Chemistry for Sustainable Development **14** (2006) 379–388

Study of Water Interaction with High-Sulphide Waste Products from Karabash Copper-Smelting Combine (Chelyabinsk Region)

N. V. OZHERELYEVA and S. B. BORTNIKOVA

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

E-mail: sveta@uiggm.nsc.ru

(Received November 10, 2005; revised April 4, 2006)

Abstract

Natural experiment with underground draining of high-sulphide waste products from Karabash Copper-Smelting Combine (Chelyabinsk Region) by natural neutral water has been performed. An oxyntic potential and a quantity of Cu, Zn, and Fe that passed into solution has been determined; a change in fractional distribution of chemical forms of these elements in the solution and in saturation indexes of mineral phases with an increase in the water/rock ratio (W/R) during the course of the experiment has been calculated. It has been demonstrated that interaction of natural neutral water with the material of waste products yields acids and results in that more than 50 % Cu and Zn, and about 30 % Fe passes into solution to yield the ratio W/R = 400 : 1. It has been observed that at low W/R ratios in acidic medium, copper and zinc exist in the form of sulphate neutral complexes and activated ions, and zinc additionally forms an anionic sulphate complex. As washing of acid proceeds, the fraction of sulphate complexes decreases; the metals remain preferentially in the form of aqua ions. Iron that exists in the solution predominantly in a sulphate complex during the beginning of the experiment then changes to a hydroxide form. Processes of dissolution and deposition of mineral phases actively proceed during the experiment. Ferrihydrite $Fe(OH)_3$ and goethite FeOOH that are produced by the end of the experiment facilitate sorption and coprecipitation of copper and zinc. Formation of a secondary sulphate, jarosite $KFe_3(SO_4)_2(OH)_6$, during the experiment is confirmed by data of X-ray crystal analysis.

INTRODUCTION

Sulphide-containing waste products from ore beneficiation attract the attention of researchers, for they represent a source of environmental pollution and simultaneously technogenic deposits [1–3]. Studying transformation processes of sulphide material, as well as regularities in leaching of most toxic elements and their migration with aqueous flows, has the purpose to obtain a prospective quantitative estimation for the hazard of waste products from mining production. Basic directions of the research in this field are an experimental investigation of sulphide oxidation kinetics [4–7], a determination of migration speciations for toxic elements and their influence on the environment [8–11], and an assessment of acidic drainage flow that takes metals away from waste product reservoirs [12–15].

Performing natural experiments into underground draining of waste products by natural water represents an important stage during the estimation of hazard for waste products and during the determination of migration speciations of toxic elements depending on the degree of sulphide substance interaction with natural oxidizers. Experimental simulation of transformation processes for a technogenic system is restricted by its complex composition (elevated and contrast contents of micro- and macroelements, a great amount of secondary compounds); therefore, the quantitative thermodynamic computation is needed to be conducted [16, 17]. A combination of field approbation with the newest analytical methods of the analysis, of natural experiments with physicochemical simulation, makes it possible to obtain most integrated estimate of the potential danger of the waste products, of the mobility, and migration speciations of toxic elements.

The purpose of this work is to construct a model of interaction of sulphide-containing waste products with natural water on the basis of natural and numerical experiments. With this purpose, an oxyntic potential has been determined during the natural experiment, and based on thermodynamic simulation data, chemical forms of elements have been determined at different stages of the interaction of waste products with natural water.

OBJECTS OF THE INVESTIGATION

Waste products of Karabash Copper-Smelting Combine (KCSC) (South Ural, Chelyabinsk Region) are characterized by a high content of sulphides, for the most part pyrite FeS_2 (up to 25 mass %), yellow copper ore $CuFeS_2$ (up to 3 mass %), and up to 1 mass % of blende ZnS and galena PbS.

From 1910 until 1958, the tails from floatation dressing of complex (Cu, Zn, Pb, Ag, and Au) ores, preferentially from Karabash deposit, were discharged into the channel of the Sak-Yelga River (Fig. 1). As a consequence of this, a technogenic deposit 2.1–2.5 km^2 in area and from 0.3 to 2.0 m thick [18] has been formed there, approximately 3 km long. During the fluid wash of the river walls, sulphate efflorescences are formed on the surface of the river section. During a freshet period and storm rains, the sulphates intensively dissolve and drift into Sak-Yelga, Miass Rivers, and further into Argazinskoye Reservoir. Since the middle of the past century, the waste material is stored in tailing ponds “Novoye” and “Starogodnyeye”, each containing up to 5 million ton of waste products from dressing.

The drainage flow from storage sites for the waste products of the integrated works is characterized by acid reaction of the medium (pH 2.2), by higher than usual mineralization, and

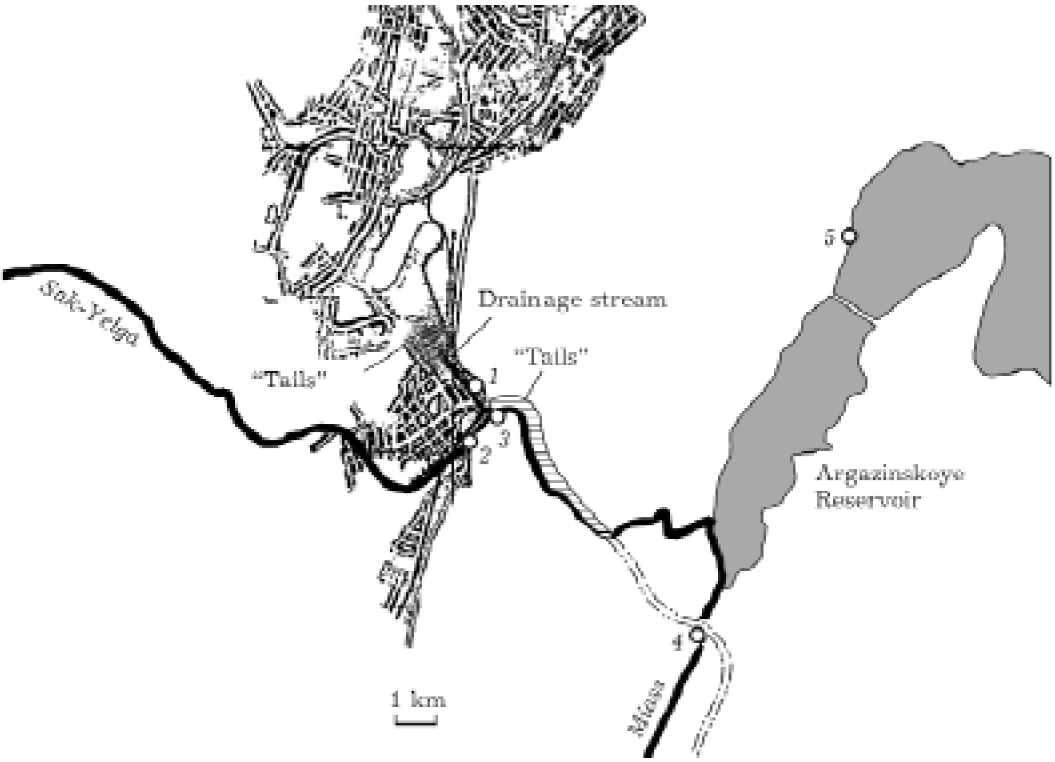

Fig. 1. Schema of sample drawing in the area of Karabash Copper-Smelting Combine: *1* – a drainage stream, *2*, *3* – the Sak-Yelga River before *(2)* and after *(3)* it merges with the drainage, *4* – the Miass River (a background point), *5* – Argazinskoye reservoir.

TABLE 1

Composition of the drainage stream that flows out of the waste product reservoir of Karabash Copper-Smelting Combine

Sample	SO_4^{2-}	Fe	Zn	Cu	Cd
Drainage solution	8100	530	16	11	0.12
MPC*	500	0.3–1	1.0	1.0	0.001
Background value**	52	0.16	0.05	0.02	0.001

*Maximum concentration limits for chemicals in the water of water bodies for household water use and amenity water needs (Hygienic standards HS 2.1.5.1315–03).

**A sample from the Miass River, 11 km far from the point of the drainage confluence into the Sak-Yelga River (see Fig. 1) has been taken as the background point.

as regards its basic ionic composition, it falls into sulphate class, calcium-magnesium type:

$$M_{9.5}\,\frac{SO_4^{2-}\,98.7Cl^{-}\,1.3}{Mg^{2+}\,77.2Ca^{2+}\,22.1Na^{+}\,0.67}\,\text{pH } 2.2$$

The background water body (the Miass River, see Fig. 1) is typified by hydrocarbonaceous calcium-magnesium mineralization type, and the total content of salts comprises 350 mg/l, which is 30 times less than in the technogenic stream.

Concentrations of iron, cadmium, zinc, and copper in the drainage stream are over the maximum concentration limits for the water of water bodies by 1800–530, 120, 16, and 11 times, respectively. The content of sulphate-ions 16 times exceeds the maximum concentration limit for water bodies (Table 1).

Due to intensive accumulation, a content of metals in ground deposits of the Sak-Yelga River and in the drainage stream that runs into it is comparable with that in the waste product material and it comprises on the average (g/t): Fe 10 000, Cu 590, Zn 510, Pb 220, Cd 3.8. Superficial waters of the river, especially the sludge solutions, show a high level of the above elements that exceed the MPC by 2–3 orders of the magnitude.

RESEARCH METHODS

A proportionated sample of the material of KCSC waste products (10 kg) was taken on a wall of Sak-Yelga River in 2004 (see Fig. 1) from the area of ~1 m^2, since the greatest quantity of contaminants is taken down into the river by seasonal streams exactly from the walls.

A sample was dried, carefully homogenised, and quartered. A portion (200 g) of the substance was enclosed in a double polyethylene package to transport into a laboratory and to assay for the content of macro and trace elements; 700 g of waste products were kept to carry out a field experiment.

A set-up that has been made to carry out these field experiments was used to pass water from Kialimskoye Reservoir through the sample (700 g) at a rate of 13–15 l/h. The pH was measured and the samples of experimental solutions were drawn for the subsequent assay for the content of metals, of sulphate, chloride, and hydrocarbonate ions upon the lapse of time terms that corresponded to W/R that were equal to 10, 70, 150, 240, 350, 400.

The hydrogen ionisation value was determined by the method of direct potentiometry with the use of a combined glass pH-electrode and a portable device of HANNA Corporation.

Samples of the outlet stream were filtered by means of a “dark blue belt” filter, were acidified with the concentrated nitric acid, and enclosed in plastic containers of capacity 50 ml to perform the laboratory analysis for the content of trace elements. Special plastic containers of capacity 500 ml were used to draw the same samples for an assay for the content of sulphate, chloride, and hydrocarbonate ions.

Concentrations of metals in aqueous samples were determined by the method of atomic emission spectrometry in an Analytical Centre of Institute of Geology and Mineralogy, SB RAS. The measurement error was as large as ±10 %.

A content of sulphate ion was determined by the turbidimetric method following a standard procedure (RD 52.24.405–95). The norm of error was ±10 %. A concentration of chloride ion was determined by a titrimetric method with silver salt; that of hydrocarbonate ion, by the procedure of titration with muriatic acid (RD-5.3.04–96). Norms of the instrumental errors were as large as ±(20–25) %.

Samples of the mother substance of the waste products and of the material that has been obtained after performing the experiment were dried, carefully homogenised, and quartered.

The dried and quartered substance of the waste products that has been taken for the experiment and the material that has been obtained after performing the experiment were grinded to reach the size less than 0.1 mm and a representative sample was taken, from which a shot of 30 mg was taken. A portion of a powder was pressed at a pressure of 100 kg/cm^2 to form tablets of diameter 10 mm. A content of elements was determined with the use of XRD-SI [19, 20] at a VEPP-3 station of the Institute of Nuclear Physics, SB RAS. Measurements were conducted with the activation energy that was equal to 30 keV, with the use of a method of internal standards. Processing of the emission spectra was conducted by means of the AXIL code. Standard samples RUS-1 (copper-zinc ore ST SEV 2028–79), RUS-2 (copper-pyrite ore ST SEV 2029–79), RUS-3 (copper-zinc ore 793–76), and RUS-4 (copper-zinc ore 794–76) [21] were chosen as reference stan-

TABLE 2

Variation in the basic ionic composition and in the content of metals of the outlet stream in the course of the interaction of waste product substance with natural water

Parameter	Sample						
	Ref.	T1	T2	T3	T4	T5	T6
Time, h	0	0.5	3.5	7.5	12	20	22
Volume of the passed water, l	0	8	48	104	168	248	280
Water/rock ratio	–	10/1	70/1	150/1	240/1	350/1	400/1
Flow rate, l/h	–	20	20	20	20	18	17
Filtration coefficient, m/h	–	3.8	3.8	3.8	3.8	4.4	4.4
pH	6.54	2.04	2.54	2.88	3.07	3.57	4.00
E_h, mV	400	750	710	700	590	580	530
			Content, mg/l				
Ca	11	22	134	11	23	10	8.2
Mg	3.0	36	8.9	5.4	13	4.7	3.2
Na	1.8	0.30	1.1	1.1	1.1	1.1	0.80
K	0.8	2.3	2.4	2.2	2.6	2.2	2.2
SO_4^{2-}	34	7500	1300	540	560	350	88
Cl^-	2.8	0.46	1.8	1.7	1.7	1.8	1.3
HCO_3^-	200	n/d	n/d	n/d	n/d	n/d	n/d
Al	0.1	29	4.4	1.9	1.2	0.7	0.3
Si	4.1	4.2	4.1	4.1	4.5	4.1	4.1
Fe	0.2	520	43	16	9.8	6.2	2.9
Zn	0.030	2.1	0.41	0.23	0.33	0.11	0.080
Cu	0.003	2.2	0.51	0.29	0.21	0.14	0.12

Note. Ref. – the initial natural water that was taken to perform the experiment; T1–T6 – sampling points in the experiment; n/d – not detected.

dards for the substance of the tails. The elemental determination sensitivity on the basis of SI was 0.1 g/t, the method error was 15–20 %.

Phase composition of samples was determined by means of X-ray crystal analysis in a DRON-3 device.

Forms of metals at various stages of interaction of natural water with the substance of waste products were determined from results of numerical simulation by means of the WATEQ4F code [22] that is intended to reveal forms of elements in a solution and to calculate the saturation index of various mineral phases in natural low-temperature waters. The WATEQ4F database contains a description of ~300 minerals and 400 components in a solution. Results of the analysis of experimental waters (the content of micro- and macroelements, the temperature, pH and E_h of the medium) were used as the initial information during the computations.

RESULTS AND DISCUSSION

Experimental data

In consequence of non-uniform distribution of the substance during its stacking and its further transformations, zonal distribution of the waste product material can be readily noted on the walls of the pit-hole. Oxidation and dissolution of Zn, Fe, Cu, and Pb sulphide minerals with the formation of secondary compounds has been visually registered by the arising bright-red iron hydroxides. The degree of colouring of a bed gives an indication of the intensity of the transformation processes for the given substance. The mixed sample of waste products that were taken to carry out the experiment is made up of a grey close-grained material with brown hardpans from organic matter and with a high content of sulphides (the sampling depth of 0–40 cm) and a medium-grained material from the black (40–50 cm), the brown (60–70 cm) and the most oxidized, red (70–100 cm) horizon. The grey wall is covered from above by yellow crusts of sulphate efflorescences. The content of iron in various beds of the pit-hole varies within the limits of 5.7–13 %, that of zinc and copper, 200–1000 g/t, that of lead, 110–290 g/t, and that of cadmium, 2–8 g/t.

The waste product substance that was selected to carry out the experiment from the wall of the Sak-Yelga River in two points on the depths of 0–100 cm from the surface represents a short-grained oxidized material with a high content of heavy metals, predominantly iron (up to 8 %), copper (400 g/t), and zinc (300 g/t).

Mineral phases of the waste product substance that was selected for the experiment are mainly represented by pyrite, quartz, plagioclase (among the macrocomponents) and by secondary basic sulphates: jarosite $NaFe_3(SO_4)_2(OH)_6$, magnesiocopiapite $MgFe_4(SO_4)(OH)_2 \times 20H_2O$, and aluminocopiapite $(Mg,Al)(Fe,Al)_4(SO_4)_6(OH)_2 \times 20H_2O$.

Water from Kialimskoye Reservoir (Chelyabinsk Region, Karabash District), that interacts with the waste product substance during

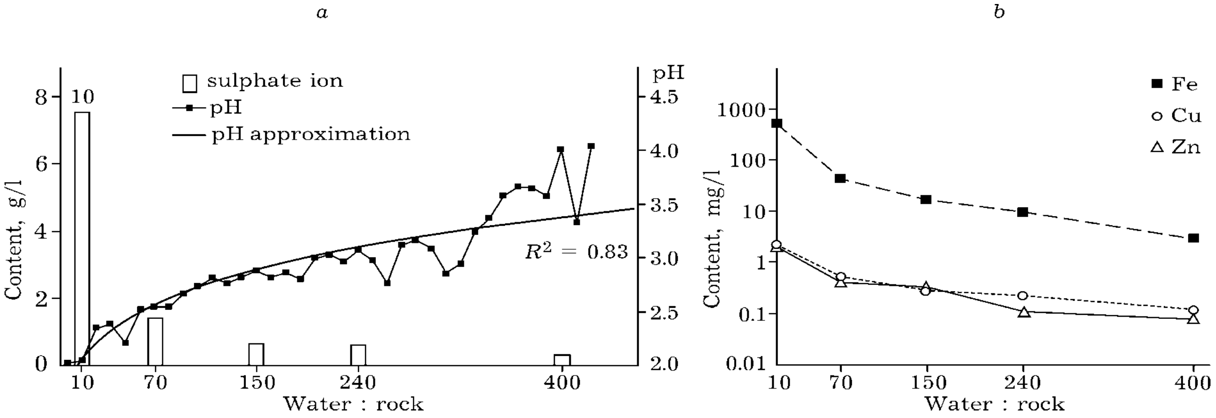

Fig. 2. Variation in pH and in the content of sulphate ion (*a*) and metals (*b*) in the solution during the experiment.

TABLE 3

Elemental content of the waste product substance before (TVV-2) and after (EP-1) the leaching experiment, g/t

Sample	Ca	K	Fe	Cu	Zn	Cd	Pb
TVV-2	3800	3400	78 000	400	380	3.7	270
EP-1	5100	5300	56 000	110	160	2.9	180

the experiment, according to O. A. Alekin's [23] classification, falls into neutral fresh hydrocarbonaceous waters of magnesium-calcium type (Table 2). The contents of copper, zinc, and iron are comparable with the MPC for water of water bodies.

A solution that is characterized by W/R = 10 : 1 is formed after 32 min lapse from the start of passing the flow of natural water through a bed of waste product substance at the rate of 13.3 l/h and with the filtration coefficient of 3.8 m/h. The hydrogen ionization value of the solution is 2.04; the macrocations are dominated by iron (III), calcium (II), and magnesium (II). SO_4^{2-} is the main anion; its content ranges up to 7500 mg/l (see Table 2).

As water passes through the waste product substance with the rate and the filtration coefficient that were set up in the beginning of the experiment, the pH of the outlet portions of the solutions increases, and the content of sulphate-ion and metals drops (Fig. 2).

By the end of experiment, the water flow rate has dropped down to 17–18 l/h, the filtration coefficient was equal to 3.5 m/h, the pH of the solution at the reactor outlet at W/R = 350 : 1 was equal to 3.57. The content of sulphate ion, copper, zinc, and iron in the solution has dropped considerably as compared to the initial portions of the solution. Upon 280 l of natural water passed through the sulphide material (W/R = 400 : 1), a pH of 4.0 has been fixed; the content of sulphate ion was at a level of its content in natural water. Concentrations of zinc, iron, and copper exceed those in water of Kialimskoye Reservoir by 2.5, 14.5, and 40 times, respectively (see Table 2). The main cations are Ca^{2+}, Mg^{2+}; anions are dominated by SO_4^{2-}.

Content of Fe, Cu, Zn in the waste product substance decreases by the end of the experiment by 1.4, 2.1, 2.6 times, respectively, as compared to the initial one (Table 3); 28 % Fe, 73 % Cu, 58 % Zn passes from the material of tails into water solution. According to X-ray diffraction analysis, quartz, clay minerals, and aluminosilicates of Na, Mg, Fe comprise the main part of solid matter in the column after the experiment. Sulphates are represented in the material by gypsum and jarosite; no sulphides were found.

Simulation results

Water of Kialimskoye Reservoir contains copper and zinc preferentially in carbonate, hydrocarbonate, and ionic forms. Main part of iron is represented by $Fe(OH)_2^+$ and $Fe(OH)_3^0$ type hydroxocomplexes, the fraction of which amounts to 70.3 and 29.5 %, respectively, from the total content. The remaining 0.2 % fall on $FeOH^{2+}$ and $Fe(OH)_4^-$.

The first portions of a solution that is formed upon the interaction with sulphide waste products contain iron in the oxidized trivalent form. $FeSO_4^+$ and $Fe(SO_4)_2^-$ sulphate complexes prevail over Fe^{3+} ionic form (Fig. 3, *a*). There is also hydrosulphate $FeHSO_4^{2+}$ and a minor amount of $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ hydroxide complexes. Copper and zinc are present in the form of $CuSO_4^0$(aq.) and $ZnSO_4^0$(aq.) aquated neutral sulphate complexes and in the free ionic form. Zinc also forms a negatively charged $Zn(SO_4)_2^{2-}$ complex (see Fig. 3, *a*).

When the natural water : waste products ratios are equal to 70/1, 150/1, 240/1, the fraction of Fe^{3+} free ion does not exceed 5 % from the total content of all iron compounds; $FeSO_4^+$ remains the predominant form, the fraction of $Fe(SO_4)_2^-$ and $FeHSO_4^+$ considerably drops, the contribution of $FeOH^{2+}$ hydroxide complex and the content of $Fe_2(OH)_2^{4+}$ increase (see Fig. 3, *b–d*). At W/R = 70 : 1, a $Fe(OH)_2^+$ hydroxocomplex appears, the content of which grows as it interacts with water. Copper and zinc are present in the solution within sulphate complex-

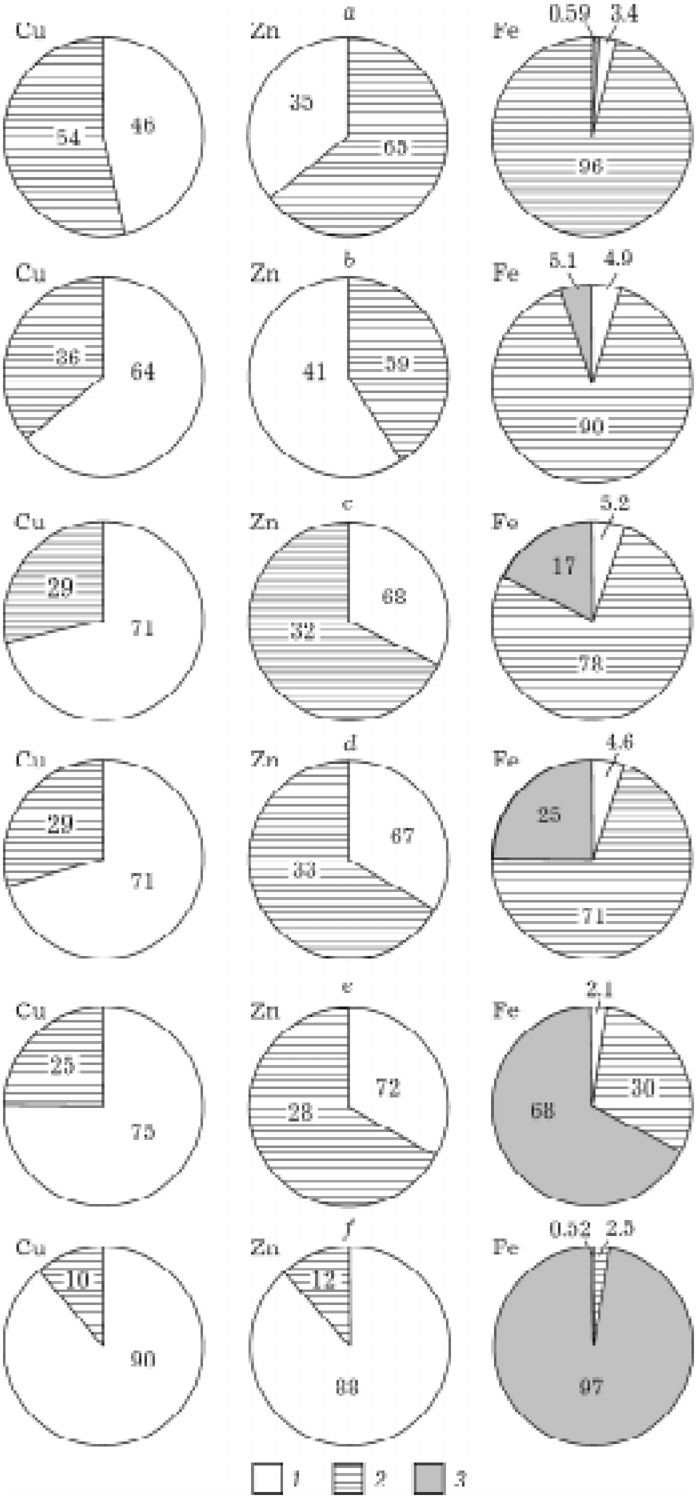

Fig. 3. Modification of chemical forms of metals that are present in the solution at the stages of the experiment (in %), these forms corresponding to the water : rock ratios equal to 10 : 1 (*a*), 70 : 1 (*b*), 150 : 1 (*c*), 240 : 1 (*d*), 350 : 1 (*e*), 400 : 1 (*f*): *1* – aquo ions, *2*, *3* – sulphate and hydroxide complexes, respectively.

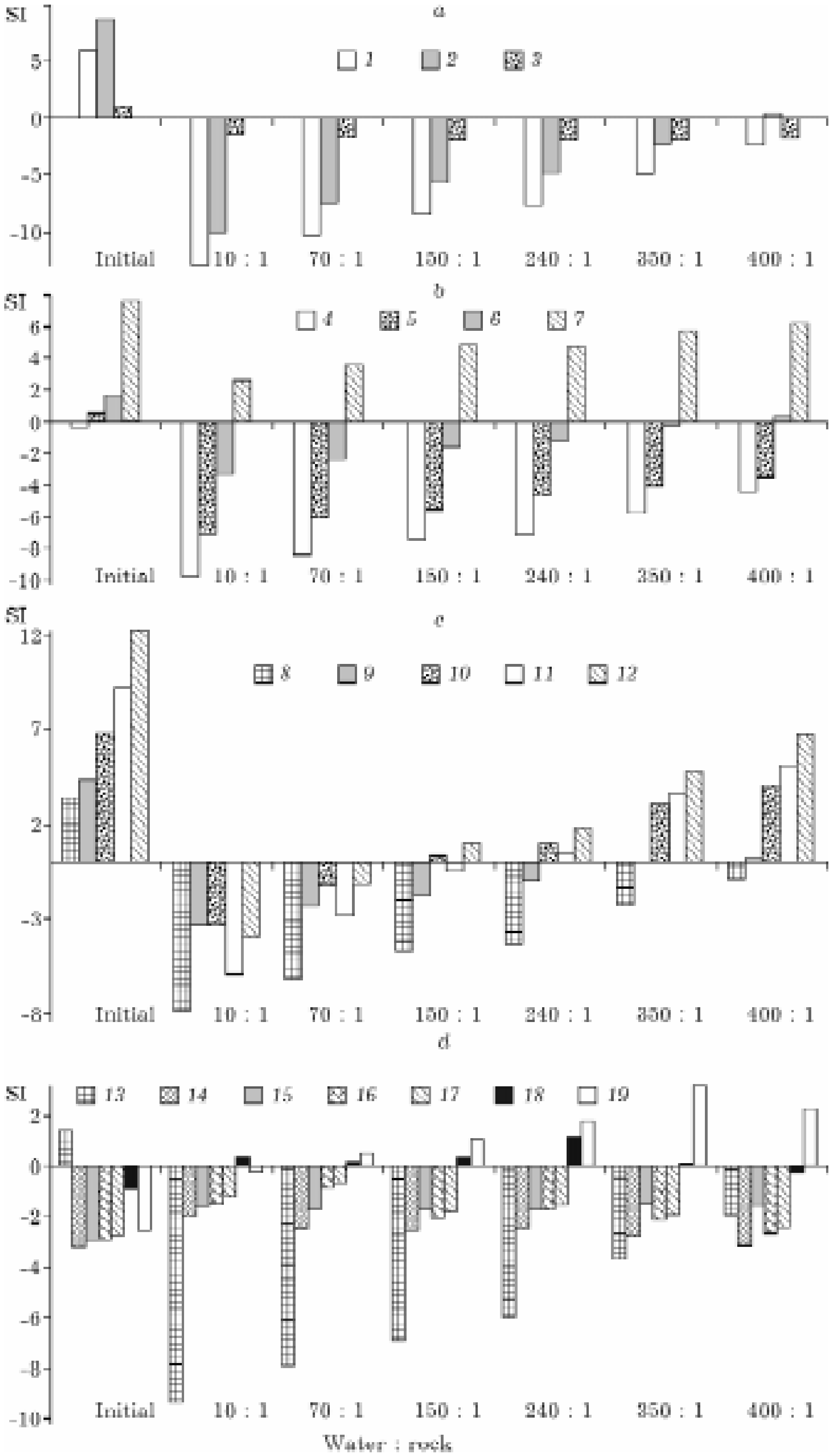

Fig. 4. Equilibrium composition of silica-alumina (*a*), hydroxide (*b*), oxidic (*c*), and sulphate phases (*d*) in initial natural water and in solutions during the course of the experiment (water : rock = 10 : 1–400 : 1): *1* – kaolinite $Al_2Si_2O_5(OH)_4$, *2* – pyrophyllite $Al_2Si_4O_{10}(OH)_2$, *3* – allophane $[Al(OH)_3]_{1-x}[SiO_2]_x$, *4* – oxyhydroxides of aluminium (III), *5* – manganite MnOOH, 6 – ferrihydrite $Fe(OH)_3$, 7 – goethite FeOOH, *8* – cuproferrite $CuFeO_2$, 9 – oxides of manganese MnO_2, *10* – maghemite Fe_2O_3, *11* – magnetite Fe_3O_4, *12* – cupriferrite $CuFe_2O_4$, *13* – rock alum $KAl(SO_4)_2(OH)_6$, *14* – celestine $SrSO_4$, *15* – urbanite $AlOHSO_4$, *16* – gypsum $CaSO_4 \times 2H_2O$, *17* – anhydrite $CaSO_4$, *18* – barite $BaSO_4$, *19* – jarosite $KFe_3(SO_4)_2(OH)_6$.

es and in the free ionic form; in so doing, the fractions of Cu^{2+} and Zn^{2+} grow during the experiment, whereas those of $CuSO_4^0$(aq.) and $ZnSO_4^0$(aq.) drop. The contribution of $Zn(SO_4)_2^{2-}$ also decreases.

By the end of the experiment, iron is represented in the solution for the most part by hydroxide complexes $Fe(OH)_2^+$ and $FeOH^{2+}$ (see Fig. 3, *e, f*). At W/R = 400 : 1, a $Fe(OH)_3^0$ neutral complex appears (see Fig. 3, *f*). The fraction of $FeSO_4^+$ and $Fe(SO_4)_2^-$ sulphate forms drops by the end of the experiment to reach 3 and 0.04 %, respectively; the fraction of Fe^{3+} comprises 0.5 % from the content of all iron compounds. Copper and zinc are present in the solution for the most part in the free ionic form. Fractions of $CuSO_4^0$ and $ZnSO_4^0$ drop to 10.2 and 11.5 %, respectively, from the content of all compounds of copper and zinc (see Fig. 3, *e, f*).

During the experiment, the solutions that correspond to various W/R ratios (from 1 : 1 to 400 : 1) are incompletely saturated as regards silica-alumina minerals (Fig. 4, *a*), but as water passes through the waste product substance, the saturation indexes (SI) increase, and pyrophyllite and kaolinite are likely to form even at the W/R ratios that are equal to 350 : 1 and 400 : 1.

In a similar way, hydroxide minerals (amorphous $Al(OH)_3$, gibbsite, manganite, ferrihydrite) are characterized by low SI values in the beginning of the experiment (W/R = 1 : 1–150 : 1), and the SI values grow during the process of interaction of the waste products with water (see Fig. 4, *b*). The solution is close to saturation with respect to ferrihydrite; its precipitation is possible even at W/R = 150 : 1 and down to the termination of the experiment, as well as the formation of gibbsite in the end of the experiment (W/R = 400 : 1). The formation of amorphous hydroxides has been registered visually due to the emergence of a colloidal brown suspension in the experimental solutions starting with the ratios W/R = 350 : 1, when the medium pH is equal to 3.57, and up to the W/R = 400 : 1 at pH 4.0.

The natural water is supersaturated with respect to Fe, Cu, and Mn oxides (see Fig. 4, *c*). Upon the interaction of water with waste product substance at W/R = 10 : 1, a solution is formed that is incompletely saturated in relation to oxides. During the experiment, the SI of minerals increase, and precipitation of maghemite, magnetite, and cupriferrite is possible even at W/R = 150 : 1. Upon the subsequent adding water to the waste product substance to reach the ratio W/R = 400 : 1, a solution is formed that is supersaturated in relation to Fe and Cu oxides and that is close to an equilibrium as regards pyrolusite and cuproferrite (see Fig. 4, *c*).

The initial natural water is considerably incompletely saturated in relation to Ca, Na, K, Ba, and Fe sulphates (see Fig. 4, *d*). After water interacts with the waste product substance (W/R = 10 : 1), SI of the sulphates increase; jarosite and barite are likely to form. When W/R = 70 : 1, gypsum and anhydrite are also close to saturation. Further water addition leads to dissolution of sulphates of Ca, to supersaturation in relation to sulphates of Ba and in relation to various modifications of jarosite (sulphates of Na, K and Fe) right up to W/R = 400 : 1 (see Fig. 4, *d*).

Analysis of the results

During the long-term interaction of the material of KCSC waste products with seasonal streams in natural conditions, sulphides are oxidized, secondary sulphate salts akin to jarosite $NaFe_3(SO_4)_2(OH)_6$, magnesiocopiapite $MgFe_4(SO_4)(OH)_2 \times 20H_2O$, and aluminocopiapite $(Mg,Al)(Fe,Al)_4(SO_4)_6(OH)_2 \times 20H_2O$ are formed, the solution is characterized by acidic reaction of the medium. The conducted experiment suggests that a great amount of sulphate ions passes into solution as a result of the further interaction of the oxidized waste product substance with fresh neutral water, acidic brine is formed with the mineralization up to 8 g/l and with higher than usual content of Fe, Cu, Zn in the form of sulphate complexes. With a high filtration coefficient (4 m/h) over the course of 22 h, acid is washed away from the waste products, total concentrations of SO_4^{2-} and metals in the solution drop, sulphate complexes are replaced by free ions in the case of Cu and Zn, and by hydroxide compounds of iron. According to experimental and calculated data, sulphate minerals akin to gypsum and jarosite precipitate from the solution, quartz and aluminosilicates comprise the main part of solid matter after the interaction with water. In spite of a decrease in the content of metals in the solution to reach the level of natural water, as much as 6 % of iron, up to 200 g/t of copper, zinc, lead, and about 3 g/t of cadmium remains in the waste product substance that are potentially capable to pass into solution upon the modification of physicochemical conditions of the medium.

CONCLUSIONS

1. Interaction of natural neutral water with the material of waste products from Karabash Copper-Smelting Combine gives rise to acid up to the ratio water/rock = 400 : 1. Upon the interaction with 400 l of neutral water, every kilogram of the waste products produces 22 g of iron, 300 mg of copper, 220 mg of zinc, 54 mg of lead, and 2 mg of cadmium.

2. As the underground draining of the waste products by natural water goes on, the pH of the formed solutions increases (from pH 2.04, W/R = 10 : 1 to pH 4.00, W/R = 400 : 1), and the total content of all metals in the solution drops by two orders of magnitude under inversely proportional dependence.

3. At low W/R values in acidic medium, copper exists in the form of a sulphate neutral complex and Cu^{2+} aquo ion; meanwhile, zinc forms an anionic sulphate complex $Zn(SO_4)_2^{2-}$. As the washing of acid proceeds, the fraction of the sulphate complexes decreases, the metals remain preferentially in the form of aqua ions, and the sulphate anionic complex of zinc disappears. Iron that stays in the solution predominantly within a sulphate complex at the beginning of the experiment transforms to a hydroxide form and abundantly precipitates at the pH 3.5–4.0.

4. Active dissolving–deposition of mineral phases proceeds in the course of the experiment. Formation of pyrophyllite $Al_2Si_4O_{10}(OH)_2$ is possible from silica-alumina compounds in the end of experiment; ferrihydrite $Fe(OH)_3$ and goethite FeOOH is formed from hydroxides. Oxides (cupriferrite $CuFe_2O_4$, magnetite Fe_3O_4, maghemite Fe_2O_3) start precipitating even in the middle of experiment, when W/R = 150 : 1. Barite ($BaSO_4$) and jarosite ($KFe_3(SO_4)_2(OH)_6$) are formed at the initial stage of the process; at W/R = 70 : 1, the formation of gypsum $CaSO_4 \times 2H_2O$ and anhydrite $CaSO_4$ is also possible, which dissolve then.

REFERENCES

1 Ekologiya i okhrana prirody pri otkrytykh gornykh porodakh, Izd-vo MGU, Moscow, 1994.
2 L. K. Yakhontova, V. P. Zvereva, Osnovy mineralogii gipergeneza, Dal'nauka, Vladivostok, 2000.
3 V. T. Kalinnikov, V. N. Makarov, I. P. Kremenetskaya, *Chem. Sust. Dev.*, 5, 2 (1997) 163.
4 P. Holmes, F. Crundwell, *Geochim. Cosmochim. Acta*, 64 (2000) 2.
5 A. M. Plyusnin, V. I. Gunin, Prirodnye gidrogeologicheskiye sistemy, formirovaniye khimicheskogo sostava i reaktsiya na tekhnogennoye vozdeystviye (na primere Zabaykal'ya), Ulan-Ude, 2001.
6 D. V. Makarov, T. N. Vasilieva, V. N. Makarov, *Zh. Prikl. Khim.*, 72 (1999) 406.
7 D. V. Makarov, V. N. Makarov, T. N. Vasilieva, *Ibid.*, 73 (2000) 425.
8 W. Salomons, *J. Geochem. Explor.*, 52 (1995).
9 D. Nordstrom., C. Alpers, C. Ptacek, D. Blowes, *Environ. Sci. Techn.*, 34 (2000) 2.
10 E. Dinelly, F. Lucchini, M. Fabbri, G. Cortecci, *J. Geochem. Explor.*, 74 (2001).
11 S. B. Bortnikova, O. L. Gaskova, A. A. Ayriyants, Tekhnogennye ozera: formirovaniye, razvitiye i vliyaniye na okruzhayushchuyu sredu, Izd-vo SO RAN, Novosibirsk, 2003.
12 N. Hoth, S. Wagner, F. Hafner, *J. Geochem. Explor.*, 73 (2001).
13 Freire P. A´vila, Santos Oliveira J. M., Ferreira da Silva E., Cardoso Fonseca E., *J. Geochem. Explor.*, 85 (2005).
14 S. Audry, G. Blanc, J. Schafer, *Appl. Geochem.*, 20 (2005).
15 Lei Liangqi, R. Watkins, *Ibid.*, 20 (2005).
16 S. R. Kraynov, Yu. V. Svarov, D. V. Grichuk *et al.*, Metody geokhimicheskogo modelirovaniya i prognozirovaniya v gidrogeologii, Nedra, Moscow, 1988.
17 S. I. Mazukhina, S. S. Sandimirov, Primeneniye fiziko-khimicheskogo modelirovaniya dlya resheniya ekologicheskikh zadach Kol'skogo Severa, Apatity, 2005.
18 G. G. Korablev, in: Mineralogiya tekhnogeneza, Miass, 2002, pp. 316–321; G. G. Korablev, *Mineral. Tekhnogeneza,* (2002).
19 V. A. Baryshev, Yu. P. Kolmogorov, G. N. Kulipanov, A. N. Skrinsky, *Zh. Anal. Khim.*, 41 (1986).
20 V. B. Baryshev, G. N. Kulipanov, A. N. Scrinsky, *Handbook Synchr. Rad.*, 13 (1991).
21 N. V. Arnautov, Standartnye obraztsy khimicheskogo sostava prirodnykh mineralnykh veshchestv, Novosibirsk, 1990.
22 J. Ball, D. Nordstrom, User's Manual for WATERQ4F, with Revised Thermodynamic Database, Geological Survey, USA, 1991.
23 O. A. Alekin, Obshchaya gidrokhimiya: khimiya prirodnykh vod, Gidrometeoizdat, Leningrad, 1948.