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Physicochemical Modeling of the Impact of Tailings Dumps in the Kavalerovskii Tin-Ore District of the Russian Far East on the Hydrosphere

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Abstract—Physicochemical modeling was applied to determine Eh and pH parameters of anthropogenic mineral formation in the Kavalerovskii mining district, study crystallization of supergene minerals from solution, examine the qualitative and quantitative ion compositions of solutions, estimate the role of supergenesis in the pollution of surface and ground water, and assess environmental situation in the district.

Keywords: Supergenesis, physicochemical modeling, tailings, tailing dumps, environmental monitoring, verification.

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INTRODUCTION

Nowadays, environmental consequences are among the most important problems related to the development of mining industry. Tailings dumps in mining areas occupy hundreds hectares and withdraw these areas from beneficial land-use. The results of numerous studies have shown that tailings dumps strongly affect the atmosphere, lithosphere, biosphere, and hydrosphere in the respective regions [1–8].

Mining facilities in the Kavalerovskii district (Khrustal'nenskii Mining and Processing Works) are located mainly in the river Zerkal'naya catchment area. They include six mines and four ore-dressing plants. The Khrustal'nenskii Works was put into operation in 1941 as Tsentral'nyi Mine (Dubrovskoe deposit). The other mines and the second plant were launched in 1960–1970s, and 15 deposits have been developed by 1992, mainly by the underground technique. Tin has always been the main (and the only) element mined in the Kavalerovskii district, though in recent years indium and silver were concomitantly extracted, whereas sulfides containing copper, lead, and zinc in commercially significant amounts were always dumped as tailings. There are five tailings dumps in the Kavalerovskii district; they occupy an overall area of 17.7 ha and comprise 37.72 million tons of mine wastes (tailings). Most deposits have been exhausted and shut down long ago. During the Perestroika period, only the Iskra copper–tin ore deposit was developed, and waste materials from the first tailings dump with a tin content of 0.5 to 1.0% were reprocessed. In 2001 tin-ore mining industry in the Kavalerovskii district ceased to exist, though the ore reserves have not been depleted.

The tailings in all tailings dumps are grey finely dispersed material consisting of pyrite, pyrrhotite, galenite, sphalerite, arsenopyrite, chalcopyrite, quartz, fluorite, tourmaline, chlorite, and other minerals. Sometimes iron hydroxides formed as a result of oxidation of sulfides endow tailings with brown color with various tints. Qualitative and semiquantitative spectral analysis of seven samples taken from three tailings dumps showed the presence of the following elements (%): Sn, 0.04–0.10; Cu, 0.0062–0.2600; Pb, 0.0039–0.0760; Zn, 0.08–1.00; As, 0.01–0.05; Ni, 0.0014–0.0033; Co, 0.0002–0.0009; Cr, 0.0019–0.0030; V, 0.0043–0.0100; Ag, 0.0003–0.0030; Ga, 0.0011–0.0016; B, 0.01–0.05; Bi, 0.0001–0.0003; Sr, $\leq$0.01, Ca, $\leq$ 0.1.

Increase of the surface of contact of finely dispersed sulfides with weathering agents activates supergene processes in the bulk material, which lead to crystallization of such minerals as chalcanthite, gypsum, halotrichite, melanterite, pitticite, etc.; these minerals by now should be regarded as anthropogenic. Some of them are "seasonal" since they form in a drought period and disappear in the rains as a result of dissolution.

The goal of the presence work to assess by physicochemical modeling the effects of supergene and anthropogenic processes occurring in the tailings dumps on the hydrosphere of the Kavalerovskii tin-ore mining region. In keeping with that goal, we set ourselves the following tasks:

(1) Examine the sulfide oxidation process in five tailings dumps located in the district;

(2) Identify anthropogenic minerals crystallizing from drainage and slime waters;

(3) Determine the qualitative and quantitative ion compositions of drainage and slime waters;

(4) Assess their impact on the hydrosphere;

(5) Verify the obtained data.

METHODS

Anthropogenic processes in mine wastes (tailings) were simulated with the aid of Selektor-S for Windows. Analogous problems for other systems were successfully solved by Karpov [9], Khudolozhkin [10], Dutov [11], Bychinskim et al. [12], and other authors. Supergene processes in the Kavalerovskii anthropogenic mining region were simulated for the first time. The temperature was assumed to be equal to 25°C, and pressure, to 1 atm. The water-to-rock ratio was taken as 10 : 1. The annual precipitation (800 kg/m^2) and seasonal variation of the air temperature (–35 to +35°C) were taken into account [13]. Rainwater was assumed to contain the following ions and neutral species [9]: N_3^-, N_2^- NH_4^+, NH_4N_3, HNO_2, NH_4NO_3, NH_4OH, NH_4NO_2, NH_3, H_2CO_3, HCO_3^-, CO_3^{2-}, $C_2O_4^{2-}$, CH_4, O_2, H_2, N_2, Ar, He, Kr, Ne, OH^-, H^+, H_2O, NO_3^-, HNO_3 (pH = 5.66). The models used were exposed to atmosphere whose chemical composition was calculated according to [14]: 10 kg of atmosphere contained 3.209 of argon, 0.1036 of carbon, 539.478 of nitrogen, and 144.8472 of oxygen. The calculations involved 19 independent components (Al, Ar, As, B, C, Ca, Cu, Fe, K, Mg, N, Na, Pb, S, Si, Zn, H, O) and 373 dependent components, among which 284 dissolved species, 18 gases, and 69 minerals and solid solutions, i.e., most probable hypogene and supergene minerals.

RESULTS AND DISCUSSION

All steps during the existence of a tailings dump and processes occurring with tailings may be represented as a set of physicochemical models. The initial transformation of tailings begins at the stage of ore processing, separation of concentrate, and discharge of slurry into the tailings dump through a pipeline. This step involves partial but short-term interaction of ore and tailings with reagents; therefore, it may not be taken into account. Once being dumped, liquid tailings are subjected to the action of supergene agents (water, atmospheric oxygen, etc.), and the slurry is diluted with rainwater and meltwater. While a mining enterprise operates and discharges wastes, the tailings dump is considered to be active, and it is covered by a slurry lake. During this period, the tailings are liquid (model I). Slime water partly drains away and enters into surface and ground waters. The period after termination of waste dumping until the slurry lake has dried out amounts to decades (model II). The tailings then remain dry over decades (model III). A combination of models II and III is applied from the moment when wastes are no longer dumped to the disappearance of the slurry lake. Depending on the age and degree of development of the mining industry, each tailings dump passes through all three stages, and the duration of each stage may vary. At present, two tailings dumps are completely dry, and the other three are partly (by no more than 1/5) covered by slurry lakes. Each tailings dump was considered in two versions, with the ratios host rock–sulfides equal to 95 : 5 and 90 : 10, due to non-uniform composition of wastes in different sites of tailings dumps.

The model of oxidation of sulfides in contact with the host rock in three tailings dumps of the Khrustalnoe deposit was constructed using the mineral compositions given in table.

Aqueous solution in the tailings dumps under consideration is weakly alkaline (pH 8.98 to 9.12), and its Eh value ranges from 0.68 to 0.69 V. The following supergene zone and weathering crust minerals crystallize from solution: goethite, duftite, magnesite, gibbsite, hydromuscovite, kaolinite, and amphiboles

Concentrations (%) of hypogene and supergene minerals in tailings used in the simulation of sulfide oxidation in contact with the host rock

Mineral	Khrustal'noe deposit			Vysokogorskoe deposit	Dubrovskoe deposit
	1	2	3		
Hypogene minerals					
Pyrite	11.3	29.3	18	15	30
Pyrrhotite	1.3	8.7	4.7	20	10
Arsenopyrite	14.7	6.7	5.3	20	10
Chalcopyrite	9.3	19.3	23.3	5	20
Galenite	43.3	29.3	43.3	5	20
Sphalerite	20	29.3	43.3	10	20
Supergene minerals					
Hydromuscovite	12.2	12.1	12.3	9.3	19.2
Amphibole (monoclinic)	13.2	13.9	13.2	0.5	–
Amphibole (rhombic)	21.5	20.1	22.2	1.3	–
Kaolinite	0.9	0.9	0.7	9.3	29.4
Goethite	24.3	24.9	24.7	15.2	15.3
Gibbsite	4.6	4.3	4.7	23.2	23.4
Magnesite	9.1	9.1	8.6	9.3	9.1
Duftite	14.2	15.5	13.7	3	1.1
Woodwardite	–	–	–	1.1	3.8
Gypsum	–	–	–	4.8	–

(see table); the presence of these minerals in the given region is confirmed by mineralogical studies [8]. The solution contains a lot of sulfur (as sulfate ion SO_4^{2-}; 1140 to 2980 mg/L) and lead ($PbHCO_3^+$; 354 to 2820 mg/L). Also, potassium, sodium, calcium, magnesium, and aluminum (as AlO_2^-) ions are present. Aluminum gives rise to supergene minerals gibbsite and kaolinite, whereas its concentration in solution is low. Iron is a component of goethite, and its concentration in aqueous phase is also insignificant. Zinc resides in solution as $ZnHCO_3^+$ and $ZnCO_3^+$ ions at an overall concentration of 674 to 1340 mg/L. Arsenic forms supergene mineral duftite, and it exists in solution as $HAsO_4{}^{2-}$ ions with a concentration of 135 to 285 mg/L. Silicon in solution is represented by insignificant amounts of SiO_2, $NaHSiO_3$, and $HSiO_3^-$ ions; it crystallizes mainly in the form of kaolinite, hydromuscovite, and amphiboles. The total mineral content of the aqueous phase in the Khrustal'noe tailings dumps (nos. 1–3) is 8590, 8690, and 9400 mg/L, respectively.

The oxidation of sulfides in contact with the host rock in the Vysokogorskoe tailings dump was simulated using the mineral composition given in table. The aqueous solution has a pH value of 8.39–7.63 and Eh value of 0.72–0.77 V. It contained woodwardite (1.1%) and gypsum (4.8%) in addition to the above listed minerals found in the Khrustal'noe tailings dumps. The concentrations of goethite, duftite, hydromuscovite, and amphiboles is lower, and of gibbsite and kaolinite, considerably higher than in the foregoing systems. As in the previous cases, the solution is characterized by high concentrations of sulfur-, arsenic-, zinc-, and lead-containing ions. The following concentrations of elements in solution were obtained for the host rock-to-sulfide ratios 95 : 5 and 90 : 10, respectively, mg/L: S, 1570, 3150; Pb, 229, 458; Zn, 352, 709; As, 464, 928; Si, 0.17, 2.3. The total mineral content of the aqueous phase reaches 14100 mg/L, i.e., it is higher than in the above sulfide oxidation models.

Likewise, the model of sulfide oxidation in contact with the host rock in the Dubrovskoe tailings dump gave pH 8.57 and 9.06 and Eh 0.68 and 0.71 V of the aqueous solution. This values approach those obtained for the systems considered above. The total mineral content is 9710 and 11200 mg/L. The solution features a high concentration of sulfur. Goethite, gibbsite, and magnesite crystallize from the solution in almost the same amounts as in the Vysokogorskoe tailings dump model, the concentration of hydromuscovite, kaolinite, and woodwardite is considerably higher, the amount of duftite is three times lower, and amphiboles are completely absent. The concentrations of elements in solution are as follows, mg/L: Zn, 702, 1400; As, 25, 52; Pb, 340, 686; S, 1550, 3100.

Simulation of the interaction of tailings with atmospheric water showed that the aqueous solution in all tailings dumps in the Kavalerovskii district should be enriched in (mg/L) sulfur (7.95 to 1690), boron (1.51 to 1070), magnesium (13.4 to 949), sodium (1.08 to 757), calcium (0.001 to 181), silicon (0.169 to 2.88), potassium (0.04 to 0.41), and aluminum (0.0001 to 0.028). Snowmelt and rainfalls increase the aqueous component and dilute pore solutions. Therefore, the oxidation of wastes in all tailings dumps was simulated assuming increase of the aqueous component in the system by factors of 10, 100, and 1000. The overall concentration of minerals in the pore water with and without account taken of dilution was estimated at, g/L: Vysokogorskoe, 0.24 to 2.36; Dubrovskoe, 0.2 to 9.17; Khrustal'noe 1, 0.23 to 12.58; Khrustal'noe 2, 0.165 to 6.06; and Khrustal'noe 3, 0.159 to 5.15. The overall concentration of elements throughout the Kavalerovskii mining district varies from 0.159 to 12.58 g/L.

Our results showed that the tailings dumps of the Vysokogorskoe and, to a lesser extent, Dubrovskoe deposits exert a stronger effect on the surface water as compared to each of the three Khrustal'noe tailings dumps; on the other hand, the overall discharge from the latter is twice as large as that from each of the former two. The highest concentration of copper was detected in the pore water of the Vysokogorskoe and Dubrovskoe tailings dumps, of lead, in the Dubrovskoe and Khrus-tal'noe 3 tailings dumps, and of sulfur, in the Vysokogorskoe and Khrustal'noe 2 tailings dumps. The concentrations of iron and silicon in all the examined systems are approximately equal. The pore water of the Vysokogorskoe and Dubrovskoe tailings dumps contained larger amounts of Na, Ca, and B, while the highest Mg content was found for the Khrustal'noe 2 and 3 tailings dumps. The overall amount of elements discharged from the five tailings dumps was estimated at about 500 g/L. Clearly, the greater the sulfide fraction of the tailings, the higher the mineral content of solutions formed as a result of sulfide oxidation and the higher the probability for crystallization of anthropogenic minerals therefrom. Correspondingly, the concentration of elements in drainage water and their transfer to surface and ground waters also increase.

The results of physicochemical modeling were verified by comparing the ion and mineral compositions [8] of aqueous solutions, as well as element concentrations therein, with the data of hydrochemical monitoring of slime and drainage waters [2, 5–8]. By simulation of supergene processes occurring year-round in mine wastes under different conditions we obtained a complete pattern of interactions in the system atmosphere–water–rocks. Pore water in tailings gives rise to highly mineralized solutions containing a broad spectrum of toxic elements. After dilution with ground and surface water, these solutions (as unpurified drainage water) contaminate surface water over decades. It should be noted that drinking water for Kavalerovo village is supplied from Vysokogorskaya and Zerkalnaya rivers just where slime water flows. Regardless of the source of pollution, whether is it a mine opening or tailings dump with various mineral composition, the hydrosphere is subjected to very high anthropogenic load with elements from both sulfide components (S, Zn, Cu, Pb, Fe) and host rock (B, Mg, K, Na, Ca, Si, Al). The concentration of some elements attains tens grams per liter, and most of them exceeded the corresponding background values and maximum allowable concentrations by one, two, and even three orders of magnitude. Pollution of surface and ground waters changes hydrochemical background in the region.

Taking into account that oxidation of sulfides lasts for centuries [7], tailings dumps remain potential sources of hydrosphere pollution with toxic elements until complete oxidation of all sulfide minerals. Therefore, it is desirable to perform reclamation of the tailings dump areas after preliminary extraction of useful components, especially toxic ones. In fact, tailings dumps are anthropogenic deposits ready for processing.

CONCLUSIONS

Physicochemical modeling of the main steps in the life of tailings dumps in the Kavalerovskii tin-ore district allowed us to reveal a comprehensive picture of sulfide oxidation processes, determine conditions for the formation of supergene minerals, assess the intensity of discharge of toxic elements, and evaluate their effect on the hydrosphere. It has been shown that supergene minerals containing Cu, Pb, Zn, Fe, and As (sulfates, arsenates, silicates, oxides, and hydroxides) crystallize from highly concentrated aqueous solutions. Pore solutions containing a broad series of heavy metal ions predetermine the composition of slime and drainage waters. The mineral content of these solution reaches 14 g/L, and the overall discharge from all tailings dumps amounts to 500 g/L. The role of supergenesis in environmental pollution is considerable throughout the existence of anthropogenic mining system. The concentrations of major elements from sulfides and host rocks, most of which are toxic, exceed the background values and maximum allowable concentrations by 1–3 orders of magnitude. Physicochemical modeling provides an assessment of the state of anthropogenic mining system across space and time, future forecast, and new parameters and scope of modern anthropogenic mineral formation. The obtained results may be used for environmental monitoring in the Kavalerovskii tin-ore district.

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