Arsenic occurrence and geochemical evolution of the abandoned ore mine Kank in the Czech Republic

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Abstract The Kank ore mine (abandoned since 1991) is located in the Czech Republic, close to the historical mining town of Kutna Hora. During mining oxidizing conditions prevailed and solute concentrations were relatively low. During flooding solute concentrations increased and secondary minerals dissolved. When the water level reached the sough highly mineralized water was discharged. Since 2001, the mine water has become more reductive and sulphides are likely to be precipitated. This has caused the concentration of most metals to decrease. Arsenic behavior is more complicated because of a reduction of As(V). The mine water is stratified. Layers of distinct characteristics were studied by logging (temperature and resistivity) and zonal sampling.

Key Words mine flooding, stratification, redox conditions, arsenic, logging

Introduction

Many unprofitable ore mines were closed in the Czech Republic in 1990s. Subsequent flooding led in many cases to a rise in water levels and acid mine discharge. This affected the ecological system of the studied areas. There are many such affected sites in the Czech Republic and one of the most interesting is Kank.

The abandoned mine Kank is located in Central Bohemia, to the east of the capital of the Czech Republic – Prague, close to the town of Kutna Hora. Silver had been exploited there since the 14th century. After depletion of silver, exploitation was focused on lead and zinc. The mine was closed in 1991 and flooding began.

Mining activities completely changed the hydrochemical conditions. Changes in redox conditions during mining and flooding resulted in dissolution of minerals and solute concentration increase. Arsenic concentrations reached 100 mg/L which is also globally quite unique. The area is currently under intensive research aimed at the identification of key chemical processes, mine water stratification and environmental risk assessment. The aim of this text is to present the site, discuss the conditions leading to the extreme solute concentrations and mine water stratification.

Site characterization

In the center of the Kank site is the Turkank mineshaft. It has a depth of 556 m and has 7 floors. Regular monitoring of mine water has been performed since 1993. In 2001 the water table reached the level of the sough – 210.3 meters above sea level. Currently, the water level ranges about 96.8 meters below the surface (203.5 meters above sea level). Mine water is pumped to a treatment plant. The mine water type is Fe-SO_4.

Mineralization of the Kank district is polymetallic in character and is represented by carbonate and quartz veins with sulfides of Fe, As, Pb, Zn, Cu, Sb, Sn, and Ag. The most important primal sources of arsenic are arsenopyrite, As-pyrite and pyrrhotite.

Methods

Standard procedures were used for sampling and analysis. The pH, Eh, temperature and conductivity were measured on site using a WTW Multi 340i multimeter with the appropriate original electrodes. The samples were taken 10 m below the groundwater level. The samples were taken and analyzed in the certified laboratories of the company AQUATEST a.s. Samples for heavy metal analysis were stabilized immediately after sampling by the addition of 1 mL of concentrated nitric acid. Samples were cooled during transport and analyzed within 48 hours.

Results and discussion

Time Evolution

Long-term monitoring of mine water at the Kank site (Turkank shaft) allows observation of changes related to seasonal effects and trends in concentrations of the contaminants. Concentrations of all significant anions and cations, pH, Eh, conductivity, etc. are measured. Time series of Fe, As and pH are shown in Figure 1. The monitored parameters have only minor seasonal fluctuation.

Three time periods related to changes in the water regime can be identified.

- The first period corresponds to active mining with relatively low concentrations of solutes in the mine water (Figure 1 – until the end of 1993).
- The second period (since 1994) corresponds to the flooding of the mine, which led to an increase in concentrations in the first two years after flooding began. Then a gradual decrease followed, until water levels in the mine reached the sough. After reaching the level of the sough (in the second half of 2001), solute concentrations increased sharply. Iron concentrations increased to 7 g/L, and arsenic to 60 mg/L.
- The third period is characterized by decreasing concentrations of all studied elements (except As) – see Figure 1.

The changes in concentrations correspond to changes in the redox conditions of the mine. Before the start of mining activities at the Kank site the rock under the groundwater table was under anoxic conditions and mineralization was low. When the mine was opened the groundwater level decreased and rocks and ore minerals were exposed to oxygen. Rocks weathered rapidly and solute concentrations increased. Heavy metals were dissolved, water was significantly acidified and secondary minerals were precipitated. After closure and flooding, redox conditions gradually changed from oxidizing to reducing conditions. Precipitated oxides and hydroxides were dissolved and the adsorbed components were released. Mine water was sampled not far from the surface.

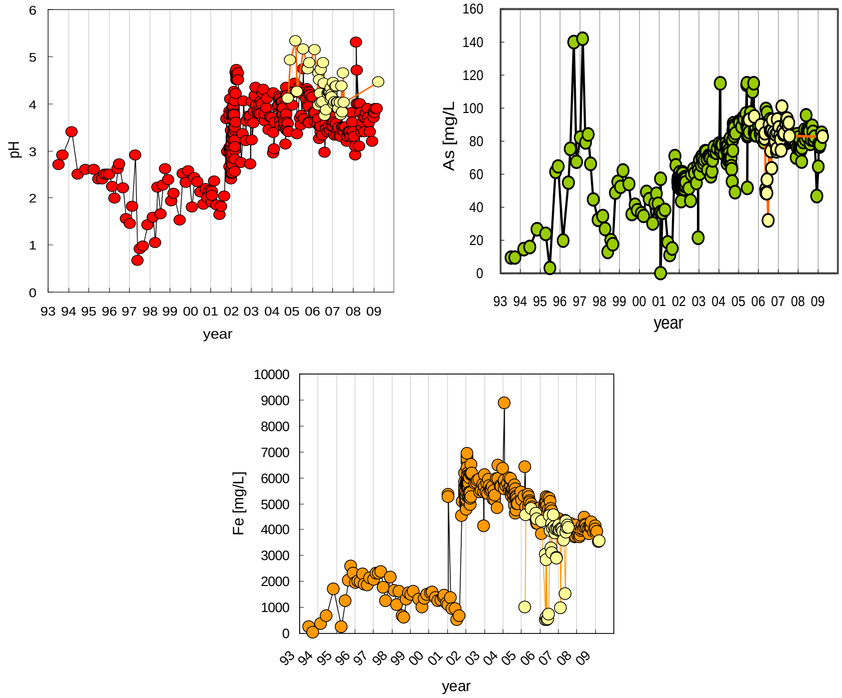

***Figure 1** Long-term trend for As, Fe and pH between 1993 and 2009*

Arsenic behavior in the third time period differs significantly from the behavior of most solutes. Concentrations of sulfates, Zn, Mn and Fe decrease for the whole third time period (since 2001). Concentration of arsenic rose for four years and then the trend reversed. Eh is decreasing during the 3rd period and the mine water is becoming more reductive. Sulfates are being reduced and precipitated as sulfides. This leads to the immobilization of metals. The four-year increase in arsenic was probably caused by a reduction of As(V) to As(III). As(III)-minerals are more soluble than As(V) and moreover dissolved As(III) is less adsorbed than As(V). In the long term (tens of years) the reducing environment usually leads to a progressive immobilization of soluble components and the system slowly returns to the state before mining activities.

Stratification

Mine water in the Turkank shaft is not homogeneous. In the time periods when water was not drawn from the mine, several layers with different chemical composition were established. The top layer which is several meters deep has low solute concentrations and is influenced by the recharge of infiltrated water. The bottom layer is strongly mineralized and corresponds to highly concentrated pore water. Three logging measurements were carried out in the shaft in the past decade. The first logging was performed in 2004 and the second one in 2007. The last deep continuous measurement of temperature and resistivity of the whole vertical profile was made in October 2009. These results are in Figure 2.

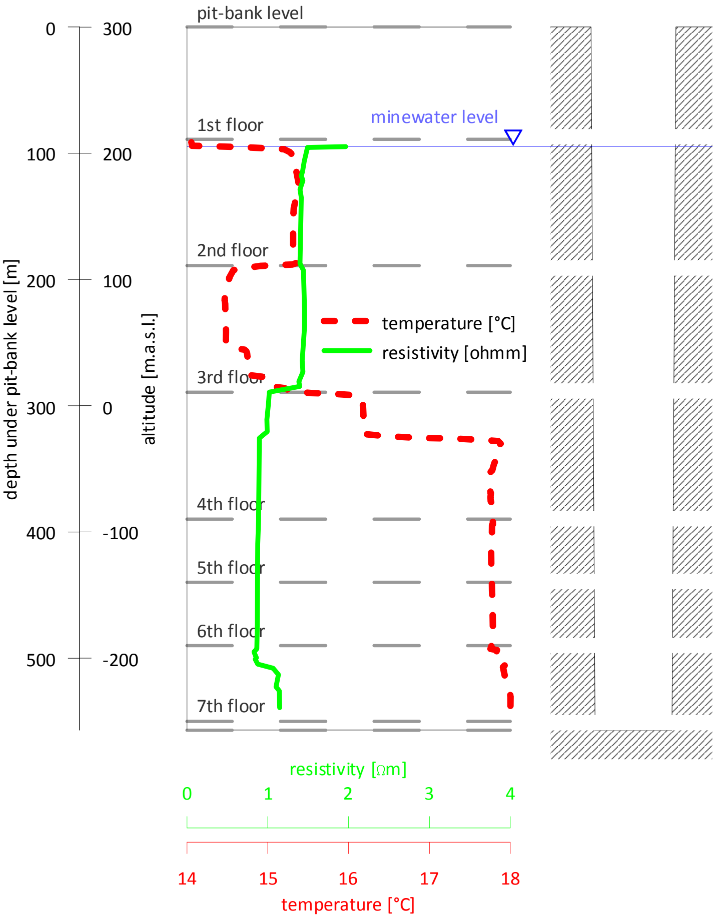

Figure 2 *Logging measurement (September 2009)*

Sharp temperature and resistivity changes were discovered in a few underground levels. Depths of major temperature and resistivity changes are from 187.0 to 191.2 m, 288.5 to 291.0 m, 323.5 to 326.5, and 507.0 m. The next logging measurement and zonal sampling were planned for March 2010, but the shaft was partly blocked at a depth of 123 m. Therefore the measurement could not be carried out. Currently, the problem is being addressed.

Zonal samples for chemical analysis were taken in 13 (14 resp.) depth levels in 2004 (2007 resp.). pH levels were from 2.8 (upper layer) to 4.7 (middle layer). Considering the significant increase in pH of 0.4 on average between 2004 and 2007, we can expect very interesting results in the case of the planned zonal sampling. The stratification of Eh values was interesting because of a large decrease of 250 mV. Stratification of Fe, Mn, Zn and Pb corresponded to electrolytic conductivity. Their concentrations were highest in the lower layer. Contrariwise concentrations of Cd and As were the lowest there.

Conclusion

Mining activity significantly affects the redox conditions of the site. The district of Kank close to Kutna Hora is a system which is unique due to the high concentrations of contaminants and significant changes in real time. This system is ideal for studying and identifying hydrochemical processes, generalizing and applying the knowledge gained to other sites of similar type.

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