

Hydrogeochemistry at Mining Districts

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Abstract—The Southern Urals exemplifies hydrogeochemical environments at mining districts. Information obtained by studying the geochemistry of nonferrous-metal industrial wastes (both mine and dump drainage) is important not only because these wastes are potential sources of base metals but also in the context of geoecological problems. The Southern Urals is one of Russia's principal producers of Cu and Zn concentrates for metallurgical processing: the region produces 12–15% Cu and 49% Zn concentrates in the country and 35% Cu and 69% Zn concentrates in the Urals. The Yubileinoe, Podol'skoe, Sibai, Uchaly, Novy Uchaly, and Gai deposits are the largest in the Urals. The ores of these deposits contain certain components (Se, Te, Cd, Co, Ga, Ge, In, Be, etc.) that are environmental contaminants. The volume of mine and dump drainage in the Southern Urals amounts to 9 million m³/year, and its mineralization varies from 3.0 to 30–40 g/L, occasionally as high as 365 g/L, with a sulfate, chloride–sulfate calcic–magnesian, magnesian–sodic, and magnesian–calcic composition of the waters. The minor and trace elements of the regional waste waters whose concentrations exceed the regional background values are Cu, Zn (one to four orders of magnitude), As, Cd (one to three orders of magnitude), Li and Be (one to two orders of magnitude). All waste waters transfer various contaminants into environmental subsystems and most actively modify the composition of the groundwaters. At the same time, dump drainage is a potentially important secondary source of valuable mineral components.

Keywords: mine and dump drainage waters, trace-element geochemistry, radioactive elements, secondary mineral

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INTRODUCTION

The Southern Urals is one of Russia's principal producers of metallurgical Cu and Zn concentrates, with more than thirty mineral deposits developed in the area over the past three centuries. Mineral deposits can actively modify the composition of the groundwaters because ore masses at these deposits are thermodynamically unstable in the geochemical environments of upper aquifers, and when these waters reach equilibrium with the new environments, much of their components are transferred into the aqueous phases of the hydrogeochemical systems (Krainov et al., 2004).

Tectonically, the area is located in the western and partly central part of the Magnitogorsk megasynclorium (Fig. 1). The Southern Urals is a classic province of Devonian sulfide deposits. Currently actively developed deposits belong to the Uchaly (Uchaly and Uzelga), Sibai (Sibai and Kamagan), and Buribai (Oktyabr'skoe) groups of the Southern Urals type, with Cu sulfide and Cu–Zn sulfide ores. Along with Ural-type deposits, the area also hosts mineral deposits belong to the Baimak type (Prokin et al., 1988, Seravkin, 2010) and are widespread in the Baimak mining district (Bakr-Tau, Tash-Tau, Balta-Tau, Maiskoe,

and other deposits). The ores of these deposits are noted for elevated contents of Pb, Ba, Mo, Ag, and Au contents. All deposits of this type are now practically completely depleted.

The complicated hydrogeological conditions at the Magnitogorsk megasynclorium are caused by the diversity of the rocks; their variable tectonic fracturing, faulting, and folding; and by the local specifics in the charge, flow, and discharge of groundwaters. The dominant groundwater type is fracture and vein waters in tectonized zones. In addition to typical intrusive and metamorphic hydrogeological massifs, which correspond to outcrops of acid (granite and granite-gneiss), intermediate (diorite, andesite, and porphyrite), mafic (basalt and diabase), and ultramafic (peridotite, pyroxenite, and serpentinite) rocks, the area hosts widespread hydrogeologic massifs hosted by Silurian, Devonian, and Carboniferous volcano-sedimentary rocks. The waters hosted in the Paleozoic volcanic and volcano-sedimentary rocks are usually five- to six-component: sulfate–hydrochloride magnesian–calcic–sodic, hydrocarbonate–sulfate–chloride calcic–magnesian–sodic, etc. The salt composition of waters in this hydrogeochemical situation is

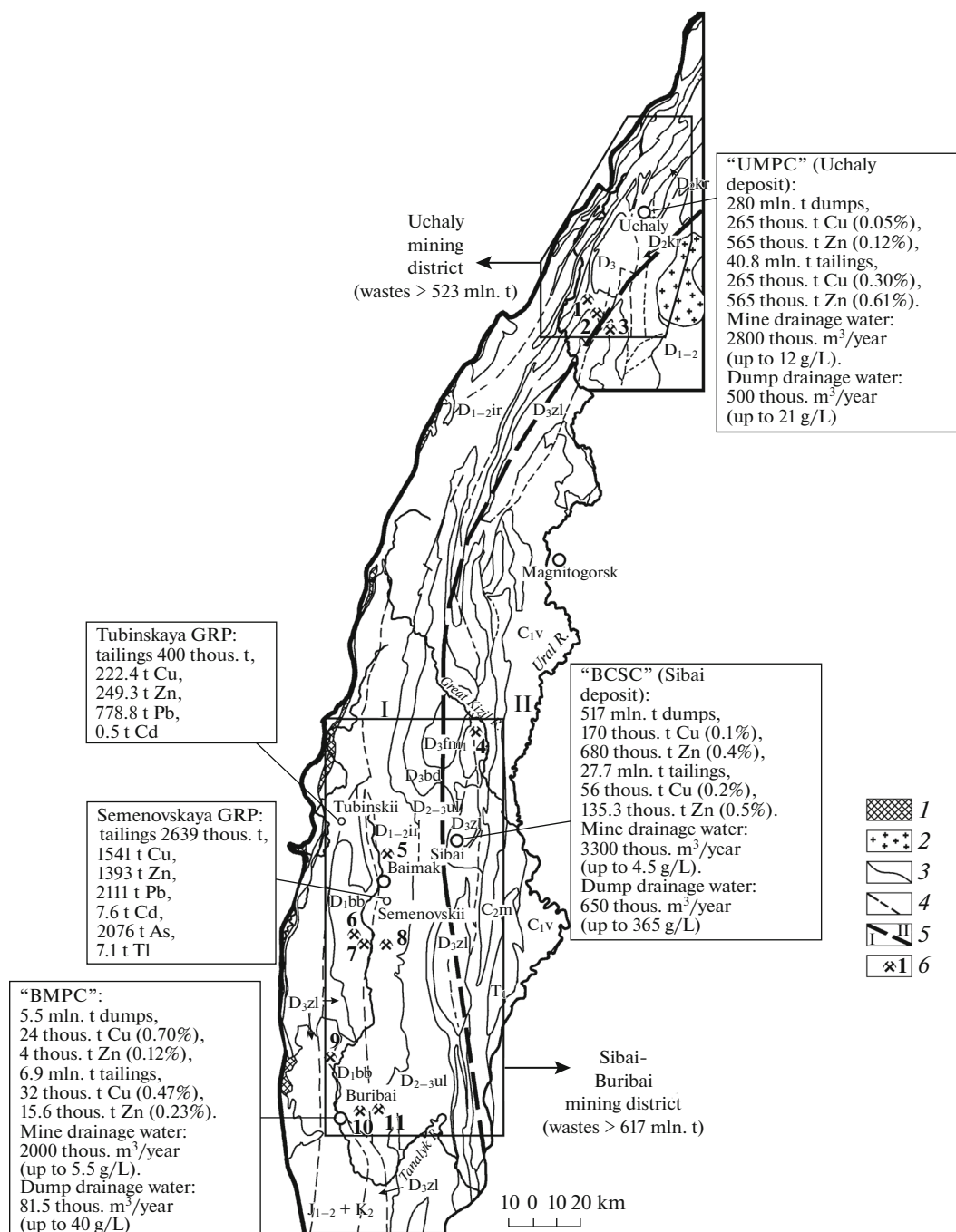


Fig. 1. Mining and processing complexes in the Southern Urals, their geochemical profiles, and amounts of wastes (Akhmetov, 2010). 1—Serpentinite; 2—granite massifs; 3—stratigraphic boundaries; 4—faults; 5—boundary between the western and central parts of the Magnitogorsk megazone; 6—major mineral deposits: (1) West Ozernoe, (2) Uzel'gin, (3) Molodezhnoe, (4) Bakr-Uzyak, (5) Kul-Yurt-Tau, (6) Bakr-Tau, (7) Tash-Tau, (8) Balta-Tau, (9) Yubileinoe, (10) Oktyabr'skoe, (11) Makanskoe.

complicated, and the waters contain practically all salt associations, with the dominance of NaCl, Ca(HCO₃)₂, and MgSO₄ and with subordinate concentrations of CaSO₄, Na₂SO₄, Mg(HCO₃)₂, and MgCl₂.

The chemical composition of the waters hosted in the Paleozoic magmatic and volcano-sedimentary

rocks is controlled mostly by hydrolysis (CO₂ leaching) of aluminosilicate and silicate minerals (Abdrakhmanov and Popov, 2010; Popov and Abdrakhmanov, 2013). Hydrogen ions, which are generated by the dissociation of carbon dioxide and partly water itself, affect metal ions in silicates and form hydrocarbonate waters of variable cation composition, depend-

ing on the mineralogy of the rocks (containing albite, anorthite, microcline, olivine, and others minerals), their lithology, and genesis.

In the Southern Urals, short-time interaction between infiltrating waters and low-solubility polymineralic silicate and aluminosilicate rocks, which consist of Mg_2SiO_4 , Fe_2SiO_4 , Fe_3O_4 , and others minerals, does not lead to establishing lithologic–hydrogeochemical equilibrium in the system water–primary aluminosilicates, and the waters thereby generated possess low mineralization and a usually mixed cation composition. In this situation, waters leaving the rocks are significantly undersaturated with respect to chemical compounds. Also, equilibrium is not reached because of the low concentrations of CO_2 and the genetically related H^+ ion, the fracture type of the reservoirs (and hence, the relatively low areas at which the solid and liquid phases can interact), and the occurrence of passivating films of SiO_2 , Al_2O_3 , and Fe oxides on the surface of the minerals. Metals (Na, Ca, K, or Mg) can be transferred into solution if they can be substituted by the H^+ ion in the crystal structures of minerals, leave the rock, and pass through the “armoring” film.

MATERIALS AND METHODS

Now more than 50 deposits and occurrences of ore mineralization of base and precious metals (Cu, Zn, Au, etc.) are known in the Urals. Ores at the pyrite and base-metal sulfide deposits are mined and processed by the OJSC Bashkir Copper–Sulfur Complex (BCSC), OJSC Uchaly Mining and Processing Complex (UMPC), and CJSC Buribai Mining and Processing Complex (BMPC). BCSC developed the Sibai deposit and also, at various times, mined the Kamagan, Bakr-Uzyak, Kul-Yurt-Tau, Bakr-Tau, Balta-Tau, and others deposits. Now the company develops lower orebodies at the Sibai and Kamagan deposits. BMPC produced ore from the Buribai and Makan deposits and now runs underground mining at the Oktyabr'skoe deposit. UMPC has developed three deposits (open-cast mining): Uchaly, XIX Parts'ezd, and Molodezhnoe. Now the company carries out underground ore production at the Uzelgy and Uchaly deposits. Gold was produced at the Semenovskaya and Tubinskaya gold-recovery plants (SGRP and TGRP, respectively). SGRP processed gold ores from the following deposits in the Southern Urals: Gornaya Baikara, Sankym, Balta-Tau, Krasnoural'skoe, Gai, etc. The plants are now decommissioned, and the territory is under rehabilitation (demercurization and recultivation).

Wastes are produced during all operation phases of mining complexes. The wastes are dumps of overburden and barren rocks, off-standard ores, tailings of ore-processing byproducts, and non-liquid pyrite concentrates; open-pit and underground mine drainage, dump drainage, tailing drainage; and gas and dust emissions, which are generated during drilling and

blasting operations, deflation from the dump and tailing surface, and during ore processing. Mining complexes in the Bashkortostan Republic alone annually produce 11.1 million tonnes of wastes, which is 58% of the total waste amount. Calculations indicate that overburden rocks and off-standard ores make up 44% of the total amount of wastes, and processing wastes (flotation tailings) account for 43%. Nowadays the amount of overburden rocks accumulated by mining companies in Bashkortostan exceeds one million tonnes. Solid wastes accumulate anthropogenic migrants and are the principal source of environmental contamination in the area. The concentrations of heavy metals in the wastes are usually higher than the background values. Data on solid wastes at BCSC, UMPC, and BMPC are summarized and graphically represented in Fig. 1.

We have analyzed the chemical composition of groundwaters near mining works and mine drainages¹. The analyses were carried out at analytical laboratories of the Institute of Geology of the Ufa Research Center, Russian Academy of Sciences, at the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, in Moscow by ICP-MS on a MS PLASMA QUAD (VG Instruments), at the Federal Government-Financed Health-Service Organization Center for Hygiene and Epidemiology of the Republic of Bashkortostan, and at the Federal Government-Financed Organization of the Republic of Bashkortostan Department for Government-Financed Analytical Control. Soils and groundwaters were analyzed on a Spectr AA-110 atomic absorption spectrometer, Spectr AA-280Z atomic absorption spectrometer, Julia-5K Hg analyzer, Fluorat-02-2M liquid analyzer, and UNICO-1200 spectrophotometer.

The hydrochemistry of the mining districts was studied more actively over the past decades, after the ecological geochemical status of these territories had been elucidated. This work was launched in the Ural mining district. Mining-related processes in the Urals were most actively studied by Chernyaev et al. (1970), Emlin (1991), Tabaksblat (1994), Abdrakhmanov (2010, 1997), and others. Elpat'evskii (2000), Yazikov et al. (2006), Zverev et al. (2013), and other research-

¹ Groundwaters are systematized according to their chemical composition in compliance with (Alekhin, 1970; Posokhov, 1975). In this systematics, type I (hydrocarbonate–sodic or sodic) is distinguished at $rCl^- < rNa^+$ with $rHCO_3^- > rCa^{2+} + rMg^{2+}$ and type II (sulfate–sodic) with $rHCO_3^- < rCa^{2+} + rMg^{2+}$. If $rCl^- > rNa^+$, type IIIa (chloride–magnesian) is recognized at $rCl^- < rCa^{2+} + rMg^{2+}$ and type IIIb (chloride–calcic) at $rCl^- > rCa^{2+} + rMg^{2+}$. If the HCO_3^- concentration in water is zero, this water is classed with type IV. Waters are named according to their dominant anions and cations in ascending order of their concentrations. Ions are considered dominant if their concentrations are 20% or higher if the total of anions and cations is 100%.

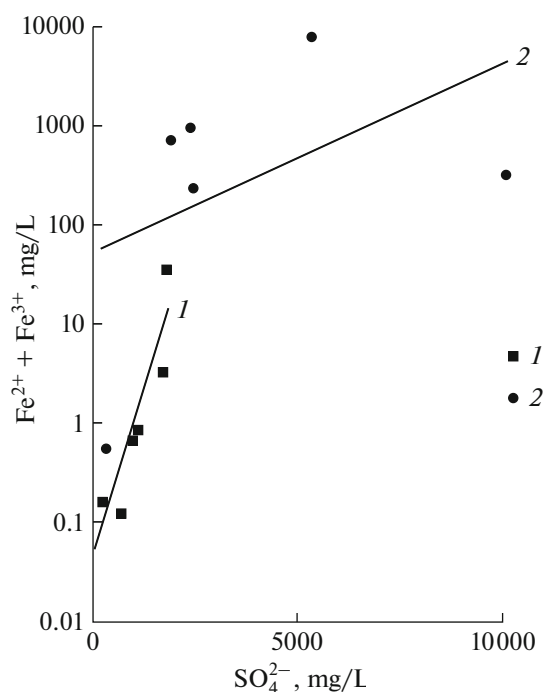


Fig. 2. Correlation between the concentration of the sulfate ion and total concentration of Fe ions (Fe^{+2} and Fe^{+3}) (1) in mine drainage and (2) dump drainage.

ers conducted analogous studies east of the Urals. Fundamental reviews on the geochemistry of groundwaters was compiled by Krainov et al. (2004). The geochemistry of mineral deposits was studied abroad by Nordstrom (1982), Doyle (1990), Stromberg et al. (1999), and others.

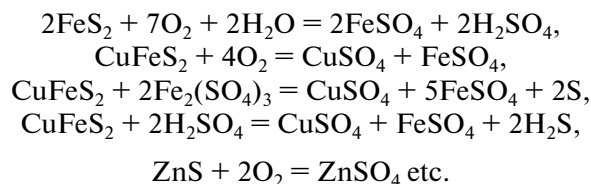
Interest in mineral associations produced in relation to various anthropogenic activities was lately whetted because of the principal possibility of utilizing anthropogenic mineral associations as a new type of mineral resources (Talalai et al., 1997; Chanturiya and Koryukin, 1998; Makarov, 2006).

DISCUSSION

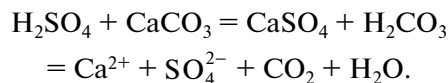
The geological environment as a whole plays the following four major ecological roles: resources, geodynamic, geochemical, and geophysical (Trofimov, 2004). The composition of rocks and ores predetermines the geochemistry of natural waters interacting with them. The dominant ore minerals at sulfide deposits in the Southern Urals are pyrite FeS_2 , chalcocopyrite CuFeS_2 , and sphalerite ZnS . The ores also sometimes contain subordinate amounts of magnetite Fe_3O_4 , tennantite $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$, bornite Cu_5FeS_4 , arsenopyrite FeAsS , and pyrrhotite Fe_{1-x}S . Sulfide ores at the Sibai deposit contain (on average) 1.14% Cu, 2.8% Zn, 41.1% S, 0.0009% Cd, 0.0083% Se, 0.0047% Te, 0.0003% Ge, 0.0006% Ga, and 0.00045% In. The Au–Cu–Zn ores of the Balta-Tau,

Bakr-Tau, and Tash-Tau deposits contain 1.18–7.43% Cu, 1.58–6.94% Zn, and 10.2–31.1% S. The sulfide ores of the Uchaly, Uzelgin, and Molodezhnoe deposits contain 0.4–3.5% Cu, 0.4–5.0% Zn, 0.1–0.3% As, 0.01–0.6% Sb, 0.2–7.0% Ba, 0.1–0.3% Pb, 0.006–0.012% Cd, etc. Ore of the Oktyabr'skoe deposit contain 3.81% Cu, 1.97% Zn, 39.4% S, and minor amounts of Cd, Se, Te, and In. Obviously, the natural and anthropogenically induced hydrogeochemical backgrounds are controlled by minerals containing a broad spectrum of major and minor elements.

One of the modes in which toxicants can migrate from anthropogenic mineral associations (AMA) is hydrogenic fluxes in the form of liquid industrial wastes (opencast- and underground-main drainage, dump drainage, and the liquid phase in tailings). Supergene alterations of minerals at deposits of the sulfide association transform low-solubility sulfides (pyrite, chalcocopyrite, sphalerite, etc.) into much better soluble sulfates (Krainov et al., 2004)



Thereby H_2SO_4 synthesized is neutralized in certain lithologic–geochemical environments by carbonates and thus gives rise to sulfate calcic and magnesian–calcic waters whose mineralization reaches 8–12 g/L (at the Uchaly, Sibai, Buribai, and other deposits)



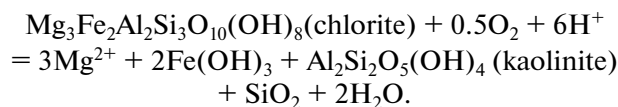
Interacting with oxygen-bearing waters and participating in redox and hydrolysis reactions $\text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+ + \bar{e}$, Fe^{2+} is transformed into Fe^{3+} . Such supergene transformations of ore masses are a hydrogeochemical consequence of the increase in the concentrations of the sulfate ion and ferric iron (Fig. 2), which are Eh–pH controlling systems, and also several ore elements. In this situation, Fe is the principal typomorphic Eh–pH controlling element, whose effect is not mitigated by any other Eh–pH controlling compounds (OH^- , CO_3^{2-} , HCO_3^- , HSiO_4^- etc. (Krainov et al., 2004).

All these redox transformations are associated with the transfer of much H^+ into the mine and solid-waste drainage, with this ion thus decreasing the pH of these waters and drastically increasing their Eh (up to +800 mV). Thereby waters of type IV are produced, whose HCO_3^- concentration is zero. The continuous synthesis of H_2SO_4 , H_2S , $\text{S}_2\text{O}_2^{2-}$, S^0 , and SO_3^{2-} , saturation with atmospheric CO_2 , and a decrease in pH are favorable for promoting sulfuric-acid leaching. Acidic

Table 1. Mine drainage waters at sulfide deposits in the Southern Urals

Sampling site	Sampling depth, m	pH	M, g/L	Concentrations of components, mg/L						Cu, mg/L	Zn, mg/L
				HCO ₃ ⁻	SO ₄ ⁴⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺ + K ⁺		
Water-drainage roadway, level 120 m, UMPC	—	3.9	9.62	0	4947.0	175.4	294.6	417.0	1137.3	59.4	204.1
				0	95.5	5.0	13.6	31.8	45.8		
General drainage sump, level 120 m, UMPC	—	4.1	5.24	0	3024.0	147.9	400.8	221.3	510.6	40.3	153.9
				0	93.7	6.3	29.8	27.1	33.1		
Mine drainage, Sibai deposit	—	5.9	4.5	0	2600.0	108.0	14.6	18.1	1705.0	20.0	200.0
				0	96.0	4.0	1.9	2.0	97.1		
Open-pit mine waters, Kul-Yurt-Tau deposit	4	2.5	2.29	0	1850.0	31.2	187.0	65.0	36.0	2.7	2.6
				0	97.77	2.23	39.9	22.9	6.7		
Open-pit mine waters, Kul-Yurt-Tau deposit	40	2.6	2.99	0	2170.0	19.0	209.0	82.0	54.5	2.5	3.2
				0	98.83	1.17	26.0	16.8	5.9		

mine and dump drainage waters actively dissolve the ambient rocks, for example,



Along with other S-bearing species, H₂S is utilized by certain bacteria (*Thiobacillus*) as an energy source, and this even further decreases pH and affects the mobility of the hydrolyzates (Tabaksblat, 1994). As a result, the influence zones of mines and other anthropogenic constructions are surrounded by newly formed hydrogeochemical fields with anomalously acidic sulfate waters with high concentrations of heavy metals and certain other elements (Krainov et al., 2004). The latter can be classified into two groups. One of these groups comprises chalcophile elements of the oxidizing sulfides themselves: Fe, Cu, Zn, Pb, Cd, Co, Ni, As, Mo, Se, and Te. The other group includes elements that are transferred into the chemically aggressive acidic waters from the host rocks; these are Al, Be, Si, Sc, Ga, Nb, Li, Cs, etc.

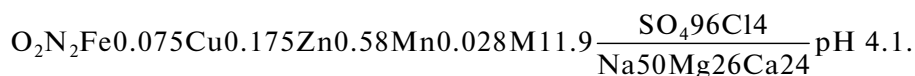
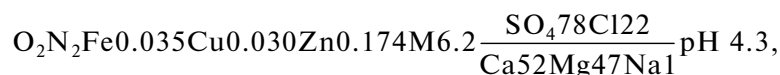
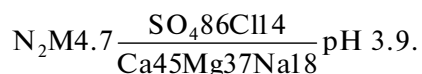
Among species contained in waste waters at mining complexes, the most ecologically hazardous ones are not the typomorphic elements of the mineral deposits (Cu, Zn, and Pb) but such accompanying minor elements as Cd, Hg, As, and Sb, whose maximum permissible concentrations (MPC) in drinking waters are the lowest. These elements are hazardous also because most of them are susceptible to methylation and form various species, such as Cd(CH₃)⁺, Hg(CH₃)⁺, and As(CH₃)₃, whose toxicity is several orders of magnitude higher than that of the respective cation species. These elements are known to be locally contained in groundwaters and cause mass poisoning of the local human population with As and Hg (for example, in the Urals and some mining districts in the western United States) (Krainov et al., 2004).

The inflow of mine waters (from open-pit and underground mine workings) is formed when certain levels exposed in mine workings are drained (Table 1). The territory of the Sibai deposit is dominated by hydrocarbonate calcic and sodic waters, whose mineralization is 0.26–0.95 g/L and pH is 6.8–7.7. The concentrations of minor components in these waters are close to the background ones (mg/L): Cu 0.5–1.0, Zn 1.3–11.0, Pb 0.1–0.2, Mn 0.4, and Hg 0.01. In the zone of the geochemical influence of the deposit, mixing groundwaters and mine drainage generates natural–anthropogenic solutions of hydrocarbonate–sulfate composition with high concentrations of minor components (mg/L): Fe up to 45, Cu 0.002–0.6, Zn 0.03–2.0, etc. In zones adjacent to orebodies, sulfate waters are produced whose mineralization is 0.66–1.5 g/L, pH 6.7–7.6 and which contain a broad spectrum of minor components (mg/L): Fe (1.5–160), Cu (0.007–1.75), Zn (0.04–62.5), Mo up to 0.003, etc. The opencast-mine drainage at the Sibai deposit is produced at a rate of 9120 m³/day and have the following parameters (mg/L): anhydrous residue up to 3216, Cu (0.067), Zn (8.68), Cd (0.007), Fe (3.6), Mn (5.94), Cr (0.07), and Sr (2.6). The underground-mine waters have the following parameters (mg/L): Fe (0.12), Cu (13.36), Pb (1.12), Cr(0.6), Hg (0.02), NO₃²⁻ (6.06); the pH of the opencast-mine drainage is 5.9 and that of the underground-mine drainage is 7.21.

Waters in the area of the Kul-Yurt-Tau deposit are chloride–hydrocarbonate sodic and sodic–calcic and possess mineralization of 0.1–0.53 g/L and pH 6.5–7.1; these waters contain Fe < 1.0, Cu < 0.007, and Zn < 0.05 mg/L. The composition of the water systematically varies with decreasing distance from the sulfide orebody: the water evolves from hydrocarbonate–sulfate to typical sulfate acidic, with mineralization up to 2.5 g/L and pH decreasing to 4–2. The sulfate waters contain (mg/L): Fe²⁺ (2.5–564), Cu (0.1–

1.0), Zn (0.1–0.4), and Mo up to (2.0). The minor admixtures are Au, Bi, Pb, Cr, Ti, V, Mn, Sr, etc. The opencast-mine (“lake”) waters of the deposit have a calcic–ferric composition (Table 1). The mineralization of the groundwater at a distance of 100–150 m from dumps at the Kul-Yurt-Tau deposit reaches 25 g/L, and the waters contain (mg/L): Cu up to 6.9 (0.02), Zn up to 5.9 (0.014), Pb up to 0.05 (0.01), Co 3.8, Ni 1.3 (0.012), Mn 47.5 (0.65), Mo 0.01 (0.004), Sr 0.9 (0.9), Cd 0.05 (0.0002), Be 0.03 (0.00009), Y 0.4, Ce 1.8, Tl 0.0004, Th 0.1, U 0.5 (numerals in parentheses are the average concentrations of the elements in waters hosted in the weathering zone in the Ural hydrogeological folded area).

The area of the Buribai deposit hosts mostly chloride sodic waters with mineralization 6–3 g/L and pH 6.4–8.1. The mine waters of the Byribai deposit are sulfate magnesian–calcic, their mineralization is <4.7 g/L, pH 3–5.2. The maximum concentrations of metals in them are as follows (mg/L): Fe³⁺ (225), Fe²⁺ (375), Cu (140), Zn (66), and Mo (1.1). The formula of the chemical composition of the mine waters is



In the general drainage sump at the Uchaly deposits, the water has pH 4.5, anhydrous residue of 7.2 g/L, and contains the following components (mg/L): Cu (32.5), Zn (212), Fe (62.2), Mn (36.96), Cd (0.6), and NH₄⁺ (10.4). The total production rate of mine drainage waters at the UMPC amounts to 2200–2800 thousand m³/year.

The most unusual composition of drainage at the mining and processing complex was found in the dump drainage waters, whose mineralization amounts to 365 g/L (Table 2) and often exceeds that of the mine drainage. The coefficients of aquatic migration of the typomorphic elements are high. The vast volumes of the dumps produce comparably large volumes of dump drainage, which are formed under the effect of atmospheric precipitation. The local atmospheric precipitation is 400 mm/year at evaporation of 280 mm/year.

Tables 2 and 3 summarize our results obtained in 2005–2014 by studying the chemical composition of dump drainage at UMPC, BCSC, and BMPC. The concentrations of some minor elements increase so much that they become major elements, and the waters become highly mineralized sulfate polymetallic with low pH (2.6–2.8) and high Eh (from +365 to +565 mV) and contain no hydrocarbonate ion (Table 2).

The underground-mine waters at the Oktyabr’skode deposit (356.6 thousand m³/year), which is developed by BMPC, have pH 3.5, anhydrous residue of 3.8 g/L, and the following concentrations of components (mg/L): Cu (16), Zn (18), As (53.3), Cd (0.2), Pb (0.04), Se (0.0003), Sr (1.4), Fe (37.5), Br (0.2), and B (0.2).

The area of the Uchaly deposit hosts hydrocarbonate calcic, rarely sodic, waters whose mineralization is 0.65 g/L, pH 6.4–7.2. In the vicinity of orebodies, the oxidation of sulfides gives rise to sulfate waters with mineralization 1–3 g/L and pH 4.0–6.5. These waters contain elevated concentrations of the following metals (mg/L): Fe²⁺ (0.2–200), Fe³⁺ (0.2–19.5), Cu (0.01–7.6), Zn (0.4–110), Pb (0.012–0.074), Mo up to 0.002, and Mn up to 0.5. The concentrations of iron and other metals are sometimes so high that these ions become dominant in the ionic–salt constituent of the waters. Unusual mineral waters are formed in the close proximity to the deposits: these are so-called *polymetallic waters* with high mineralization. Waters of the following composition are known at the deposit (Abdrakhmanov, 2014):

The dump waters were analyzed for both with the dominant metals and trace elements, REE, and radioactive elements (RE). Although the rocks are poor in these elements, processes related to anthropogenic activities result in enrichment of the waste waters in these elements (Abdrakhmanov and Popov, 2010). The waters are typically rich in trace and radioactive elements. We have analyzed the most toxic (Classes 1 and 2) elements of this group.

One of the most hazardous metals in mine drainage is *lithium*. According to their impacts on the human organism, Li and its compounds belong to Class 2 (highly toxic elements). Its maximum permissible concentration (MPC) in domestic drinking waters is 0.03 mg/L.

Lithium is an element relatively widely spread in nature, and its average concentration in rocks is 0.0032%. Its highest concentrations (tenths of a percent) are found in micas, amphiboles, pyroxene, and halloysite- and montmorillonite-group minerals. Being a cation-producing element, Li most commonly occurs in natural waters in the form of low-charge free ions and passively migrates mostly with clay suspensions. Natural waters are extremely poor in Li (7×10^{-8} to $2.5 \times 10^{-7}\%$) (Chernyaev et al., 1970). The regional background Li

Table 2. Chemical composition (mg/L) of dump drainage at sulfide deposits

Component, mg/L	Sampling site and sample number					
	Buribai, 23	Sibai, 30	Sibai, 31	Uchaly, 40	Uchaly, 41	Kul-Yurt-Tau, 50
HCO ₃ ⁻	—	61.0	—	—	—	—
SO ₄ ²⁻	32143	1857	194048	17976	5102	47738
Cl ⁻	382	5.9	232	27.3	122	19
Ca ²⁺	2138	389	48597	140	802	72
Mg ²⁺	2713	367	62515	101	438	238
Na ⁺ + K ⁺	238	80.2	7.7	17.7	254	23.1
Fe _{tot}	732	0.15	29400	1824	134	9675
Al	1273	13	14153	525	222	818
Cu	443	0.11	3560	178	34	30.5
Zn	196	7.27	12235	207	228	12.2
Mn	145	0.06	409	53	39	18.0
Ni	7.6	<0.01	6.65	0.7	0.57	1.15
Co	8.4	<0.01	22.5	2.66	1.2	5.92
Cd	1.8	0.01	40.5	0.62	0.58	0.062
pH	2.6	7.0	2.1	2.3	3.0	1.6
Anhydrous residue, g/L	40.4	2.8	365.2	21.1	7.4	58.7

concentrations in groundwaters in the Southern Urals is 0.005 mg/L. Elevated Li concentrations occur in waters hosted by clayey rocks (>0.02 mg/L) and by granitoids and diabases (>0.01 mg/L).

A typical lithophile element. Li is atypical of the sulfide-forming hydrothermal process, and most mineral deposits produced by this process contain Li mostly in rock-forming minerals. The highest Li concentrations are found in acid and alkaline rocks. The samples from the Buribai deposit contain up to 16.5 ppm Li. Supergene processes in solid wastes at mining complexes lead to Li involvement in migration with waste waters. The highest Li concentrations are found in the dump waters: 0.2–0.4 mg/L (Buribai) to 3.14 mg/L (Sibai). In the mine waters, Li is positively correlated with the mineralization of the solutions and with Mg and Rb and is negatively correlated with Ca (Fig. 3). Calcium sulfate, whose solubility is at a minimum, likely precipitates. Bottom sediments in the dump drain ditch at the Bakr-Tau deposit contain up to 4 ppm Li, and the local soil contains up to 51 ppm of this element.

Lithium is genetically related to *beryllium* (Fig. 4), which behaves as a typical lithophile element in various geochemical processes. According to its abundances in groundwaters, Be is a rare element. In all of its compounds, Be is bivalent. Much Be is transferred into waters when rock-forming minerals with disseminated Be mineralization are weathered. Trace Be concentrations (0.0003–0.0005 mg/L) were found in groundwater at the XIX Parts"ezd deposit, Kul-Yurt-

Tau deposit, and Gai deposit (Chernyaev et al., 1970). Although the Be concentrations are very low (0.3–0.6 ppm), processes related to anthropogenic activities enrich this element in waste waters, in which Be concentrations vary from 0.001 to 0.13 mg/L. Iron hydroxides at the Bakr-Tau territory contain up to 9 ppm beryllium, and the dry precipitate of water at the discharge site of drainage of the Southern Dump of the Sibai deposit contains 6.6 ppm of this element. The group of beryllium also includes *barium* (0.04–0.7 mg/L) and *strontium* (0.2–6.3 mg/L).

Cadmium is typomorphic chalcophile element of sulfide deposits. It is genetically related to Zn and, not as strongly, to Pb and In. A principal Cd concentrator is sphalerite. The concentrations of this element in groundwaters are very low. It was detected by spectral analysis only in a few samples of groundwaters from Southern Ural sulfide deposits, with these waters sampled in the close vicinity of high-grade Zn ores. The Cd concentrations of these water samples range from traces to 0.01 g/L. Cadmium is likely transported in the form of sulfate. Its concentrations in the dump drainage are relatively high, from 0.02 mg/L (at the Kul-Yurt-Tau deposit) to 40.5 mg/L (at the Sibai deposit). Cadmium concentrations in dump drainage waters at the Sibai deposit reach 380 mg/L (Emlin, 1991), and the wastes are also rich in As.

Arsenic is widespread in ores at sulfide deposits and is contained mostly in arsenopyrite. Minerals of this element are unstable in the supergenesis zone and are

Table 3. Minor elements (wt %) in dump drainage at mineral deposits in the Southern Urals in comparison with the average regional concentrations in the hydrosphere

Element	Sampling site and sample number						Regional clarke (Chernyaev et al., 1970)
	Buribai	Sibai		Bakr-Tau	Uchaly		
	23	30	31	36	40	41	
Li	0.001	0.0009	0.001	0.002	0.003	0.004	0.0005
Be	0.00003	0	0.00004	0.0002	0.00007	0.0002	0.00002
Sc	0.002	0.0005	0.002	0.003	0.001	0.002	0.000014
Ti	0.006	0.006	0.0054	0.014	0.02	0.005	0.001
Cr	0	0	0	0.003	0.06	0	0.0001
Co	0.02	0.0007	0.006	0.03	0.009	0.01	0.00008
Ni	0.02	0.002	0.003	0.02	0.007	0.009	0.00014
Ga	0.00007	0	0.00004	0.00005	0.0001	0.0001	0.000016
Ge	0	0	0	0.00002	0.000005	0	0.00006
Rb	0.00008	0.00007	0.00024	0.00008	0.0005	0.00006	0.0001
Sr	0.005	0.08	0.002	0.02	0.02	0.005	0.001
Y	0.003	0.00024	0.002	0.006	0.003	0.01	0.000012
Nb	0.00003	0.00001	0.00004	0.000005	0.00002	0.00002	0.0001
Mo	0.00005	0.00002	0	0.00003	0.009	0	0.00006
Cd	0.005	0.003	0.01	0.02	0.0024	0.008	0.000014
Sn	0.00044	0.05	0.00002	0	0.001	0.001	0.00007
Cs	0.000006	0.00001	0.000009	0.000004	0.00002	0	0.00003
Ba	0.004	0.0003	0	0	0	0	0.00012
La	0.00054	0.00004	0.0003	0.001	0.0006	0.0014	0.00001
Ce	0.002	0.00009	0.0007	0.003	0.0014	0.004	—
Pr	0.0003	0.00001	0.0001	0.0004	0.0002	0.0006	—
Nd	0.0014	0.000054	0.0006	0.002	0.0009	0.003	—
Sm	0.0005	0.00004	0.0002	0.0006	0.00034	0.001	0.00002
Eu	0.0001	0.000007	0.00008	0.0001	0.0009	0.0003	—
Gd	0.0006	0.00004	0.0004	0.001	0.0006	0.002	—
Tb	0.000094	0.000006	0.00008	0.0002	0.0001	0.0004	—
Dy	0.0005	0.00004	0.0005	0.001	0.0007	0.002	0.00004
Ho	0.0001	0.00001	0.00009	0.0002	0.000134	0.0005	—
Er	0.0003	0.00003	0.0003	0.0004	0.0003	0.0014	0.00001
Tm	0.00004	0	0.00003	0.00007	0.00005	0.0002	—
Yb	0.0002	0.000007	0.0002	0.0005	0.0004	0.001	0.000008
Lu	0.00003	0.000003	0.00003	0.00007	0.00004	0.0002	—
Hf	0	0	0.000001	0	0.00001	0.000006	—
Ta	0.00004	0.000004	0	0	0	0	0.0001
Tl	0.000002	0.000002	0.000003	0.000002	0.000007	0.000001	0.000012
Bi	0.000003	0.000004	0	0.000001	0.000001	0.000004	0.00001
Pb	0.00009	0.0001	0.0004	0.0009	0.0008	0.0007	0.00012
Th	0.00002	0.000003	0.00004	0.0005	0.00008	0.00014	—
U	0.0002	0.0001	0.0003	0.00003	0.0002	0.0005	—

decomposed in several processes. The concentrations of As in the mine waters amount to 10–400 mg/L and even more. In the Ural groundwaters, As concentrations range from traces to 0.054 mg/L in 35–62% of the samples. The highest As concentrations were found in dump drainage at the Sibai and Kul-Yurt-Tau deposits (up to 7.55 mg/L).

The distribution of RE in the wastes is still understood inadequately poorly because these elements have not be regarded as pollutants previously. Concentrations of these elements in the rocks at the territory are illustrated in Fig. 5. Note that in some Paleozoic formations in the Magnitogorsk zone, K, U, and Th concentrations increase from older to younger rocks. This tendency is not absolute and is of cyclic character because of alternation of tholeiitic petrogenetic series (Baimak–Buribai and Karamalytash) and calc–alkaline ones (Irendyk and Ulutau) (Kosarev et al., 2000).

Composite sulfide ores in the Tagil–Magnitogorsk trough are noted for relatively strong paragenetic relationships with U and Th (Taraborin, 2004). Ores at the Gai Cu sulfide deposit are characterized by fairly high radioactivity (up to 400 μ R/h) and contain 0.03% U in the form of colloid U compounds and uraninite. Anomalously high radioactivity (61–63 μ R/h) was also detected in the Mesozoic–Cenozoic cover.

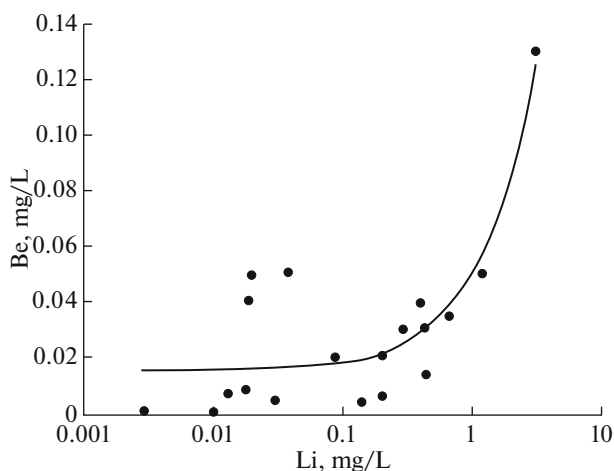


Fig. 4. Correlation between Li and Be concentrations in dump drainage in the Southern Urals.

Although the concentrations of RE in the rocks are relatively low, processes associated with anthropogenic activities result in the accumulation of these elements in the liquid wastes (mg/L): U up to 1 and Th up to 0.8. Radioactive elements always accompany REE, and the U concentrations of practically all of the samples are positively correlated with Y (Fig. 6).

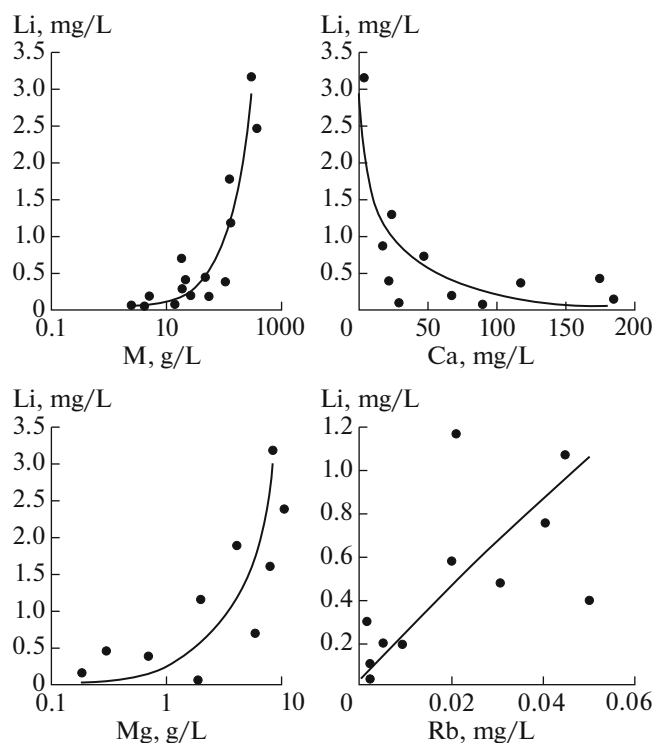


Fig. 3. Correlations of the Li concentration with the total mineralization and the Ca, Mg, and Rb concentrations in mine drainage in the Southern Urals.

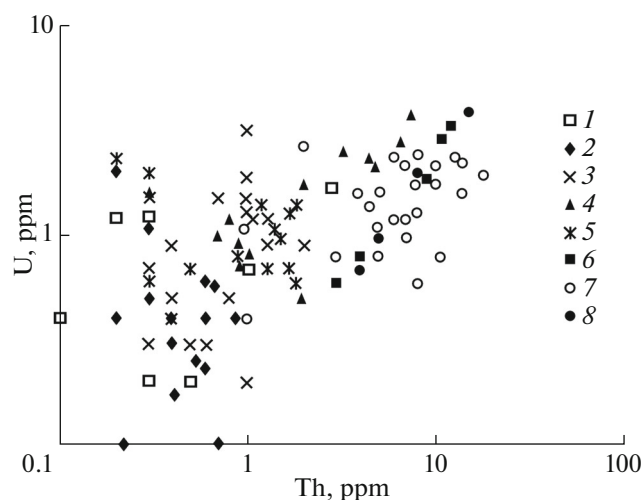


Fig. 5. Correlation between U and Th concentrations in Ordovician–Early Carboniferous volcanic rocks in the Magnitogorsk megazone (Kosarev et al., 2000). 1—Ordovician–Silurian basalt in the Voznesensko–Prisakmarskaya zone; 2—Early Devonian volcanic rocks of the Baimak–Buribai Formation; 3—Early Devonian volcanic rocks of the Upper Karamalytash Formation; 4—Early to Middle Devonian volcanic rocks of the Irendyk Formation; 5—Middle Devonian volcanic rocks of the Karamalytash Formation; 6—Late Devonian volcanic rocks (average values); 7—Early Carboniferous volcanic rocks of the Berezovskaya and Kizil Formations; 8—same, average values.

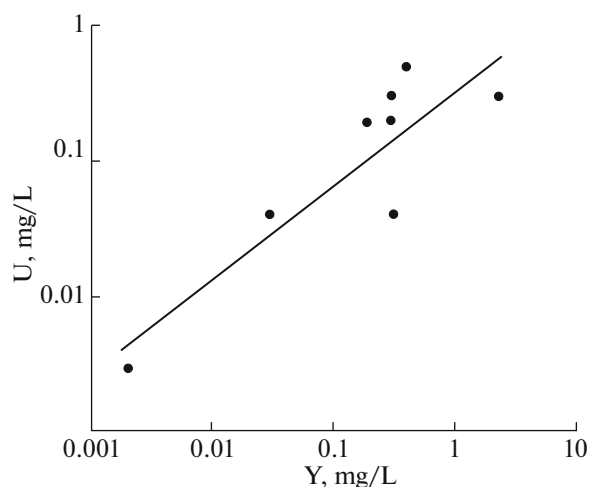


Fig. 6. Correlation between Y and U concentrations in dump drainage in the Southern Urals.

Weathering processes enrich their products in Ca, Ce-group elements, and Th. Simultaneously, Mg, Y, Y-group elements, and U are transferred from the rocks to waters (Fig. 7).

The minerals likely concentrating Y and REE are sphene, magnetite, barite, gypsum, jarosite, limonite, calcite, zircon, feldspars, hydromicas, galena, and pyrite. The possible sources of trace elements and REE may be brunkite and thorbastnaesite (Tabaksblat, 1994), which were identified by XRD analysis in the water-hosting rocks, loose surface sediments, and the anhydrous residue of groundwaters and mine waters in the Urals.

The dump drainage contains (mg/L): Y up to 6.3, Ce up to 2.2, La up to 0.94, Pr up to 0.3, Nd up to 0.6, Sm up to 0.2, Eu up to 0.25, Gd up to 0.4, Tb up to 0.25, Dy up to 1.6, Ho up to 0.28, Er up to 0.94, Tm up to 0.1, Yb up to 0.6, and Lu up to 0.09. Oxide mottles on soil in the close vicinity of Bakr-Tau dumps contain

189 ppm Y and 31 ppm La (Akhmetov and Abdrahmanov, 2009). The REE whose MPR in drinking water are stipulated are Sm and Eu: 0.024 and 0.3 mg/L, respectively.

The U concentrations in the dump drainage vary from 0.006 to 1 mg/L. According to the systematics (Alekhin, 1970), this value, which is 0.0005% of the mineralization, is very high. At low pH, U starts migrating (mostly in the form of the uranyl ion UO_2^{2+}) and can be accumulated in the soil, bottom sediments, etc. as the acidity of the solutions decreases. The probable sources of Th and U are pyrite, rock-forming minerals (feldspars, micas, etc.), thorbastnaesite, and to a lesser extent, zircon. Uranium forms rims around rock-forming minerals, with these rims operating as adsorption films, so that uranium concentrations in the films are 1000–10000 higher than in the minerals themselves (Titaeva, 2002).

An important regional hazard is environmental contamination with *mercury*. Its high concentrations are typical of the hydrothermal process because this element possesses chalcophile characteristics. The main Hg concentrators in the Southern Urals are fahlores, sphalerite, galena, and to a lesser degree also chalcopyrite and pyrite. Mercury concentrations in ores at the deposits broadly vary and are often relatively high, for example, 800 ppm at the Uzel'gin deposit, 560 ppm at the Uchaly deposit, and 88 ppm at the Novo-Uchaly deposit. Rocks from the oxidation zone at the deposit contain Hg in the form of metacinnabarite and in Au amalgame (a mineral phase of composition close to $Au_{0.81}Hg_{0.19}$). When ores are mined and processed, Hg is partly transferred into wastes: dumps of barren rocks and off-standard ores, flotation residues, and waste waters. Because it was found out in 1996 that the blood of residents in the village of Semenovskaya contains Hg (0.00085 to 0.12975 mg/L) and the drinking water contains up to 59 MPC, the waters drawn off for the village and the materials in tailings of the Semenovskaya gold-recovery plant

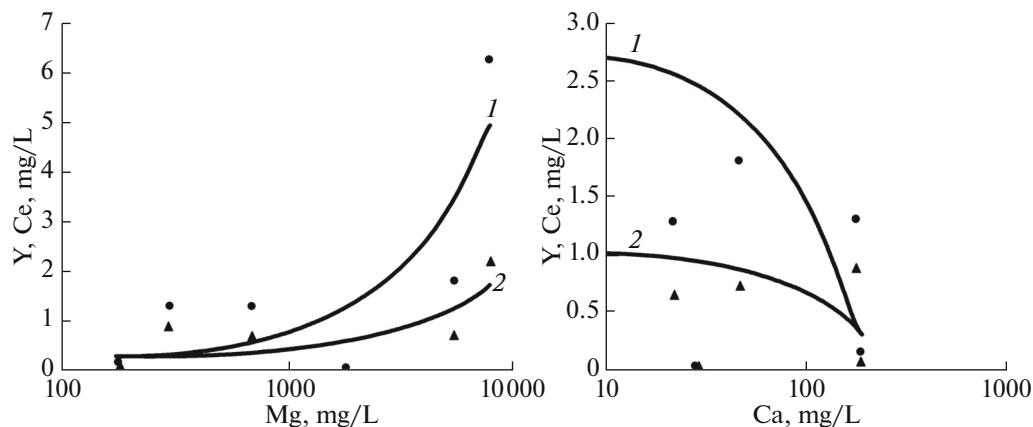


Fig. 7. Correlation between (1) Y and Mg and (2) Y and Ca concentrations in dump drainage in the Southern Urals.

(which was closed down in 1996) were sampled and analyzed in 1996–2000. The very first data (obtained in 1996) have shown that Hg concentrations in the tailings vary from 8.8 to 42.3 ppm in all samples. The follow-up studies in 2012–2013 have shown that Hg concentrations in soils at the tailing dump and at the industrial estate of SGRP have significantly decreased: from >40 ppm in 1996–2000 to 0.79–6.7 ppm in 2012–2013. The latter values are 3.2 times higher than the MPC for soils. There seems also to be a tendency toward a decrease in Hg concentration in the groundwaters. The Hg concentrations in the waters in 1996 were 0.0121 mg/L (24.2 MPC) and in times were as high as 678 MPC. Systematic monitoring of the chemical composition of the groundwaters in 2012 (in August) detected Hg contaminati

on only in two wells (2.4 and 3.2 MPC). Replicate analysis of water samples in December of 2012 did not identify Hg in the groundwaters of any of the monitoring wells within the detection threshold of the equipment. Thus comparative analysis of earlier data and information obtained nowadays shows that Hg concentrations in the groundwaters have significantly diminished, to 3 MPC or even zero, which suggests natural demercurization (Abdrakhmanov, 2013; Akhmetov, 2013).

CONCLUSIONS

Territories of mining and processing complexes are characterized by the strong impact of processes related to anthropogenic activities on the geological environment (down to a depth of 500 m). These processes are most active at territories where closely spaced mineral deposits are developed simultaneously (as in the Baimak, Uchaly, and other mining districts). This results in an unusual “sulfuric” landscape, and hydrogeochemical fields of modified waters that are newly formed in the areas of mining districts (Perel'man, 1961).

The anthropogenically induced degradation of the underground hydrosphere at mining districts in the Southern Urals is a long-lasting process associated with the accumulation of vast amounts of solid wastes (>1 billion tones). The fracture and fracture-vein nature of the groundwaters and the thin and discontinuous cover of overlying rocks are favorable for the easy infiltration of highly concentrated mine waters contaminated with toxic elements into aquifers. Highly acidic (pH 2–5) sulfate waters are generated at the Buribai, Sibai, and Uchaly sulfide deposits. These waters bear mineralization up to 20 g/L and possess high concentrations of Fe (up to 564 mg/L), Cu (up to 140 mg/L), Zn (up to 200 mg/L), and other metals. The most geochemically reactive liquid wastes and dump drainage waters, whose mineralization amounts to 365 mg/L. All of these wastes are typical of the active metamorphism of groundwater.

Anthropogenically produced mineral associations and liquid wastes at sulfide deposits in the Southern Urals may be regarded in the future as serious secondary potential sources of valuable mineral components. Dump and mine drainage contain concentrations of principal ore components comparable with their average concentrations in the ores. The Government of the Russian Federation ordered (Resolution Pr-1640) “to prepare suggestions on long-term investment programs aimed at treating solid domestic and industrial wastes and implement pilot projects of waste processing”. Our studies in the Southern Urals provided estimates of the average concentrations of metals in the discharged mine drainage. These data indicate that the mine waters at the Sibai deposit alone annually leach $n \times 10^5$ kg Cu, $n \times 10^5$ kg Zn, $n \times 10^5$ kg Fe, and $n \times 10^4$ kg Pb. The processing of anthropogenically produced mineral associations and main drainage waters shall improve the ecological situation in the area and relieve the environmental load.

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