municipal waste waters and intensive agriculture. [7]

Heaps of industrial wastes containing various hazardous materials may be dangerous to the surrounding environment. Pollutants released from the heaps can contaminate the water, soil and air, and can affect human health. Therefore, areas where dangerous wastes are stored must be monitored to prevent contamination.

Industrial waste heaps can cause water pollution. For instance, contaminants such as metals, hydrocarbons, organic solvents and polycyclic aromatic carbons can be released from the heap. [8]

In the aquatic environment, sediments have been widely used as environmental indicators for the assessment of metal pollution in the natural water. The principal comportment of metals is a function of the suspended sediment composition and water chemistry in the natural water body. During transportation of heavy metals in the riverine system, it may undergo frequent changes due to dissolution, precipitation and sorption phenomena, which affect their performance and bioavailability. Sediment is an essential and dynamic part of the river basin, with the variation of habitats and environments. The investigation of heavy metals in water and sediments could be used to assess the anthropogenic and industrial impacts and risks posed by waste discharges on the riverine ecosystems. Therefore, it is important to measure the concentrations of heavy metals in water and sediments of any contaminated riverine ecosystem. [9]

Recently, studies of bottom sediments have gained an importance. Adsorption of heavy metals by bottom sediments leads to the so-called hidden pollution, which could turn into a real pollution under external factors.

Just because sediments play an important role in contaminant accumulation and transport, they are frequently used to identify contamination sources, study dispersion pathways and mechanisms, and determine the extent of the area involved in contamination and its time duration and evolution.

However, several studies focus their attention only on a few specific abiotic characteristics of sediments (geochemistry or mineralogy) to trace back their origin and/or contamination degree. On the contrary, other studies have shown that the use of multiple approaches is more useful in this research type to understand and highlight the different mechanics involved in the investigated area. [10].

The bottom sediments of rivers are the element of the upper part of the lithosphere section and the lower part of the hydrosphere. They contain the data about structure, composition and conditions for formation of the river valley and drainage basin. The great amount of the man-made materials are added to the natural sources of the sediments in the regions of huge anthropogenic pressure and in the territories of industrial, especially mining, centers. It comes with sewage, surface runoff, by direct movement of material stored in the coastal zone to the riverbed. The technogenic component is included in the general cycles of migration and sedimentation of sedimentary substance. In areas of man-made impact and downstream the alluvial sediments are a collection of particles with natural and unnatural origin. [11,12]

Studies of modern alluvium have shown the presence of significant amount of marketable products of mining and processing enterprises in the bottom sediments of the Ingulets River. This fact testifies not only to significant pollution of the environment, but also to the economic losses of these enterprises. Because waste is what can be sold. The results of such studies prove the need to find and implement new integrated technologies that will minimize production losses, and thus reduce the amount of waste and pollution of geocosystems.
3. Purpose and methodology
The aims of the study:

- to assess the possibility and the feasibility of using river alluvium in the industrial regions in order to recover lost marketable products of metallurgy and mining and processing;
- to show the advantages of using the integrated technologies for cleaning bottom sediments;
- to demonstrate the economic benefits.

To achieve this goals, a number of methods were used:

- the analysis of granulometric composition of bottom sediment by the sieve method. According to particles' size 12 fractions were got after sieving. Then they were divided on four types: psephites (>2 mm), psammites (2-0,1 mm), siltstones (0,1-0,05 mm) and pelites (<0,05 mm).
- the determination of specific density by the quantitative hydrostatic method. Five parallel experiments were conducted for realistic results. If standard error was more than 0,2, additional five experiments were conducted.
- the evaluation of magnetic component in river alluvium (described [13]). The total compound of magnetic component was compared with the average compound of magnetic component for concrete type of sediments.
- the qualitative and quantitative mineralogical analysis of selected samples of river bottom sediment. The preparation of samples for mineralogical analysis was carried out in accordance with the method of slag analysis with the author’s additions and improvements. [14]
- the separation of river alluvium in the vortex air-mineral flow. The initial sample with weight 3-5 kg was divided on two parts by the quartering method. About 1 kg was used for the mineralogical analysis. An other part of the initial sample called the joint sample and was used for the technological research on the possibility of its use. The proposed technological algorithm:
  (i) The comminution of the joint sample by rotary mill of the author’s design. The first sludge part is obtained: dusty product.
  (ii) The sieving and the air-gravity separation. A vortex air-mineral flow was activated in rotary mill’s working chamber. With its help, the growths and lumps of sediment were divided into several products depending on the specific gravity, size, morphology and other properties of mineral grains. The second sludge part is obtained: quartz sand.
  (iii) The obtained products after the second step of algorithm were divided into several size classes. Each class was further cleaned in a magnetic and gravitational field to improve product quality.
  (iv) The quality of separation was controlled by the testing of obtained products with optical microscope. In addition the chemical and the spectral analysis, the electron microscopy and the microprobe analysis were used.

This technology allowed not only to identify the commodity products of industrial enterprises of the Kryvyi Rih basin in the composition of the river sediment, but also to distinguish them into the individual products and to compare with the similar products of the enterprises that produce it.

4. The results of the research
4.1. Sampling and samples
Over the last ten years, 214 samples were taken from the Ingulets river system with tributaries. Of these, 105 different depth samples from 35 wells (the number of layers in the well varies from
two to six - depending on the depth of drilling); 58 samples from 12 cross-sections across the river valley: 51 point test.

Sites of sampling, profiling and drilling were selected on the basis of preliminary analysis of the river system taking into account the structure and shape of the riverbed and the nature of the watercourse - the presence of meanders, narrows, dams, reservoirs. Because the conditions of bottom sediments' formation and informativeness of testing materials depends on it. The analysis also took into account environmental conditions - the proximity of enterprises, settlements, agricultural lands and more.

The samples were taken for the purpose of comprehensive assessment of bottom sediments, special emphasis was placed on the determination of anthropogenic load. It means the presence of man-made non-natural components. The analysis of granulometric composition was performed, the specific density, magnetic component, radiological, chemical and qualitative mineralogical analysis were determined for all samples. The presence of marketable products of mining and concentrating enterprises was revealed during the qualitative mineralogical analysis.

According to the sites of sampling the samples are grouped in three zones:

- Zone I relatively low industrial load - samples, taken upstream the Kriviy Rih city
- Zone II extremely industrial load - samples, taken in the southern part of Kriviy Rih
- Zone III post industrial load - samples, taken after Kriviy Rih

The average results are grouped the same way.

4.2. Particle size distribution

Psephites and pelites have almost equal parts in bottom sediments from zone I and zone III. In zone II pelites have little part - only 3,5 %, but psephites and psammites fraction are increase in twice. It means that a great amount of additional rough particles are added to the bottom sediments in this part of river system. (table 1)

| Sites of sampling | Psephites (>2 mm) | Psammites (2-0,1 mm) | Siltstones (0,1-0,05 mm) | Pelites (<0,05 mm) |
|-------------------|-------------------|----------------------|--------------------------|-------------------|
| Zone 1            | 10,1              | 43,2                 | 3,5                      | 43,3              |
| Zone 2            | 20,2              | 75,2                 | 1,1                      | 3,5               |
| Zone 3            | 10,4              | 35,9                 | 4,1                      | 49,7              |

4.3. Specific density

The similar regularity is approved by results of measuring of specific density of bottom sediments. The indexes of density are increase and have wide range in zone II. (table 2)

The specific density indicator allows to identify quite accurately the beginning of the zone of influence of mining and processing plants on the river ecosystem. However, for the final identification of this man-made element and clarification of the zone of its distribution downstream, it is necessary to investigate the presence and amount of magnetic product, petrographic and mineralogical composition of samples in addition to the particle size distribution. But regardless of further studies of lithological characteristics, we can talk about the area within the industrial region, where the specific density and particle size distribution of bottom sediments have significant differences from natural indicators. This allows to single
Table 2. Specific density of bottom sediments of the Ingulets River.

| Sites of sampling | Specific density, g/sm³ |
|-------------------|-------------------------|
| Zone 1            | 2.34 ... 2.48           |
| Zone 2            | 2.70 ... 3.11           |
| Zone 3            | 2.34 ... 2.49           |

out the area where the formation of bottom sediments occurs under the influence of factors of man-made origin.

4.4 Magnetic component
Mining operations in the Kryvbas have a direct impact on such lithological characteristics of bottom sediments as particle size distribution and specific density. Since we are talking about the extraction and processing of iron ore, it is advisable to determine the presence of magnetic particles in the samples. Below are the results of studies of the presence and distribution of magnetic particles in the bottom sediments in the study area. According to table 3 we can see regularity: in samples from zone I part of magnetic component is too low, but in samples from zone II it is too great. Then in samples of zone III part of magnetic component become lower.

Table 3. Part of magnetic component in the bottom sediments of the Ingulets River.

| Sites of sampling | Part of magnetic component, % |
|-------------------|-------------------------------|
| Zone 1            | 0.09                          |
| Zone 2            | 2.10 ... 59.55                |
| Zone 3            | 0.12 ... 0.28                 |

So large part of magnetic components in samples from zone II confirms the presence of mining and processing and metallurgical waste in the bottom sediments of the Ingulets River on territory of Kriviy Rih. The mineralogical analysis was performed to further confirmation of this statement. Due to it the percentage of natural and man-made elements with magnetic properties was evaluated.

4.5 Mineralogical analysis
A large number of allotigenic and autigenic components, mineral formations of industrial origin, as well as organic residues were diagnosed as part of the modern sediment of the Ingulets River.

Iron minerals are very common in the modern sediment of the Ingulets River. They are represented by magnetite, hematite (martite and iron mica), goethite, lepidocrocite, hydro hematite (emulsion hematite). Their presence is constantly observed. It is natural for the river and its tributaries, because they intersect the outcrops of rocks of the iron-siliceous formation of the Kryvyi Rih series.

In addition to the deposited products of the weathering crust, there are unchanged (not oxidized) varieties of rocks and ores of iron-siliceous formation in the sediments. Among the fragments of quartzites dominate the "fresh" appearance, the angular proportions of low-ore (poor) species, such as red-layered, gray-layered, and light gray. There is quartz, magnetite,
unchanged grains of silicates and sulfides in their composition. According to these features, they correspond to the poor magnetite-quartz growths accumulated in the tailings of mining and processing plants located in the valley of the Ingulets River. (figure 1, figure 2)

![Figure 1. Fragment grains of magnetite quartzite. Magnification 30X.](image1)

![Figure 2. Martite ore. Magnification 40X.](image2)

Besides, in the samples from zone II was found the iron ore concentrate figure 3, figure 4. The samples of bottom sediments from the Saksagan river

![Figure 3. Magnetite concentrate from processing plant in a mixture with quartz and other minerals of alluvium (+0.04-0.063).](image3)

![Figure 4. Lost magnetite concentrate of processing plant (+0.063-0.1 mm).](image4)

The quantitative part of components of bottom sediment in grams per ton (g/t) was determined during the mineralogical analysis.

The combination of natural and man-made iron minerals transform the bottom sediments of the Ingulets River into deposits of iron ore.
4.6. Separation of river alluvium in the vortex air-mineral flow

The technology for separation of river alluvium in the vortex air-mineral flow is based on the physical properties of the particles. The difference in magneticity of the alluvium components provides opportunities for dividing sediments on parts due to influence of the magnetic fields of varying strength.

The Ingulets alluvium from zone II has a great amount of iron oxides, especially magnetite (328538 g/t), hematite (41804 g/t) and goethite (19874 g/t). These are the maximum of the known concentrations of these minerals in the modern alluvium of the studied rivers. Also, in this area, the maximum number of iron-containing man-made formations was determined: magnetic spheres (24 g/t) and particles of metallurgical slag (16 g/t). The share of ore minerals in the joints with quartz is 90-95%.

Enrichment of this man-made placer was performed according to the scheme shown in figure 5.

![Figure 5. Algorithm of enrichment of river alluvium.](image)

The dried sample material was divided into sieves in the class of 0.5 mm. Particles larger than 0.5 mm, composed mainly of quartz and carbonates, were sent to the tailings of separation. Class 0-0.5 mm was separated in a magnetic field with an intensity of 0.2 T. The non-magnetic fraction was sent to the tailings, and the magnetic product was ground in a rotary mill to a particle size of 0.04 mm to reveal the growths of ore and non-ore minerals and again subjected to magnetic separation in a magnetic field of 0.35-0.7 T. This made it possible to obtain iron ore concentrate in the form of a magnetic fraction and non-magnetic tailings. (figure 6, figure 7)

The enrichment tailings formed at the various stages of separation were combined. The total iron content in the resulting concentrate was 65.4%. This corresponds to the composition of
iron ore concentrate of medium quality, produced by mining and processing plants. But the compound and type of this product is different from products of mining and processing plants, because raw stuff is consist of complex of iron minerals with natural and technogenic origin.

Figure 6. Iron ore concentrate from the processing of river alluvium.

Figure 7. Tailing of enrichment of river alluvium.

5. Conclusions
The authors established the presence of commercial products of mining and processing enterprises in the sediments during studying the pollution of river sediments with industrial waste. It includes crushed granite, metallurgical slags, ores and concentrates, coal and other products. Amount of this materials so great that it will be advisable to use for economic purposes. It is enough to develop and implement the appropriate technology. All products generated in the process of applying the proposed technology can be used in industries. This is a waste-free processing technology.

Lost iron ore concentrate of mining and processing plants as a result of erosion and transportation by storm streams, falls into the river alluvium. In the river system, it mixes with other man-made and natural iron minerals. Among them: hematite, magnetic oxide and metal balls, etc. Due to gravitational differentiation, secondary (redeposited) natural-man-made deposits of heavy iron minerals are formed. These minerals and industrial products can be re-removed from the sludge and produce marketable iron-containing raw materials in the vortex air-mineral flow, according to our technology. Unlike products from processing plants, it consists not only of magnetite, but also contains hematite, goethite, oxide and metal balls, fragments of iron ore agglomerate, particles of metallurgical slag and sludge that fell into the river sediment from various natural and industrial sources.

The main benefit of the proposed technology is water-free enrichment of iron ore. There are no need for any additional reagents and toxic or hazardous agents.

The areas of the riverbed contaminated with man-made components coincide with the places of natural accumulation of iron minerals due to erosion of the weathering crust of iron-siliceous rocks. It also accumulates heavy mineral grains from the heaps of mining and processing plants, tailings and other industrial facilities and morphostructures. The joint sedimentation of ore crystal and lithoclasts coming from three sources significantly changes the natural properties, mineral and chemical composition in some parts of the river.

Not only Kriviiy Rih is faced with this problems. Similar tasks are actual and important for other industrial regions, especially regions of iron ore mining and processing. For example,
Anshan town with the Shane river (China), Eisenhüttenstadt with the Oder river (Germany), Parauapebas with the Rio-Parauapebas river (Brazil) and many-many others.

Significant volumes of industrial inputs into the ecosystems encourage the development of special technologies aimed at additional production of mineral products through the complex processing of modern river alluvium. It shows a great potential for economic use. In addition to economic benefits, the implementation of these projects will improve the state of the environment in regions with large technogenic load.

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