Mineral and geochemical characteristics of soils and bottom sediments in the area affected by mining dumps (a case study of the Sibay ore deposit)

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Abstract. The article focuses on the chemical composition of hydrosulfates formed in bottom sediments and soils as a consequence of sulfide minerals oxidation in mining waste rock dumps. An alkaline geochemical barrier formed under the dumps reduces pollution of natural territorial complexes. High concentrations of Zn up to 1.29%, Cu - 0.74%, and Cd - 27.3 mg/kg are found in the hydrosulfates formed in the river bottom and in the soils. The percentages of exchangeable copper, zinc and cadmium in their total content are 33%, 28% and 22%, respectively. Metals are actively involved in lateral and radial migration, which is regulated by alkaline and evaporation geochemical barriers. The hydrosulfates’ mineralogical composition was studied using microscopy and thermodynamic modeling. Among the secondary minerals, gypsum and iron oxyhydroxides are of primary importance, and to a lesser extent barite, epsomite, and jarosite. Secondary minerals of Cu and Zn in scattering halos are not found, which indicates the leading role of adsorption processes in their phase transitions.

1. Introduction

The development of ore deposits is a significant factor in the chemical pollution of the environment. The specificity of pollution has a certain climatic zoning, which is well expressed in the pyrite deposits of the Urals [1]. The migration of heavy metals in landscapes of the steppe zone is regulated by alkaline and evaporation barriers. The development of a chalcopyrite deposit in the area of Sibay-city has been carried out for 70 years. During the enterprise operation period, mining waste rock dumps, bearing dispersed sulfide mineralization, were formed. For a long time, quarry water was discharged into the Karagaily river without treatment. Over this time, secondary technogenic flows [2] and scattering halos were formed [3, 4].

The main metals of secondary scattering halos formed during the development of chalcopyrite deposits include Cu, Zn, Cd and other chalcophile elements [1, 5-8]. Sulfuric acid is formed during the oxidation of sulfides, which leads to a decrease in the pH of natural waters and soil solutions. Water-soluble sulfates (hydrosulfates) in the oxidation zone of sulfide ores are of great importance in the deposition of toxic elements. According to E. Emlin [1], the highest concentrations are typical for Cd (exceeds regional averages (Cc) more than 10,000), Cu and Zn (Cc 1,000-10,000). The chalcophile...
elements are most accessible to plants in sulfate forms. Experiments have shown that during polycyclic dilution of sulfate brine, only 0.5-1.2% of these metals are deposited in them, while for Fe this value is 22%, and As - 99% [1]. The radial migration of chalcophile elements is well manifested during seasonal changes in the groundwater level in floodplain soils and grounds. An evaporation barrier forms on the surface. Hydrosulfate crusts are formed on the surface and are dissolved during rainfalls.

Despite the large number of studies focused on pollution during the development of sulfide ores, research in this area has not lost its relevance. One of the least studied aspects of this problem is the role of dumps in chemical pollution and secondary mineral formation in bottom sediments and soils of subordinate landscapes. These processes are stimulated by high metal concentrations and contrasting physicochemical environmental conditions (pH-Eh). When developing chalcopyrite deposits, waste rock dumps are considered as the main source of highly concentrated sulfate sulfuric acid solutions and crystalline hydrates of Fe, Cu, Zn, Se [1]. Thus, the purpose of this work is to study the influence of mining dumps of the Sibay chalcopyrite habitat on the mineral and chemical composition of the main components of the landscape.

2. Materials and Methods

The study area is located on the southeastern slope of the Southern Urals within the forest-steppe subzone of the foothills and the steppe chernozem subzone of the abrasive platform of the Trans-Urals. The prevailing soils are ordinary and typical chernozems. The bedrock consists of Paleozoic gneisses, porphyries, diabases, limestones etc. The Sibay habitat is located within the Krasnouralsk-Sibay-Gai chalcopyrite metallogenic zone. The main ore-forming minerals include pyrite, pyrrhotite, chalcopyrite, and sphalerite. Galena, tennantite, arsenopyrite, hematite, greenockite, freibergite, enargite, and cinnabar are present in smaller amounts, while Cu, Zn, Cd, and As are the main indicators of secondary scattering halos [9, 10].

The object of study is bottom sediments and soils in the upper reaches of the Karagaily River. The river flow is formed under the overburden dumps of the Sibay quarry. Here acid mine drainage accumulates and groundwater (fissure waters) flows out [2]. Downstream quarry water was discharged into the watercourse until 2019. The river is about 11 km long, it crosses the Sibay City from west to east (in the middle course) and flows into the Khudolaz River, a tributary of the Ural River.

The total contents of heavy metals and metalloids (HMM - Cu, Zn, Ni, Co, Fe, Mn, Cr, Pb, Cd, Ba, As, Sb, Ca, V, Sc) in bottom sediments and soils were measured with complete acid decomposition of samples by inductively coupled plasma mass spectrometry (ICP-MS) in the Central laboratory of A.P. Karpinsky Russian Geological Research Institute (Saint Petersburg, Russia). The mercury was analyzed by the "cold vapor" method on an autonomous device "Yulia-5m". Micromineralogical studies were carried out on the equipment of the Resource Center "Microscopy and Microanalysis" (Science Park of St. Petersburg State University) using a scanning electron microscope (SEM) Quanta 200 3D (FEI, Netherlands) with an analytical complex Pegasus 4000 (EDAX, USA) in backscattered and secondary electrons mode. Electron probe microanalysis was carried out on an energy dispersive diffractometer of the said microscope under high vacuum conditions at an accelerating voltage of 20 kV. Thermodynamic modeling of TMM forms in soils and bottom sediments was carried out using the Selector-S software package, which is a set of software procedures that implement the algorithm for minimizing free energy using the convex programming method [11].

3. Results and Discussion

The mixing of acid mine drainage and slightly alkaline groundwater leads to the formation of an alkaline geochemical barrier. The acid drainage is neutralized and water flows out from under the dumps, has a slightly acidic or neutral reaction (table 1). The water of streams forming the runoff of the Karagaily River is characterized by sulfate-magnesium type and relatively high mineralization ranging from 2.5 to 9.0 g/l. It contains high concentrations of SO$_4^{2-}$, Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ (table 1). The river bottom from the outlet of the acid mine drainage at a distance of one km downstream is covered
with white powdery sediment with very high concentrations of sulfate sulfur, Cu, Zn, Cd, and also Mn with low contents of SiO$_2$ and Ba. The content of the remaining studied elements is close to the background level (table 2).

**Table 1.** Content of chemicals (mg / l) in acid mine drainage, river, and quarry waters [2].

| Chemicals | Acid mine drainage | Quarry | River | Background |
|-----------|--------------------|--------|-------|------------|
| K$^+$     | 2.66               | 2.2    | 2.3   | 0.91       |
| Na$^+$    | 154.3              | 165.4  | 104   | 24.2       |
| Mg$^{2+}$ | 1463.1             | 450.4  | 224   | 14.7       |
| Ca$^{2+}$ | 369.2              | 248.7  | 114.6 | 60.2       |
| Cl$^-$    | <1.0               | <1.0   | 66.7  | 35.5       |
| SO$_4^{2-}$ | 7392              | 2917   | 1340  | 49.4       |
| HCO$_3^-$ | <1.0               | <1.0   | 115   | 169        |
| Zn        | 111.0              | 49.0   | 12.5  | 0.02       |
| Cu        | 21.0               | 8.1    | 0.296 | 0.007      |
| Cd        | 0.59               | 0.15   | 0.0254| 0.001      |
| Ni        | 0.24               | 0.12   | 0.021 | 0.02       |
| Mn        | 1.117              | N/d    | N/d   | N/d        |
| Fe        | 0.324              | N/d    | 0.240 | 0.256      |
| pH        | 4.95-6.83          | 3.32   | 4.80-7.16 | 7.92 |

N/d – no data

**Table 2.** Chemical composition of hydrosulfates and soils in the zone of influence of the mining waste rock dumps.

| Chemicals | Hydrosulfates | Soils, valley of the Karagaily River |
|-----------|---------------|------------------------------------|
|           | Bottom sediments | Soil crust | Near the mining waste rock dumps | Downstream of the river, 9 km from the dumps |
| SiO$_2$, % | 9.0            | N/d        | N/d            | N/d       |
| CaO, %     | 1.20           | 1.37       | 10.0           | 4.25      |
| SO$_3^2-$  | 19.8           | N/d        | N/d            | N/d       |
| Sc         | 45.7           | 22.4       | 15.5           | 15.9      |
| V          | 27.3           | 31.9       | 110            | 126       |
| Cr         | 13.3           | 19         | 36.1           | 96.7      |
| Mn         | 1082           | 2866       | 1550           | 1010      |
| Fe, %      | 3.78           | 2.44       | 4.28           | 5.00      |
| Co         | 16.5           | 110        | 26.1           | 23.7      |
| Ni         | 11.0           | 49.8       | 24.4           | 61.9      |
| Cu         | 7436           | 6190       | 388            | 184       |
| Zn         | 11570          | 12900      | 1530           | 309       |
| Cd         | 9.2            | 27.3       | 3.59           | 0.86      |
| Sb         | 0.86           | 1.19       | 1.73           | 1.76      |
| Ba         | 26.2           | 52.7       | 180            | 481       |
| Pb         | 10.6           | 8.38       | 22.7           | 26.6      |
| As         | 13.8           | 25.5       | 26.7           | 28.0      |
| Hg         | 0.08           | 0.09       | 0.15           | 0.12      |
In general, the processes of interaction of solutions (formed during mixing of acid mine drainage and ground water) with the environment are non-equilibrium. The composition and pH value of the solutions are not constant, since they depend on the ratio of acid mine drainage, the volume of which is determined by the amount of precipitation (or melt water), and fissure waters, which have a relatively constant inflow. The composition of hydrosulfates at the bottom of the river also depends on this to a certain extent.

The mineralogical composition of hydrosulfates from the bottom sediments was studied by optical and scanning electron microscopy. The sediment is represented by a dense clayey mass of light brown (to milky-white) color with fragments of dark-colored minerals (figure 1). The size of the fragments does not exceed 0.05 mm. The sample is a mixture of various clay minerals with a particle size of less than 5 microns, which cements the larger particles. Among the clay minerals, the most common representatives are probably present: kaolinite, montmorillonite, beidellite and halloysite. The latter two are typical of the weathering crusts of the basic rocks of the Southern Urals (beidellite) and sulfide deposits (halloysite). The illite admixture is also possible. Composite spectra show an aluminosilicate matrix with small impurities of K, Na, Ca, Mg. Clay minerals have a very low contain of Fe. It forms microcrystalline aggregates in pores, cavities and on the surface of samples, sometimes individual grains (figure 1). The sample contains gypsum and barite. At the same time, gypsum covers the entire surface of the sample in the form of individual crystallites, intergrowths and microaggregates "gypsum roses" (figure 2). Barite is less common. Some spectra show distinct peaks of Zn, Mn, and Cu are visible (figure 3), high concentrations of which are noted in hydrosulfates (table 2). However, no independent phases containing these metals were identified. They are found in the formations of microcrystalline aggregates together with iron compounds. These can be iron (III) hydroxides, which are formed at the oxidative stage of the process and act as sorbents. Probably, some of the ore metals are adsorbed by clay minerals, especially montmorillonite and beidellite, which have a high cation exchange capacity. The adsorption of metals is confirmed by the study of their mobile forms using an acetate-ammonium extractant with a pH of 4.8, which, at a low carbonate content, mainly extracts surface-sorbed (exchange) forms. The share of exchangeable forms of the total content is 33% Cu, 28% Zn and 22% Cd.

![Figure 1](image1.png)

**Figure 1.** General view of iron oxides/hydroxides (a); microcrystalline aggregates and individual grains (b). SEM images.
The high content of Zn and Cu in water and in hydrosulfates suggests that some of the Zn can crystallize into goslarite, and Cu into chalcanthite. This is confirmed by the results of thermodynamic modeling, which showed that as a result of the interaction of wastewaters with sediment at the lowest stages of the process, intensive mineralization occurs. (Modeling conditions: per 1 liter of wastewater there is 10 g of sediment, which corresponds to the maximum set value of mineralization). Amorphous silica, gypsum (Ca(SO$_4$)$_2$×2H$_2$O), jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$), antimony anhydrite (Sb$_2$O$_3$), barite (BaSO$_4$), and at the final stages - epsomite (Mg (SO$_4$) × 7H$_2$O), goslarite (ZnSO$_4$ × 7(H$_2$O)), chalcanthite (CuSO$_4$×5(H$_2$O)), iron oxides and hydroxides. Epsomite, amorphous silica, goslarite, and gypsum prevail among the secondary minerals.

The crusts of hydrosulfates formed on the evaporation barrier near the soil surface are represented by loose lumpy white aggregates. In chemical composition, they are very close to hydrosulfates from the bottom of the river, but with a higher content of Co (concentration coefficient is 6.7), Ni (4.5), Cd (3.0), Mn (2.6) and As (1.8) (table 2). This probably reflects the concentrating function of the evaporation barrier. Small amounts of quartz and aluminosilicates K and Na are noted. Secondary
minerals are represented by gypsum in the form of a large number of columnar and tabular crystals that form a dense crust. The voids contain accumulations of fibrous and acicular magnesium sulfates, probably epsomite (figure 4), as well as sulfur crystals. Iron oxyhydroxides are found in small amounts in the form of small grains or in aggregates, possibly containing jarosite. Among the accessory minerals, individual grains of pyrite, chalcopryte, sphalerite, zircon, and apatite are identified.

Chemical analysis of the soil from the river floodplain, where hydrosulfates are formed, showed (table 2) that, in comparison with the chemical composition of soils in the catchment area outside the zone of influence of waste rock dumps, Zn (concentration coefficient is 5.0), Cd (4.2), CaO (2.4), Cu (2.1). The concentration of Cr, Ni and Ba in the floodplain soils is rather low. The contents of the rest of the studied elements are close to each other.

According to the results of microscopic analysis, the parent minerals quartz and potassium and sodium aluminosilicates, represented by altered feldspars, form the basis of the soil. Clay minerals and micas are present. Secondary phases are represented by sulfates: gypsum forms clusters of columnar and tabular crystals filling cracks and cavities, barite grains are noted (figure 5). The secondary ones include iron hydroxides in the form of concretions and clay aggregates (figure 6). Accessory minerals include grains of pyrite, chalcopryte, sphalerite, zircon, and apatite. Ilmenite and, probably, secondary titanium oxide (rutile/anatase) are presented. The sample contains a manganese-bearing mineral and inclusions of chromium-bearing minerals in the form of a vein of submicron sizes. Iron compounds are represented by oxides and hydroxides, iron sulfates (jarosite) are also found. Magnetite crystals are presented. Native iron was found, represented by a rounded formation of about 20 μm, consisting of balls less than a micron in size (figure 6). The independent phases of Zn and Cu have not been determined, which may indicate their high mobility and being in an adsorbed state. In this regard, it should be noted that, according to the results of the analysis of the acetate-ammonium extract from the polluted soils, Cd (74% of sorption-carbonate forms), Zn (49%), and Cu (24%) are characterized by high mobility. In soils outside the zone of influence of mining waste rock dumps, the proportion of mobile forms of these metals does not exceed 29%, 13 and 4%, respectively.

According to the results of thermodynamic modeling of the evaporation of sulfate solutions from the soil, the spectrum of secondary minerals formed in soils under the influence of acid mine drainage is wider. Hydroxides and bicarbonates appear. However, only gypsum, chlorites, amorphous silica, muscovite, anthophyllite (\(\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8\)) are deposited in noticeable amounts. Carbonates, willemite (\(\text{Zn}_2\text{SiO}_4\)), and cerussite (\(\text{PbCO}_3\)) crystallize in microscopic quantities.
Figure 5. Aggregates of gypsum (a) and inclusions of barite (white mineral) (b). SEM image, backscattered electrons.

Figure 6. Native iron: (a) oxyhydroxides (white on the surface of the aggregates); (b) native iron. SEM image, backscattered electrons.

4. Conclusion
The alkaline barrier, formed in natural waters under the influence of the dumps of the Sibay quarry, largely regulates the technogenic metals flows and reduces the load on the adjacent natural-territorial complexes. Its effectiveness is due to a small amount of atmospheric precipitation, which increases the proportion of groundwater during mixing under dumps and increases the pH of the water that forms the runoff of the Karagaily. Probably, the formation of melanterites occurs under the dumps at the alkaline barrier, which reduces the supply of iron and other metals to the super-aquatic and sub-aquatic elementary landscapes. In the composition of sulfate solutions, Zn, Cd, Cu, S retain high mobility. This leads to their active lateral migration in technogenic scattering flows and an increase in concentration in water and bottom sediments. The radial migration of elements in soils in an arid climate is regulated by an evaporation barrier. Secondary minerals in halos and scattering streams are mainly sulfates, among which gypsum predominates. During microscopic studies independent phases of Zn and Cu have not been found, it confirms the leading role of adsorption processes in their phase transitions [2].

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