ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 13, pp. 2750–2753. © Pleiades Publishing, Ltd., 2013.
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Modeling of Sulfide Oxidation in Tailings Dumps of the Kavalerovsky District and Their Impact on the Hydrosphere (Primorsky Krai, Russia)

V. P. Zvereva[a, b], A. D. Pyatakov[a], and A. M. Kostina[a,b]

[a] *Far Eastern Federal University, ul. Sukhanova 8, Vladivostok, 600091 Russia*
e-mail: zvereva@fegi.ru

[b] *Far Eastern Geological Institute, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, Russia*
pr. 100-letiya Vladivostoka156, Vladivostok, 690049 Russia

Received September 9, 2013

Abstract—The results obtained in modeling of drainage waters in tailings dumps of deposits in the Kavalerovsky district in the temperature range from 0 to +45°C are reported. The Eh-pH parameters of the technogenic mineral formation systems at various rock sulfide ratios in the tailings (95 : 5, 90 : 10, 80 : 20, and 60 : 40) were determined. The crystallization of supergene minerals from micropore solutions was studied. The qualitative and quantitative ion composition of the minerals and their effect on the surface and ground waters in the district were determined.

Keywords: Physical and chemical modeling, hypergenesis, tailings, tailings dump, assessing the environmental status, verification.

DOI: 10.1134/S1070363213130227

INTRODUCTION

In our previous study [1] we showed based on the literature data that mining systems exert the negative effect on the ecosphere as whole, and hydrosphere in particular. The study was concerned with the extent of mining technological system of tin sulfide deposits in the Kavalerovsky district, the volume and composition of accumulated wastes (tailings), and the effect exerted by supergene processes on the surface and ground waters at +25°C.

The main goal of this study was to assess the impact of supergene and technogenic processes proceeding on the same five tailings dumps in the wide temperature range, from 0 to +45°C. By climatic characteristics [2], the temperature in the district varies from –35 to +35°C. At the same time, in oxidation of sulfides, it increases. For this reason, the upper value of the temperature in the study was higher by 10°C. Taking into account the goal of the study, we have formulated the following tasks: (1) to study sulfide oxidation in five tailings areas in the temperature range from 0 to +45°C; (2) to determine technogenic minerals crystallizing in solutions of drainage and slime waters; (3) to determine the qualitative and quantitative ion composition of these waters; (4) to assess their impact on the hydrosphere of the district; and (5) to verify the data obtained.

EXPERIMENT

The technogenic processes in mining wastes (tailings) were simulated using the “Selector-Windows” Program (adapted version of the Selector–C Program Package). We used for modeling the same thermobarometric conditions: temperature was from 0 to +45°C, pressure, 1 atm, and the water rock ratio, 10 : 1. In modeling we took into account the annual rainfall (800 kg/m^2) and used the selected temperature interval. The rain water contained [3]: 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, NO_3^-, and HNO_3 (pH = 5.66). The model systems were open to the atmosphere. The chemical composition of the atmosphere was calculated according to a Horne’s monograph [4]. The atmosphere (10 kg) contains (moles): Ar 3.209, C 0.1036, N 539.478, and O 144.8472. We used in calculation 19 independent components (Al, Ar, As, B, C, Ca, Cu, Fe, K, Mg, N, Na, Pb, S, Si, Zn, H, O, e), 373 dependent components, 284 of which were dissolved particles, 18, gases, and 69 were minerals and solid solutions, i.e. the most probable hypogene and supergene minerals.

RESULTS AND DISCUSSION

Mining waste (tailings) on all tailings dumps is a finely disperse gray mass constituted by pyrite, pyrrhotite, galena, sphalerite, arsenopyrite, chalcopyrite, quartz, fluorite, tourmaline, chlorite, and other minerals. For sulfide oxidation in contact with the host rock minerals we used model systems of varied composition (see table). Because in different parts of the tailings dumps, the waste composition is different, the rock sulfide ratios used for modeling systems were 95 : 5, 90 : 10, 80 : 20, and 60 : 40 for each tailings. The content of the supergene minerals precipitated from the concentrated model solutions is also given in table.

In model systems of three tailings of the Khrustal'ny deposit and one tailings of the Dubrovsky deposit, the compositions of the solutions are close (pH 6.26–10.10, Eh 0.68–0.82 V). Compared to +25°C [1], in this temperature range, a wider spectrum of the minerals of a supergene zone and crust weathering is formed in the model systems (see table). The minerals classed with oxides, hydroxides, sulphates, carbonates, silicates, and arsenates are crystallized in them from highly concentrated solutions. These are minerals of the following cations (g): Fe (goethite), from 21 to 32, Fe and Pb (plumbojarosite), 16–21 (only the first tailings, 60 : 40), Pb (anglesite), 5.10 (three tailings of the Khrustal'noe deposit), Pb and Cu (duftite) 0.6–13, Cu and Al (woodwardite) 0.3 (second tailing , 95 : 5), Al (gibbsite, kaolinite, and alunogen) 1.6–4, 1–54, and 0.0002–34, respectively, Mg (magnesite) 0.9–9.5, Ca (gypsum) 0.3–2.9 (60 : 40), K and Al (hydromuscovite and muscovite) 1.2–15 and 7.3–13.2, Mg, Al, and Fe (montmorillonite) 0.003–18.7 (60 : 40).

Sulfide oxidation in contact with a host rock on the tailings of the Vysokogorskoe deposit is somewhat different than on the above systems. The model solutions have pH = 6.17–9.08 and Eh = 0.72–0.82 V.

In this system, the following minerals were formed (g): goethite up to 35, alunogen 80, magnesite 10, hydromuscovite 16, muscovite 13, quartz 16, kaolinite 43, gypsum 4, duftite 3, and gibbsite 2. A considerable amount of woodwardite (up to 1) is precipitated from the solutions, whereas anglesite, plumboarosite, and montmorillonite are not precipitated. Gibbsite is formed in model solutions only at the ratio 95 : 5, and duftite, at the ratios 80 : 20 and 60 : 40.

In the temperature range studied, some precipitated minerals are always present in all model solutions: goethite, duftite, and hydroxymuscovite. The latter crystallizes up to +30°C and converts into muscovite with loss of the molecular water at higher temperatures. The formation of some minerals (such as gibbsite and anglesite) in the systems is constantly growing with increasing temperature, whereas the formation of another minerals (such as magnesite, caolinite, alunogen, and gypsum), on the contrary, decreases. In some systems, the dependence of the behavior of some minerals is different. For example, the content of duftite in the systems (tailings of the Dubrovsky deposit, the ratios 80 : 20 and 60 : 40) first decreases to a temperature of +25°C and then increases. The content of woodwardite crystallized in the systems of tailings of the Vysokogorsky deposit at the ratio 95 : 5 remains practically at the same level (1.35–1.36 g); at the ratios 90 : 10 and 80 : 20 it decreases from 2.42 to 1.84 and from 5.1 to 3.78, respectively, to a temperature of +25°C and then begins to increase (to 2.54 and 4.18 g, respectively). At the ratio 60:40 the mineral content decreases and increases twice in the entire temperature range by the following scheme: 10.16 (0°C), 8.52 (+10°C), 8.96 (+15°C), 10.7 (+30°C), and 7.88 (+45°C). For example, montmorillonite occurs in the systems only at the ratio 60:40 from 0 to +10°C (tailings 1, 2 of the Khrustal'ny and Dubrovsky deposits) in an amount of 8.40–8.27, 18.7–0.0026, and 7.57 g, respectively.

The elements of sulfide ores in the solutions are in the form of the following ions: AsO_4^{3-}, $Cu(CO_3)_2^{2-}$, Cu^{+2}, $CuCO_3$, $CuHCO_3^+$, CuO, $CuOH^+$, $CuSO_4$, $HCuO_2^-$, $H_2AsO_4^-$, H_3AsO_4, $HAsO_4^{2-}$, $HFeO_2$, FeO^+, FeO_2^-, $FeOH^{2+}$, $HZnO_2^-$, ZnO_2^{2-}, $NaAsO_4^{2-}$, $Pb(SO_4)_2^{2-}$, Pb^{2+}, $PbCl^+$, $PbHCO_3^+$, $PbNO_3^+$, PbO, $PbOH^+$, $HPbO_2^-$, $PbSO_4$, $Pb(CO)_2^{2-}$, SO_4^{2-}, HSO_4^-, $Zn(CO_3)_2^{2-}$, $Zn(SO_4)_2^{2-}$, Zn^{2+}, $ZnCO_3$, $ZnHCO_3^+$, ZnO, $ZnOH^+$, $HZnO_2^-$, and $ZnSO_4$. Owing to the destruction of the host rocks and their interaction with sulfide components, the following ions are formed in the solutions: $Al(OH)^{2+}$, Al^{3+}, AlO^+, AlO_2^-, $B(OH)_3$, BO_2^-, $Ca(HCO_3)^+$, $CaHSiO_3^+$, Ca^{2+}, $CaCO_3$, $CaOH^+$, $CaSO_4$, H_2O_2, $HAlO_2$, HCO_3^-, $HSiO_3^-$, K^+, KCl, $KHSO_4$, KSO_4^-, KOH, $Mg(HCO_3)^+$, $MgHSiO_3^+$, Mg^{2+}, $MgCO_3$, Na^+, $NaHSiO_3$, NaOH, $NaSO_4^-$, and SiO_2. A variety of the ion composition grows with increasing temperature.

The content of hypogene and supergene minerals in model systems in oxidation of tailings in contact with the host rock[a]

Mineral	Khrustal'ny deposit			Dubrovsky deposit	Vysokogorsky deposit
	tailings 1	tailings 2	tailings 3		
	Hypogene, %				
	Sulfides				
Pyrite FeS_2	11.3	29.3	18	30	15
Pyrrhotite $Fe_{1-x}S_n$	1.3	8.7	4.7	10	20
Arsenopyrite FeAsS	14.7	6.7	5.3	10	20
Chalcopyrite $CuFeS_2$	9.3	6.7	5.3	10	30
Galena PbS	43.3	19.3	23.3	20	5
Sphalerite ZnS	20	29.3	43.3	20	10
	Host rock				
Chlorite	78.38			59.46	45.94
Sericite	11.89			13.51	13.51
Tourmaline	5.95			21.62	35.14
Epidote	2.16			3.24	3.24
Calcite	1.62			2.16	2.16
	Supergene, g				
Goethite FeOOH	21.04–30.12			24.21–32.02	24.19–35.43
Gibbsite $Al(OH)_3$	1.55–3.33			2.5–4.14	0.37–2.42
Magnesite $MgCO_3$	0.91–8.69			2.14–9.45	0.33–9.92
Anglesite $PbSO_4$	5.30–10.06			–	–
Duftite $PbCu[AsO_4](OH)$	0.61–8.50			1.16–13.33	0.14–3.61
Plumbojarosite $Pb_{0,5}Fe_3(SO_4)_2(OH)_6$	21.34–21.37			14.66	–
Woodwardite $Cu_4Al_2[SO_4](OH)_{12}\cdot H_2O$	0.30			–	1.35–10.70
Gypsum $CaSO_4\cdot 2H_2O$	0.26–1.92			2.86–2.91	0.01–4.11
Alunogen $Al_2[SO_4]_3\cdot 18H_2O$	1.05–30.26			0.20–53.85	1.08–79.90
Hydromuscovite $K[Al_3Si_3O_{10}](OH)_2\cdot 4H_2O$	8.81–13.95			1.16–14.99	0.0001–15.82
Muscovite $K[Al_3Si_3O_{10}](OH)_2$	7.26–11.59			8.18–13.15	7.69–13.14
Quartz SiO_2	0.0001–7.0			0.34–9.20	0.57–16.25
Kaolinite $Al_2[SiO_3]_2(OH)_4$	10.56–25.21			0.0002–33.86	2.62–43.09
Montmorillonite $m\{Mg_3[Si_4O_{10}](OH)_2\}\cdot p\{Al, Fe^{+3})_2[Si_4O_{10}](OH)_2\}\cdot nH_2O$	0.0026–18.70			7.57	–

[a] (–) no mineral is in the model system.

Model solutions of drainage water on all tailings contain the high amount (mg/L) of the metals, including from 1160 to 10800 sulfur, 13–6280 lead, 354–12000 zinc, 13–3850 arsenic, and 0.6–944 copper (the latter present only in tailings of the Dubrovsky and Vysokogorsky deposits). In them, potassium, sodium, calcium, magnesium, aluminum, and boron ions are present.

The total mineralization of the solutions on tailings 1, 2, and 3 of the Khrustal'ny deposit lies within (g/L) 8.63–51.9, 9.27–51.2, and 10–57.1, respectively, at a rock sulfide ratio varied from 95:5 to 60:40. For the Dubrovsky and Vysokogorsky deposits, the corresponding values are 11–44.8 and 14–35.6, respectively. Assessment of the impact exerted by each individual tailings shows that Khrustal'ny deposit has maximal damage to the hydrosphere and Vysokogorsky deposit, minimal. The total removal of elements from all tailings at the rock sulfide ratio 95 : 5 is (g/kg): 54.2 (95 : 5), 95.6 (90 : 10), 163.4 (80 : 20), and 223.7 (60 : 40), i.e., ranges from 54 to 224.

The ion and mineral composition [5] and the hydrochemical data for slime and drainage waters [5–7] confirmed the correctness of the results obtained.

CONCLUSIONS

Our physico-chemical modeling of the main phases of existence of dry tailings of the Kavalerovsky tin ore district in the temperature range from 0 to +45°C provides a complete picture of the formation of drainage water. Untreated water around the clock for decades enters the surface waters and pollutes them. The hydrosphere is subjected to a strong anthropogenic load by the elements of sulfides (S, Zn, Cu, Pb, and Fe) and host rocks (B, Mg, K, Na, Ca, Si, and Al).

From the results obtained we may follow sulfide oxidation process, determine conditions of formation of supergene minerals, estimate probable intensity of removal of toxic elements, and to evaluate their impact on the hydrosphere. The physico-chemical models of sulfide oxidation showed that supergene minerals (Fe, Cu, Pb, Al, Mg, K, and Ca) of sulfates, carbonates, silicates, oxides, and hydroxides are crystallized from highly concentrated solutions. The composition of drainage waters is determined by equilibrium pore solutions containing a wide spectrum of the ions of heavy metals and host rocks. Mineralization of these solutions reaches 224 g/kg. The concentration of the main elements of sulfides and host rocks, most of which are toxic, exceeds their background level and MPC values (set for fishing industry) by one, two, and even three orders of magnitude. The modeling makes it possible to estimate the state of mining technological systems in space and time, to make a forecast for the future, obtain new data on parameters of modern technogenic mineral formation, and to show the range of their existence.

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