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Study of water-rock interaction in sulfide mining tailings using geochemical and geoelectrical methods

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Abstract

Sulphide-bearing mill wastes of the Ursk Ore Processing Plant situated in the Kemerovo region (Russia) were investigated in the 2013 – 2015. Multipurpose studies of the Ursk mining tailings allowed to determine the composition of the wastes pore waters, acid mine drainages and affected groundwater. Electrical resistivity tomography (ERT) was used to trace the geoelectric zoning of the wastes, expressed as a consistent change of the electrical resistivity from zone to zone. Layers with low resistivity indicate areas with pore spaces filled by highly mineralized solutions with high concentrations of Cu, Zn, Cd, As, and Sb up to 12 g/L in total.

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Keywords: Mining tailings; geoelectric zoning; monitoring; ground water pollution;

1. Introduction

Mining activity entails the accumulation of sulfide–bearing mill wastes with high concentrations of ore and impurity elements. Hundreds thousands tons of waste and mined ores with contents of Fe, Cu, Zn, Cd, and impurities (As, Sb) lower than industry level dumped in the tailings and discharged spontaneously in the river beds for decades[1-4]. Vertical electrical sounding allow outlining the mine tailing dump, detecting the depth of the waste, the penetration area of the highly mineralized fluids into underground water[5,6].

The authors proposed the first attempt to develop the monitoring method that allows determining the composition of the mine tailings using both geochemical and geoelectrical approaches on the example of the Ursk

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Processing Plant wastes (Kemerovo region, Russia).

2. Study area and methods

Ursk sulfide-bearing mill wastes after the enrichment of the barite-metallic ores from the oxidation zone were stored in the natural ravine in 1950-1990s as a bulk heaps with a height of 8 m and a width of 500 m (Fig. 1). It is dried during the summer and covered by water in a flood. The described conditions support the intensive transformation of the sulfide-bearing wastes due to the oxidation by atmospheric and water oxygen, there is an intensive removal of the dissolved metals in the river network. Pyrite is the most common mineral (75 - 90% of the total sulfide) among the sulfide minerals in wastes. Less common are sphalerite (8-19 %), galena (2-14 %), and single grains of chalcopyrite.

Methods include:

- The electrical resistivity tomography and electromagnetic frequency sounding[7] for the construction of the storage sections on the two co-directional profiles (Fig. 1) and for the revealing of the geo-electric zoning in the subsurface environment. The length of the profile#1 is 45 m, the distance between the electrodes - 1 m, the maximum probing depth is 8 m, the length of the profile # 2 is 150 m, the distance between the electrodes is 5 m, depth - 30 m.
- Sampling of eight pits in areas with the lowest resistivities to a depth 0.5 - 1.6 m.
- pH, Eh, and conductivity measurements in the pastes prepared in-situ with sampled wastes and distilled water (2:1 by mass), packaging of the samples in double plastic bags for the transporting to the laboratory.
- X-ray fluorescence with synchrotron radiation (XRF SR) was used for elemental composition (Si, Ti, Al, Fe, Mn, Ca, Mg, K, Na, Ba, Cu, Zn, Cd, Pb, As, Sb) at the VEPP-3 station in the Institute of the Nuclear Physics SB RAS, Novosibirsk[8].
- Preparation of the aqueous extracts in the ratio wastes : water = 1:10 (by mass), the measurements of pH, Eh by potentiometry, conductivity by conductometry, concentrations of the anions (Cl^-, HCO_3^-, SO_4^{2-}) using the titrimetric and turbidimetric methods, concentrations of the elements Ca, Mg, K, Na, Al, Mn, Fe, Cu, Zn, Cd, Ni, Co, Pb, As, and Sb by mass spectrometry with inductively coupled plasma (ICP-MS) in water samples.
- The element and mineral composition of the waste were analyzed using a scanning electron microscope (SEM) Jeol JSM-638OLA and X-ray diffraction analysis (XRD).
- Determination of the resistivity, particle size, density, porosity, moisture content in the solid samples.

Accuracy and precision of used methods were estimated to be 10-15 % or better.

3. Results

Investigated wastes are represented by «grey non-oxidized» and «red oxidized» materials (Table 1, Fig. 1), which contain 14 and 5 mas. % of sulfide sulfur respectively, about 5 mas. % of Fe and wide range of metals, As and Sb. Pore waters produced are acid (pH 3 for Red wastes) and weak-acid (pH 5 for Grey) with high concentrations of Fe (4 – 5 g/L), Cu, Zn, As (Table 1).

The section on the profile #1 («Red» wastes) is characterized by a range of resistivities from 5 up to 80 ohm·m. The upper part of the section (0-1 m vertically) shows the most conductive rocks with resistivities 5 to 10 ohm·m (Fig. 1). This layer is apparently confined to the highly mineralized wastes. High-impedance (50-80 ohm·m) heaps represent bulk soil.

The section on the profile #2 («Grey» wastes) is characterized by a range resistivities from 0.1 up to 80 ohm·m. The bigger part of the section shows the conductive rocks with resistivities 2 to 10 ohm·m (Fig. 1). Three zones with lower resistivities (0.1 – 5 ohm·m, Pits 5, 7) are located on a depth about 1.5 m and represent layers which are apparently confined to the highly mineralized wastes.

The «layer by layer» compositions of pits were compared with geo-electric profiles. The layer with high concentrations of sulfide sulfur, low resistivity, acid paste pH values and high concentrations of Cu, Hg, Ag, and Te, was found in Grey tailings on a 30 cm depth (Profile 2, Pit 5, Fig. 2).

The humidity of this layer (5 %) is lower, then in other horizons. So high electric conductivity (low resistivity) of this material is probably caused by presence of sulfides (23 mas. %). Pore waters produced contain Fe 11 g/L, Al 29 g/L, Cu 47 mg/L, As 29 mg/L, Zn 11 mg/L. The main mineral phases in dry residue from the water extract are sulfates and arsenates: $Fe(SO_4)H_2O$ $(Fe^{3+})_2(AsO_4)(SO_4)(OH)*7H_2O$, $Na_2Fe_4(AsO_4)_3(OH)_57H_2O$, $MnHAsO_4H_2O$.

Anomalous zones can be specified as "geochemical barriers" – specific layers where the mobility of the elements is reduced.

Table 1. Composition of wastes and pore waters (average from 16 samples)

Parameter	Grey ppm	Red ppm	Pore water Grey ppm	Pore water Red ppm
R, ohm·m	2.3	10	1	5
Sulfide sulfur, mas. %	14	5.3	-	-
Fe, mas. %	5.4	5.2	5300	4000
Pb	3300	1100	1.9	0.041
Sb	570	250	0.83	0.049
Mn	520	410	1.97	8.6
Cu	160	64	25	9.0
Zn	140	170	10	18
Hg	130	48	n/a	n/a
As	110	380	12	3.0
Ag	47	29	0.017	0.0041
Te	35	29	0.27	0.0092
Bi	26	14	0.0060	0.00005
Sn	22	10	0.0043	0.0048
Ni	17	13	0.037	0.24
Mo	7.7	7.0	0.095	0.016
Cd	1.7	1.1	0.013	0.022

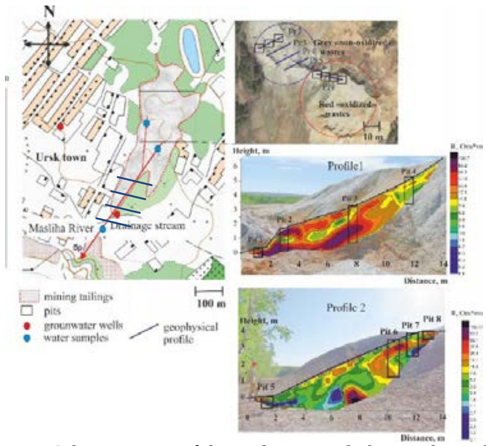

Fig. 1. Schematic map of the study area with the geophysical profiles

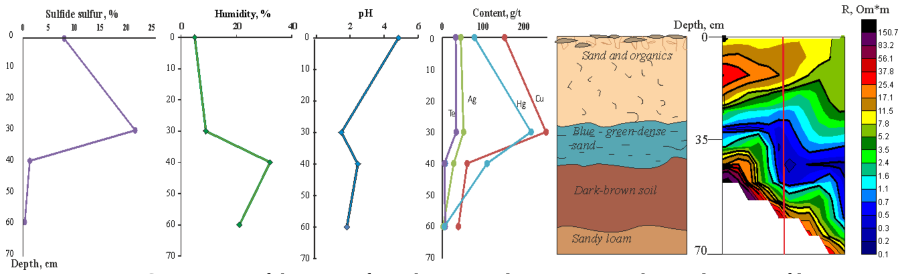

Fig. 2. Composition of the wastes from the Pit 5 and comparison with geo-electric profile

Data of vertical electrical sounding in the south part of the Ursk techno-genic valley (Fig. 1) allow us to delineate the horizons with low electric resistivity on the 15 m depth (Fig. 3). This high conductive zone represent the contamination: the high concentrations of chemical elements (Cd, Zn, Be, Ni, Cu) found in the ground water samples. Moreover, the southeast direction of the underground drainage penetration in the ground water horizon mismatch the southwest surface drainage direction (Fig. 3).

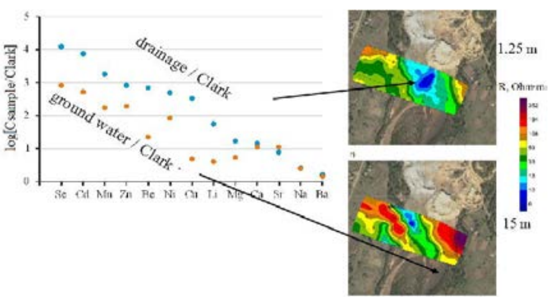

Fig. 3. Chemical elements in drainage and ground waters and geo-electric maps

Conclusion

Electrical resistivity tomography was used to trace the geoelectric zoning of the wastes, expressed as a consistent change of the electrical resistivity from zone to zone. Layers with low resistivity indicate areas with pore spaces filled by highly mineralized solutions with high concentrations of Cu, Zn, Cd, As, and Sb up to 12 g/L in total. Anomalous zones can be specified as "geochemical barriers" – specific layers where the mobility of the elements is reduced due to pH-Eh conditions and Fe(III) hydroxides precipitation so the concentration of the elements caused by co-precipitation and sorption with Fe (III) compounds. Mineral phases contained Fe and As were found by X-ray analysis: bukovskyte - $Fe_2(AsO_4)(SO_4)(OH)7H_2O$, pharmacosiderite – $Na_2Fe_4(AsO_4)_3(OH)_5*7H_2O$, krautite – $MnHAsO_4H_2O$. The layers with low resistivity and high mineralized pore solutions extend to depths of 15 m, indicating the penetration of toxicants into the groundwater horizon. The pollution of groundwater was confirmed by chemical analysis, according to which the concentrations of As, Zn, Cd, and Be in water samples from the wells are 2-3 orders of magnitude higher than the Maximum Permissible Concentration (MPC).

Conductivity of the wastes also caused by presence of high amounts of sulphide minerals. The electrical resistivity tomography allow delineating the Ursk tailings, predicting the direction of the subsurface drainage stream and contamination of ground waters.

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