GEOCHEMISTRY OF INTERACTION OF MINE DRAINAGE OF MEDNOGORSK GEOTECHNICAL SYSTEM WITH RIVERS AS A NATURAL HYDROCHEMICAL BARRIERS

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ABSTRACT

Mednogorsk industrial area shows a high level of anthropogenic pollution, due to exploitation of copper-zinc massive sulfide deposits that causes accumulation of heavy metals in all components of the environment and leads to a critical environmental situation.

The authors determine the composition of a rivers in the Mednogorsk geotechnical system (a combination of natural and technogenic objects, whose functioning depends on each other.) that is impacted by acid- and neutral-mine drainages, evaluate dominant geochemical processes controlling the composition, and assess dissolved metal speciation and saturation indexes using a combination of laboratory, field and modeling studies.

Anomalies of heavy metals concentrations in water are stretched over long distances from the source of technogenic pollution, forming the most contrasting halos of Zn, Cd, Mn, Cu in the downstream of river Blyava. Concentrations of Fe, Cu, Zn, Mn and Cd are increased in the river Kurgan, which is due to insufficient natural buffering capacity of a river.

Secondary minerals and solid phases formed on a hydrochemical barriers are defined, and their role in removing heavy metals from solution are shown. The migration of chemical elements in anthropogenic water flows are caused by the cyclic process of deposition and dissolution of mineral phases. The iron concentration is a dominant factor in the removing of metals from solutions: even in an acidic conditions (pH 3.5) the formation of iron hydroxides leads to a decrease in metal concentrations more than an order of magnitude due to a proportional sorption of cationic and neutral complexes.

Keywords: Mine drainage, mixing zone, environmental impact, heavy metals.

1. INTRODUCTION

The weathering of iron sulfides, other metal sulfides, and gangue minerals associated with mineral deposits, their host rocks, and mine wastes releases acidity, metals, sulphate and other elements to the environment.

Importance of this research work is dictated by a large-scale pollution of natural ponds and rivers which occurs when mine drainage, containing high concentration of heavy metals, sulfate and other components, discharges into otherwise uncontaminated waters.

Today there are a lot of investigations in the field of oxidation of sulfidic wastes, formation of acid mine drainage and mechanisms of transporting metals in streams. These aspects have been reported in various papers by Banks [1], Hammarstrom [2], Younger and Robins [3], Lottermoser [4] and others. This problem was also addressed by Ural geologists such as Chesnokov and Bushmakin [5], Udachin [6], in monographies and articles by Bortnikova and Gaskova [7] and others.

However, the problem of hydrochemical barriers (such as natural ponds, rivers, streams) received less attention. In spite of this, the significance of hydrochemical barrier is very great: neutralization and dilution of highly mineralized mine waters, formation of suspension of hydrogenic minerals and alteration of chemical forms of elements occurs on it.

Thus, the purpose of this study is to define mechanisms of interaction «mine drainage - natural waters» with an ecological estimation of influence on hydrogeochemical composition of waters.

2. OBJECTS OF STUDY

The Urals is one of the most important regions in the world for the occurrence of volcanogenic massive sulfide deposits. One of them is Blyavinskoe copper-pyrite deposit located on the western slope of the Southern Urals within the Sakmara zone of the Zilair synclinorium (7 km north-east of Mednogorsk city). It was opened in 1930 and developed from 1936 to 1970 by open pit and underground ways. The ore body lies at the western contact of a large subvolcanic massif of liparit porphyries, breaking through the thick pillow lavas of the Silurian age. The genesis of deposits is hydrothermal. Its ores could be formed on the sea bottom in the near-surface conditions as a result of volcanic exhalations. Due to prolonged exposure to weathering processes the oxidation zone in which have been developed hematite, limonite, hydrohematite, siderite, brimstone, gypsum, sulfates of iron and copper, malachite and native copper was formed on an ore deposit. From ores of Blyavinskoe deposit were extracted copper, sulfur, zinc and some rare elements that are processed at the Mednogorsk copper-sulfur plant (Richter and Varlamova [8]). The main features of this deposit are relatively high content of Cu in ore, extensive colloform structures and significant thickness of the zone of secondary sulfide enrichment.

The aquatic system in Mednogorsk industrial complex is under a strong anthropogenic impact. The main sources of pollution of rivers are waste rock dumps and substandard copper-zinc sulfide ores. Sulfide wastes are oxidized intensively and as a result aggressive waters with high concentration of soluble metallic salts are formed. These waters radically differ from chemical composition of surface waters in the region.

In geotechnical system under study the main migration flows, forming technogenic anomaly of toxic elements, are connected with acid mine drainage from waste rock dumps and substandard ores of Bljavinskoe and Jaman-Kasinskoe deposits. All streams run into the rivers Zhiriklja and Khersonka which are tributaries of second order of Bljava river.

3. METHODS OF ANALYSIS

Research methods include sampling of water and sediments from drainage streams, mixing zones and natural rivers, spectrometry and classical methods of analytical chemistry to determine elemental, anionic and mineral compositions of samples, thermodynamic modeling to calculate the chemical species of elements in the solution.

3.1. Field sampling

The surface waters at all sampling points of Mednogorsk geotechnical system were collected in 10-20 cm water layer into plastic (polyethylene) bottles (0.5 – 1 L). Samples were taken directly at the drainage outflow, in mixing zones with rivers and in the rivers upstream and downstream of mixing zones. Part of the water samples were filtered through 0.45 μm filter and acidified to pH~2 with suprapure HNO_3 for subsequent elemental analysis. Another part of water samples were left unchanged. Samples were stored at ambient temperature in the dark not exceeding 14 days. Water pH and Eh were measured immediately on site.

Bottom sediments were collected into double plastic bag for transportation to the laboratory where they were dried at room temperature. Fraction +0.25 mm were sieved. The remains were abraded in a porcelain mortar and pestle to a size <0.1 mm. After careful homogenization and repeated quartering, 30 mg of each sample was pressed into 10 mm pellets on a hydraulic press under a 100 kg/cm^2 pressure for XRF-SR analysis.

3.2. Water and sediment analysis

A number of chemical analytical methods of determination the composition of water and sediments were used:

1. titrimetric and turbidimetric methods to determine major anions (Cl^-, HCO_3^-, SO_4^{2-});
2. ICP-AES method to determine major cations (Ca, Mg, K, Na, Al, Si) and trace elements (Mn, Fe, Cu, Zn, Cd, Ni, Co, Pb, As, Sb) in water;
3. SR-XRF analysis to determine chemical composition of sediments;
4. electron microscopy (Jeol JSM-638OLA) to define mineral composition of heavy fraction of bottom sediments;

5. chemical species of elements and saturation indexes in solution were calculated using program WATEQ4F (Ball and Nordstrom [9]). It uses field measurements of temperature, pH, Eh, dissolved oxygen and alkalinity, and the chemical analysis of a water sample as input and calculates the distribution of aqueous species, ion activities, and mineral saturation indices that indicate the tendency of a water to dissolve or precipitate a set of minerals.

The mineral saturation index (SI) describes the tendency of the drainage to dissolve or precipitate a set of minerals, and it is defined by the following relationship:

$$SI = \log \frac{IAP}{K_{sp}} \qquad (1)$$

where IAP is the ion activity product calculated from the water sample, and K_{sp} is the theoretical solubility product, both adjusted to the sample's temperature. When SI > 0, the IAP exceeds the solubility product (K_{sp}) and a state of saturation or supersaturation is achieved. In such situations, secondary minerals would precipitate. A negative SI means that $IAP < K_{sp}$ and conditions for mineral dissolution are achieved. SI equal to 0 indicates equilibrium conditions, more precisely, dissolution or precipitation of a certain mineral phase controls the concentration of the dissolved components contained in that phase. The formation and dissolution of secondary minerals affect the chemical composition of the drainage. Precipitation of less soluble minerals such as alunite, jarosite or anglesite can cause significant attenuation of metal concentration in solution. On the other hand, the precipitation of soluble minerals has a temporary effect on acidity and metal concentrations in solution. Such minerals seem to be removed from solution during dry period, and then released back into solution as soon as the wet season begins, resulting in seasonal and cyclical variations in acidity and metal concentrations.

6. Mobility of elements in the system 'bottom sediments - surface water' were calculated using the following formula:

$$C_{mobility} = \lg \frac{Me_{solid}}{Me_{solution}} \qquad (2)$$

Where Me_{solid} is the concentration of element in bottom sediment (ppm), and $Me_{solution}$ is concentration of element in water (ppm). The lower $C_{mobility}$ the higher the mobility of element in the system.

4. RESULTS

Water samples were analyzed to elucidate both the effects of continuous and episodic transport of metal contaminants as they were released from the source upon oxidation of the sulfide minerals and the stages of their sequestration.

As presented in Table 1, the mine water samples showed extremely high concentrations in most metal pollutants.

Table 1 Chemical composition of water samples, ppm

Parameter	Blue stream	Green stream	Background*
pH	6.9	3.4	7.6
Eh, mV	510	760	233
Conductivity, µS/cm	4340	12000	365
Cl^-	40	411	54
SO_4^{2-}	2800	9300	88
HCO_3^-	510	-	260
Ca^{2+}	630	450	81
Mg^{2+}	370	1800	18
K^+	2.3	1.5	4
Na^+	74	160	27
Fe	0.1	33	0.03
Al	0.2	440	nd
Mn	18	120	0.009
Cu	1.5	170	0.014
Zn	6.1	100	0.03
Pb	<0.1	0.2	nd
Cd	0.02	0.7	0.0002
Ni	0.2	2.9	0.0014

** - as a background was chosen a sampling point in the upper stream of Blyava river remoted from waste rock dumps; nd - not determined*

Anomalies of heavy metals in water are stretched over a long distances from the source of contamination, forming the most contrasting halos of Zn, Cd, Mn, Cu downstream of the Blyava river (Fig. 1).

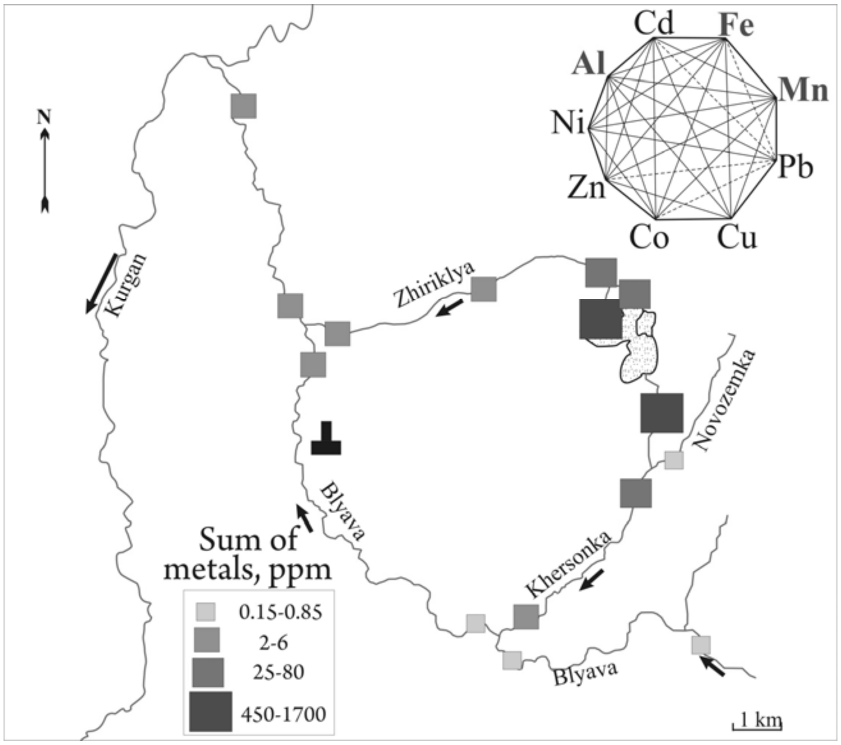

Fig. 1 The total concentration of metals (Al, Fe, Mn, Cu, Zn, Ni, Co, Cd, Pb, Ba) and correlation diagram in water of Mednogorsk geotechichal system

Concentrations of Fe, Cu, Zn, Mn and Cd increased in the Kurgan river because of insufficient natural buffering capacity of a natural water stream. An explanation to this facts can be found in the correlations between elements. There is a high positive correlation between Al, Fe, Mn and heavy metals Cd, Zn, Co, Cu, Pb, and Ni, which indicates on its joint migration in waters.

Studying of chemical forms of metals in a surface waters is a prominent aspect at ecological researches and in particular in mixing zones with technogenic streams since change of physical and chemical properties and alteration of chemical forms of elements might occur.

The main chemical forms of elements in acidic waters are sulfate complexes ($Me(SO_4)_2{}^0{}_{aq}$, $Me(SO_4)_2{}^{2-}$) and free cations (Me^{2+}). In neutral mine water drainage, carbonate and hydroxide complexes ($MeCO_3{}^0{}_{aq}$, $Me(CO_3)_2{}^{2-}$, $MeHCO_3{}^+$, $Me(OH)_{2aq}$, $MeOH^+$) significantly increase, creating the base for the formation of a big group of minerals, primarily hydroxides. A significant metal concentrations can also be transported by colloidal material in surface waters. Colloidal iron precipitates with adsorbed metals can represent important transport modes for metals in mine environments and streams beyond the mine site.

Saturation indexes showed that Al, Fe, Mn can form amorphous hydroxides, which in turn may be in the form of thin colloids and migrate as suspension (Fig. 2).

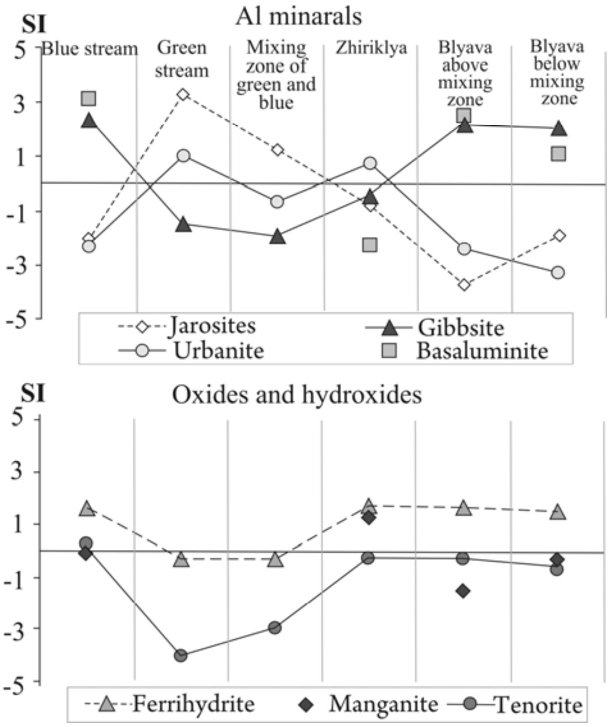

Fig. 2 Saturation indexes of minerals in waters in Mednogorsk GTS

It should be noted that the parameter pH showed only a negative correlation with all metals, and electrical conductivity showed a significant at 99% a positive association with all components. It has been noted that sulfate and electrical conductivity are more reliable indicators of mining effluents than pH and heavy metals are. This was attributed to the fact that sulfate is a conservative anion in mining environments and is less affected by sorption processes or fluctuations in pH than heavy metals (Gray [10]).

The presence of colloids is confirmed by saturation indexes of minerals – basaluminite, urbanite, gibbsite at different points of the geotechnical system. Indeed, in that type of solutions hydroxides, oxides and sulphates may form, but some of them are unstable in such conditions and able to dissolve.

The chemical composition of sediments and ocher suspension is a sensitive indicator of natural and anthropogenic processes within the catchment area. The major components of a Blue stream ochers contain Al (14%), Ca (1.2%), K (0.4%), Mn (0.05%), Fe (0.05%) and in Green stream - Al (7.2%), Ca (0.9 %), K (0.6%), Ti (0.1%), Cr (0.07%), Mn (0.2%), Fe (47%). Bottom sediment of Blue stream according to thermal analysis consists of Al_2O_3 (41%), SiO_2 (3.4%), P_2O_5 (1.1%), SO_3 (16%), CaO (0.8%), FeO (0.6%) and H_2O (38%). This composition corresponds to hydrobasaluminite $Al_4(SO_4)(OH)_{10}$•12-36H_2O as a product of a neutralizing Al-containing high sulfate waters formed by oxidation of pyrite and the subsequent dissolution of sericite, chlorite and acid plagioclases from the aluminosilicate rock dumps. Basaluminite and urbanite $Al_4(SO_4)(OH)$•5H_2O formed as a products of dehydration of hydrobasaluminite.

Comparison of two contrast streams showed that ferrihydrite ocher sorbs largely Al, Mn, Cu, Ti, Cr, Zn, and white aluminum ocher mainly accumulates Cu, Zn, Ni, Y, Mo (Fig. 3).

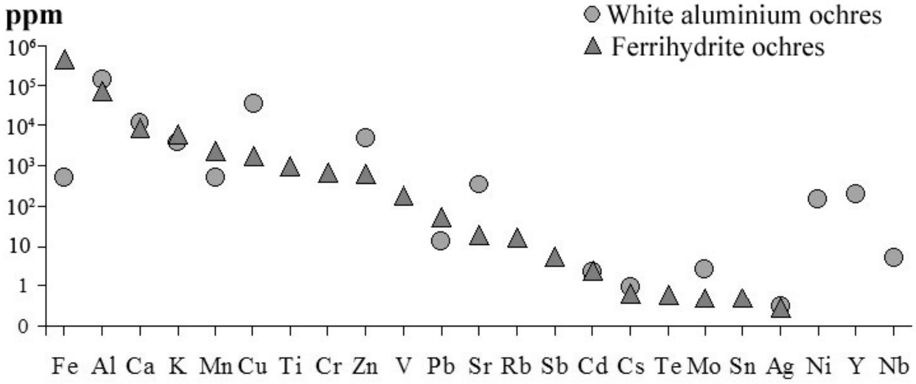

Fig. 3 Elemental composition of suspension ochers

The formation of Fe-hydroxides causes a decrease of concentrations of metals more than one degree (due to a proportional adsorption of cationic and neutral complexes). Under neutral and alkaline conditions, along with the sorption on hydroxides, metals form their own mineral phases and coprecipitate with Al and Fe hydroxides (Fig. 4, 5). Generally, solid compounds adsorb more anions at low pH and more cations at neutral pH.

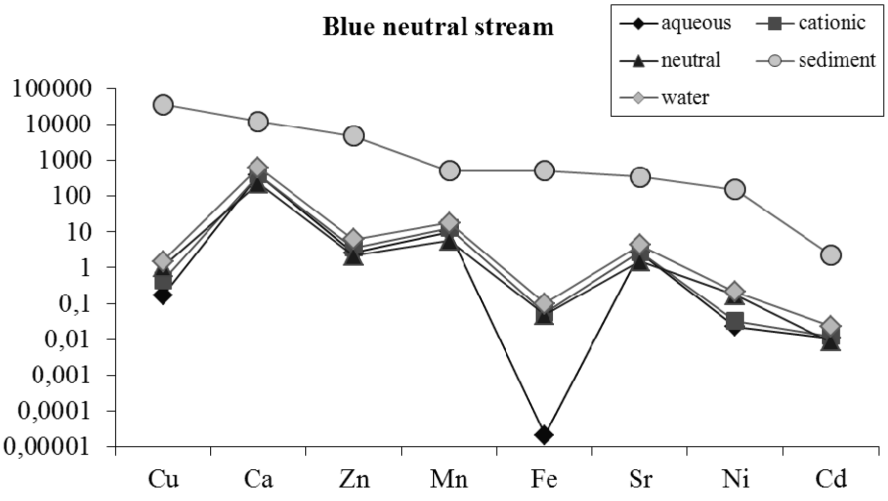

Fig. 4 Forms of concentration of elements in bottom sediments of Blue stream

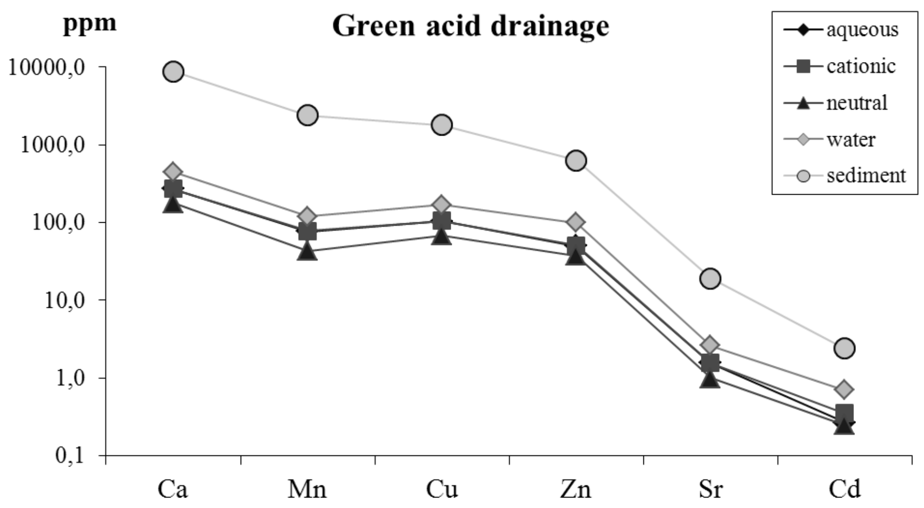

Fig. 5 Forms of concentration of elements in bottom sediments of Green stream

The coefficient of mobility of element were calculated and compiled in a corresponding rows in order of decreasing the mobility:
1) pH=3.4 (Green stream) $Cd_{0.5}>Zn_{0.8}>Cu_{1.0}>Mn_{1.3}>Al_{2.2}>Pb_{2.4}>Fe_{4.2}$;
2) pH=6.9 (Blue stream) $Mn_{1.4}>Cd_{2.0}>(Ni, Zn)_{2.9}>Fe_{3.7}>Cu_{4.4}>Al_{5.6}$;
3) pH=4.1 (MZ of two streams) $Cd_{0.7}>Mn_{1.2}>Cu_{1.3}>Zn_{1.4}>Ni_{1.6}>Al_{2.7}>Pb_{3.2}>Fe_{4.3}$;
4) pH=7.0 (MZ of Blyava and Zhiriklya)
$Mn_{3.1}>Pb_{3.5}>Ni_{3.6}>Cd_{3.9}>Zn_{4.2}>Cu_{5.7}>Al_{5.9}>Fe_{6.4}$.
Analyzing the mobility of elements in the system 'bottom sediments - surface water' we can see that Al ocher traps metals more effectively than in green stream. After mixing in Zhiriklya river the elements become less mobile, but further downstream their mobility rises again because of desorption process.

5. CONCLUSIONS

Mine waters are highly mineralized sulfate solutions, forming a new type of anthropogenic waters, in which trace elements constitute the main part of cation composition, that allows to consider them as a major components.
The migration path of chemical elements in anthropogenic flows are determined by cyclic processes of deposition and dissolution of mineral phases. Secondary hydrogenous metal compounds can change their mineral forms and may dissolve due to local variations of physical and chemical conditions. Dissolved iron is the main factor of metal removal from solutions: even in acidic environment (pH=3.5) the formation of Fe-hydroxides causes a decrease of concentrations of metals more than one order of magnitude (due to a proportional adsorption of cationic and neutral complexes). In neutral and subalkaline conditions, along with the sorption on hydroxides, metals can form their own mineral phases and coprecipitate with Al and Fe hydroxides.

The maximum concentration of Cu, Zn, Mn, Cd, Ni, Co are found in bottom sediments with high concentration of Fe and Al, which can form amorphous hydroxides and hydroxosulphates. Trace elements in ferryhydrite ochres form the following series of decreasing contents: Mn> Cu> Ti> Cr> Zn> V> Pb> Sb> Cd, which corresponds to the decrease of cation and neutral complexes in these conditions. In Al-bearing ochres, from 2 to 3 times higher concentration of chalcophile elements were observed.
Mine waters of Mednogorsk geotechnical system contain elevated metal and metalloid concentrations. Such waters are of environmental concern because the elements tend to remain in solution, despite pH changes. The elements can be transported for long distances downstream of their source, and they may adversely impact on the quality of natural waters.

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