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Investigation of Hypergene Processes in Copper and Nickel Sulphide Ore Concentrating Tailings

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Abstract

Hypergene processes in the waste products of concentration of copper and nickel ores (tailing dumps in the Afrikanda settlement, Murmansk Region) were investigated by means of physicochemical modelling using the Selektor software. New formations in the solid phase are represented by goethite (over sulphides) and three-layered layered silicates. The appearance of gypsum is observed in the case of substantial interaction. The concentration of nickel in the pore fluid exceeds the MPC even under a 0.01 % change in volume. The results indicate that the concentrations of heavy metals are rather high in pore fluid, though its pH is higher than 8 as a mean in all the samples, which brings real danger to the environment.

INTRODUCTION

Hume amount of tailing rocks and concentrating tailings accumulated by present brings about essential economical and ecological problems in mining regions, since the tailings are sources of atmospheric pollution with dust while water and soil get polluted with heavy metals. Hypergene processes in mining wastes have a higher rate than those under natural geological conditions [1]. Many heavy metals (copper, nickel, cobalt, lead, zinc, bismuth, antimony, arsenic, *etc.*) are present in mining wastes in the form of sulphides or as an isomorphous admixture in them. Because of this, sulphides, which are easily oxidized, are an essential source of environmental pollution. The rate of sulphide oxidation is affected not only by climatic and hydrological conditions but also by the composition, disperse state and stability of non-metal minerals towards weathering [2]. In this connection, it seems interesting to determine the composition of pore fluids of concentrating tailings after storage for a long time and to estimate the danger of environmental pollution with heavy metals, both during the operation of a mining plant and after a plant is withdrawal from operation.

EXPERIMENTAL

A tailing dump of the experimental concentrating mill in the Afrikanda settlement (Murmansk Region) which had been processing sulphide copper and nickel ores from the Pechenga ore deposit in early 1970s was chosen as a model object. Hypergene processes in concentrating wastes were investigated both by means of the direct observation at this man-made object and by means of physicochemical modelling.

About 200 samples of tailings were collected within the tailing dump. The mineral and

TABLE 1

Changes in the minerals of concentrating tailings of copper and nickel ores during storage

Mineral	Content in tailings, mass %	Changes during storage
Serpentines*	50–80	Substitution with hydrochlorites, partial leaching
Peridot	0–10	No visible changes; partial leaching
Augite	2–15	No visible changes
Talc	0.3–20	Hydration of the surface
Magnetite	5–15	No visible changes
Calcite	0–5	Substitution with gypsum and dolomite
Dolomite	0–5	No visible changes
Sulphides	1–3	Substitution with iron hydroxides

*Chrysotile, lisardite, antigorite.

chemical composition of the samples was investigated, the composition was analysed, pH and E_h of pore fluids were determined using the methods of mineralogical, X-ray phase, differential thermal, chemical analyses, IR spectroscopy, optical and scanning electron microscopy, standard methods of evaluation of physical and mechanical properties. The analysis showed that storage for 30–35 years is accompanied by almost complete oxidation of sulphides, partial substitution of serpentine minerals with hydrochlorites, dolomitization of calcite. No changes were discovered in the primary magmatic minerals of the tailings – augite, peridot, amphiboles, magnetite. A qualitative description of the observed hypergene processes is presented in Table 1. We took these results into account when developing a model to describe functioning of the man-made object under investigation.

When carrying out physicochemical modeling of weathering processes in mining wastes, we used the PC Selektor software [3]. A basic multisystem was composed with the help of this software; the following aspects were modelled:

– chemical equilibrium in the interaction of water, rock and atmosphere, depending on the degree of rock interaction with water (P = 1 bar, T = 25 °C), which allowed us to reveal the main features of changes in water composition;

– interaction of water saturated with atmospheric components [4] with the beds of tailings, in order to study the oxidation process in space and in time.

RESULTS AND DISCUSSION

Chemical composition of the tailings was established, mass %: SiO_2 47.1, AlO_3 6.64, Fe 10.81, MgO 16.93, CaO 2.62, Ni 0.166, Cu 0.043, TiO_2 0.96, S 1.04. When describing hydrochemical processes, we took into account the rates of arrival or removal of the components, so not the whole rock mass but only its soluble part was introduced into the mass balance of the system "a rock + 1 kg of H_2O" [5]. All the calculations were carried out per 1 kg of water. The system was investigated under the conditions of free air access (1 kg of the atmosphere). Taking into account the results of observations of hypergene processes, we found that the rate of oxidation of sulphide minerals was an order of magnitude higher than the rate of interaction of the formed solutions with non-metal minerals. According to the data of the author of [6], the coefficients of water migration of S, Cl are 1–2 orders of magnitude larger for Ca, Na, Mg. This aspect was modelled by the difference in the degrees of interaction of elements. The results of modelling of the equilibrium in the system water–rock–atmosphere are shown in Table 2.

The data provide evidence that the new formations in the solid phase are represented by goethite (for sulphides), three-layered layered silicates (named talc conventionally in Table 2, talc 1 (containing nickel) and montmorillonite). The appearance of gypsum is observed in the case of active interaction. The concentration of nickel in pore fluid

TABLE 2

Computer analogue of the newly formed phases and ion composition of pore fluids as a result of interactions in the system water–rock–atmosphere ($T = 25$ °C, $P = 1$ bar)

Rock mass, g	Amount, mol					Concentration, mg/l							pH
	TiO_2	FeOOH	Talc	Talc 1	Montmorillonite	Mg^{2+}	SO_4^{2-}	HCO_3^-	Ni^{2+}	Cu^{2+}	Ca^{2+}	$CaSO_4$	
$86.315 \cdot 10^{-6}$	$1.40 \cdot 10^{-8}$	$2.27 \cdot 10^{-7}$	0	0	$2.30 \cdot 10^{-7}$	9.01	0.04	0.15	0.0027	0	0	0	5.73
$86.315 \cdot 10^{-5}$	$1.25 \cdot 10^{-7}$	$1.81 \cdot 10^{-6}$	0	0	$1.19 \cdot 10^{-6}$	0.10	0.32	0.29	0.009	0.004	0.041	0	6.03
$86.315 \cdot 10^{-4}$	$1.20 \cdot 10^{-6}$	$7.88 \cdot 10^{-6}$	$4.38 \cdot 10^{-6}$	0	$8.06 \cdot 10^{-6}$	0.95	3.06	1.75	0.016	0.004	0.26	0	6.80
$86.315 \cdot 10^{-3}$	$1.20 \cdot 10^{-5}$	0	$8.58 \cdot 10^{-5}$	0	$8.10 \cdot 10^{-5}$	9.30	30.40	16.23	0.169	0.027	2.59	0.27	7.76
$86.315 \cdot 10^{-2}$	$1.20 \cdot 10^{-4}$	$7.72 \cdot 10^{-5}$	$1.18 \cdot 10^{-3}$	$1.13 \cdot 10^{-8}$	$8.10 \cdot 10^{-4}$	66.23	295.64	29.27	1.69	0.221	22.32	14.55	8.07
$86.315 \cdot 10^{-1}$	$1.20 \cdot 10^{-3}$	$2.22 \cdot 10^{-3}$	$1.19 \cdot 10^{-2}$	$1.74 \cdot 10^{-6}$	$8.09 \cdot 10^{-3}$	606.44	2830	16.21	16.95	3.43	171.64	325.10	7.68

TABLE 3

Computer analogue of the newly formed phases and ion composition of pore fluids for the three-reservoir model of tailing dump

Time, rel. units	Amount, mol							Concentration, mg/l							pH
	FeOOH	Dolomite	TiO_2	Talc	Talc 1	Montmorillonite	SiO_2	Ca^{2+}	$CaSO_4$	Mg^{2+}	SO_4^{2-}	HCO_3^-	Ni^{2+}	Cu^{2+}	
							The first reservoir								
1	0	0	0.000012	0.000085	0	0.000081	0.0000866	5.016	0.916	18.46	60.227	32.272	0.336	0.064	7.96
3	0	0	0.000013	0.000095	0	0.00009	0.000096	5.017	0.916	18.46	60.226	32.238	0.337	0.063	7.96
7	0	0	0.000013	0.000095	0	0.00009	0.000097	5.015	0.927	18.47	60.220	32.283	0.337	0.063	7.96
10	0	0	0.000013	0.000095	0	0.00009	0.000096	5.019	0.912	18.47	60.230	32.303	0.337	0.063	7.96
							The second reservoir								
1	0	0	0.00003	0.00028	$5.19 \cdot 10^{-9}$	0.000201	$1.9 \cdot 10^{-5}$	12.244	4.923	37.940	154.13	34.358	0.871	0.165	7.97
3	0	0	0.000046	0.000444	$1.42 \cdot 10^{-9}$	0.000311	$6.54 \cdot 10^{-8}$	16.261	7.986	49.308	208.492	35.542	1.187	0.226	7.99
7	0	0.000039	0.000096	0.00094	$6.41 \cdot 10^{-8}$	0.000645	0	28.461	24.437	98.473	428.443	43.996	2.469	0.446	8.10
10	0	0.000039	0.000178	0.001749	$1.58 \cdot 10^{-9}$	0.001197	0	43.868	52.041	178.448	791.872	36.685	4.588	0.891	8.04
							The third reservoir								
1	$3.75 \cdot 10^{-9}$	0.000036	0.000057	0.000564	$7.76 \cdot 10^{-8}$	0.000384	0	20.188	13.201	68.476	301.452	26.415	1.718	0.222	8.45
3	0.000027	0.000131	0.000219	0.002163	$1.24 \cdot 10^{-7}$	0.001478	0	24.430	17.511	82.367	368.675	24.765	2.109	0.286	8.43
7	0.000205	0.000601	0.000836	0.008243	$1.46 \cdot 10^{-7}$	0.005633	0	36.084	35.246	129.679	589.034	21.460	3.398	0.512	8.35
10	0.001249	0.001268	0.001812	0.017872	$7.97 \cdot 10^{-7}$	0.012209	0	51.829	63.670	193.416	884.335	18.985	5.144	0.843	8.28

exceeds the MPC even when the change in volume is as small as 0.01 %.

As a result of modelling of the composition and concentrations of the components of ore-forming elements and magnesium oxide in solutions, a good agreement of the resulting values with the measured ones was observed in the case if 1–10 % of sulphide minerals and silicates entered the reaction.

In real tailing dumps, the processes of sulphide oxidation and interaction of solutions with non-metal minerals do not coincide in space, because the formed solutions are partially filtered into deeper horizons. In order to describe this process, we considered a model involving three reservoirs. According to this model, mining wastes stored in a tailing dump differ in degree of compaction, humidity and gas phase content, which allows us to separate them into three interacting systems (reservoirs) connected with each other by mass transfer.

It was assumed in modelling that each reservoir contained 863.15 g of rock and the reservoirs were characterized by different degree of openness to the atmosphere (1, 0.1, 0.001 bar, respectively) at a temperature of 10 °C. The first reservoir of the mega system receives 0.5 kg of water; the resulting solution passes to the lower reservoirs and reacts to a definite extent with the rock in each reservoir (4, 3.8, 3.6, respectively). The acidity of water (0.5 kg) saturated in 1 kg of the atmosphere at $T = 10$ °C and $P = 1$ bar is 5.62, $E_{\mathrm{h}} = 0.904$. The newly formed mineral phases in part remain in their reservoir (about 10 %), in part enter the next reservoir.

The first system is equated with the upper layer of tailings in the beach zone where it undergoes periodic drying and wetting. The solid phase in this zone is in unstable equilibrium in weakly compacted state. The second system is represented by the lower-lying zone of tailings fully saturated with water and compacted under the action of upper layers. The ground solutions are filtered into the lower-lying third zone. The third system, which is represented by the deepest horizons of a tailing dump, is characterized by the maximal degree of solid phase compaction. The filtration coefficient here is low; it decreases with time because of the accumulation of solid products of the synthesis of newly formed minerals due to the substances arriving from the upper horizons. Under the conditions of humid climatic regime characteristic of the Kola Peninsula, the products of hypergenesis are carried into the second and third reservoirs. Due to the limited character of drainage, the first two reservoirs have a very low volume capacity. The third reservoir was considered as an accumulator. Recurrence of such events, provided that the degree of water interaction with the rock in the second and the third reservoirs increases by 0.1, allows us to consider this process using relative time units.

The results of physicochemical modelling are presented in Table 3. One can see that the transformation of two-layered layered silicates into three-layered ones occurs in all the three zones, while nickel-containing three-layered hydrosilicates occur within the second and the third zones. Nickel content of pore fluids in the three zones is much higher than the MPC within the whole period of modelling.

CONCLUSIONS

It is generally believed in the scientific community that the ecological danger is associated with mining wastes in which pore fluids are acidic. The results obtained in the present work show that the concentrations of heavy metals are rather high in all the samples, though the acidity of pore fluids in these samples is characterized by pH < 8; this brings actual danger to the environment. The concentrations of ore-forming elements and magnesium oxide in pore solutions of old tailings are controlled by two consecutive processes: sulphide oxidation with the formation of acidic solutions and the interaction of these solutions with the most reactive non-metal minerals – serpentines and carbonates.

The investigation provides unambiguous evidence that sulphide-containing wastes can be dangerous for environments for many years after withdrawal from operation.

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