A GEOCHEMICAL AND GEOPHYSICAL CHARACTERIZATION OF ACID MINE DRAINAGE AND SULFIDE TAILINGS AT KARABASH MINE SITE (SOUTH URAL, RUSSIA)

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Abstract- The Karabash mine area was chosen as the research site for its potential hazardous influence on the environment of Chelyabinsk region. This work presents the results of a geochemical and geophysical characterization of an old tailing containing high contents of sulfide minerals, primarily pyrite (up to 25 wt%), chalcopyrite (3 wt%) and up to 1 wt% of sphalerite and galena. In order to obtain a representative characterization of the study area, geochemical analysis of surface water samples, groundwater composition, bottom sediments analysis and thermodynamic modelling were selected. In all compounds, high levels of trace elements (including Pb, Zn, Cu, Cd, Co, Ni, Fe, Mn) were observed. A thermodynamic modelling study (WATEQ4f) revealed the mobilization of heavy metals mostly through the aqueous and sulfate complexes. Due to the large amounts of dispersed sulfide minerals, the pyrite-rich tailing characterized by an electrically conductive geophysical signature in comparison to the surrounding resistive bedrock. Meteoric water, getting on a tailings surface, gradually penetrates, on the way dissolving secondary minerals and metal salts, being saturated with them. Poorly permeable grounds are capable to accumulate waters, forming underground reservoirs. The distribution of layers with low resitivities suggests that the infiltration of highly mineralized solutions spreads in a direction transverse to the river flow zone. These layers extend to depths of 1–15 m, indicating the penetration of toxicants into the groundwater horizon. The pollution of groundwater confirmed by chemical analysis, according to which the concentrations of Zn, Pb, Ni, Cu and Cd in groundwater samples are two to three orders of magnitude higher than the maximum permissible concentrations (MPC). ERT technique combined with 3D models suggests along with the vertical penetration into groundwater, there is a lateral spread of low resistivity within water-saturated layers, which in this case may be termed an "acid wave".

Keywords- Acid mine drainage, pollution, heavy metals, electrical resistivity tomography, WATEQ4f.

I. INTRODUCTION

Mining and related activities have often produced by-products that pollute the environment. Hence, it is not surprising that new geophysical systems have been developed by the mining community to characterize these related pollutants [1]. Activities conducted over the centuries associated with mining of metal sulfides, mineral processing and smelting have generated large accumulations of wastes and structures such as tailing dams and ponds. Furthermore, when waste rock contains sulfide minerals such as pyrite (FeS_2), reactions can occur with oxygen and water [2]. These reactions produce an acidified leachate ($pH \leq 3$) known as acid mine drainage (AMD). Although the AMD phenomenon has been studied for many years [3-5], it may induce detrimental consequences for surface and groundwater quality, and thus remains a major environmental concern for the mining industry.

Over the years, geochemical approaches to the delineation of mine tailings leachate have gained tremendous popularity [6, 7]. The environmental challenges of waste dumps include contamination of groundwater by pollutants generated by waste dumps; migration of pollutants away from sites via groundwater, surface water, or air routes; a combination of the above; fire and explosion at the site; and direct contact with hazardous substances [8]. Geophysical methods increasingly demonstrate their potential for solving environmental problems such as: delineating areas contaminated with potentially harmful elements and compounds, including acidic seepage at industrial landfills and mine waste sites; and defining petrophysical properties and internal structure of tailing impoundments and waste rock piles [9-12].

This paper focuses on Karabash, a city of the Soviet-era industrial belt located on the Chelyabinsk region of the southern Ural Mountains, Russia. A legacy of chemical, heavy metal emissions, and radiation leaks, including one worse than Chernobyl, earned the Karabash region a reputation as the most polluted location on Earth in the 1990s. The fact that the local population in this mining center is at great risk seems to be categorically ignored by the responsible authorities. This study were based on multidisciplinary analyses using geochemical, geophysical, hydrogeological and modelling techniques.

Non-destructive geophysical methods have proven effective tools in detecting contaminated sites and can be used in the detection of AMD generation and its flow paths, for instance in groundwater [9-13]. This investigation aimed to understand the processes that led to the current conditions and AMD generation, and the possible attenuation mechanisms mitigating the effects of highly mineralized solutions at the Karabash mine site. These aims were approached by using the above-mentioned techniques, and as a

whole, they comprised a comprehensive study providing crucial information about the distribution of highly mineralized solutions in horizontal and vertical direction.

II. MATERIALS AND METHODS

2.1. Study area

The city of Karabash is located in the Chelyabinsk region in the Southern Ural Mountains (Fig. 1).

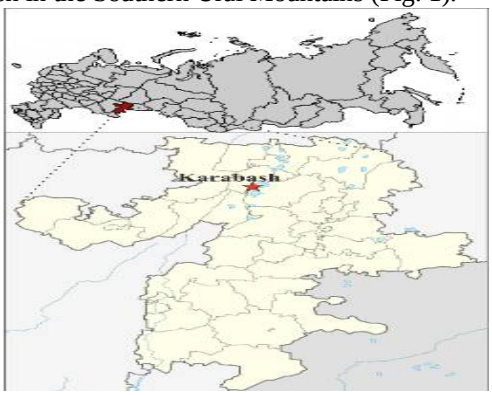

Fig.1. Map showing the location of the Karabash town (Cheljabinsk region).

Copper was extracted at Karabash from ore supplied by deposits in the area and in Kazakhstan. Between 1910 and 1958, a fine grained slurry of processing wastes was dumped along and in the Sak-Elga River. It is a tributary of the Miass River (Tobol basin) and has a length of 19 km. The drainage basin is 135 km2. The Sak-Elga River flows into the Miass River on its western bank. The solid process wastes have been accumulated over a ~3 km length of the riverbed that covers an area of 2.1–2.5 km2 with a thickness from 0.3 to 2.0 m. When the river banks erode, sulfate minerals (such as gypsum ($CaSO_4 2H2O$), barite ($BaSO_4$), jarosite ($NaFe_3(SO_4)_2(OH)_6$), magnesiocopiapite ($MgFe_4(SO_4)(OH)_2 \cdot 20H_2O$), aluminocopiapite ($(Mg,Al)(Fe,Al)_4(SO_4)_6(OH)_2 \cdot 20H_2O$) and antlerite ($Cu_3(SO_4)(OH)_4$), together with scorodite ($FeAsO_4 2H_2O$) form on the exposed surfaces (Yurkevich et. al., 2012). These secondary minerals are dissolved and carried by the Sak-Elga River into the Miass River, and Argazi Reservoir. The Argazi reservoir is a major source of fresh water for the city of Chelyabinsk (1.2 million inhabitants). Beginning in the middle of the twentieth century, wastes were stored in two tailings dumps. The Karabash mine tailings contain high contents of sulfide minerals, primarily pyrite (up to 25 wt%), chalcopyrite (3 wt%) and up to 1 wt% of sphalerite and galena. The amount of carbonaceous material in Karabash tailings is up to 10–15 wt%. The concentration of sulfide-S in the Karabash wastes is up to 6 wt% [14].

2.2. Sampling, preparation and analysis

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

The surface waters at all sampling points of Karabash geotechnical system were collected in 10-20 cm water layer into plastic (polyethylene) bottles (0.5 – 1 L). Part of the water samples were filtered through 0.45 μm filter and acidified to pH~2 with suprapure HNO3 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. The pH, Eh, electrical conductivity (EC) were measured in situ using the "HANNA" portable pH-Eh meter and a "WTW Cond 315i" conductivity meter with automatic temperature compensation. In addition, a groundwater sample was collected from a well in the area of storage of pyrite sands.

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 were pressed into 10 mm pellets on a hydraulic press under a 100 kg/cm2 pressure for XRF-SR analysis.

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

1. Titrimetric and turbidimetric methods to determine major anions (Cl-, HCO_3-, SO_4^{2-});
2. ICP-MS 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 samples;
3. SR-XRF analysis to determine chemical composition of sediments at the VEPP-3 station of the Novosibirsk Institute of Nuclear Physics SB RAS;
4. Chemical species of elements and saturation indexes in solution were calculated using program WATEQ4F [15].

We used deep electrical resistivity tomography (ERT), a non-destructive, geophysical technique that analyses the materials in the subsoil, their electrical behavior and distinguishes between them by measuring their apparent electrical resistivity [16].

The ERT equipment used in this study was a SiBER-48 multi-electrode resistivity surveying set manufactured by KB Electrometry Ltd in Novosibirsk, Russia. As for limitations of usage the ERT technique, the depth of investigation is directly connected with length of the profile. For example, the "SIBER-48" with 240 meters profile length has maximum investigation depth of 45 meters. Current source has a power up to 200 watts. The maximum output current is 1.5 A, the maximum voltage is 750 V. Accuracy of electrical measurements on the average is 0.1%.

In this study, we undertook 11 parallel ERT profiles with a spacing of 5 m between the electrodes (total number of electrodes is 48) to obtain approximate maximum penetration depth of 40 m and one long profile (№ 10-14) of 590 m to obtain a full characterization of the haphazard tailing in the Sak-Elga river valley (Fig. 4). The electrodes penetrated into the tailings transverse to the Sak-Elga River flow. The surveyed area, delimited by ERT lines, covers about half of the tailings surface, which spreads gently to the southeast toward the Argazi reservoir. The tailings surface is considered as a flat surface for the resistivity measurements and interpretation.

III. RESULTS AND DISCUSSION

3.1. Geochemistry

Surface water and groundwater sampling and analysis were performed in order to evaluate the water chemistry affected by low-quality mine drainage and the mobilization of elements.

Surface water in the zone of the smelter activity considerably differs from natural ones and their chemical composition reflects the nature of anthropogenic pollution. The results obtained from the analysis of the water samples showed high variability in Eh-pH and ionic concentrations, illustrating the great diversity of geochemical conditions in the drainage systems (Table 1).

Table1: Concentrations of elements in water samples

	Sak-Elga	AMD	Mixing zone	MPC[a]
Al	0.25	65	0.42.	0.2
Ba	0.07	0.08	0.05.	0.7
Li	0.004	0.10	0.03	0.03
Mn	0.4	40	7	0.1
Zn	0.66	65	12	1.0
Cd	<0.003.	0.3	0.032	0.001
Cu	0.08	30	4.1	1.0
Co	<0.002	0.585	0.01	0.1
Ni	0.03	2.0	0.04	0.02
Fe	0.32	180	54	0.3

The guidelines for the maximal allowed concentrations of elements (in mg/L) are also included

[a]-MPCs of Harmful Substances Contained in Potable, Household and Social Water Bodies (See Hygienic Standards GN 2.1.5.1315-03 "Maximum Permissible Concentrations (MPCs) of Chemical Substances Occurring in the Water of Water Bodies Used for Household and Amenity Needs" approved by the Public Health Chief of Russia on April 27, 2003).

Thus, acid mine drainage most often is a sulfate/chloride type water with moderate mineralization (4.5 g/L) and extremely high concentrations of metals. These characteristics are typomorphic for the Karabash mine site: Fe, Al, Zn, Mn and Cu. The measured values of metals in AMD exceed the MPC levels for several constituents. The high content of Fe caused by acidic decomposition of iron disulfide - pyrite, and aluminum by hydrolysis of aluminum silicate phases in mine wastes and tailings.

In addition to the liberation of SO_4^{2-}, the oxidation of sulfides gives rise to large quantities of iron and H^+. The concentrations of dissolved Fe in the water samples under study varied greatly: from 0.1 to 1600 mg l-1. Concentrations of Ca and Mg were especially high (the values being 330 and 270 mg/l, respectively) as were those of Si (27 mg/l) and Al (65 mg/l). The strong correlation between Si and Al ($r=0.9923$, $P<0.001$) reflects the origin of Al, which is principally from the alteration of silicates.

The processes of oxidation of sulfides and of mineral hydrolysis have given rise to the mobilization of heavy metals, causing abnormally high concentrations of these in AMD [17]. This outcome was especially the case for Zn, for which values of up to 65 mg/l were seen. Concentrations of Mn, Zn, Cu, Co, Ni and Cd were strongly correlated with one another and with SO42- (coefficients of correlation between 0.95 and 0.99, $P<0.001$).

The chemical analyses of the groundwater samples from the well located in the river valley indicate high concentrations of Cu, Zn, Cd, Pb, Co, Ni and SO_4^{2-} (15 g/L) in the groundwater. The manganese concentrations are the highest compared with the other heavy metals, except iron: up to 56 mg/L (samples G-7/2, G-7/3, Table 2).

Table2: The pH, Eh, electrical conductivity and total concentrations of elements in water samples from wells, mg/L

Sample	G-7/1	G-7/2	G-7/3	MPC
Depth	5 m	10 m	15 m	-
pH	6.2	4.5	4.2	-
Eh, mV	330	400	440	-
γ, μS/cm	5100	8600	11000	-
HCO3-	60	12	12	-
Cl-	9	11	9	350
SO42-	5300	10500	14600	500
NH4+	3.3	30	80	2
Ca	340	340	250	-
Fe	190	220	220	0.3
Mg	1000	1800	2500	50
K	3.4	2.4	2.1	-
Na	13	14	13	200
Cd	0.07	0.1	0.2	0.001
Co	<0.2	1.3	1.8	0.1
Cu	<0.3	1.4	6.0	1
Mn	33	56	56	0.1
Ni	<0.3	8	12	0.02
Pb	<0.5	0.8	1	0.01
Zn	<0.2	5.8	10	1

One of the most objective and reliable indicators of the overall condition of river systems is the content of heavy metals in bottom sediments. In the bottom sediments of rivers and in AMD, the high content of

Fe in the acidic stream sediments (40%) and in the river sediments (on average 8-10%) represent the bulk of pyrite in the waste rock (up to 20%) [14].
High concentrations of metals in bottom sediments are associated with the mechanical transfer of solids and intense precipitation of insoluble compounds of the elements found in AMD and their subsequent accumulation. Due to mechanical disintegration of material by the river, the content of all metals in sediments are higher after the mixing of AMD and the Sak-Elga River than before its confluence (Table 3).
At a site with decreased water velocity (mixing zone) concentrations of microcomponents such as Cu, Zn, Cd, Ti, As and Sb are higher than below the mixing zone. In stagnant waters with little disturbance of bottom sediments, the processes of oxidation, dissolution, which lead to increasing concentrations of dissolved metals in solution, occur with less intensity. Moreover, extensive precipitation of Fe(III)-bearing muds is taking place throughout the whole area as a result of the mixing of acid mine-waters with local Rivers.

3.2. Geochemical modelling

The migration forms of heavy metals and other compounds were computed using thermodynamic modelling. Metal species enable to identify the pollution sources and intensity of their influence. The presence of a chemical element in the water in different state is reflected in ion exchange, as well as sorption and precipitaion processes, since not only common cations and anions, but also the compounds charged differently (in size and sign) participate in the exchange and sorption processes. Therefore, in order to understand the formation of chemical composition of surface water and groundwater and distribution of chemical elements in the water–deposit system and prognosticate the changes caused by natural and technogenic factors, it is necessary to know their complex compounds.

The important migration forms of chemical elements are those the content of which makes at least 10–20% of the total content of a certain element. According to migration forms in acid mine drainage, metals mainly migrated as ions (Cu, Zn, Mn, Ni) and sulphate complexes (Al, Fe). Cadmium migrates equally as ions (50 %), and as sulfate complexes (35 %) and the rest as chloride forms ($CdCl^{+}$,$CdCl2^{0}$(aq).
Mixing of AMD and Sak-Elga River certainly affects the distribution of the migration forms of elements, since there is an abrupt change of thermodynamic conditions that lead to the transformation of the metal species in the solution. The result of these changes depends on the ratio of flow rates of watercourses and initial water content. On the site of the mixing zone there is a low flow rate [18] and a substantial dilution of AMD occurs. Although pH value of water samples from Sak-Elga river after mixing with AMD are slightly acidic (pH = 5.25) there is still elevated concentrations of heavy metal and sulfates.
WATEQ4f modelling suggested the water to be supersaturated with respect to ochre phases (goethite and jarosite in AMD, and ferrihydrite, goethite and jarosite $KFe3(SO_4)_2(OH)_6$ after mixing AMD with ambient Sak-Elga river waters). Moreover, saturation indices indicated that AMD solution was supersaturated to barite BaSO4, magnetite $Fe^{2+}Fe_2{}^{3+}O_4$ and amorphous silica (SiO_2(am)).

The upper sample of groundwater (5 m) is supersaturated with respect to Fe-hydroxide minerals goethite FeOOH, $Fe_3(OH)_8$ and also cupric ferrite $CuFe_2O_4$. The calculations indicated that, of mineral phases likely to be controlling aqueous concentrations in AMD environments [19](Nordstrom and Alpers, 1999), the groundwater was close to saturation with respect to gypsum $CaSO_4 \cdot 2H_2O$, anhydrite $CaSO_4$, siderite $FeCO_3$ and undersaturated with respect to calcite. Seeping through the pore space, solutions are initially supersaturated with respect to the sulfate minerals of the jarosite group and to maghemite Fe_2O_3. In low-pH conditions the incongruent early release of K from mica (sericite) provides the main source of K for jarosite precipitation [20].
Seeping deeper as oxidation processes continue and thus pH values decrease makes the solution to be undersaturated with respect to other mineral phases such as goethite, maghemite, cuprous ferrite, etc. are formed

3.2. Geometry of the Sak-Elga valley

Geophysical methods have been applied to further clarify geoelectrical zoning of pyrite-rich tailings, the structure of the waste to a depth of 40 m, the total survey area of mine wastes, and to find evidence of drainage infiltration to groundwater.
The carried-out electrotomography defined the internal zonality caused by change of sites with a different specific electric resistance (SER). Low resistivities (5 Ωm) are typical for the entire upper layer of tailings up to 15-20 meters, as seen in the profile sections that correspond to the groundwater horizon (Fig. 9). These low values corresponded to dispersed conductive waste materials with an abundance of sulfides, mainly pyrite.
We believe that highly conductive zones of blue color are formed owing to saturation of a pore space of a dump by solutions. An atmospheric precipitation (rainfalls, snowmelt water), getting on a tailings surface, gradually penetrates, on the way dissolving secondary minerals and metal salts, being saturated with them. Poorly permeable grounds, waters are capable to accumulate, forming underground reservoirs (in the form of lenses colored blue – low-resistance water saturated substance (Fig. 2a). The distribution of the geoelectrical profiles suggests also that the infiltration of water spreads in a direction transverse to the river flow zone (Fig. 2b).

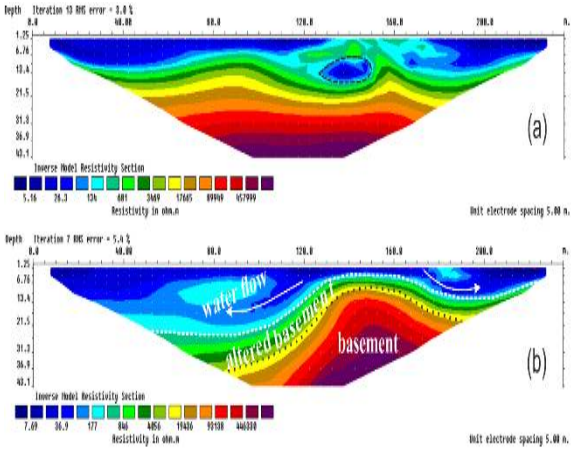

Fig. 2. Interpretation of the electrical resistivity imaging profiles 6 (a) and 10 (b): apparent resistivity sections in the river valley are covered by pyrite-rich tailings. The positions of the profiles are shown in Fig. 4

Deeper (15–25 m vertically) there is a layer with a resistivity from 100 to 200 Ohm m belonging to the waterproof horizon. Increases in electrical resistivity in the deepest portion of the ERI profiles indicate a resistivity signature of less-permeable, unsaturated metamorphic rocks represented by sulfidized chlorite-sericite-quartz slates that form the underlying resistive bedrock at the base of the tailings.

To evaluate spread of pyrite tailings and structure of the valley one long ERT profile has been made (Fig. 3). The bedrock topography is generally flat and the upper conductive layer extended along whole ERT profile laterally and thinning out to the northwest. Medium-resistivity values of <80 Ohm.m are found below the highly conductive zone (from 0 m to the 70 m of the ERT profile), indicating that contaminated solutions seeping through pore space deeper than 22 m. The use of electrical tools allows us to estimate the amount of pyrite sand on the investigated area of 130x590 m about 467 m^3. It could be helpful to estimate the reserves of metals in the tailings for further re-extraction.

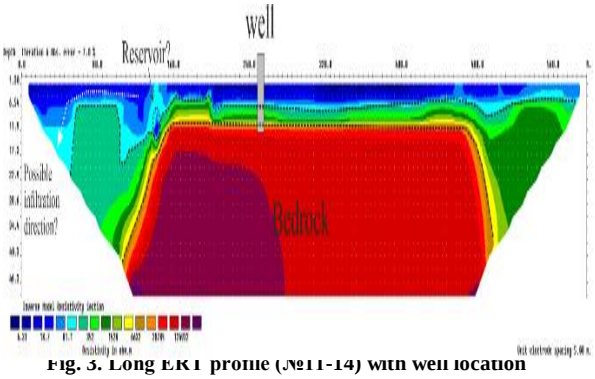

Fig. 3. Long ERT profile (№11-14) with well location

The composition of the groundwater shows that the conductive zones at depths of 10-15 meters corresponds to highly mineralized solutions with elevated concentrations of metals and sulfates, increasing on depth. A significant increase in concentration with depth were observed for Ni, Zn and Cu (Fig. 4).

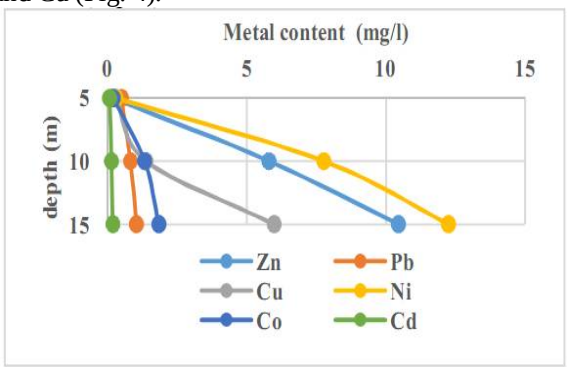

Fig. 4. Distribution-with-depth profiles for trace elements

Application of the deep ERT method allowed constructing a 3D model of the tailing pond, displaying the distribution of apparent resistance values based on topography (Fig. 5)

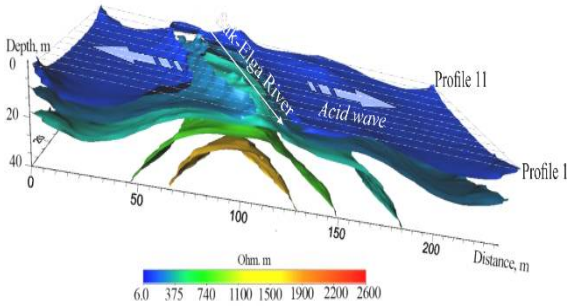

Fig. 5. 3D Voxler image of electrical resistivity isosurfaces at the tailing pond

The model provides insight into the spatial distribution of highly conductive zones (marked blue in Fig. 5) over large areas, and illustrates the seepage of highly mineralized leachates to a depth of 20 m and spread over both sides of the riverbed.

Most likely, there is an influx of toxic solutions into the groundwater horizon, which leads to its contamination. ERT profiles combined with 3D models show us that, along with the vertical penetration into groundwater, there is a lateral spread of low resistivity within water-saturated layers, which in this case may be termed an "acid wave". Action of an "acid wave" can be recorded, doing annual supervision over change of a landscape in the territory adjacent to storage: the partial, then total disappearance of vegetation farther and farther from the tailings dam, leaving behind a “Martian” landscape

CONCLUSIONS

Pyrites and other sulfide materials under influence of aeration, atmospheric precipitations, solar radiation, and sulfur dioxide are oxidized and transform from sulfide to sulfate form with formation of watersoluble toxic compounds, which contaminate water sources.

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 affect the quality of natural waters.

The entire Sak-Elga's floodplain is filled with pyrite deposits and is deprived of soil cover. Thus, the Sak-Elga River receives almost all pollutants from the smelter, abandoned mines, and is the source of secondary pollution. Knowing migration forms of chemical species analyzed in surface water and groundwater samples of the Karabash mine site consider the basis for prognostication and interpretation of migration of chemical elements and their distribution due to interaction of water with rocks as well as assessment of changes going in these compounds under the technogenic impact.

The leaching of metals from the pyrite-rich tailings and the migration of mine drainage solutions lead to significant pollution of local rivers and groundwater in the Karabash industrial area, causing irreparable damage to adjacent territories and to the supply of clean drinking water at the regional level, and thus affecting the health of local residents. The potentially toxic metal content is different but high enough to exceed the MPC limits for drinking water. It is likely that a geochemical halo forms around the metal hotspot, and a dilution occurs with distance from the mine waste.

The electrical resistivity tomography survey revealed the spread of acid wave on lithological barrier. Integrated geophysical and geochemical approaches allowed studying the distribution of highly mineralized solutions to a depth of approximately 15 meters, although the thickness of pyrite-rich tailings is approximately 1 meter. Weathering of sulfide tailings and oxidation processes amplifying with seasonal meteoric events, leads to permanent acidifying of the water environment causing groundwater pollution. Concentration of toxic elements forming ionic and sulfate complexes increases on depth exceeding maximum permissible concentrations (MPC) several times.

Geophysical surveys used in the present study were able to provide a rapid, inexpensive tool that can be used to identify potential mine drainage seeps from mine tailings and to determine the extent of migration of the mine drainage in lateral and vertical scale. This approach can be combined with conventional groundwater monitoring techniques to form a holistic solution to manage the water pollution from mine tailings.

ACKNOWLEDGMENTS

The authors would like to thank Prof. Svetlana Bortnikova for valuable recommendations and operators of analytical devices Yuri Kolmogorov, Olga Saeva. This study was supported by RFBR grants № 14-05-31431, № 14-05-00293 and № MK-5724.2014.5 of the Foundation of the Russian Federation President.

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