Impact of ore deposits and anthropogenic activities on local hydrochemistry at "Silberberg", S-Germany

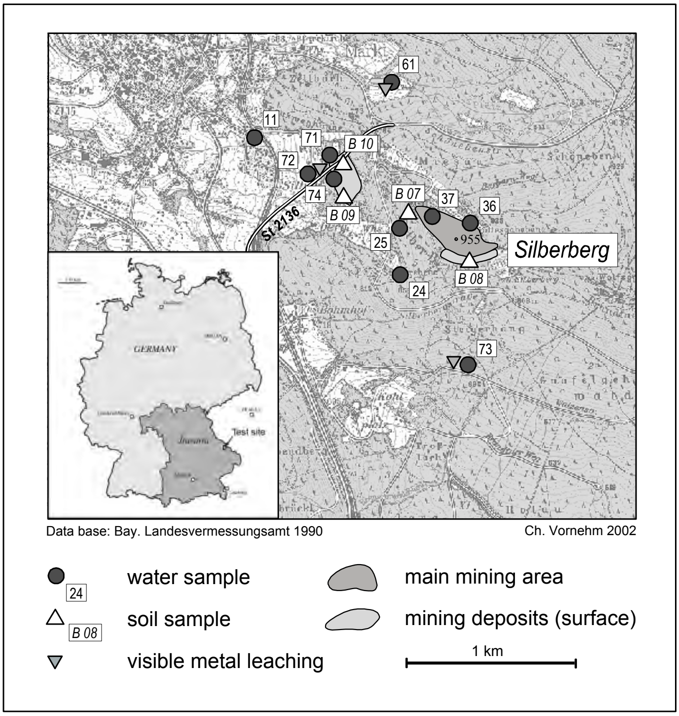
Christine Vornehm[1], Steffen Bender[1], Gerhard Lehrberger[2]

[1]Department for Geo- and Environmental Sciences, Ludwig-Maximilians-University Munich, Luisenstr. 37, D-80333 Munich
[2]Lehrstuhl für Allgemeine, Angewandte und Ingenieur-Geologie, Technische Universität München, Arcissstr. 21, D-80290 München

Abstract. Massive sulfide ores have been mined at the mountain „Silberberg" in Bavaria, South Germany. Metal- and sulfur-rich tailing dumps were deposited at the surface. Due to road construction the tailing dump material has been moved, which result in a remobilization of anions and cations. Four water types can be classified: mine water, shallow ground water and a mixture of both types. One well with deeper ground water does not fit in this scheme. Experimental results point to an impact of ore oxidation processes or an influx of high mineralized water.

Introduction

The aim of the investigation at the former sulfide mine at "Silberberg" mountain in the Bavarian Forest (South Germany) (Fig. 1) is to investigate the drainage system and hydro chemical processes. Possible impacts for the hydrochemistry are 1) the ore deposit and 2) anthropogenic activities (road construction and traffic, tourism, forestry). The study, which is part of the project "LOWRGREP" (land use optimization in hard rock areas with regards to ground water resources protection), is funded by the European Community. Main task of this project is focused on the impact on ground water beside of anthropogenic activities and the challenges for water management in hard rock areas.



Data base: Bay. Landesvermessungsamt 1990

Ch. Vornehm 2002

Fig. 1. Investigations in the “Silberberg” area

The ore deposit

General overview

The ore deposit is situated in Cordierit-Sillimanit-paragneisses, which are part of the moldanubic monotonous group (BayGLA 1998). These metamorphic units are part of the Bavarian section of the Bohemian Massif (BayGLA 1996). Up to now, the genesis of the ore deposit is not totally identified. The ore of the “Silberberg” is part of a massive zone of deposits that had been built during Palaeozoic or Praecambrian age. It originated in a submarine sedimentary basin, where tectonical activity in a sheer zone favored the inflow of iron-, zinc- and sulfur-bearing hydrothermal fluids. Chemical reactions with surrounding sea water and regional metamorphic processes finally generated the iron- and zinc-sulfides. High contents of barium in ores and feldspars found in the region support the theory of their hydrothermal origin (Obermüller 1993, Linhardt 1985).

The ores predominantly consist of sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), pyrite (FeS_2) and phyrrhotite (FeS). Generally, these minerals are associated by Ag, As, Au, Cd and Ni. (Alloway 1996). Inside the mine "stalactites" of mostly iron hydroxide (62 % Fe_2O_3) were formed by precipitation out of iron-rich acidic drop-water (pH 2.6). RFA-analysis show that these iron oxides contain further amounts of sulfur, fluorine, small amounts (< 1 %) of SiO_2, Al_2O_3, MgO, K_2O and the trace elements Zn (66 ppm), V (49 ppm), Ni (27 ppm), Cr (25 ppm), U (15 ppm) and Cu (12 ppm) (Vornehm et al 2002).

Mining activities

Since the Middle Ages massive sulfide ore has been excavated in open pit and underground mining (Blendinger and Wolf 1971). Main purpose was the production of sulfates and concentrated sulfuric acid for the chemical industry and iron oxide powder ("Polierrot") for polishing in the glass industry. During the mining activities until 1962, large quantities of ore and rocks have been excavated. On the surface sulfur- and metal-rich dumps were deposited near adits and shafts. Furthermore, around the former roasting and leaching plants, tailings were deposited.

After the ending of mining activities, the residual dumps, that have been stored in terraces around the mine, were covered with soil material, which was the base for forest vegetation. In the end of the 1990s parts of these tailing dumps were removed due to road construction, stored next to the other tailing dump material and protected with plastic canvas covers. With beginning of the road constructing activities, heavy metal concentration in surface runoff and seepage water increased significantly. The leaching of the metals can be observed at a dam of a new constructed road and in a nearby pond (Fig. 1).

Characterization of the covering material

Several samples have been taken in July 2001 from the tailing dumps (B 09 and B10 in Fig. 1), at the former roasting sites (B 08) and from soil in uninfluenced parts of the region ("base value"). Geochemistry was investigated by RFA-analysis and leaching behavior was determined by batch experiments.

Geochemistry

Compared to the local chemical situation of the soil, all tailings are characterized by higher contents of Fe_2O_3, S and F^- and lower contents of SiO_2 and Al_2O_3 (Fig. 2). The highest contents of Fe_2O_3 and S are found in the tailings of the former roasting plant (B08), because the iron-sulfate had not yet been leached like in the tailing dumps (B09, B10).

Regarding trace elements, the concentration of Zn is a characteristic marker for the tailing material. It derives from sphalerite (ZnS), the most important ore of the "Silberberg" mine. Whereas the "base value" ranges between 30 and 60 ppm (Fig. 3), the amount in the tailings is clearly higher (800 and 10,000 ppm). Copper, lead and barium can be used as characteristic elements, too. Arsenic has been found only in the material of the former roasting plant (B08) with a quantity of 53 ppm, in the other tailing material it is below detection limit (20 ppm).

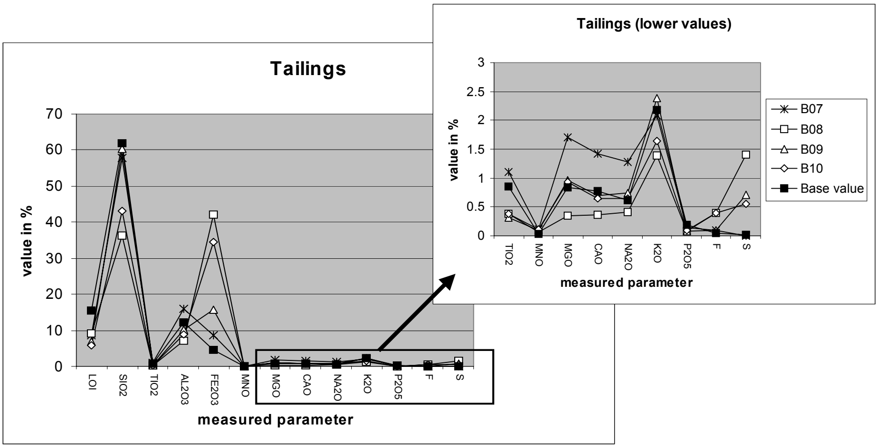


Fig. 2. RFA-analysis of the tailing material, main components

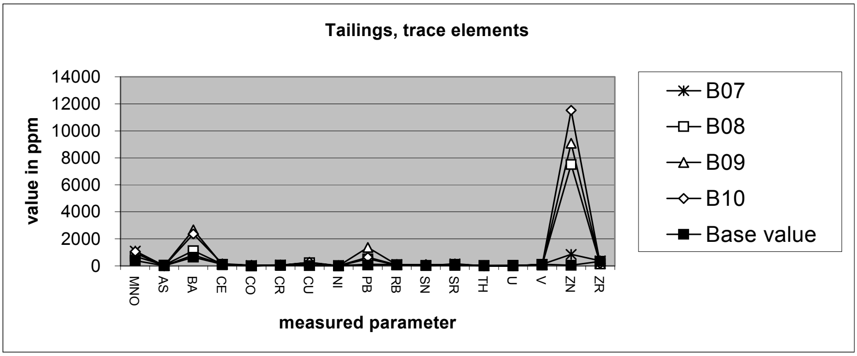


Fig. 3. RFA-analysis of the tailing material, trace elements (Vornehm et al. 2002)

Increased contents of manganese seems to be bound to manganese bearing garnets, which are often associated with phyrrhotite and galena-bearing rocks (Obermüller 1993), two typical ores of this deposit. A maximum of 1093 ppm MnO was analysed at soil sample B07 at the foot of "Silberberg" mountain. The tailing dump material has values between 900 and 1060 ppm MnO (B09, B10) whereas the base values range between 200 and 800 ppm.

The geochemistry of the soil sample B 07, taken at the foot of the “Silberberg” mountain, follows the general trend of the local “base value” with only slightly higher contents of the characteristic “Silberberg”-metals Zn and Fe_2O_3 (Fig. 2 and 3).

Leaching behavior

To determine the leaching capacity with water, selected samples of uninfluenced soil (“base value) and tailing dump material were leached according to DIN (1984). The eluat of the tailing dumps (B08, B09, B10) has a specific electric conductivity over 2000 µS/cm and pH ranges between 3.4 and 3.8. In comparison the eluat of sample B07, taken at the foot of “Silberberg” mountain, has a conductivity of 39 µS/cm and a pH of 4.2, lying in “base value” range (EC 30 – 130 µS/cm, pH 2.9 – 4.5). Figure 4 and 5 depict the leached amounts of selected cations and anions. Sample B06 represents the “base value” soil (EC 92, pH 3.4).

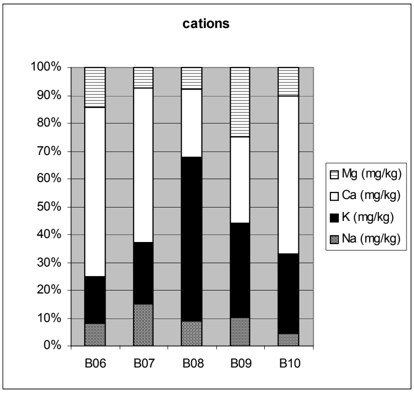


Fig. 4. cations of leaching experiment

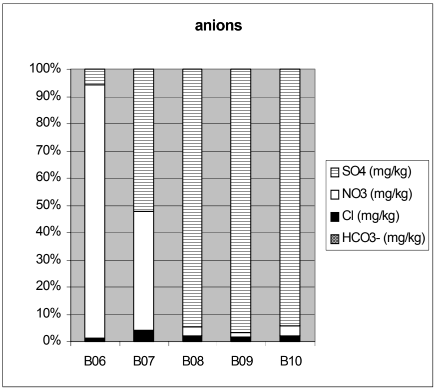


Fig. 5. anions of leaching experiment

The results of the leaching experiment show that calcium is the dominating alkaline and earth-alkaline ion in most samples of soil and tailing damp material. In sample B08 (tailing dump material), potassium is predominant (60 %). Compared to the local “base value” potassium is increased in all samples from tailing dump material (>20 %). Therefore it can be used as characteristic for the mining area. Both calcium and potassium can be leached as well from feldspars and clay minerals. Compared to potassium, magnesium can not be used as a marker, because no significant difference between tailing dump material and the “base value” can be monitored. Concerning sodium, no significant difference can be seen between the samples, too (Fig. 4).

Using SO_4^{2-}, NO_3^- and Cl^- simplifies the classification of the samples. In tailing dump material sulfate is the most important anion (over 90 %), whereas the local soil is dominated by nitrate (around 80 %). The soil sample B07 from the foot of the “Silberberg” mountain is characterized by a domination of sulfate (almost 70 %) and additionally increased amounts of nitrate (30 %). Bicarbonate does not leach from any of the soils, neither from tailing dump material nor from local uninfluenced soil, which points to the poor buffering capacity of the rocks (Fig. 5).

Concerning the most important metals for this region, iron was leached in very small amounts (below 0.3 mg/kg), whereas for zinc, concentrations between 0.4 and 11.4 mg/kg (tailing dump material) and 0.4 mg/kg (former roasting places) were found. Amounts of dissolved Zn up to 0.4 mg/kg have been observed in local soil as well.

Water conditions

Hydro geological overview

To describe the hydro chemical situation at the “Silberberg” several springs and one well were sampled. The springs, which are located in gneisses are mostly captured in the weathering zone (3–6 m). Some wells in the region further show influence of higher mineralized water originated in deeper circulating water. Their hydro chemical composition is hard to describe because local wells seldom exceed depths over 40 m. But investigations and models in similar regions point to the possible mixing of the deeper ground water from the fractured aquifer with the shallow ground water in the porous weathering zone (Bender 2000).

Hydro chemical situation

Three different types of water can be found in the surroundings of the “Silberberg”: mine water, shallow ground water and mixtures of both types (Vornehm et al 2002). The origin of the water from a well at the foot of “Silberberg” mountain is not cleared yet: it could be either influenced by the ore deposit or by deeper cycling ground water (fourth water type). The equivalent concentrations of the most important dissolved species are depicted in the vertical diagram (Fig. 6).

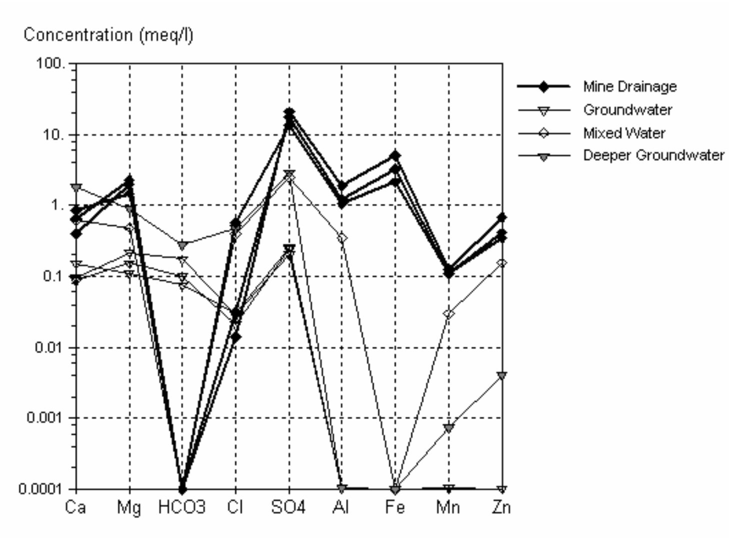


Fig. 6. Classification of the waters, using a vertical diagram (Vornehm et al. 2002)

The mine water is characterized by low pH-values (2.4 – 3.0) and high specific electric conductivities (EC) between 800 and 1900 µS/cm. It can be classified as Fe-SO_4-type. Compared to the other local water the amounts of Al, Zn, Mn and Cu are increased.

Shallow ground water is low mineralized (EC: 50 – 60 µS/cm) with pH-values about 5.5 to 6.0. The alkaline earth-HCO_3-water type shows regionally higher contents of Na^+ and SO_4^{2-}. The amounts of heavy metals are very low (Vornehm et al. 2002).

The mixed water found in the drainage system of the mine is acidic (pH-values about 4) with a mineralization below 300 µS/cm. Due to the alkaline earth metals that are added with the inflow of ground water, this water is of a CaMg-SO_4-type. Whereas nearly no dissolved iron can be detected, the following dissolved metal were found: Al, Zn, Mn, Cu, Co, Ni, Cd, Pb, As and Cr.

Deeper cycling ground waters have pH-values like the shallow ground water (5.5 – 6.0) and a mineralization of about 350 µS/cm. The CaMg-SO_4-water type shows increased HCO_3^- concentrations (up to 20 mg/L) in comparison to the shallow ground water (1–12 mg/L).

Hydro chemical processes

Besides leaching of the ores and surrounding rocks by infiltrating rainwater, oxidation is the most important hydro chemical process. Main oxygen sources for the reaction are atmospheric oxygen and saturated oxygen in rainwater and seepage water. The oxidation releases sulfates such as melantherite, which characterize the waters in the vicinity of the ore deposit. Due to the oxidation processes of the ores, heavy metals (such as Fe^{2+}, Zn^{2+}, Cu^{2+} and so on) and high amounts of H^+ are released. All mine waters show pH-values between 2.5 and 3.0. However pH-values under 2.5 do not appear, not even in very concentrated drop water inside the mine, which can be due to buffering by products of silicate-weathering. Considering the very high amounts of sulfates in the mine water (around 1000 mg/L) it can be supposed that bacteria catalyze the process of ore oxidation (Nordstrom 2000).

The increased pH-values of the shallow ground water (up to 6.0) are the result of buffering reactions (Vornehm et al. 2002), but the sulfate domination still points to the ore oxidation.

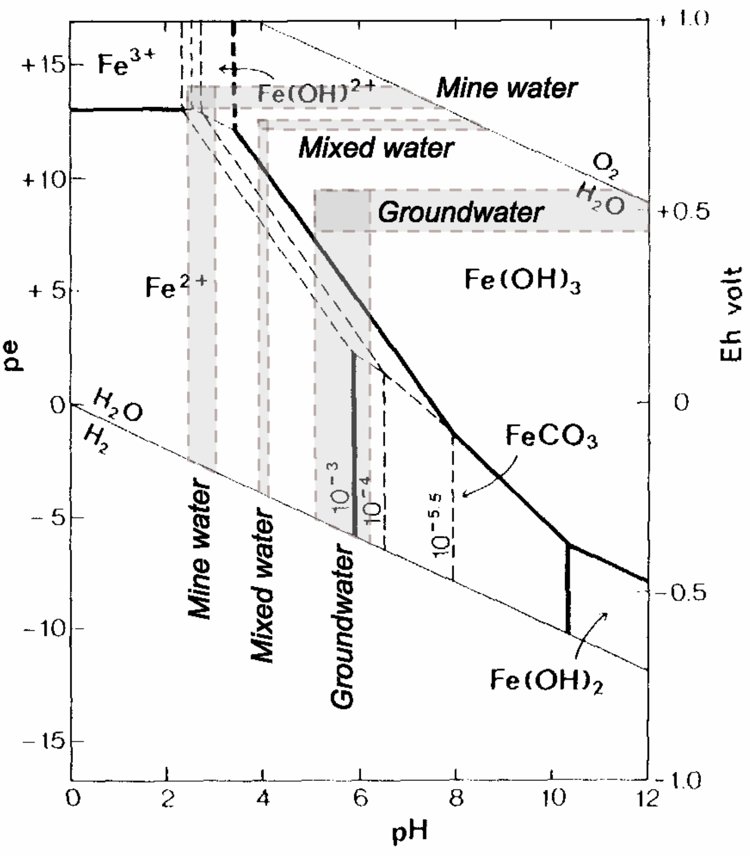


Fig. 7. pH-Eh-diagram for iron species (Appelo and Postma 1999) with the different water types

As a result of redox-processes and buffering reactions, the pH-Eh-conditions are changing along the flowpathes. Fig. 7 shows the pH-Eh-diagram for the iron species according to the observed water types. Regarding to mine water, different combinations of species are possible (Fe^{2+}, Fe^{3+}, $Fe(OH)_3$ and $[FeOH]^{2+}$). On site measurements of iron species (Fe^{2+}) showed that in the mine water (sample 37), 98 % of the total iron is present as Fe^{3+}. In water outlet no. 72, still 80 % of iron is dissolved as Fe^{3+}. Due to the abundant supply of oxygen and protons inside the mine, the ferrous iron from the oxidation of the ores is converted to dissolved ferric iron according to the following equation:

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ = Fe^{3+} + \frac{1}{2} H_2O$$

In shallow ground water the existence of ferrous iron is still possible, but no dissolved iron can be detected in the water. One reason for this fact is shown by the leaching experiments, where no iron can be leached from the solid phase.

A further source for iron decrease in the water can be observed at the mine water outlet. Due to a super saturation regarding Fe_2O_3, an iron-oxide-phase is precipitating (Vornehm et al. 2002).

Conclusion

Four different water types are typical for the "Silberberg" area: 1) acidic mine waters, 2) shallow ground water, 3) mixed waters of mine water and shallow ground water and 4) deeper cycling ground water. However the genesis of the last water is not totally identified.

Leaching experiments show that calcium is the predominant earth alkaline and alkaline cation. Some samples show increased values of potassium (tailing dumps) and magnesia. The leaching behavior can be identified more clearly by the anions. Samples influenced by the ore deposit contain sulfate as predominant anion, whereas in other samples nitrate is dominating. Iron in soil and tailing dump material seems to be strongly fixed.

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