Water quality of the abandoned sulfide mines of the Middle Urals (Russia)

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Abstract Dozens of sulfide mines have been flooded in the Ural region. At Levikha mine (Sverdlovsk region), the discharge of acidic groundwater was formed after filling the depression cone. The reason for its formation is the dissolution of minerals in the collapse zone – the technogenic sulfuric acid weathering crust. Lateral flow from adjacent areas dilutes the solution in the collapse zone. The flow time here is 6-8 years, and during this period extremely high values of all constituents were observed. According to the inverse geochemical modeling, the composition of the rocks was determined. Their dissolution and precipitation produce the composition of the groundwater after flooding. The longevity of acidic waters formation was estimated in dozens of years.

Keywords AMD, copper-pyrite mines, dewatering, flooding, oxidation, geochemical and geofiltrational modeling

Introduction

The Urals ore region is one of the largest pyritic provinces in the world and is the leading mining center of Russia. The complex of former and current town attached the mine works traces the Greenstone lane – the regional province of massive sulfide deposits (Emlyn, 1991). Deposits of the Ural Paleozoic geosynclinal system were formed in the period from the late Cambrian – early Ordovician to early Carboniferous.

In recent decades, a large number of mines have been closed and flooded, including copper pyrite, one of the most dangerous in terms of the degree of influence on the hydrosphere. However, despite the mine abandonment and flooding, the formation of acid mine drainage in many of them continues. On the territory of Sverdlovsk region, the acid mine drainage of the flooded mines is one of the leading sources of contamination: 10% of the total amount of pollutants enters the river on the watershed, where such objects are located. Concentrations of components in groundwater and surface water significantly exceed the maximum permissible values.

The processes of oxidative weathering of pyrite and other sulfide minerals are the cause of increased acidity and the source of metals in mine waters. (Smirnov, 1951, Emlyn, 1991, Nordstrom and Alpers, 1999; Appelo and Postma, 2005). During the dewatering period (which lasted for several decades), secondary minerals were formed in the drained zone, which include efflorescent salts and Fe- and Al-hydroxy sulfate minerals (Hammarstrom et al, 2005, Belogub et al, 2009, Nordstrom, 2011). The unsteady nature of the change in the hydrochemical constituents was fixed in many closed mines and was called “first flush”, which lasts dozens of years (Younger, 1997; Wolkersdorfer, 2008).

The aim of the work was to identify the regularities of hydrogeochemical processes leading to the formation of acid mine drainage in the copper pyrite mines of the Middle Urals. To achieve this goal the following tasks have been solved: 1) analysis of the processes of the formation of acid mine drainage at various stages of the mine development; 2) hydrogeochemical characteristic of groundwater types within disturbed areas; 3) assessment of trends in groundwater quality changes after flooding; 4) calculation of the degree of solutions saturation; 5) determination of the migration forms of dissolved components; 6) determination of the hydrodynamic balance of the flow in the zone of acid waters formation.

The hydrogeochemistry of groundwater and the features of its unsteady nature are considered on the basis of the data obtained as a result of long-term observations at the flooded mines of the Levikha group of copper pyrite deposits (Sverdlovsk Region, Middle Urals, Russia).

Case study

The Levikha group of copper pyrite deposits is located 120 km to the north of Yekaterinburg. The mine was being worked out from 1927 to 2003. More than 10 million tons of copper ore have been extracted. The ore field has a length of 6 km. The ore-bearing formation reaches an apparent thickness of about 2 km. The geochemical type of Levikha deposits is copper-zinc. The main minerals are pyrite, chalcopyrite, sphalerite, bornite, fahlore, pyrrhotite, magnetite, galena, chalcocite, covellite, native gold. A feature of the Levikha deposits is a large number of ore bodies (about 800, about 100 worked) and an abundance of disseminated ores that surround the bodies of massive pyrite. The copper content in sulfide ores varies considerably, ranging from sulfur ore without copper to ores with a copper content of 10-12%. The copper content in the disseminated ores does not exceed 1.5%.

According to the content of associated components, the ores are complex, they contain selenium, tellurium, indium, gold, silver, gallium, cadmium, germanium, arsenic and other elements. The main types of ore-bearing rocks are diabase (5%), albitophyre (10%), porphyrites (10%), quartz-sericite and quartz-chlorite schists (75%). Rock-forming minerals are represented by plagioclase, albite, chlorite, sericite, quartz.

Mining operations were conducted both open (to a depth of 70 m) and underground (to a depth of 618 m) way. The upper horizons of up to 205 m had been worked out by 1960; the deposits were worked out with the collapse of overlapping strata of rocks (floor height 30-80 m). Within the mine field, extensive zones of displacement and collapse of rocks with funnel-shaped depressions of up to 30 m in depth have been formed. Zones are elongated in the meridional direction and have a total length of about 4 km and a width of 200 to 500 m. The length of the underground mine workings is about 100 km.While the deposit was being worked out, the amount of the dewatering varied from 34 to 66 l/s, accounting to 55 L/s in the normal year.

After the cessation of pumping in December 2003, there was a flooding of the mine workings, the water rose to a depth of about 20 – 40 m from the surface of the earth. The filling of the depression cone from a depth of 285 m had been lasting for 36 months. Since April 2007, the mine water has been discharged to the surface at the lowest point of the collapse zone in the Levikha-II mine area. A technogenic basin with a depth of about 20 m was formed here in the caving (collapse zone). Acid mine drainage is pumped over from the basin to the neutralization station, then after treatment with lime milk, it flows into the clarification pond and further, by gravity, through the old riverbed of the Levikha into the river Tagil (the valley of the river Tagil is 4 km East of the mine). The pumping rate varies from 15 L/s at a low water to 30 l/s at a high water (the average annual value is about 20 L/s, which is 2 times less than the value of the mine dewatering during working out).

As a rule, mining with roof caving goaf is usually used in the copper-mines of the Middle Urals. Cavings to a depth of 15-35 m and more, zones of collapse and subsidence of tens and hundreds of hectares are formed on the ground surface. These factors contribute to a more intensive penetration of infiltration water into the disturbed zone and active formation of anthropogenic sulfuric acid weathering crust. The hydrodynamic situation is determined by geomechanical processes, resulting in the formation of collapse and subsidence zones. Here the basic parameters of rock mass significantly differ from the background ones: infiltration, coefficients of filtration and porosity of the collapse zones are one or two orders of magnitude greater than the parameters of the undisturbed rock mass. Both during working out and after flooding one of the main income items in the balance of dewatering is the uptake of atmospheric precipitation within the zones of collapse.

Testing and chemical analysis

The composition of groundwater in the area of the Levikha mine is analyzed on the basis of monitoring data for the period from the early 1950s to the present. Since the release of groundwater to the surface in April 2007, the pH, As^{2+}, Cu^{2+}, Fe_{tot} Mn_{2+}, SO_4^{2-}, Zn^{2+}, TDS, suspended solids have been determined daily. In addition, since 2007 we have annually performed advanced laboratory studies of main and micro – component composition of water samples using methods of mass spectrometry with inductively coupled plasma ICP-MS.

To process the data obtained, statistical analysis methods were used, hydrodynamic and geochemical modeling was performed (using the Visual MINTEQ ver. 3.0/3.1 program code and MODFLOW, PMPATH software codes).

Hydrogeochemical conditions after flooding

After filling the depression cone, groundwater quality is characterized by the essentially non-stationary hydrochemical regime: in the early years there is a sharp increase in the concentration of most of the components, then begins the gradual decline that can last for decades or more.

At the Levikha mine, the chemical composition indicators are up to now higher than when working out. The composition of groundwater in the zone of discharge is sulfate, hydrocarbonate ion is absent, chlorine is detected in the amount of 25-53 mg/L; among cations, aluminum, iron, and magnesium predominate (Table 1). Groundwater temperature is 10°C, **E**h = 266 mV, Fe^{2+} = 1,209 mg/L, Fe^{3+} = 53 mg/L (sampling November 29, 2016).

Table 2 *Characteristics of the chemical composition of groundwater in the Levikha mine at the stage of development and after flooding (t is the time after completion of filling of the depression cone and release of groundwater to the surface, in parentheses is the date of sampling)*

Component	Stage, object, date			
	mining	flooding, the zone of discharge		
	1990-2000	t = 10 month (26.02.2008)	t = 90 month (15.09.2014)	t = 116 month (29.11.2016)
pH	2.35	3.86	3.18	3.57
TDS (g/L)	11.6	59.5	14.5	14.2
SO_4^{2-} (mg/L)	5,970	25,672	9,954	6,985
Ca^{2+} (mg/L)	260	495	423	382
Mg^{2+} (mg/L)	340	1,876	703	587
Al^{3+} (mg/L)	375	1,093	603	412
Cu^{2+} (mg/L)	154	62	11	16
Zn^{2+} (mg/L)	317	1,755	323	183
Fe_{tot} (mg/L)	730	4,112	1,373	1,262

The unsteady nature of changes in the composition of groundwater in the discharge zone is observed for all indicators. However, the patterns of these changes, both in absolute values and in the rates of ascent and decline differ (Figure 1).

For all indicators, their sharp rapid growth for 4-7 months is common. Elevated values of the concentrations of components remain for 3 to 5 years. Ranked list in the degree of concentration in relation to the period of working-out is as follows:

$K_{Mg} > K_{Mn} > K_{Fe} > K_{SO4} > K_{Al} > K_{Zn}$.

Modeling the formation of solutions in flooding

The results of calculating the saturation of groundwater in the discharge zone show that they are supersaturated with respect to hematite, magnetite, goethite, lepidocrocite, jarosite; are in equilibrium with gypsum, anhydrite, ferrihydrite; are unsaturated with respect to epsomite, chalcanthite, melanterite, etc. High concentrations of sulfate sulfur determine the form of migration of metals in the form of sulfate complexes: Al^{3+} and Fe^{3+} almost completely; the divalent cations in the amount of about 50%; the monovalent cations in the amount, not more than 10%.

With a sufficient amount of reliable data on the composition of groundwater, the composition of the rocks can be determined, the dissolution and precipitation of which forms specific constituents of water. For this, the solution of inverse problems is performed by calculating the mass balance (Nordstrom, 2011). In table 2 the results of solving the inverse problems are given for three models that simulate the likely geochemical scenarios for the formation of groundwater in the Levikha mine (for the situation 90 months after the start of discharge of groundwater to the surface).

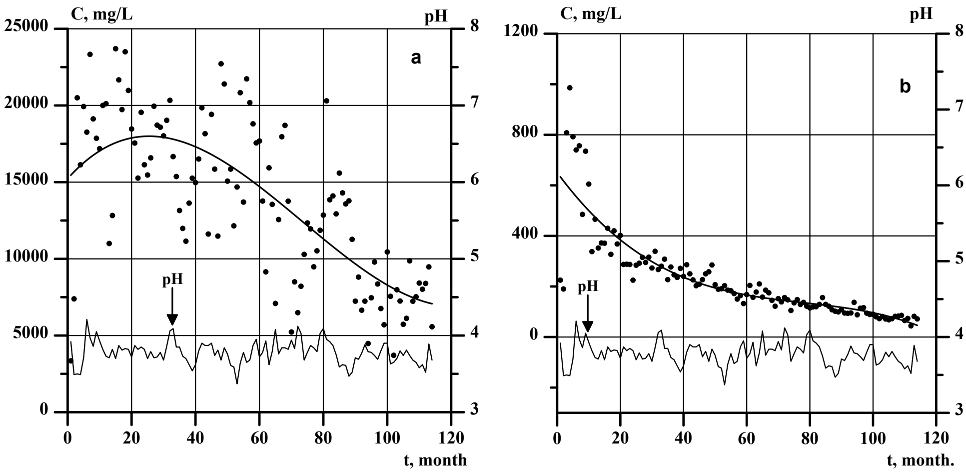

__Figure 1__ Change in the content of components and pH in the groundwater of the discharge zone after flooding (solid line – polynomial approximation of the third degree): a – sulfate ion (R2 = 0.52), b – manganese (R2 = 0.74)

Mineral phase (mmol/kg)	Model number		
	1	2	3
Chlorite	10	10	10
Sericite	10	10	10
Calcite	11	11	11
Pyrite	50	0	0
Sphalerite	7	0	0
Chalcopyrite	0.3	0	0
Manganite	2	2	2
Melanterite	0	100	0
Goslarite	0	7	7
Chalcanthite	0	0.3	0.3
Jarosite	0	0	50
Quarz	-40	-40	-40
Goethite	-25	-75	-125

__Table 2__ Results of calculation of mass balance for mine waters of the Levikha mine 90 months after flooding for various models of composition formation (negative values – precipitation, positive values – dissolution)

The first model assumes oxidative dissolution of sulfides (pyrite, sphalerite, chalcopyrite); the second – the dissolution of sulfate crystalline hydrates crystalline hydrates of sulfates (melanterite, goslarite, and chalcanthite); in the third, jarosite takes the place of melanterite. The composition of the host rocks for all models is identical – it is chlorite, sericite, calcite. The rate of dissolution of sulfates is currently (5±10)·10³ mol in hour and is comparable to the dissolution rate of sulfides during working out (Rybnikova and Rybnikov, 2017). For comparison, the oxidation rate in the Iron Mountain mine, where negative pH values are fixed, is an order of magnitude higher (Nordstrom, 2011).

The phenomenon of growth of the values of the components in the discharge zone and their subsequent decrease ("first flush") can be explained using the regularities of groundwater flow formation and its balance components. These data were obtained as a result of geofiltrational modeling in a multi-layered system (using MODFLOW and PMPATH software codes (Chiang and Kinzelbach, 2001). The longevity of flooding of the collapse zone is 3 years. During this period, the secondary minerals formed earlier in the sulfuric acid weathering crust were dissolving; the solution in the fractures and pores was being saturated with sulfates, metals, and other components. After filling of the depression cone, the discharge of groundwater into the caving begins. The groundwater flow, discharged into the caving, at elevated concentrations contains dissolved substances accumulated in a solution filling the free space of the collapse zone. It is this process that determines the extremely high values of the components in the initial period.

In steady state conditions, the lateral inflow begins to acquire the leading importance in the hydrodynamic balance, which comes from the adjacent territories. Its composition is slightly different from the background, the contribution to the unloading discharge to the caving is 50%, its value is manifested in dilution of the solution contained in the collapse zone (Figure 2). The time of groundwater movement in the collapse zone (from the border to the caving) is from 6 to 8 years, during this period extremely high concentrations of practically all indicators are observed. Subsequently, the dilution of groundwater will play a crucial role and the value of the indicators will be reducing.

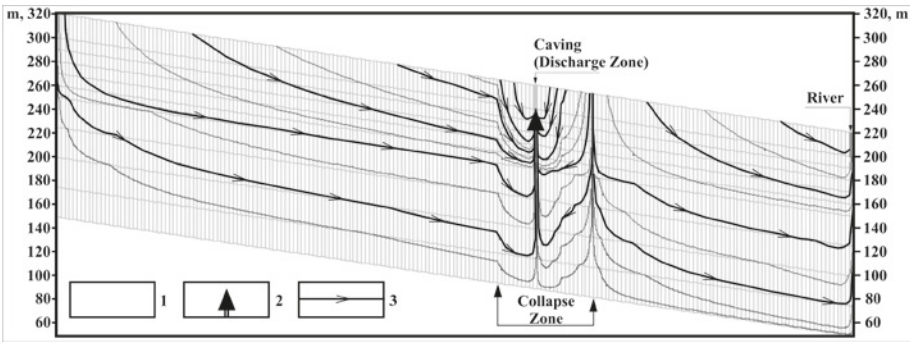

Figure 2 *The scheme of groundwater movement after flooding (on the left – the surface watershed, the impermeable boundary; to the right – the river; the size of the block horizontally – 50 m, the number of layers – 10). 1 – grid layout; 2 – groundwater discharge into the caving; 3 – the direction of groundwater flow.*

If the initial concentration of sulfides in the host rocks is about 10% and porosity (fracturing) 3%, then the duration of the acidic water flow to the earth surface will be about 50 years. The mass of dissolving minerals reaches 5-10 thousand tons per year, while in the underground space more than 1 thousand cubic meters of voids are formed annually. This explains the fact that for many years the formation of collapses continues in the worked out mines.

Conclusions

The behavior and migration forms of elements in acid mine drainage after the flooding of the Levikha sulfide mine have been considered. The regularities of unsteady hydrogeochemical processes after the flooding of the mine have been established: a sharp (by a factor of 5-6) increase in the content of all components within 4-6 months, the preservation of the elevated values within 3 to 5 years, with a subsequent decrease.

Some components (for example, copper and manganese) have an abnormal character of behavior, both in terms of the maximum values of the concentration coefficients relative to the working period (0.5 and 21, respectively), and in a sharp decline in time (less than 1 year). The ranked concentration series of the main components in relation to the working period is as follows: $K_{Mg} > K_{Mn} > K_{Fe} > K_{SO4} > K_{Al} > K_{Zn}$.

The solution of the inverse problems has allowed establishing: 1) the composition of rocks, the dissolution of which leads to the formation of acidic groundwater in the collapse zone; 2) the rates of removal of sulphates: currently they account for about $(5 - 10) \cdot 10^3$ mol per hour and are comparable to the values that were recorded during the mining in the period 1990-2000.

Analysis of the results of geochemical and geofiltrational modeling makes it possible to state the following hypothesis of the formation of groundwater quality. The discharge rate in the caving consists of a flow that forms in the collapse zone and a lateral flow that comes from the adjacent areas (40% and 60%, respectively). In the initial period of flooding the increased values of all indicators in the water of the discharge zone are provided by the solution mainly from the collapse zone. Time of flow in the collapse zone (from its border to the unloading site) is 6-8 years, during this period extremely high values of practically all indicators in the technogenic reservoir are observed. Over time, the role and importance of the lateral flow from adjacent areas in the dilution of the solution in the collapse zone increases. This leads to a decrease in the concentration of components in the unloading zone. Longevity of formation of acid mine drainage within Levikha mine will be about 50 years.

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