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Thermodynamic Modeling of Hypergene Processes in Copper-Nickel Ore Tailings under Different Temperature and Moisture Regimes

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Abstract

Thermodynamic modelling of hypergene processes in copper-nickel ore tailings was performed with the variations of temperature (3 and 20 °C) and water evaporation processes in the upper layers of tailings during summer months at low filtration coefficients. It is established that the major cations of pore solutions are magnesium, calcium, nickel and copper ions, while predominant anions are sulphate and hydrocarbonate ions. The main newly formed phases in the system are the minerals of smectite group, as well as goethite, carbonates, silica, chlorite and gypsum.

Keywords: thermodynamic modelling, copper-nickel ore tailings, hypergene processes, pore solutions, newly formed mineral phases

INTRODUCTION

Investigation of the effect of climate changes on the stable performance and development of the enterprises of the mining complex under arctic conditions is an urgent scientific and practical problem [1].

At present, the processes of mineral raw material mining and processing have a negative effect on the environment. A characteristic feature of modern mining industry is depletion of the mineral resource basis and a decrease in the quality of ores [2]. This is in full true for many enterprises of the Arctic zone of Russia. Concentrating of lean and difficult-to-concentrate raw material leads not only to the losses of valuable components but also to a substantial increase in the amount of industrial wastes.

The observed and predicted climate change affects the mechanisms and intensity of hypergene processes during waste storage and their

impact on the environment. Climate change affects also the technological properties of potentially extractable useful minerals from wastes used as technogenic deposits. It is possible to improve the conditions for hydrometallurgical processing of substandard raw materials [3].

Computer modelling methods are applied to study hypergene transformations of minerals and to provide evaluation and prediction of environmental pollution during the development of mineral deposits and storage of the wastes from mining and ore concentrating [4–9]. In our country, the software package used for this purpose is Selektor [10]. A number of interesting studies of technogenic systems in Siberia and the Far East were carried out with the help of this software during recent years.

For instance, the authors of [11] developed a multi-reservoir model of the annual discharge of mine and natural waters of the Bom-Gork-

hon tungsten deposit through an adjacent tailing dump into the ecological system of the Zuntignya river (the Zabaikalye Territory).

A potential ecological danger of the most widespread ore minerals of the Prasolovo (Au, Ag) deposit (Kunashir Island, the Sakhalin Region) was demonstrated in [12]. It was stressed that the degree of the toxic effect on the environment increases by several orders of magnitude if not only separate minerals but their entire natural associations undergo oxidation and dissolution. The highest ecological danger is characteristic of ore minerals extracted to the surface and stored as mining dumps or tailings.

Evaluation of the negative effect of ore concentrating wastes from the scarn-polymetallic deposits in the Dalnegorsk District (the Primorsky Territory) on the water network was carried out with the help of computer modelling of physicochemical transformation processes in these wastes [13]. The qualitative and quantitative composition of mineralized pre fluids forming drainage waters was determined on the basis of thermodynamic calculations of the behaviour of minerals under hypergene conditions.

Results of the simulation of physicochemical parameters of the crystallization of hypergene minerals from mine, slime and drainage waters in technogenic systems of sulphide-containing deposits of the Dalnegorsk District were presented in [14]. It was established that minerals are crystallized within a broad range of the values of oxidation-reduction potential E_h (0.6–1.2 V) and hydrogen ion exponent pH (0.3–13.7). A decisive role of ore composition and the ratio of sulphides to the host rock in the formation of mineral parageneses and potential ecological danger of the tailings from tin-polymetallic and silver-lead-zinc ore concentrating were revealed. It was demonstrated that hypergene processes take place also at negative temperatures (modelling was carried out within a temperature range from –25 to 45 °C). Under the conditions of negative temperatures (in comparison with positive ones), micro-

pore solutions with higher concentrations are formed.

Previously we carried out thermodynamic modelling of hypergenesis of the dumps of the Allarechensk deposit of copper-nickel ores in the Pechenga District of the Murmansk Region [15].

The goal of the present work was to study hypergene processes in concentration tailings from copper-nickel ores under the conditions of different temperatures and watering modes by means of physicochemical modelling (Selektor software package).

EXPERIMENTAL

Object of investigation

The tailing dump of the concentrating plant (CP) No. 1 of Pechenganikel plant, JSC Kolskaya GMK in Zapolyarniy town (the Pechenga District, the Murmansk Region) which is under operation since 1965 till present, occupies an area of more than 1000 ha and is one of the largest technogenic objects of nonferrous metallurgy in Russia.

Ore minerals of the tailings are represented by sulphides: pyrrhotine, pentlandite and chalcopyrite, as well as magnetite (Table 1).

A comparison of the tailings of the current production and old tailings showed that long-term storage causes changes in the technological characteristics of the minerals [16, 17]. A transition of nonferrous metals into mobile forms is observed, the ratios of sulphide to silicate forms of nickel are changed. These processes cause a decrease in the value of technogenic raw material. The ecological danger of tailings is conserved during several decades.

Climatic characteristics of the region

The climate of the Murmansk Region is subarctic marine, with many features of the continental one [18]. The temperature regime is unstable during the year, which causes frequent

TABLE 1

General characterization of the concentration tailings of copper-nickel ores

Resources	Composition	Prevailing size of sulphide intergrowths
Total ~320 mln t	Ore: pentlandite, chalcopyrite, pyrrhotine, magnetite	3.0–20 μm
Ni ~550 thousand t	Non-ore serpentines (~60 % of total composition), amphiboles, talc, chlorite, carbonates (calcite and dolomite), olivine, pyroxenes	
Cu ~270 thousand t		

thaws in winter and sharp cooling in summer. The annual mean air temperature decreases from 0 °C at the coast of the Barents and White Seas to –2 °C in the central part of the peninsula and down to –3 ... –4 °C in mountainous regions [18]. Warming manifests itself to some extent over the whole territory of Russia and especially in its Arctic zone. Warming manifests itself both in the changes of mean annual and seasonal temperatures.

Thermodynamic modelling

Physicochemical modelling of hypogene processes in the minerals of tailings was carried out using the Selektor software package [19], which is equipped with a system of built-in thermodynamic databases and the unit forming the models of different complexity. The algorithm, which is based on convex-programming minimization [10] of the Gibbs potential of the system to be modelled, allows calculating complicated chemical equilibria under isobar-isothermal, isochoric and adiabatic conditions in multisystems which may simultaneously include an aqueous electrolyte solution, gas mixture, liquid and solid hydrocarbons, minerals in the form of solid solutions and one-component phases. The software package may be used to study either multicomponent heterogeneous systems or megasystems composed of the interacting systems (reservoirs) connected with each other and the environment through the fluxes of matter and energy. In the present work, we applied a basic model “water – rock – gas” which includes 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 an electron. The model takes into account 996 dependent component, in particular, 369 in the aqueous solution, 76 in the gas phase, 111 liquid hydrocarbons, 440 solid phases, organic and mineral substances. The necessary thermodynamic information was taken from databases built into the software package [10, 19].

Table 2 shows the mineral composition of tailings which was involved in the model to calculate equilibrium in the system “water – rock – gas”, where rock stands for 100 g of tailings, water is atmospheric precipitation, and gas is atmosphere. The composition of 1 kg of the atmosphere, mol, is: Ar 0.3209, C 0.01036, N 53.9478, Ne 0.000616, O 14.48472 [10]. The boundary conditions of the model are rock composition, the amount of water, and 1 kg of the atmosphere.

Calculations were carried out at a temperature of 3 and 20 °C, total pressure 105 Pa. The volume of water in the system was 0.5 L. The calculated model values of rainwater pH at the indicated temperatures were 5.60 and 5.65, respectively. Water evaporation was studied with water volumes equal to 0.05 and 0.001 L.

It should be stressed that the matter of tailings undergoes differentiation in particle size and density even at the stage of hydrotransportation and stacking, and then this process goes on during storage as a result of suffusion and hypogene processes. This leads to a substantial non-homogeneity of the substantial composition of concentration tailings.

Due to non-homogeneity of the composition of tailings, the model involves a hypothetical averaged mineral composition. The processes taking place in concentration tailings are much more complicated.

So, the model demonstrates general trends of hypogene processes, changes in mineral composition and pore solutions of the tailings depending on external conditions.

The amount of the solid phase participating in the interaction, or the degree of interaction (v , mol) is the amount of tailings that entered the reaction; this value simulates the rate of chemical processes. Interaction degree v was varied from 10^{-6} to 1 mol. The dependences are presented in Tables and Figures in the logarithmic scale: $v = 10^{\xi}$ or $\xi = \lg v$.

RESULTS AND DISCUSSION

Table 3 shows the Eh and pH values of the system, along with the concentrations (C, mg/kg

TABLE 2

Mineral composition of concentration tailings of copper-nickel ores

Mineral	Formula	Content, %
Olivine	$(\text{Fe}, \text{Mg})_2[\text{SiO}_4]$	5.0
Avgite	$\text{Ca}(\text{Mg}, \text{Fe}, \text{Al})[(\text{Si}, \text{Al})_2\text{O}_6]$	5.0
Actinolite	$\text{Ca}_2(\text{Mg}, \text{Fe})_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$	8.0
Serpentine	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	60.0
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	3.0
Chlorite	$\text{Mg}_{4.5}\text{Al}_3\text{Si}_{2.5}\text{O}_{10}(\text{OH})_8$	2.0
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	0.6
Calcite	CaCO_3	0.4
Magnetite	Fe_3O_4	13.0
Pyrrhotine	FeS	1.8
Pentlandite	$(\text{Ni}, \text{Fe})_9\text{S}_8$	0.8
Chalcocite	CuFeS_2	0.4

$_2\text{O}$) of ions dominating in the system depending on ξ and temperature (3 and 20 °C).

One can see that Eh is maximal for $\xi = -6$, then it decreases monotonously to $\xi = -5$. Then a sharp decrease in Eh to the minimum at $\xi = -1.5$ is observed, followed by an insignificant increase in the potential. It should be noted that the appearance of Eh(ξ) curves is identical for 3 and 20 °C, while the oxidation-reduction potential of the system at 3 °C is higher by 0.02–0.03 V than at 20 °C.

The pH values of the system at 20 °C are higher (by 0.05–0.11) than at 3 °C. The minimal pH value is observed at $\xi = -6$, then a shift of the acid-base equilibrium to the alkaline region is observed, at first only slight, and then more substantial. The maximum of pH corresponds to $\xi = -1.5$.

It should be stressed that, according to field and laboratory studies carried out previously, pH of pore solutions of concentration tailings of copper-nickel ores was 7.9–8.7 [20]. These values correspond to the degree of interaction v within the range from $10^{-2.5}$ to 10^0 mol of the solid phase.

The concentrations of magnesium and calcium ions (major cations) increase regularly with an increase in interaction degree and practically coincide at 3 and 20 °C.

The dependences of concentration on temperature for nickel ions are more interesting. At 3 °C, Ni concentration increases with an increase in ξ , while at 20 °C, starting from $\xi = -2$, an increase in the concentration of metal ions slows down substantially. So, for interaction degree $v \geq 10^{-2}$ mol, nickel ion leaching is more intense at a temperature of 3 °C.

The concentration of copper ions increases with an increase in the interaction degree. An increase is slowed down starting from $\xi = -3$ (at 3 °C) and from $\xi = -2.5$ (at 20 °C).

The major anion in the system is sulphate ion. Its concentration increases with an increase in the degree of interaction and is practically the same at 3 and 20 °C.

Hydrocarbonate ion is characterized by substantially lower concentrations in comparison with sulphate ion. The dependences of the concentration on ξ at a temperature of 3 and 20 °C have maxima at $\xi = -1.5$, and starting from $\xi = -3$, HCO_3^- concentration in solution is higher at 3 °C.

It was interesting to compare the results of modelling with the data of the analysis of pore solutions from concentration tailings of different ages. The concentrations of nickel, copper and magnesium ions in the pore solutions of the tailings of the actual tailing dumps (a, c, e) and

out-of-production dumps (b, d, f) are shown as an example in Fig. 1. The data were taken from [21].

One can see (see Fig. 1) that the tailings of the current works are characterized by lower metal content. For nickel and copper, this is connected with the initial stage of sulphide leaching, and with the deceleration of their oxidation due to the presence of floatation reagents. Substantially lower concentrations of magnesium are due to the higher rate of sulphide oxidation than the rate of the interaction of solutions with nonmetal minerals.

Comparison of the data shown in Table 3 and Fig. 1 allows us to conclude that the model provides an adequate description of the composition of tailing solutions after their long-term storage. It is probable that under these conditions the system “solution – solid phase – atmosphere” is closer to the equilibrium. The degree of interaction v is within the range from $10^{-2.5}$ to 10^0 mol of the solid phase.

Dependences of the content (%) of major newly formed mineral phases on ξ at different process temperatures (3 and 20 °C) are shown in Fig. 2.

Aluminium hydroxide (gibbsite, see Fig. 2, a) is formed within the range $-5 < \xi < -3$ in insignificant amounts, then at $\xi > -1$ (3 °C) and at $\xi > -0.5$ (20 °C).

Goethite is a substantially more significant mineral. This mineral dominates within the range $-5.5 < \xi < -3.5$, which is explained by the most rapid reactions proceeding in the system, namely sulphide oxidation; goethite is the product of this reaction. With an increase in the degree of interaction, goethite content decreases substantially. Nevertheless, it remains one of the major phases (see Fig. 2, b). Dependences of its content on ξ are almost identical for the temperature of 3 and 20 °C.

Silica is not formed at a temperature of 20 °C (see Fig. 2, c). At 3 °C it appears in noticeable amounts within the range $-3.5 < \xi < -1.5$. Its maximal content (about 38 %) is detected for $\xi = -2.5$. This is connected with the fact that at 3 °C no hydroxysilicates (smectite, chlorite, and kaolinite) are formed.

Within the interaction degree range studied by us, carbonates are formed: calcite (see Fig. 2, d) and dolomite (see Fig. 2, e). Mineral content is only weakly dependent on temperature and is maximal at $\xi = 0$ (7 and 10 %, respectively).

Now the behaviour of layered hydrosilicates is to be considered.

Kaolinite content in the system is essentially dependent on temperature (see Fig. 2, e). This

TABLE 3

Dependences of Eh, pH and the concentrations of prevailing ions on ξ at a temperature of 3 and 20 °C in the model system "water – rock – gas"

ξ	Eh, V	pH	Concentrations of prevailing ions, mg/kg H ₂ O																					
			Ca ²⁺				Mg ²⁺				Ni ²⁺				Cu ²⁺				SO ₄ ²⁻				HCO ₃ ⁻	
			3 °C	20 °C	3 °C	20 °C	3 °C	20 °C	3 °C	20 °C	3 °C	20 °C	3 °C	20 °C	3 °C	20 °C	3 °C	20 °C	3 °C	20 °C				
-6.0	0.91	0.89	5.62	5.67	4.29 · 10 ⁻⁴	4.27 · 10 ⁻⁴	2.11 · 10 ⁻³	2.10 · 10 ⁻³	1.98 · 10 ⁻⁴	1.98 · 10 ⁻⁴	2.73 · 10 ⁻⁵	2.26 · 10 ⁻⁵	4.39 · 10 ⁻³	4.38 · 10 ⁻³	1.56 · 10 ⁻¹	1.40 · 10 ⁻¹	1.56 · 10 ⁻¹	1.40 · 10 ⁻¹						
-5.5	0.91	0.89	5.65	5.70	1.61 · 10 ⁻³	1.62 · 10 ⁻³	8.38 · 10 ⁻³	8.54 · 10 ⁻³	6.32 · 10 ⁻⁴	6.36 · 10 ⁻⁴	9.52 · 10 ⁻⁵	8.43 · 10 ⁻⁵	1.44 · 10 ⁻²	1.45 · 10 ⁻²	1.68 · 10 ⁻¹	1.52 · 10 ⁻¹	1.68 · 10 ⁻¹	1.52 · 10 ⁻¹						
-5.0	0.90	0.88	5.76	5.82	5.86 · 10 ⁻³	5.88 · 10 ⁻³	2.83 · 10 ⁻²	2.85 · 10 ⁻²	2.47 · 10 ⁻³	2.49 · 10 ⁻³	6.38 · 10 ⁻⁵	5.61 · 10 ⁻⁵	4.70 · 10 ⁻²	4.70 · 10 ⁻²	2.14 · 10 ⁻¹	1.99 · 10 ⁻¹	2.14 · 10 ⁻¹	1.99 · 10 ⁻¹						
-4.5	0.89	0.86	6.04	6.11	1.96 · 10 ⁻²	1.96 · 10 ⁻²	9.18 · 10 ⁻²	9.18 · 10 ⁻²	9.52 · 10 ⁻³	9.49 · 10 ⁻³	1.30 · 10 ⁻⁴	1.48 · 10 ⁻⁴	1.54 · 10 ⁻¹	1.54 · 10 ⁻¹	4.10 · 10 ⁻¹	3.92 · 10 ⁻¹	4.10 · 10 ⁻¹	3.92 · 10 ⁻¹						
-4.0	0.87	0.84	6.48	6.57	6.32 · 10 ⁻²	6.33 · 10 ⁻²	2.93 · 10 ⁻¹	2.93 · 10 ⁻¹	3.20 · 10 ⁻²	3.20 · 10 ⁻²	3.72 · 10 ⁻⁴	4.55 · 10 ⁻⁴	4.92 · 10 ⁻¹	4.92 · 10 ⁻¹	1.12 · 10 ⁰	1.12 · 10 ⁰	1.12 · 10 ⁰	1.12 · 10 ⁰						
-3.5	0.84	0.81	6.97	7.04	2.01 · 10 ⁻¹	2.01 · 10 ⁻¹	9.26 · 10 ⁻¹	9.26 · 10 ⁻¹	1.03 · 10 ⁻¹	1.03 · 10 ⁻¹	1.28 · 10 ⁻³	1.26 · 10 ⁻³	1.56 · 10 ⁰	1.55 · 10 ⁰	3.50 · 10 ⁰	3.29 · 10 ⁰	3.50 · 10 ⁰	3.29 · 10 ⁰						
-3.0	0.81	0.78	7.47	7.53	6.33 · 10 ⁻¹	6.38 · 10 ⁻¹	2.91 · 10 ⁰	2.91 · 10 ⁰	3.28 · 10 ⁻¹	3.28 · 10 ⁻¹	4.35 · 10 ⁻³	2.30 · 10 ⁻³	4.86 · 10 ⁰	4.86 · 10 ⁰	1.10 · 10 ¹	1.03 · 10 ¹	1.10 · 10 ¹	1.03 · 10 ¹						
-2.5	0.79	0.76	7.97	7.93	1.97 · 10 ⁰	2.02 · 10 ⁰	9.04 · 10 ⁰	7.73 · 10 ⁰	1.04 · 10 ⁰	1.04 · 10 ⁰	7.43 · 10 ⁻³	2.14 · 10 ⁻³	1.48 · 10 ¹	1.49 · 10 ¹	3.46 · 10 ¹	2.56 · 10 ¹	3.46 · 10 ¹	2.56 · 10 ¹						
-2.0	0.77	0.74	8.21	8.14	5.99 · 10 ⁰	6.38 · 10 ⁰	1.80 · 10 ¹	1.59 · 10 ¹	3.28 · 10 ⁰	3.28 · 10 ⁰	3.16 · 10 ⁻³	2.95 · 10 ⁻³	4.43 · 10 ¹	4.45 · 10 ¹	5.93 · 10 ¹	4.11 · 10 ¹	5.93 · 10 ¹	4.11 · 10 ¹						
-1.5	0.76	0.74	8.35	8.21	1.02 · 10 ¹	1.16 · 10 ¹	3.73 · 10 ¹	3.53 · 10 ¹	1.04 · 10 ¹	4.23 · 10 ⁰	1.71 · 10 ⁻³	6.97 · 10 ⁻³	1.27 · 10 ²	1.26 · 10 ²	7.95 · 10 ¹	4.76 · 10 ¹	7.95 · 10 ¹	4.76 · 10 ¹						
-1.0	0.77	0.75	8.24	8.07	1.49 · 10 ¹	2.66 · 10 ¹	7.93 · 10 ¹	7.96 · 10 ¹	2.64 · 10 ¹	9.17 · 10 ⁰	3.04 · 10 ⁻³	4.30 · 10 ⁻²	3.46 · 10 ²	3.36 · 10 ²	6.05 · 10 ¹	3.33 · 10 ¹	6.05 · 10 ¹	3.33 · 10 ¹						
-0.5	0.78	0.76	8.09	7.92	3.19 · 10 ¹	7.57 · 10 ¹	1.63 · 10 ²	1.65 · 10 ²	5.13 · 10 ¹	1.80 · 10 ¹	6.05 · 10 ⁻³	2.24 · 10 ⁻¹	7.77 · 10 ²	7.36 · 10 ²	3.78 · 10 ¹	2.06 · 10 ¹	7.77 · 10 ²	7.36 · 10 ²						
0	0.78	0.76	8.04	7.93	6.86 · 10 ¹	2.23 · 10 ²	3.44 · 10 ²	3.41 · 10 ²	8.08 · 10 ¹	2.79 · 10 ¹	1.01 · 10 ⁻²	7.04 · 10 ⁻¹	1.64 · 10 ³	1.54 · 10 ³	2.09 · 10 ¹	1.02 · 10 ¹	1.64 · 10 ³	1.54 · 10 ³						

Note. Here and in Table 4: Eh is the oxidation-reduction potential; pH is hydrogen ion exponent; $\xi = \lg v$, where v is the degree of interaction, mol.

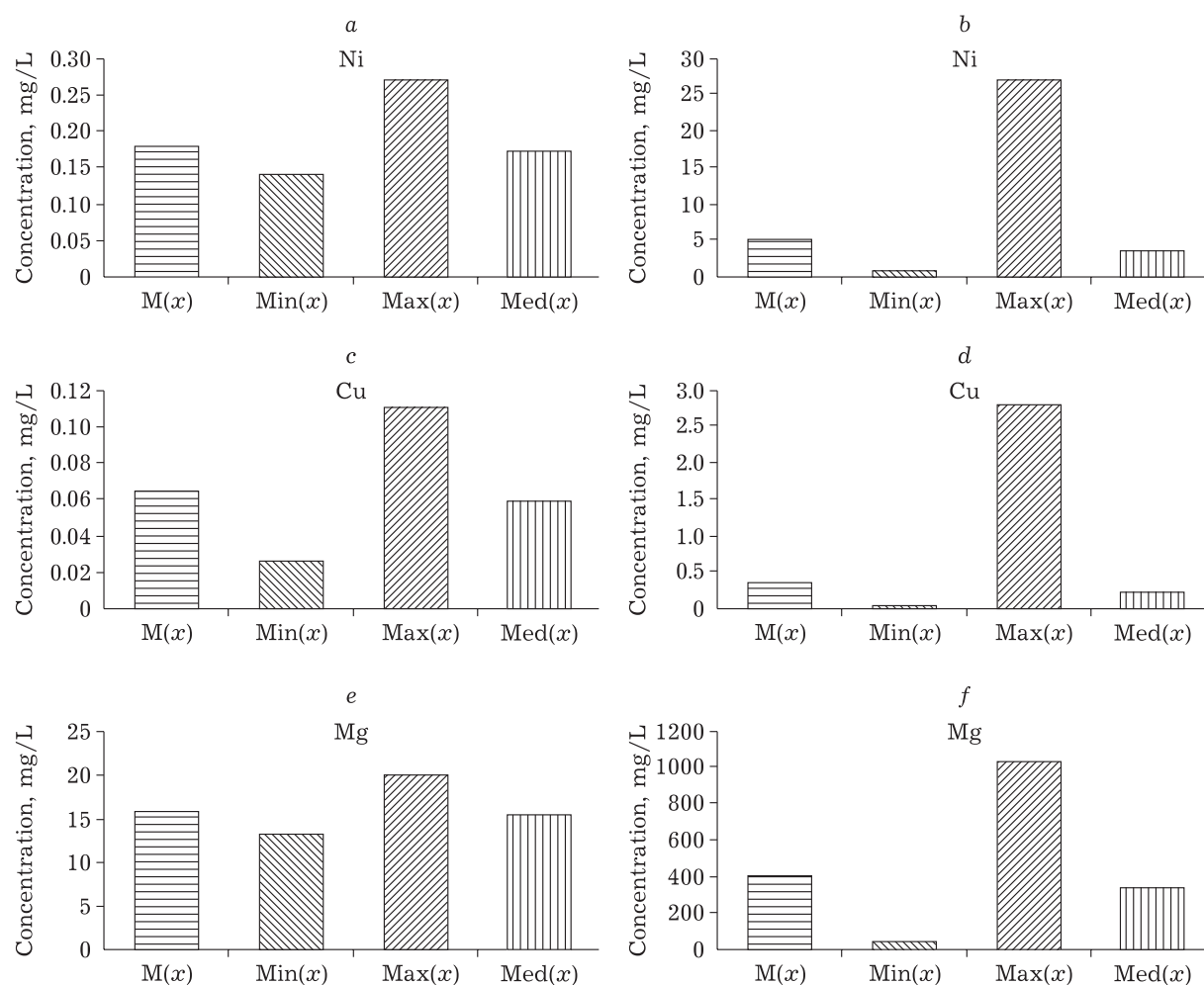


Fig. 1. Concentrations of nickel, copper and magnesium ions in the tailings of the operating (a, c, e, 27 samples) and out-of-operation (b, d, f, 104 samples) tailings: M(x) is the mean value; Min(x) is the minimal value; Max(x) is the maximal value; Med(x) is the median.

mineral is stable at $\xi > -4$ and a temperature of 3 °C, its maximal content is about 3 %. At 20 °C, kaolinite is formed within the range $-3.5 < \xi < -2$, and then it appears at $\xi > -0.5$. Under these conditions, its maximal content is about 3 %.

Within the interaction degree range presented by us, the newly formed chlorite is observed only at a temperature of 20 °C, and its content is about 3 % (see Fig. 2, g).

The major layered hydrosilicates in the system are the minerals from the group of smectites (see Fig. 2, h). The phases appear at $\xi > -3$ (20 °C) and $\xi > -2.5$ (3 °C). Their maximal content exceeds 50 %. Somewhat higher smectite content is characteristic of the system at a temperature of 20 °C. It should be pointed out that the phases of this type were extensively detected by us in the studies of the fine fractions of oil tailings from copper-nickel ore concentrating [22].

Finally, the appearance of liebenbergite should be stressed (see Fig. 2, i). This mineral is formed

at $\xi > -2.5$ (20 °C) and $\xi > -2$ (3 °C). Higher content is characteristic of 20 °C.

Now the results of evaporation modelling are to be considered. The Eh and pH values of the system at different ξ and water volumes in the system are presented in Table 4.

The dependences of the oxidation-reduction potential of the solution have a clearly pronounced minimum. For water volume 0.05 L, the maximal Eh is 0.88 V and corresponds to $\xi = -6$. A decrease in Eh continues till 0.74 V ($\xi = -2.5$), then this parameter starts to increase and reaches its plateau (0.77 V) at $\xi = -1$. With a decrease in water volume in the system to 0.001 L, the maximal Eh (at $\xi = -6$) decreases (0.81 V). The minimal Eh (0.73 V) is observed for the high degree of interaction ($\xi = -4.5$), then an increase in Eh to 0.80 V follows.

With a decrease in water volume in the system, a shift of the maximal pH values is observed. For instance, for water volume 0.05 L, the degree

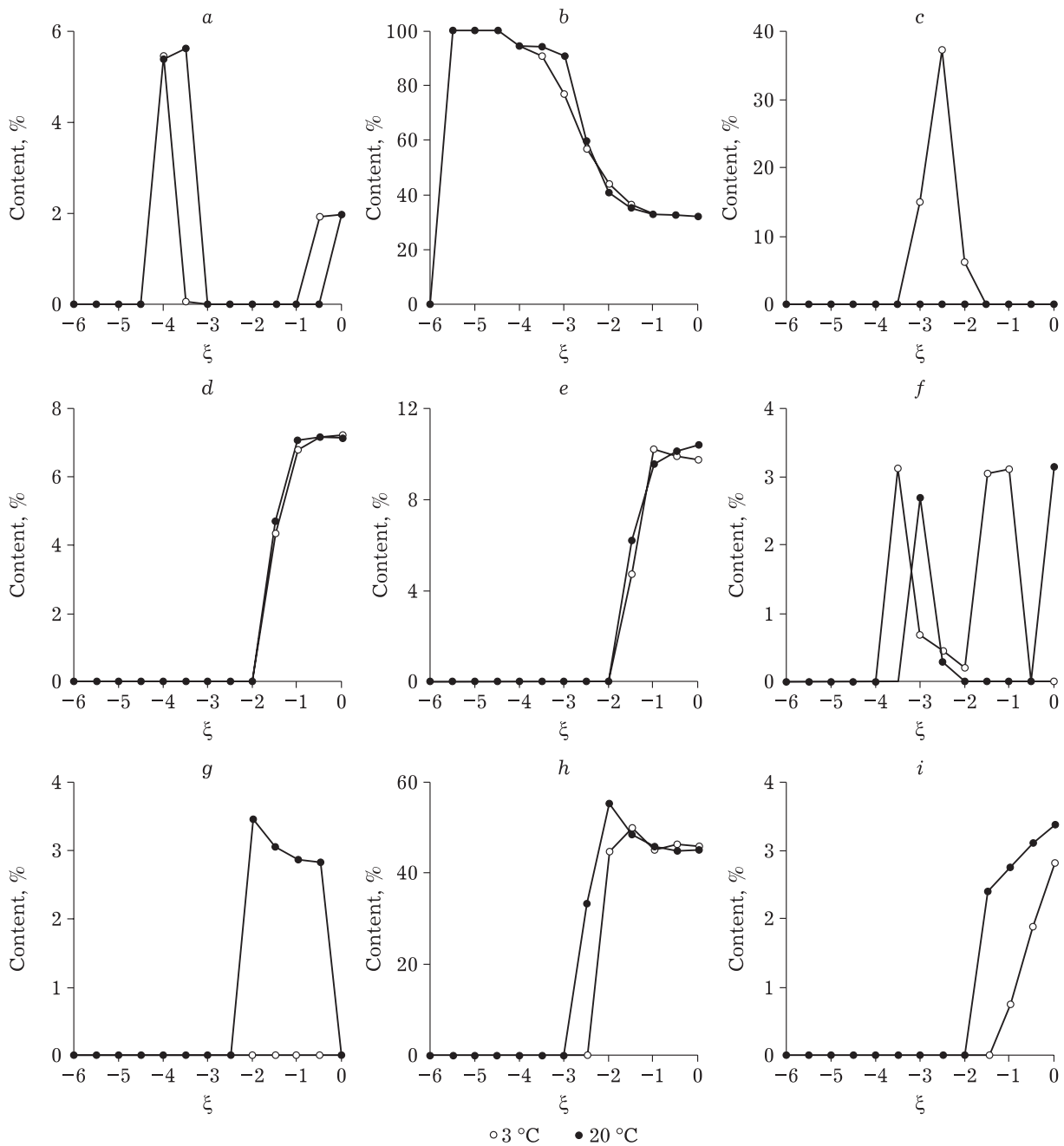


Fig. 2. Phase content depending on ξ ($\xi = \lg v$, where v is the degree of interaction, mol) at a temperature of 3 and 20 °C. Mineral phases: gibbsite (a); goethite (b); silica (c); calcite (d); dolomite (e); kaolinite (f); chlorite (g); smectite (h); liebenbergite (i).

of interaction v of mineral phases corresponding to the acidity of pore solutions detected in natural experiments is within the range from $10^{-3.5}$ to 10^{-2} mol, while for 0.001 L it is within the range from 10^{-5} to $10^{-3.5}$ mol of the solid phase.

The dependences of the concentrations of ions dominating in the system on ξ and water volume are shown in Table 4, too.

One can see that the solutions become more concentrated with respect to major cations with a

decrease in water volume in the system and an increase in the degree of interaction. The concentrations of magnesium and nickel ions increase monotonously. In general, the concentration of nickel ions is substantially higher than that of copper ions, which agrees with the field studies of the pore solutions from tailings of copper-nickel ore concentrating.

The concentration of sulphate ions increases in the solution with an increase in the degree of

TABLE 4

Dependences of Eh, pH and the concentrations of prevailing ions on ξ for water volume 0.05 and 0.001 L in the system "water – rock – gas"

ξ	Eh, V	pH	Concentration of prevailing ions, mg/kg H ₂ O											
			Ca ²⁺			Mg ²⁺			Ni ²⁺			Cu ²⁺		
			0.05 L	0.001 L	0.05 L	0.001 L	0.05 L	0.001 L	0.05 L	0.001 L	0.05 L	0.001 L	0.05 L	0.001 L
-6.0	0.88	0.81	4.23 · 10 ⁻³	2.12 · 10 ⁻¹	2.10 · 10 ⁻²	1.05 · 10 ⁰	1.61 · 10 ⁻³	9.56 · 10 ⁻²	1.74 · 10 ⁻⁴	8.30 · 10 ⁻³	4.32 · 10 ⁻²	2.16 · 10 ⁰	1.89 · 10 ⁻¹	3.63 · 10 ⁰
-5.5	0.86	0.77	1.59 · 10 ⁻²	7.83 · 10 ⁻¹	8.50 · 10 ⁻²	4.18 · 10 ⁰	2.77 · 10 ⁻³	3.06 · 10 ⁻¹	5.90 · 10 ⁻⁴	1.07 · 10 ⁻²	1.42 · 10 ⁻¹	6.96 · 10 ⁰	3.55 · 10 ⁻¹	1.50 · 10 ¹
-5.0	0.83	0.75	5.84 · 10 ⁻²	2.86 · 10 ⁰	2.84 · 10 ⁻¹	9.68 · 10 ⁰	2.17 · 10 ⁻²	1.23 · 10 ⁰	4.36 · 10 ⁻⁴	2.52 · 10 ⁻³	4.68 · 10 ⁻¹	2.24 · 10 ¹	1.06 · 10 ⁰	3.10 · 10 ¹
-4.5	0.80	0.73	1.96 · 10 ⁻¹	9.21 · 10 ⁰	9.17 · 10 ⁻¹	2.28 · 10 ¹	4.42 · 10 ⁻³	3.53 · 10 ⁰	1.34 · 10 ⁻³	2.91 · 10 ⁻³	1.54 · 10 ⁰	6.99 · 10 ¹	3.25 · 10 ⁰	6.04 · 10 ¹
-4.0	0.78	0.74	6.28 · 10 ⁻¹	1.62 · 10 ¹	2.90 · 10 ⁰	5.00 · 10 ¹	1.05 · 10 ⁻⁴	6.52 · 10 ⁰	2.16 · 10 ⁻³	1.33 · 10 ⁻²	4.84 · 10 ⁰	2.08 · 10 ²	1.03 · 10 ¹	5.02 · 10 ¹
-3.5	0.76	0.75	1.97 · 10 ⁰	3.73 · 10 ¹	7.82 · 10 ⁰	1.24 · 10 ²	5.96 · 10 ⁻⁶	1.58 · 10 ¹	1.97 · 10 ⁻³	8.27 · 10 ⁻²	1.49 · 10 ¹	5.77 · 10 ²	2.60 · 10 ¹	3.56 · 10 ¹
-3.0	0.75	0.76	6.02 · 10 ⁰	9.37 · 10 ¹	1.61 · 10 ¹	3.08 · 10 ²	1.20 · 10 ⁻⁵	3.95 · 10 ¹	3.19 · 10 ⁻³	1.27 · 10 ⁻²	4.50 · 10 ¹	1.49 · 10 ³	4.15 · 10 ¹	2.52 · 10 ¹
-2.5	0.74	0.77	1.15 · 10 ¹	1.25 · 10 ²	3.53 · 10 ¹	6.38 · 10 ²	2.63 · 10 ⁻⁵	7.49 · 10 ¹	7.51 · 10 ⁻³	2.29 · 10 ⁻²	1.28 · 10 ²	2.93 · 10 ³	4.92 · 10 ¹	1.82 · 10 ¹
-2.0	0.75	0.78	2.21 · 10 ¹	6.97 · 10 ¹	7.81 · 10 ¹	1.24 · 10 ³	5.78 · 10 ⁻⁵	1.27 · 10 ²	4.66 · 10 ⁻²	3.59 · 10 ⁻²	3.36 · 10 ²	5.26 · 10 ³	3.40 · 10 ¹	1.45 · 10 ¹
-1.5	0.76	0.78	4.76 · 10 ¹	3.82 · 10 ¹	1.70 · 10 ²	2.34 · 10 ³	1.27 · 10 ⁻⁴	2.29 · 10 ²	2.82 · 10 ⁻¹	6.33 · 10 ⁻²	7.71 · 10 ²	9.72 · 10 ³	2.31 · 10 ¹	1.08 · 10 ¹
-1.0	0.77	0.79	8.76 · 10 ¹	2.32 · 10 ¹	3.60 · 10 ²	4.68 · 10 ³	2.19 · 10 ⁻⁴	4.40 · 10 ²	1.45 · 10 ⁰	1.23 · 10 ⁻¹	1.63 · 10 ³	1.93 · 10 ⁴	1.61 · 10 ¹	7.75 · 10 ⁰
-0.5	0.77	0.80	5.10 · 10 ¹	1.20 · 10 ¹	6.56 · 10 ²	7.51 · 10 ³	4.88 · 10 ⁻⁴	6.54 · 10 ²	5.27 · 10 ⁰	1.95 · 10 ⁻¹	2.72 · 10 ³	3.08 · 10 ⁴	1.23 · 10 ¹	4.70 · 10 ⁰
0	0.77	0.79	3.09 · 10 ¹	1.47 · 10 ¹	1.28 · 10 ³	1.87 · 10 ⁴	9.52 · 10 ⁻⁴	1.00 · 10 ³	1.52 · 10 ¹	3.80 · 10 ⁻¹	5.15 · 10 ³	7.57 · 10 ⁴	6.71 · 10 ⁰	2.11 · 10 ⁰

Note. For designations, see Table 3.

interaction of mineral phases. With a decrease in the volume of water in the system from 0.05 to 0.001 L, SO_4^{2-} concentration increases by more than an order of magnitude.

Dependences of hydrocarbonate ion concentrations on ξ are characterized by the presence of maxima, which shift for water volume 0.05 L to $\xi = -2.5$, and for 0.001 L to $\xi = -4.5$.

The contents of the major newly formed mineral phases depending on water volume are

shown in Fig. 3. The same newly formed mineral phases are prevailing (see Fig. 2). Specific features of the system are the absence of silica, very low kaolinite content (it is not shown), and the appearance of gypsum (see Fig. 3, b). Its noticeable content is outside the range $-3.5 < \xi < -2$ for 0.05 L of water in the system, while for 0.001 L it is outside the range $-5 < \xi < -3.5$. At the same time, the presence of gypsum was detected by us previously in the investigation of fine clay-like

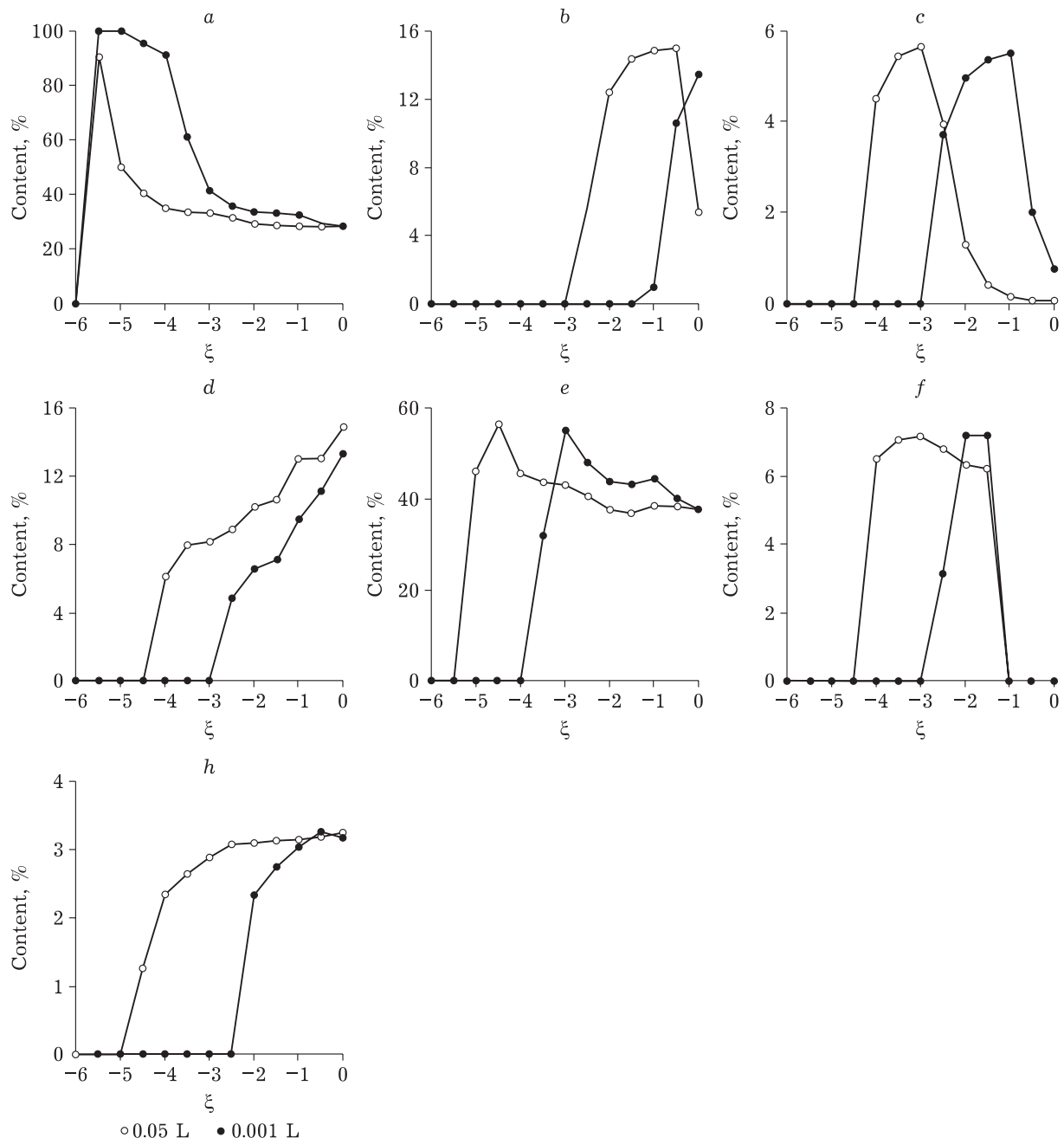


Fig. 3. Content of phases depending on ξ ($\xi = \lg v$, where v is the degree of interaction, mol) and water volume in the system – 0.05 and 0.001 L. Mineral phases: goethite (a); gypsum (b); calcite (c); dolomite (d); smectite (e); chlorite (f); liebenbergite (g).

fractions of tailings with low filtration coefficient [20, 22]. Gypsum was not determined in the fractions of larger size. It was likely to get dissolved and washed out as a consequence of a higher filtration coefficient. It should be noted that the formation of cementing layers with almost zero filtration coefficient is characteristic of many old tailings [23–25]. A similar phenomenon was observed also in the out-of-production tailing dumps of copper-nickel ores in Afrikanda settlement (the Murmansk Region) [22]. In our model, a decrease in filtration coefficient may be taken into account through an increase in the degree of interaction.

In general, the phases dominating in the system are the minerals of smectite, goethite, carbonate, and chlorite groups, independently of water volume in the system (see Fig. 3).

CONCLUSION

Thermodynamic modelling of hypergene processes in the concentration tailings of copper-nickel ores allows us to draw the following conclusions:

1) The major cations of pore solutions are magnesium, calcium, nickel, and copper ions; the major anions are sulphate and hydrocarbonate ions. Ion concentrations are approximately the same at a temperature of 3 and 20 °C, except nickel, which is more intensively leached at lower temperatures with an increase in the interaction degree. With a decrease in water volume in the system and an increase in the interaction degree, the solutions become more concentrated with respect to major cations and anions.

2) The major newly formed phases in the system are the minerals of smectite group and goethite, carbonates, silica, chlorite, gypsum. For small interaction degree in the system, which corresponds to filtration of a part of water through coarse-grained fractions of tailings and to relatively short interaction time, the prevailing phase is goethite. With an increase in the degree of interaction – filtration through fine fractions of tailings – layered magnesium hydrosilicates from smectite group dominate.

3) Modelling results demonstrate that an increase in the seasonal mean temperatures and in the duration of frost-free period would lead to intensification of hypergene processes during the storage of tailings, and an increase in the negative effect on environmental components of the surrounding territories. In spring and autumn, at a temperature insignificantly higher than

0 °C, the transition of nonferrous metals into soluble forms is observed practically in the same manner as during the summer. In summer, the composition and ratios of the phases formed in the upper layers of tailings change due to evaporation and low rate of water filtration.

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