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Formation of mine drainage in the Far Eastern region and its impact on the ecosphere and public health

V.P. Zvereva[1] ✉, **K.R. Frolov**[2], **A.I. Lysenko**[1]

[1] *Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russian Federation*

[2] *Far Eastern Federal University, Vladivostok, Russian Federation*

✉ *zvereva@fegi.ru*

Abstract

The long-term development of the mining industry in the Komsomolsky, Kavalerovsky and Dalnegorsky districts of the Far East of Russia caused origination of large-scale mining technogenic systems. During the period of so-called “perestroika”, mining production in the region was suspended, while mine workings (pits, adits) and tailings dumps were not subjected to any kind of preservation or reclamation. Only the boron and lead-zinc mining sectors in the Dalnegorsk district are currently in operation. The purpose of this paper is to assess the composition of mine waters, reveal the conditions of their formation, the presence of various aqueous species (coordination compounds and ions) of different elements and establish the parameters of precipitation of a number of hypergenic natural and technogenic minerals from these waters. This paper provides the hydrochemical characteristics of mine waters in the mining technogenic systems of tin-sulfide, copper-tin, tin-polymetallic, and polymetallic deposits, indicates the conditions of their formation and describes the adverse impact on the hydrosphere, as well as on human health in these districts. The studies of sulfide oxidation and mine water formation processes were carried out by the method of physicochemical simulation involving the use of the Selektor software package. The Eh–pH parameters of solutions, their composition with respect to stable aqueous species (complex compounds and simple ions), paragenetic associations (paragenesis) of precipitating hypergenic minerals with respect to the primary composition of ores and host rocks were established in a wide temperature range (from −25 to +45 °C). It has been established that the simulated micropore solutions participating in the formation of mine waters exhibit a wide range of Eh–pH parameters: Eh from 0.55 to 1.24 V and pH from 0.3 to 13.8. The technogenic minerals Fe, Cu, Zn, Pb and Sb belonging to oxide and hydroxide, sulphate, and arsenate classes are precipitated from them. Mine waters of high concentration, prior to and after the precipitation of technogenic minerals (weight of which reaches the hundreds of grams), are released into the hydrosphere. The simulated solutions contain all the elements of sulfide ores: Cu, Zn, Pb, Fe, Ag, As, Sb and S, whereas their concentrations in the form of aqueous species reach the tens of grams, while under cryogenic conditions the concentrations are by one or two orders of magnitude higher as a result of ice formation. The forms of migration of the elements depend on the temperature conditions. The negative impact of mine waters on the region hydrosphere and human health was demonstrated. In the districts under consideration, obvious trend of increasing morbidity (for almost all types of diseases) by 2 times both in adults and in children as compared to other Far Eastern regions was revealed. In addition, the morbidity of the child population for almost all the diseases under consideration proved much higher than in adults.

Keywords

mine slurry and drainage water, physicochemical simulation, sulfide minerals, hypergenesis, technogenesis, hypergenic natural minerals, technogenic minerals, processing tailings, paragenetic associations, toxicant, morbidity, Far East

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ТЕХНОЛОГИЧЕСКАЯ БЕЗОПАСНОСТЬ В МИНЕРАЛЬНО-СЫРЬЕВОМ КОМПЛЕКСЕ И ОХРАНА ОКРУЖАЮЩЕЙ СРЕДЫ

Научная статья

Формирование рудничных вод в Дальневосточном регионе России и их влияние на экосферу и здоровье населения

В. П. Зверева[1], **К. Р. Фролов**[2], **А. И. Лысенко**[1]

[1] *Дальневосточный геологический институт ДВО РАН, г. Владивосток, Российская Федерация*

[2] *Дальневосточный федеральный университет, г. Владивосток, Российская Федерация*

✉ *zvereva@fegi.ru*

Аннотация

Длительное развитие горнорудной промышленности в Комсомольском, Кавалеровском и Дальнегорском районах Дальнего Востока России позволило сформироваться крупномасштабным горнопромышленным техногенным системам. В период перестройки работа горнопромышленного производства была приостановлена, а горные выработки (карьеры, штольни) и хвостохранилища не подвергались какой-либо консервации или рекультивации. В настоящее время работает только борная и свинцово-цинковая промышленность в Дальнегорском районе. Цель данной статьи – оценить состав рудничных вод, показать условия их формирования, наличие ионов и молекул различных элементов и установить параметры кристаллизации из них ряда гипергенных природных и техногенных минералов. В публикации приведена гидрохимическая характеристика рудничных вод в горнопромышленных техногенных системах олово-сульфидных, медно-оловянных, олово-полиметаллических и полиметаллических месторождений, показаны условия их формирования и негативное воздействие на гидросферу, а также здоровье людей, проживающих в данных районах. Исследования процессов окисления сульфидов и формирования рудничных вод выполнены методом физико-химического моделирования с использованием программного комплекса «Селектор». В широком интервале температур (от –25 до +45 °C) установлены Eh–pH параметры растворов, их состав в отношении устойчивых водных частиц (комплексных соединений и простых ионов), парагенетические ассоциации (парагенезисы) осаждающихся гипергенных минералов в зависимости от первичного состава руд и вмещающих пород. Установлено, что моделируемые микропоровые растворы, формирующие рудничные воды, имеют широкий спектр Eh–pH параметров: Eh от 0,55 до 1,24 В и pH от 0,3 до 13,8. Из них кристаллизуются техногенные минералы Fe, Cu, Zn, Pb и Sb из классов оксидов и гидроксидов, сульфатов и арсенатов. Высококонцентрированные рудничные воды до и после осаждения из них техногенных минералов, масса которых составляет сотни грамм, попадают в гидросферу. Полученные моделированием растворы содержат все элементы сульфидных руд: Cu, Zn, Pb, Fe, Ag, As, Sb и S, а их концентрации в форме водных частиц достигают десятков грамм, причем в криогенных условиях они на порядок и два выше за счет кристаллизации льда. Формы миграции элементов зависят от температурного режима. Показано отрицательное воздействие рудничных вод на гидросферу региона и здоровье населения, проживающего в нем. Установлено, что в рассматриваемых районах отмечается тенденция роста практически всех видов болезней в два раза как у взрослых, так и у детей, причем заболеваемость детского населения практически по всем рассматриваемым болезням значительно выше, чем у взрослых.

Ключевые слова

рудничные шламовые и дренажные воды, физико-химическое моделирование, сульфидные минералы, гипергенез, техногенез, гипергенные природные минералы, техногенные минералы, хвосты обогащения, парагенетические ассоциации, токсикант, заболеваемость, Дальний Восток

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Introduction

The mining industry in the Komsomolskiy, Kavalerovskiy and Dalnegorskiy districts of the Far East has been developing for 70 to 120 years. Cassiterite-sulfide and polymetallic deposits were mined by both open-pit and underground methods. In the region, cassiterite-sulfide, cassiterite-silicate, and polymetallic deposits were developed, from ores of which Sn, Cu, Pb, and Zn were extracted. During perestroika, from 1996 to 2000, mining and processing facilities located in the Komsomolsky, Kavalerovsky and Dalnegorsky districts (Krasnorechenskaya processing plant) were abandoned. The major sulfide minerals in the areas under consideration are: pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena and sphalerite. The deposits development was carried out both by open-pit and underground methods, resulting in increased access of weathering agents (water, oxygen, etc.).

The intensification of hypergenic processes in underground mine workings (adits) contributes to the formation of mine waters with high concentrations of sulfide ore elements: Cu, Zn, Pb, Fe, As, Sb and S. Cu, Zn, Pb, Fe, As, Sb and S. Studies of the composition of technogenic waters and their impact on natural waters were carried out both in Russia and abroad. Many authors have reported their adverse impact on natural waters in the Komsomolsky, Kavalerovsky [1–3], and Dalnegorsky districts [2–4] of the Far East, in the Kemerovo region [5], the Urals [6], and in the world: New Zealand [7], America [8, 9], Turkey [10], Spain [11], Argentina [12].

The study of the chemical composition of mine waters by the authors was carried out in the period from 2001 to 2019 by the method of atomic emission spectroscopy using a Plasmaquant-110 spectrometer (Table).

Table

Chemical characteristics of mine waters (mg/l)

Sampling location (district, deposit)	Cu	Pb	Zn	Fe	As
Komsomolsky District					
1. Perevalnoye, 2002	36.600	1.320	77.500	71.400	0.130
2. Festivalnoye, 2004	153.000	0.002	24.970	14.800	0.200
3. Perevalnoye, 2004	48.300	1.200	60.100	32.200	0.600
4. Festivalnoye, 2010	46.510	0.013	10.230	17.430	0.003
5. Perevalnoye, 2010	16.150	1.560	25.64	42.300	0.187
6. Festivalnoye, 2015	85.152	0.034	10.510	5.730	0.120
7. Perevalnoye, 2015	2.080	0.054	4.480	2.580	0.299
Kavalerovsky District					
8. Vysokogorskoye, 2008	0.032	0.003	0.175	0.410	0.002
9. Dubrovskoye, 2008*	0.222	0.001	4.314	0.080	0.002
10. Dubrovskoye, 2008**	0.110	0.002	2.290	0.830	0.002
11. Vysokogorskoye, 2009	0.012	0.001	0.120	0.230	0.001
12. Dubrovskoye, 2010*	0.250	0.002	2.970	1.080	0.003
13. Dubrovskoye, 2010**	0.361	0.003	2.090	5.770	0.002
14. Vysokogorskoye, 2010	0.420	0.001	0.530	0.770	0.001
15. Dubrovskoye, 2011	0.450	0.001	2.010	2.970	0.012
16. Dubrovskoye, 2012	0.687	0.011	2.440	3.190	0.019
17. Dubrovskoye, 2013	0.159	0.001	2.700	0.550	0.003
18. Dubrovskoye, 2014	0.081	0.001	1.512	1.323	0.009
19. Dubrovskoye, 2015	0.482	0.007	2.725	3.625	0.009
20. Dubrovskoye, 2016	0.160	0.001	50.460	3.210	0.018
21. Dubrovskoye, 2017	0.166	0.001	1.748	0.713	0.002
22. Dubrovskoye, 2018	0.067	0.004	1.971	0.020	0.001
23. Dubrovskoye, 2019	0.034	0.001	0.749	0.017	0.001
24. Dubrovskoye, 2021	0.053	0.001	1.161	0.005	0.001
Dalnegorsky District					
25. Sovetsky Mine, 2001	0.001	0.123	0.216	0.593	0.023
26. Sovetsky Mine, 2003	0.015	0.200	0.614	0.918	0.018
27. Sovetsky Mine, 2006*	0.011	0.584	1.281	2.895	0.056
28. Sovetsky Mine, 2006**	0.003	0.262	0.687	1.252	0.029
29. Sovetsky Mine, 2007	0.008	1.033	0.937	9.309	0.033
30. Sovetsky Mine, 2010	0.002	0.121	0.390	0.330	0.015
31. Sovetsky Mine, 2011	0.114	5.350	9.790	27.222	0.041
32. Sovetsky Mine, 2012**	0.004	0.246	0.532	0.938	0.030
33. Sovetsky Mine, 2013**	0.004	0.085	0.650	1.080	0.026
34. Sovetsky Mine, 2014**	0.014	0.447	1.208	2.148	0.034
35. Krasnorechenskoye, 2015	0.031	0.076	0.001	2.928	0.006
36. Sovetsky Mine, 2016	0.189	0.920	0.040	0.350	0.614
37. Sovetsky Mine, 2017	0.001	0.034	0.131	0.036	0.011
38. Sovetsky Mine, 2018	0.001	0.041	0.273	0.026	0.009
39. Sovetsky Mine, 2019	0.001	0.016	0.156	0.004	0.010
40. Sovetsky Mine, 2020	0.001	0.013	0.134	0.004	0.016
41. Sovetsky Mine, 2021	0.001	0.107	0.066	0.002	0.002

Notes: * – samples were taken in summer, if the sampling was performed repeatedly in that year: ** – samples were taken in autumn, *** – samples were taken in spring. The content of S in the mine waters of the Kavalerovsky district varies from 7.2 to 216 mg/l, and in the Dalnegorsky district, from 18.4 to 192 mg/l.

In the Komsomolsky district, in the mine waters of the Festivalnoye deposit (copper-tin ores), the concentration of Cu reaches 153 mg/l, which is 76,500 times higher than the background characteristics, so its extraction from such waters was even recognized to be profitable. In the mine waters of Perevalnoye deposit (tin-polymetallic ores), the concentrations (mg/l) of Zn reaches 78, that of Pb, 1.56, exceeding the background values by 8,611 and 1,560 times, respectively. The waters are also distinguished by extremely high concentrations of Fe, 71.4 mg/l, As, 0.6 mg/l, exceeding the background values by 6490 and 1000 times, respectively (see Table 1). In the Kavalerovsky district, the maximum concentrations were detected for Cu, Pb, Zn, Fe, As at the Dubrovskoye deposit (mg/l): 0.687, 0.007, 50.46, 3.625, 0.019, respectively, exceeding the background values in 343.3, 7, 5,606, 329.5, 9.5 times, respectively. The mine waters of the 1st Sovetsky Mine in Dalnegorsky district contain: Cu, Pb, Zn, Fe, As in concentrations up to 0.189, 5.35, 9.79, 27.222, 0.614 mg/l, which exceed the background values by 94.5, 3,147, 1,088, 2,593, 1,023 times, respectively.

The mine drainage flow rate is inconsistent and varies considerably from mine to mine in the Kavalerovsky district, reaching 3,600 m^3/day. The volume of effluents at the mines of cassiterite-sulfide ores in this region in 1985–988 was (thousand m^3): 296 (Silinsky), 316 (Vysokogorsky), 758 (Ternisty), 895 (Tsentralny), 1208 (Yubileiny) and 1750 (Arsenievsky). In this period, the following quantities of a number of elements in the mine waters were found (kg): Fe, from 18 to 859, Cu, 2, and Zn, 62.

These high concentrations of sulfide ore elements are observed in the mine waters after precipitation of a wide range of technogenic minerals: posnjakite, serpierite, woodwardite, wroewolfeite, pitticite, glockerite, hisingerite, etc. They form stalactites, stalagmites or simply speleothems of white, blue, green, brown, and black colors of different shades permanently occurring in underground mine workings. Their thickness can reach 0.5 m [13–15].

Highly concentrated mine water was discharged year-round for many decades, untreated and unconfined, and polluted surface water and groundwater. Notice that some river waters, e.g. from the Silinka River (Komsomolsky district) and the Vysokogorka River (Kavalerovsky district) are actually used for supplying drinking water.

The purpose of this work is to assess the composition of mine waters, study the conditions of their formation, ionic/molecular speciation, establish the parameters of precipitation of a number of hypergenic natural and technogenic minerals from them and show their possible paragenetic associations using the 18–20 physicochemical simulation software package. One more objective is to demonstrate their adverse impact on the hydrosphere and the public health of those residing in the districts under consideration. To achieve this goal, the following tasks were addressed:

1. Establishing the Eh-pH parameters of micropore solutions and the composition of technogenic minerals that precipitate from them.
2. Determining the temperature conditions of their formation in the range of −25 to +45 °C.
3. Determining the paragenetic associations of precipitating (from solution) minerals.
4. Establishing the speciation of elements of sulfide ores in mine waters (aqueous species, coordination compounds and ions).
5. Demonstrating their impact on the hydrosphere and the public health in these districts.

Research techniques

In the simulation, the "Selektor" software was used (developed by I. K. Karpov et al., the A. P. Vinogradov Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences), which was based on a convex programming mathematical approach, making it possible to establish equilibrium in heterogeneous systems by minimizing thermodynamic potentials (Gibbs free energy). The Selektor allows to calculate the phase and component composition of a thermodynamic multisystem under various temperatures and pressures, considering the activity coefficients. Isothermal changes in thermodynamic functions were calculated using equations of dependence of the change in the volume of condensed phases on temperature, pressure and semi-empirical equations of state of gases at the given parameters.

For model formation, thermodynamic parameters of the components were required at the initial stage: the independent ones – the chemical composition of the system, the dependent ones – the potentially formed in the system. The dependent components were represented by the following phases: gaseous (atmospheric and formed as a result of sulfide oxidation reactions), liquid aqueous (ions and molecules formed in solutions) and solid (hypogenic, hypergenic natural and technogenic minerals present in the mining technogenic system of the district) [16, 17]. Both thermodynamic parameters inherent in the software [18–20] and those found in the references [21, 22] were used in the simulation.

Models of the system are represented by the following chemical composition [23]: atmosphere (Ar – 3.209, C – 0.1036, N – 53.9478, O – 144.8472, moles), 10 kg [24], water (H_2O) – 1 kg, and ore–mineral (oxidizing), 0.1 kg. The calculations were performed taking into account both independent (Ar–N–C–Fe–Cu–Pb–Zn–Ag–S–As–Sb–H–O–ē) and dependent components: speciation of elements in solution (aqueous species, coordination compounds and ions), gases, minerals, solid solutions, and ice. The following thermobarometric conditions were defined for the simulation: temperature from −25 to +45 °C (varying in increments of 5 °C) at a constant pressure of 1 atm.

All of the above parameters were inputted into the “Selektor” software, which calculated the equilibrium composition of the gaseous, liquid and solid phases of the system. The obtained simulation results have been analyzed and verified.

The mineral composition of primary ores (weighing 0.1 kg) in the simulation for each of the three districts under consideration (Komsomolsky [25, 26], Kavalerovsky [27], Dalnegorsky [28]) was obtained from the relevant literary sources. The simulation of the mine water formation was undertaken for the oxidation conditions of various sulfides (chalcocite, covellite, bornite, pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena, and sphalerite), and, in the Dalnegorsky district, Ag sulfides (argentite and acanthite) and Sb sulfides (pyrargyrite and jamesonite) were additionally input. The oxidation models for each sulfide were generated (at a rate of 100 %), then the oxidation was simulated in combinations of sulfides (in various combinations from 5 to 20 % of each mineral), and then with one mineral alternately excluded from the entire list of minerals involved (100 model variations were considered).

In the Komsomolsky district, when simulating, the calculations took into account: 11 independent and dependent components, of which: from 90 to 222 aqueous species, 18 gases, 3 to 40 minerals, including ice. In the Kavalerovsky district, the calculations took into account: 11 independent and dependent components, of which: from 99 to 238 aqueous species, 18 gases, 12 to 34 minerals, including ice. For the Dalnegorsky district, the calculations took into account: 13 independent and dependent components, of which: from 86 to 257 aqueous species, 18 gases, 1 to 30 minerals, including ice.

Research Findings and Discussion

The sulfide minerals forming the ore bodies at the deposits, which can be both monomineral and polymineral, have been chosen as the object of simulation. Hypergenic processes in the ore bodies of mine workings have been investigated both by direct observation [13, 15] and by the method of physicochemical simulation [29, 30]. Numerous micropore solutions formed during the oxidation of sulfides at various points of an ore body enter mine waters (drainage) and flow (untreated) from the workings outwards around the clock and all year round.

The simulation of the cementation zone minerals oxidation (chalcocite, covellite, and bornite) at negative temperatures in the Komsomolsky district showed that the simulated solutions (micropore) had the following Eh-pH parameters: Eh from 0.74 to 1.13 V and pH from 1.6 to 10.0, and the following minerals precipitated from the solutions: goethite $FeO \cdot OH$, chalcanthite $Cu[SO_4] \cdot 5H_2O$ and wroewolfeite $Cu_4[SO_4](OH)_6 \cdot 2H_2O$. At positive temperatures, the parameters were as follows: Eh 1.02–1.06 V and pH 1.6–3.3, and additional minerals posnjakite $Cu_4[SO_4](OH)_6 \cdot H_2O$ and antlerite $Cu_3[SO_4](OH)$ formed. The solutions for the simulation of sphalerite oxidation at negative temperatures had the following parameters: Eh 1.13–1.17 V and pH 1.3–1.9, and at positive temperatures, Eh 1.14–1.15 V and pH 1.3–1.5, and only at temperatures from −25 to −20 °C goslarite $ZnSO_4 \cdot 7H_2O$ precipitated, while at all other temperatures zinc and sulfur remained in solution. The oxidation of galena led to the formation of anglesite $PbSO_4$ in the entire temperature range under consideration, and the Eh-pH parameters of the solutions varied in the ranges of Eh 1.05–1.16 V and pH 1.5–2.6. During the oxidation of pyrite and pyrrhotite over the entire temperature range, solutions with parameters of Eh 1.17–1.21 V and pH 0.04–1.0 originated, from which goethite precipitated. The simulation of chalcopyrite oxidation showed precipitation of chalcanthite and goethite from solutions with parameters of Eh 1.16–1.2 V and pH 0.05–1.2. When arsenopyrite was oxidized at negative temperatures, goethite and scorodite $Fe[AsO_4] \cdot 2H_2O$ precipitated from solutions, while at positive temperatures only goethite precipitated, at the following parameters of micropore solutions: Eh 1.16–1.19 V and pH 0.6–1.3.

The rest eleven variants of sulfide oxidation (pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena, sphalerite, chalcocite, covellite and bornite) with alternate exclusion of each of the minerals listed in parentheses showed that Eh-pH parameters of the solutions were in the range of Eh 0.55–1.19 V and pH 0.5–2.0. At the same time, the following minerals precipitated from the solutions: goethite, chalcanthite, plumbojarosite $PbFe_6^{+3}[SO_4]4(OH)_{12}$ and scorodite. The absence of arsenopyrite in the system excluded scorodite from the paragenetic association of technogenic minerals, while the lack of galena excluded plumbojarosite.

It should be noted that under cryogenic conditions here and elsewhere, the concentrations of most species in solutions (liquid phase of water) reached hundreds g/l, since most of water was present in the system as a solid phase (ice). The solutions contained the following species (Fig. 1). In the range of positive temperatures, species $Cu(CO_3)_2^{2-}$, $Pb(SO_4)_2^{2-}$, $FeSO_4$ disappeared from the solutions, while the concentrations of the residual species decreased by an order of magnitude.

The simulation of oxidation of the minerals of the cementation zone: chalcocite, covellite, and bornite showed that under cryogenic conditions Eh-pH parameters of the solutions obtained for the Kavalerovsky district coincided with those obtained for the Komsomolsky district, while goethite disappeared from the paragenesis of the precipitated minerals and fibroferrite $Fe^{+3}[SO_4](OH) \cdot 5H_2O$ appeared. In the range of positive temperatures, the value of redox potential (Eh) reached 1.13 V, but the resulting paragenetic association of the technogenic minerals remained practically unchanged, with the exception of the change from goethite to fibroferrite. The simulated solutions for the oxidation of sphalerite had the following parameters at negative temperatures: Eh 1.16–1.17 V and pH 1.3–1.4, while at positive temperatures, Eh 1.14–1.15 V and pH 1.1–1.3. Same to the Komsomolsky district, at temperatures from −25 to −20 °C, goslarite precipitated, while in the other variants (scenarios) zinc and sulfur remained in the solution. The oxidation of galena also contributed to the precipitation of anglesite in the entire temperature range under consideration with the same Eh-pH parameters of solutions. With the oxidation of pyrite and pyrrhotite over the entire temperature range, fibroferrite precipitated, and the solutions exhibited the following parameters: Eh 0.84–1.24 V and pH 0.1–5.7. The simulation of chalcopyrite oxidation demonstrated the precipitation of chalcanthite with fibroferrite from solutions with the following parameters: Eh 1.08–1.14 V and pH 1.6–3.0. During the oxidation of arsenopyrite only fibroferrite was precipitated over the temperature range considered, and the Eh-pH parameters of the solutions were as follows: Eh 1.14–1.20 V and pH 0.7–1.2.

The following eleven sulfide oxidation variants (pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena, sphalerite, chalcocite, covellite, and bornite) with the successive exclusion of each of the minerals listed in parentheses showed that at negative temperatures Eh-pH parameters of the solutions came to the following limits: Eh 1.1–1.2 V and pH 0.6–2.3. At the same time, the following minerals precipitated from them: fibroferrite, chalcanthite, and anglesite. The absence of pyrite in the system led to the precipitation of duphthite $CuPb[AsO_4](OH)$ and bayldonite $Cu_3Pb[AsO_4]_2(OH)_2$, and when galena was excluded, chalcanthite and fibroferrite precipitated.

The solutions contained the following aqueous species (coordination compounds and ions), see Fig. 2. In the range of positive temperatures, Pb^{2+} ion and $PbSO_4$ neutral specie appeared in the solution, and the concentration of all ions, which occurred under cryogenic conditions, decreased by an order of magnitude or two.

The simulation of oxidation of the minerals of the cementation zone: chalcocite, covellite, and bornite over the considered temperature range in the Dalnegorsky district (on the example of the ores of the Sovetsky Mine) demonstrated the formation of paragenesis of chalcanthite and brochantite $Cu_4[SO_4](OH)_6$, while in the presence of bornite, goethite also precipitated. In this case, Eh-pH parameters of the solutions were as follows: Eh 0.66–1.13 V and pH 1.6–4.4 at positive temperatures and up to 11.7 at negative temperatures. The oxidation of sphalerite over the entire temperature range contributed to transfer of zinc and sulfur into the solution, which exhibited the following

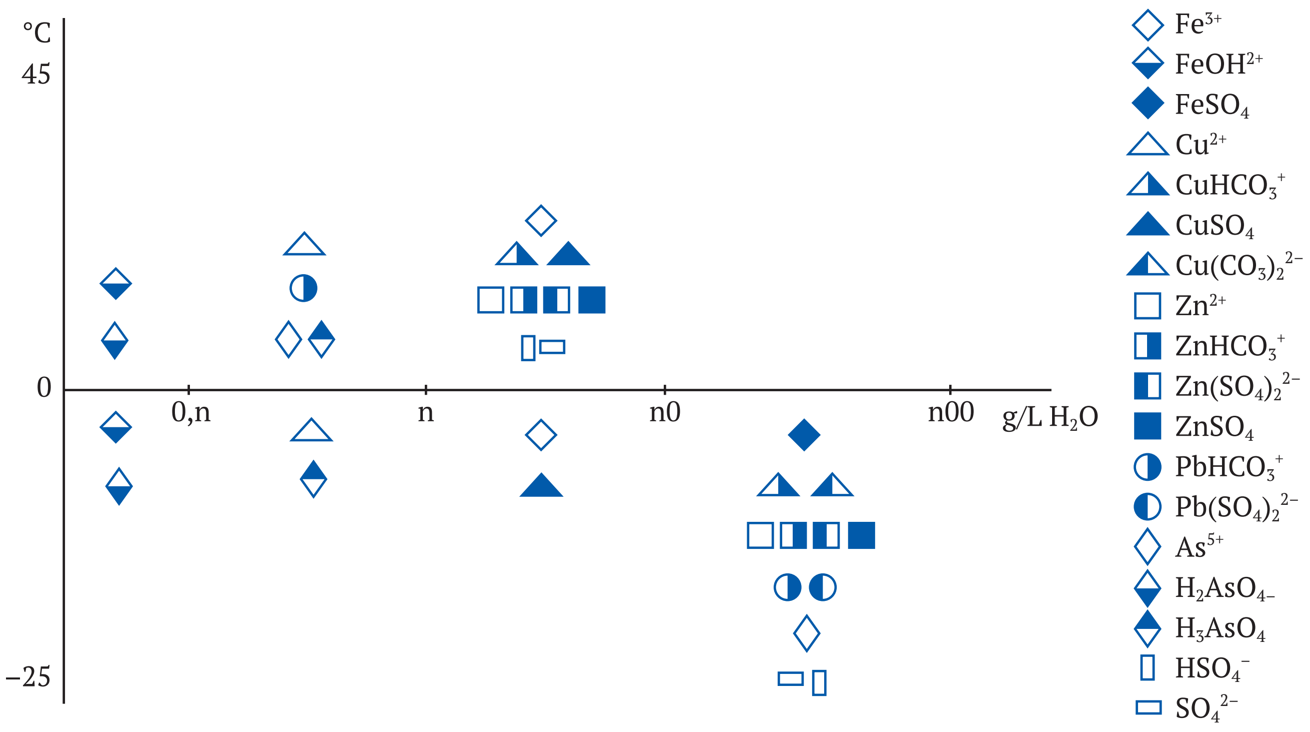

Fig. 1. Concentrations of aqueous species – speciation of elements of sulfide ores in micropore solutions forming mine water (g/l H_2O)

parameters: Eh 1.12–1.17 V and pH 1.3–1.9. The oxidation of galena in the range from −25 to +45 °C, same to the previous cases, led to precipitation of anglesite, while Eh–pH parameters of the solutions were as follows: Eh 1.05–1.19 V and pH 0.8–2.6. In the case of the oxidation of pyrite and pyrrhotite over the entire temperature range, goethite precipitated, and the solutions exhibited the following parameters: Eh 1.13–1.17 V and pH 0.7–2.1. The simulation of the chalcopyrite oxidation indicated the precipitation of chalcantite and goethite from solutions at the following parameters: Eh 1.13–1.16 V and pH 0.9–2.2. The oxidation of arsenopyrite resulted in the precipitation of goethite at the following parameters of solutions: Eh 1.11–1.14 V and pH 1.9–2.3.

Ag is extracted from the ores of the Dalnegorsky district containing argentite, acanthite, pyrargyrite, jamesonite. Then, let us simulate the oxidation of these minerals in an ore body, both separately and with their inclusion in the other variants. The oxidation of argentite, acanthite, and pyrargyrite contributed to the transition of silver to solutions both at negative and positive temperatures, and the parameters of the solutions were as follows: Eh 1.05–1.2 V and pH 0.6–2.5. In the case of the oxidation of jamesonite over the entire temperature range, anglesite and plumbojarosite precipitated at the following parameters of the solutions: Eh 1.16–1.2 V and pH 0.7–1.1.

The following fifteen sulfide oxidation variants (pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena, sphalerite, chalcocite, covellite, bornite, argentite, acantite, pyrargyrite and jamesonite) will be considered further with the successive exclusion of each of the minerals listed in parentheses. The oxidation simulation in eleven variants at negative temperatures showed the formation of goethite, chalcanthite (from −25 to −5 °C), plumbojarosite and adamine $Zn_2[AsO_4](OH)$ in the solutions with Eh 1.12–1.18 V and pH 0.8–2.3. The removal of arsenopyrite from the oxidizing sulfide association excluded, from the paragenesis (paragenetic association) of the precipitated minerals, goethite and adamine (at Eh 1.16–1.2 V and pH 0.6–1.2), the removal of pyrite excluded goethite (at Eh 1. 11–1.19 V and pH 0.7–2.1), the removal of sphalerite excluded adamine (at Eh 1.11–1.16 V and pH 1.1–2.3), and the removal of minerals of the cementation zone excluded plumbojarosite (at Eh 1.12–1.15 V and pH 1.3–2.2).

In eight variants of the association of the above-listed sulfides the oxidation in the range of positive temperatures led to the precipitation of goethite, plumbojarosite, and adamine at the following solution parameters: Eh 1.15–1.18 V and pH 0.8–1.3. The presence of argentite and acanthite in the association of oxidizing sulfides led to the formation of solutions with the following parameters: Eh 1.15–1.16 V and pH 0.9–1.1 and the replacement of plumbojarosite with anglesite in the list of the precipitated minerals. The absence of arsenopyrite and sphalerite in the initial association excluded adamine from the paragenesis of the precipitated minerals, and the parameters of the solutions became as follows: Eh 1.15–1.18 V and pH

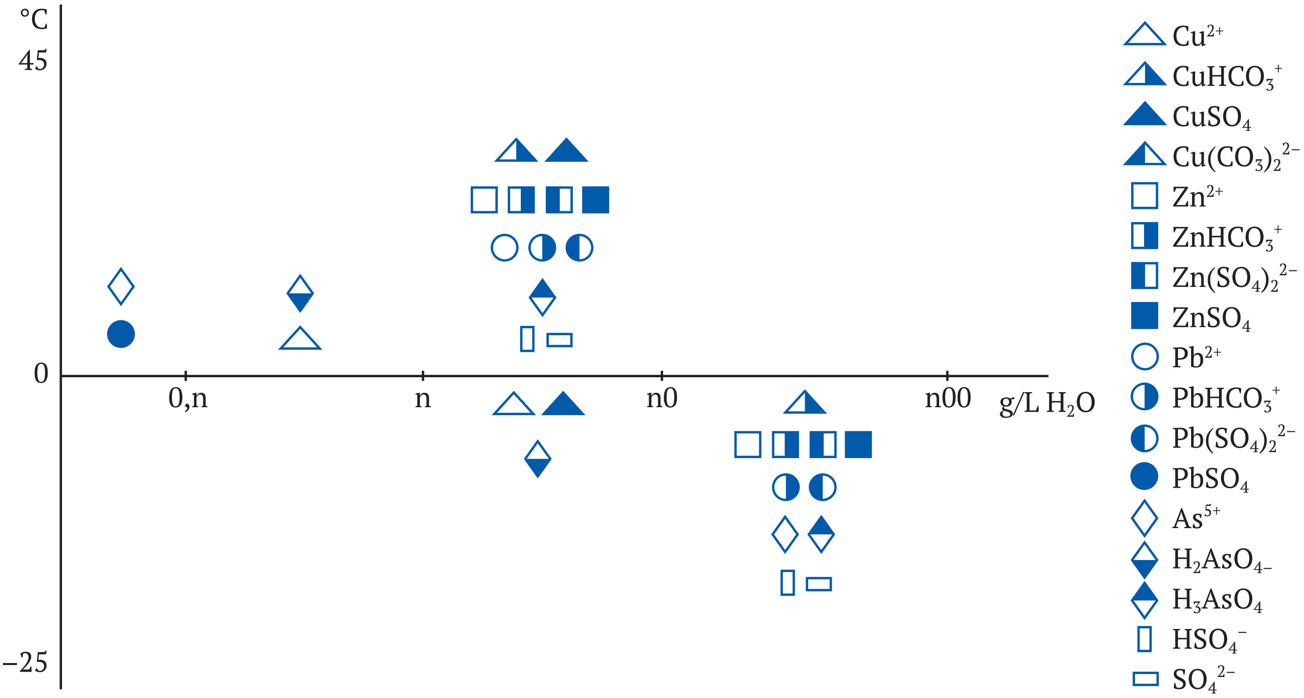

Fig. 2. Concentrations of aqueous species – speciation of elements of sulfide ores in micropore solutions forming mine water in the Kavalerovsky district (g/l H_2O)

0.8–1.2. The absence of chalcopyrite and galena in the initial association excluded goethite (Eh 1.14–1.18 V and pH 0.8–1.2) from the paragenesis of the precipitated minerals. Solutions with an Eh of 1.15–1.16 V and a pH of 0.8–1.3 were formed in the presence of pyrargyrite, resulting in the absence of plumboyarosite among the precipitated phases.

The solutions contained the following aqueous species (coordination compounds and ions), see Fig. 3. Over the range of positive temperatures, the following species were absent: $Cu(CO_3)_2^{2-}$, $Pb(SO_4)_2^{2-}$, Ag^+, while $FeOH^{2+}$, FeH_3AsO_4, $AgNO_3$ appeared. At the same time, the concentration of most species in the solution decreased by an order of magnitude.

The simulation of oxidation of the minerals of the cementation zone, chalcocite and covellite, over the range from −25 to +45 °C in the Dalnegorsky district (on the example of Krasnorechenskoye deposit) led to the transition of Cu and S into a solution with the following Eh-pH parameters: Eh 0.58–1.12 V and pH from 1.9 to 8.8 at positive temperatures and up to 13.8 at negative temperatures. The oxidation simulations for bornite solely and in combination with other minerals of the oxidation zone (covellite and chalcocite) at negative temperatures demonstrated the formation of solutions as follows: Eh 0.55–0.76 V and pH 8.6–13.8, from which fibroferrite precipitated. At positive temperatures, the parameters were as follows: Eh 0.72–0.76 V and pH 7.4–8.7, and, besides, goethite precipitated. When sphalerite was oxidized at temperatures from −20 to −15 °C (same to the two previous districts), goslarite precipitated additionally from the solutions with the following parameters: Eh 1.16–1.17 V and pH 1.4. At all other temperatures Zn and S remained in the solution (1.12–1.15 V and pH 1.3–1.5). The oxidation of galena over the considered temperature range, in accordance with usual practice, led to the precipitation of anglesite at the following Eh-pH parameters of the solutions: Eh 1.06–1.16 V and pH 1.5–2.6. In the case of the oxidation of pyrite over the entire temperature range, fibroferrite precipitated (the solution parameters: Eh 1.19–1.21 V and pH 0.3–0.7). The oxidation of pyrrhotite at negative temperatures resulted in the precipitation of fibroferrite (Eh 1.11–1.16 V and pH 1.5–2.1), while at positive temperatures goethite appeared (Eh 0.88–0.92 V and pH 5.2–5.6). The simulation of the chalcopyrite and arsenopyrite oxidation revealed the precipitation of fibroferrite (regardless of temperature) from the solutions exhibiting the following parameters: Eh 1.09–1.21 V, pH 0.3–2.0 at negative temperatures, and Eh 1.09–1.19 V, pH 1.2–9.9 at positive temperatures. The oxidation of argentite and acanthite contributed to the accumulation of Ag and S in solution over the entire temperature range, with the same parameters as in the previous variant considered (the oxidation of the Sovetsky Mine's ores). In the case of the oxidation of pyrargyrite and jamesonite in the entire temperature range, anglesite, fibroferrite and valentinite Sb_2O_3 precipitated, and the solutions exhibited the following parameters: Eh 1.18–1.21 V and pH 0.5–0.9.

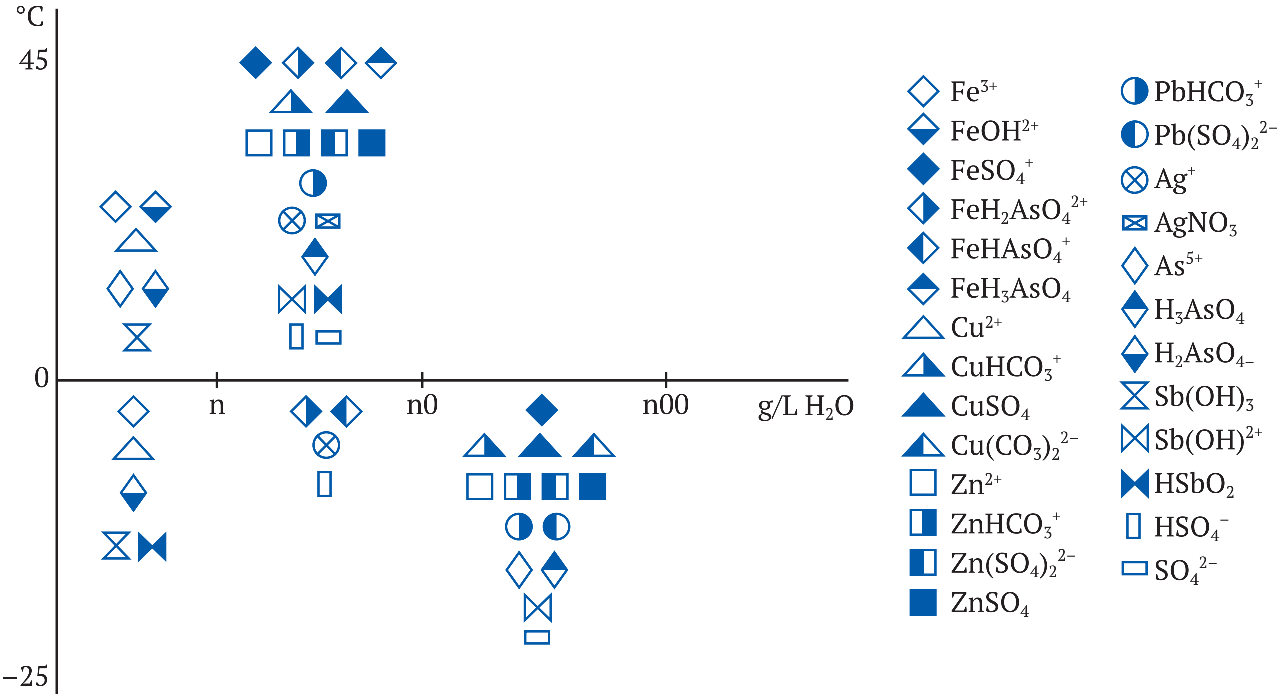

Fig. 3. Concentrations of aqueous species - speciation of elements of sulfide ores in micropore solutions forming mine water in the Dalnegorsky district (on the example of the Sovetsky Mine ores), g/l H_2O)

The following fifteen sulfide oxidation variants (pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena, sphalerite, chalcocite, covellite, bornite, argentite, acanthite, pyrargyrite and jamesonite) will be considered further with the successive exclusion of each of the minerals listed in parentheses. Wherever pyrargyrite and jemesonite (regardless of temperature) were present in the initial mineral association, the following mineral paragenesis was precipitated from solution under oxidation conditions: anglesite, fibroferrite and valentinite. The solutions exhibited the following Eh-pH parameters: Eh 1.11–1.19 V and pH 0.8–2.2. For the other variants, anglesite and fibroferrite were precipitated over the entire temperature range and the solution parameters were as follows: Eh 1.03–1.2 V and pH 0.7–3.5. The exclusion of galena from the initial association led to the disappearance of anglesite from the paragenesis of the precipitated minerals at the following solution parameters: Eh 1.11–1.17 V and pH 1.0–2.3.

The solutions contained the following aqueous species (coordination compounds and ions), see Fig. 4. Over the range of positive temperatures, the following species were absent in the solutions: Pb^{2+}, Ag^{2+}, $Pb(SO_4)_2^{2-}$ (which were present at negative temperatures), but Ag^+ appeared. Similar to the previous case, the concentrations of most aqueous species in solutions decreased by an order of magnitude at positive temperatures compared to negative temperature conditions.

Over the range of negative temperatures, non-freezing aqueous solutions contained free, bound and vaporous water, as well as osmotically absorbed and capillary one [31–33]. The amount of water in the systems decreased along with decreasing temperature due to the increasing mass of crystallising ice, so concentrations of aqueous species could reach 900 g/l or even more.

Highly concentrated mine water has been entering surface water and groundwater around the clock for decades, as noted above. Therefore, to prevent their environmental impact, it is necessary to dilute them tens, hundreds, and even thousands of times, that is not the common case in nature. A study of river and underground (in wells) waters in the Far Eastern region [2, 3, 34] showed that they contained a wide range of sulfide ore elements in concentrations above the maximum permissible levels (both for fishery reservoirs and domestic waters) tens, hundreds, and even thousands of times, so their use as drinking water is unacceptable. For example, in the well waters in the villages of the Kavalerovsky district, the concentrations of elements are as follows (mg/l): Fe, 5.1–10.3, Cu, 0.09–1.5, Pb, 0.01–0.07, Zn, 0.3–17.2, As, 0.03–0.8, which are significantly higher than the corresponding permissible levels [35]. Both deficiencies and excesses of vital elements are well known to cause numerous diseases among people residing in mining districts [36, 37]. The toxic effects of elements on human health depend on: their chemical nature, the concentration and composition of their ions and compounds, as well as the individual characteristics of an organism [38], so it was important to establish the forms of migration of the elements under consideration.

It is well known that Pb is one of the strongest toxicants for living organisms, and its inorganic compounds, which contain Pb^{2+} ion, disrupt metabolism and act as enzyme inhibitors. Long-term consump-

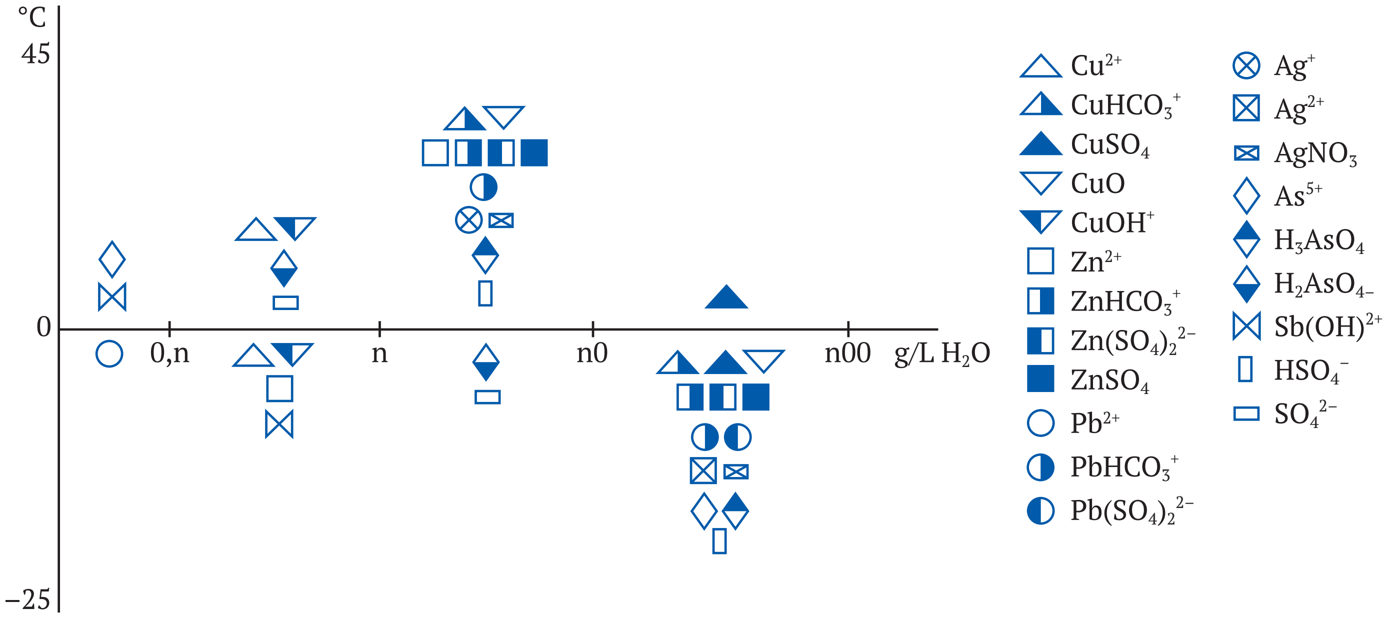

Fig. 4. Concentrations of aqueous species – speciation of elements of sulfide ores in micropore solutions forming mine water in the Dalnegorsky district (on the example of the Krasnorechenskoye deposit ores) (g/l H_2O)

tion of Pb-containing water, even with low Pb concentration, is one of the causes of acute and chronic diseases. Zinc is an element that is necessary for humans and animals, but both a deficiency and an excess of it is harmful to living organisms. It migrates in six different forms, and at low temperatures Zn^{2+} form prevails, while with increasing temperature $ZnOH^{+}$ specie becomes dominant [39]. Cu compounds reacting with tissue proteins have a sharp irritating effect on the mucous membranes of an upper respiratory tract and gastrointestinal tract, and also cause acute poisoning. $CuSO_4$ ingestion is toxic for humans and causes nausea, vomiting, diarrhea, the rapid appearance of hemoglobin in the blood plasma and in the urine, jaundice, anemia, etc. Arsenic compounds act on a nervous system, the walls of blood vessels, cause an increase in permeability and paralysis of capillaries. Chronic exposure to As compounds leads to gastrointestinal disorders, lack of appetite, nausea, stomach pain, dyspepsia, recurrent enterocolitis, chronic hepatitis, and in severe cases, cirrhosis. Sulfur and its compounds are also highly toxic [36].

The author's analysis of the population morbidity in the period from 1991 to 2001 showed that the intensive morbidity rate in the Kavalerovsky district is steadily higher than in the Komsomolsky district. Among the most common diseases are: the digestive apparatus diseases, which affected up to 20 % of children and adults in the Komsomolsky district and up to 40 % and 70 %, respectively, in the Kavalerovsky district; respiratory diseases, which affected up to 20 % of children and 60 % of adults in the Komsomolsky district, and up to 20 % of children and 17 % of adults in the Kavalerovsky district; and diseases of nervous system, which affected up to 10 % of children and 10 % of adults in both Kavalerovsky and Komsomolsky districts. During the period under review, there was a trend towards a twofold increase in the morbidity rate for almost all types of disease in both adults and children, with the morbidity of the child population for almost all diseases being significantly higher than the morbidity rate for adults. It should be noted that during this period, due to “perestroika” in the country, the volumes of ore extraction and processing in the region decreased significantly, and the population decreased by 6 % in the Kavalerovsky district and by 18 % in the Komsomolsky district [15]. Intensive morbidity rates in the Kavalerovsky district are higher than in the Komsomolsky one. They are much higher or at the same level as compared to the Primorsky Krai as a whole for most of the diseases under consideration: digestive and respiratory organs, pancreas, nervous system, blood and hematopoietic organs, chronic bronchitis, allergic rhinitis, epilepsy, metabolic disorders, chronic rheumatic heart disease and acute myocardial infarction.

The results of analysis of biological material (hair of children under 14 in the village of Fabrichny, Kavalerovsky district) indicated that its content of heavy metal compounds exceeds such in other areas of Russia (Non-Black Earth Belt, Central Black Earth Zone, Crimea, etc.) by 1.8 or more [35]. The studies on the elemental status of children and adolescents residing in the Komsomolsky district made it possible to establish a correlation between the level of technogenic pollution of the natural environment and the changes in the elemental status of children and adolescents [40]. The authors found high levels of contamination in children and adolescents with heavy metals, including Pb, Cr, As, and calculated their individual and population carcinogenic risks (CR). The obtained value of individual carcinogenic risk $CR = 1{,}05 \cdot 10^{-3}$ belongs to the fourth range and is unacceptable neither for the population, nor for occupational groups.

Conclusion

The relationship between minerals and pollutants in the form of aqueous species (coordination compounds and ions) present in mine waters is a topical issue and a major problem in environmental mineralogy and geochemistry. The primary purpose of this type of research is to develop models that will be able to correlate the data obtained with macroscopic observations in the mine workings.

Minerals play a key role in controlling the mobility and spread of inorganic contaminants in the environment, including surface water and groundwater, because they are involved in the processes of alteration of primary phases (hypogenic) and the formation of secondary (hypergenic natural and technogenic ones).

The simulated micropore solutions that form mine waters are characterized by wide range of Eh–pH parameters: Eh from 0.55 to 1.24 V and pH from 0.3 to 13.8. From the solutions, technogenic minerals of Fe, Cu, Zn, Pb, and Sb, including oxides and hydroxides, sulfates, and arsenates precipitate. Mine waters of high concentration, prior to and after the precipitation of technogenic minerals, reaching up to hundreds of grams in weight, are released into the hydrosphere. The use of modern methods of analysis and thermodynamic simulation makes it possible, apart from assessing the elemental composition of waters and determining their chemical forms, to identify their potential transformation under changing physical conditions (temperature, etc.). The solutions obtained as a result of the simulation contain all the elements of sulfide ores: Cu, Zn, Pb, Fe, Ag, As, Sb, S, and their concentrations (in the form of aqueous species) reach tens of grams per liter, and under cryogenic conditions (at negative temperatures) they are one-two orders of magnitude higher due to ice formation. The forms of the elements migration depend on the temperature conditions.

It should be emphasized that this study involved thermodynamic simulation only. The simulation revealed thermodynamically equilibrium solution compositions and thermodynamically stable solid phases under the considered physicochemical conditions. In the case of real processes of hypergenesis at the considered deposits, at sufficiently low ambient temperatures, and, in particular, at negative temperatures, thermodynamic simulation provides only a rough estimation of the potential composition of solutions and precipitated phases. Under such conditions, the kinetics of mineral dissolution and precipitation reactions can play an extremely vital role. In this regard, the kinetic studies may constitute the subject of the subsequent stage of the study of hypergenic mineral formation, the identification of forms and paths of metal migration in the conditions of sulphide deposit development (in the considered and other mining districts).

Assaying hydrochemical samples of mine waters collected in the districts under consideration and the compositions of highly concentrated solutions obtained in the course of the simulation, which enter into surface water and groundwater prior and after precipitation of hypergenic minerals, showed the adverse impact of hypergenic natural and technogenic processes on the hydrosphere as a whole. Consumption of such waters by the local population has led to its high morbidity in the mining districts of the Far Eastern region.

It has been established that in the districts under consideration, there is a clear upward trend of the increasing morbidity (for practically all types of diseases) among both adults and children in two times compared to the other Far Eastern regions. Furthermore, the morbidity rate among the child population proved to be much higher than that among adults for practically all the diseases under consideration.

The application of simulation results makes it possible to assess the temporal evolution of water systems in the mining districts and may become a useful tool for monitoring and remediation activities.

References

1. Grehnev N.I. Mining enterprises wastes that create economic and ecologic problems to subsoil usage in the Russian Far Eastern region. *Mining Informational and Analytical Bulletin*. 2014;(7):337–343. (In Russ.) URL: https://www.giab-online.ru/files/Data/2014/07/55_337-343_Grehnev.pdf

2. Yurkevich N.V., Bortnikova S.B., Saeva O.P. Directions of groundwater and surface runoff from the mining tailings according geophysical and geochemical research. In: *XI International Scientific Congress "Interexpo GEO-Siberia-2015". Sat. materials in 3 volumes. Novosibirsk, April 13–25, 2015*. Vol. 2. Pp. 305–310. (In Russ.) URL: http://www.ipgg.sbras.ru/ru/science/publications/publ-napravleniya-podzemnogo-i-poverkhnostnogo-stokov-305310-2015

3. Shulkin V.M., Chernova E.N., Khristoforova N.K., Kozhenkova S. I. Influence of mining activity on the chemical composition of water ecosystems. *Geoekologiya. Inzheneraya Geologiya, Gidrogeologiya, Geokriologiya*. 2014;(6):483–494. (In Russ.)

4. Opekunov A.Y., Opekunova M.G., Somov V.V. et al. Influence of the exploitation of Sibay Deposit (the Southern Urals) on the transformation of metal migration in subordinate landscapes. *Vestnik Moskovskogo Universiteta. Seriya 5. Geografiya*. 2018;(1):14–24. (In Russ.)

5. Ashley P.M., Lottermoser B.G. Arsenic contamination at the mole river mine, northern New South Wales. *Australian Journal of Earth Sciences*. 1999;46(6):861–874. https://doi.org/10.1046/J.1440-0952.1999.00748.X

6. Nordstrom D.K., Alpers C.N. Geochemistry of Acid Mine Waters. In: Plumlee G.S., Logsdon M.J. (eds.) *The Environmental Geochemistry of Mineral Deposits*. Society for Economic Geologists; 1999. Pp. 133–160.

7. Nordstrom D.K., Blowes D.W., Ptacek C.J. Hydrogeochemistry and microbiology of mine drainage: an update. *Applied Geochemistry*. 2015;57:3–16. https://doi.org/10.1016/j.apgeochem.2015.02.008

8. Kacmaz H. Assessment of heavy metal contamination in natural waters of Dereli, Giresun: an area containing mineral deposits in northeastern Turkey. *Environmental Monitoring and Assessment*. 2020;192(2):1–12. https://doi.org/10.1007/s10661-019-8057-0

9. González R.M. Seasonal variability of extremely metal rich acid mine drainages from the Tharsis mines (SW Spain). *Environmental Pollution*. 2020;259:113829. https://doi.org/10.1016/j.envpol.2019.113829

10. Murray J., Nordstrom D.K., Dold B., Kirschbaum A. Seasonal fluctuations and geochemical modeling of acid mine drainage in the semi-arid Puna region: The Pan de Azúcar Pb–Ag–Zn mine, Argentina. *Journal of South American Earth Sciences*. 2021;109:103197. https://doi.org/10.1016/J.JSAMES.2021.103197

11. Zvereva V.P. Man-made water of tin deposits in the Far East. *Geoekologiya. Inzheneraya Geologiya, Gidrogeologiya, Geokriologiya*. 2007;(1):51–56.

12. Zvereva V.P. Impact of technogenic wastewaters of Kavalerovskii and Dalnegorskii mining districts on the hydrosphere of Primorsky Krai. *Russian Journal of General Chemistry*. 2019;89(13):2808–2817. https://doi.org/10.1134/S1070363219130115

13. Postnikova V.P., Yakhontova L.K. *Mineralogy of supergene zone of tin deposits of Komsomolsky district.* Vladivostok: DVNTs AN USSR (Far Eastern Branch of the USSR Academy of Sciences); 1984. 122 p. (In Russ.)

14. Postnikova V.P., Yakhontova L.K. Glockerite, giesingerite and pitticite from the zone of hypergenesis of tin ore deposits of the Far East. *Mineralogicheskiy Zhural*. 1990;12(1):63–66. (In Russ.)

15. Zvereva V.P. *Environmental consequences of hypergenic processes in tin ore deposits of the Far East.* Vladivostok: Dalnauka Publ.; 2008. 165 p. (In Russ.)

16. Karpov I.K., Kiselev A.I., Letnikov F.A. *Computer simulation of natural mineral formation*. Moscow: Nedra Publ.; 1976. 255 p. (In Russ.)

17. Yokokawa H. Tables of thermodynamic properties of inorganic compounds. *Journal of the National Chemical Laboratory for Industry*. 1988;83:27–121. (In Japanese)

18. SUPCRT Database 1992–1998 Geopig, Arizona State University. http://geopig.asu.edu/sites/default/files/slop98.dat

19. Robie R.A., Hemingway B.S. *Thermodynamic properties of minerals and related substancies at 298.15 K and 1 bar pressure and at higher temperatures.* Washington; 1995. 461 p.

20. Chudnenko K.V. *Thermodynamic simulation in geochemistry: theory, algorithms, software, and applications.* Novosibirsk: Geo Publ.; 2010. 287 p. (In Russ.)

21. Yeremin O.V., Vinnichenko S.V., Yurgenson G.A. Estimation of standard Gibbs potentials of copper sulfates by means of linear programming techniques. *Vestnik Otdeleniya nauk o Zemle RAN* (*Bulletin of the Department of Earth Sciences of the Russian Academy of Sciences*). 2006;(1):19–20. (In Russ.)

22. Charykova M.V., Krivovichev V.G., Depmeir W. Thermodynamics of arsenates, selenites, and sulfates in the oxidation zone of sulfide ores: I. Thermodynamic constants at ambient conditions. *Geology of Ore Deposits*. 2010;52(8):689–700. https://doi.org/10.1134/S1075701510080015 (Orig. ver.: Charykova M.V., Krivovichev V.G., Depmeir W. Thermodynamics of arsenates, selenites, and sulfates in the oxidation zone of sulfide ores: I. Thermodynamic constants at ambient conditions. *Zapiski RMO (Proceedings of the Russian Mineralogical Society)*. 2009;(6):105–117. (In Russ.))

23. Chudnenko K.V., Karpov I.K. *Selektor-Windows. Brief instruction.* Irkutsk; 2003. 90 p. (In Russ.)

24. Horn R. *Marine chemistry*. Moscow: Mir Publ.; 1972. 398 p. (In Russ.)

25. Radkevich E.A., Korostelev P.G., Kokorin A.M. et al. *Mineralized zones of the Komsomolsky district.* Moscow: Nauka Publ.; 1967. 115 p. (In Russ.)

26. Radkevich E.A., Asmanov V.Ya., Bakulin Yu.I. et al. *Geology, mineralogy and geochemistry of the Komsomolsky district*. Moscow: Nauka Publ.; 1971. 335 p. (In Russ.)

27. Gonevchuk V.G. *Tin-bearing systems of the Far East: magmatism and ore genesis*. Vladivostok: Dalnauka Publ.; 2002. 295 p. (In Russ.)

28. Bulavko N.V. *Mineralogy of skarn deposits of the Dalnegorsk ore field (Primorye)*. Vladivostok: Far Eastern Book Publisher; 2000. 219 p. (In Russ.)

29. Zvereva V.P., Frolov K.R. Assessment of the Impact of Technogenic Processes Occurring at the Central Concentrating Mill Tailing Dump (Komsomolsky Tin-Ore District) on the Hydrosphere in a Wide Temperature Range. *Russian Journal of General Chemistry.* 2017;87(13):3133–3136. https://doi.org/10.1134/S1070363217130047

30. Zvereva V., Lysenko A., Frolov K. Modern minerals formation genesis in Kavalerovsky tin-ore district technogenic system (Primorsky Krai). *Minerals*. 2020;10(2):9. https://doi.org/10.3390/min10020091

31. Ananyan A.A. The movement of moisture in frozen loose rocks under the influence of electroosmosis forces. *Colloidal Journal*. 1952; 14(1):1–9. (In Russ.)

32. Ptitsyn A.B., Abramova V.A., Markovich T.I., Epova E.S. *Geochemistry of cryogenic oxidation zones.* Novosibirsk: Nauka Publ.; 2009. 88 p. (In Russ.)

33. Vakulin A.A. *Fundamentals of Geocryology.* Tyumen: Tyumen State University Publ.; 2011, 220 p. (In Russ.)

34. Krupskaya L.T., Zvereva V.P., Mayorova L.P. et al. *Ecological and geochemical bases for assessing the impact of the technogenic system on the environment and its protection (on the example of the closed mining enterprise "Solnechny GOK")*. Khabarovsk: Pacific State University Publ.; 2019. 260 p. (In Russ.)

35. Krupskaya L.T., Melkonyan R.G., Gul L.P. et al. *Assessment of the impact of tailings ponds of the closed mining enterprise "Khrustalnensky GOK" of the Primorsky Territory on the ecosphere and reclamation of its surface.* Khabarovsk: DalNIILKH Publishing House; 2017. 144 p. (In Russ.)

36. Lazarev N.V., Gadaskina I.D. *Hazardous Substances in Industry. Handbook for chemists, engineers and doctors. Vol. 3. Inorganic and organometallic compounds*. Leningrad: Khimiya Publ.; 1977. Pp. 332–333. (In Russ.)

37. Ivanov V.V. *Ecological geochemistry of elements*. Moscow: Ekologiya Publ.; 1994. Vol. 1. 304 p. (In Russ.) 1995. Vol. 4. 416 p. (In Russ.) 1996. Vol. 3. 352 p. (In Russ.) 1997. Vol. 5. 576 p. (In Russ.)

38. Moiseenko T., Megorsky V., Gashkina N., Kudryavtseva L. Water pollution effect on population health in an industrial northern region. *Water Resources*. 2010;37(2):199–208. https://doi.org/10.1134/S0097807810020077

39. Linnik P.N., Nabivanets B.I. *Forms of metal migration in fresh surface waters*. Leningrad: Gidrometeoizdat Publ.; 1986. 270 p. (In Russ.)

40. Rastanina N.K., Kolobanov K.A. Impact of technogenic dust pollution from the closed mining enterprise in the Amur Region on the ecosphere and human health. *Mining Sciences and Technologies* (*Russia*). 2021;6(1):16–22. https://doi.org/10.17073/2500-0632-2021-1-16-22

Information about the authors

Valentina P. Zvereva – Dr. Sci. (Geol. and Min.), Chief Researcher, Laboratory of Hypergene Processes Geochemistry, Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russian Federation; ORCID 0000-0001-8288-0993, Scopus ID 14628094500, ResearcherID D-6017-2014; e-mail: zvereva@fegi.ru

Konstantin R. Frolov – Cand. Sci. (Chem.), Associate Professor, Department of Petroleum Technology and Petrochemicals, Far Eastern Federal University, Vladivostok, Russian Federation; ORCID 0000-0002-6122-2980, Scopus ID 55570105700, ResearcherID Q-1471-2016; e-mail: frolov.kr@dvfu.ru

Anastasiya I. Lysenko – Cand. Sci. (Chem.), Researcher, Laboratory of Hypergene Processes Geochemistry, Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russian Federation; ORCID 0000-0002-6439-0736, Scopus ID 55569808000; e-mail: lion8888@inbox.ru

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