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Physicochemical Modeling of the Effect of Mine Waters from Polymetallic and Cassiterite–Sulfide Deposits of Dalnegorskii Region on the Hydrosphere

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Abstract—The effect of mine waters from polymetallic and cassiterite–sulfide deposits of Dal'negorskii region on the hydrosphere has been estimated by physicochemical modeling. Hypergene processes in ore bodies of the deposits lead to formation of highly concentrated mine water solutions which continuously over decades contaminate surface and ground waters, New Eh/pH parameters of equilibrium solutions over a wide temperature range (0 to 45°C), their elemental compositions, and probable composition of hypergene and modern minerals crystallizing from mine waters have been determined.

Keywords: hypergenesis, technogenesis, hypergene minerals, physicochemical modeling, mine waters

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INTRODUCTION

Dal'negorskii region of Primorskii Krai in the Russian Far East is rich in polymetallic and cassiterite–sulfide deposits. Deposits are developed both within the Dal'negorsk territory (polymetallic ores) and in Krasnorechensk village (tin-polymetallic ores) which is located in close vicinity to the city. The city and the village lie on the river Rudnaya bank, and untreated mine waters were discharged continuously over decades into the river, River Rudnaya is the dirtiest in the world, Mining industry in the region has been developed for more than 110 years. There are three plants and four tailings dumps, old and new of the Krasnorechensk ore-dressing plant (KODP) and old and new of the Central ore-dressing plant (CODP). At present, only the Central ore-dressing plant operates, and its wastes are disposed in the new tailings dump.

Until ore bodies consisting of sulfides or including them remain buried, they almost do not change. Open-pit (quarry) or underground mining (galleries) provides access of weathering agents (water, oxygen, carbon dioxide, etc.) to ore bodies during both blasting operations and ore extraction, which favors hypergenesis and technogenesis processes in excavations and hence pollution of the hydrosphere. Modern hypergene formation is observed everywhere on the walls and roofs of mine drifts. These minerals are represented by dark and light blue, green, yellow, and brown dripstones, stalactites, and stalagmites with a size of up to 0.5 m [1–3]. The goal of the present study was to simulate over a wide temperature range (0 to 45°C) chemical composition of pore solutions which, in combination with surface and ground waters, constitute mine water. For this purpose it was necessary to determine the composition of probable hypergenesis and technogenesis minerals crystallizing from highly concentrated solutions, ionic composition of these solutions, and Eh and pH parameters.

The simulation study was performed with two kinds of ores, polymetallic ore from Dal'negorsk deposits and cassiterite–sulfide ore from Krasnorechensk deposits, both isolated and in contact with each other with account taken of most widely occurring sulfide minerals.

EXPERIMENTAL

Physicochemical modeling was carried out using Selektor software (developed by I.K. Karpov, K.V. Chudnenko, and V.A. Bychinskii) which makes it possible to estimate the amount of chemical elements transferred to the hydrosphere from mine drifts. The procedure is based on minimization of the Gibbs energy and is a universal software tool; the set of potential phases included therein is most exhaustive, It meets all requirements imposed on computer programs for the calculation of chemical equilibria. Analogous problems with other systems were successfully solved by I.K. Karpov, V.A. Bychinskii, and other researchers [4–10], Oxidation of sulfides in tailings dumps in the region under study was simulated previously by V.O. Khudolozhkin [11] and I.A. Tarasenko [3], but we are the first to study generation of mine waters.

The construction of physicochemical models requires a set of thermodynamic parameters of components of the aqueous, gaseous, and solid phases. It is clear that computer models of sulfide oxidation processes are incapable of including all factors affecting the direction and rate of chemical reactions which are responsible for the concentration and qualitative composition of chemical elements in pore solutions and mine waters, as well as the degree of their dilution with ground, rain, and snow waters. Therefore, all data obtained by physicochemical modeling, in particular mineral phase ratios and concentrations of elements in solution, should be regarded as probable and most approaching those in real mine water systems. Models may reflect hypergene and technogene processes in mine drifts. In addition, they may characterize quailtative and quantitative aspects of potential environmental hazard of unprocessed ores exposed to weathering agents in functioning and abandoned mines.

All models were constructed assuming the following conditions: temperature range 0 to 45°C, pressure 1 atm, water-to-rock ratio 10 : 1 (1 kg of water per 100 g of tailings); rain water composition: N_3^-, N_2^- NH_4^+, $NH_4N_3^0$, HNO_2^0, $NH_4NO_3^0$, NH_4OH^0, $NH_4NO_2^0$, NH_3^0, $H_2CO_3^0$, HCO_3^-, CO_3^{2-}. $C_2O_4^{2-}$, CH_4^0, O_2^0, H_2^0, N_2^0, Ar^0, He^0, Kr^0, Ne^0, OH^-, H^+, H_2O^0, NO_3^-, HNO_3^0 (pH = 5.66) [12]. The models were exposed to atmosphere. The chemical composition of atmospheric air was calculated according to Horne [13]: 10 kg of air contains, mol: Ar, 3.2, C, 0.10; N, 539.48; O 144.85. Depending on the system version, the calculations were carried out considering 3 to 14 independent components (Ar, C, N, Fe, S, As, Cu, Pb, Zn, Ag, Sb, H, O, e) and 107–304 dependent components, among which 86–257 were dissolved species, 18 were gases (Ar, H_3N, CO_2, CO, C_2H_6, H_2, H_2S, CH_4, NO, N_2, NO_2, N_2O, O_2, C_3H_8, S_2, O_2S, O_3S, H_2O), and 3–29 were hypogene or hypergene minerals.

The following primary sulfide minerals were included: sphalerite, galenite, pyrite, pyrrhotite, chalcopyrite, and arsenopyrite; secondary sulfide enrichment minerals (chalcosine, covellite, and bornite) were also added taking into account deep ore mining. For the oxidation of sulfides in contact with each other, primary minerals were taken as major ones, and the fractions of chalcosine, covellite, and bornite were assumed to be 5% each. Insofar as Krasnorechensk deposits are enriched in silver and bismuth sulfides, the corresponding models were supplemented with argentite, acanthite, pyrargyrite, and jamesonite. These minerals enriched hypergene solutions in silver, antimony, lead, and sulfur. The ratio of sulfides in the models was determined on the basis of published data (see table) [3, 14, 15].

RESULTS AND DISCUSSION

Sulfide ores may be both single-mineral and polymineral, Let us consider the results of simulation of the oxidation of single-mineral sulfide ores assuming isolated minerals (see table). The total ionic composition of the simulated solutions is given by O_2^0, H^+, H_2O^0, HSO_4^-, SO_4^{2-}, N_2^0, NO_2^-, NO_3^-, HNO_2^0, CO_2^0, HCO_3^-, Ag^+, $AgNO_3^0$, $AgOH^0$, As^{5+}, $H_2AsO_4^-$, $H_3AsO_4^0$, $HAsO_4^{2-}$, Cu^{2+}, $CuHCO_3^+$, CuO^0, $CuOH^+$. $CuSO_4^0$. $CuCO_3^0$, CuO_2^{2-}, $HCuO_2^-$. $Fe(OH)_2^+$, Fe^{2+}, Fe^{3+}, $FeAsO_4^0$. $FeH_2AsO_4^+$, $FeH_2AsO_4^{2+}$, $FeHAsO_4^+$, FeO^+, $FeOH^{2+}$, $FeSO_4^0$, $FeSO_4^+$, $Pb(SO_4)_2^{2-}$, Pb^{2+}, $PbHCO_3^+$, $PbNO_3^+$, $PbOH^+$, $PbSO_4^0$, $Sb(OH)_2^+$, $Sb(OH)_3^0$, SbO_2^-, $HSbO_2^0$, $Zn(SO_4)_2^{2-}$, Zn^{2+}, $ZnHCO_3^+$, $ZnOH^+$, and $ZnSO_4^0$.

The data in table show that the oxidation of secondary sulfide enrichment minerals, chalcosine (entry no. 1), bornite (2), and covellite (3) in Dal'negorsk (Eh 0.75–1.12 V, pH 1.88–8.66; version 1) and Krasnorechensk deposits (Eh 0.98–1.13 V, pH 1.64–4.35, version 2) gives rise to solutions with somewhat different Eh and pH values. The following technogene minerals crystallize from these solutions: in the first case. Fibroferrite $Fe^{3+}[SO_4](OH)\cdot 5H_2O$ (6–51 g) and goethite α-FeO·OH (2–15 g, only at 40°C), and in the second case, chalcanthite $Cu[SO_4]\cdot 5H_2O$ (6–166 g), brochantite $Cu_4[SO_4](OH)_6$ (22–87 g), and goethite (17 g). The mineral content of solutions is 84

Oxidation of Dal'negorsk and Krasnorechensk Sulfide Ores

Entry no.	Hypogene mineral (%)	Dal'negorsk ore (version 1)			Krasnorechensk ore (version 2)		
		technogene mineral	pH	Eh, V	technogene mineral	pH	Eh, V
1	Chalcosine Cu_2S (100)	–	8.7839	0.7475	Brochantite Chalcantite	4.3503	0.9867
2	Bornite Cu_5FeS_4 (100)	Fibroferrite Goethite (40–45°C)	8.6570	0.7542	Brochantite Chalcantite Goethite	4.3486	0.9868
3	Covellite CuS (100)	–	1.8561	1.1221	Chalcantite	1.6384	1.1335
4	Chalcosine, bornite, covellite	Fibroferrite Goethite (45°C)	8.5894	0.7579	Brochantite Chalcantite Goethite	4.3486	0.9868
5	Sphalerite ZnS (100)	–	1.3475	1.1495	–	1.3475	1.1495
6	Galenite PbS(100)	Anglesite	1.6984	1.1300	Anglesite	1.6983	1.1300
7	Pyrite FeS_2 (100)	Fibroferrite	0.3324	1.2048	Goethite	1.2020	1.1578
8	Pyrrhotite $Fe_{1-x}S$ (100)	Fibroferrite	5.5970	0.9189	Goethite	1.2186	1.1566
9	Chalcopyrite $CuFeS_2$ (100)	Fibroferrite	1.7011	1.1302	Goethite Chalcantite	1.2876	1.1528
10	Arsenopyrite FeAsS (100)	Fibroferrite	1.2110	1.1566	Goethite	1.8672	1.1215
11	Argentite Ag_2S (100)	–	1.2181	1.1567	–	1.2181	1.1567
12	Acanthite Ag_2S (100)	–	1.2181	1.1567	–	1.2181	1.1567
13	Pyrargyrite Ag_3SbS_3 (100)	Valentinite	0.8765	1.1752	–	1.0681	1.1649
14	Jamesonite $Pb_4FeSb_6S_{14}$ (100)	Anglesite Valentinite Fibroferrite	0.5456	1.1928	Plumbojarosite Anglesite	0.8239	1.1778
15	Sphalerite (15), galenite (15), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15)	Anglesite Fibroferrite	0.7777	1.1802	Plumbojarosite Adamite Goethite (40–45°C)	0.8220	1.1780
16	Sphalerite (10), galenite (10), pyrite (20), pyrrhotite (20), chalcopyrite (10), arsenopyrite (10) argentite (10), acanthite (10)	Anglesite Fibroferrite	0.8372	1.1771	Plumbojarosite Adamite Goethite (15–45°C)	1.0964	1.1632

Table. (Contd.)

Entry no.	Hypogene mineral (%)	Dal'negorsk ore (version 1)			Krasnorechensk ore (version 2)		
		technogene mineral	pH	Eh, V	technogene mineral	pH	Eh, V
17	Sphalerite (10), galenite (15), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), pyrargyrite (5)	Anglesite Fibroferrite Valentinite	0.7897	1.1796	Plumbojarosite Adamite Goethite (40–45°C)	0.8661	1.1757
18	Sphalerite (10), galenite (15), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), jamesonite (5)	Anglesite Fibroferrite Valentinite	0.7765	1.1803	Plumbojarosite Adamite Goethite (45°C)	0.7526	1.1818
19	Sphalerite (10), galenite (10), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (10), covellite (5), bornite (5), chalcosine (5)	Anglesite Fibroferrite	0.9170	1.1726	Plumbojarosite Adamite Goethite (5–45°C)	1.1792	1.1587
20	Sphalerite (10), galenite (10), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), jamesonite (5), pyrargyrite (5)	Anglesite Fibroferrite Valentinite	0.7670	1.1808	Plumbojarosite Adamite Goethite (20–45°C)	1.0078	1.1680
21	Sphalerite (10), galenite (10), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), covellite (10)	Anglesite Fibroferrite	0.8193	1.1780	Plumbojarosite Adamite Goethite (5–45°C)	1.1674	1.1593
22	Sphalerite (10), galenite (10), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), bornite (10)	Anglesite Fibroferrite	0.8779	1.1748	Plumbojarosite Adamite Goethite (5–45°C)	1.2633	1.1541
23	Sphalerite (10), galenite (10), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), chalcosine (10)	Anglesite Fibroferrite	0.9310	1.1719	Plumbojarosite Adamite Goethite (5–45°C)	1.2663	1.1540

Table. (Contd.)

Entry no.	Hypogene mineral (%)	Dal'negorsk ore (version 1)			Krasnorechensk ore (version 2)		
		technogene mineral	pH	Eh, V	technogene mineral	pH	Eh, V
24	Sphalerite (15), galenite (15), pyrite (20), pyrrhotite (20), chalcopyrite (15).covellite (5), bornite (5), chalcosine (5)	Anglesite Fibroferrite	0.8962	1.1738	Plumbojarosite Goethite (40–45°C)	0.7926	1.1796
25	Sphalerite (15), galenite (15), pyrite (20), pyrrhotite (20), arsenopyrite (15), covellite (5), bornite (5), chalcosine (5)	Anglesite Fibroferrite	0.8745	1.1749	Plumbojarosite Adamite	0.7601	1.1814
26	Sphalerite (15), galenite (15), pyrite (20), chalcopyrite (20), arsenopyrite (15), covellite (5), bornite (5), chalcosine (5)	Anglesite Fibroferrite	1.5850	1.1364	Plumbojarosite Adamite (0–5°C)	0.8538	1.1762
27	Sphalerite (15), galenite (15), pyrrhotite (20), chalcopyrite (20), arsenopyrite (15), covellite (5), bornite (5), chalcosine (5)	Anglesite Fibroferrite	1.8646	1.1213	Plumbojarosite Adamite (0–5°C)	0.8589	1.1759
28	Sphalerite (15), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), covellite (5), bornite (5), chalcosine (5)	Fibroferrite	0.9674	1.1700	Adamite Goethite	1.2683	1.1540
29	Galenite (15), pyrite (20), pyrrhotite (20), chalcopyrite (15), arsenopyrite (15), covellite (5), bornite (5), chalcosine (5)	Anglesite Fibroferrite	1.0586	1.1650	Plumbojarosite Goethite (20–45°C)	1.2061	1.1572

to 100 (version 1) and 36–84 g/L (version 2). In the oxidation of chalcosine, covellite, and bornite in contact with each other (entry no. 4), the Eh and pH parameters of the solutions, mineral content thereof, and the composition of minerals crystallizing therefrom are similar to the results obtained for the preceding systems. In the first version, Fibroferrite (17 g) and goethite (only at 45°C, 5.6 g) crystallize from the solution, and in the second version, brochantite (up to 34 g), chalcanthite (up to 105 g), and goethite (58 g). The mineralization is 155 to 160 g/L (version 1) and 65–130 g/L (version 2).

We consider next the models of oxidation of hypogene sulfide minerals (see table, entry nos. 5–10). The Eh and pH values for these systems range from 0.92 to 1.2 V and from 0.33 to 5.6, respectively. Oxidation of sphalerite in all deposits gives rise to highly concentrated solutions, but no technogene minerals crystallize therefrom, and zinc and sulfur are completely transferred to solution. The mineralization of solutions is always high and is 172 g/L. Decomposition of galenite leads to separation of lead sulfate (anglesite, $PbSO_4$) in an amount of 114 to 125 g, and the mineralization ranges from 11 to 90 g/L. Pyrite and pyrrhotite favor formation of fibroferrite (version 1; goethite crystallizes at 15°C) or goethite (version 2). The mineralization ranges from 90 to 206 and from 0.01 to 140 g/L for pyrite and pyrrhotite, respectively. The oxidation of chalcopyrite and arsenopyrite leads to crystallization of fibroferrite (version 1; 141 and 159 g) or goethite (version 2; 27–41 g) and chalcanthite (version 2; 9–54 g). The mineral contents are as follows: 99 (version 1) and 129–156 g (version 2) in the oxidation of chalcopyrite and 94 (version 1) and 165–178 g (version 2) in the oxidation of arsenopyrite. Thus, fibroferrite (iron sulfate) crystallizes from concentrated mine water solutions as a result of oxidation of hypogene sulfides from Dal'negorsk deposits, and goethite (iron hydroxide) crystallizes from mine water solutions in Krasnorechensk deposits, In the first case pore solutions contain almost no iron, while in the second case the iron content of pore solutions ranges from 1.5 to 43 g/L.

Simulation of the oxidation of silver sulfides (argentite and acantite; entry nos. 11, 12) present only in Dal'negorsk deposits showed that no any hypergene silver mineral is formed in these models and that silver is completely held in solution where its concentration changes from 87.2 to 87.4 g/L.

Pyrargyrite and jamesonite (entry nos. 13, 14) were found in ores of both deposits, valentinite (Sb_2O_3) was found to precipitate from solution in version 1 (oxidation of pyrargyrite), whereas in version 2 hypergene minerals were not formed, and the elements remained in solution. The mineralization of the latter is fairly high, 133 to 151 g/L. The behavior of jamesonite upon oxidation is the most interesting, In version 1, anglesite (58 g), valentinite (42 g), and Fibroferrite (12.5 g) crystallized from the solution, and in version 2, anglesite (9 g) and plumbojarosite $\{PbFe_6^{3+}[SO_4]_4(OH)_{12}$, 56 g), while antimony was transferred to solution (35 g/L), the total mineralization of the solutions being 45 and 92 g/L, respectively. The Eh and pH values of solutions in the oxidation of antimony sulfides range from 1.16 to 1.19 V and from 0.54 to 1.07, respectively.

Taking into account that not necessarily all primary minerals were present simultaneously in sulfide ore veins, ore models for further simulation contained different natural combinations of minerals, i.e., minerals were alternately removed from the system. Then the most typical combination containing most abundant primiry sulfides (sphalerite, galenite, pyrite, pyrrhotite, chalcopyrite, and arsenopyrite; entry no. 15 in table) was simulated, and covellite, bornite, and chalcosine were added both jointly (entry no. 19) and separately (in the alternate mode; entry nos. 21–23, respectively); next, arsenopyrite (24), chalcopyrite (25), pyrrhotite (26), pyrite (27), or sphalerite (29) was removed. In all these models (Dal'negorsk deposits) anglesite (12–19 g) and fibroferrite (106–164 g) separated from micropore solutions. The Eh values changed from 1.12 to 1.18 V, and pH, from 0.77 to 1.86. The mineralization of solutions ranged from 85 to 90 g/L.

When pyrargyrite (entry no. 17) and jamesonite (18) were added either separately or simultaneously (20) to the combination of minerals given by entry no, 15 (see table), the following hypergene minerals crystallized from concentrated solutions: anglesite (15–22 g), fibroferrite (144–145 g), and valentinite (1.3–3 g); Eh 1.17–1.18 V, pH 0.77, respectively; mineralization 73 to 82 g/L. After removal of pyrrhotite from the system (entry no. 28), only fibroferrite (165 g) precipitated from the solution containing 112 g/L of mineralization.

Let us consider analogous models for Krasnorechensk deposits (version 2). The base model was constructed for joint oxidation of sphalerite, galenite, pyrite, pyrrhotite, chalcopyrite, and arsenopyrite (see table, entry no. 15); covellite, bornite, and chalcosine were then added jointly (19) or separately (21–23). Further models were obtained by addition to the base model (15) of one of the following silver minerals: acantite (16), pyrargyrite (17), and jamesonite (10); jamesonite and pyrargyrite were then added jointly (20), and covellite (21), bornite (22), or chalcosine (23) was added separately. In all cases, plumbojarosite (47–82 g), adamite $Zn_2[AsO_4](OH)$ (4–15 g; only at 0° C), and goethite (0.6–14 g; 5–45°C) crystallized from micropore solutions; Eh 1.15–1.18 V; pH 0.75–1.27; mineralization 109–145 g/L.

Exclusion of either arsenopyrite (entry no. 24) or sphalerite (29) from the base combination of minerals in Krasnorechensk ores (19) leads to generation of plumbojarosite (71 g) and goethite (0.4–10 g) from solutions characterized by the following parameters: Eh 1.15–1.18 V, pH 0.79–1.2, mineralization 119–139 g/L, If chalcopyrite (entry no. 25), pyrrhotite (26), or pyrite (27) was removed from the base model, plumbojarosite (71 g) and adamite (9–21 g) crystallized from solutions, adamite being formed in the temperature range from 0 to 5°C. The corresponding solutions had Eh and pH values of 1.18 V and 0.76–0.85, respectively, and their mineralization was 93 to 122 g/L. Exclusion of galenite from the base model (entry no. 28) leads to formation of adamite (13 g) and goethite (20–40 g); mineral content 177–189 g/L.

All hypergene minerals formed in the simulated systems were observed on the walls and roofs of mine drifts both in the regions under study and in other mining regions [1–3].

CONCLUSIONS

Physicochemical modeling of the formation of highly concentrated mine waters entering surface and ground waters and subsequent crystallization of hypergene and technogene minerals showed the following. Iron and lead sulfates (fibroferrite and anglesite) can be formed as a result of oxidation of the sulfide component of ores from Dal'negorsk deposits, and Krasnorechensk ores give rise goethite (iron oxide/hydroxide mineral) and plumbojarosite (lead sulfate). Oxidation of secondary sulfide enrichment minerals (covellite, bornite, and chalcosine) leads to crystallization of chalcantite and brochantite only from acid solutions formed in Krasnorechensk deposits. Zinc from sphalerite in Dal'negorsk deposits is completely transferred to solution, whereas adamite is produced, though only at low temperature (0 to 5°C), from Krasnorechensk ores. By contrast, goethite does not crystallize from solutions above 0°C,.Silver is transferred completely to solution where its concentration reaches 87 g/L. Antimony crystallizes as an oxide mineral, valentinite, and its concentration in solution is estimated at below 35 g/L. The total mineralization of solutions is generally high, 36 to 206 g/L, but it should be taken into account that 2 to 178 g of technogene minerals precipitates from there.

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