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# Bottom Sediments in a River Under Acid and Alkaline Wastewater Discharge

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**ABSTRACT**

The drainage flows of metal loads into the drainage and infiltration waters of mine dumps of enterprises have a dramatic effect on small rivers in industrial regions. The paper considers the outcomes of geochemical monitoring of the Karagaily River and assesses the transformation of the acid-base conditions depending on the influence of the facilities of the enterprise. The results of engineering and environmental surveys, including sampling of bottom sediments, laboratory preparation, chemical elemental analysis of samples and X-ray diffraction analysis of mineral composition, were presented. A complex technogenic alkaline sorption-hydroxide barrier was found at the mixing point of acidic river waters (the influence of dump and quarry waters) and alkaline wastewater of treatment facilities, where the deposited iron hydroxide adsorbs ore minerals, which reduces their outflow into larger rivers and increases the self-purification potential of the river. Further interaction of iron hydroxide with the acid mine drainage and calcium bicarbonate of wastewater results in pyritization of bottom sediments. Excavation and dewatering of the pyrite-containing bottom sediments will allow their joint use with tailings and ore-processing waste for re-extraction useful components.

**Keywords:** rivers' pollution; bottom sediments; metal pollution; technogenic sediment; pyrite formation; geochemical barrier; x-ray diffraction analysis

## INTRODUCTION

In Russia, approximately half of the total streamflow volume accounts for small rivers [Kuznetsov & Petrov 2017, Nevskaya et al. 2019]. Due to minor runoff volumes in small rivers, the self-remediation process is slower, and the long-term anthropogenic impact leads to the degradation of water ecosystems [Kremcheyev et al. 2020, Puzanov et al. 2015]. The impact of mining industries results in increased silting and technogenic sedimentation [Chalov et al. 2015a, Chukaeva et. al. 2020]. The issue of the environmental state of minor rivers and other water bodies was considered in numerous works, and much attention was paid to the development of the environmental protection measures to prevent pollution of small rivers by enterprises of various industries [Isakov & Chukaeva 2016, Strakhovenko et al. 2016]. Nevertheless, despite the state of knowledge, the problem of environmentally efficient and economically expedient technogenic sediment utilization remains unsolved [Chalov 2015b, Pashkevich et al. 2017a, Pashkevich et al. 2020].

The Urals is one of the largest mining regions in the world. As the development of chalcopyrite deposits started here in 1635, millions of tons of various types of waste have been accumulated by now [Plokhov et al. 2019]. This includes mine dumps, tailings, and technogenic materials over a vast area, represented by atmospheric precipitation and bottom sediments [Pashkevich 2017]. The residues of extraction and processing of sulfide copper-pyritic ores at the Sibay Mining and Processing Plant (Sibaysky GOK) are an example of such mining legacy.

The Sibaysky GOK is located in the Southern Urals next to the town of Sibay in the Karagaily River basin of the top commercial fishing importance. The Karagaily belongs to minor rivers and is the initial link in the formation of hydrological, biological, and biochemical cycles of medium and major watercourses, such as the Khudolaz River and the Ural River.

The riverbed in the study area is 2-6 m wide with spills of up to 20 m; it was transformed during the Sibay quarry development. The river headwaters are under the overburden dumps of the Sibay quarry. Technogenic mine dump drainage and natural fissure springs are the source of river water. The riverside quarries, tailings, waste rock and overburden dumps, and drainage channels contribute to the water flow alongside the processing plant that discharges treated wastewater into the watercourse (Fig. 1) in the Sibay industrial agglomeration [Kharko & Plokhov 2019].

The chemical composition of river water depends on dump and mine drainage, as well as on the infiltration from the tailings storage facility. It is also determined by the presence of technogenic alkaline barriers in the river, where the transition of some metals to the solid phase occurs [Alekseenko et al. 2017].

The theoretical and applied significance of the research are high, as theoretically, acid formation is neutralized where sulfide ores occur alongside more alkali minerals, since alkali is the opposite of acidic. Each is caustic, but combined they neutralize each other. Carbonate rocks are a typical alkali mineral sometimes associated with sulfides. Where acid and alkali minerals co-occur, the ratio of acid-generating material to neutralizing material is an important component of predicting whether a mine will have acid mine drainage. For example, metal at the historic Kennecott Copper Mine in Alaska was found in conjunction with large amounts of carbonate that neutralized any acid-forming compounds [Kennecott Copper Mine, 2020].

The river water is characterized by contrasting acid-base conditions. At point No. 1 (Fig. 1), the water pH is 7.7-8.2. The quarry water is discharged into the river 1 km downstream. Its qualitative element composition is similar to that of the dump drainage. In summer, the flows of the stream and the river are comparable at the confluence. At this point, the pH value decreases to 3.5-5.0. The metal content in water depends on the pH value, as cations are highly mobile in the acidic environment. Thus, the contents of copper, zinc, iron, and manganese exceed the background levels by 10-1,000 times. As the pH increases, the metal concentrations decrease; nevertheless, their average levels remain at a very high level, as compared to the background conditions [Opekunov et al. 2018, Opekunov & Mitrofanova 2016].

These authors note that until 2011, abnormally high concentrations of metals in the Karagaily River were found throughout its entire length downstream to the confluence with the Khudolaz River. After 2011, the company began to discharge the water from treatment facilities into the Karagaily River 2.5 km below the river source, changing the metal migration patterns. This is since the treated water discharged into the Karagaily River had a pH of about 10.5, exceeding the maximum permissible level. A complex technogenic sorption alkaline barrier was formed at the discharge point (No. 3, Fig. 1). This barrier caused an increase in the self-cleaning potential of the river by decreasing the metal concentrations and salinity of river waters and, consequently,

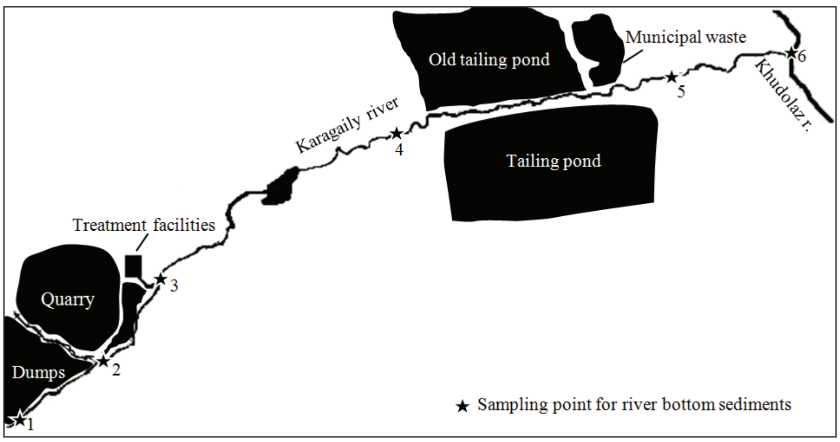


**Figure 1.** Map of bottom sediment sampling

remediating the influx to the Khudolaz River. Thus, the geochemical barrier currently improves the situation with self-purification of the river on the one hand, but, leads to the formation of a geochemical anomaly in the technogenic bottom sediments of the watercourse on the other hand. The geochemical barrier has a saturation stage, and over time, it loses its effectiveness.

The formation of a geochemical barrier is associated with the deposition and accumulation of man-made metals, which leads to the eutrophication of river sections. The hydrological observations marked a flood in the shallowest sections of the Karagaily River downstream from the geochemical barrier in 2014.

In retaliation against this, the Karagaily riverbed was completely cleared of the man-made sediments in 2015. According to the *Bashinform* news agency, the declared width of the riverbed would be at least 4 m along the river bottom. In the city, the river depth would reach 0.5 m. The extracted bottom sediments are dried on the river bank and sent to the solid waste landfill [The Karagaily riverbed in Sibay…, 2020].

When sampling bottom sediments in 2017, the depth of the river in the riverbed was about 0.4 m. Hence, the approximate annual bottom sediment layer thickening is ca. 0.10-0.15 m. Therefore, we assume the maximum increase in bottom sediments by 2021 that will lead to another gradual flooding of the superaqual landscapes in the Sibay industrial agglomeration. The development of such a scenario is unacceptable, due to the progressive development of urban areas, as well as their simultaneous pollution due to the presence of abnormally high concentrations of metals in the river water. Pollutants directly enter the soil, harming phytocenoses and soil biocenosis [Pashkevich et al. 2020, Lytaeva & Isakov 2017a]. Thus, it is necessary to dredge the sediments, since untimely removal of the contaminated geochemical barrier can lead to an even stronger environmental disaster.

In order to reduce the anthropogenic load on the Karagaily River, it is necessary to monitor the current state of the bottom sediments of the river.

The purpose of this study was to assess the state of bottom sediments of the Karagaily River, which is a receiver of the drainage and wastewater of the Sibaysky GOK.

The bottom sediment samples of the Karagaily River and Kultuban Lake were studied. The research consisted of field and laboratory parts.

During the environmental survey, the investigated river was divided into 7 zones: 1 – not affected by the enterprise, 2 – probably affected by the dump drainage, 3 – a point of mixing with the discharges from wastewater treatment plants, 4 – before the tailings of the processing plant, 5 – after the tailings, 6 – confluence with the Khudolaz River, and 7 – the background uncontaminated Kultuban Lake. The sampling points for river bottom sediments are shown in Figure 1 [Kharko & Plokhov 2019].

### Sample preparation and research techniques

One of the authors of the article carried out the sampling of bottom sediments in the summer period (August 2017) under the Russian national standard [GOST 17.1.5.01-80]. The first stage of sample preparation (drying) of bottom sediments was carried out in the laboratory of the enterprise at room temperature. Further preparation of the bottom sediment samples was carried out in the laboratory at the Common Use center of Saint Petersburg Mining University. This Center has accredited environmental monitoring laboratories with all necessary equipment for analysis. A ball mill was used to grind the samples; 5 grams of cellulose were added to a 7 grams sample, ground and mixed it together, to make "tablets" using a manual press. Then, the mineralogical composition of bottom sediments was carried out using the standard method on the Shimadzu XRD-7000 X-ray diffractometer. The water-soluble, mobile and total forms of elements in the samples of bottom sediments were also determined by atomic emission spectrometry with inductively coupled plasma.

## RESULTS AND DISCUSSION

The results of the method of atomic emission spectrometry confirm the studies of other authors (Table 1).

Sample No. 1 is already characterized by an excess of the content of aluminum and manganese relative to the background. When storing pyrite-containing rocks, acid drainage is formed due to the filtration of atmospheric, surface, or underground water through the dump, under the oxygen influence according to the following scheme (Eq. (1)) [Kulikova 2010].

**Table 1.** Content of water-soluble, mobile and total forms of metals in bottom sediments of the Karagaily River

| Metals | Total forms. mg of element/kg of sample | Mobile forms. mg of element/kg of sample | Water-soluble forms. mg of element/kg of sample |
|---|---|---|---|
| Sample No. 1 | | | |
| Al | 48541.6 | 12.6 | 0.2 |
| Cu | <0.05 | <0.05 | <0.05 |
| Fe | 38833.3 | 391.3 | 1.5 |
| Mn | 644.5 | 64.5 | 0.7 |
| Zn | <0.05 | <0.05 | <0.05 |
| Sample No. 2 | | | |
| Al | 3027.6 | 71.7 | <0.05 |
| Cu | 1263.5 | 210.9 | <0.05 |
| Fe | 46221.4 | 33.2 | <0.05 |
| Mn | 890.1 | 82.8 | 2.5 |
| Zn | 446.1 | 165.3 | <0.05 |
| Sample No. 3 | | | |
| Al | 73328.1 | 3293.8 | 1102.9 |
| Cu | 8847.5 | 3101.4 | 1986.5 |
| Fe | 238256.2 | 4007.7 | 60.6 |
| Mn | 742.9 | 112.7 | 96.3 |
| Zn | 2981.2 | 2728.8 | 2578.5 |
| Sample No. 4 | | | |
| Al | 57191.4 | 143.0 | <0.05 |
| Cu | 622.8 | 50.5 | <0.05 |
| Fe | 57191.4 | 310.2 | 0.2 |
| Mn | 1421.3 | 218.0 | 17.3 |
| Zn | 1167.1 | 405.6 | 10.4 |
| Sample No. 5 | | | |
| Al | 55827.0 | 100.0 | <0.05 |
| Cu | 794.8 | 242.9 | <0.05 |
| Fe | 68185.6 | 276.9 | <0.05 |
| Mn | 724.5 | 159.5 | 2.7 |
| Zn | 2237.3 | 1246.5 | <0.05 |
| Sample No. 6 | | | |
| Al | 36924.3 | 1439.6 | <0.05 |
| Cu | 1342.1 | 502.0 | <0.05 |
| Fe | 49785.6 | 813.1 | <0.05 |
| Mn | 1344.2 | 434.5 | 9.3 |
| Zn | 5186.0 | 3485.0 | 4.3 |
| Background sample | | | |
| Al | 19439.0 | 9.3 | 2.8 |
| Cu | 44.7 | 0.7 | <0.05 |
| Fe | 38877.9 | 304.1 | 2.4 |
| Mn | 592.2 | 78.9 | 0.3 |
| Zn | 48.1 | 3.1 | <0.05 |

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

The resulting sulfuric acid reduces the pH of the river water. The alkaline wastewater from the treatment facilities of the company has a bicarbonate-calcium composition. At the confluence of the alkaline effluents of treatment facilities with the acidic waters of the river, an alkaline barrier occurs. In the river, when the alkalinity of the water increases, the process of formation of iron bicarbonate begins (Eq. (2)) with its conversion to hydroxide (Eq. (3)).

$$FeSO_4 + Ca(HCO_3)_2 \rightarrow Fe(HCO_3)_2 + CaSO_4\downarrow(\text{anhydrite}) \quad (2)$$

$$2Fe(HCO_3)_3 \rightarrow Fe(OH)_3\downarrow + 6CO_2 \quad (3)$$

This was manifested in the ochre coloration of the sediments and the abnormally high concentration of total iron in them (up to 24%) (Table 1). The freshly formed $Fe(OH)_3$ actively adsorbs ore metals [Lytaeva & Isakov 2017, Pashkevich et al. 2017a, Pashkevich et al. 2017b]. This is indicated by the high concentration of Cu (up to 0.885%) and Zn (up to 0.298%) in bottom sediments (Table 1).

The further interaction of iron hydroxide with the dump-drainage sulfuric acid remaining after the neutralization reaction with calcium bicarbonate of wastewater forms pyrite (Eq. (4)).

$$Fe(OH)_3 + H_2SO_4 \rightarrow H_2O + O_2 + FeS_2 \quad (4)$$

Thus, the artificial barrier caused an active accumulation of metals at the bottom of the river in the area of alkaline effluent discharge. After the geochemical barrier, there is a sharp drop in the metal and a further decrease in the metal content downstream of the river. The mechanism of barrier formation is schematically depicted in Figure 2.

The result of X-ray diffraction analysis of the composition of sediment samples is a diffraction pattern, which shows the registered peaks of detected minerals. Table 2 shows the mineral composition of sample No. 3. It was noted that the major minerals of bottom sediments are quartz and albite. Sample No. 2 is characterized by high calcite and dolomite contents. These minerals are natural components of the river bottom sediments.

Sample No. 3 significantly differs in terms of the pyrite ($FeS_2$) and cronstedtite content (($Fe^{2+}$ ,$Fe^{3+}$)$_3$(Si,$Fe^{3+}$)2$O_5$(OH)$_4$), found in associations with pyrite and has admixtures of aluminum and calcium [Cronstedtite…]. This also confirms the formation of pyrite at the site of the artificial geochemical barrier.

According to the studies of the authors [Opekunov et al. 2018, Opekunov, Mitrofanova 2016] artificial alkaline sorption barrier caused an increase in the self-purification potential of the river. The concentrations of iron, zinc, and copper in water decreased by 20-100 times at the confluence of the Karagaily River into the Khudolaz River. This is confirmed by the high content of metals in bottom sediments, which may be associated with a mechanical natural geochemical barrier in the form of a change of velocity and direction of the water flow due to which there is a delay of metals in the bottom sediments of the river.

Thus, a preliminary assessment of the self-purification capacity of the river, taking into account the concentrations of metals in the water and the flow of the river upstream and downstream, suggests that before 2011, about 50% of the zinc entering the Karagaily River was carried out into the Khudolaz River. After the start-up of the treatment plant, this value decreased to 5%. For Cu, a similar figure changed from 25 to 0.3%.

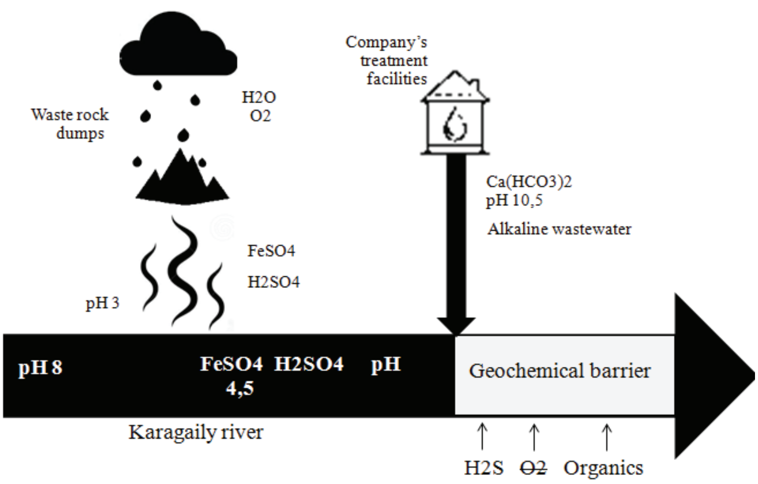


**Figure 2.** Iron migration processe

**Table 2.** Mineral composition of sample No. 3

| No. | Card | Chemical formula | Chemical name (Mineral name) |
|---|---|---|---|
| 1 | 6-0710 | $FeS_2$ | Iron sulfide (Pyrite, syn) |
| 2 | 17-0470 | $Fe_3(Si,Fe)2O_5(OH)_4$ | Iron silicate hydroxide (Cronstedite-\IT) |
| 3 | 33-1161 | $SiO_2$ | Silicon oxide (Quartz, syn) |

## CONCLUSIONS

Mining and industrial production lead to significant pollution of the environment with ore (Cu, Zn) and associated (Fe) metals. Small natural water bodies and rivers are the most vulnerable to pollution. The processes of migration and accumulation of metals in the aquatic landscape are conditioned by the structure of anthropogenic physical and chemical barriers, among which alkaline ones play the leading role. The saturation of the flow of metals leads not only to their concentration on the geochemical barriers, but also to their removal outside the geotechnogenic system.

The monitoring studies have shown that an alkaline barrier occurs at the confluence of the alkaline effluents of the treatment facilities of the company with the acidic water of the Karagaily River. Iron hydroxide deposited in man-made sediments adsorbs ore minerals, which causes an increase in the self-cleaning potential of the river.

This markedly reduces the volume of transported metals into the Khudolaz River, which is a tributary of the Ural River. The final transformation of iron in the bottom sediments of the river at the site of the geochemical barrier may be the formation of pyrite.

The formation of artificial geochemical barriers leads to increased siltation of rivers and sediment accumulation. It should be noted that the authors are currently working on the development of measures for the removal, dewatering and utilization of pyrite-containing river bottom sediments. In the future, such sediments may be used along with tailings and ore processing dumps as a technogenic deposit for additional extraction of useful components.

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