The Evolution of the Waters Chemical Composition in the Areas of Lead-Zinc Deposits Mining in East Transbaikalia

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Abstract A feature of the studied objects is the formation of waters under conditions of combination in the mineral composition of the tailings of sulfide and carbonate mineralization. The studied drainage waters are mainly fresh (salinity 0.33-1.82 g/L), neutral and alkaline (pH 7.25-8.30). They belong to the bicarbonate, sulfate-bicarbonate, bicarbonate-sulfate and sulfate magnesium-calcium and calcium-magnesium chemical types. Arsenic, zinc, cadmium, lead, antimony and manganese in the microelement composition of drainage waters are predominant. Drainage waters of lead-zinc deposits are characterized by a significant excess of the heavy metals concentrations (As, Zn, Cd, Pb, Sb, Mn, Mo, U, La, Se) over the average composition of leaching zone waters, with a maximum for arsenic – more than 800 and for zinc – 200 times. The waters are saturated with respect to secondary carbonates and arsenates, which indicates the existence of thermodynamic conditions for the removal from the solution of Ca, Mg, Cu, Zn, Pb, As into the solid mineral phase. The neutralizing effect of host rocks carbonates and ore bodies carbonates causes a neutral reaction of waters and low heavy metal concentration.

1. Introduction
The beginning of an active quantitative study of the water migration of pollutants in mining areas dates back to the last quarter of the 20th century. It was found that acidic drainage from mines contains abnormal amounts of heavy metals that have a negative impact on biotic components of the landscape [1].

Significant increases in sulfate concentrations, high concentrations of suspended particles, metal concentrations above 100 mg/L are noted in acidic wastewater from waste copper and lead-zinc mines in Macedonia [2], coal and gold deposits in South Africa [3] and Canada (Yellowknife Mine) [4]. The development of deposits in the Donetsk and Kuzbass coal basins contributed to the formation of mine drainages with a maximum mineralization of up to 17 g/L and maximum concentrations (g/L): SO₄ – 12, Na – 3.4, Mg – 1.2, Fe – 0.5, Mn – 0.07 [5, 6]. Drainages of dumps and waters of the tailing dump waters of the Taseevsky gold ore deposit (Eastern Transbaikalia) are characterized by an increase in concentrations (g/L): SO₄ – up to 5.54; Al – up to 0.15; Fe – up to 0.77; Mn – up to 0.09 and mineralization – up to 7.30 g/L [7]. There are many similar examples around the world.

Neutral and alkaline mine runoffs, which are formed in the case of the carbonate composition of the host rocks, also pose a no less threat. The contents of Pb, Zn and Cd in such waters are low, but anionic highly toxic elements, including As, Sb, Se and Mo, are highly mobile [2, 8, 9, 10, 11, 12].
The purpose of this work is to study the degree of the waters technogenic transformation in the mining areas of sulfide lead-zinc deposit localized in carbonate rocks.

2. Objects and methods of research

The hydrochemical samples in the area of three previously developed lead-zinc deposits (Blagodatsky, Akatuevsky and Kadainsky), located in the southeastern part of the Transbaikal Region were carried out (figure 1).

Figure 1. The location of the deposits: 1 – Akatuevsky, 2 – Blagodatsky, 3 – Kadainsky mines.

The deposits belong to the galena-sphalerite-carbonate-quartz ore formation of the Lower Paleozoic age [13, 14]. Ore bodies are represented by sheet-like deposits, stocks and lenses. They occur among carbonate rocks of the Lower Paleozoic (dolomites and limestones with interbedded of siltstones and mudstones) and are localized at the contacts of carbonate and alumsilicate rocks and within carbonate rocks, at the intersection of faults. The carbonates (dolomite, ankerite and calcite) are play an important role in the composition of vein minerals. The pyrite-galena-sphalerite (Blagodatsky deposit) and galena-sphalerite (Kadainsky and Akatuevsky deposits) types of polymetallic ores are prevalent.

At the Blagodastky deposit the waters of the Maly Zerentuy brook, in the valley of which a tailing dump is located, were tested. Water samples above the tailing dump (number of sample – GZ-13-1), in its central (GZ-13-2) and lower parts (GZ-13-3), as well as under the lower dam (GZ-13-4) were taken. The adit drainage waters in the western side of the tailing dump (AK-15-1) and the seepage waters under lower dam of the tailing dump (AK-15-1) at the Akatuevsky field were tested. The tailings pond (SB-13-1) at the Kadainsky field was tested.

Chemical-analytical studies of waters were carried out by using generally accepted methods [15] in a certified laboratory of the Institute of Natural Resources, Ecology and Cryology of the Siberian Branch of the Russian Academy of Sciences (Chita). The determination of metal concentrations was carried out by the atomic absorption method on a SOLAAR M6 spectrophotometer. Additionally, the analysis of water samples was carried out by the ICP-MS method at the Institute of Geochemistry SB RAS (Irkutsk) on an ELEMENT2 device by Finnigan MAT.
3. Results
The waters of the deposits, despite the predominantly sulfide composition of the ores, are characterized by a neutral and slightly alkaline reaction (table 1 – pH), which is due to the high neutralization potential of the enclosing carbonate rocks and minerals are present in the ores [16, 17]. The investigated waters are predominantly fresh, with the exception of the pond of the Kadainsky tailing dump (the amount of ions is 1.8 g/L). The slowed down water exchange and evaporation contributed to the growth of mineralization of the pond water.

| Parameter | Number of samples | Average composition of waters |
|-----------|-------------------|-------------------------------|
| pH        | 7.70 8.04 8.26 8.30 7.80 7.58 7.25 | 6.75 |
| Eh, mV    | 295 - 293 255 262 220 -92 | - |
| HCO₃, mg/L| 215.0 216.0 204.0 448.0 73.2 281.2 262.9 | 146 |
| SO₄²⁻     | 33.0 73.5 111.3 107.5 1150 307.5 478.2 | 12.4 |
| Cl⁻       | 2.20 2.30 2.20 2.00 3.70 1.52 1.60 | 10.1 |
| F⁻        | 0.21 0.20 0.21 0.21 0.72 0.36 0.49 | 0.23 |
| Ca²⁺      | 74.7 57.0 69.3 86.8 459.2 147.7 155.1 | 27.4 |
| Mg²⁺      | 2.32 24.4 26.2 58.9 112.5 43.3 42.9 | 11.2 |
| Na⁺       | 5.02 4.82 4.67 6.47 16.2 7.25 12.8 | 13.8 |
| K⁺        | 0.96 0.91 1.05 0.67 5.73 1.21 4.49 | 1.84 |
| Si        | 5.13 4.96 4.69 3.31 1.10 6.65 10.3 | 6.78 |
| Σ ions    | 333.4 379.1 418.9 710.6 1821 789.7 958.0 | 239.0 |
| Li, µg/L  | 6.70 7.30 7.30 10.1 29.0 11.5 11.9 | 6.20 |
| Al        | 945.0 28.0 18.0 174.0 14.2 38.0 19.0 | 190.0 |
| Ti        | 7.30 0.46 0.25 3.33 0.27 1.22 0.63 | 6.96 |
| V         | 1.96 0.51 0.14 0.86 0.03 0.24 0.22 | 1.01 |
| Cr        | 1.28 0.52 0.39 0.43 0.64 0.13 0.15 | 2.78 |
| Mn        | 37.0 54.0 220.0 49.0 1106 17.0 2361 | 34.3 |
| Fe        | 852.0 88.0 177.0 269.0 87.0 66.0 8435 | 424.0 |
| Ni        | 1.76 2.99 2.28 1.46 11.8 7.20 2.10 | 3.11 |
| Co        | 0.51 0.40 0.44 0.24 3.61 0.09 1.05 | 0.33 |
| Cu        | 2.05 5.30 13.8 0.50 3.51 3.30 2.00 | 4.00 |
| Zn        | 53.0 412.0 982.0 2.82 7846 2111 425.0 | 30.3 |
| As        | 18.0 28.0 99.0 2.79 7.50 60.0 1097 | 1.34 |
| Br        | 7.90 10.4 8.60 12.6 41.0 7.80 7.50 | 40.8 |
| Rb        | 1.37 0.64 0.57 0.50 13.8 3.11 2.70 | 1.81 |
| Sr        | 212.0 226.0 241.0 369.0 2526 567.0 1148 | 88.7 |
| Mo        | 4.57 6.60 6.10 0.23 2.21 3.07 5.90 | 1.16 |
| Cd        | 0.18 1.02 2.66 0.009 19.0 1.70 0.68 | 0.20 |
| Sb        | 2.46 8.60 25.0 0.56 19.0 3.36 0.91 | 0.64 |
| Ba        | 27.0 25.0 27.0 31.0 21.0 8.30 67.0 | 14.4 |
| Pb        | 7.90 42.0 150.0 0.19 57.0 2.56 14.4 | 2.18 |

*GZ – Blagodatsky, SB – Kadainsky, AK – Akatuevsky deposits.

Average composition of leaching zone waters [18].

After waters filtration in the sediments of the Blagodatsky and Akatuevsky tailing dumps, a noticeable enrichment of them with ions of SO₄²⁻, HCO₃⁻, Mg²⁺ and others is recorded (table 1), which contributes to an increase in salinity and a change in the chemical composition from HCO₃⁻ Ca to SO₄²⁻.
HCO₃ Ca-Mg and HCO₃-SO₄ Mg-Ca. The pond waters of the Kadainsky tailing dump are characterized by SO₄ Mg-Ca composition and maximum concentrations of macro-components and salinity (table 1).

The migration of metals in neutral and alkaline waters by the low solubility of their hydroxides is limited; the concentrations are usually the first tens, units, or less μg/L (table 1). A noticeable increase in metal concentrations in the waters under the lower dams of the Akatuevsky and Blagodatsky tailing dumps and of the pond of the tailing dump of the Kadainsky deposit was recorded.

The greatest excess of the components concentrations over the average composition of the leaching zone waters [18] are characteristic for metals belonging to the group of the deposits ore-forming elements – Zn, Pb, Fe, As (table 1).

The carbonate composition of the enclosing rocks, as well as the presence of carbonate minerals in the composition of ore bodies, contribute to the rapid saturation of waters with CO₃²⁻ ions and the achievement of their equilibrium with calcite in the mining areas and natural conditions (figure 2).

**Figure 2.** The HCl-H₂O-Al₂O₃-Na₂O-CaO-CO₂-SiO₂ system at 25°C and lg [H₄SiO₄] = -3.5 with plotting data on the waters composition: 1 – Blagodatsky, 2 – Akatuevsky, 3 – Kadainsky mines and 4 – natural waters in these areas.

Analysis of data on the composition of waters and the nature of mineral equilibriums, in accordance with the classification proposed by S.L. Shvartsev [18, 19] indicates their belonging to two geochemical types – siliceous-calcium-magnesium and siliceous carbonate-calcium. Detailed description of these geochemical types is given in [20].

The siliceous-calcium-magnesium geochemical type includes waters with a salinity of less than 0.6 g/L (table 1 – number of sample GZ-13-1, GZ-13-2, GZ-13-3), equilibrium relative to clay aluminosilicate minerals (montmorillonite, illite). More saline waters (table 1 – number of sample GZ-13-4, AK-15-2, SB-13-10), equilibrium with calcite and clays (kaolinite, montmorillonite, illite) belong to the siliceous carbonate-calcium geochemical type [20].

In addition to calcite, the studied waters are characterized by saturation relative to dolomite, malachite, azurite and cerussite (figure 3 a, b, d, e, f). High concentrations of arsenic in waters (table 1) determine their saturation relative to copper and zinc arsenates – lammerite and legrandite (figure 3 g, h).

The above indicates the existence of thermodynamic conditions for the removal of components from solution into the solid phase in the form of secondary carbonates and arsenates, which, nevertheless, does not contribute to their purification.

Similar conditions of formation of the studied waters determine the noticeable similarity of their chemical composition. The main factor controlling the change in the composition of the studied waters is the intensity of water exchange (surface or underground run-off), which determines the duration of interaction in the water-rock system and the corresponding level of its evolutionary development.
The presence of sulfide mineralization in the composition of ores, as well as the placement of the products of their processing on to a daylight area in direct contact with atmospheric oxygen, contribute to the intensification of the oxidation processes of sulfide minerals. However, the localization of ores in carbonate rocks contribute to neutralization of the resulting acidity. As a result, neutral and alkaline waters are formed that are unfavorable for the migration of most ore components that precipitate from solution in the form of secondary hydroxides and carbonates. In this case, the main processes of water enrichment with chemical elements are oxidation, leaching and dissolution.

At the same time, the forming waters are favorable for the migration of such highly toxic elements as arsenic and antimony, the contents of which reached values tens and hundreds of times higher than the average for leaching zone waters (table 1), which are a threat to environmental of the adjacent territories.

4. Conclusions
A feature of the studied objects is the formation of waters under conditions of combination in the composition of the tailings dumps of sulfide and carbonate mineralization. The anionic composition of waters is bicarbonate, sulfate-bicarbonate, bicarbonate-sulfate and sulfate, the cationic composition is magnesium-calcium and calcium-magnesium. The waters are fresh and brackish, neutral and slightly alkaline. As, Zn, Cd, Pb, Sb and Mn are predominant in the trace element composition of drainage effluents. The neutralizing effect of carbonates of host rocks and ore bodies of deposits determine waters...
neutrality, low concentrations of heavy metals, which, however, does not make waters environmentally friendly.

5. References

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