Research Article
Concentrating Mill Wastes are the Source of Pollution of Human Environment and Natural Ecosystems with Heavy Metals: A Case Study in Primorsky Krai, Russian Federation

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Elevated contents of hazardous elements in natural ecosystems are often associated with human activities. Significant quantities of these elements, including heavy metals, are concentrated in tailings. The goal of the study was to assess the mineralogical and geochemical features of the old tailings of the decommissioned Krasnorechenskaya concentrating mill (located in Primorsky Krai, Russian Federation), which was processing complex tin-polymetallic and silver-lead-zinc ores, the chemical features of tailings pond waters, and the extent of environmental impact on the nearby Rudnaya river. In addition to the analysis of rock and water samples, the software modeling of the water-rock-gas system was carried out. In the study area, the minerals and rocks undergo changes that lead to the formation of highly mineralized, acidic waters saturated with various elements. In the tailings ponds, the maximum permissible concentrations were exceeded for Zn, Cd, Cu, Mg, Fe\text{total}, Pb, Mn, Al, As, Co, Be, Sr, Ni, and Ba. The drainage from the tailings pond tripled the total mineralization of the Rudnaya river relative to the background values. However, the intoxication of the ecosystem by tailing products is partially inhibited by the secondary minerals in the tailings ponds. The negative impact is of a local nature, and 500 m downstream the concentration of many of the above elements is reduced. Despite this, the system that forms the chemical composition of highly mineralized waters is far from the equilibrium state. The oxidation of sulfides, dissolution of other minerals, and migration of oxidation and hydrolysis products will continue affecting the environment. In this regard, it is necessary to conduct environmental monitoring and undertake activities aimed at the recovery of mature concentration tailings or at suppressing the activity of hazardous elements by the conservation of tailings ponds.

1. Introduction

Tailings are a source of high concentrations of heavy metals, harmful elements, and substances accumulated in significant quantities in tailings. This is a serious issue for many mining regions widely discussed by the researchers [1–21]. Sulfides in oxidized leach cap that are not extracted during the enrichment are intensively acidified. As a result, the oxidation products of ore minerals become mobile. This leads to acid rock drainage with elevated contents of heavy metals fundamentally different from the waters in the region. The specific composition of acid drainage may cause the destruction of hydrobiont association in watercourses impacting their self-purification ability [22–30].

Therefore, the task of reliable assessment of the impact of acid rock drainage on the human environment and natural ecosystems through chemical and mineralogical analyzes is particularly relevant [31, 32].
The technology of processing of ore in Russian Federation has not been perfect for a long time [4, 33, 34]. The extraction ratio of base metals into lead and zinc concentrates was 92–98% for galena and sphalerite and 80–85% for silver. The remainder together with other metallic sulfides was discharged into pulp consisting of up to 87% of non-metallic minerals. About 10% of silver, 2–8% of lead in galenic form, and 1–5% of zinc in sphalerite form were discharged into tailings. Incorporated into magnetite, pyrrhotite, pyrite and marcasite, 56.3% to 93.8% of iron, 66–98% of arsenic, 10–15% of antimony, and 38–46% of silicon earth in the form of quartz, hedenbergite, and other silicates were discharged into tailings, as well as Se, Te, In, Ge, Tl, Ga, and F [4].

The tailings ponds of the Krasnorechenskaya concentrating mill (KCM) have been filled for 40 years (from 1956 to 1995), and now they contain more than 6.8 million tons of waste, with large amounts of sulfides. These wastes act as potentially toxic metal sources to the surrounding ecosystem and residential areas [4]. The migration of metals offsite is primarily through airborne dispersion of fine particles and waterborne transport of dissolved and particulate metals [35]. Various geochemical characteristics of the tailings, specifically solid-phase speciation, particulate size, and metal concentrations, determine the potential for the metals to migrate offsite and expose humans and animals to potentially toxic metal concentrations [36–38].

The mineralogical and geochemical features of mature concentration tailings, the chemical composition of the water in the tailings ponds, and the scale of the environmental impact of the tailings drainage on the Rudnaya river are discussed in this paper. To achieve this, we used the concentration tailings of KCM accumulated in the “old” and “new” tailings ponds as the study material.

2. Materials and Methods

2.1. Study Area. The KCM and its tailings ponds are located in the Dalnegorsk district of the Primorsky Krai, Russian Federation (Figure 1). During the operation period (1956–1995), the mill was processing complex tin-poly-metallic and silver-lead-zinc ores from the Smirnovskoe and Yuzhnoe deposits. The minor valuable components were silver, antimony, cadmium, bismuth, copper, and indium [39–42].

2.2. Sample Collection and Analysis. The samples were collected from the surface of the mature tailings ponds of KCM and through sinking the pits 2.0–2.5 m deep with a scoop. In addition, we used the results of our earlier geochemical sampling of five holes set on an optimally predetermined network by the five-spot pattern at the depth of 10–15 m. The distance between the holes was 100 and 150 m.

The samples for geochemical, mineralogical, and hydrochemical analyzes were collected in 2015. Geochemical samples were collected by the vertical channel method in each visually distinguished layer with the greatest variability in composition and structure of the mature tailings. The mineralogical samples were collected by pit sampling method into the sealed glass sample bottles. The samples for hydrochemical analysis were collected in the tailings ponds and in the Rudnaya river, which receives the drainage. The samples in the river were taken directly at the site of the drainage spontaneous discharge, above the discharge (1 km) and below the discharge (0.5 km), according to the Russian sampling standard GOST 17.1.5.04–80 [43].

Hydrochemical samples for the analysis of cations and sulfates were filtered through a 0.45 μm filter at the sampling site and acidulated with nitric acid. For detection of anions, the samples were also filtered and collected in polyethylene containers without acidulation. Unstable parameters were measured at the sampling site.

The laboratory analytical studies were carried out at the Analytical Center of the Far East Geological Institute FEB RAS. The contents of elements in the samples were detected by mass spectrometry with inductively coupled plasma using the Agilent 7700 C spectrometer (Agilent Technologies, USA) and atomic-emission spectrometry with inductively coupled plasma using the iCAP 6500Duo spectrometer (Thermo Scientific Corporation, USA). The contents of H2O, losses on ignition, and SiO2 were determined by gravimetric analysis. The sample preparation of solid samples for instrumental analysis consisted of open acid decomposition (HNO3+HClO4+HF) according to the Russian certified method NSAM No. 499-AES/MS [44].

Mineralogical studies were performed by X-ray spectral microanalysis using the INCA-sight energy dispersive spectrometer (Oxford Instruments, UK) and X-ray analysis using the DRON-3 diffractometer with monochromatic radiation and the D8-Discover microdiffractometer. The micromorphology and the composition of the mineral phases were studied using the scanning electron microscopes JSM-6490LV and ZEISS EVO 50XVP equipped with...
X-ray energy-dispersive INCA energy spectrometers, in secondary and reflected electron modes with the accelerating voltage of 20 kilovolt and beam currents $n \times 10^{-12}$, and also using the Nikon Eclipse LV100 Pol light microscope.

To determine the patterns of hydrogeochemical processes in tailings and possible stable transformations of minerals and their assemblages, we modeled the water-rock-gas system using the software package “Selektor” (© 2007 by K. V. Chudnenko), which is based on minimizing the isobaric-isothermal potential (or Gibbs potential) [45]. The modeling technique consisted of a series of calculations of the equilibrium state for the water-rock-gas system. The external conditions of the system (temperature, total pressure, and chemical potentials of each boundary value component) were entered into the software. The reliability of the results of the equilibrium-nonequilibrium state calculations was determined by using the actual ion concentrations rather than gross masses of the chemical components. The natural chemical composition of the rocks composing the tailings was calculated based on the number of moles of each component and entered into the software. A set of phases and forms of chemical elements in the modeled system was compiled. The model of the water-rock-gas system was represented as a matrix of 57 dependent components and 392 independent components, including 347 aqueous phase components, 37 mineral phase components, and 8 gaseous phase components. We used the thermodynamic properties of minerals, gases, and aqueous solution components from the following databases (adapted to the Selektor software package): a_Shock [46–51], g_Reid [52], s_dump, s_Robie Hemingway [53], and s_Yokokawa [54].

The model simulated the dissolution of rocks in a closed system ($CO_2$ was 0.01 kg/L per 1 kg of $H_2O$, and the atmospheric gas was 0.3 kg/L per 1 kg of $H_2O$). The equivalence of the models to real natural objects was assessed by the correspondence of the calculated ratios of chemical elements in the waters, pH of the medium, and mineralogical composition of the newly formed solid phases to the natural parameters.

3. Results and Discussion

3.1. Mineralogical Composition. The concentration tailings are represented by a mixture of mineral particles of different sizes: from a fraction of a micron to 3 mm. According to the particle composition, they are characterized by the presence of coarse-grained sandy variations (+0.4 mm)—2%, medium-sized soils (−0.4 . . . +0.2 mm)—10%, small-sized soils (−0.2 . . . +0.07 mm)—36%, and silty variations (−0.7 mm)—52%, which are cemented together with hydrosiderous-ferruginous, clay-limonite, and sulfate monocristalline material [4]. The aggregate concentrations of hydroxide-ferruginous, clay-limonite, and sulfate monocristalline material [4].

The total sum of sulfides in the mature concentration tailings of KCM ranges from 5 to 35% (Figure 2), where 80% are pyrite and marcasite, 15% sphalerite and galena, and about 4-5% pyrrhotite, chalcopyrite, stannite, and arsenopyrite. There are grains of silver minerals represented by argentite, hessite, and sulphosalts of pearceite-polybasite order, which are deposited in the form of emulsion spots in galena, jamsonite, and less often in pyrrhotite and sphalerite [19].

The oxidized ores are typical for the mature tailings. The hypogene galena is transformed into anglesite, cerussite, and plumbojarosite, which is found as a result of mineralogical studies (Figure 2). The oxidized zinc phase is represented by smithsonite and goslarite.

3.2. Chemical Composition. Significant amounts of different elements are accumulated in the tailings of KCM, including As, Pb, Zn, Cd, Fe, Mn, and Sn. The content of tin, for example, varies from 170 to 1000 gm/ton, and zinc concentrations amount to 13,920 gm/ton, lead 11,700 gm/ton, arsenic 10,000 gm/ton, and silver 75 gm/ton (Table 1).

As a consequence of the oxidation processes, which are active in the tailings due to the interaction of the minerals that make up the ephemeral sands with the natural waters (precipitation), with the active participation of oxygen, a part of the solid phase blends into the solution. In the “new” tailings pond of KCM, the soft sulfate calcium waters are formed (154.2 mg/dm$^3$ mineralization). The maximum permissible concentrations in the waters are exceeded in Fe$_{total}$ (17.7 times), Zn (42.2 times), and Mn (168.1 times). The content of the remaining components is normal (Table 2).

A different situation is typical for the “old” tailings pond of KCM, where high-mineralized, brackish (6844.6–12807.3 mg/dm$^3$ mineralization) and acidic (pH = 2.3–2.5) sulfate calcium waters are formed as a result of hypergene transformations with elevated content of Zn, Cd, Cu, Mg, Fe$_{total}$, Pb, Mn, Al, As, Co, Be, Sr, Ni, and Ba (Table 2).

Zinc is an active water migrant, and in the water of the tailings ponds under study, its concentration reaches 111.6 mg/dm$^3$ in the “old” tailings pond at the permissible levels of 0.01 mg/dm$^3$ for river water [56] and 5.0 mg/dm$^3$ for drinking water [57].

The mobility of cadmium is much lower in reducing conditions than in oxidizing ones. The content of Cd in the water of the “old” tailings pond (pH = 2.3–2.5) is 0.04 mg/dm$^3$ at the permissible levels of 0.005 mg/dm$^3$ [56] and 0.001 mg/dm$^3$ [57]. In the water of the “new” tailings pond (pH = 7.4), the concentration of Cd does not exceed 0.0012 mg/dm$^3$ (Table 2).

Copper in the oxidized leach cap migrates well in acidic media [58], and apparently due to this characteristic, its content in the water of the “old” tailings pond amounts to 0.27 mg/dm$^3$ at the permissible level of 0.005 mg/dm$^3$. Nickel fits into the same group with Zn, Cd, and Cu, which are mobile or poorly mobile in oxidizing and gley environment [58]. In the water under study, its content varies from 0.53 to 0.06 mg/dm$^3$ at the permissible level of 0.01 mg/dm$^3$.

In terms of migration, cobalt differs from nickel. It is mobile in reducing gley environments, but it deposits both on the hydroxysulfuric and on the oxidation barriers.
probably the reason of its accumulation in the tailing dumps and insignificant migration in the water under study. Its content in the tailings waters varies from 0.002 to 0.017 mg/dm$^3$, which is insignificantly higher than the Russian permissible level for fishery water bodies (0.01 mg/dm$^3$) [56].

Lead accumulated in significant quantities is a poor migrant. Due to the effectiveness of the sulfide and carbonate barriers, its content in the tailings waters varies within the range from 0.003 to 0.009 mg/dm$^3$ at the permissible level of 0.006 mg/dm$^3$.

At the low pH and oxidation-reduction potential levels iron is mainly found in the bivalent form, which contributes to the accumulation of its significant concentrations in the water of the “old” tailings. In general, the acidic geochemical

| Table 1: The content of elements in the tailings of KCM. |
|----------------------------------------------------------|
| Element | Clark in the Earth’s crust, gm/ton [55] | “New” tailings pond, V = 3.9 mln t, n = 20 | “Old” tailings pond, V = 2.9 mln t, n = 86 |
|---------|----------------------------------------|----------------|----------------|
|         | Range | Mean | Range | Mean | Range | Mean |
| Zn      | 93.0 | 700.0–1000.0 | 905.0 | 300.0–13920.0 | 3094.2 |
| Pb      | 20.0 | 710.0–1400.0 | 1071.5 | 680.0–11700.0 | 2459.9 |
| As      | 12.0 | 650.0–2500.0 | 1027.5 | 400.0–10000.0 | 2325.0 |
| Sn      | 6.4 | 260.0–630.0 | 389.0 | 170.0–1000.0 | 531.3 |
| Fe      | 44200.0 | 59082.0–199080.0 | 108031.0 | 13682.0–460740.0 | 144989.0 |
| Al      | 77200.0 | 41022.0–62487.0 | 51417.6 | 6837.0–57028.0 | 44567.1 |
| Mn      | 800.0 | 3580.0–10069.0 | 5808.3 | 467.0–24554.0 | 7032.67 |
| Ag      | 0.07 | 10.0–220.0 | 10.8 | 5.0–2100.0 | 196.0 |
| Cu      | 48.0 | 120.0–220.0 | 155.5 | 40.0–2100.0 | 202.4 |
| B       | 100.0 | 40.0–220.0 | 135.5 | 76.0–500.0 | 41.8 |
| V       | 130.0 | 21.0–47.0 | 34.6 | 21.0–95.0 | 36.4 |
| Ni      | 74.0 | 20.0–35.0 | 25.1 | 14.0–78.0 | 29.0 |
| Cr      | 94.0 | 12.0–44.0 | 21.7 | 14.0–49.0 | 28.0 |
| Bi      | 0.097 | 0.10–2.5 | 1.8 | 0.10–105.0 | 28.0 |
| Cd      | 0.42 | 2.50–3.5 | 2.8 | 0.1–380.0 | 23.5 |
| Co      | 19.0 | 6.0–19.0 | 14.6 | 3.0–53.0 | 16.7 |
| Ga      | 22.0 | 8.0–17.0 | 11.4 | 5.0–17.0 | 9.9 |
| Li      | 65.0 | 0.5–30.4 | 15.1 | 3.9–40.5 | 28.1 |
| Be      | 0.3 | 0.9–1.3 | 1.1 | 0.7–1.7 | 1.2 |
| Sc      | 13.0 | 4.6–10.0 | 7.8 | 3.4–8.9 | 6.1 |
| Rb      | 150.0 | 61.1–97.0 | 87.6 | 8.9–98.1 | 72.1 |
| Sr      | 330.0 | 55.2–106.5 | 86.7 | 30.2–201.7 | 54.7 |
| Y       | 30.0 | 8.7–12.5 | 10.7 | 5.3–80.9 | 12.7 |
| Zr      | 170.0 | 20.7–33.0 | 28.9 | 6.4–47.8 | 37.3 |
| Nb      | 18.0 | 5.8–8.6 | 6.8 | 0.8–8.1 | 6.2 |
| Mo      | 2.6 | 0.6–0.9 | 0.7 | 0.6–2.6 | 1.0 |
| Cs      | 6.5 | 7.9–17.3 | 10.6 | 1.2–17.6 | 10.5 |
| Ba      | 660.0 | 238.2–360.7 | 301.3 | 181.7–388.3 | 257.1 |

Figure 2: The prevailing mineral forms in mature concentration tailings: (a) isometric grains of galena in pyrite metacrystals, eroded pyrite crystal, and new formations of iron sulfates; (b) plumbojarosite and other hypogene and hypogene minerals: Bt, biotite, Gn, galena, Py, pyrite, Qz, quartz, Sp, spherelite, Pb-jrs, plumbojarosite, and FeSO$_4$·H$_2$O in the form of cementing phases. Photographed using the energy-dispersive spectrometer INCA-sight (Oxford Instruments, Great Britain).
environment is favorable for transfer to water and accumulation of various elements that concentrate in the rocks of the tailings, which is clearly shown in Table 2.

3.3. Physical-Chemical Modeling of the Water-Rock-Gas System. To quantify the patterns of hydrochemical processes in the tailings, we carried out the physical-chemical modeling of the water-rock-gas system.

It is known that primary minerals mineralize the water at the dissolution rate equal to or higher than $10^{-10}$ g/cm². In the studied rocks, the primary minerals are feldspars (albite, orthoclase, and anorthite), calcite, quartz, apatite, pyrite, biotite, sphene etc. [59]. Assuming the mineral dissolution rate is constant with an increase of the reacting rock mass, then, according to B. N. Ryzhenko and S. R. Kraynova [60, 61], the rock-water mass ratio (R/W) takes the meaning of the time of interaction between the rock and water solution. Based on the above, we selected the following R/W mass ratios for the modeling: 0.0022 (step 1); 0.0035 (step 2); 0.004 (step 3); 0.006 (step 4); 0.013 (step 5); 0.026 (step 6).

The model showed that, even with the shortest contact of 2.2 grams of rock and 1kg of water (step 1 of the computational experiment), the mineralization of water reaches 3391.59 mg/dm³. The waters had sulfate anionic and calcium (magnesium-calcium) cationic composition. The hydrogen index (pH) varied within 2.1–2.5. With the increase of R/W mass ratio (steps 1 to 6), the mineralization of the water solution rises and a characteristic directed change in the composition of the aqueous phase is observed (Figure 3).

The calculations of the electrolytic dissociation in the waters under study indicate that the components migrate both in the form of intrinsic uncomplexed ions and in the form of complex compounds. With an increase in the R/W mass ratio (the time of interaction) and increase in mineralization, the proportion of complex compounds grows. As a result of this, mainly sulfate complexes are formed in the “old” tailings pond, and hydrocarbonate and carbonate complexes in the “new” tailings pond. An example is presented in Figure 4, showing a decrease in the fraction of uncomplexed ions and an increase in calcium and magnesium complex compounds with rising mineralization of

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**Table 2: The chemical composition of the water in the tailings ponds of KCM.**

| Components | Maximum permissible concentration [56] | Toxicity-dependent hazard class [56] | “Old” tailings | “New” tailings | Content, mg/dm³ |
|------------|--------------------------------------|-------------------------------------|----------------|----------------|----------------|
| Min | 1000.0 | – | – | 154.2 | 12807.3 6844.6 | 46.6 | 1340.6 1680 |
| pH | 6.5–8.5 | – | – | 7.4 | 2.5 2.3 | 6.9 | 4.6 6.7 |
| HCO₃ | 100.0 | – | – | 29.3 | <0.06 <0.04 | 18.3 | 8.0 23.2 |
| SO₄ | 100.0 | – | – | 78.4 | 9364.0 5250.0 | 12.9 | 933.9 101.7 |
| Cl | 300.0 | 4e | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Ca | 180.0 | 4e | 31.8 | 544.0 408.1 | 8.7 | 277.1 26.9 |
| Mg | 40.0 | 4 | 7.5 | 216.0 248.5 | 1.5 | 105.4 9.1 |
| Na | 120.0 | 4e | 3.4 | 4.9 3.3 | 4.3 | 13.7 5.2 |
| K | 50.0 | 4e | 1.6 | <0.01 <0.01 | 0.4 | 5.6 0.8 |
| Si | – | – | 5.1 | 48.6 35.2 | 9.9 | 8.7 5.9 |
| Fe total | 0.1 | 4 | 1.8 | 2677.0 934.5 | 0.05 | 4.4 0.7 |
| Oil products | 0.05 | 3 | 0.05 | <0.05 <0.05 | N/D | <0.05 N/D |
| Pb | 0.006 | 2 | 0.0004 | 0.003 0.009 | 0.0004 | 0.01 0.01 |
| Zn | 0.01 | 3 | 0.4 | 111.6 94.4 | 0.006 | 3.3 2.1 |
| Cu | 0.001 | 3 | 0.001 | 0.3 0.2 | 0.0004 | 0.01 0.004 |
| Mn | 0.01 | 4 | 1.7 | 527.5 43.4 | 0.008 | 8.3 0.98 |
| Al | 0.04 | 4 | 0.03 | 82.2 46.8 | 0.03 | 6.5 0.5 |
| Cd | 0.005 | 2 | 0.001 | 0.04 0.04 | 0.00002 | 0.01 0.004 |
| As | 0.05 | 3 | 0.006 | 0.2 0.05 | 0.001 | 0.004 0.001 |
| Cr total | 0.02 | 3 | 0.00003 | 0.01 0.007 | 0.0002 | 0.02 0.0001 |
| Co | 0.01 | 3 | 0.002 | 0.02 0.02 | N/D | 0.02 N/D |
| Be | 0.0003 | 2 | 0.00002 | 0.002 0.002 | N/D | 0.002 N/D |
| B | 0.5 | 4 | <0.01 | <0.01 <0.01 | 0.01 | 0.02 0.01 |
| Sr | 0.4 | 3 | 0.3 | 1.2 1.3 | 0.06 | 2.1 0.3 |
| Li | 0.08 | 4 | 0.006 | 0.02 0.03 | 0.003 | 0.06 0.01 |
| Ni | 0.01 | 3 | <LD | 0.05 0.06 | 0.0001 | 0.06 0.002 |
| Se | 0.002 | 2 | 0.00006 | <LD 0.0004 | 0.0002 | 0.01 0.0003 |
| Rb | 0.1 | 4 | 0.001 | 0.0003 0.0004 | N/D | 0.003 N/D |
| Cs | 1.0 | 4 | 0.0001 | 0.0003 0.0007 | 0.0005 | 0.0003 0.001 |
| V | 0.001 | 3 | 0.00002 | 0.003 0.001 | N/D | 0.0002 N/D |
| Ba | 0.74 | 4 | 0.05 | 1.7 0.0004 | 0.006 | 0.02 0.01 |

–, no data; N/D, not detected; <LD, below the level of detection; components exceeding the MPC are in italics.
the water in the “old” tailings pond, as well as variations in
the behavior of iron ions, probably caused by new of mineral
forms.

The most notable changes in the behavior of chemical
components in water are inherent to the elements found in
the structures of the resulting secondary minerals (Figure 3).
During the modeling, it was found that, as the solution gets
saturated with certain components, the secondary mineral
phases are formed (illite—K.064Na.03Al1.83Fe.0, jarosite—
KFe3(SO4)2(OH)6, anglesit—PbSO 4, bianchite—ZnSO 4
· 6H2O, and gypsum—CaSO4·2H2O).

The obtained results of physicochemical modeling are in
good agreement with field observations. The water with the
salinity of >15000 mg/dm³ is supersaturated with calcium
ions, which is indicated by gypsum formations (CaSO4·2H2O) identified by mineralogical and the X-ray
diffraction study.

The main sources of Fe in the studied water are iron
sulfides and aluminosilicate minerals, mainly hornblendes,
pyroxenes, biotite, epidote, etc. As these minerals dissolve,
the chemical elements are transferred into the aqueous
solution. Iron exists in two oxidation states under the
considered conditions (Fe²⁺ and Fe³⁺) and, as shown in
Figure 4, it is transported by the aqueous solution, mainly in
the form of Fe³⁺ ions and FeOH²⁺ compounds.

3.4. Morphology of Secondary Minerals. Due to the effec-
tiveness of geochemical barriers, as well as evaporation and
freezing out, various sulfate mineral forms of iron are
formed [62–66]. High pH and/or redox potential create
stable conditions for trivalent iron, which hydrolyzes to form
the insoluble iron hydroxide (Fe(OH)₃). Iron hydroxides, in
turn, are a geochemical barrier to arsenic, a very strong
toxicant. Iron hydroxides efficiently sorb its migration
forms, especially arsenate [17, 67–69]. Iron sulfates are a
barrier for the reduced As (III), which is described by Ya. E.
Yudovich and M. P. Ketris [58] and is clearly traced by us in
the study of the mineralogy of the tailings ponds and the
microprobe analysis of mineral formations.

Through the example of the study of the micromor-
phology and composition of a newly formed fibroferrite
(Fe(SO4)₃·(OH)·5H2O) (Figure 5(a)), identified by the X-ray
diffraction method, we showed that it is characterized by the
raised content of arsenic (1.46%), zinc (1.21%), manganese
(1.66%), aluminum (0.89%), and magnesium (1.9%) (Fig-
ure 6; Table 3). A characteristic feature of the debyeogram of
fibroferrite is the increase of the intensity of some arcs near
the equatorial line. Fibroferrite is formed mainly due to the
direct oxidation of pyrite, pyrrhotite, and chalcopyrite as a
result of exothermic reactions.

In addition, newly formed minerals such as melanterite
(Figure 5(b)), ferrohexahydrite, rozenite, copiapite
(Figures 5(c) and 5(d)), hydroalumogoethite, and gypsum,
found in the tailings under study, control the content in
water of such components as As, Fe, Zn, Ca, Cu, Al, Mg, and
Mn.

3.5. Effect of Elevated Contents of Heavy Metals on Human
Health and Natural Ecosystems. The elements contained in
elevated concentrations in the waters of the tailings ponds
(Table 2) are classified as priority environmental pollutants
in Russia [56].

For example, zinc is among mutagenic, gonadotoxic, and
embryotoxic elements. Prolonged exposure (5–20 years) to
its compounds leads to gastrointestinal disorders, increase in
the number of acute respiratory infections and dental caries,
changes in morphological composition of blood, and in-
crease in incidence of illness in children [70].
Cadmium is a polytropic poison. Chronic intoxication can lead to anosmia, headaches, nosebleeds, increased mortality in cardiovascular diseases, effects on the gastrointestinal tract, damage to the central and peripheral nervous systems, diseases of the liver, kidneys, skeletal muscles, and bone tissue.

Copper is carcinogenic and gonadotoxic. In compounds, it irritates the mucous membranes of the upper respiratory tract and the gastrointestinal tract. In chronic intoxication, it causes functional disorders of the nervous system and impaired renal function and liver.

Lead is a polytropic poison that causes pathological changes in the nervous system, blood, and blood vessels. It causes lung disease in children. Inorganic lead compounds \(\text{Pb}^{2+}\) disrupt the body’s metabolism and are inhibitors of blood and tissue enzymes. Lead can enhance the

**Figure 4:** Inorganic migration of Ca (a), Mg (b), and Fe (c) in the waters of the "old" tailings pond.
development of diseases of the anemia group. Diseases of the peripheral nervous system (cephalgia, ischialgia, and myoneuralgia) are associated with an excess of lead in soils and waters. Lead accumulates in bones, hair, tissues of the aorta, liver, and kidneys, causing paralysis of the nervous system, anemia, and intestinal spasms. In areas near polymetallic mines, there is often a direct correlation between the distribution of lead in soils and the incidence of atherosclerosis and caries [4].

Arsenic and its compounds are highly toxic. First of all, they affect the nervous system vascular walls, increase the permeability and paralysis of capillaries, and develop the necrotic lesions in the liver, kidneys, heart, and intestines [4]. In addition, they cause disorders of fat and hydrocarbon metabolism, dermatitis in children, and skin cancer. High concentrations of arsenic in the soil lead to plant death.

Water-soluble toxic salts, which include components such as $\text{CO}_3^{2-}$, $\text{HCO}_3^-$, $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Na}^+$ in various concentrations, inhibit the growth and development of plants.

### 3.6. Impact on the Local Rudnaya River

The drainage from the “old” tailings pond exudes through the dam and flows into the Rudnaya river (Figure 7). This river is the largest

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**Figure 5**: The morphology of sulfates formed in the tailings: (a) laminal fibroferrite, (b) sheaf-like melanterite, (c) hexagonal prisms of copiapite with a truncated bipyramidal tail, and (d) tetragonal prisms of copiapite. Microscopes JSM-6490LV and ZEISS EVO 50XVP.

**Table 3**: Chemical composition of fibroferrite

| Element | Weight (%) | Atomic (%) | Oxide form Formula | Mass (%) |
|---------|------------|------------|--------------------|----------|
| Mg      | 1.90       | 1.84       | MgO                | 3.14     |
| Al      | 0.89       | 0.78       | $\text{Al}_2\text{O}_3$ | 1.68     |
| S       | 24.72      | 18.16      | $\text{SO}_3$      | 61.72    |
| Mn      | 1.66       | 0.71       | MnO                | 2.14     |
| Fe      | 21.68      | 9.15       | FeO                | 27.89    |
| Zn      | 1.21       | 0.44       | ZnO                | 1.51     |
| As      | 1.46       | 0.46       | $\text{As}_2\text{O}_3$ | 1.92     |
| O       | 46.49      | 68.47      |                    |          |
| Total   | 100.00     | 100.00     |                    | 100.00   |

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**Figure 6**: The morphology and composition of fibroferrite (microscope ZEISS EVO 50XVP).
waterway in the area. It flows from the Northwest to the Southeast from the watershed of the Sikhote-Alin ridge and into the Rudnaya Pristan bay. The length of the river is 73 km, the catchment area is 1140 km² with an average height of 395 m, the total fall of stream is 942 m, and the average slope is 12.9%. The average flow width varies from 3.5 m (in winter) to 11.5 m (in summer), the average depth is from 0.15 to 0.34 m, and the average speed is from 0.13 to 0.19 m/s.

The waters of the river in the upper reach (background) are fresh (mineralization 46.58 mg/dm³) bicarbonate calcium (Table 2). The content of all the components is normal and does not exceed the maximum permissible concentrations [56].

The analysis of the impact of the water from the “old” tailings pond of KCM on the composition of water in the Rudnaya river showed that the water flowing from the tailings triples the total mineralization of the watercourse relative to the background values (Table 2), saturating the waters of the river with SO₄ (933.9 mg/dm³), Ca (277.1 mg/dm³), Mg (105.4 mg/dm³), Fe_{total} (4.39 mg/dm³), Pb (0.01 mg/dm³), Zn (3.31 mg/dm³), Cu (0.014 mg/dm³), Mn (8.33 mg/dm³), Al (6.48 mg/dm³), Cd (0.01 mg/dm³), Co (0.023 mg/dm³), Be (0.002 mg/dm³), Sr (2.08 mg/dm³), and Ni (0.062 mg/dm³). The pH of the river’s water at the discharge point is 4.61. However, the negative impact is of a local nature, probably due to the substantial volume of the river in the year of sampling (2015). Already 500 m downstream the concentration of many of the above elements is reduced to safe permissible levels. The maximum permissible concentrations are exceeded only for SO₄ (101.73 mg/dm³), Fe_{total} (0.73 mg/dm³), Zn (2.08 mg/dm³), Cu (0.004 mg/dm³), Mn (0.98 mg/dm³), Al (0.49 mg/dm³), and Sr (0.27 mg/dm³) (Table 2; Figure 7).

 Apparently, the mineralization of the river water depends, inter alia, on the volume of the river in the study period. For instance, according to the data from 2004 [71], the concentrations of metals decreased insignificantly downstream from the discharge point and a small amount of clean water inflow did not contribute to a noticeable dilution of contaminated water. The mineralized waters of the Rudnaya river retain abnormally high concentrations of sulfates and Zn, Cd, and As at a considerable distance from the influx of acid rock drainage.

4. Conclusions

In this study, we explored the physical and chemical processes that lead to the formation of acid tailings drainage and its impact on the river water. Based on the geochemical studies and the results of physicochemical modeling, we showed that the geochemical specificity of the tailings

![Figure 7: The diagram of changes in the content of iron, zinc, manganese, copper, aluminum, and sulfate anion in the Rudnaya river under the influence of the drainage from the “old” tailings pond of KCM: (a) Rudnaya river above the discharge; (b) point of discharge; (c) below the discharge.](image-url)
drainage is formed in the catchment area and transformed in the direction of the filtration flow. Geochemical features are determined by the ratio of interacting masses of rock, water, and gas. Secondary minerals as cementing phases and surface formations control the content of elements in the water.

In the study area, the minerals and rocks undergo changes that lead to the formation of highly mineralized (mineralization 684.6–12807.3 mg/dm³ and more), acidic (pH 2.3–2.5) waters saturated with various elements. The maximum permissible concentrations were exceeded for Zn, Cd, Cu, Mg, Fe₅₀₆₅, Pb, Mn, Al, As, Co, Be, Sr, Ni, and Ba. The tailings are the sources of pollution of the human environment and natural ecosystems with heavy metals.

However, the intoxication of the ecosystem by tailing products is partially inhibited by the secondary minerals in the tailings. Nevertheless, the assessment of the impact of the water of the "old" tailings pond of KCM on the composition of water in the Rudnaya river showed that the drainage from the tailings pond triples the total mineralization of the watercourse relative to the background values, saturating the waters of the river with SO₄, Ca, Mg, Fe, Pb, Zn, Cu, Mn, Al, Cd, Co, Be, Sr, and Ni. Still, the negative impact is of a local nature, and already 500 m downstream the concentration of many of the above elements is reduced.

The system that forms the chemical composition of highly mineralized waters in the tailings ponds under study is far from the equilibrium state. The oxidation of sulfides and dissolution of other hypogene minerals and rocks, as well as the migration of oxidation and hydrolysis products, will continue indefinitely affecting the environment.

In this regard, it is necessary to conduct environmental monitoring and undertake activities aimed at the recovery of mature concentration tailings or at suppressing the activity of hazardous elements by the conservation of tailings ponds.

Data Availability

The data used for the study are presented within this paper.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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