Thermodynamic Modeling of Hypergenesis of the Allarechensky Deposit Dumps under the Conditions of Different Temperatures and Moistening Modes

S. I. MAZUKHINA, S. S. SANDIMIROV, D. V. MAKAROV

Institute of North Industrial Ecology Problems, Subdivision of the Federal Research Centre Kola Science Centre of the Russian Academy of Sciences,
Apatity, Russia

E-mail: simazukhina@mail.ru

Abstract

Processes occurring in the dumps of sulphide-bearing rocks had drawn the researchers' attention for a long time. Environmental hazards connected with the activity of mining industry facilities under the conditions of climate change can be estimated by modeling. Modeling was performed in the water-rock-atmosphere systems (software suite Selector), where rock is an average mineral composition of rocks from the Allarechensky Deposit Dumps of copper-nickel ores. The conditions for the carryover of different components during weathering of rocks in the dump were determined, and the effect of climatic factors on the formation of new phases was evaluated. It was demonstrated that abrupt temperature changes promote rock weathering. In addition to copper and nickel, potassium and aluminium will pass into solution during the cold period. Gibbsite and aluminium silicates will be formed during the warm period. Comparison of modeling results with field studies revealed the adequacy of the model and high degree of the interaction of rocks and atmospheric precipitation in the dumps. Evaporation gives rise to more acid solutions, increased transfer of nickel, copper, iron and sulphates into solutions. The basic premise is that the destruction of wastes mineral matrix occurs practically all year round under the regional climatic conditions, due to the formation of highly mineralized solutions inside the dump body and on its surface. Atmospheric precipitation, filtered through rock fragments with high sulphide content, affects the hydrosphere causing an increase in the concentration of all the major ions (Cl^-, SO_4^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) by a factor of several units, compared to pure natural waters.

Keywords: surface water, deposit dumps, physicochemical modeling, patterns of migration, newly formed phases

INTRODUCTION

The largest enterprises of the mineral and raw material complex of the Arctic zone of the Russian Federation (AZRF) and the country as whole are concentrated at the territory of the Murmansk Region. More than 150 million t of mining wastes are annually impounded in the region: unpayable ores, rock dumps, mill tailings and slag, the total amount being up to 8 billion t by the present. Maintenance of the dumps of overburden rocks and slag, tailings and sludge pits requires substantial capital and material expenses, and large areas of land are eliminated from the economic turnover. Dusting from dumps and tailings, the ingress of reagents and heavy metals into natural surface and ground waters have a negative effect on the ecosystems and human health.

The problems of sustainable development of the mining industry under the conditions of climate change are urgent for all Arctic countries, which is evidenced by the publications that appeared during the recent years, for example [1–12].

It is necessary to predict the consequences of climate change for the enterprises of the mining complex in the zones of intense nature management in the AZRF and take the results into account in the following aspects:

– development of hypergene processes in the wastes of the mining industry, which leads to the environmental migration of toxic elements and heavy metals, flotation reagents generating acid sewage;

– technological properties of potentially extractable minerals from the wastes of the mining complex as technogenic deposits and the possibilities to intensify hydrometallurgical geotechnologies for processing substandard raw materials of natural and technogenic origin.

Canadian researchers carried out laboratory studies and field observations of real objects to reveal the features of chemical and frost weathering of minerals from the dumps of sulphide-containing rocks under the conditions of the Arctic [11, 12].

Previous studies showed that the changes of the composition and properties of minerals during the storage of wastes occur at a much higher rate than under the natural geological conditions. This causes damage to the environment, in particular after the completion of mining at deposits [13].

The effect of the conditions of waste storage on the technological properties of potentially extractable minerals was considered in [14]. The authors studied the parameters of the exothermal heating of the dump of sulphide copper-nickel ore in Sudbury (Canada) for 7 months (since May till December) and assessed the effect of external meteorological factors (temperature, air humidity, wind velocity, atmospheric pressure) on these parameters. The discovered effects include inflation of nickel resources and worsening of the flotation activity of pentlandite during pyrrhotite due to the formation of elemental sulphur after the storage of the ore.

Investigation of the concentration tailings of copper and nickel ores in the Murmansk Region and model experiments showed that hypergene action leads to substantial changes in the technological properties of sulphides and nonmetallic minerals [13].

The authors of [15, 16] established that the stored pyrrhotite concentrate from the Norilsk mining and smelting plant differs in its composition and properties substantially from the concentrate of the current works. The formation of dense surface films is observed on pyrrhotite grains. Pyrrhotite content in these aggregates is sharply decreased. Only its relics in the form of particles not larger than 30–40 μm are conserved. The major phases are represented by goethite and elemental sulphur. The content of nickel and sulphur in the products of pyrrhotite oxidation increases.

It should be noted that slow but steady warming in the Arctic regions is a general trend pronounced all over the territory of the AZRF [17].

The goal of the present work was to evaluate the effect of the changes of temperature and the amount of atmospheric precipitation on the processes involved in physicochemical weathering, the amount and composition of newly formed mineral phases, and on the intensity of the transfer of nonferrous metals into mobile forms. Thermodynamic modeling of equilibria in the water – rock system was used as a tool to study the dumps of the Allarechensky deposit of copper-nickel ores as an example.

EXPERIMENTAL

The object of investigation

The dumps of the Allarechensky deposit are situated in the Pechenga District of the Murmansk Region and are filled with the mining wastes from the primary Allarechensky deposit of sulphide copper and nickel ores. Mining had been carried out using the open-pit method and ceased in 1971 (Fig. 1). The major mineral resources were nickel, copper and cobalt [18]. The rocks of the dump are represented, to different extents, by mineralized peridotite, olivinite, contact amphibolite, etc. Ores include two morphological types: massive (continuous) and disseminated. The major ore minerals are pyrrhotite, pentlandite and (more rarely) chalcopyrite, in chats with magnetite (Table 1).

Atmospheric impact on the primary ores during their long-term presence in the rock dump and the related hypergene processes provided the formation of oxidized ores. As a result of oxidation, the major part of ore had lost its primary qualities. For instance, while rich kinds of primary ores contain 18 % Ni, 8 % Cu, 0.3 % Co, the content of these elements in their oxidized analogues does not exceed 3.3, 2.0, 0.05 %, respectively [18].

Massive ores of pyrrhotite-pentlandite line are especially prone to hypergenesis because of the instability of their major mineral components, which is observed visually: the fragments of these ores get covered with a shell composed of
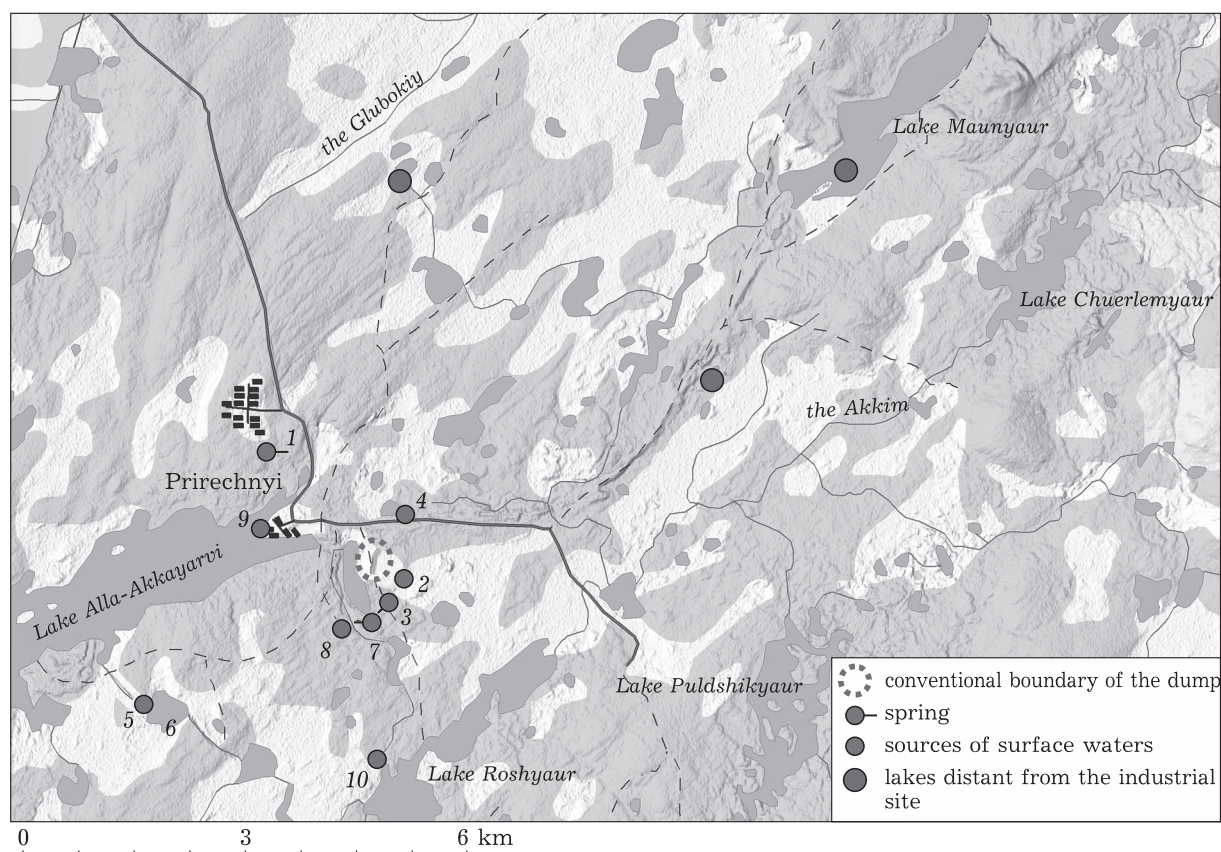
Fig. 1. Scheme of surface and ground water sampling [18]: *1* − spring (N69°01'35.2", E30°15'30.5"); *2* − a nameless lake (N69°00'35.9", E30°18'13.1"); *3* − bog (N69°00'28.1", E30°18'01.5"); *4* − a nameless lake (N69°01'00.2", E30°17'40.3"); *5* − the mouth of the bypass channel (N68°59'32.1", E30°14'37.0"); *6* − a nameless lake (N68°59'34.4", E30°14'37.0"); *7* − a drowned open pit (N69°00'28.3", E30°17'26.0"); *8* − a bog (N69°00'32.5", E30°17'26.2"); *9* − the Alla-Akkayarvi lake (N69°00'51.7", E30°16'01.0"); *10* − the mouth of the Alla river at the site where it flows into the Roshyaur lake (N68°59'15.5", E30°17'19.9") (the data from JSC Tellur SPb).

TABLE 1

General characterization of the Allarechensky deposit

Resources	Content of nonferrous metals, %	Mineral composition	Prevailing size of sulphide sinters
~1 million t (commercial and unpayable ores of different types containing not less than 5−6 thousand t of Ni according to approximate estimation)	Ni − 1.57[a] Cu − 1.34Co − 0.029	Ore: pentlandite, chalcopyrite, pyrrhotite, magnetite Nonmetal: plagioclase, microcline, quartz, biotite, muscovite, amphiboles, serpentine, chlorite	20.0−200.0 μm

[a] The data relate to the rocks of the ore mass of the dump [18].

iron hydroxides, they start to peel off and go to pieces. In addition to physical destruction, chemical reactions leading to typical hypergene minerals proceed in the ores continuously. The permanent presence of violarite (Ni_2FeS_4) in the ores and ubiquitous propagation of (α-$NiSO_4 \cdot 6H_2O$) forming clearly noticeable blue-green sinters on host rocks attract attention.

Retgersite mineral is partially accumulated in the fine-grained fraction and also, due to its easy solubility, it is carried with atmospheric precipitation and flood waters into lower horizons and away from the dump [13, 18]. According to the data of X-ray phase analysis of sulphate sinters on the samples of massive ores, gypsum $CaSO_4 \cdot 2H_2O$ was identified as the major phase, as well as hexa-

TABLE 2

Major ions in surface and ground waters [18]

Parameter	Sampling sites										MPC[a]
	1	2	3	4	5	6	7	8	9	10[b]	
Concentration, mg/L											
HCO_3^-	28.06	6.71	–	11.59	12.20	14.03	34.16	19.52	15.86	7.1	1000
SO_4^{2-}	23.04	84.77	911.88	10.70	3.70	6.17	37.45	16.87	3.29	3.4	500
F^-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	–	1.5
Cl^-	1.95	0.71	2.3	1.42	<0.35	<0.35	2.84	1.06	0.53	1.9	350
NO_2^-	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	–	3
NO_3^-	0.33	<0.1	0.33	0.10	<0.1	0.11	<0.1	<0.1	<0.1	0.001	45
Ca^{2+}	13.0	24.00	–	6.00	3.60	4.00	20.00	8.00	4.00	2.16	180
Mg^{2+}	2.54	5.81	–	0.24	0.24	0.97	2.42	1.45	0.36	0.74	50
Na^+	2.15	1.98	8.53	1.98	1.48	1.41	3.28	2.73	1.73	1.62	200
K^+	1.23	4.60	10.87	0.90	0.58	0.52	3.15	2.04	0.62	0.42	12
Al^{3+}	<0.04	<0.04	0.22	<0.04	<0.04	<0.04	0.05	<0.04	<0.04	0,035	0.2
NH_4^+	0.16	<0.05	0.61	0.13	0.22	0.22	<0.05	0.12	0.12	0.013	1.5
H_4SiO_4	3.47	5.71	4.59	4.27	<0.32	<0.32	<0.32	<0.32	<0.32	–	34
Fe_{total}	<0.05	<0.05	–	0.12	<0.05	0.05	<0.05	0.05	0.06	0.1	0.3
pH	6.46	6.18	3.65	6.63	7.06	7.06	7.57	7.11	6.36	6.31	6−9
Mineralization, mg/L	66.83	134.76	–	36.41	23.48	26.70	88.63	46.23	26.97	17.4	1000
Concentration of oil products, mg/L	–	–	–	–	–	–	0.017	–	<0.005	–	0.1

Note. 1. Sampling sites (see Fig. 1). 2. Dash − not detected.

[a] The MPC values are given according to SanPiN 2.1.4.1074−01 [19].

[b] Average values of hydrochemical parameters in the lakes that are remote from the industrial site.

hydrite $MgSO_4 \cdot 6H_2O$, nickelhexahydrite $NiSO_4 \cdot 6H_2O$, retgersite $NiSO_4 \cdot 6H_2O$, moorhouseite $CoSO_4 \cdot 6H_2O$, beaverite $CoSO_4 \cdot 7H_2O$, langite $Cu_4SO_4(OH)_6 \cdot 2H_2O$ [13].

Experimental modeling of hypergenesis revealed a substantial rate of the transformation of nonferrous metals into soluble forms during the interaction of rocks in the dump with diluted sulphuric solutions. The absence of chemically active nonmetal minerals able to neutralize the acid drainage and possible precipitation of acid rain in the region cause a sharp increase in the rate of hypergene changes of sulphide minerals and the transformation of ecologically dangerous elements into mobile forms [13, 18].

Analysis of surface waters within the framework of ecological monitoring revealed that all water reservoirs situated in the direct vicinity to the dump are polluted with nickel (the excess over the MPC is 3−79 times on average, the highest value is 4736 times). Not less polluted were the soils. For instance, in the upper organogenic soil horizon of the bog located to the south from the dump, the revealed concentrations of heavy metals exceeded the conventional

background levels: Ni − by a factor of 877, Cu − 227, Co − 61 [18] (see Fig. 1, Table 2).

As a result of technogenic load, increasing degradation of the ecosystems is observed at the territories adjacent to the dump. Some pieces of land had turned into technogenic waste areas. The area of the affected territories is much larger than the area of the foot of the dump itself [13, 18].

Research procedure

The climate of the zone in which the dumps of the Allarachensky deposit are situated is characterized by relative mildness and humidity for the latitude of 69°, which is due to the effect of the Gulf Stream, a warm current. Changeable weather with cold snaps in summer, frequent thaws in winter, icing and snowdrifts is characteristic of the region. The annual amount of precipitation is 450−480 mm with approximately uniform distribution over months. The annual temperature is about 0 °C. The average annual number of days with negative temperature is about 200. The snow cover is stable since early November to middle May.

Thermodynamic modeling is one of the methods to predict the changes of technogenic objects and their effect on the hydrosphere. Within the investigation of water − rock interactions, the influence of climate is assessed with such parameters as temperature and amount of precipitation. The composition of rocks was determined by means of chemical analyses; water imitates atmospheric precipitation. Possible thermodynamic states are considered, those that may change from the washing action in the water − rock system (rains, snow melting) to the process of water evaporation causing concentrating of chemical elements and precipitation of secondary minerals. To calculate chemical equilibria, the authors used a Selektor software package (SP) of the newest modification [20]. The basic "water − rock − gas" model was applied to the hydrochemical systems under investigation. The model included a broad range of independent components (Al−B−Br−Ar−He−Ne−C−Ca−Cl−F−Fe−K−Mg−Mn−N−Na−P−S−Si−Sr−Cu−Zn−Ni−Pb−V−Ba−Co−Cr−Hg−As−Cd−H−O−e^-, where e^- is electron), 996 dependent components (in particular, 369 components in the aqueous solution, 76 in the gas phase, 111 liquid hydrocarbons, 440 solid phases, organic and mineral substances). A set of solid phases within the multisystem was formed taking into account the mineral composition of the crystal rocks of the Fennoscandian (Baltic) Shield. The necessary thermodynamic information was taken from the databases built in the SP [20, 21]. The SP is based on the minimization of thermodynamic potentials. The algorithm [20] allows carrying out the calculations of complicated chemical equilibria under the isobar-isothermal, isochoric and adiabatic conditions in multisystems in which an aqueous electrolyte solution, a gas mixture, liquid and solid hydrocarbons, minerals in the form of solid solutions and single-component phases, melts and plasma may be present at the same time. The SP proved itself to be a good tool for solving many ecological, geochemical and technological problems arising for the Arctic region.

The averaged mineral composition of the rocks in the dump according to the data reported in [18] is presented in Table 3. These data were used to calculate the equilibria in the 'water − rock' system where the rock is represented by 100 g of the rock from the dump, and water is atmospheric precipitation. The system is open; the composition of 1 kg of the atmospheric air is (in moles): Ar 0.3209, C 0.01036, N 53.9478, Ne

TABLE 3

Mineral composition of the ore-containing rock of the dump

Mineral	Formula	Content, %
Plagioclase	$NaAlSi_3O_8$, $CaAl_2Si_2O_8$	47.4
Microcline	$KAlSi_3O_8$	7.7
Quartz	SiO_2	11.5
Biotite	$KMgFe_2(AlSi_3O_{10})(OH)_2$	5.0
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	3.5
Amphiboles	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	11.6
Serpentine	$Mg_6Si_4O_{10}(OH)_8$	3.6
Chlorite	$Mg_{4.5}Al_3Si_{2.5}O_{10}(OH)_8$	2.3
Magnetite	Fe_3O_4	2.5
Pyrrhotite	FeS	2.0
Pentlandite	$(Ni,Fe)_9S_8$	1.8
Chalcopyrite	$CuFeS_2$	1.1

0.000616, O 14.48472 [22]. The boundary conditions of the model are: rock composition, amount of water, 1 kg of the atmosphere.

Calculations were carried out at a temperature of 3, 10 and 20 °C, total pressure $1 \cdot 10^5$ Pa (1 bar). The amount of water in the system varied from 0.2 L/dm² (the amount of precipitation in summer months) to 0.5 L/dm² (the annual amount of precipitation). The acidity of model rainwater at the listed temperature is pH 5.60, 5.62, 5.65, respectively. Evaporation was studied with the amount of water 0.05 and 0.001 L. The upper layer of the dump represented in Table 3 is the first to get in contact with atmospheric precipitation, which involves rock weathering depending on the degree of interaction (ξ), imitating the differences in the size of rock grains and associated rates of chemical interaction [23].

RESULTS AND DISCUSSION

Results of modeling water - rock interaction at a temperature of 20 °C, pressure $1 \cdot 10^5$ Pa and annual amount of precipitation 0.5 L/dm² are presented in Table 4.

Analysis of the data obtained shows that sulphide oxidation develops with an increase in the degree of water − rock interaction, and the acidity of the solution changes from pH 5.65 to pH 3.46 (see Table 4). This is accompanied by the carryover of aluminium, iron, copper and nickel from the rock; the formation of new mineral phases is observed: iron and aluminium hydroxides, alunite, aluminosilicates. The concentrations of the elements that have been determined during the

TABLE 4

Changes of the component and phase composition, acidity (pH) and oxidation-reduction potential (Eh) in water − rock interaction (temperature: 20 °C, pressure: $1 \cdot 10^5$ Pa)

ξ	Concentrations of the aqueous solution, mg/L						
	K^+	Ca^{2+}	$CaSO_4$	Na^+	Mg^{2+}	Cu^{2+}	Ni^{2+}
6.0	$8.40 \cdot 10^{-5}$	$1.48 \cdot 10^{-4}$	$2.95 \cdot 10^{-9}$	$3.28 \cdot 10^{-5}$	$2.07 \cdot 10^{-4}$	$2.76 \cdot 10^{-5}$	$3.47 \cdot 10^{-4}$
5.5	$3.14 \cdot 10^{-4}$	$4.86 \cdot 10^{-4}$	$2.81 \cdot 10^{-8}$	$1.14 \cdot 10^{-4}$	$8.13 \cdot 10^{-4}$	$7.37 \cdot 10^{-5}$	$1.19 \cdot 10^{-3}$
5.0	$9.38 \cdot 10^{-4}$	$1.78 \cdot 10^{-3}$	$3.79 \cdot 10^{-7}$	$3.20 \cdot 10^{-4}$	$3.14 \cdot 10^{-3}$	$1.26 \cdot 10^{-4}$	$5.04 \cdot 10^{-3}$
4.5	$3.67 \cdot 10^{-3}$	$6.89 \cdot 10^{-3}$	$4.85 \cdot 10^{-6}$	$1.57 \cdot 10^{-3}$	$1.22 \cdot 10^{-2}$	$3.89 \cdot 10^{-4}$	$1.82 \cdot 10^{-2}$
4.0	$1.29 \cdot 10^{-2}$	$2.36 \cdot 10^{-2}$	$5.28 \cdot 10^{-5}$	$7.19 \cdot 10^{-3}$	$4.13 \cdot 10^{-2}$	$1.31 \cdot 10^{-3}$	$5.94 \cdot 10^{-2}$
3.5	$4.17 \cdot 10^{-2}$	$7.62 \cdot 10^{-2}$	$5.31 \cdot 10^{-4}$	$2.52 \cdot 10^{-2}$	$1.33 \cdot 10^{-1}$	$4.57 \cdot 10^{-3}$	$1.90 \cdot 10^{-1}$
3.0	$1.33 \cdot 10^{-1}$	$2.42 \cdot 10^{-1}$	$5.16 \cdot 10^{-3}$	$8.21 \cdot 10^{-2}$	$4.21 \cdot 10^{-1}$	$1.50 \cdot 10^{-2}$	$6.01 \cdot 10^{-1}$
2.5	$4.21 \cdot 10^{-1}$	$7.56 \cdot 10^{-1}$	$4.79 \cdot 10^{-2}$	$2.61 \cdot 10^{-1}$	1.31	$4.80 \cdot 10^{-2}$	1.90
2.0	1.33	2.31	$4.27 \cdot 10^{-1}$	$8.28 \cdot 10^{-1}$	3.97	$1.52 \cdot 10^{-1}$	6.02
1.5	$5.63 \cdot 10^{-1}$	6.82	3.02	2.61	$1.15 \cdot 10^1$	$4.82 \cdot 10^{-1}$	$1.90 \cdot 10^1$
1.0	$3.33 \cdot 10^{-2}$	$1.88 \cdot 10^1$	$1.91 \cdot 10^1$	8.17	$3.06 \cdot 10^1$	1.52	$6.02 \cdot 10^1$
0.5	$1.35 \cdot 10^{-4}$	$4.82 \cdot 10^1$	$9.82 \cdot 10^1$	$2.53 \cdot 10^1$	$7.54 \cdot 10^1$	4.82	$1.90 \cdot 10^2$
0.0	$2.98 \cdot 10^{-4}$	$1.23 \cdot 10^2$	$4.10 \cdot 10^2$	$7.71 \cdot 10^1$	$1.85 \cdot 10^2$	$1.52 \cdot 10^1$	$6.03 \cdot 10^2$

ξ	Concentrations of the aqueous solution, mg/L						
	$AlSO_4^+$	$Al(SO_4)_2^-$	Al^{3+}	$FeSO_4^+$	HSO_4^-	SO_4^{2-}	HCO_3^-
6.0	$1.90 \cdot 10^{-10}$	0.00^a	$1.89 \cdot 10^{-5}$	$1.03 \cdot 10^{-11}$	$8.62 \cdot 10^{-7}$	$4.65 \cdot 10^{-3}$	$1.36 \cdot 10^{-1}$
5.5	$2.49 \cdot 10^{-9}$	$2.84 \cdot 10^{-14}$	$7.62 \cdot 10^{-5}$	0.00^a	$2.86 \cdot 10^{-6}$	$1.50 \cdot 10^{-2}$	$1.32 \cdot 10^{-1}$
5.0	$4.23 \cdot 10^{-9}$	$1.80 \cdot 10^{-13}$	$3.62 \cdot 10^{-5}$	$1.38 \cdot 10^{-14}$	$1.02 \cdot 10^{-5}$	$4.96 \cdot 10^{-2}$	$1.23 \cdot 10^{-1}$
4.5	$2.16 \cdot 10^{-8}$	$3.27 \cdot 10^{-12}$	$6.09 \cdot 10^{-5}$	$7.66 \cdot 10^{-14}$	$3.98 \cdot 10^{-5}$	$1.64 \cdot 10^{-1}$	$1.03 \cdot 10^{-1}$
4.0	$2.58 \cdot 10^{-7}$	$1.25 \cdot 10^{-10}$	$2.42 \cdot 10^{-4}$	$9.68 \cdot 10^{-13}$	$2.02 \cdot 10^{-4}$	$5.25 \cdot 10^{-1}$	$6.53 \cdot 10^{-2}$
3.5	$1.16 \cdot 10^{-5}$	$1.77 \cdot 10^{-8}$	$3.31 \cdot 10^{-3}$	$4.10 \cdot 10^{-11}$	$1.51 \cdot 10^{-3}$	1.67	$2.75 \cdot 10^{-2}$
3.0	$5.74 \cdot 10^{-4}$	$2.73 \cdot 10^{-6}$	$5.46 \cdot 10^{-2}$	$2.02 \cdot 10^{-9}$	$1.18 \cdot 10^{-2}$	5.26	$1.10 \cdot 10^{-2}$
2.5	$1.06 \cdot 10^{-2}$	$1.53 \cdot 10^{-4}$	$3.48 \cdot 10^{-1}$	$8.77 \cdot 10^{-8}$	$8.79 \cdot 10^{-2}$	$1.65 \cdot 10^1$	$4.59 \cdot 10^{-3}$
2.0	$1.57 \cdot 10^{-1}$	$6.83 \cdot 10^{-3}$	1.82	$1.83 \cdot 10^{-6}$	$5.06 \cdot 10^{-1}$	$5.09 \cdot 10^1$	$2.43 \cdot 10^{-3}$
1.5	1.03	$1.13 \cdot 10^{-1}$	5.27	$1.20 \cdot 10^{-5}$	1.78	$1.37 \cdot 10^2$	$1.80 \cdot 10^{-3}$
1.0	7.00	1.98	$1.73 \cdot 10^1$	$8.13 \cdot 10^{-5}$	6.42	$3.89 \cdot 10^2$	$1.35 \cdot 10^{-3}$
0.5	$3.74 \cdot 10^1$	$2.51 \cdot 10^1$	$5.51 \cdot 10^1$	$9.42 \cdot 10^{-5}$	$1.24 \cdot 10^1$	$1.10 \cdot 10^3$	$1.81 \cdot 10^{-3}$
0.0	$1.35 \cdot 10^2$	$1.95 \cdot 10^2$	$1.59 \cdot 10^2$	$1.34 \cdot 10^{-3}$	$5.23 \cdot 10^1$	$3.05 \cdot 10^3$	$1.05 \cdot 10^{-3}$

ξ	pH	E_h, B	Composition of newly formed phases, %				
			Gibbsite	Goethite	Alunite	Al-Si	SiO_2
6.0	5.65	0.889	−	−	−	−	−
5.5	5.64	0.890	−	100	−	−	−
5.0	5.61	0.892	13.33	86.67	−	−	−
4.5	5.53	0.896	17.11	82.89	−	−	−
4.0	5.33	0.908	18.60	81.4	−	−	−
3.5	4.96	0.929	18.58	81.42	−	−	−
3.0	4.56	0.953	14.67	81.86	−	3.48	−
2.5	4.17	0.975	−	76.86	−	23.14	−
2.0	3.89	0.991	−	68.15	−	16.68	15.17
1.5	3.76	0.999	−	59.43	12.30	3.51	24.76
1.0	3.62	1.007	−	57.97	13.83	0.97	27.25
0.5	3.73	1.001	−	57.88	13.84	−	28.28
0.0	3.46	1.016	−	57.77	13.81	−	28.41

Note. 1. Al-Si − aluminosilicates, SiO_2 − amorphous silica. 2. Dash means the absence of a phase.
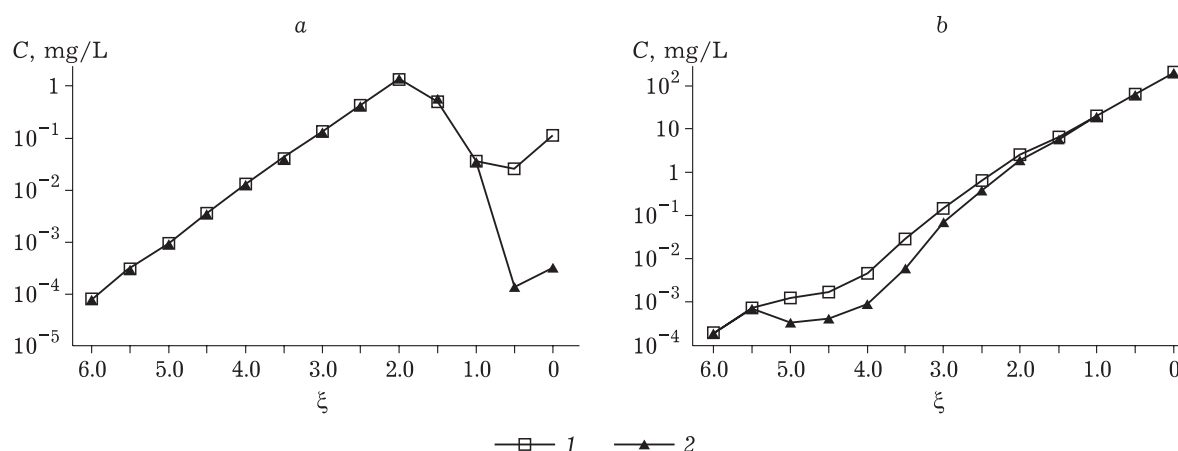[a] Concentration is below the prescribed accuracy of calculation ($1 \cdot 10^{-14}$).

Fig. 2. Changes of the concentration C of ions: K (a) and Al (b) in solution depending on the degree of interaction, %, at a temperature of 3 (1) and 20 °C (2). Water content: 0.5 L, pressure: $1 \cdot 10^5$ Pa.

analysis of the samples of surface waters in the neighbourhood of the dump (see Table 2) are printed in boldface font in Table 4. Thus, water in the bog situated near the dump and filled due to drainage waters coming from the dump is acidic (pH 3.65) (see Table 2, sampling site 3), for other water reservoirs the medium varies from weakly acidic to weakly alkaline. Investigation of the microelement composition of the water reservoirs under study revealed that the concentrations of Cu and Ni in the water of the bog are 1.28 and 94.75 mg/L, respectively. Sulphate concentration in surface waters was varying from 3.29 to 911.88 mg/L, the maximal value was detected in bog water, which exceeded the MPC by a factor of 1.8. This points to the fact that drainage waters entering this bog contain sulphates because atmospheric precipitation is filtered through rock fragments with high sulphide content. In other water reservoirs under investigation, sulphate concentrations were substantially lower except for the lake situated in the direct vicinity of the dump, where sulphate concentration is equal to 84.77 mg/L (see Table 2, sampling site 2), while the concentrations of Ni and Cu are 1.57 and 0.004 mg/L, respectively [18]. In the surface waters of the objects situated at a larger distance from the industrial site, the average concentrations of elements were: Ca − not higher than 2.16, Na − 1.62, Mg − 0.74, K − 0.79, SO_4^{2-} − 3.4, HCO_3^- − 7.1 mg/L. The comparison of modeling results with the results of field studies points to a high degree of the interaction of rocks with atmospheric precipitation in dumps. The effect of dump-related processes on the hydrosphere is pronounced as an increase in the concentrations of all major ions by several times in comparison with pure natural waters.
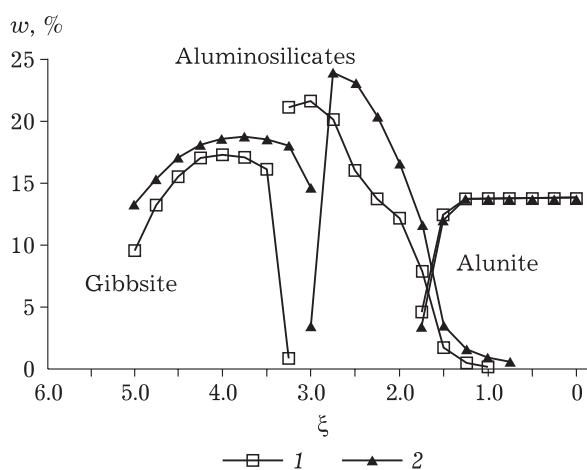

Fig. 3. Changes of phase content w depending on the degree ξ of interaction at a temperature of 3 (1) and 20 °C (2). Newly formed phases: alunite − $KAl_3(OH)_6(SO_4)_2$, gibbsite − $Al(OH)_3$, aluminosilicates: $Al_2Si_2O_5(OH)_4$, $Al_{12}Si_4O_{10}(OH)_2$, $Al_2Si_2O_5(OH)_4$, $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$.

The effect of temperature on the migration of potassium and aluminium is presented in Fig. 2. Changes of the content of phases depending on temperature are shown in Fig. 3.

Thermodynamic calculations showed that an increase in temperature (see Fig. 3) will promote the formation of gibbsite and aluminosilicates, and will have no effect on carry-over of copper, nickel and sulphate ions. The formation of theoretically predicted phases is possible only in the case of continuous water filtration through the rocks at a rate sufficient for the establishment of partial equilibria between the effluent solution and newly formed minerals. Very strong drainage and high filtration rate lead to the formation of the upper zone (goethite − gibbsite) because the
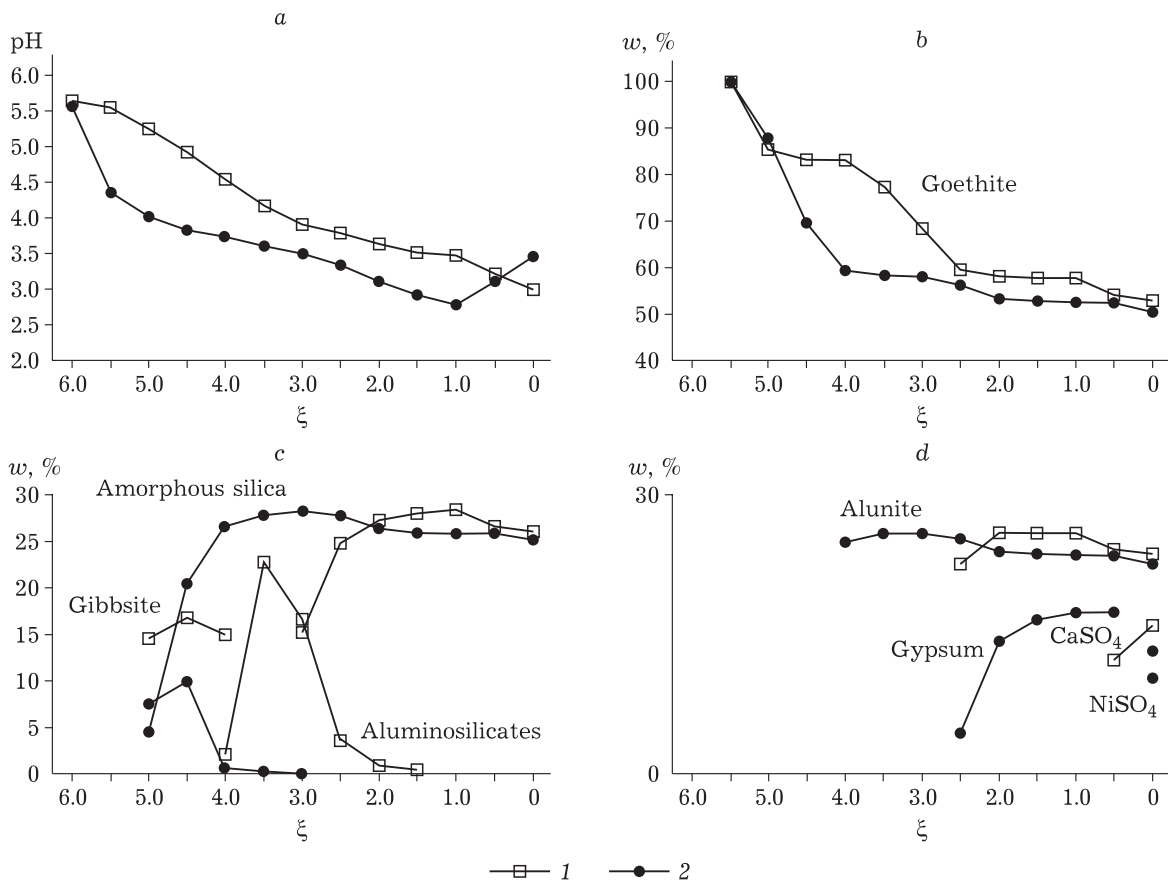
Fig. 4. Dependence of solution acidity (a) and content of phases w (b–d) on the degree ξ of interaction and the amount of water in the system: 0.05 (*1*) and 0.001 L (*2*). Temperature: 20 °C, pressure: $1 \cdot 10^5$ Pa. Alunite - $KAl_3(OH)_6(SO_4)_2$, gibbsite - $Al(OH)_3$.

concentration of dissolved components is maintained at a level close to the initial process conditions due to a very short time of the contact of circulating solution with initial rocks. Quite the contrary, in the case of the stagnant hydrodynamic regime in the weathering zone, mineral associations corresponding to high degrees of rainwater interaction with the rocks in the dump are developing: goethite-aluminosilicate-silica. For instance, S. I. Beneslavskiy marked the formation of gibbsite at the surface emergences of the Khibiny deposits after summer rains [24]. This points to the transient character of gibbsitization.

Potassium concentration in surface waters in the vicinity of the dump varied from 4.6 mg/L in the lake to the maximal value (10.87 mg/L) in the bog; it was 3.15 mg/L in the drawn open pit. In surface waters at a larger distance from the dump, potassium concentration varied from 0.52 to 0.9 mg/L. Aluminium concentration in the water of the bog was 0.22, in the drawn open pit − 0.05, in all other cases it did not exceed 0.04 mg/L (see Table 2, sampling sites **2**, **3** and **7**).

So, the results of tests indicate carry-over of potassium and aluminium from the dumps. Comparison with modeling results (see Fig. 2 and 3) allows us to conclude that at low temperatures (off-season, thaws in winter) potassium and aluminium are more mobile, while during rains in the warm season they promote the formation of gibbsite and aluminosilicates.

Evaporation is arranged as the change in the amount of water: 0.05−0.001 L at a temperature of 20 °C. Calculation results are presented in Fig. 4. One can see that the solution becomes more acidic with a decrease in the content of water in the solution (see Fig. 4, *a*). In this process, gibbsite disappears (5.5 ≤ ξ ≤ 4); an insignificant amount of aluminosilicates (5.5 ≤ ξ ≤ 3) and amorphous silica (5.5 ≤ ξ ≤ 0) are formed instead (see Fig. 4, *c*).

With a decrease in pH, the content of goethite is the system decreases, and the transition of iron into solution increases (see Fig. 4, *b*). Iron concentration in some surface water reservoirs varies from 0.05 to 0.12 mg/L (see Table 2). In addition, active formation of nickel, copper,
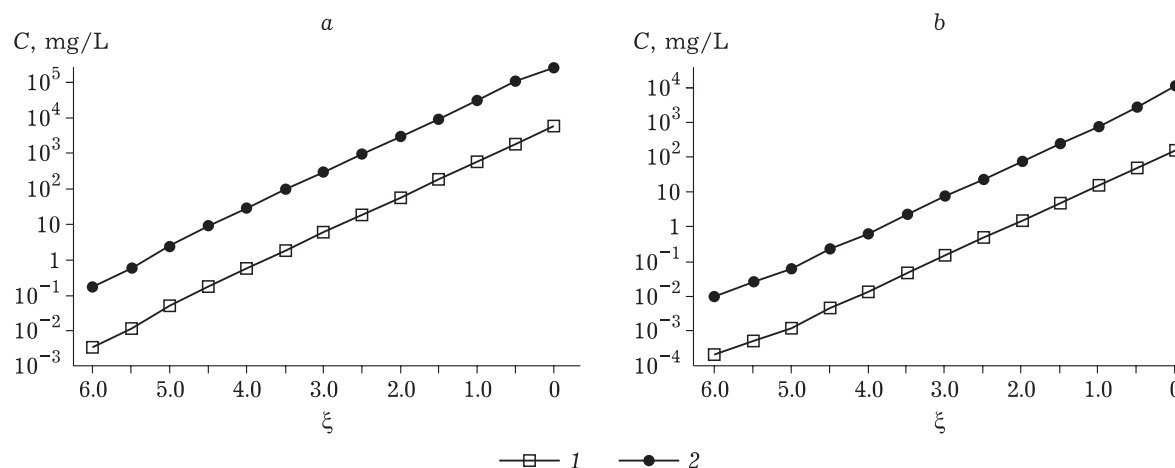
Fig. 5. Effect of the amount of water in the water − rock system: 0.05 (*1*) and 0.001 L (*2*) on the concentrations of Ni (*a*) and Cu (*b*) ions. Temperature: 20 °C, pressure: $1 \cdot 10^5$ Pa.

calcium and potassium sulphates takes place (see Fig. 4, *d*). The concentrations of nickel and copper (Fig. 5), sulphate ion and iron in this solution increase.

So, the model analogue of evaporation is represented by two states of the system:

the amount of water in the system is 0.05 L, practically a monthly norm of precipitation during summer;

the amount of water in the system is 0.001 L, which means evaporation itself. The formation of metastable compound $NiSO_4$ and gypsum occur, which corresponds to field observations.

Solution concentrating due to freezing and due to a decrease in the amount of the aqueous phase is similar to evaporation model [25], so we may assume that the destruction of the mineral matrix of wastes as a result of the formation of highly mineralized solutions inside the dump and on its surface proceed almost all year round.

CONCLUSION

The mineral and chemical composition of the dump of the Allarechensky deposit of copper-nickel ores and surface waters, both background (relatively pure) and those situated in the vicinity of the dump, was investigated.

Thermodynamic modeling allowed us to draw the following conclusions:

As a result of the interaction of minerals with atmospheric precipitation and the formation of highly mineralized solutions during the dump storage, the destruction of the mineral matrix of rocks occurs inside the dump body and on its surface.

Sharp changes of temperature will promote rock weathering. Copper, nickel, potassium and aluminium will pass into solution during cold seasons, while the formation of gibbsite and aluminosilicates will take place during warm seasons.

Evaporation promotes the formation of more acid solutions, carry-over of nickel, copper, iron and sulphates into the solution.

Processes taking place in the dumps affect the hydrosphere causing an increase in the concentrations of all major ions by a factor of several units in comparison with pure natural waters.

Acknowledgements

REFERENCES

1 Petukhov V. I. (Ed.), Integrated sustainable waste management. Mining industry: teaching guide, Publishing House of the Academy of Natural History, Moscow, 2016. 638 p. (in Russ.).

2 Van Dam K., Scheepstra A., Gille J., Stepien A., Koivurova T., in: Mining in the European Arctic. The Changing Arctic and the European Union: A book based on the Report "Strategic Assessment of Developement of the Arctic: Assessment Conducted for the European Union", Stepien A., Koivurova T., Kankaanpaa P. (Eds.), Vol. 89, Leiden − Boston: Brill / Nijhoff, 2016, P. 163−185.

3 Askaer L., Schmidt L. B., Elberling B., Asmund G., Jonsdottir I. S., Environmental impact on an Arctic soil-plant system resulting from metals released from coal mine waste in Svalbard (78° N), *Water, Air & Soil Pollution*, 2008, Vol. 195, P. 99−114.

4 Heikkinen P. M., Raisanen M. L., Johnson R. H., Geochemical

characterization of seepage and drainage water quality from two sulphide mine tailings impoundments: acid mine drainage versus neutral mine drainage, *Mine Water and the Environment*, 2009, Vol. 28, P. 30−49.

5 Plante B., Benzaazoua M., Bussiere B., Predicting geochemical behavior of waste rock with low acid generating potential using laboratory kinetic tests, *Mine Water and the Environment*, 2011, Vol. 30, P. 2−21.

6 Moncur M. C., Ptacek C. J., Hayashi M., Blowes D. W., Birks S. J., Seasonal cycling and mass-loading of dissolved metals and sulfate discharging from an abandoned mine site in northern Canada, *Appl. Geochem.*, 2014, Vol. 41, P. 176−188.

7 Lindsay M. B. J., Moncur M. C., Bain J. G., Jambor J. L., Ptacek C. J., Blowes D. W., Geochemical and mineralogical aspects of sulfide mine tailings, *Appl. Geochem.*, 2015, Vol. 57, P. 157−177.

8 Moncur M. C., Ptacek C. J., Lindsay M. B. J., Blowes D. W., Jambor J. L., Long-term mineralogical and geochemical evolution of sulfide mine tailings under a shallow water cover, *Appl. Geochem.* 2015, Vol. 57, P. 178−193.

9 Pedersen K. B., Jensen P. E., Sternal B., Ottosen L. M., Henning M. V., Kudahl M. M., Junttila J., Skirbekk K., Frantzen M., Long-term dispersion and availability of metals from submarine mine tailing disposal in a fjord in Arctic Norway, *Environ. Sci. Pollut. Research.*, 2018, Vol. 25, Issue 33, P. 32901−32912. https://doi.org/10.1007/s11356-017-9276-y

10 Amos R. T., Blowes D. W., Bailey B. L., Sego D. C., Smith L., Ritchie A. I. M., Waste-rock hydrogeology and geochemistry, *Appl. Geochem.*, 2015, Vol. 57, P. 140−156.

11 Langman J. B., Blowes D. W., Sinclair S. A., Krentz A., Amos R. T., Smith L. J. D., Pham H. N., Sego D. C., Smith L., Early evolution of weathering and sulfide depletion of a low-sulfur, granitic, waste rock in an Arctic climate: A laboratory and field site comparison, *J. Geochem. Explor.*, 2015, Vol. 156, P. 61−71.

12 Langman J. B., Blowes D. W., Amos R. T., Atherton C., Wilson D., Smith L., Sego D. C., Sinclair S. A., Influence of a tundra freeze-thaw cycle on sulfide oxidation and metal leaching in a low sulfur, granitic waste rock, *Appl. Geochem.*, 2017, Vol. 76, P. 9−21.

13 Masloboev V. A., Seleznes S. G., Makarov D. V., Svetlov A. V., Assessment of eco-hazard of copper-nickel ore mining and processing waste, *Journal of Mining Science*, 2014, Vol. 50, No. 3, P. 559−572. (in Russ.).

14 Ozdeniz A. H., Kelebek S., Effect of ambient conditions on self-heating characteristics of a Ni-Cu sulphide ore stockpile and consequent process behavior of principal sulphide minerals, *Inzynieria Mineralna*, 2015, No. 2, P. 249−255.

15 Naphtal' M. N., Shestakov R. D. Platinum-containing pyrrhotite concentrates of Norilsk − a new look at the problem of complex processing, *Non-ferrous Metals*, 2001, No. 6, P. 43−48. (in Russ.).

16 Ertseva L. N., Dyachenko V. T., Sukharev S. V., Tsemekhman L. Sh., Volkov V. I. Recovering heat treat process of pyrrhotite concentrate, *Non-ferrous Metals*, 1998, No. 1, P. 20−22. (in Russ.).

17 Demin V. I., General climatic tendencies on the Kola Peninsula during the meteorological measurements period, Transactions of the Kola Scientific Centre, *Applied Ecology of the North*, 2012, Issue 3 (10), P. 98−108. (in Russ.).

18 Seleznev S. G. The Allarechensky Deposit Dumps of sulfide copper-nickel ores. Specificity and development problems, PhD Thesis, Ekaterinburg, 2013. 147 p. (in Russ.).

19 Sanitary Regulations and Norms 2.1.4.1074-01 "Drinking water. Hygienic requirements for water quality of centralized systems for drinking water supply. Quality control. Hygienic requirements for safety measures of hot water supply systems" (with amendments dated April 2, 2018). (in Russ.).

20 Chudnenko K. V. Thermodynamic Modeling in Geochemistry, Novosibirsk, Geo, 2010. 287 p. (in Russ.).

21 Mazukhina S. I., Genesis of the Surface and Ground Waters of the Khibiny Massif, KSC RAS, Apatity, 2012. 173 p. (in Russ.).

22 Horne R. A., Marine Chemistry. The Structure of Water and the Chemistry of the Hydrosphere, J. Wiley, New York-London, 1969. 568 p.

23 Ryzhenko B. N., Ryabenko A. E., Modeling the composition of mine (waste rock) water at the deposits of the Balkhach gold bearing field, *Geochemistry International*, 2013, Vol. 51, No. 11, P. 920−930. (in Russ.).

24 Beneslavsky S. I., Mineralogy of Bauxites, Subsoil Resources, Moscow, 1974. 168 p. (in Russ.).

25 Gas'kova O. L., Strakhovenko V. D., Ovdina E. A., Composition of brines and mineral zoning of the bottom sediments of soda lakes in the Kulunda steppe (West Siberia), *Russian Geology and Geophysics*, 2017, Vol. 58, No. 10, P. 1199−1210. (in Russ.).