Chemistry for Sustainable Development **18** (2010) 189–200

UDC 504.4.054

Geochemical Characteristics of Interaction Mechanism between Neutral Man-Caused Flow and Natural Waters of the Salair Ore Field

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(Received August 6, 2009; revised January 18, 2010)

Abstract

Geochemical investigation of the Ekaterininskiy brook draining the Salair ore field from the temporarily abandoned culvert (Salair city, Kemerovo Region) was carried out. Changes of the overall composition of element concentrations in water and in bottom sediments in the brook under investigation, the Malaya Talmovaya River and the zone of their mixing were determined. Model chemical species of element occurrence and the indices of saturation of mineral phases in solution were calculated. The major mechanisms of element deposition at the geochemical barrier were revealed. It was demonstrated that the interaction between the brook and river waters causes substantial changes of the basic ion composition in the mixing zone, the concentrations of heavy metals decrease substantially but the level of background values is not achieved. The main forms of the occurrence of zinc (as the pollutant of priority for the system under consideration) in the surface water of the Ekaterininskiy brook are sulphate and aquated complexes. In water and bottom sediments of the Malaya Talmovaya River, zinc is represented mainly by aqua ions and carbonate complexes. For all regions under investigation, iron occurs in the form of hydroxide complexes, which was confirmed by calculated saturation indices. The latter values showed that the waters of the brook and the river are supersaturated with respect to goethite FeOOH and ferrihydrite $Fe(OH)_3$, and the latter compounds promote sorption and co-precipitation of a number of heavy metals.

Key words: heavy metals, mixing zone, mine water, chemical species of elemental occurrence, saturation indices

INTRODUCTION

One of the main problems connected with the mining industry inherent in different countries is represented by draining and seasonal flows from operating and spent mines with a high content of metals, sulphates and other components [1, 2]. Crucial influence upon the migration of heavy metals leached in the zones of oxidation from the substance waste piles of ore rock or waste products of ore dressing is exerted by the processes of mixing with naturally occurring waters. The efficiency of a similar type of geochemical barriers is determined by the contrast of the composition of carrying flows and by the buffer properties of a depositing medium.

By the example of the neutral drainage Ekaterininskiy brook located within the area of the Salair mining-beneficiation complex (MBC, Kemerovo Region) we studied changing in the content of main ions and toxic metals in surface water and bottom sediments. The neutral mine drainage is formed, mainly, as the result of the processes of pyrite oxidation and carbonate dissolution. Besides this fact, the drainage formation is influenced by such processes as the precipitation and dissolution of iron hydroxides and sulphates, the adsorption of the dissolved metals, *etc.* [3].

The purpose of the present work consisted in quantitative description of hydrochemical processes in the course of interaction between a neutral drainage flow and river water, including: 1) determining the changes in the total concentration of the components carried out by a drainage flow; 2) revealing the chemical species of elements in solutions and their transformation in the zones of mixing; 3) revealing the precipitation mechanisms on a hydrogeochemical barrier for the elements

RESEARCH OBJECTS AND METHODS

We investigated the drainage Ekaterininskiy brook, revealed within Salair ore field which unites several barite/multimetal deposits. The brook represents an outflow of mine waters from ancient temporarily abandoned Ekaterininskaya culvert flowing into the Malaya Talmovaya River. The brook is not deep; its width varies within the range from several centimetres to 2 m on some sites. The brook bed is abundantly covered by red ochre (Fig. 1).

General characteristic of the ore field

The geological structure of the Salair barite/multimetal deposits located in the northeast part of the Salair range, the structure, morphology and material composition of ores were described in the literature in detail [4–6]. Limestone and dolomite serve as enclosing rocks of the ore field. Besides quartz, feldspar, mica and carbonates (up to 15 %) the structure of minerals includes barite in significant amounts. The content of sulphides amounts to 2–3 %, the main sulphide mineral is presented by pyrite FeS_2. In addition, there are sphalerite, galenite, chalcopyrite, tetrahedrite present whose content is an order of magnitude lower. Within the Salair ore field a oxidation zone is intensively developed causing the segregation of two types of ores such as barite/multimetal and oxidized barite/multimetal ores with accompanying gold and silver mineralization.

Background lake of the Salair ore field

As a background point we chose an artificial Gavrilovo water storage basin created by means of impounding the Gavrilovka River, 5 km to the north from the Salair City. The water storage basin is located on the calcareous basis (Lower Cambrian limestones of the

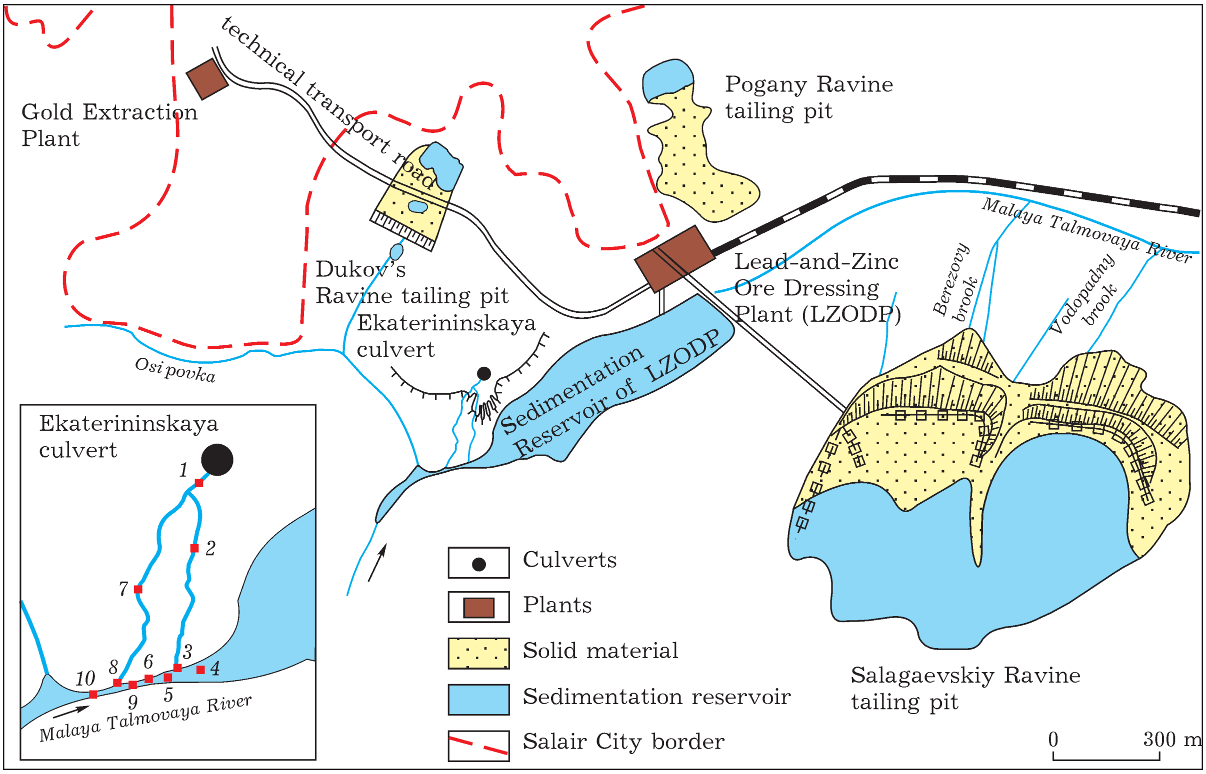

Fig. 1. Schematic map of the Ekaterininskiy brook arrangement with sampling points.

Gavrilovo series); it is distant from industrial platforms and to the least extent suffers from the man-caused impact of open-cut mines and concentration plants. The water of Gavrilovo water basin is alkalescent (pH 7.9) and according Alekin's classification [7] it belongs to the hydrocarbonate/sulphate class, calcium/magnesium type. The composition of water according to the Kurlov's formula looks like:

$$M_{0.45}\,\frac{HCO_3^- 52 SO_4^{2-} 31 Cl^- 17}{Ca^{2+} 70 Mg^{2+} 21 Na^+ 9}\,\mathrm{pH}\,7.9$$

Notwithstanding the fact that the Gavrilovo water storage basin exhibits no visible connection with the deposits of the ore field, the concentration almost all the elements under determination are to a considerable extent exceeded in its water as compared to average data for river water [9] (Table 1). Moreover, the content of four elements such as cadmium, nickel, antimony and arsenic exceeds the maximum permissible concentration (MPC) limit for chemical substances in water objects for domestic, potable as well as cultural and welfare water consumption [8].

The field testing of water and bottom sediments of the background water basin and the Ekaterininskiy brook was carried out in the summer period of time from 2006 to 2008. Surface water was sampled into plastic containers from the layer 5–10 cm in thickness directly in the mouth the drainage brook, within the zone of mixing and at some distance from this zone downstream and upstream of the Malaya Talmovaya River. Water from the background reservoir was also sampled into plastic containers within the layer of 5–10 cm in thickness. The samples were filtered on the spot through the filter 0.45 μm being conserved then with purified HNO_3 for the subsequent elemental analysis. Determining of the content of metals in water samples was carried out by means of an inductively coupled plasma atomic emission spectroscopy method (ICP-AES).

Under field conditions, we determined pH by the method of direct potentiometry with the use of a combined glass electrode, E_h with the help of a platinum electrode, the content of chloride ions by means of a silver chloride electrode. The content of sulphate ion was determined using a turbidimetric method by means of a standard technique (RD 52.24.405–95). The concentration of hydrocarbonate ion was determined using the hydrochloric acid titration technique (RD-5.3.04–96).

The bottom sediments of drainage brooks were sampled with the help of a plastic sampler, the samples were dried and grinded to obtain grain size <0.1 mm. After careful homogenization and repeated quartering, we took 30 mg portions from each sample to press them

TABLE 1

Data concerning the composition of water from the Gavrilovo water storage basin, elemental concentration average values for river water ($[Me]_{av}$ and MPC value (pH 7.9), mg/L

Components	Background	$[Me]_{av}$*	MPC value [8]	Components	Background	$[Me]_{av}$*	MPC value [8]
Cl^-	45	7.8	350	Zn	0.01	0.02	1
SO_4^{2-}	110	11	500	Cu	0.003	0.007	1
NO_3^-	0.4	no data	no data	Co	n/d	0.0001	0.1
HCO_3^-	240	no data	no data	Ni	0.096	0.0003	0.02
Na	5.7	6.3	200	Pb	0.009	0.001	0.01
K	0.78	2.3	no data	Cd	0.02	0.00001	0.001
Ca	44	15	no data	Rb	0.013	0.001	0.1
Mg	8.0	4.1	50	Sr	0.2	0.07	1
Fe	0.03	0.04	0.3	Sb	0.02	0.0001	0.005
Al	n/d	0.05	0.2	As	0.03	0.002	0.001
Mn	0.006	0.007	0.1	Ba	0.07	0.02	0.7

Note. n/d – not detected.

*Average concentration values for elements in river waters according to [9].

to obtain 10 mm tablets under a pressure of 100 kg/cm^2. The content of elements was determined using SR XFA equipment at the station of the elemental analysis on the base of VEPP-3 synchrotron radiation of the Institute of Nuclear Physics, SB RAS (Novosibirsk). Sensitivity of determining the elements was equal to 0.1 g/t, the relative standard deviation of the method amounted to 20 %.

Chemical species of of metals in solutions were determined with the help of thermodynamic calculations using WATEQ4F software [10]. Saturation indices (SI) were simultaneously calculated those indicate the potential undersaturation or supersaturation level of the solution with respect to various mineral phases. The calculation of SI value is based on the data of the analysis for water samples or for the model solution, as well as on the measured or estimated physicochemical parameters such as E_h, pH, *etc.*

There are several approaches for the estimation of the pollution level for surface waters. The most widespread among them consists in comparing the data obtained concerning the content of heavy metals in water with the clarke values of element concentration for river waters, background concentrations, MPC value. In this case, the concentration coefficient for the element under investigation in surface water (K) represents the ratio of between the concentration of the element in water ($[\mathrm{Me}]_{\mathrm{smpl}}$) and its background value ($[\mathrm{Me}]_{\mathrm{bgr}}$):

$K_{\mathrm{poll}} = [\mathrm{Me}]_{\mathrm{smpl}}/[\mathrm{Me}]_{\mathrm{bgr}}$

In order to estimate the mobility of elements in the water – bottom sediment system we used the distribution coefficient (K_{dist}) determined as $K_{\mathrm{dist}} = \log\,[\mathrm{Me}]_{\mathrm{solid}}/[\mathrm{Me}]_{\mathrm{soln}}$ [11]

Here $[\mathrm{Me}]_{\mathrm{solid}}$, $[\mathrm{Me}]_{\mathrm{soln}}$ are the concentration of an element in solid substance of bottom sediment and in solution, respectively. In this case the less K_{dist} value, the more mobile is the element in the system.

The concept of the mobility of heavy metals in the system solution–solid substance implies the estimation of a flow of different heavy metal species from one medium of the system to another under the action of physical and chemical processes and the factors promoting or inhibiting this directed flow (so-called barrier) [12]. Among the inhibiting factors one should note physical processes of heavy metal adsorption on the particles of bottom sediment (or a suspended substance).

For the characterization of bottom sediment pollution, we used the ratio between the content of chemical elements and the background value (MPC) and the parameter of total pollution (Z_t) which is determined according to the formula [13]

$$Z_t = \sum_{i=1}^{n} K_c - (n-1)$$

Here K_c is the concentration coefficient for an element in bottom sediments; n is the number of elements taken into account with $K_c > 1.5$.

RESULTS AND DISCUSSION

The content of heavy metals in water of drainage brooks depends on a number of physical and chemical parameters. So, depending on the acidity of solutions, the composition of ore, enclosing rocks and other parameters the total content of heavy metals in water could amount up to 4000 mg/L, whereas in some cases this value can be equal to ten thousand milligrams per litre (Fig. 2).

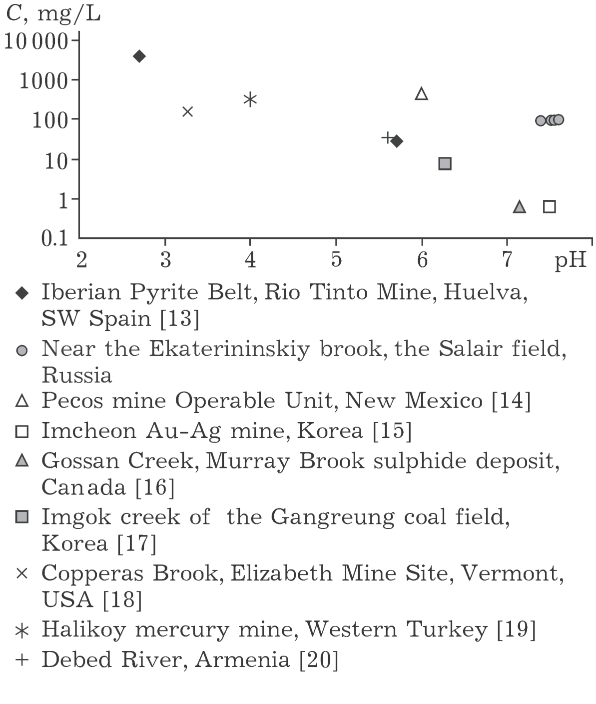

Fig. 2. Diagram of total metal concentration in the solution depending on pH value for various mine drainages of the world.

In our case, the total content of metals in the Ekaterininskiy brook water at neutral pH values amounted up to 90–95 mg/L, which is comparable with the data for subacidic mine waters in Mexico, Spain and Armenia. At the same time, for brook neutral water draining sulphide sediment in Canada and gold-silver ores in South Korea, this value amounts to about 0.6 mg/L.

Composition of water

The surface water of the Ekaterininskiy brook is characterized by neutral pH value (7.4–7.6) and according to the ionic composition belongs to man-caused magnesium/calcium/zinc sulphate type with a high mineralization level. In the composition of water, there are Ca (280–290 mg/L) and Mg (265–275 mg/L) cations prevailing. A high content of zinc and manganese in water allows one to attribute them to macrocomponents (Table 2).

The main anion is represented by sulphate ion SO_4^{2-} (10 000–10 900 mg/L) determining an increased mineralization level of the brook water (11 g/L). The water composition can be presented according to the Kurlov's formula as it follows:

$$M_{11}\,\frac{SO_4^{2-}99Cl^{-}1}{Mg^{2+}58Ca^{2+}34Zn^{2+}5Mn^{2+}3}\,pH\,7.5$$

The main source of sulphates is represented in surface waters by the processes of chemical aeration and dissolution of sulphur-containing minerals. The total content of heavy metals in the solution (Cd, Cu, Mn, Ni, Zn, Co) ranges from 91 up to 96 mg/L, whereas the elements can be ranged as it follows: Zn > Mn > Cd > Co> Ni > Cu.

The Ekaterininskiy brook water contains a prevailing pollutant element such as zinc, whose content amounts to 60–64 mg/L. It should be noted that the concentration of zinc exhibits a 1.5-fold decrease as compared to the data of investigations carried out earlier on this site [22]. Most likely, this fact is caused by the sorption of zinc ions on iron hydroxides. The content of manganese in the brook water 300 times exceeds the MPC value, whereas the content of cadmium is 400 times higher than the MPC. Such high values of the content of these elements, certainly, indicate the anthropogenous character of their supply.

The high content of zinc and manganese in the surface water of the Ekaterininskiy brook is caused by the mineral ore composition of the

TABLE 2

Chemical composition of water samples from the drainage brook, mixing zone and the river, mg/L

Components	Ekaterininskiy brook				Zone of mixing			Malaya Talmovaya River		
	Ek-1	Ek-2	Ek-3	Ek-7	Ek-4	Ek-8	Ek-9	Ek-5	Ek-6	Ek-10
pH	7.5	7.5	7.6	7.4	7.5	7.4	7.6	7.7	7.7	7.8
SO_4^{2-}	10 000	10 900	5550	5800	1100	1150	750	25	15	10
HCO_3^-	0.06	0.08	0.07	0.07	0.01	0.12	115	140	170	190
Cl^-	37	35	25	40	23	20	15	20	17	9.3
Ca^{2+}	280	300	280	290	65	65	62	65	60	60
K^+	5.5	5.7	5.8	5.5	1.7	1.7	1.8	1.9	2.7	1.6
Mg^{2+}	260	280	270	270	8.7	8.8	7.7	9.1	7.9	8.0
Na^+	14	14	15	14	7.3	7.3	7.3	8.0	9.2	7.1
Si	86	70	67	72	60	60	61	61	67	60
Fe_{total}	0.9	0.2	0.02	0.04	0.04	0.04	0.01	0.01	0.01	0.01
Mn	31	32	31	29	0.02	0.05	0.003	0.003	0.002	0.002
Zn	61	63	64	62	0.6	0.6	0.08	0.4	0.05	0.2
Cu	0.01	0.01	0.008	0.005	0.007	0.004	0.005	0.007	0.01	0.007
Co	0.2	0.2	0.2	0.2	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cd	0.4	0.4	0.4	0.4	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ba	0.06	0.03	0.03	0.06	0.12	0.13	0.12	0.11	0.13	0.12

TABLE 3

Correlation coefficients between the elements in the surface water of the Ekaterininskiy brook, mixing zone and the Malaya Talmovaya River (number of samples $n = 15$)

Elements	Ba	Ca	Cd	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Si	Sr
Ca	**−0.930**												
Cd	*−0.585*	**0.858**											
Co	*−0.501*	**0.962**	**0.946**										
Cu	−0.468	0.370	*−0.544*	**−0.795**									
Fe	−0.456	*0.563*	0.186	0.197	0.396								
K	**−0.848**	**0.945**	**0.661**	0.406	*0.518*	*0.554*							
Mg	**−0.935**	**0.996**	**0.886**	**0.965**	0.316	*0.555*	**0.919**						
Mn	**−0.940**	**0.968**	**0.674**	**0.679**	0.426	*0.559*	**0.887**	**0.969**					
Na	**−0.852**	**0.943**	**0.940**	**0.848**	0.221	*0.489*	**0.927**	**0.947**	**0.894**				
Ni	−0.445	0.419	0.135	0.277	0.112	**0.631**	0.370	0.430	0.291	0.225			
Si	0.071	−0.006	**0.682**	**0.861**	**−0.752**	0.057	−0.134	0.060	−0.062	0.208	0.091		
Sr	**−0.937**	**0.979**	**0.720**	**0.701**	0.425	*0.537*	**0.928**	**0.975**	**0.992**	**0.933**	0.229	−0.050	
Zn	**−0.903**	**0.918**	*0.594*	*0.594*	0.380	*0.505*	**0.810**	**0.926**	**0.986**	**0.842**	0.151	−0.054	**0.966**

Note. The semiboldface type indicates the values at б > 0.99, italics indicates the values at $\alpha \geq 0.95$.

Salair ore field. Zinc enters into water as the result of dissolution of sulphide minerals remained after the development of ancient culvert (sphalerite, zincite, smithsonite), as well as with wastewater from ore dressing plants. Supplying the manganese into surface water flows, mainly in the form sulphate, is connected with its leaching from rock-forming minerals.

The surface water within the zone of mixing the Ekaterininskiy brook and the Malaya Talmovaya River is characterized by an abrupt decrease of the mineralization due to the reduction of sulphate ion concentration of (740–1150 mg/L), belongs to sulphate class, calcium/magnesium type according to the ionic composition. In turn, with the reduction of the content of sulphate ions the concentration of heavy metals is abruptly reduced, too. The total content of the dissolved heavy metals amounts to 0.8 mg/L.

$$M_{1.3}\,\frac{\mathrm{SO_4^{2-}95Cl^{-}5}}{\mathrm{Ca^{2+}69Mg^{2+}15Na^{+}14K^{+}2}}\,\mathrm{pH}\,7.6$$

The surface water of the Malaya Talmovaya River according to the chemical composition belongs to calcium/magnesium/sodium type, hydrocarbonate/sulphate class, the mineralization level amounting to 0.5 g/L. The total content of heavy metals (Cd, Cu, Mn, and Zn) in the solution is equal to 0.06–0.4 mg/L.

$$M_{0.5}\,\frac{\mathrm{HCO_3^{-}56SO_4^{2-}36Cl^{-}8}}{\mathrm{Ca^{2+}68Mg^{2+}15Na^{+}15K^{+}2}}\,\mathrm{pH}\,7.8$$

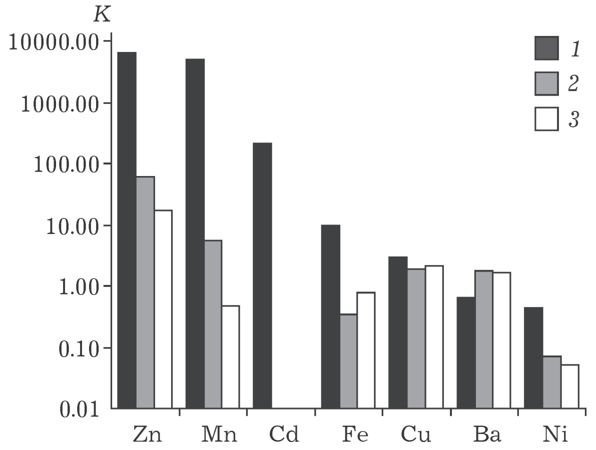

Fig. 3. Data concerning the concentration coefficient for heavy metals (K_c) in the surface water of the Ekaterininskiy brook (*1*), the mixing zone (*2*) and the Malaya Talmovaya River (*3*).

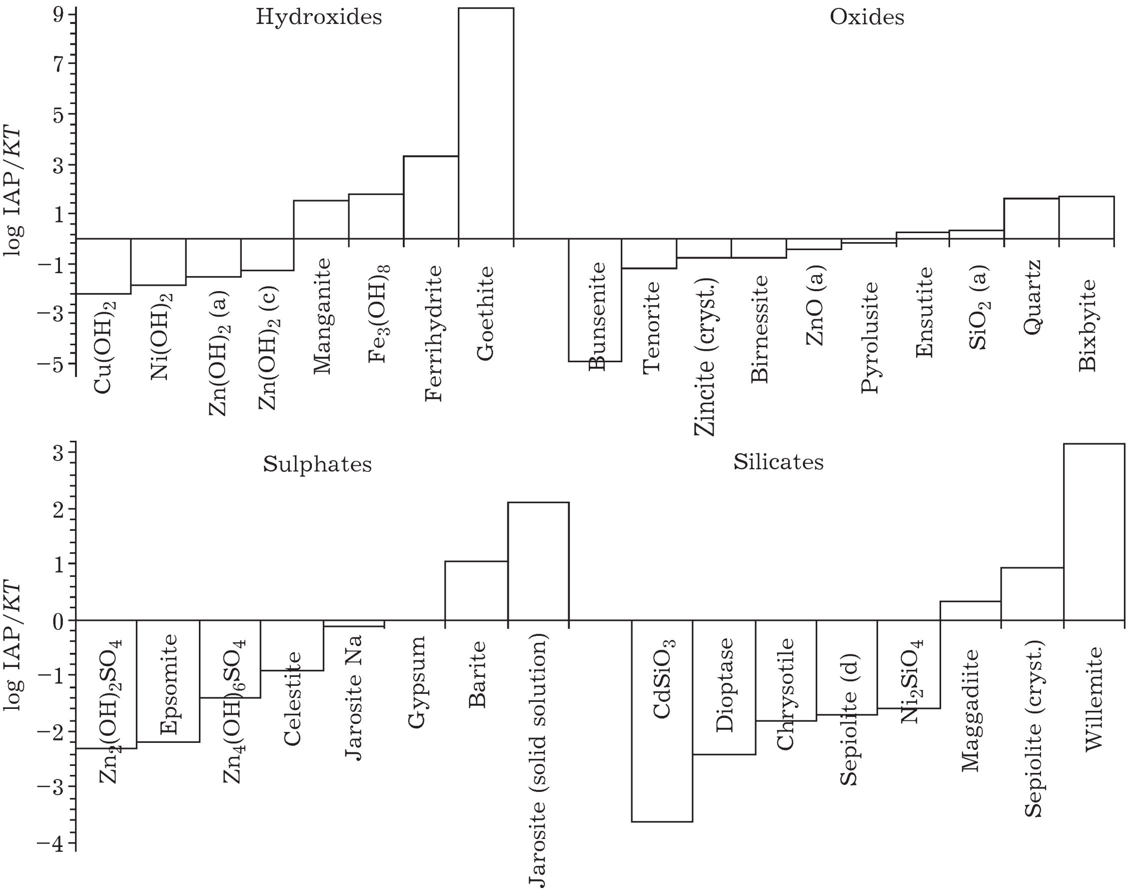

Fig. 4. Saturation indices of mineral phases in the surface water of the Ekaterininskiy brook.

Thus, a rather high content of sulphates in the Malaya Talmovaya River water indicates that it is exposed an intense man-caused impact.

The relative concentration coefficient (log K_c) is used for the estimation of excess metal concentration at the point with man-caused loading higher than the background value; it reflects the purification level for waters entering directly into the river. The calculation of this parameter for the water of the Ekaterininskiy brook demonstrated that the highest values of K_c are inherent in Zn, Mn, and Cd (Fig. 3). For water of the zone of mixing a considerable reduction of this value is observed, whereas for the Malaya Talmovaya River water the concentration coefficient of heavy metals reaches minimal values. An exception is represented by barium, whose K_c value for water of the mixing zone and of the river demonstrates a 2–3-fold increase.

The main chemical species of the occurrence of metals reflect changes in physical and chemical conditions in surface waters and their basic ionic composition. The fractional ratio between chemical species of metals in brook water and the zone of mixing is different. As it was mentioned earlier, the solution of Ekaterininskiy brook contains a prevailing concentration of Zn (62–64 mg/L) which belongs to a number of active microelements influencing the growth and normal development of organisms. At the same time, many compounds of zinc are toxic, in particular zinc sulphate and chloride [23]. The chemical species of its occurrence are presented mainly by sulphate complexes ($ZnSO^0_{4\,aq}$, $Zn(SO_4)_2^{2-}$) and aqua ions (Zn^{2+}_{aq}) (Table 3). For the mixing zone water, the fraction of Zn aqua ions (55 %) and hydroxide complexes (1 %) exhibit an increase, whereas the fraction of sulphate ions almost does not change. In this case, for the water of the Malaya Talmovaya River (after the brook confluence), one can observe zinc mainly in the form of carbonate compounds (50–60 %) and aqua ions (35–50 %). Cad-

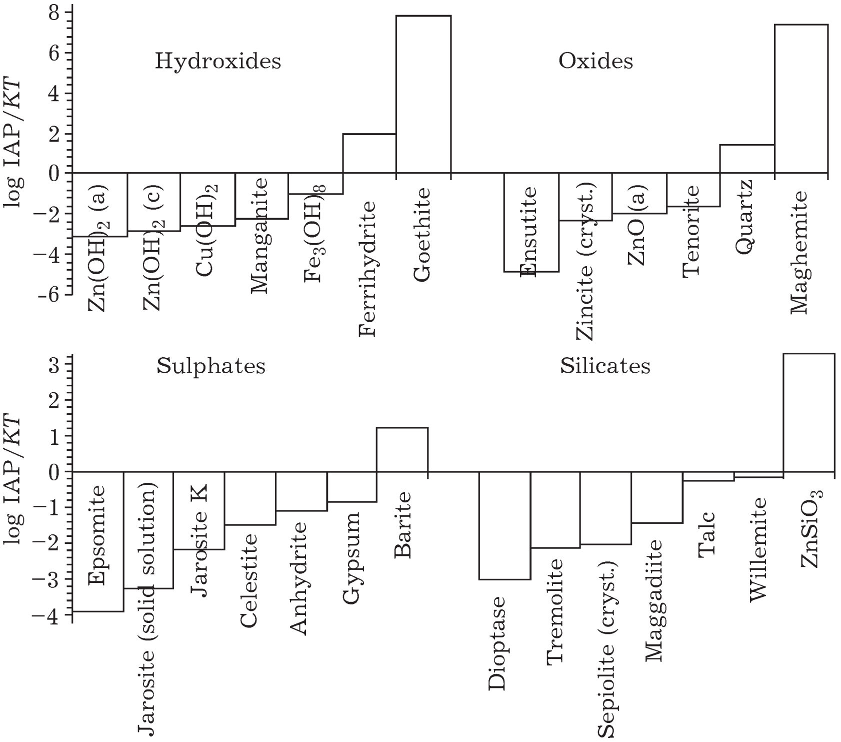

Fig. 5. Saturation indices of mineral phases in the surface water of the zone of mixing.

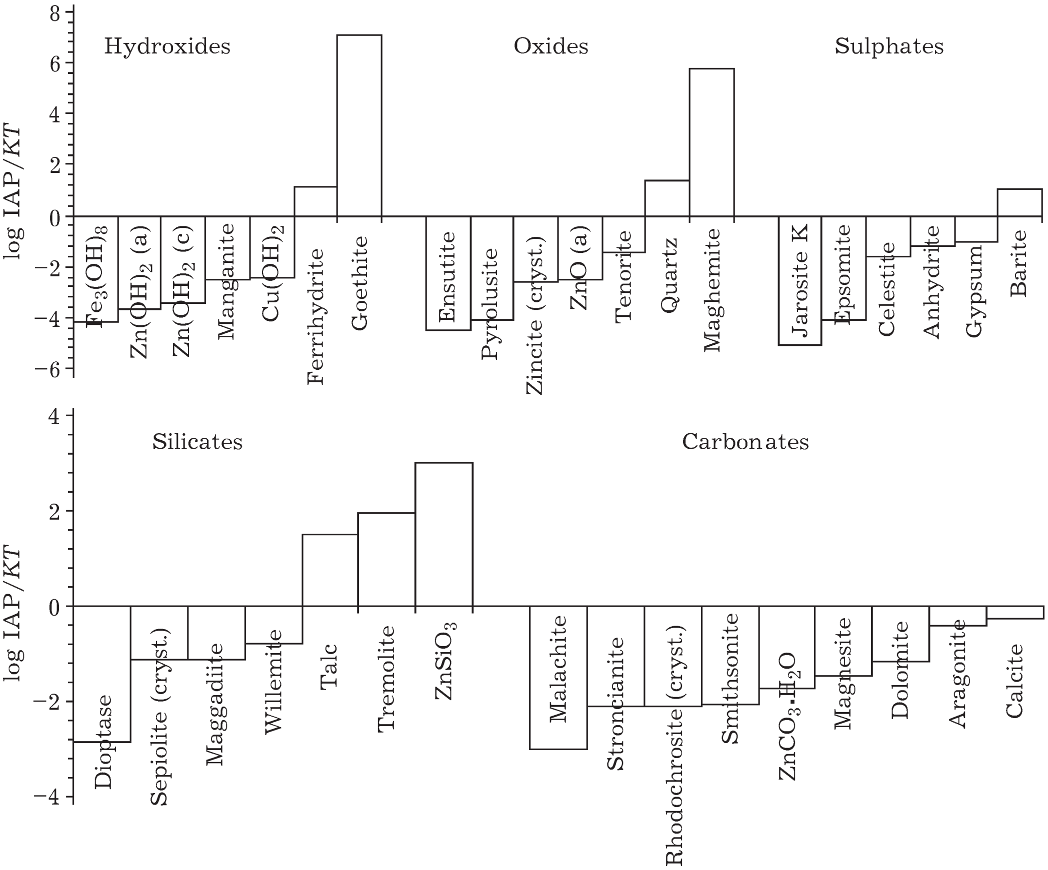

Fig. 6. Saturation indices of mineral phases in the surface water of the Malaya Talmovaya River.

mium exhibiting the properties close to those of zinc forms in the brook mainly sulphate complexes (75–80 %) though the fraction of its aqua ions is significant, too, amounting in the river up to 89 %. Iron (III) occurs exclusively in the form of hydroxide complexes. Chemical species of copper are presented by hydroxide (66–86 %), sulphate (16–17 %, in brook water), aqua ions and hydrocarbonate (after the confluence of the brook and the river). Manganese and nickel in the Ekaterininskiy brook water are presented in the form of aqua ions and sulphate complexes. At the confluence of the brook and the river, hydrocarbonate species of these metals are inherent in water.

The main chemical species of barium in brook water are presented by barium sulphate ($BaSO^0_{4\,aq}$, 81 %) and aqua ions (Ba^{2+}_{aq}, 19 %). As far as the mixing zone water is concerned, the fraction distribution of chemical species changes insignificantly: the fraction of aqua ions (37 %) grows and the fraction of sulphate complexes (62–63 %) decreases. No formation of neutral carbonate complexes was registered. In the Malaya Talmovaya River water, barium prevails in the form of aqua ions (93–95 %), whereas the fraction of sulphate complexes abruptly decreases (2–5 %) and the fraction of neutral carbonate complexes increases insignificantly (1.2–2.0 %).

The results obtained are in a good agreement with data from [24] according to which the drainage waters of the oxidation zone with pH close to neutral value contain free metal ions and sulphate metal complexes as prevailing species.

Thermodynamic calculations have demonstrated, that the waters of the drainage brook, mixing zone and of the river oversaturated with respect to iron (III) hydroxide. Fe^{3+} ions are precipitated in the form of goethite FeOOH and ferrihydrite $Fe(OH)_3$, forming brown ochre, covering the brook bed (Figs. 4–6). The precipitation of ferrihydrite occurs at $pH \geq 6$. Goethite (α-FeOOH) can be formed under neutral conditions or in the case when the acidic solution ($pH < 4$) with a low content of sulphates (<1000 g/L) is neutralized by carbonate-containing waters [25].

The presence of sulphates in the Ekaterininskiy brook water could result in the formation of jarosite, barite and gypsum. Also designed values SI demonstrated possible oxides' formation, such as maghemite Fe_2O_3, bixbyite Mn_2O_3, quartz SiO_2, and Mg, Ca, Zn silicates. Most likely, it should result in the formation of a suspension with the subsequent precipitation to form a deposit.

According to data of [26], the loss of jarosite into the deposit could occur owing to a decrease of water pH value. Moreover, jarosite can be partly replaced by goethite as the pH value increases. The low content of copper could be caused by a high content of Fe hydroxides such as goethite whereon the sorption of ions occurs.

For the mixing zone water one can observe a similar picture; however jarosite under the mentioned conditions is dissolved. As oxides in the zone of mixing are concerned, the oversaturation of the solution occurs only with respect to maghemite and quartz, whereas for sulphates the oversaturation occurs with respect to barite $BaCO_3$ (see Fig. 5).

The indices of saturation for carbonates in the Malaya Talmovaya River water upstream the confluence with the Ekaterininskiy brook exhibit equilibrium values with respect to calcite $CaCO_3$ and to dolomite $CaMg(CO_3)_2$. After the confluence of the brook and the river these minerals are dissolved in water. At the same time, the water of the river before and after the confluence with the brook are still oversaturated with respect to iron (III) hydroxides (goethite, ferrihydrite and maghemite), amorphous SiO_2 and Fe oxide (maghemite) (see Fig. 6).

Bottom sediments

The macrocomponental composition of bottom sediments at the sampled sites is presented by Ca, Fe, K, Ti, and Mn. Thus the greatest concentrations in the bottom sediment of the Ekaterininskiy brook are observed for Ca and Fe on the average amounting to 3.4 and 15 %, respectively. The content of K, Ti and Mn amounts to 2.1, 1.3 and 0.45 %, respectively. As a whole, the macrocomponental composition in all the sites studied is almost identical. An exception is represented by iron whose content in bottom sediments of the zone of mixing and the river decreases amounting to 2–6 %. A high content of heavy metals in bottom sediments was revealed. A considerable excess with respect to background values was regis-

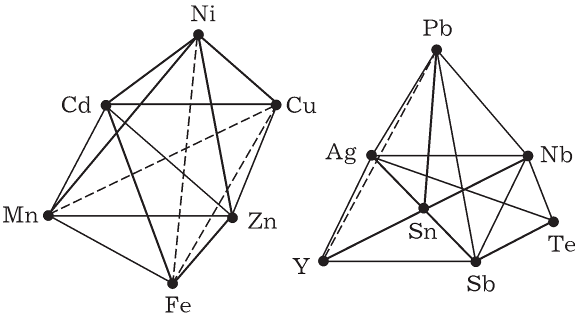

Fig. 7. Correlation diagrams for interrelation between elements in the bottom sediments of the Ekaterininskiy brook, mixing zone and Malaya Talmovaya River.

tered for all the elements under investigation, especially cadmium, amounting to a 150–1000 fold excess level for Cd, whereas there are excess level values for Zn 70–500, for Ag 60–300, for Pb 30–125, for Sb 20–120 times observed. To all appearance, this could be connected with the fact that bottom sediments are capable of accumulate elements, and first of all heavy metals and their compounds.

The distribution coefficients calculated are rather variable. Such elements as Mn, Zn, Cd belong to rather mobile elements contained in water Ekaterininskiy brook (K_{distr} = 1–3). The highest values of this parameter ($K_{\text{distr}} > 5$) are inherent in Fe and Mn. Thus, a hypothetical order of increasing the mobility could be presented as: Fe < Cu < Ni < Zn, Cd < Mn for the bottom sediment–surface water system of the Ekaterininskiy brook; Fe < Mn < Cu, Cd < Zn for the mixing zone; Fe < Mn < Zn < Cu < Ni for the Malaya Talmovaya River.

The correlation analysis of bottom sediments revealed the presence of two groups wherein the elements are closely connected between each other (Fig. 7). The groups of basic man-caused components (Zn, Mn, Cd, Cu, and Ni) and the groups of trace elements (Y, Sb, Te, Sn, Ag, Nb, and Pb) are distinctly selected. Besides, the correlation analysis has revealed a significant interconnection between the elements in the bottom sediment and in water. For example, zinc and manganese in water are closely connected exhibiting a positive correlation with K, Mn, Fe, Ni, Cu, Zn, Cd in the bottom sediment.

From the calculation results for pair correlation, various associations of elements can be discriminated with significant correlation coefficients for the surface water at the points of sampling those are inherent in a man-caused impact (see Table 3). Taking into account an almost full iron and manganese correlation in bottom sediment with heavy metals (Fig. 7), one could conclude that the precipitation of these elements occurs simultaneously, as zinc, cadmium, copper and nickel ions adsorbed onto the surface of iron and manganese hydroxides. In this case, the highest correlation coefficients are exhibited by zinc and cadmium. An interrelation between trace elements of rock-forming minerals and chalcophile elements such as was revealed, too. Hence, as the result of the interaction with mine waters, a rocky matrix is destroyed, which is accompanied the withdrawal a significant amount of chemical elements.

The total pollution parameters (Z_t) obtained for bottom sediment according to Yu. I. Saeta's estimation scale [13] correspond to a high pollution level. The maximal Z_t value for bottom sediment (in the Ekaterininskiy brook) amounts to 172, the minimal value (in the Malaya Talmovaya River) amounts to 47.9. The main contribution to the pollution is made (in a decreasing order) by Cd, Zn, Ag, Pb, and Sb.

Features of elemental redistribution in the zone of mixing

As a rule, on a hydrogeochemical barrier there are the processes of the dilution, sorption and the formation/dissolution of newly formed man-caused origin minerals occurring, which results in decreasing the concentration of heavy metals in the solution. In our case, the zone of mixing the waters of the Ekaterininskiy brook and the Malaya Talmovaya River represents an example of such hydrogeochemical barrier, where in the course of confluence with a highly mineralized drainage the total content of heavy metals in water is abruptly reduced. Besides the dilution, there are also the processes of solid phase formation/dissolution occurring. Manganite formed in the brook water is dissolved in the mixing zone and the river water to produce bixbyite (manganese oxide). Sulphate minerals jarosite and gypsum are also dissolved under confluence the waters of the brook and the river, in this case carbonate minerals are formed in the river water. These mineral formation processes cause also changing the chemical species of occurring the elements in the solution.

Sulphate complexes of zinc in the zone of mixing decrease due to increasing the fraction of aqua ions, and their content in the Malaya Talmovaya River decreases due to the occurrence of hydrocarbonate and carbonate complexes. The active reduction of zinc content under mixing the waters is caused by the sorption of ions on iron hydroxides, which mechanism is prevailing for removing zinc from the solution [27, 28]. The chemical species of occurring manganese confirm the fact that there is a man-caused origin of the mentioned element. It should be reminded that the prevailing chemical species of manganese in the Ekaterininskiy brook are presented by manganese sulphate (55 %) and free ions (45 %), whereas the water of the river exhibits a decrease of the fraction of sulphate species due to the fact that there are carbonate and hydrocarbonate complexes present.

An abrupt decrease of Zn and Cd concentration in the Ekaterininskiy brook water within the zone of mixing is in a good agreement with the data of [29] whose author concluded that arsenic and lead are more efficiently adsorbed from the solution at low pH values, whereas zinc, cadmium and nickel are adsorbed at the solution pH close to a neutral value.

The increase in barium concentration in the solution within the zone of mixing and in the river could be explained by the fact that the supply of heavy metals into the Malaya Talmovaya riverbed occurs both resulting from point pollution sources (drainage flows and a direct uncontrollable drain from the Salair MBC where barite/multimetal ores are processed), and from areal sources (drainage flows and a filtering the solutions from the Talmovaya's sand). To all appearance, changing the chemical species of barium by more mobile chloride complexes also causes an increase in its concentration in water of the riverbed (*i.e.* there is a change of ligands) though the thermodynamic modelling does not reveal any presence of barium chloride species.

High concentrations of metals in bottom sediments are established to occur, and the metals are not in the form of their proper phases, but as sorbed species on iron hydroxides. This indicates to the fact that only the compounds of zinc (such as zinc silicate Zn_2SiO_4) are characterized by high SI values in bottom sediments of the Ekaterininskiy brook mouth. Bottom sediments within the zone of mixing and further in the river are characterized by a sharp decrease of iron, zinc, cadmium and copper content, whereas the content of lead and antimony remains high. Notwithstanding the fact that the content of these elements in brook water was low (below the detection limit), their accumulation in bottom sediments indicates an intense withdrawal and steady migration ability. It has been earlier demonstrated for the Vodopadny and Berezovy brooks draining from the Salagayevskiy Ravine depository that the basic form of lead migration under the conditions of drainage is presented by a suspension [30]. It is obvious that the same species is prevailing in the Ekaterininskiy brook, which determines the formation of lengthy lead anomalies under gradual precipitation of suspended particles.

CONCLUSION

The drainage Ekaterininskiy brook represents a highly mineralized sulphate solution forming a new type of man-caused waters. Taking into account a high content of Zn and Mn therein (3 and 5 % of the total partial content, respectively, these metals can be attributed to a number of macrocomponents in the mentioned system.

Within the zone of mixing te river and man-caused waters, the behaviour of microelements is determined by the processes of dilution, formation/dissolution of mineral phases and a sorption barrier whereby the metals are withdrawn from the migration flow within a short time. The major factor of man-caused sedimentogenesis consists in supersaturation saline waters by mineral phases and forming secondary minerals of man-sorigin.

It is demonstrated that the association of man-caused elements in transporting and depositing media reflects geochemical features of rocks and ores. An abundant precipitation of iron hydroxides, sorbing Mn, Cu, Cd, Zn and other elements, is supported by the calculated values of the saturation index and the distribution coefficient. The calculations the concentration coefficients and the total pollution parameter for bottom sediments confirm the thesis concerning the fact that operating and abandoned mining areas represent the territories with a high risk of ecological catastrophes. The pollution of the Malaya Talmovaya River bottom sediment, conserved for a long time is doubtlessly hazardous, since it could result in the secondary pollution of surface waters.

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