Metal mobilization from AMD sediments in connection with bacterial iron reduction

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Abstract

Ochreous sediments, dominated by schwertmannite mineral from the acid mine drainage effluent from the Smolník abandoned sulfide mine, and biogenic schwertmannite prepared under laboratory conditions, were subjected to leaching by the acidophilic iron-reducing bacterium *Acidiphilium* SJH. Different kinetics of the mobilization of sulfur and iron entities from the schwertmannite during the bacterial leaching indicated incongruent dissolution of the mineral. Due to bacterial iron reduction, all of the dissolved iron was in divalent state. Contrary to the progressive sulfate extraction, the leaching of iron showed saturation behaviour, caused either by the sorption of ferrous ions onto the mineral surface or by the precipitation and formation of new mineral phase. Mobilization of arsenic from the sediment in the early stage of leaching was followed by its later disappearance from the solution due to sorption or co-precipitation onto/with a newly formed iron mineral phase.

Chemical analysis of the acid mine drainage (AMD) water and related sediments formed from the stream revealed selective scavenging potential of the iron precipitates for arsenic and some other species. The iron oxidizing and iron reducing bacteria play a vital role in the successive dissolution and immobilization of elements in the mine drainage systems in connection with the biogeochemical destruction and reconstruction of metal sulfides, iron hydroxides and iron hydroxysulfate minerals.

Key words: AMD, schwertmannite, acidophilic bacteria, iron, sulfate, precipitation, oxidation, reduction

Introduction

Iron and sulfur oxidizing bacteria play an important role in the metal mobilization in AMD, as they accelerate the oxidation of iron and sulfur entities in the pyrite and other metal sulfides, leading to mineral dissolution and acid generation (Singer and Stumm, 1970; Nordstrom, 1982). On the other hand, bacterial oxidation of Fe^{2+} to Fe^{3+} affects the iron speciation and as a result of that it contributes to the formation of the secondary iron minerals. After the ferric iron in the AMD systems reaches saturation, it hydrolyses and precipitates in various forms of iron oxides and hydroxysulfate minerals. Schwertmannite (Eq. 1) is considered to be the major secondary ferric iron mineral that forms in moderately acidic (pH 2.8 – 4.5) sulfate waters impacted by AMD (Bigham et al., 1996).

$$8\ Fe^{3+} + SO_4^{2-} + 14\ H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 22\ H^+ \quad (1)$$

Sediments of AMD recipients receive significant amount of iron, sulfur and other elements that co-precipitate with or adsorb onto these secondary mineral phases. The formation of these iron minerals may play an important role in the transient storage of metals.

Heterotrophic acidophilic bacteria, that occupy acid mine streams, have been shown to use the dissimilatory reduction of ferric iron to growth in oxygen-limited conditions (Coupland and Johnson, 2008). Reductive dissolution of solid ferric iron minerals by these bacteria causes mobilization and down-stream transportation of iron, sulfate and other potentially toxic elements associated with the precipitates through sorption or solid solution. The cycling of Fe between the oxidized and reduced solid phases thus involves successive solubilization and immobilization of elements from these transient storages. Iron oxides are in general compounds with low- to very low solubility. In natural environments, reductive dissolution is by far the most important dissolution mechanism (Cornel and Schwertmann, 2003).

In this work, heterotrophic bacterium *Acidiphilium* SJH was applied in the leaching test, as the ability of this bacterium to reduce both soluble and solid phase ferric iron has been reported previously (Bridge and Johnson, 2000).

Material and methods

Preparation of the minerals

Ochreous precipitates were collected from the sediments of AMD effluent from the shaft Pech that concentrates the majority of waters draining the flooded Smolník mine area.

The sediment was air dried at the ambient temperature, homogenized and stored in desiccators for further use.

The biogenic schwertmannite was prepared in the laboratory from ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$) by its biological oxidation to ferric sulfate followed by the ferric iron hydrolysis and precipitation. Psychrotolerant iron-oxidizing bacterium *Acidithiobacillus ferrooxidans* SS3 (Kupka et al., 2007) was inoculated to the ferrous iron-containing medium. The schwertmannite formation was achieved in the absence of potassium and at low level of other monovalent cations to prevent the precipitation of jarosites (Wang et al., 2006; Gramp et al., 2008) salts medium for schwertmannite synthesis contained 1.6 mM $MgSO_4 \cdot 7H_2O$, 6.1 mM $NH_4H_2PO_4$ and 120 mM $FeSO_4 \cdot 7H_2O$ in 4.05 mM H_2SO_4. The initial pH of the medium was 2.8. The incubation was carried out at 4 °C in 500 ml flasks stored in cooling thermo cabinets and magnetically stirred at 180 rpm. Samples of the solutions were taken in intervals for the iron speciation, sulfate, pH and redox analysis. All synthesis conditions involved 10 days of equilibration before the samples of precipitates were separated from the rest liquid medium by centrifugation at 5 000 rpm, washed by distilled water and air dried.

Bacterial leaching

The leaching tests of the sediment samples were done with the iron reducing bacteria *Acidiphilium* SJH (Bridge and Johnson, 2000) in the special tubes with a screw cap and a septum. Each tube contained 0.05 g of dried sediment and 10 ml of liquid medium (final pulp density 5 g · l^{-1}). The medium contained (per liter) 6.25 g $(NH_4)_2SO_4$, 2.5 g $MgSO_4 \cdot 7H_2O$, 0.13 g tryptic soy broth, 0.9 g D-galactose, and 1 mL solution of the trace elements. The medium was acidified with 5M H_2SO_4 to final pH 2.5. The bacterial inoculum was taken from the aerobically grown culture. The cells were separated from the nutrient solution by filtration through a 0.20 µm pore size Milipore filter. Washed cell pellets were suspended in fresh medium and diluted to adjust the final cell concentration equal to optical density $OD_{600} = 1.0$. Ten milliliters of the cell suspension were added to each tube. The tubes were air tightly closed, and incubated dynamically on a rotator at 60 rpm in a thermostat at 25 °C. Experiments were carried out in triplicates and each series included one abiotic control.

Because of the observing anoxic conditions and excluding the sample contamination, the samples were taken in regular intervals through the cap´s septum by using sterile needles and syringes. The samples were filtered in order to separate the solid and liquid phases before analysis.

Chemical analyses

Chemical composition of the solid phases was determined by atomic absorption spectrometry (AAS) with GTA furnace after the digestion with concentrated nitric and hydrochloric acid (1 : 1) in a microwave digester. Ferrous iron was measured by o-phenantroline colourimetric method, ferric iron by UV-spectrophotometric method at $\lambda = 300$ nm. Sulfate concentration was determined by $BaCl_2$ nephelometric method. Concentrations of the total iron and arsenic in the leaching liquors were determined by AAS and pH and the redox potential of the solutions by the potentiometric method.

The XRD patterns were measured using a Philips PW 1820 powder diffractometer working in the 2Θ geometry with CuKα radiation. The JCPDS PDF database (JCPDS-PDF, 2004) was utilized for the phase identification.

Results and discussion

The XRD spectrum of the Smolník precipitate (Fig. 1) gave characteristic schwertmannite XRD pattern with 8 broad peaks and a high background, indicating poor crystallinity. The spectrum contained the phases: iron oxide sulfate hydroxide $Fe_{16}O_{16}(SO_4)_3(OH)_{10} \cdot 10H_2O$ (JCPDS 47-1775), iron oxide hydroxide FeO(OH) (JCPDS 13-87), and ferrihydrite $Fe_5O_7(OH) \cdot 4H_2O$ (JCPDS 29-712).

Chemical composition of the sediment is given in Tab. 1.

The two major elements of the precipitate are iron and sulfur. Schwertmannite, with the ideal formula $Fe_8O_8(OH)_6(SO_4)$, implies an Fe/S molar ratio of 8. However, the sulfate content is variable in natural samples of schwertmannite and varies from 10 to 15 wt.%, yielding Fe/S mole ratios ranging from 8 to 4.6 (Bigham et al., 1994; Murad et al., 1994; Bigham et al., 1996). The weight % of iron and sulfur in the "Smolník" precipitate (Tab. 1) are 44.89 and 5.53 respectively, yielding Fe/S molar ratio of 4.7. This value belongs to the range of naturally occurred schwertmannites published by Bigham et al. (1994).

Fe(III)-hydroxysulfates from the acid mine drainages have been shown to contain As, Cr, and a variety of the rare earth elements (Schroth and Parnell, 2005). Relatively high content of arsenic (0.28 wt.%) in the "Smolník" precipitates indicates their ability to accumulate oxyanions from the surrounding water. The concentration of arsenic in the AMD stream in which the precipitates were formed was 30 µg · l^{-1}. The concentration of iron and sulfate in the AMD was 380 mg · l^{-1} and 2 320 mg · l^{-1} respectively. The pH of the water was 3.9 and temperature 14 °C. Natural precipitates in the sediments of streams, where the water has attained a pH of 3 to 4, are dominated by schwertmannite.

Tab. 1
Chemical analysis of precipitates taken from AMD (shaft Pech) in Smolník abandoned mine (April, 2009)

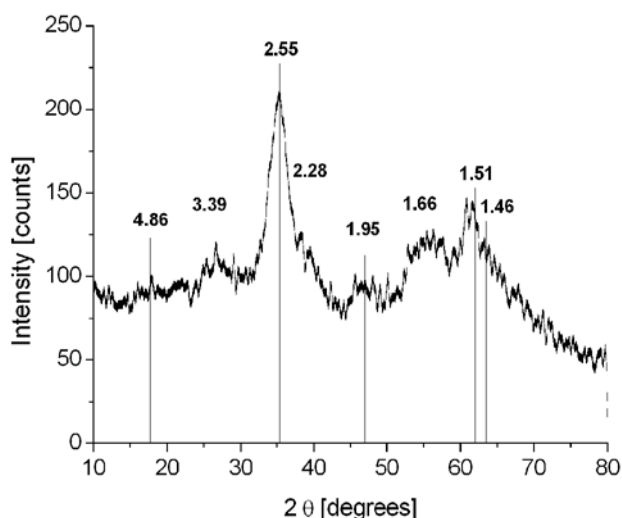| Fe	S	Al	Ca	Mg	Na	K	As	Cu	Zn	Mn	Pb
%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	ppm
44.89	5.53	0.38	0.1	0.07	0.02	47.5	0.28	112.5	72.5	35	16.8

Fig. 1. X-ray diffractogram of precipitates collected from the shaft Pech in the Smolník abandoned mine. The d-spacing (Å) and peak positions for schwertmannite (PDF 47-1775) are given as vertical lines.

Schwertmannite was the major component of all collected and studied AMD precipitates formed between pH 2.5 and 4 by Murad et al. (1994).

Preparation of the biogenic schwertmannite from ferrous salt solution using psychrotolerant iron oxidizing bacteria *Acidiphilium* SS3 was done at 4 °C. Ferrous iron was completely oxidized to ferric iron within 10 days (Fig. 2A). The solution pH initially increased due to the acid--consuming iron oxidation. Subsequent reaction of ferric iron hydrolysis, leading to schwertmannite formation is acid producing and the final pH value depends on the extent of ferric iron precipitation (Fig. 2B).

Due to bacterial oxidation of Fe^{2+} to Fe^{3+} ferric iron eventually reached supersaturation with respect to
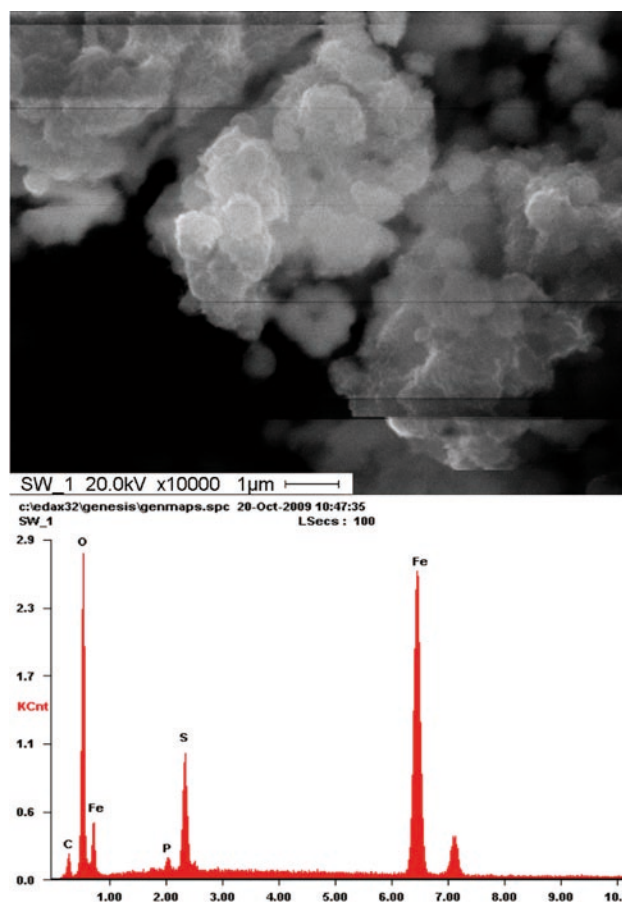

Fig. 3. SEM micrographs of biogenic Schwertmannite prepared in laboratory (top) and EDX analysis (bottom), which revealed 65.6 % Fe and 6.87 % S content in the mineral, yielding Fe/S molar ratio of 5.48. This value belongs to the range of naturally occurred schwertmannites published by Bigham et al. (1994).
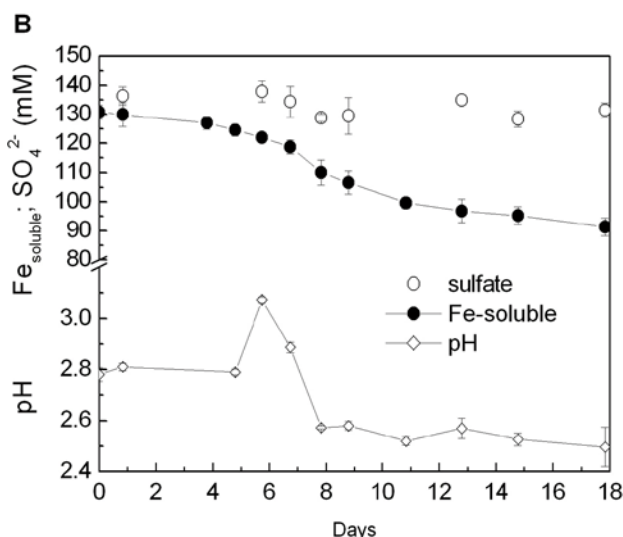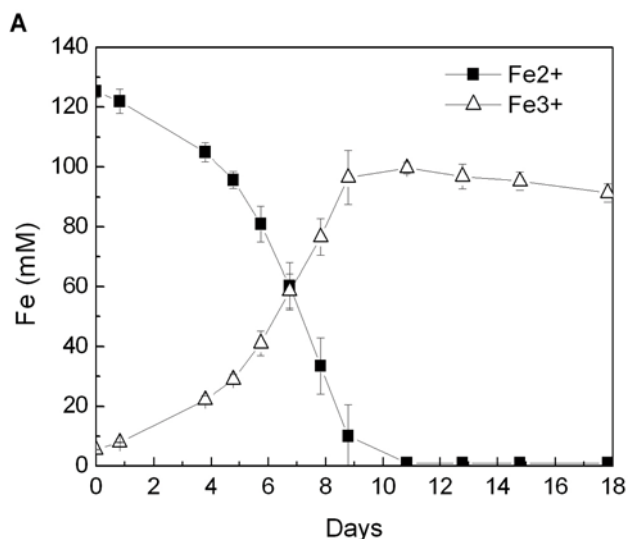

Fig. 2. Bacterial oxidation of Fe^{2+} to Fe^{3+} (2A), pH changes and precipitation of iron and sulfate in the course of schwertmannite formation (2B) at 4 °C. Symbols indicate averages ± standard deviations from triplicate flasks.

schwertmannite, which formation diminished iron and sulfate concentration in the solution. Schwertmannite was synthesized in the absence of potassium and other monovalent cations, to eliminate the formation of jarosite minerals. The SEM and EDX analysis of schwertmannite formed is done in Fig. 3. The XRD analysis of this reference schwertmannite sample revealed characteristic 8 broad peaks pattern (data not shown), similar to those in Fig. 1.

Reductive dissolution of the iron precipitates

Fig. 4 shows bacterial leaching of AMD sediment and biogenic schwertmannite. The reductive dissolution of ferric hydroxysulfate (schwertmannite) $Fe_8O_8(OH)_6(SO_4)$, releases ferrous iron and sulfate and generates net alkalinity (Eq 2).

$$3Fe_8O_8(OH)_6(SO_4) + C_6H_{12}O_6 + 6H_2O \rightarrow 24Fe^{2+} + 6CO_2 + + 3SO_4^{2-} + 42OH^- \qquad (2)$$
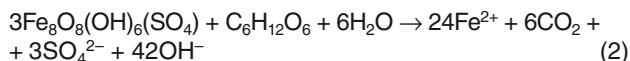
In the course of bacterially mediated dissolution of ferric iron minerals, Fe^{III} from the solid phase accepts electrons from the oxidation of organic matter. Reduction of Fe^{III} to Fe^{II} destabilizes the coordination sphere of the iron, both as a result of the loss of charge and because of the larger size of the bivalent iron ion and thus induces detachment of iron as Fe^{2+} from the structure (Cornel and Schwertmann, 2003). The higher initial rate of the iron extraction was observed at laboratory prepared schwertmannite (Fig. 4 closed symbols) compared to iron extraction from the AMD sediment (Fig. 4 open symbols). The concentrations of dissolved iron, from which Fe^{2+} was the dominant iron species, reached approximately 16.5 mM (913 mg · l⁻¹), which corresponds to 31.6 % yield. The rate of the leaching gradually decreased and reached zero after 5 days at pure schwertmannite and 20 days in the case

of AMD sediment sample. Laboratory studies of bacterial reductive dissolution of the crystalline ferric iron oxides typically revealed only minor degrees of the iron extraction (Phillips et al., 1993; Bridge and Johnson, 2000; Roden et al., 2000). There are a number of reasons of decelerating the iron dissolution rate. The mineral surface passivation due to the accumulation of surface bound divalent iron is assumed to be the major factor prohibiting the complete dissolution of mineral in batch systems (Roden et al., 1999, 2000). Adsorbed and exchangeable iron fraction of the solid phase was not quantified in these experiments. Unlike dissolved iron, the concentration of sulfate does not follow asymptotic behaviour and gradually increased in the observed interval (data not shown), indicating incongruent dissolution of the mineral phases. The high initial concentration of sulfate (approx. 120 mM) in the medium prohibited the exact determination of net sulfate extraction from the mineral phase during the leaching. Mobilization of arsenic from the Smolník sediment was observed in the early stage of leaching (Fig. 4B), followed by its disappearance from the liquid phase after 12 days.

Schwertmannite is a poorly crystalline, metastable mineral that transforms spontaneously to goethite, releasing all its structural sulfate and producing protons (Eq. 3) (Bigham et al., 1996).

$$Fe_8O_8(OH)_6SO_4 + H_2O \rightarrow 8FeOOH + 2H^+ + SO_4^{2-} \qquad (3)$$

Transformation of the mineral schwertmannite to thermodynamically more stable goethite was observed in laboratory conditions at room temperature during 543 days (Bigham et al., 1996). In the presence of the iron reducing bacteria, the degradation of the parent iron mineral is accelerated and the reconstruction of the new mineral phase could be substantially affected due to the alteration of the ion speciation and the abundance of divalent iron
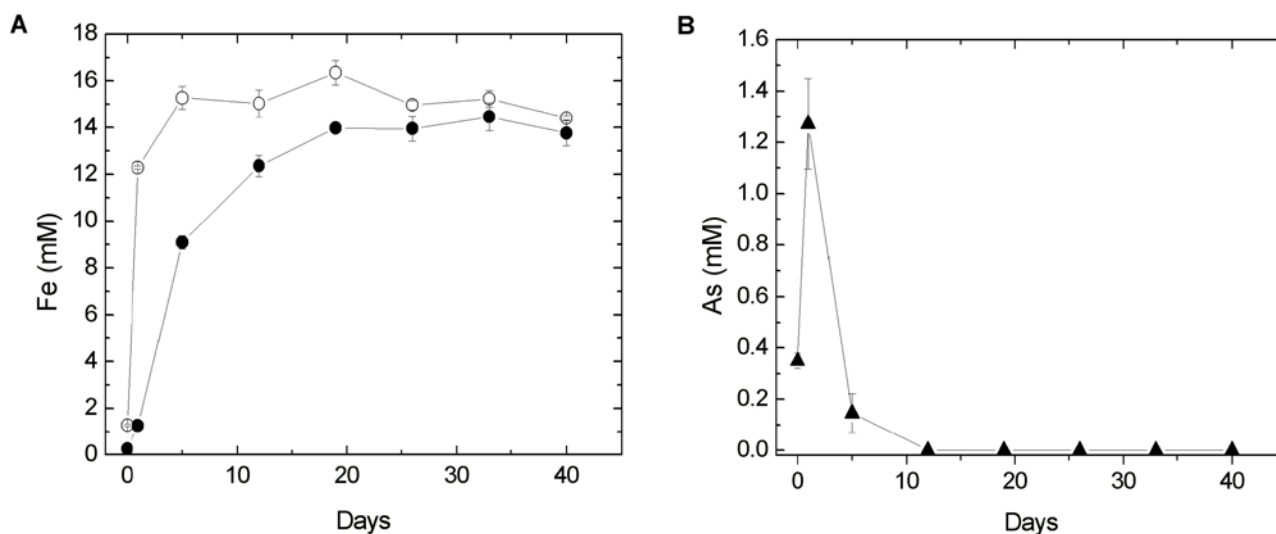

Fig. 4. Mobilization of iron and arsenic in the course of bacterial reductive dissolution of iron hydroxysulfate minerals. 4A extraction of iron from the biogenic schwertmannite (open symbols) and AMD sediment (closed symbols). 4B mobilization of arsenic from the AMD sediment in the course of bacterial leaching. Symbols indicate averages ± standard deviations from triplicate flasks.

species. Besides goethite, the formation of other phases is possible. At higher pH, which is achieved due to alkalinity producing reaction 2, the formation of magnetite is more likely as accumulation of this mineral has been observed during anaerobic bacterial iron reduction.

Conclusions

Bacterial oxidation of ferrous iron to ferric iron in the acid mine effluents contributes to attenuation of dissolved species in these systems. As ferric iron concentration in the solutions increased, it eventually reached supersaturation and co-precipitates with sulfate to the form of insoluble iron hydroxy sulfates. Schwertmannite is considered to be the major secondary ferric iron mineral that forms in the moderately acidic sulfide mine waters. The XRD pattern of both, the Smolník AMD precipitate and biogenic schwertmannite prepared in the laboratory corresponds to published X-ray spectra of AMD precipitates taken from other sites, where schwertmannite was the dominant Fe(III) mineral phase (Bigham et al., 1990). Chemical analysis of the Smolník sediment has proved retention of arsenic, Al, Cu, Zn and Pb from AMD stream and hence the capacity of iron precipitates for the transient storage of iron, sulfur and heavy metals. The paragenesis of ochreous AMD minerals and the fate of associated species depend on immediate environmental conditions. The cycling of Fe between oxidized and reduced solid phases may also involve solubilization or immobilization of associated potentially toxic metals or other ions during mineral destruction and transformation.

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