K. Martyčák · J. Zeman · M. Vacek-Veselý

Supergene processes on ore deposits — a source of heavy metals

Abstract The study of supergene processes (i.e., secondary processes running in ore deposits and driven by thermodynamic nonequilibrium between ore-and rock-forming minerals and natural waters, gasses, etc.) is important in order to understand the migration of heavy metals from ore into their adjacent surroundings. The contamination of the local environment can be characterized by the composition of pore waters. The Pb–Zn–Cu ore deposits of Zlaté Hory (Czech Republic) have been chosen for a detailed study of pore solutions. A simple model has been created to describe the evolution of supergene processes in the ore deposits. This model is based on the determination of chemical composition of pore solutions. The dilution of pore solutions of such mineral deposits results in acid mine drainage. Pore solutions can have, during specific stages of their evolution, relatively high concentrations of Cu (0.09 mol/kg), Zn (0.1 mol/kg), SO_4 (0.8 mol/kg) and an extremely low pH (1.38). The supergene alteration of pyrite is the most important process determining the character of pore water. This reaction causes significant acidification and is a leading source of acid mine drainage. The leached zone originates from the interaction of pyrite and limonite. Increased concentrations of heavy metals and sulfates occur in pore waters. The dynamic composition of pore waters within ore deposits undergoing the supergene process can be used to distinguish: (1) three main zones— limonite, transition, and primary zone and (2) two areas—an area with the highest intensity of weathering processes and an area of weathering initiation. In these areas the rate of sulfide oxidation is higher as a result of low pH. From the study of these zones and areas we can further our knowledge of ore body, pore solution, acid mine drainage, and contamination of the local environment.

K. Martyčák (✉) · J. Zeman
Department of Mineralogy, Petrography and Geochemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

M. Vacek-Veselý
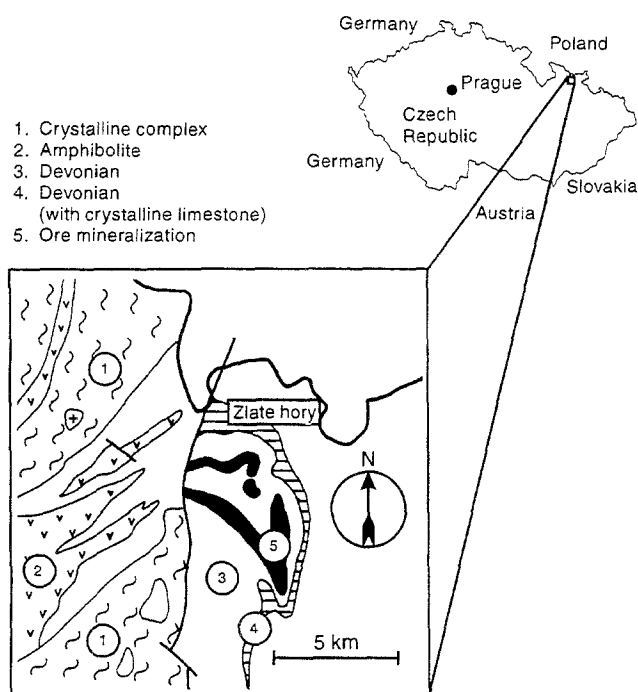Department of Geography, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Introduction

The oxidation of sulfide minerals is the main source of acidity and increased content of heavy metals and sulfates in surface waters and groundwaters. Acid mine drainage, a major source of contamination in mining regions, originates from the dilution of ore body pore waters. It results from the supergene alteration of ore deposits and in the weathering of tailing piles, which results in the generation of acid pore solutions.

The Cu–Zn–Pb district of Zlaté Hory, Czech Republic (Fig. 1), has been chosen for the study of these processes. This historic mining district has been exploited by periodic mining since the turn of the 12th and 13th centuries. For economic reasons, the mining activity is in the process of closing. It occupies an area of approximately 25–30 square km. All known ore deposits are found in low metamorphic Devonian volcanosedimentary rocks (Hettler and others 1977). A genetic relationship between ore mineralization and basic volcanism was determined by geochemical study of volcanosedimentary rocks (Patočka 1987). Patočka and Vrba (1989) considered the Zlaté Hory ore deposit as the Rosebery type deposit and some part as the Kuroko type. Ore mineralization occurs especially in quartzite rocks, occasionally in various types of schist, and rarely in crystalline limestones. Additionally, a horizontal zoning in this district can be observed. Cu ore mineralization is found in disseminated, banded, and sporadically massive ore deposits.

Pyrite is the dominant sulfide mineral. Sphalerite, chalcopyrite, and pyrrhotite are abundant, also; of the minerals present, galena is the least plentiful. Quartz is the main mineral of the waste rock. Additionally, there are carbonates (particularly dolomite types) in some areas of the deposit. Micas and chlorites have been recorded (Fojt 1968). Secondary minerals have been described in large

1. Crystalline complex
2. Amphibolite
3. Devonian
4. Devonian
   (with crystalline limestone)
5. Ore mineralization

Fig. 1. Sketch of geologic structure of the Zlaté Hory deposit (after Hettler and others 1977)

ture ranges from 7 to 8°C. The third area is also water-bearing, and it is located approximately 150 m below the surface. A decrease in the SO_4/HCO_3 ratio is caused by inorganic reactions and increases with the depth. The total water quantity drained into the surface streams ranges from 50 to 70 l/s.

Methodology

Sampling procedures

Two sets of samples were collected to represent the main stages of ore evolution from primary ore to the ore totally consumed by the supergene alteration. The first set was taken from the 100-m-thick vertical profile in the mono-metallic Cu ore mineralization of the Zlaté Hory–Hornické skály ore deposit (samples HS 01–18). The second set was taken near a conspicuous dislocation line in the polymetallic Pb–Zn–Cu ore mineralization of the Zlaté Hory West deposit (samples W 01–18). The samples were put in double polyethylene bags to avoid fluctuation of moisture content, which is relevant for calculation of the pore water volume.

quantities (about 50 species), but mostly with only miner-alogical importance. Limonite is a widespread mineral formed by the decomposition of sulfides (pyrite and pyrrhotite). Relatively frequently, secondary pyrite and marcasite are found, arising by alteration of pyrrhotite. Chalcocite is abundant and bare Cu also occurs in some places. Malachite and cerrusite are found in small quan-tities. Allofanoides and halloysite are plentiful within the other supergene minerals originating from acid mine drainage or by alteration of rock-forming minerals, respec-tively (Fojt and others 1973; Bulka and Zeman 1987).

The groundwaters of the Zlaté Hory region, in general, have low concentrations of dissolved species (25–100 mg/l at 105°C) and the circulation of water is fast. Where waters of shallow circulation are found, they are of the Ca–HCO_3–SO_4 or Ca–SO_4–HCO_3 type. Magnesium content increases with depth. Waters flowing through the oxidized zone are highly mineralized and pH values are relatively low (frequently below 3.5). These waters are of the Ca–SO_4 or Ca–Mg–SO_4 type; Fe, Mn, Cu, Zn and Pb contents are often high (Tišnovská 1977).

Hettler and others (1979) determined that the water level could be characterized as three vertical areas. The first area is permanently found above the groundwater level (approximately 50 m below the land surface). The concen-trations of dissolved mineral species increase considerably after precipitation because of washing through the oxi-dized zone. Water temperature is near the surface tempera-ture and the water is acidic. The second area is below the water table and reaches a depth of approximately 150 m below the surface. Water chemistry is relatively stable, and the pH varies from slightly acid to neutral. Water tempera-

Laboratory work

The quality of acid mine drainage (pH and concentration of dissolved species) does not accurately characterize the conditions of heavy metal release during supergene pro-cesses, as the waters are diluted and are not in contact long enough with rocks and ores. A better idea of the weathering processes can be acquired by studying pore solutions in the laboratory. These pore solutions characterize better the environment where the weathering of sulfides occurs. The modified Lisicin method (Lisicin 1967) was used to study pore solutions. This method was successfully used by Thornber (1975) in the Kambalda Ni ore deposit in Australia. The method is based on the presumption that the pore solutions are primarily diluted by the interaction with the disintegrated ore, and the associated leachate is considered to be the dilute pore solution. The complete transition of the pore solution into the leachate is indicated by the stabilization of the pH and the Eh of the leachate.

One hundred- or 300-g samples of crushed ore (with the grain size of 5–20 mm) were used to prepare the leachate. Distiled water (150 or 700 ml) was poured into polyethyl-ene flasks containing the disintegrated ore. The flasks were shaken daily, and the pH was measured with an Radelkis pH meter (OP 208/1) using a comparing Radelkis calomel electrode and a measuring Radelkis glass electrode. After pH stabilization, Eh was also measured by Radelkis OP 208/1, comparing Radelkis calomel electrode, and measur-ing Pt net. The pH meter was calibrated before each run using pH 2 and 7 buffers (Russel) and Eh was calibrated by ZoBell's solution (Nordstrom 1977).

After stabilization of pH and Eh, leachates were de-

canted, filtered, and stabilized by 1 or 2 ml of concentrated HNO_3 pure for analysis. Sample moisture was determined using a 0.5-g charge at 105°C. Fe, Ni, Co, Mn, Ca, Mg, Pb, Zn, and Cu were determined by atomic absorption spectrophotometry (AAS). Na and K were determined by flame photometry. Al was arranged by titration with complexone III, and sulfates were arranged by gravimetry or by titration. These methods were used for analyses of both the leachate and the solid ore.

Interpretation

Data obtained from chemical analyses of the leachates and stabilized values of pH and Eh were used as input parameters for PHREEQE, a computer program (Parkhurst and others 1980). Their data base was completed with data from the program WATEQ2 (Ball and others 1981). The results were recalculated for the volume of pore solution on the assumption that the pore solution is in balance with atmospheric CO_2 ($p = 10^{-3.5}$ Pa). The volume of pore solution was calculated from known weight and moisture in this model. The dilution (DI) is evaluated using the equation:

$$DI = (m_1 + V_1)/m_1 \qquad (1)$$

where m_1 is the weight of pore solution in the solid sample, and V_1 is the volume of distilled water added.

The concentration of the pore solution is given by:

$$C_{ps} = C_0 \cdot DI \qquad (2)$$

where C_{ps} is the concentration in the pore solution, and C_0 is the concentration in the leachate.

Model verification

Discontinuous changes of pH were observed during the first 40 h of leaching, then pH evolution in the leachates was relatively smooth. Figure 2 presents a characteristic profile. Selected samples were used for repeated leaching and pH, Eh, and Cu concentration determination. In these repeated leachates, the pH values were higher in all cases and the Cu concentration was low (Table 1). We can suppose that the interaction between the ore and water has no inherent influence on the composition of the leachate (during a given time).

The simultaneous leaching of 19 sample pairs was carried out to verify values obtained by the program PHREEQE. After the stabilization of pH and Eh, one of each pair of these samples was poured and evaporated for volume of pore solution. During the process of evaporation, the pH and Eh values were observed continually; evolution is shown in Fig. 3a and b. Evidently, the evolution of pH is tied to the initial pH value. The pH of those samples with initial pH values of approximately 6 increase over time, while initial pH values lower than 5 decrease over time. This relation to initial pH values is caused by
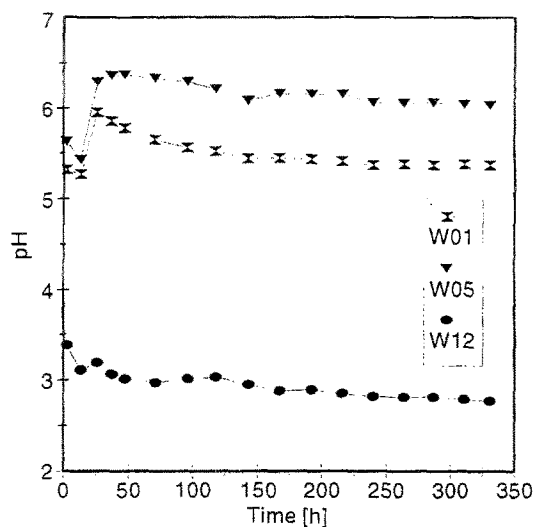

Fig. 2. Time evolution of pH in leachates of selected samples

Table 1. Comparison of pH and Cu concentrations in leachates (1) and repeated leachates (2)

|	1	2	3
pH (1)	2.82	4.18	3.59
Cu (1) (mol/kg)	1.02E − 02	7.46E − 03	8.76E − 02
pH (2)	3.02	4.82	4.41
Cu (2) (mol/kg)	7.26E − 04	4.51E − 04	2.83E − 03

the acidic (base) neutralizing capacity of dissolved CO_2 in the pore solutions (for detail see Stumm and Morgan 1981).

It was not possible to prove time dependence of Eh on pH during the evaporation of the leachates; however, this dependence is often observed in natural waters and acid mine drainage. In some samples discontinuous changes occurred. In one case, the initial value of pH was reached when Eh was reduced to 70 mV at the end of the experiment. By comparison between pH calculated by PHREEQE and pH measured during the evaporation of the leachates (Fig. 4), it was found that pH and the concentrations calculated by PHREEQE can be considered to be comparable.

Good agreement was reached by the comparison of final Eh measured in the leachates and Eh measured in the evaporated leachates (Fig. 5). The standard deviation was 42 mV (minimum observed deviation 14 mV, maximum observed deviation 94 mV). This testifies to the fact that the ion activity ratio of the oxidation–reduction pair does not change significantly, even at great dilution. Accordingly, oxidation–reduction potential measured in the leachates can be used to determine the oxidation–reduction potential of the pore solution. Comparable values between measured and calculated Eh occurred for the oxidation–reduction pair Fe^{2+}/Fe^{3+} on the assumption that Fe^{3+} concentration is controlled by dissolution of $Fe(OH)_3$. In this way Zeman (1987) and Martyčák (1988) calculated the Eh values for pore solutions from different
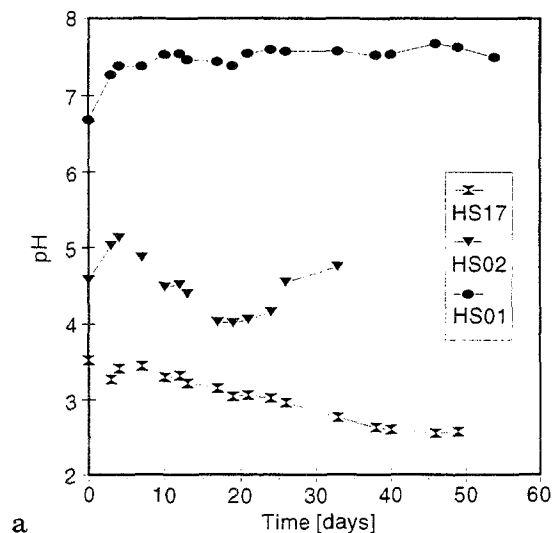
a
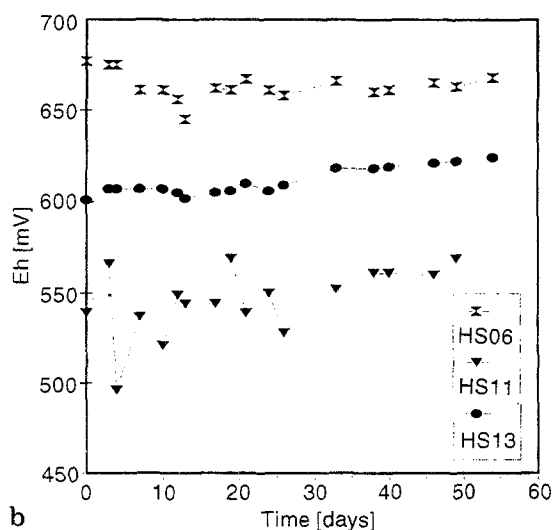
b

Fig. 3a, b. Time evolution of pH during evaporation of leachates **b.** Time evolution of Eh during evaporation of leachates
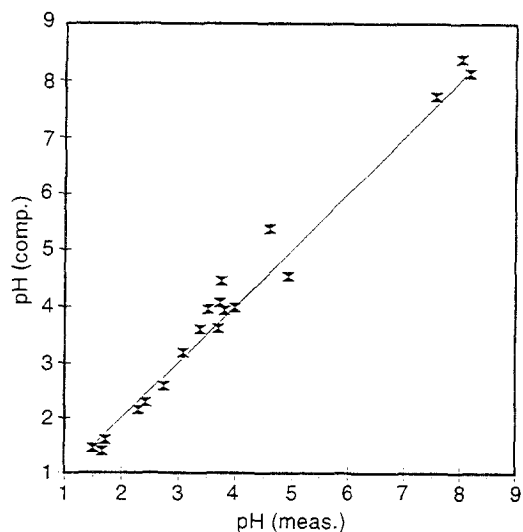

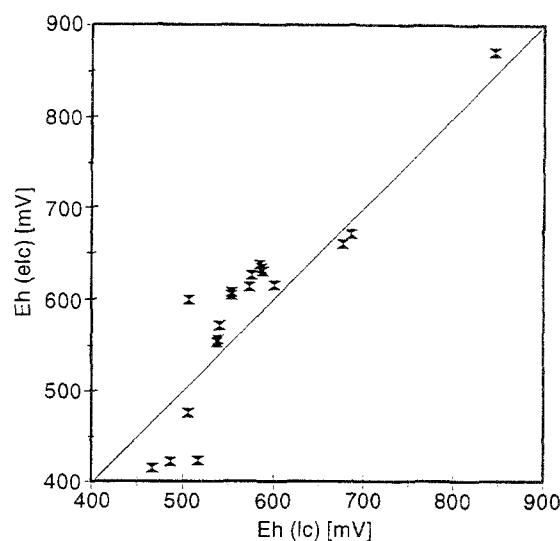**Fig. 4.** Comparison of calculated and measured pH values

Fig. 5. Comparison of Eh values observed in final leachates, Eh(1c), and Eh values observed in evaporated leachates, Eh(elc)

Table 2. Comparison of Eh measured in leachates and Eh calculated for pore solutions on presumption that Fe^{3+} ion concentration is determined by equilibrium with $Fe(OH)_3$

	1	2	3	4	5	6
Eh (obs.) (mV)	642	610	537	589	525	−21
Eh (comp.) (mV)	640	624	543	599	543	98

part of Zlaté Hory ore deposits (Table 2). Similar evidence for oxidation–reduction potential controlled by the oxidation–reduction pair Fe^{2+}/Fe^{3+} in acid mine drainage was also given by Nordstrom and others (1978, 1992). Partial coincidence also occurred between Eh measured in evaporated leachates and Eh calculated by PHREEQE (in seven of 19 samples). Differences between calculated and measured Eh were much higher in the other samples. The Mn concentrations were mostly higher than Fe concentration. The standard deviation between calculated and measured Eh was 240 mV (minimum observed deviation 7 mV, maximum observed deviation 456 mV.

Results and discussion

Profiles

The main parameters computed by the program PHREEQE are statistically summarized in Table 3. On the basis of these results, three main zones (limonite, transition, and primary) can be distinguished along the 100-m vertical profile on the Hornické skály deposit. The limonite zone is located from the surface (approximately 885 m above the sea level) to the depth at the elevation of about 850 m above sea level. The beginning of the transition zone is at the

**Table 3.** Statistic summary of selected characteristic of pore solutions

	pH	Em (mV)	Ionic concentration (mol/kg)						
			Fe (tot.)	Mn	Al	Cu	Zn	Pb	SO$_4$
HS									
N	18	18	18	18	18	18	18	18	18
Average	3.78	544	4.37E − 02	1.11E − 03	8.86E − 03	1.65E − 02	3.13E − 03	1.43E − 05	1.13E − 01
Std	1.89	106	1.25E − 01	1.92E − 03	2.78E − 02	2.19E − 02	4.49E − 03	5.78E − 05	1.89E − 01
Min	1.40	376	7.27E − 06	0.00E + 00	0.00E + 00	8.07E − 06	1.02E − 04	0.00E + 00	1.13E − 02
Max	8.13	832	5.22E − 01	7.22E − 03	1.19E − 01	6.62E − 02	1.80E − 02	2.46E − 04	8.09E − 01
W									
N	23	23	23	23	23	23	23	23	23
Average	4.42	617	4.48E − 03	2.31E − 04	1.31E − 03	8.65E − 03	7.88E − 03	2.26E − 04	3.31E − 02
Std	1.93	95	1.07E − 02	1.79E − 04	2.73E − 03	1.19E − 02	1.46E − 02	6.81E − 04	3.52E − 02
Min	1.38	512	0.00E + 00	0.00E + 00	0.00E + 00	4.33E − 05	6.24E − 05	0.00E + 00	2.48E − 03
Max	8.26	777	3.96E − 02	5.81E − 04	9.36E − 03	4.10E − 02	4.91E − 02	3.13E − 03	1.13E − 01

elevation of about 800 m above sea level; the primary ore occurs in the lowest part of profile. The area with the highest intensity of the weathering is between the limonite zone and the transition zones, the area of initialization of weathering is between the transition zone and the zone of primary ore (Fig. 6a and b). In these areas, the rate of sulfide oxidation is high at pH below 2. This is caused both by the direct influence of pH on the rate of oxidation (Moses and others 1987) and by increasing dissolution of Fe(III) hydroxides. Released Fe^{3+} is an important oxidation species.

The values of pH, Eh, Fe, and in some cases the Cu and Zn concentrations, show the most evident dependence on depth. A similar relationship can also be observed in the horizontal profile surrounding of the dislocation line in the West deposit. In this case the intensity of the weathering decreases very quickly proportional to the distance from the dislocation. This trend is represented by the course of pH values. Differences of the element concentrations between zones are not so significant. They are caused by intensive washing of the area closest to the dislocation line by infiltrating water (Fig. 7).

Iron and pH

The lowest pH values found in pore solutions occurred in the area near the boundary of the limonite and transition zones, where the highest intensity of weathering occurs. The values of pH increase with depth or with an increase in distance from the dislocation line respectively (Fig. 6a and 7). The oxidation of pyrite is the main source of acidity:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$
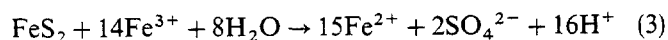
This reaction is the primary mechanism at pH < 4 (Nordstrom 1982). According to the same author, the following reaction is valid for higher pH:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4)$$
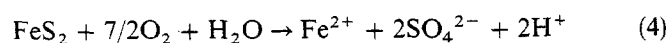
Fe^{2+} released by the reaction is relatively mobile at low

pH values and under these conditions can migrate to the part of deposit with high pH. There it can be oxidized by dissolved oxygen. This rate is significantly increased with an increase in pH (Sinnger and Stumm 1970). Some hydrogen ions released by pyrite oxidation are consumed during this reaction:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (5)$$
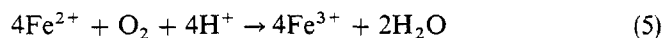
This reaction may also buffer pH. As soon as all pyrite is consumed, reaction 3 stops and the rapid precipitation of $Fe(OH)_3$ occurs:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ \quad (6)$$
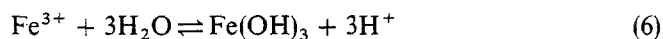
At this stage of reaction pH is controlled by hydrolyzed Fe, and hydroxocomplexes of Fe(III) are formed. Further pH decrease occurs on sites where the primary ore is adjacent to the transition zone. This part can be specified as the area of weathering initiation. With respect to low pH values, pyrite oxidation predominates according to equation 3.

The decrease of pH in the upper part of the ore deposit (above the zone of primary ore) is caused by consumption of H^+ ions during the dissolution of alumosilicates (feldspar, muscovite, sericite) and limonite. For instance, muscovite consumes H^+ ions in acidic solution by the following reaction (Knauss and Wolery 1989):

$$KAl_2[Si_3AlO_{10}](OH)_2 + 10H^+ \rightarrow K^+ + 3Al^{3+}$$
$$+ 3Si(OH)_4 \quad (7)$$
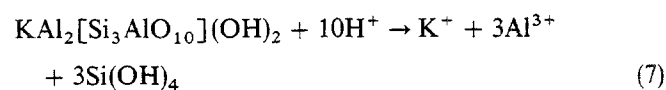
The exchange of H^+ ions on clay minerals can influence pH. Alumosilicate dissolution is the main source of K, Na, Ca, and Mg. On the other hand, the influence of carbonate minerals is not so significant because of their small quantities (in this part of the deposits). The pH values and the Fe concentration can also be altered by microbiological activity; *Thiobacilus ferrooxidans* bacteria have been identified in acid mine drainage (Mandl 1991, personal communication).
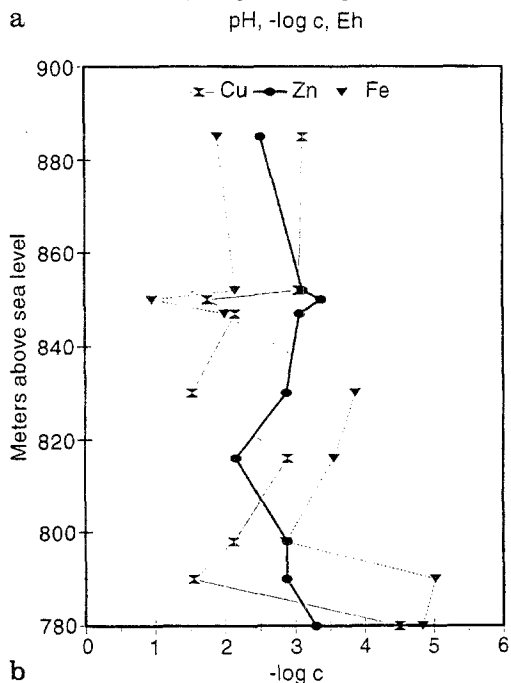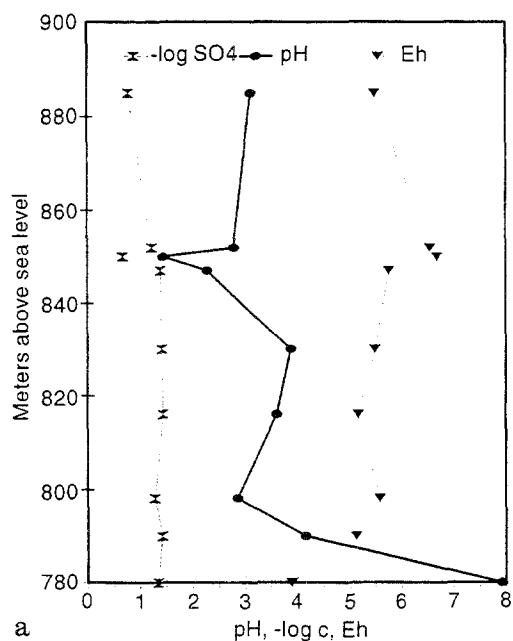
The average Eh values are higher in the West deposit

a

b

Fig. 6a, b. Evolution of average concentrations of SO_4^{2-} (mol/kg), pH, and Eh (mV/100) along the vertical profile in the Hornické Skály deposit b. Evolution of average concentrations of Cu (mol/kg), Zn (mol/kg), and Fe (mol/kg) along the vertical profile in the Hornické Skály deposit
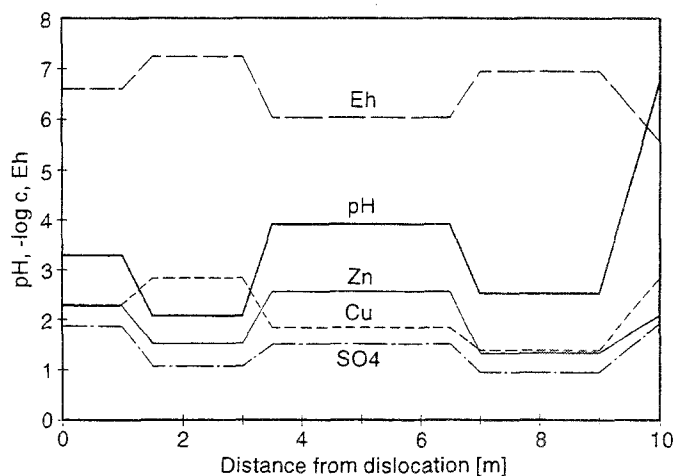

Fig. 7. Evolution of average concentrations along the horizontal profile in the West deposit; c (mol/kg), Eh (mV/100)
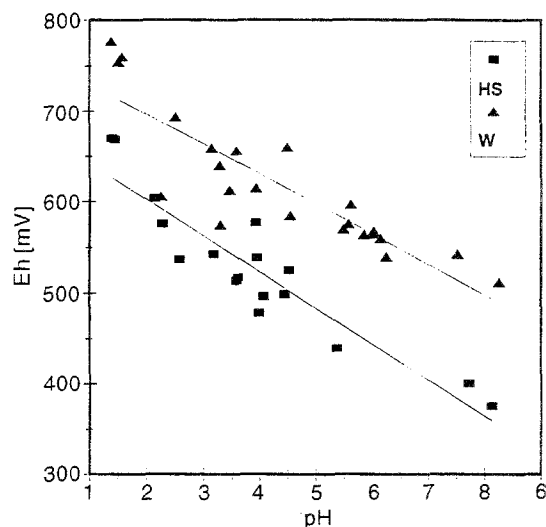

Fig. 8. Plot of pH vs Eh

than in the HS deposit (approximately 70 mV, Table 3). In both cases the Eh values are dependent on pH (Fig. 8). This dependence is given by similar linear functions:

$$Eh_w = -33.07pH + 763 \tag{8}$$

$$Eh_{HS} = -39.60pH + 682 \tag{9}$$

Correlation coefficients are significant in both cases ($R_W^2 = 0.762$, $R_{HS}^2 = 0.854$).

Iron concentration varies from 7.27×10^{-7} to 5.21×10^{-1} mol/kg for HS samples and from trace amounts to

3.96×10^{-2} mol/kg for W samples. The concentration significantly decreases with depth to a minute quantity in the lowest part of profile (Fig. 6b). The Fe concentration also decreases with an increase in pH. The highest Fe concentration can be found everywhere that pyrite is still preserved and limonite already precipitated.

The leached zone is an interesting phenomenon associated with the pyrite–limonite interactions. This zone is a residuum of former rock or ore that underwent intensive supergene alteration. It can be considered as the last alteration stage of rock with high sulfide content. Zeman (1990) described its origin by the evolution of the stationary state between the Fe^{3+} released from $Fe(OH)_3$ and the Fe^{3+} consumed during the pyrite oxidation.

The limonite zone is a region of stable Fe^{3+} concentration. On the other hand, Fe^{3+} ions are consumed in regions containing pyrite. In parts of the system with high pyrite content, the sink of Fe^{3+} is high and the thickness of the leached zone is increased to 10 m. In cases when the pyrite
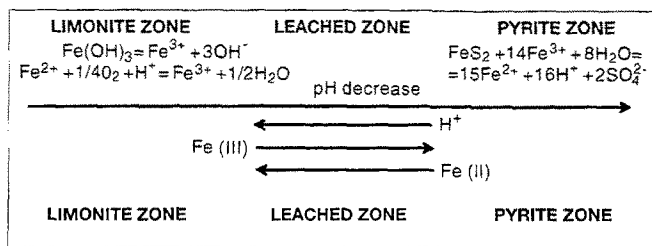
LIMONITE ZONE	LEACHED ZONE	PYRITE ZONE

$Fe(OH)_3 = Fe^{3+} + 3OH^-$

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

$FeS_2 + 14Fe^{3+} + 8H_2O =$

$= 15Fe^{2+} + 16H^+ + 2SO_4^{2-}$

pH decrease

$\longleftarrow H^+ \longrightarrow$

Fe (III) $\longrightarrow$

$\longleftarrow$ Fe (II)

LIMONITE ZONE	LEACHED ZONE	PYRITE ZONE

Fig. 9. Origin and evolution of leached zones

content is low, the stable leached zone occurs as a border of pyrite grains (tenth mm).

A schematic diagram of the origin and an evolution of the leached zone is presented in Fig. 9. The composition of the leached zone depends on the composition of primary rock. If the leached zone is developed during weathering of schist containing mainly muscovite and feldspars, quartz and halloysite (identified by IR spectroscopy) are the main products. This zone is relatively homogeneous. Because of H^+ consumption during weathering of alumosilicate, pH values are higher than in the case when quartzite is the primary rock and quartz is almost the only rock-forming mineral. In this case, the leached zone is porous and is formed mostly by quartz with some amount of pyrite. The evolution of the leached zone is the same in both cases, although pH values differ. Both types of leached zone are observed in the surroundings of the dislocation line. The pH values of the acid leached zones range from 1.35 to 3.46 and pH of the neutral zones varies from 5.48 to 8.26. Secondary earthy chalcocite is frequent in the leached zone and coats pyrite grains or disseminated halloysite. Even gold is concentrated in some parts of these zones.

In spite of the initial assumption of dilution of pore solutions in the leached zones it, was found that the concentrations of the pore solutions increase. With regard to
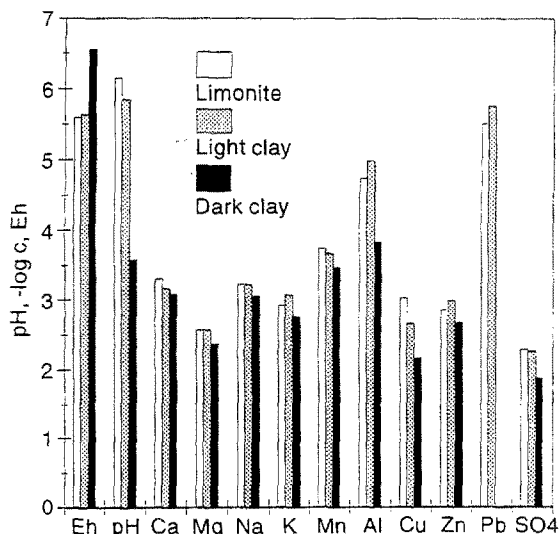
Fig. 10. Change of composition of pore solution in leached zone; c (mol/kg), Eh (mV/100)

the high concentrations of heavy metals and high permeability, the leached zones represent an important source of heavy metals for acid mine drainage. A rapid enrichment of the leached zone and the precipitation of $Fe(OH)_3$ occur when the amount of diffused Fe^{3+} from the limonite zone is less than is needed for pyrite oxidation. The detail of the leached zone that was formed by the alteration of schist consisting of limonite, and light and dark clay is presented in Fig. 10. The thickness of the particular zones is about 5 cm. The pH values increase from 3.87 to 6.11 within 15 cm and Cu content in the solution decreases.

In the middle part, there can be found a large amount of secondary chalcocite, which is the only source of Cu for the pore solution. "Limonite" is mainly formed by halloysite with sorbed Fe(III). Chalcocite is often precipitated onto the surface of halloysite. Fe is the only element whose concentration in pore solution and then in acid mine drainage can be limited by a newly forming phase— the precipitate of Fe oxohydroxide.

Aluminum

The total concentration of Al slowly decreases with an increase in pH and varies from trace amount to 1.19×10^{-1} mol/kg for HS samples and from trace amount to 2.15×10^{-2} mol/kg for W samples. In many cases, the Al concentration was lower than the detection limit of the method used. Nordstrom (1982) suggests that the Al concentration in acid mine drainage can be limited by the precipitation of Al sulfates [alunite $KAl_3(SO_4)_2(OH)_6$, jurbanite $Al(SO_4)(OH) \cdot 5H_2O$, and basalunite $Al_4(SO_4)$ $(OH)_{10} \cdot 5H_2O$, or alunogen $Al_2(SO_4)_3 \cdot 17H_2O$ respectively]. The SI values for alunite, jurbanite, basalunite, and gibbsite calculated by the WATEQ4F program (Ball and others 1987) show increased saturation and supersaturation in the upper part of the profile. The SI values decrease significantly with depth, only the SI value for jurbanite is constant (SI = 0). Halloysite was identified in some samples by IR spectroscopy based on the comparison with the halloysite spectrum by van der Marel and Beutelspacher (1976). Fojt and others (1973) stated alunite as basic sulfate from a different part of the deposit. The same author also found a high concentration of leachable H_2SO_4 in a mixture of the secondary Al and Si products. Comparing this to the data given by Nordstrom (1982), the formation of basic Al sulfates is a relatively slow process connected with the sorption of SO_4^{2-} on fine particles of Al hydroxide. This fact suggests that the Al concentration in pore solution is controlled by the newly forming phase. Solubility depends on pH and the SO_4^{2-} concentration, although it is not necessary that its compound stoichiometry must be exactly defined.

Copper

Cu concentration varies from 9.66×10^{-5} to 9.36×10^{-2} mol/kg for W samples and from 7.22×10^{-6} to $6.66 \times$

source of Zn. The Zn concentrations in a pore solution from polymetallic ore mineralization (W samples) are on the average higher than the concentrations in the pore solution from Cu monometallic ore mineralization (HS samples). These correspond to the increased content of sphalerite. A dependence of the Zn concentration on pH was not observed. A small amount of Zn is moved from the region with higher Zn content in primary ore.

According to Mann and Deutscher (1980), gosslarite or $Zn_4(SO_4)(OH)_6$ phases are limiting for Zn mobility in solution containing SO_4^{2-} at $Pco_2 = 10^{-3.5}$ Pa and lower pH. $Zn(OH)_2$ is a limiting phase at pH > 7. The authors consider that smithsonite occurs at higher Pco_2.

High concentrations of sulfates lead to formation of basic sulfates, even though Zn concentrations are not sufficient for the formation of this phase. Lower SI values for smithsonite, $ZnCO_3$, gosslarite, $Zn_2(OH)_2SO_4$, and $Zn_4(OH)_6SO_4$ correspond to this fact. The SI values for smithsonite, $ZnCO_3$ and $Zn_2(OH)_2SO_4$ slightly exceed zero only in the lower parts of profile because of increased pH and CO_3^{2-} concentrations.

The minerals mentioned above were not identified in solid samples. When leachate was poured from the samples, gosslarite crystallized on remaining crushed ore (identified by IR spectroscopy).

Zn concentration in the pore solution is also limited by adsorption or coprecipitation, mainly with $Fe(OH)_3$. Zn removed from solution by sorption increases with an increase in pH values. Kiniburg and others (1976) pointed out extensive Zn adsorption on the surface of Fe and Al oxide gels at pH > 5.5. Zn mobility in the supergene environment can influence the coprecipitation of Zn with $Fe(OH)_3$, Thornber (1983).

Zn concentrations are not limited by the precipitation of some secondary minerals and depend on rate of input (the rate of sphalerite weathering or the inflow from the surroundings) and output (the dilution of the pore solution into acid mine drainage). Zn mobility makes it difficult to remove from acid mine drainage by reaction on the carbonate barrier.

Lead

In many cases Pb concentrations were below the detection limit. The concentrations in the pore solutions from the monometallic ore mineralization vary from 2.11×10^{-6} to 2.43×10^{-4} mol/kg and from 3.55×10^{-6} to 7.12×10^{-3} mol/kg for the polymetallic ore mineralization. The SI values were observed for anglesite and cerrusite. The majority of the pore solutions from the polymetallic ore mineralization is supersaturated with respect to anglesite (SI $= -0.32 \sim 3.41$) and undersaturated with respect to cerrusite (SI $= -10.86 \sim -1.55$). Anglesite tends to be supersaturated in solutions with lower pH and higher SO_4^{2-} concentrations. Cerrusite tends to the opposite: SI value increases with an increase in pH because the CO_3^{2-} concentration also increases. With regard to the fact that the model presumes equilibrium with atmospheric CO_2,

the concentration of CO_3^{2-} is not high enough for cerrusite precipitation. The SI values for anglesite and cerrusite are very low in the region of Cu monometallic ore mineralization. These minerals were not identified in the solid samples. A dependence of the Pb concentration on pH was not observed. The dependence of Pb is influenced by low concentration of Pb in samples.

Conclusion

A simple model has been created to describe the evolution of supergene processes in ore deposits. This model is based on the determination of chemical composition of pore solutions.

Cu and Zn concentrations in pore solutions are not controlled by the solubility of any secondary mineral, even for cases in which solutions are supersaturated. The crystallization of soluble sulfates (chalcantite and gosslarite) is more prevalent during the evaporation of samples, even though other phases should be formed according to equilibrium calculations. Zn and Cu have very high mobility in the environment where their precipitation should occur. Their concentrations are occasionally reduced by the coprecipitation of $Fe(OH)_3$ or by adsorption on its surface or on the surface of clay minerals.

A significant increase in concentrations of heavy metals occurs in the leached zone surrounding ore deposits. This zone is formed by the interaction of pyrite and limonite. With regard to an intensive water circulation in this zone, pore solutions represent the main source of heavy metals.

Secondary minerals or nonstoichiometric solid phases can locally control Al concentrations in pore solutions. Only Fe^{3+} concentrations are influenced by the $Fe(OH)_3$ precipitation. Its various modifications were found in observed samples and in precipitates originating from running acid mine drainage.

Results suggested that the oxidation–reduction potential is determined by the Fe^{2+}/Fe^{3+} activity ratio. The Fe^{3+} concentration is mostly controlled by the solubility product of $Fe(OH)_3$. The values of oxidation–reduction potential do not significantly change during dilution of pore solutions in acid mine drainage.

As a result of their high mobility, heavy metals generally do not precipitate out from acid mine drainage (e.g., by reaction on a simple carbonate barrier). The decrease in Cu and Zn concentrations did not significantly occur during the experiment based on the model flow acid mine drainage through carbonate. The pH values increased from 2.5 to 6. The lowering of Cu and Zn element concentrations occurred only during a circulation experiment when Cu concentration was lowered 10 times within 250 h and Zn concentration changed only slightly.

The oxidation of sulfide minerals—a main source of acidity—is a process determining the quality of surface water and groundwater and soil in ore mining areas. From the study of pore solutions, we can characterize in detail

the environment where heavy metals are primarily released into their adjacent surrounding.

References

Ball JW, Nordstrom DK, and Jenne EA (1981) Additional and revised thermochemical data and computer code for WATEQ2—computerized chemical model for trace and major elements speciation and mineral equilibria of natural waters: US Geological Survey Water Resource Investigations 78-116, pp 1–109

Ball JW, Nordstrom DK, and Zachmann DW (1987) WATEQ4F—personal computer FORTRAN translation of the geochemical model WATEQ2 with revised data base. US Geological Survey Open Report 87-50, pp 1–108

Bulka V and Zeman J (1987) The sorption behavior of allofane, limonite, and wad from Zlaté Hory ore district Scripta Fac Sci Nat Univ Purk Brun 17:247–258 (in Czech, English abstract)

Fójt B (1968) Chalcographic characteristic of the sulphide deposits in Zlaté Hory ore district in Silesia. Folia Univ Purk Brun 5:5–50 (in Czech, English abstract)

Fojt B and others (1973) Mineralogy of supergene product of sulphide deposits in Zlaté Hory ore district, Research report of Department of Mineralogy, JE Purkyně University, pp 1–58 (unpublished)

Hettler J, Skácel J, and Tomšik J (1977) Zlaté Hory—ore district, Sbor Geological Průzk Ostrava 13:1–149 (in Czech, English abstract)

Hettler J, Novotný M, Mátl M, Grym V, and Pišl P (1979) Zlaté Hory—primary aureoles. Research report of Geological Exploration Zlaté Hory Comp. (unpublished)

Kiniburg DG, Jackson ML, and Syers JK (1976) Adsorption of alkaline earth, transition heavy metal cations by hydrous oxide gels of iron and aluminium. Soil Sci Soc Am J 40:796–799

Knauss K G and Wolery TJ (1989) Muscovite dissolution kinetics as a function of pH and time at 70°C. Geochim Cosmochim Acta 53:1493–1501

Lisicin AK (1967) Method of investigation of equilibrium values of Eh and pH in system: solution–rocks–minerals, Geokhimia 8:994–1002 (in Russian, English abstract)

Mann AV and Deutsher RL (1980) Solution geochemistry of lead and zinc in water containing carbonate, sulphate and chloride ions. Chem. Geol 29:293–311

Marel van der HW and Beutelspacher H (1976) Atlas of infrared spectroscopy of clay minerals and their admixtures, Amsterdam: Elsevier 396 pp

Martyčák K (1988) The study of the pore solutions of Zlaté Hory ore deposits. MSc thesis. JE Purkyně University. pp 1–69 (unpublished)

Moses CO, Nordstrom DK, Herman JS, and Mills AL (1987) Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim Cosmochim Acta 51:1561–1571

Nordstrom DK (1977) Thermochemical redox equilibria of ZoBell's solution. Geochim Cosmochim Acta 41:1835–1841

Nordstrom DK (1982) The effect of sulfate on aluminium concentration in natural waters: Some stability relations in the system Al_2O_3–SO_3–H_2O at 298K. Geochim Cosmochim Acta 46:681–692

Nordstrom DK, Jenne EA, and Ball JW (1978) Redox equilibria of iron in acid mine wares. In: Jenne EA (Ed), Chemical modeling in aqueous systems: Washington, DC: ACS Symposium Series 93. pp 51–79

Nordstrom DK, McNutt RH, Puigdomenech I, Smellie JAT, and Wolf M (1992) Ground water chemistry and geochemical modeling of water-rock interaction at the Osamu Utsumi mine and the Morro do Ferro analogue study sites, Pocos de Caldas, Minas Gerais, Brazil. J Geochem Explor 45:249–287

Parkhurst DL, Thorstenson DD, and Plummer LN (1980) PHREEQE—computer program for geochemical calculations. US Geological Survey Water Resource Investigations 80-96, pp 1–193

Patočka F (1987) The geochemistry of mafic metavolcanics: Implications for the origin of the Devonian massive sulphide deposits of the Zlaté Hory, Czechoslovakia. Miner Dep 22:144–150

Patočka F and Vrba J (1989) The comparison of strata-bound massive sulphide deposits using the fuzzy linguistic diagnosis of the Zlaté Hory deposits, Czechoslovakia, as an example. Miner Dep 24:192–198

Pešková H (1984) Distribution of Cu in Zlate Hory ore deposit. MSc thesis. JE Purkyně University, pp 1–65, (unpublished)

Sinnger PC and Stumm W (1970) Acid mine drainage: The rate determining step. Science 167:1121–1123

Stumm W and Morgan JJ (1981) Aquatic chemistry, 2nd ed. New York: Wiley, 780 pp

Thornber MR (1975) Supergene alteration of sulphides. II. A chemical study of Kambalda nickel deposits. Chem Geol 15:117–144

Thornber MR (1979) Supergene alteration of sulphides. V. Laboratory studies on the dispersion of Ni, Cu, Co and Fe. Chem Geol. 26:135–149

Thornber MR (1983) The chemical processes of gossan formation. In: Smith RE (Ed), Geochemical Exploration in Deeply Weathered Terrains CSIRO Division of Mineralogy, Short Course/Workshop, Floreat Park, W.A. pp 67–73

Thornber MR and Wildman JE (1979) Supergene alteration of sulphides. IV. Laboratory study of the weathering of nickel ores. Chem Geol 24:97–110

Thornber MR and Wildman JE (1984) Supergene alteration of sulphides. VI. The binding of Cu, Ni, Zn, Co and Pb with gossan (iron bearing) minerals. Chem Geol 44:399–434

Tišnovská V (1977) Hydrogeologic situation of Zlaté Hory ore district and chemistry of groundwater. Geol Průzk 13:83–87 (in Czech)

Zeman J (1987) The processes of supergene alteration of sulphide, the Zlaté Hory ore deposits, as an example. PhD thesis. JE Purkyně University. pp 1–124 (unpublished)

Zeman J (1990) Dynamic of reaction between Fe(III) and pyrite and origin of leached zones in Zlaté Hory ore deposits. In: Skřivan P (Ed), Geochemistry and environment Geological Institute of Czech Academy of Science, Prague pp 83–87, (in Czech)