

Processes of Chemical Weathering of Minerals in Sulphide-Containing Tailing Dumps: Modeling of the Composition of Vadose Water and Secondary Phases

O. L. GASKOVA, S. B. BORTNIKOVA and G. P. SHIRONOSOVA

Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Koptyuga 3, Novosibirsk 630090 (Russia)

E-mail: gaskova@uiggm.nsc.ru

(Received July 5, 2006; revised October 5, 2006)

Abstract

Thermodynamic model of the oxidative leaching of sulphide-rich tailings from dressing of gold-containing ores (Berikul settlement, West Siberia) is investigated. When calculating the water – rock interactions, we applied some special approaches allowing one to determine the effect of the degree of reaction progress and change of the parameters of the medium (E_h , pH) on the composition of the formed secondary minerals that restrain the development of acid drainage at the objects of this kind. Substantiation of several stages of the formation of a technogenic system in time and space is presented, depicting the approach of the system to equilibrium with the environment. The distinguished stages correspond to the zoning of mineral associations described at the object. These associations were formed during 50 years of storing the tailing mounds from the lowest weakly oxidized sulphide parageneses with gypsum and covellite to the capping jarosite-quartz-gypsum zones. The results of modelling provide evidence that an increase in rock affection by atmospheric water brings about the conditions favourable for the formation of the “final” association (goethite and quartz); however, this association is not stable even on the surface of the Berikul tailing dump. It is concluded on the basis of preliminary evaluation that hypergenesis processes in the objects of this kind may proceed hundreds of years till complete depletion of the acid-producing and toxic potential of industry-related wastes.

INTRODUCTION

One of the problems concerning environmental pollution is directly connected with the facilities of mining and metallurgical industries: an increase in the level of metals, oxy anions (SO_4^{2-} , AsO_4^{3-} , SbO_3^- etc.) and radionuclides in the biosphere. Since hypergenesis of sulphide-containing waste rock piles, tailing heaps and impoundments forms acid sulphate wastewater rich in sulphate, the investigation of sulphide oxidation processes has become an important direction of investigation during the recent decades [1–11]. The authors of those works demonstrated that the total pH of solutions is a function of the balance between the acid-producing and acid-neutralizing reactions depending on the relative rates of these reactions and the availability of the minerals to

chemical decomposition (weathering). The factors promoting the formation, development and attenuation of the acid mine drainage, which has a different character at different sulphide-containing industry-related objects, can be divided conventionally into the internal and external ones. The former include composition, amount and distribution of sulphide minerals; type of host rocks and vein minerals; particle size determining porosity, permeability and water-saturation. The latter factors are: climate, amount of atmospheric precipitation, hydrogeological situation, amount of wastes, efficiency of preliminary isolation, and measures aimed at the conservation.

The goal of the work was to build up a physicochemical model of oxidative leaching of sulphide-rich industry-related tailing stored in the form of a mound above the level of subsoil

water. The possibility of comparing the results of thermodynamic calculations with the geochemical and mineralogical information concerning this object [12–14] serves to test the model, allows us to reveal the major chemical reactions responsible for the formation of the composition of water in the zones of oxidation and secondary associations, and to provide a quantitative characterization of the degree of process propagation in time.

OBJECT OF INVESTIGATION

Staro-Berikul deposit is a part of the Berikul ore field (South-West Siberia, Kemerovo Region) and relates to the vein gold-sulphide-quartz type. The geological structure of the deposit and the mineral composition of veins were studied in detail in [15].

Processing of the ore from this deposit at the Berikul Gold-Recovery Plant (GRP) was mainly connected with the extraction of gold (content: 1–5 g/t). Wastes from cyanidation of the sulphide floatation concentrate (cakes) were stored at the territory of the plant along the Mokry Berikul River in the form of a pile 245 m long and 3–6 m high. About 70 thousand ton of waste material had been accumulated there during the years 1942–1972. The vertical sections of the band of wastes, tested during 1997–2000, were formed in early 1950s. Then the process tailings were used to pile the road leading to later tailings. The plant was in operation till 1991.

The data of the analyses of general chemical composition of the substance (Table 1) allow us to consider the ratios of rock-forming oxides, sulphide and sulphate sulphur. It should

be noted that the Berikul cakes are characterized by high arsenic content (0.2–4.5 %, the average value being 2 %). The grain size after crushing followed by grinding is 0.01–0.2 mm. According to the archive data of the plant, initially the waste material contained about 40 % pyrite, 5 % arsenopyrite, and several per cent of sphalerite, chalcopyrite and galena. Pyrrhotine was also observed; it is marked with secondary minerals along the cleavage cracks. The residual part includes quartz (15 %), mica (5–10 %), feldspar and plagioclase (5–10 %), chlorite (5 %) and carbonates (about 5 %). Heavy schlich contains pyrite 75–90 %, arsenopyrite 8–20 %. Due to the use of aggressive leaching solutions (sodium cyanide, lime) and the agents neutralizing the industrial sewage (ferrous sulphate, lime chloride) in the technological process, cake storage leads to the formation of a more reactive medium than that formed in the stored gravity flotation wastes.

Four zones were clearly distinguished in the investigation of vertical walls of several shafts:

Zone 1. The upper 20–40 cm of the wastes are composed of fine-grained jarosite yellow-coloured material having the following composition: jarosite – about 50 %, quartz – up to 35 %, impregnated gypsum up to 2 mm long (with gypsum content up to 10 %). Sulphides are present in the form of relics in gypsum or seams in the clay material.

Zone 2. At a depth of 40–150 cm, melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) horizon with the melanterite content about 10 % is located. This mineral fills the entire space; sometimes it occurs in the form of druses, sometimes as the jointing material. Large fragmental blocks of the lower-lying horizon are discovered in this layer. This is an evidence of the propagation of

TABLE 1

Total chemical composition of the substance of the Berikul sulphide cakes, mass %

Content	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	S _{sulph}	SO ₄	CO ₂
Average	20.97	2.12	7.47	27.91	1.81	3.86	6.83	2.14	2.76	14.89	11.88	1.98
Minimal	16.89	0.37	4.17	16.09	0.03	1.58	4.34	0.47	0.75	0	3.14	0.02
Maximal	36.05	0.73	8.42	37.06	0.28	2.96	9.77	0.49	1.69	21.6	20.0	2.32
Standard deviation	5.41	0.1	1.28	5.43	0.08	0.47	1.51	0.008	0.26	6.70	5.55	0.60

Note. *n* – number of determinations (*n* = 17).

oxidation front. This layer also contains sludge-like water-saturated mass composed of sulphides (up to 25–30 %) jarosite (20 %), quartz (15–20 %), gypsum (10–15 %), ferric sulphoarsenates (10 %), ferrous chlorite, hydromica and plagioclase (~10 %). Melanterite very rarely occurs in the upper, loose and humid part of the horizon.

Zone 3. At a depth of 150–200 cm, a lithified grey horizon is observed. It is penetrated by leaching crevices. The structure of this layer is formed by a small-grained mass strengthened with large gypsum metacrystals. The mass consists of sulphides (30 %), quartz (15 %), plagioclase (5–10 %), hydromica, chlorite (~10 %), relics of carbonates (5 %). The crevices are formed in jarosite, amorphous ferric sulphoarsenates, and gypsum. The fraction of the secondary minerals is about 25 %. In general, the layer looks like a newly formed solid rock.

Zone 4. The foot of dumps is composed of non-lithified sulphide material with weak indices of modification. Mean sulphide content is 45 %. Covellite CuS occurs only rarely. The total content of secondary compounds represented by gypsum, amorphous ferric sulphoarsenates is about 15 %.

So, ferric sulphates are confined mainly to the upper part of the oxidation zone but they are also characteristic of the whole section. They are represented by jarosite solid solutions; hydroxonium jarosite is the first to be formed, then comes the potassium one with the high lead content. In the discoloured association formed at the slopes of sulphide heaps, ferrous and ferric sulphates were detected, such as roccenite ($\text{Fe}^{2+}\text{SO}_4 \cdot 4\text{H}_2\text{O}$) containing Zn, as well as copyapite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) and rhomboclase ($\text{HFe}^{3+}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) with the content of arsenic up to 0.9 mass %. Arsenates and sulphoarsenates described in zones 2–4 are cryptocrystalline wandering formations and red-brown films. The author of [16] distinguished three groups of amorphous compounds with different iron and arsenic content in which Al, Si, Zn, Pb and Cu are present as impurities. According to the data of structural and thermal investigations, each group is a mixture of an arsenate like scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ and sulphoarsenates, such as zicaite $\text{Fe}_4(\text{AsO}_4)_3(\text{SO}_4)(\text{OH}) \cdot 15\text{H}_2\text{O}$, sarmentite

$\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$, bukovskyite $\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}$. It is typical that arsenic is present in the upper zone 1 in the form of water-soluble salts (passes into water extracts), which points to its high mobility. It should also be noted that water-soluble and ferric hydroxide related forms are characteristic of Zn, Cd and Cu but they are detected above the cemented layer, that is, under the oxidative conditions of the aeration zone.

A representative sample of chemical analyses of different types of water according to the data reported in [14] is presented in Table 2. Surface water was sampled near cakes immediately after atmospheric precipitation and washing the discoloured matter off, while pore water was sampled only from zone 2 above the lithified horizon. Prevailing drainage also follows the profile of this layer and flows into the river. It is this circumstance that explains the fact that even correct storage of sulphide cakes on the surface of alluvial material composed of carbonate fragments does not give efficient results on neutralization of sewage. Water near tailings is an acid polycomponent sulphate-arsenate solution; getting into the river it forms a large amount of precipitate composed of amorphous hydroxides of iron, aluminium and silicon containing also heavy metals.

MODELING PROCEDURE

Four different modeling procedures were used in the work. They are complementary with respect to the information concerning weathering the sulphide-containing mound tailings. In the first three cases, calculations in the heterophase 16-component system H–O–Cl–K–Na–Ca–Mg–Fe–Al–Si–S–C–Zn–Pb–Cu–As were carried out at 25 °C and the pressure of 1 bar with the help of the GIBBS algorithm using the thermodynamic database UNITHERM of the HCh software package [17]. The composition of the initial rock was assigned in compiling the model in agreement with the archive data; pure water served as the initial solution. In this model, the independent calculation schemes are arranged in the following way:

1. Calculation of the interaction between the solid phase (R) and aqueous solution (W) depending on the integral ratio of their masses,

TABLE 2

Total chemical composition of different types of water of the Berikul sulphide cakes, mol/l

Component	Pore water	Drainage water	Surface water*	Water in the river near the cakes
As	0.297	0.013	0.003/0.092	4E-6 (0.3 mg/l)
Ca	0.008	0.005	0.006/0.01	0.00044
Cd	0.0002	9.8E-5	1.51E-5	3.91E-8
Cl ⁻	0.022	0.005	0.0025	5.92E-6
Cu	0.006	0.001	0.0006/0.008	7.9E-8
F ⁻	0.01	0.0049	0.003	2.63E-6
Fe	1.026	0.32	0.32/0.32	5.3E-7
HCO ₃ ⁻	8.2E-7	8.2E-7	8.2E-7	0.0013
K	0.0004	1.4E-4	0.001/1.5E-4	3.32E-5
Mg	0.26	0.021	0.01/0.043	0.00013
Na	0.003	0.0004	0.00074/0.028	6.52E-5
Pb	1.74E-4	8.2E-5	8E-6/2.4E-6	1.93E-8
SO ₄ ²⁻	1.95	0.21	0.315/0.615	0.00014
Zn	0.03	0.0094	0.0018/0.015	8.56E-6
pH	1.7	2.3	1.1/1.49	7.1
E _h , mV	621±29	649±50	635±6	359

Note. *n* – number of determinations (*n* = 6).

*The first value is the data of analyses; the second value is the calculated pH and concentrations of elements in solution.

by means of the degree of reaction progress in the system which is open with respect to the active atmospheric components. The prescribed partial pressure of carbon dioxide was $10^{-3.5}$ bar, oxygen 0.2 bar. The amount of water was constant (55.51 mol H₂O) and the amount of reacting rock was increased from 10^{-4} to $10^{-0.3}$. In this case, the rock to water ratio (R/W) is usually interpreted as the degree of rock processing completeness and characterizes the time of rock interaction with the aqueous solution [18].

2. Since gaseous oxygen is intensely consumed in the pyrite layer for reaction with pyrite, the model of vertical zoning may be built up only with the help of a system of serial flow reactors. The start of the oxidation process corresponds to the zero step of the zero wave ($i = 0, N = 0$). At each step i , 1 kg of the rock reacts with an increasing amount of H₂O (horizontal strings) imitating the increasing degree of washing the rock during the reaction with water. At each secondary wave ($N = 1-4$), the interaction of the altered rock with the effluent solution takes place. So, in each column we initially have the constant R/W ratio along the flow line,

depicting changes in the volume of the layer. As reported in [17, p. 651], such an approach allows one to compose combined models involving the conditions varying both in space and in time. In this type of calculations, for $i = 0, N = 0$, the oxygen content of solution is assigned at the excess with respect to the equilibrium with the atmosphere (0.2 mol/l instead of $0.2 \cdot 10^{-2.96}$ mol/l), that is, as if the portion of water of the upper horizons repeatedly gets saturated with oxygen. This assumption is based on the fact that the rate of reagent gas diffusion into the solution substantially exceeds the rate of its absorption due to oxidation reactions in the condensed phase [19]. Oxygen is consumed in lower-lying layers for the oxidation of sulphides, while the oxidation-reduction potential is controlled by the equilibrium association under the conditions of the closed system. If this excess is not assigned, the content of oxygen in the solution leaking to the lower horizons is so small that oxidation and dissolution processes stop.

3. Since the issue of the largest interest in the object under investigation is melanterite natural-technogenic association registered us-

ing the method of flow reactors only at $\log R/W = -1$, we have thoroughly analysed its stability for E_h values that were actually recorded in sulphide-rich tailings. For this purpose, the reference values that we used in the calculations were E_h values taken from [10]: they were measured with the help of the piezometer network in pore water from the Camp tailing (Sheridon, Canada) containing up to 60 % of pyrite and pyrrhotine. In the upper layers (50 cm), this value is 500–800 mV, in the binding layer and down to the level of underground water the values of oxidation-reduction potential decrease to 100–300 and –15...–100 mV, respectively. It is also necessary to stress the fact that the thickness of the bound layer (hardpan) in this tailing dump exceeds 1 m; the layer is composed of melanterite, roccenite, gypsum, jarosite, and goethite.

4. The program and the database Wateq4F [20] were used to calculate the forms of element occurrence in solution and saturation indices (SI) in the case of the known overall composition of solutions and measured E_h , pH values. As indicated in the User Manual, the equilibrium state of the solution and the solid phase is characterized by the value $\log SI = \pm 0.3$. The degree of deviation from these values determines the degree of non-equilibrium. It seems reasonable to carry out re-calculation of the compositions of pore water and surface water indicated in Table 2.

Since the UNITHERM database is intended for the physicochemical analysis of underground processes participated by fluids, it was supplemented with specific data describing the interactions under hypergene conditions. The major abstracted sources are concentrated in the extensive database Wateq4F (minerals of the oxidation zone, ions and complexes characteristic of surface water). The values of free energy of formation for the most disputable minerals of iron and arsenic are presented in Table 3. For ferric and ferrous sulphates, we mainly used the data taken from [21, 22], for jarosites the data were taken from [20]. For ferrous and calcium arsenates, the data were taken from [20], too, and they correspond to the values given in Handbook [23]. It is necessary to stress that more up-to-date data exist for jarosite and scorodite [24–26]; these data take into account the solubility of pure crystal forms. However, tests showed that in this case the calculated concentrations of iron in surface water are an order of magnitude smaller than the measured values, and scorodite is to appear in the upper quartz-jarosite-gypsum zone 1, though it was not discovered *in situ*. The choice of the values shown in Table 3 was due to the fact that the solubility of the crystal phase differs from that of the amorphized phase by almost two orders of magnitude [27], and it is the poorly devitrified individual species that are present in the Berikul cakes.

TABLE 3

Chemical formulas of iron- and arsenic-containing minerals and standard free Gibbs energies of formation

Mineral	Formula	$\Delta_f G_m^o$, kJ/mol
Pyrite	FeS_2	–159476
Magnetite	Fe_3O_4	–1009685
Goethite	$FeOOH$	–487620
Melanterite	$FeSO_4 \cdot 7H_2O$	–2507.75±1
Ferricopyapite	$Fe_3(SO_4)_6O(OH) \cdot 20H_2O$	–9899
Copyapite	$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$	–9971
Jarosite H	$(H_3O)Fe_3^{3+}(SO_4)_2(OH)_6$	–3231.38
Jarosite K	$KFe_3^{3+}(SO_4)_2(OH)_6$	–3298.50
Arsenopyrite	$FeAsS$	–10962
Scorodite	$FeAsO_4 \cdot 2H_2O$	–1259.80
Calcium arsenate	$Ca_3(AsO_4)_2 \cdot 4H_2O$	–4006.60
Symplesite	$Fe_3(AsO_4)_2 \cdot 8H_2O$	–3687.26

The problem of co-ordination of the thermodynamic information is improved by the fact that the values of thermodynamic potentials of ions, neutral particles and simple compounds were established with the sufficient degree of reliability under the standard conditions. However, the minerals of hypergenesis zones are often represented by nonstoichiometric, amorphous phases or contain a large amount of admixtures, while stability constants of complicated coordination compounds (of the metal-arsenate type) were determined only in a few isolated works. In this connection, we estimate the accuracy of model calculations to be within the range of ± 0.5 of the order of values (with respect to solubility).

MODELING RESULTS

1. The effect of the increasing rock/water (R/W) ratio on the composition of the solution formed in a system open to the action of the atmosphere is shown in Fig. 1. The compositions of equilibrium secondary phases are shown there, too. One can see that the acidity of surface water increases and goethite appears even in the case of the interaction of 0.0001 kg of the rock with 1 kg of water ($\log R/W = -4$). The process of sulphide oxidation develops at the early stages in such a manner that ferrous hydroxides (goethite in the model) are prevailing among the secondary minerals during a long period of time ($\log R/W$ are equal to -4 , -3 , -2); anglesite is present. Only after the amount of the reacted rock reaches 0.1 kg ($\log R/W = -1$), the association of zone 1 turned out to be stable; it is represented mainly by quartz (42 %), jarosite (36 %) and gypsum (14 %). Further increase in $\log R/W$ to -0.5 leads to the appearance of soluble ferrous sulphate – copyapite, which is characteristic of the discoloured zone [28]. For $\log R/W = -0.3$, goethite disappears, while the fraction of copyapite is 57 %. The amount of water in the system decreases from the initial level 55.5 g/mol (1 kg H_2O) to 52.9 and 49.1 g/mol in the two latter associations, respectively. In model calculations, this is due to the fact that water is consumed for the formation of water-containing sulphates, but with respect to the natural situation this fact may be interpreted

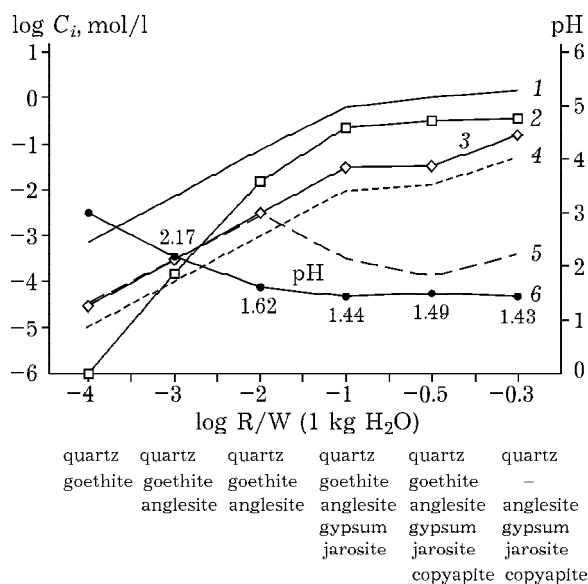
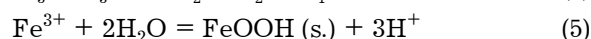
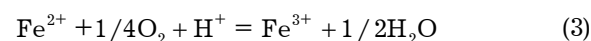
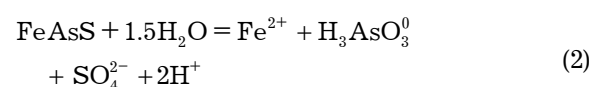
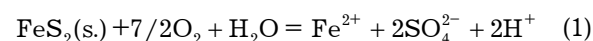


Fig. 1. Effect of increasing rock/water (R/W) ratio on the composition of the solution formed in an open system. The compositions of the equilibrium secondary phases of the upper part of the oxidation zone (zone 1) are presented under the plot.

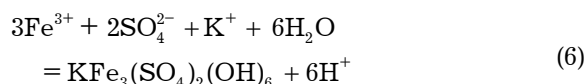
also as the demonstration of the mechanism of the formation of ferrous sulphates at the evaporation barrier.

Before the appearance of jarosite, pH of solutions decreases depending on the amount of oxidized sulphides. Since the prevailing minerals are pyrite and arsenopyrite, let us first consider the following parallel reactions:



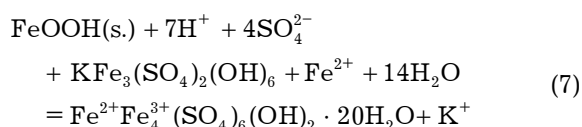
The known fact of deceleration of reaction (3) in acid solutions [29] and reaction (4) within a broad pH range [30, 31] allows us to state that reaction (1) is the main acid-producing reaction at the first stage. Model calculations with variable R/W ratio provide evidence that the acidity of water drained through the waste material of one composition can increase substantially with storage time. Accumulation of the corresponding cations and anions in the solution leads to supersaturation with respect to jarosite. This process (6) is accompanied by

further change of the acidity of the medium to stable pH ~ 1.45:



It is known that goethite and ferrihydrite are stable in less acid solutions (pH > 4), schwertmanite $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$ at pH 3–4, while jarosite at pH < 3 [32–34].

The reaction of copyapite appearance can be described as



One can see in Fig. 1 how potassium responses to the change of associations: at first it passes into solution due to leaching from the initial minerals of the rock, then it leaves solution getting deposited in jarosite, later on it is again carried into the solution with the enrichment of the solid phase with copyapite (7). The curves of the concentrations for arsenic and zinc are shown in the same Figure, too. One can see that these concentrations increase in parallel to each other. It is implied that these elements exhibit conservative behaviour in the upper part of the oxidation zone since they do not change the forms of occurrence and get accumulated only in solution till the complete disappearance of initial arsenopyrite (FeAsS) and sphalerite (ZnS). However, it is necessary to recollect, first of all, the above-indicated refinements of the free energy values for scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), and the ability of zinc to be accumulated as an admixture in secondary arsenates and sulphates. Due to the absence of the corresponding thermodynamic data, these features were not taken into account in the model. This may be the reason why the calculated arsenic and zinc concentrations turned out to be higher than the data for natural surface water flow. This Table also shows other calculated and *in situ* measured characteristics of the composition of surface water. One can see that the model solution contains almost the same concentration of iron (0.32 mol/l) and somewhat higher concentration of sulphate ions (0.615 mol/l). It should be stressed that the pH values are close to each other, which is likely to be due to pH buffer-

ing reactions. At the same time, the problem connected with the redox potential deserves attention. It was stressed in [35] that a complicated mechanism of the oxidation with atmospheric oxygen leads to such a situation that the measured potentials of aerated natural water are lower by 400 mV than those indicated by equation $E_h, \text{V} = 1.22 - 0.059\text{pH}$. Indeed, at 25 °C, $P_{\text{O}_2}(\text{g}) = 0.2$ bar and pH 1.49, the oxidation-reduction potential determined using Henry's constant is 1.13 V, while the measured value is only 0.635 V (see Table 2). We carried out estimations also for the latter E_h (for $P_{\text{O}_2}(\text{g}) \leq 10^{-20}$ bar). The composition of mineral associations turned out to be qualitatively the same, which is due to the broad field of their stability; however, the concentrations of elements with variable valence such as Fe(II)/Fe(III) change. In the opinion of the authors of [36], it is the $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair that determines the potential in iron-rich mine water. On the basis of a large number of comparisons of the measured and calculated (through the $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio) values, the authors of [37] proposed to use the measured value of the oxidation-reduction potential as a mobile quantitative indicator of the oxidation state of iron: at ~640 mV, the $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio is equal to 1, while at ~570 mV up to 95 % of iron is present in the form of Fe(II); at ~720 mV it is present in the form of Fe(III). On this basis, even without any analytical possibility to determine the concentrations of iron forms with different valence in solution, it may be concluded that the presence of Fe(III) in water flowing over the investigated object is significant. This statement is also confirmed by model calculations.

2. Table 4 (rows: step; columns: wave) shows the equilibrium parageneses and parameters of solutions (E_h , pH) for N equal to 0, 1 and 4 because no significant qualitative changes occur between the first and the fourth waves. The vertical zoning of the waste body is shown schematically in Fig. 2 to simplify understanding of calculation results.

At the zero step of the zero wave (1 kg of unweathered rock reacts with 1 kg of H_2O) all the initial minerals are conserved in the association; small amounts of magnetite and calcium arsenate characteristic of alkaline solutions at 25 °C appear. The reducing solution ($E_h =$

TABLE 4

Parameters of solutions E_h -pH and equilibrium associations formed with an increase in the degree of transformation of the initial rock

Parameter	Step $i = \log R/W$					
	0*	-1	-2	-3	-4	-6
Wave, N	0	0	0	0	0	0
E_h , V/pH	-0.536/11.58	-0.039/5.44	1.16/1.6	1.14/2.2	1.08/3.0	1.0/4.56
Association	Initial	Quartz Pyrite Galena Sphalerite Chalcocopyrite Goethite Gypsum Montmorillonite- kaolinite Symplesite	Quartz Goethite Anglesite Jarosite	Quartz Goethite Anglesite	Quartz Goethite	Goethite
Wave, N	1	1	1	1		
E_h , V/pH	-0.335/9.34	0.128/2.97	1.13/2.3	0.99/4.65		
Association	-Albite -Anortite -Chlorite -Mica + Magnetite + Gypsum + Symplesite + Montmorillonite- kaolinite	Quartz, pyrite Chalcosine Alunite Gypsum Anglesite Montmorillonite- kaolinite Melanterite Scorodite	Quartz Goethite Anglesite	Quartz		
Wave, N	4	4	4			
E_h , V/pH	-0.064/5.73	1.17/1.4	0.99/4.63			
Association	+ Goethite + Gypsum + Montmorillonite- kaolinite + Symplesite	Quartz Goethite Anglesite Jarosite	Quartz Goethite			

*Zero step means that $\log R/W = 0$, that is, $R/W = 1$. Provided that $R = 1$ kg, this corresponds to 1 kg of water. Calculation for each step may be done in this manner.

-0.536 V) has pH equal to 11.58. With a decrease in R/W ratio with an increase in the time of water exchange, the interaction of 1 kg of the fresh rock in 10 kg of water ($\log R/W = -1$, pH 5.44) gypsum, goethite, clayish minerals and ferrous arsenates (symplesite) appear, while calcite disappears from the association. With further increase in the degree of rock washing out with the oxidizing solution, typi-

cal associations of leaching zones with anglesite, jarosite and goethite are formed ($i = 2-6$). Attention should be paid to the fact that the association corresponding only to $\log R/W = -2$ is described on the surface of cakes (see Fig. 2).

Each underlying layer "lags behind" in the number of waves of solution that had passed through it. This is depicted as a diagonal displacement in the model and in Fig. 2. So, melan-

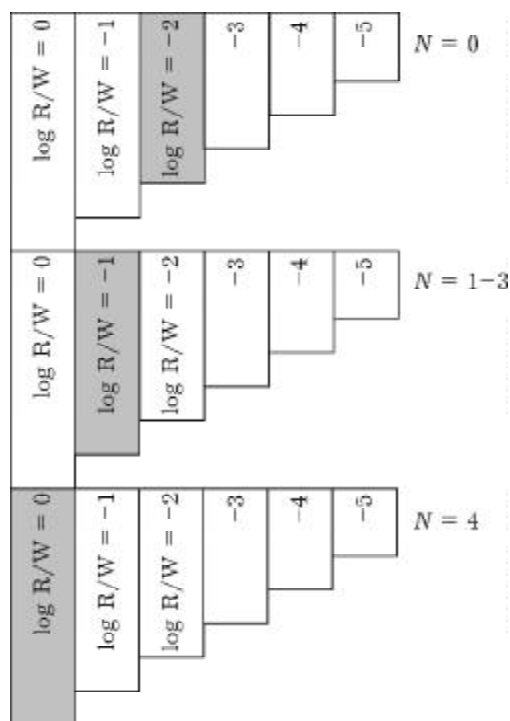
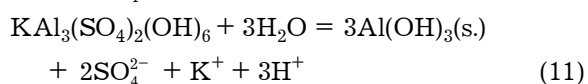
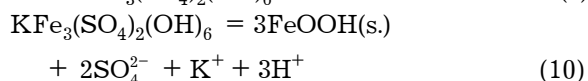
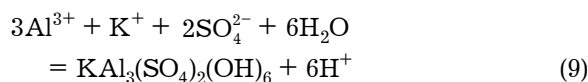
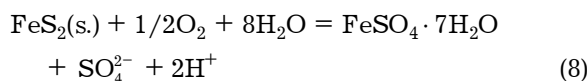


Fig. 2. Scheme of vertical zoning of the body of wastes. The rectangles decreasing in size show the modelled rock to water ratios corresponding to step (i), number of wave (N) is designated with figures; shaded areas correspond to the steady state of the system observed at present.

terite association was obtained at $\log R/W = -2$ and $N = 1-3$. It should be noted that it turns out to be stable only in the case if the condition of the interaction of the affected rock with the effluent solution (that is, the solution that had accumulated sulphate and iron leached from the upper-lying horizons) is assigned. In the case of the reaction of affected rock with the fresh portion of solution, melanterite is absent. From the first wave to the third one, E_h of the solution increases gradually (0.128–0.142–0.201 V), while its pH decreases (2.97–2.77–1.9). The species prevailing in solution are Fe^{2+} , $FeSO_4^0$ and $H_3AsO_3^0$. Analysis of the composition of the solid phase showed that the amount of pyrite on each wave decreased (2.15–1.35–0.55 g/mol, respectively), though under the above-indicated conditions melanterite was always present with pyrite (8). In addition to gypsum, the excess sulphate sulphur is deposited with potassium and aluminium in the form of alunite (9).



Reaction (9) corresponds in stoichiometry and meaning to reaction (6) and is acid-producing but to a lower extent, which is determined by the solubility of the minerals. Additional calculations showed that the occurrence of reactions (10) and (11) results in pH values equal to 1.68 and 4.0, respectively. In this situation, total iron concentrations are almost always higher by two orders of magnitude than the concentrations of aluminium. For example, for the accepted thermodynamic parameters for minerals and ions participating in reactions, the corresponding concentrations are $5.44 \cdot 10^{-3}$ and $4.42 \cdot 10^{-5}$ mol/l, respectively.

For the largest among the chosen values of $\log R/W$ equal to 0, model parageneses with sulphides and carbonates correspond to the zones in the base of cake mound (to remind, sign “+” in the second column of Table 4 means the appearance of new minerals in addition to the initial association). The diagonal displacement of the shaded rectangles in Fig. 2 conventionally shows an increase in the thickness of the underlying horizons. We failed to sample the necessary amount of pore water from this horizon to measure E_h and pH because the rocks turned out to be dry. But even the cases with very high pH (>11) are not artefacts and were recorded with instruments, for example in the pore water of the lower horizons of Mount Pleasant tailing dump in New Brunswick [38].

3. It was found for the interaction of the rock and water in an open system ($\log R/W = -1$) in which the partial pressures of oxygen were assigned by the corresponding redox potentials according to the data reported in [10] that melanterite has a broad field of stability (Fig. 3). However, in this situation, the compositions of solutions and associations undergo substantial changes. Even at $E_h \sim 0$ (pH 5) melanterite can appear in association with pyrite, galena,

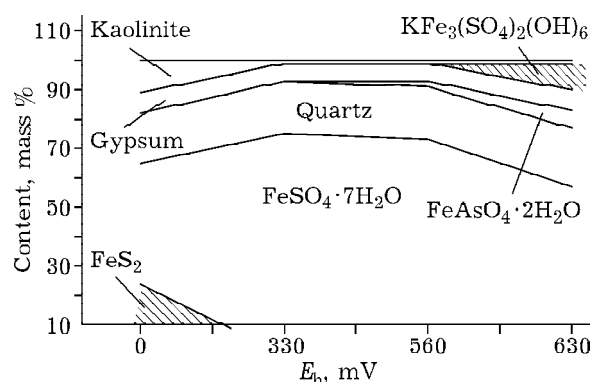


Fig. 3. Changes in the composition of associations with an increase in the oxidation-reduction potential for $\log R/W = -1$. Small fractions of sphalerite, galena and covellite are present in the field of FeS_2 .

sphalerite, chalcocine or covellite. The components prevailing in solution are iron (II), arsenic (III) in the form of H_3AsO_3^0 , sulphur in the oxidized sulphate form, which ensures the conditions for migration of these elements. Only in the case of oxidation of a part of arsenic ($E_h \geq 330$ mV), scorodite appears (it should be reminded that due to the absence of any data for sulphoarsenates, it serves as their conventional prototype). Now the solutions are clearly acidic (pH 1.5–1.3); iron is prevailing in them in the form of Fe^{2+} , FeSO_4^0 , $\text{FeH}_2\text{AsO}_4^+$ even in the case of equilibrium of melanterite with jarosite ($E_h > 560$ mV). This is evidence that the role of such oxidizer as Fe^{3+} is actually very

limited in the pore space of pyrite-rich tailings of the type of Berikul cake. In real associations of zone 2 having the thickness about 1 m, melanterite parageneses vary from above downward from jarosite- to pyrite-containing and include gypsum and amorphous sulphoarsenates. This is an indirect evidence of changes of the parameters of the medium E_h , pH, which is confirmed also by the thermodynamic calculations of equilibrium conditions.

4. Discussing the region of stability of the melanterite association, it is reasonable to pay attention to the saturation of pore water sampled from zone 2 ($E_h = 621$ mV, pH 1.7) with respect to a number of minerals that are present in the database of Wateq4F program [20]. It was discovered that, according to the composition (see Table 2), the pore water is almost equilibrium with respect to melanterite (-0.157), scorodite (+0.814), gypsum (+0.283), Na- and hydroxonium jarosite (-0.246 and +0.721, respectively), anglesite (+1.4) and goethite (+2.5). All the other minerals should get dissolved, judging from the negative values of log SI.

The composition of surface water accumulating near the mound or flowing into the Mokry Berikul River (see Table 2) deserves attention, too. Saturation indices were calculated for three expected variations of conditions E_h –pH. The values measured in the field immediately after collecting water washing the upper horizons of the cakes are presented in

TABLE 5

Logarithms of saturation indices of surface water from the Berikul cakes calculated using the Wateq4F program [20]

Mineral	log SI		
	for $\text{pH}_{\text{aff}}/E_{h \text{ aff}}$		
	1.1/649 mV	1.1/800 mV	7.1/359 mV
Allophane	-0.61	-0.67	0.60* + $\text{Al}(\text{OH})_3$
Anglesite	-0.25*	-0.49*	-0.29*
Goethite	0.68	1.89	12.81
Ferrihydride	-5.22	-4.0	6.91*
Gypsum	-0.48*	-0.84	0*
K-jarosite	-2.37	0.30*	17.7
K-Na-H jarosite (ss)	-3.1	-0.42*	15.72
Melanterite	-1.19	-3.26	-5.98
Quartz	-0.26*	-0.25*	-0.24*
Scorodite	-3.13	-1.92	3.39

*Possible phases controlling the solution composition.

the second column of Table 5. Taking into account the fact that the oxidation-reduction potential may increase with time in the acid surface water to 800–850 mV [10, 35] due to saturation with oxygen in the absence of contact with residual sulphides, the results of calculation for $E_h = 800$ mV and measured pH are presented in the next column. The situation formed during neutralization of drainage by natural water (E_h values and pH for water in the river near the cakes) is depicted in the last column of Table 5.

In the first case (see Table 5, the second column), according to calculation results, acid solutions are supersaturated only with respect to goethite because >80 % of iron remains in solution in the form of Fe(II) and 90 % of arsenic in the form of $H_3AsO_3^0$. A question arises: how can we explain the occurrence of jarosites on the surface of Berikul cakes? First of all, as it was demonstrated in [24, 33], it is necessary to take into account the decelerated kinetics of the process of deposition/dissolution of complex (oxy)sulphates of iron like jarosite; second, the redox potential increases gradually out of the contact with sulphides [10, 35]. Indeed, model calculations at 800 mV (the third column) confirm that under these conditions the composition of the solution will be controlled by the formation of K jarosite ($\log SI = +0.3$) or K–Na–H jarosite ($\log SI = -0.42$). No saturation with respect to any solid arsenic-containing phases was detected. According to the mineralogical and geochemical data, arsenic is present as an admixture in sulphates, in the form of complex soluble sulphoarsenates and in the water-soluble extract from the jarosite horizon. That is why its mobility in solution in the form of arsenate and iron-arsenate complexes, that is, oxy-forms of As(V) is observed.

In the case of the neutral reaction of the medium (pH ~ 7), the solutions are sharply supersaturated with respect to all the phases containing Fe(III) and Al(III). This implies their rapid precipitation, which is indeed observed around the cakes and along the banks of the river. Allophanes include X-ray amorphous compounds which are finely dispersed colloidal products arising most often during the joint coagulation of the gels of $Al(OH)_3$ and $SiO_2 \cdot nH_2O$ [39]. The concentrations of sulphate

and calcium are controlled by the solubility of gypsum. Formally, for scorodite $\log SI \gg 0$, but it is not typed in bold because incongruent dissolution of scorodite at an increase in pH is well known; it is accompanied by the transition of arsenic into solution with the formation of iron (hydr)oxides [27]. So, when the acid sulphate brine, to which the surface water of sulphide-rich wastes may be related, enters the river network, a large amount of amorphous hydroxides of iron, aluminium, silicon get precipitated; this precipitate is able to sorb a large amount of heavy metals. The problem of temporal stability of the compounds of this kind will be discussed by us in a number of subsequent works. However, it should be noted that the concentration of arsenic in the river water near the cakes (see Table 2) remains higher than the MPC values (according to the WHO standards, it is 0.001 mg/l since 1993). This is connected with the fact that adsorption of oxy anions decreases substantially with an increase in pH [40–42], though As(V) is sorbed most actively by soil and pure minerals in comparison with As(III) [43]. Because of this, it is reasonable to introduce an excess of iron (hydr)oxides for additional purification of solutions from arsenic.

DISCUSSION

To reveal the physicochemical parameters of the process of oxidation of the wastes from sulphide ore concentrating, we used various approaches of thermodynamic modelling. This allowed us to characterize the conditions of stability of different associations of secondary minerals and the composition of the corresponding equilibrium solutions. Substantial similarity in the compositions of real and model systems is due to the fact that it is determined by the equilibrium of solutions with secondary phases, while the absolute equilibrium in the system primary minerals–surface water of hypergenesis zones can hardly be reached during the technogenic time (sulphide residues are present in the upper horizons of piled wastes even after storing for 50 years). Each of the four modelling methods applied in the present work was useful for understanding of separate features

of chemical decomposition process. For example, the method of reaction degree in an open system allowed us to obtain associations of efflorescences with copyapite observed on the surface of cakes. At the same time, it became possible to characterize the internal zoning of the sulphide-containing mound only when we took into account oxygen absorption for sulphide oxidation under the conditions of the limited access of oxygen to deeper lying horizons (the method of flow reactors). However, using the method of flow reactors which allows us to observe the growth of the melanterite zone 2, it is impossible to achieve the conditions of equilibrium of melanterite with jarosite because the formation of the latter is accompanied by a sharp jump of E_h , pH and the disappearance of melanterite. Only in the system which is open with respect to oxygen as suggested by the measured E_h in the water of test objects, and under the fixed ratio $R/W = 0.1$, the exchange of parageneses from pyrite-melanterite to melanterite-jarosite one was obtained as it occurs at the object under investigation.

Calculations showed that the role of several stages of the development of the technogenic system under the action of oxidizing atmospheric factors (active gas components, natural precipitation) is essential. At the first stage, due to the large amount of pyrite and the presence of carbonates, intensive oxidation of sulphide and the transport of iron and sulphate ions into the acid solution occur (1). These processes are promoted also by the absorption of protons due to the conjugated rapid dissolution of calcite accompanying by rapid precipitation of gypsum. In general, the system is characterized by weakly oxidative conditions ($E_h \leq 0$) and alkaline or nearly neutral medium (pH ≥ 6). Iron (II) is prevailing in solution; iron (III) gets precipitated in the case of high concentrations of K^+ and SO_4^{2-} in the form of jarosite (4). According to the data reported in [44], at pH > 5 the expression for the rate of Fe^{2+} oxidation to Fe^{3+} exhibits the square dependence on the concentration of OH^- ions in solution, so the conditions for the formation of gypsum-cemented horizon (zone 3) are created; it goes down with time.

At the second stage, incongruent dissolution of aluminosilicates starts; the solid phase contains clayish minerals, sulphides but does not contain carbonates. Accumulation of aluminium in solution, including its stable sulphate complexes, leads to the appearance of alunite, gibbsite in the association (11). Moderately oxidative conditions ($E_h = (0.1 \pm 0.1)$ mV) and weakly acidic reaction of the medium (pH 3–6) promote accumulation of arsenic and iron in the lowest oxidation degree in solutions; aqueous ferrous sulphate – melanterite – appears (zone 2). One can see in Fig. 3 that a broad field of stability is characteristic of melanterite both in association with pyrite and with ferric sulphates and arsenates. This agrees with the data of mineralogical observations at the object.

The third stage of acid leaching at $E_h > 600$ mV and pH ~ 1 is distinguished by the stability of the quartz-jarosite-gypsum association (with anglesite). For this to occur, judging from the data shown in Table 4, 10 to 100 water volumes are to flow through the porous space of the primary rock. The amount of precipitation at the territory under investigation is 600 mm/year; dripping rate is about 10^{-8} – 10^{-6} m/s (0.3–30 m/year) according to the data of different authors (Table 6). Taking into account average density and porosity of the technogenic rocks shown in Table 6, this mode of water exchange in the upper 20–40 cm of mound is very probable within the past 50 years. It is acidic oxidative water of all the types that is characteristic of the Berikul cakes today (see Table 2). On the basis of these preliminary calculations, it may be assumed that the fourth stage (a decrease in the acidity of solutions and the development of a stable quartz-goethite association) may be expected after 100 years more. It should be noted that jarosite is only an intermediate product corresponding to some steady state of the system. Moreover, as it was demonstrated in [45], it serves as an indicator of the oxidation process under the conditions of limited access of water. The final products of chemical decomposition in equilibrium with atmospheric water saturated with oxygen are (hydr)oxides and iron and aluminium as demonstrated by calculations with high R/W .

TABLE 6

Physical parameters used by different authors when building up the hydrochemical models in the dripping zone (above the level of ground water)

Parameter	References			
	[47]	[9]	[10]	[19, 46]
Flow rate (q), m/s	$1.6 \cdot 10^{-8}$	$1.35 \cdot 10^{-8}$	$1.5 \cdot 10^{-6}$	$9 \cdot 10^{-9}$ – $1.4 \cdot 10^{-5}$
Porosity (v), %	35	25	44	40–50
Density (ρ), kg/m ³	2800	2475	–	–
Water content (θ), %	0.05	0.15	–	0.3–0.2

CONCLUSIONS

1. Thermodynamic model of the oxidative leaching of sulphide-rich wastes from ore concentrating stores as mounds is composed; the model is verified for Barikul cakes as an example.

2. The use of the consistent thermodynamic database and different approaches to modeling (taking into account the degree of reaction progress and the system of consecutive flow reactors) promoting revelation of the features of oxidation processes in the ore-rock association allowed us to provide a quantitative characterization of the determined dependence of zoning of the formed mineral parageneses on the parameters of the medium E_h , pH and the composition of solutions.

3. The stages of the development of technogenic systems of this kind were substantiated: oxidation of primary sulphides and neutralization of the solutions by carbonates present in the system ($E_h \leq 0$, pH ≥ 6); dissolution of aluminosilicates, appearance of alunite, gibbsite in the solid phase, aqueous ferrous sulphates at $E_h = (0.1 \pm 0.1)$ mV and pH 3–6; formation of acid oxidative solutions ($E_h > 600$ mV, pH ~ 1) in equilibrium with ferric, calcium and lead sulphates. A series of chemical reactions was proposed resulting in possible formation of sulphates and (hydr)oxides characteristic of oxidized (jarosite-quartz-gypsum), transient (melanterite) and weakly oxidized sulphide zones cemented with gypsum.

4. On the basis of preliminary estimations, it was concluded that hypergenesis processes at the objects of this kind may proceed during hundreds of years until complete depletion of the acid-producing and toxic potential of the technogenic wastes.

REFERENCES

- 1 M. Sato, *Econ. Geol.*, 55 (1960) 1202.
- 2 L. C. Bryner, R. B. Walker and R. Palmer, *Transact. Soc. Mining Eng.*, 238 (1967) 56.
- 3 D. K. Nordstrom, E. A. Jenne and J. W. Ball, in: *Chemical Modeling in Aqueous Systems*, in E. A. Jenne (Ed.), Am. Chem. Soc. Symp. Series 93, Washington, 1979, p. 51.
- 4 C. O. Moses, D. K. Nordstrom, J. S. Herman and A. L. Mills, *Geochim. Cosmochim. Acta*, 51 (1987) 1561.
- 5 D. K. Nordstrom, C. N. Alpers, *Proc. Nat. Acad. Sci. USA*, 96 (1999) 3455.
- 6 J. L. Jambor, D. W. Blowes (Eds.), in: *Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes*, Mineralogical Association of Canada, Toronto, 1994, vol. 22.
- 7 J. L. Jambor, D. W. Blowes, in: *Modern Approaches to Ore and Environmental Mineralogy*, in L. J. Cabri and D. J. Vaughan (Eds.), Mineralogical Association of Canada, Short Course, Toronto, 1998, vol. 27, pp. 367–402.
- 8 A. D. Paktunc, in: *Environmental Impacts of Mining Activities – Emphasis on Mitigation and Remedial Measures*, in J. M. Azcue (Ed.), Springer-Verlag, 1999, ch. 3, p. 19.
- 9 S. U. Salmon, M. E. Malmstrom, *Appl. Geochem.*, 19 (2004) 1.
- 10 M. C. Moncur, C. J. Ptacek, D. W. Blowes and J. L. Jambor, *Ibid.*, 20 (2005) 639.
- 11 G. R. Kolonin, O. L. Gaskova, K. G. Morgunov, *Geokhim.*, 2 (1999) 181.
- 12 S. B. Bortnikova, *Geokhimiya tyazhelykh metallov v tekhnogennykh sistemakh. Voprosy formirovaniya, razvitiya i vzaimodeystviya s komponentami ekosfery* (Doctoral Dissertation in Geology and Mineralogy), Novosibirsk, 2001.
- 13 O. L. Gaskova, *Geokhimicheskiye osobennosti i fiziko-khimicheskiye parametry gipergennykh protsessov v zonakh tekhnogeneza* (Doctoral Dissertation in Geology and Mineralogy), Novosibirsk, 2005.
- 14 R. Giere, N. V. Sidenko, E. V. Lazareva, *Appl. Geochem.*, 18 (2003) 1347.
- 15 Yu. G. Shcherbakov, N. V. Roslyakova, II Konf. po izucheniyu mestorozhdeniy zolota Sibiri (Proceedings), Izd-vo Tom. Un-ta, Tomsk, 1970, p. 298.
- 16 N. V. Sidenko, *Migratsiya tyazhelykh metallov i mysh'yaka v zone gipergeneza sulfidnykh otkhodov Berikul'skogo zolotodobyvayushchego zavoda* (Author's Abstract of Candidate's Dissertation in Geology and Mineralogy), Novosibirsk, 2001.
- 17 Yu. V. Shvarov, *Geokhim.*, 6 (1999) 646.

- 18 B. N. Ryzhenko, S. R. Kraynov, *Ibid.*, 10 (2001) 1052.
- 19 D. W. Blowes, J. L. Jambor, *Appl. Geochem.*, 5 (1990) 327.
- 20 J. W. Ball, D. K. Nordstrom, User's Manual for Wateq4F, with Revised Thermodynamic Database, U.S. Geological Survey, Menlo Park, California, 1991.
- 21 B. S. Hemingway, R. R. Seal and I-Ming Chou, Thermodynamic Data for Modeling Acid Mine Drainage Problems: Compilation and Estimation of Data for Selected Soluble Iron-Sulfate Minerals, Open-File Report 02-161 of United States Department of the Interior US Geological Survey, 2002.
- 22 I-Ming Chou, R. R. Seal and B. S. Hemingway, *Am. Miner.*, 87 (2002) 108.
- 23 G. B. Naumov, B. N. Ryzhenko, I. L. Khodakovskiy, Spravochnik termodinamicheskikh velichin (dlya geologov), Atomizdat, Moscow, 1971.
- 24 D. Baron, C. D. Palmer, *Geochim. Cosmochim. Acta*, 60 (1996) 185.
- 25 E. Krause, Y. A. Ettl, *Am. Miner.*, 73 (1988) 850.
- 26 K. S. Whiting, The Thermodynamic and Geochemistry of Arsenic, with Application to Subsurface Waters at the Sharon Steel Superfund Site at Midvale, Utah, Thesis of Master's – Colorado School of Mines, Golden, Co., T-4128, 1992.
- 27 O. L. Gaskova, M. Azaroual and P. Piantone, Arsenic Behavior in Subsurface Hydrogeochemical Systems – A Critical Review of Thermodynamic Data for Minerals and Aqueous Species of Arsenic, BRGM Report R40629, France, 1999.
- 28 L. K. Yakhontova, A. P. Grudev, Zona gipergeneza rudnykh mestorozhdeniy, Izd-vo MGU, Moscow, 1978.
- 29 P. C. Singer, W. Stumm, *Science*, 167 (1970) 1121.
- 30 J. A. Cherry, A. U. Shaikh, D. E. Tallman and R. V. Nicholson, *J. Hydrology*, 43 (1979) 373.
- 31 D. Craw, D. Falconer and J. H. Youngson, *Chem. Geol.*, 199 (2003) 71.
- 32 U. Schwertmann, J. M. Bigham and E. Murad, *Eur. J. Mineral.*, 7 (1995) 547.
- 33 J. Jonsson, P. Persson, L. Lovgren, *Appl. Geochem.*, 20 (2005) 179.
- 34 G. R. Kolonin, O. L. Gaskova, in: Informatsionnye materialy po teme "Osnovnye problemy okhrany geologicheskoy sredy", in V. P. Parnachev (Ed.), Izd-vo Tom. Un-ta, Tomsk, 1995, p. 82.
- 35 S. R. Kraynov, B. N. Ryzhenko, *Geokhim.*, 4 (1992) 467.
- 36 D. K. Nordstrom, Proceedings of the Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Environmental Protection Agency, EPA/600/R-02, 2000, p. 43.
- 37 J. S. Espana, E. L. Pamo, E. Santofimia *et al.*, *Appl. Geochem.*, 20 (2005) 1320.
- 38 B. M. Petrunic, T. A. Al, *Geochim. Cosmochim. Acta*, 69 (2005) 2469.
- 39 A. A. Godovikov, Mineralogiya, Nedra, Moscow, 1975.
- 40 R. G. Howell, *Appl. Geochem.*, 9 (1994) 279.
- 41 O. L. Gaskova, S. B. Bortnikova, A. A. Ayriyants, *Geokhim.*, 3 (2000) 317.
- 42 O. L. Gaskova, S. B. Bortnikova, E. P. Bessonova, *Poverkhnost'*, 12 (2003) 56.
- 43 K. P. Raven, A. Jain and R. H. Loeppert, *Environ. Sci. Technol.*, 32 (1998) 344.
- 44 R. T. Lowson, *Chem. Rev.*, 82 (1982) 461.
- 45 M. E. E. Madden, R. J. Bodnar and J. D. Rimstidt, *Nature*, 431 (2004), 821.
- 46 D. W. Blowes, E. J. Reardon, J. L. Jambor and J. A. Cherry, *Geochim. Cosmochim. Acta*, 55 (1991) 965.
- 47 B. Stromberg, S. Banwart, *Appl. Geochem.*, 9 (1994) 583.