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Prognosis of Geoecological Consequences of Development of Deposits of the Bom-Gorkhon Tungsten Deposit (Transbaikalia)

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Abstract

The main movable elements Zn, Cu, Pb, Fe, Cd, Mn, Ca, Sr, W, were found as a result of the experiments on leaching by the sulphuric-acid solutions of the ores of the deposit Bom-Gorkhon (Transbaikalia). Associations of possible mineral phases, the essential part of which is located in products of the modern mineral formation in wastes of the mountain manufacture were determined. The legitimacy of the use of the physicochemical modelling for the prognosis of geoecological consequences of mining of ore deposits was confirmed.

Key words: experimental leaching, elements migration, thermodynamic modelling, modern minerogenesis, prognosis of geoecological consequences of mountain manufacture

INTRODUCTION

The Bom-Gorkhon deposits of tungsten of hubnerite-quartz-sulphide mineral type of the greisen formation is located in the south western part of the Transbaikalia Territory, 10 km to the northeast of the village of Novopavlovka (Fig. 1). Tungsten-containing quartz veins are localized in granites of the gudzhirskiy magmatic complex of the Late Jurassic age. The veins have the northeast stretch, southeast fall at the angles of 15–25°. The veins power reaches the first meters in bulges. The main minerals of veins are quartz, microcline, muscovite, pyrite, hubnerite. Among main minerals of the oxidation zone, goethite hydrogoethite, tungstate and jarosite were found. Secondary minerals are represented by fluorite, sericite, biotite, albite, epidote, adularia, chlorite, mo-

lybdenite, sphalerite, bismuthine and cosalite, scheelite *etc.* (Table 1). The group of secondary oxidized minerals is martite, hydrohematite, bismuthite and ferromolybdenum, chalcocite, covellite. Among accessory minerals, beryl, apatite, chalcopyrite, cassiterite, magnetite, hematite, galena, stannite, pyrrhotite, tetradymite, native bismuth, cannizzarite, gladiate, hammarite were discovered [1, 2].

The extraction and beneficiation of ores on this plot have been carried out since the 80ies of the last century. In the processing of ore on the flotation-gravitation technological wolframite and sulphide concentrates are obtained. Arrays of enrichment wastes are placed downstream creeks of Zun-Tignya and Bom-Gorkhon. They are saturated by waters of the concentrating factory and atmospheric precipitation. The acidity of the waters is in limits of



Fig. 1. Location of the deposit Bom-Gorkhon.

pH 2.7–3.5. When interacting with atmospheric precipitations sulphides of ores, concentrates and enrichment tailings are oxidized, forming various sulphates on geochemical barriers. Results of the experimental study of the interaction of ores of the deposit with subacid solutions of sulphuric acid to assess the mobility of the ore elements and their possible impact on the environment are presented in this work.

EXPERIMENTAL

Materials

Samples of ores were selected from the quarry and ore waste dump adits. Samples of ores averaged on per the mineral composition were used to carry out the experiment and mapped with the samples coming to the beneficiation plant. The mineralogical analysis of samples was conducted to five classes of the coarseness (mm): 1–2, 0.5–1, 0.5–0.1, 0.1–0.074, <0.074.

Methods

Fractionation of the obtained classes was held in bromoform, as well as by the magnetic and electromagnetic separation using Sochnev magnets and an electromagnet UEM-1. All samples were weighted on the electronic balances and studied under the binocular, if necessary, in immersion preparations; microsections and polished sections were studied using a Zeiss Axio Scope A1 polarization microscope (Carl Zeiss, Germany).

The chemical analysis of technogenic water sampled from old settling basins of the mine was carried out by methods of atomic-absorption spectroscopy, photometry and potentiometry at the Laboratory of Hydrogeology and Geocology of the Geological Institute of the SB RAS, as well as by the method ICP-MS (Institute of Geochemistry of the SB RAS and SGS Vostok Limited, Chita). Solutions of sulphuric acid for the experiments on leaching were prepared from distilled water and a concentrated acid of ch. d. a. reagent grade.

TABLE 1

Rock-forming and ore minerals of the Bom-Gorkhon deposit in experimental samples

| Silicates | Ore minerals | | Accessory minerals |
|-----------|--------------|------------------------|--------------------|
| | Main | Secondary | |
| Quartz | Hubnerite | Fluorite | Apatite |
| Feldspar | Pyrite | Molybdenite | Aikinite |
| Biotite | | Sphalerite | Triplite |
| Muscovite | | Bismuthite | Stannite |
| Epidote | | Cosalite | Pyrrhotine |
| Adular | | Scheelite | Troilite |
| Chlorite | | Chalcopyrite | Tetradymite |
| Albite | | Cassiterite | Native bismuth |
| Beryl | | Magnetite | Bismutoplacionite |
| | | Galena | Zavaritskite |
| | | Tungstite | |
| | | Sulphosalts of bismuth | |
| | | Chalcosine | |
| | | Covelline | |

The X-ray diagnostics of minerals was conducted using a diffractometer DRON-3 ($\text{CuK}\alpha$ radiation) was carried out by the powder method. The study of micromorphology and chemical composition of the individual phases was performed using a LEO 1430 VP scanning electron microscope.

Processes of sulphuric-acid leaching were carried out in transparent plastic vessels with a capacity of 20 mL, where the samples of crushed ore weighing 40 g, with the coarseness of 1–2 mm and diameter of 3–4 mm were placed. The ore was initially washed with distilled water and dried in an oven at the temperature of 120 °C. For one weighed sample of ore 500 mL of the sulphuric-acid solution was used. The acidity of solutions was determined

by the pH meter “Anion-7000” with a universal pH electrode ESK-10601/7 (for initial solution with pH of 2). The regular supply of a fresh solution was provided using the peristaltic pump pp1-05 with a constant rate of 1.5 mL/min. The ore during the whole experiment was immersed in the flowing solution. The final solutions were selected by 45 mL; their chemical analysis was carried out by the ICP-84T method.

Thermodynamic modelling

The thermodynamic model of equilibriums with solid phases using the environment of the program complex “Selector” [3] was formed for microcomponents of the solution of the old

TABLE 2

Microelements in the water of the lower sump, mg/L

| Indicators | K + Na | Ca | Mg | Al | Fe | Mn | Zn | SO_4^{2-} | Cl | CO_2 |
|------------------------------------|--------|-------|-------|-------|-------|-------|-------|--------------------|------|---------------|
| Concentrations (analytical) | 2266.2 | 340.7 | 255.2 | 331.5 | 356.2 | 61.33 | 179.1 | 4623.1 | 74.8 | 356.7 |
| Calculation (oxidizing conditions) | 1757.6 | 1.9 | 0.5 | – | – | – | – | 2900 | 73.0 | 5.5 |
| Calculation (reductive conditions) | 1950.6 | 116.1 | 112.5 | – | – | – | – | 564.1 | 19.9 | 5.0 |

TABLE 3

Microelements in the water of the lower sump, $\mu\text{g/L}$

| Indicators | Sr | Cu | Cd | F |
|------------------------------------|------|------|------|------|
| Concentrations (analytical) | 2299 | 1442 | 2770 | 3400 |
| Calculation (oxidizing conditions) | – | – | – | 3373 |
| Calculation (reductive conditions) | 196 | – | – | 3050 |

settling ponds of the mine (Table 2) and microcomponents in the composition of Sr, Cu, Cd, F (Table 3). Two options were considered: a) at the contact with the modern atmosphere (oxidative conditions); b) under anaerobic (reductive) conditions of the environment.

Possible components of the model system were formed from databases of thermodynamic properties of gases, solids and components of aqueous solutions [4–8]. Chemical classes of hydroxides, sulphates, sulphides and carbonates are presented in the form of solid solutions. Calculations were carried out for the standard temperature and pressure.

RESULTS AND DISCUSSION

Mineral composition of ores

In all used classes of the ore the following minerals are present: hubnerite presented by tabular, less often prismatic grains, scheelite, almost in 50 % of cases in intergrown pieces with hubnerite (see Table 1); pirit, often in intergrown pieces with quartz; sphalerite, in plates of the irregular shape, rarely in beans, bismuthine. When studying the polished sections-briquettes it was established that the bismuth mineral was also presented by the anisotropic lead-bismuth phase the type of aikinite (PbCuBiS_3). Molybdenite was found in small amounts, as well as chalcopyrite, covellite and magnetite. The rarest mineral zavaritskite (BiOF) was revealed in single grains using the microprobe analysis. Its composition is non-uniform, however, the major components are contained in the following amounts (mass %): Bi 43.76, O 33.37, F 5.52. In addition, the following elements are present in the ore as mechanic admixtures (mass %): Al 1.74, Fe 1.77, Cu 2.46, Zn 3.61, Cd 0.86, Pb 3.85 and S 3.06.

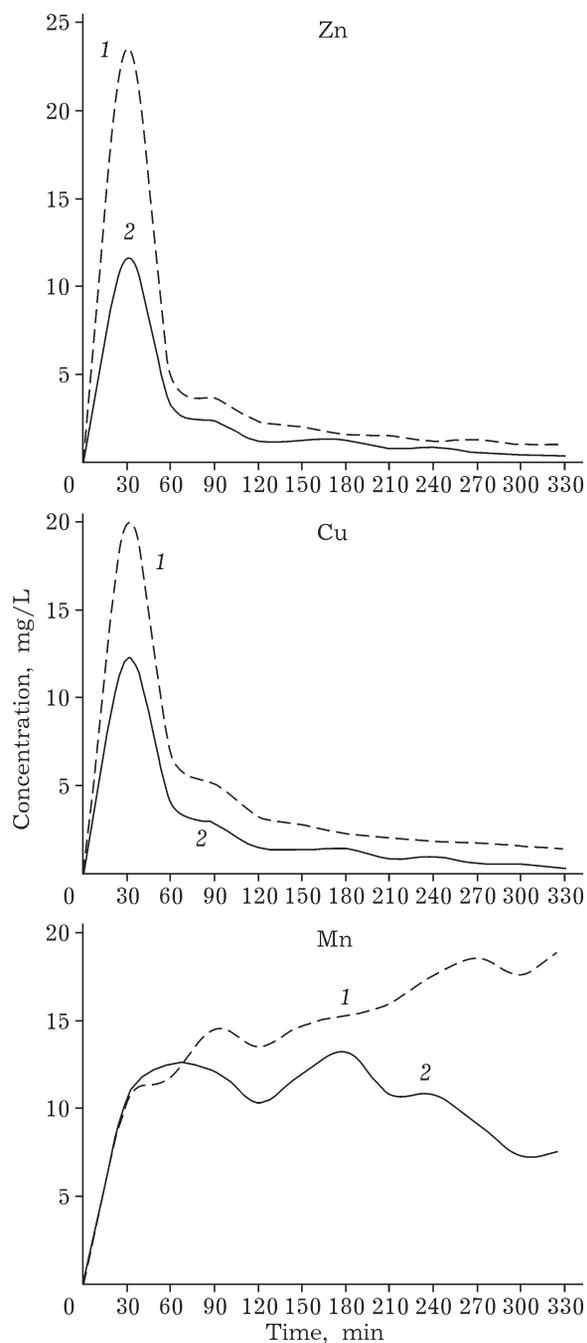


Fig. 2. Change of the concentration of Zn, Cu and Mn in the filtrate. Grain size (mm): 1–2 (1), 3–4 (2).

TABLE 4

Results of modeling of equilibrium states of technogenic water of mine Bom-Gorkhon using PC "Selector"

| Oxidizing conditions (solution: $E_h = 1034$ mV, pH 2.3) | Reductive conditions (solution: $E_h = -154$ mV, pH 6.9) |
|--|---|
| Alumosilicates | Alumosilicates |
| Biotite $K(Fe,Mg)_3(Al,Si)_4O_{10}(OH,F)_2$ (1.0 g) | Biotite (1.0 g) |
| Montmorillonite $Mg_{0.45}Fe_{0.34}Al_{1.61}Si_{3.82}O_{10}(OH)_2$ (0.1 g) | Montmorillonite (0.1 g) |
| Hydroxide (0.2 g) | Hydroxide (0.7 g) |
| Hydrogoethite $FeOOH \cdot nH_2O$ | Hydrogoethite |
| Vernadite $MnO_2 \cdot nH_2O$ | |
| Sulphates (1.4 g) | Sulphates (3.3 g) |
| Bianchite $ZnSO_4 \cdot 6H_2O$ | Bianchite |
| Gunningite $ZnSO_4 \cdot H_2O$ | Gunningite |
| Boyleite $ZnSO_4 \cdot 4H_2O$ | Boyleite |
| Goslarite $ZnSO_4 \cdot 7H_2O$ | Goslarite |
| Epsomite $MgSO_4 \cdot 4H_2O$ | Epsomite |
| Hexahydrate $MgSO_4 \cdot 6H_2O$ | Hexahydrate |
| Kieserite $MgSO_4 \cdot H_2O$ | Kieserite |
| Gypsum $CaSO_4 \cdot 2H_2O$ | Gypsum |
| Anhydrite $CaSO_4$ | Anhydrite |
| Celestine $SrSO_4$ | |
| Leonite $K_2Mg(SO_4)_2 \cdot 4H_2O$ | |
| Antlerite $Cu_3SO_4(OH)_4$ | |
| Bonattite $CuSO_4 \cdot 3H_2O$ | |
| Rostite $AlSO_4OH \cdot 5H_2O$ | Rostite |
| Carbonates (1.5 g) | Carbonates (1.7 g) |
| Dolomite $(Ca,Mg)CO_3 \cdot 2H_2O$ | Dolomite |
| Otavite $CdCO_3$ | Siderite $FeCO_3$ |
| | Kutnahorite $CaMnCO_3$ |
| | Strontianite $SrCO_3$ |
| | Sulphides (0.4 g) |
| | Marcasite FeS_2 |
| | Bornite Cu_5FeS_4 |
| | Greenockite CdS |

Among minerals of the oxidation zone, tungstate ($WO_2(OH)_2$), ferritungstite ($Fe_2W_2O_{9,3}H_2O$), ferromolibden ($Fe_2Mo_3O_{12,7}H_2O$) were registered. Rock-forming and vein minerals are presented by quartz, feldspar, epidote, muscovite and biotite, fluorite. In addition to fluorine and calcium, fluorite contains rare earths, the source of which is monazite. Feldspars are presented by microcline, albite, and adularia described earlier in ores [9, 10].

Chemical composition of solutions

The chemical analysis of filtration solutions showed a high mobility of the following elements: Zn, Pb, Cu, Cd, W, Fe, Mn, Sr, Ca. The change of concentrations of some movable elements is shown in Fig. 2.

In all cases the maximal concentrations are recorded during the first minutes of filtration, further they decrease gradually. The exception

is Ca, Sr and Mn: the content of these elements increases; moreover, this pattern is typical for materials of the dimension of 1–2 mm. As a whole, dynamic experiments showed that reactions with the participation of a smaller fraction proceed more intensely.

Thermodynamic model of equilibrium states of waters of old sedimentation tanks

Results of experiments on thermodynamic modelling are presented in Tables 2–4.

It can be seen (see Table 4) that under reductive conditions more solid-phase components by the total mass are formed than at the contact with oxygen. Herewith, such elements as Cu, Cd, Fe, Mn, Sr depending on oxidative or reductive conditions of the environment are transformed into various chemical classes from solutions. A solid solution of sulphides is formed only from Fe, Cu and Cd at reductive conditions.

Mineral structure of products of oxidation of ores and concentrates

In the course of study of products of oxidation of ores and sulphide concentrates of the Bom-Gorkhon deposit, by methods of the X-ray

and microprobe analyses (Figs. 3, 4) a large number of various sulphates were revealed: gunningite, wilcoxi ($\text{MgAl}(\text{SO}_4)_2\text{F} \cdot 18\text{H}_2\text{O}$), rostitite, startit, boyleite ($(\text{Zn},\text{Mg})\text{SO}_4 \cdot 4\text{H}_2\text{O}$), rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$), siderotil ($(\text{Fe},\text{Cu})\text{SO}_4 \cdot 5\text{H}_2\text{O}$), chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), alum ($(\text{K},\text{Na})\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) etc. In addition, the phase ($(\text{Fe}, \text{Ni})\text{SO}_4 \cdot 4\text{H}_2\text{O}$), earlier unknown among natural formation, was established.

The sample from the warehouse of the sulphide concentrate is presented in Fig. 3. Pyrite (1), on which a thin crust of goslarite (2) is formed as a result of sphalerite oxidation, can be seen well in the electron microscopic image. According to spectral data, goslarite contains admixtures of manganese iron and copper, in addition to zinc, sulphur and oxygen. Figure 4 presents a mineral association consisting of four minerals: cuprogoslarite (1) that is bases of the association containing manganese and iron as impurities; gypsum (2) containing iron, copper, zinc and cadmium that are probably present as their own mineral phases; biankit (3) and rare poatvenit ($(\text{Cu}, \text{Fe}, \text{Zn})\text{SO}_4 \cdot \text{H}_2\text{O}$) (4).

Sulphates contain cadmium, molybdenum, lead, selenium, arsenic, tellurium and other toxic elements as impurities.

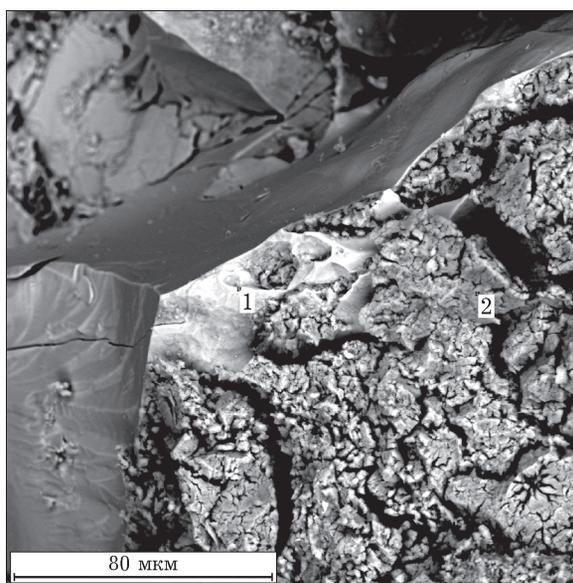


Fig. 3. Electron microscopy image of newly-formed minerals of the pyrite concentrate: 1 – pyrite, 2 – goslarite.

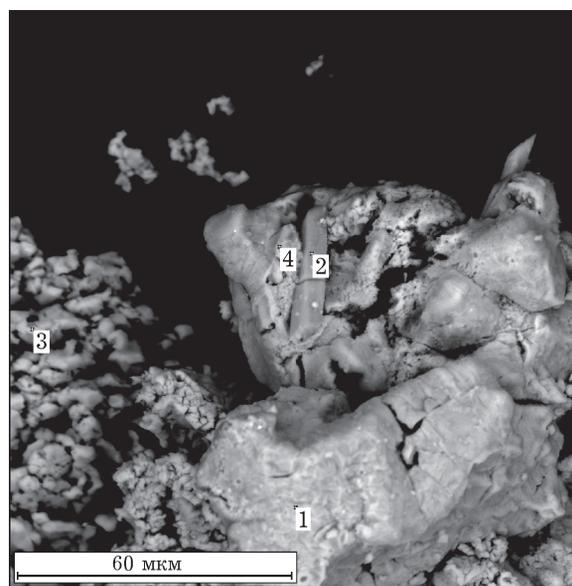


Fig. 4. Electron microscopy image of newly-formed sulphates: 1 – cuprogoslarite, 2 – gypsum, 3 – bianchite, 4 – poitevinite.

All these minerals are easily soluble in water and their component parts including sulphate anion are transferred to sedimentation tanks.

CONCLUSION

As a result of the experiments conducted on acid leaching of ores of the Bom-Gorkhon deposit of tungsten (Transbaikalia) it was established that zinc copper manganese and calcium are characterized by the maximal solubility, iron and lead by a smaller value. Cadmium, tungsten and strontium are washed out in small quantities.

Based on model calculations, all ore elements and their admixtures are mobilized when contacting with slightly acidic sulphuric solutions what helps their migration from the storage area for the products of mining into surrounding landscapes.

Mineralogical studies revealed a fairly broad spectrum of products of the modern mineral formation showed that this process was implemented on geochemical barriers from flows of water draining warehouses of sulphide concentrates and wastes arrays of ore dressing and contribute to their cleansing from toxic elements. Nevertheless, the intense migration of toxic elements leads to their concentration in water sumps, subsequent deposition as sulphates under oxidative conditions and sulphides under reductive conditions of the environment.

The data on the mineral composition of products of the modern mineral formation indicate that mineral phases obtained as a result of physicochemical modelling are generally consistent with mineral associations of natural sul-

phates forming in processes of oxidation, migration and the subsequent mineral formation on geochemical barriers.

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