Jarosite, schwertmannite, goethite, ferrihydrite and lepidocrocite: the legacy of coal and sulfide ore mining

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Abstract

The aftermaths of coal and sulfide ore mining are widespread and well documented: unless measures are taken to prevent sulfide oxidation – both during and after cessation of mining – acid mine drainage with all its detrimental effects can ensue. Improved knowledge of acid mine drainage precipitate mineralogy had recently opened up the possibility of relating the occurrence of certain “key” minerals to genetic factors such as pH and sulfate concentration. Mineral sequences may develop as a function of local changes in genetic conditions and can serve to identify such variations in the field. Temporal changes, for example seasonal fluctuations of precipitation (leading to variations of water infiltration through and runoff over mines and mine dumps), can also have noticeable effects on precipitate mineralogy.

The purpose of this paper is to provide (1) a brief review of the most important Fe3+ minerals formed as a result of acid mine drainage and (2) a case study of mine drainage precipitates from the Sokolov lignite mining district in the northwestern Czech Republic and their environmental implications.

Key Words

Oxidation, acidification, ochre, minerals.

Introduction and review

Sulfidic ores constitute the raw materials for innumerable industrial products. Two of the most common sulfides, pyrite and marcasite, FeS2, are also (undesirable) constituents of many liginites and coals. In pyrite and marcasite, both iron and sulfur are in reduced forms (Fe2+ and S2-, respectively). Other transition elements such as cobalt, nickel and copper may partially replace iron, and arsenic can replace sulfur in these minerals to some extent. Pyrrhotite, Fe1-xS, is another common iron sulfide, and numerous sulfides of more complex chemistry such as chalcopyrite, CuFeS2, pentlandite (Fe,Ni)9S8, and arsenopyrite, FeAsS, also contain iron as an “essential” element. Iron can furthermore substitute in the structures of many other sulfides to various extents, for example replacing up to 50 mole percent of the zinc content of sphalerite, ZnS.

Exposure of Fe2+-bearing sulfides to the ambient atmosphere results in the oxidation of both Fe2+ and S2-. Exemplary formulae for (overall) reactions such as

(1) \[ 2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{FeSO}_4 + 2 \text{H}_2\text{SO}_4 \]

(2) \[ 4 \text{FeS}_2 + 15 \text{O}_2 + 10 \text{H}_2\text{O} \rightarrow 4 \text{FeOOH} + 8 \text{H}_2\text{SO}_4 \]

show that this leads to the generation of abundant quantities of sulfuric acid (“acid mine drainage”, AMD), and eventually to a massive formation of ochreous Fe3+-bearing precipitates. Such processes, however, do not occur exclusively in the wake of mining operations; thus the (mis-)use of sulfide-bearing clays for landfills can bring about similar problems (cf. Fanning and Burch 1997), and the same reactions also take place naturally when Fe2+-bearing sulfides in rocks or soils are oxidized upon exposure to the atmosphere (an illustrative example has been given by Schwertmann et al. 1995). The weathering of sulfides of complex composition, such as those mentioned above, will result in the release of additional elements that are detrimental to plant and animal life into the environment.

Although a plethora of research articles has addressed the phenomenon of acid mine drainage, most of these were concerned with water and precipitate chemistry, in particular with regard to the ad- and desorption of heavy metals, whereas knowledge of the mineralogy of the ochreous precipitates formed in the course of such processes was long of a more cursory nature. A major cause for this lack of detailed information may have resulted from the poor crystallinity of many of the minerals in question, which complicates their identification. Thus, although schwertmannite is a component of many acid mine...
drainage precipitates, the first description of this iron oxyhydroxysulfate as a “new mineral” was published just a decade ago (Bigham et al. 1994).

Recent in-depth overviews of acid mine and rock drainage, including information on the mineralogy of the associated precipitates, have been published by the American Chemical Society (Alpers and Blowes 1994) and the Mineralogical Association of Canada (Jambor et al. 2003).

**Mineralogy**

Equation (1) indicates the initial stages of Fe$^{2+}$-sulfide oxidation to result in the formation of Fe$^{2+}$ sulfates. A variety of such sulfates exists, which differ only in their water content: melanterite, ideally FeSO$_4$·7H$_2$O, ferrohexahydrite, FeSO$_4$·6H$_2$O, siderotil, FeSO$_4$·5H$_2$O, rozenite, FeSO$_4$·4H$_2$O, and szomolnokite, FeSO$_4$·H$_2$O. Fe$^{2+}$ in these minerals is relatively stable under acid conditions, and they can be identified in the laboratory by X-ray diffraction because they are generally well crystallized. Upon extended exposure to the atmosphere Fe$^{2+}$ will oxidize partly or totally, forming one or several of numerous hydrated sulfates of Fe$^{2+}$/Fe$^{3+}$ or Fe$^{3+}$, and these will ultimately hydrolyze, forming the mentioned ochreous Fe$^{3+}$ oxyhydroxides or oxyhydroxysulfates. The oxidation state of iron, i.e., to what extent – if at all – Fe$^{2+}$ has been oxidized, can be readily monitored by Mössbauer spectroscopy (Figure 1).

![Figure 1. Room-temperature Mössbauer spectra of melanterite (top) and schwertmannite (bottom) from acid drainage environments. The spectra show the characteristic features of these Fe$^{2+}$- and Fe$^{3+}$-bearing minerals in the paramagnetic state (center shifts vs. metallic Fe ~ 0.36 and 1.25 mm/s, and quadrupole splitting ~ 0.65 and 3.25 mm/s, respectively).](image1)

![Figure 2. X-ray diffraction diagrams of (top to bottom) ferrihydrite, goethite, schwertmannite and jarosite. Goethite and schwertmannite intensities are expanded twofold and ferrihydrite fourfold relative to jarosite. The ferrihydrite diagram indicates the presence of traces of goethite and schwertmannite, and the schwertmannite diagram indicates a minor admixture of jarosite.](image2)
close to or below 10 nm in size, so that physical parameters (e.g. X-ray diffraction peaks and Mössbauer lines) become “smeared out”. The identity of these minerals as individual species was consequently long not recognized (Chukhrov et al. 1973; Bigham et al. 1994), and they have often been labelled with misleading designations such as “amorphous iron oxide” or “ferric hydroxide”. Because of their small particle size and accordingly large surface area, these minerals can adsorb significant amounts of elements that are frequently released simultaneously with iron upon weathering of sulfides (see above comment on the liberation of elements other than iron and sulphur in the course of sulfide weathering).

Experimental work on synthetic systems has shown that schwertmannite gradually transforms to goethite (Bigham et al. 1996, Carlson and Schwertmann 2005). Studies of a natural system by Singh et al. (1999), suggesting that ferrihydrite formed in a mine drainage environment transforms – possibly under the influence of filamentous algae – to goethite, and by Gagliano et al. (2004), showing a gradual transformation of schwertmannite to goethite in a constructed wetland, confirm goethite to be more stable in the long run.

Oxalate extraction in the dark, which leads to a complete dissolution of schwertmannite and ferrihydrite (in contrast to goethite and jarosite), enables an estimate of the relative proportions of the former minerals to be made in samples of complex mineralogy. Jarosite and goethite precipitated in acid drainage environments are generally relatively well crystallized and can therefore be identified by X-ray diffraction, even when present in subordinate amounts (Figure 2; Table 1). The different magnetic ordering temperatures (Néel temperature or, for ferrihydrite, magnetic blocking temperature) can also help make a distinction between these minerals using Mössbauer spectra taken at appropriate (low) temperatures (cf. Murad and Cashion 2004).

Table 1. Properties of Fe³⁺ minerals formed by acid mine drainage

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Colour Munsell</th>
<th>XRD peaks</th>
<th>S</th>
<th>Tₙ/Tᵦ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>n¹</td>
<td>Feₒ/Fe₆</td>
<td>m²/g</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>5YR – 7.5 YR</td>
<td>6-2</td>
<td>1.0</td>
<td>200-600</td>
</tr>
<tr>
<td>Goethite</td>
<td>7.5YR – 10YR</td>
<td>~ 25</td>
<td>~ 0.3</td>
<td>100-200</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>10YR – 2.5Y</td>
<td>8</td>
<td>1.0</td>
<td>125-225</td>
</tr>
<tr>
<td>Jarosite</td>
<td>2.5Y – 5Y</td>
<td>~ 17</td>
<td>&lt; 0.1</td>
<td>«</td>
</tr>
</tbody>
</table>

¹ Number of peaks for d > 1.5 Å  
² 2θ CoKα  
³ superparamagnetic blocking temperature  
⁴ only AMD goethites  
« small (instrumental broadening of XRD peaks and surface areas of a few m²/g)

Bigham et al. (1992) and Schwertmann et al. (1995) established a biogeochemical model of the mentioned minerals as a function of the genetic environment: jarosite forms under the most acid conditions and at the highest sulfate concentrations (pH 1.5-3, [SO₄] > 3000 mg/l) followed by schwertmannite (pH 3-4, [SO₄] = 1000-3000 mg/l) and goethite (pH < 6, [SO₄] < 1000 mg/l). Ferrihydrite, which often forms under the participation of bacteria that live at near-neutral pH, was observed at less acid (pH > 5) conditions, generally in the presence of dissolved silica or organic matter. Nevertheless, the occurrence of ferrihydrite in more acid environments cannot be ruled out, since minor amounts of this mineral could – because of its extremely broad X-ray diffraction peaks – be overlooked in the presence of other, better crystalline, components. Unnoticed contributions of ferrihydrite could, in fact, offer a possible explanation for the unusually high oxalate solubility that is characteristic of goethites formed in acid mine drainage environments (Feₒ/Fe₆ ~ 0.3, cf. Table 1).

The striking yellow to reddish-brown colours of the ochreous mine drainage precipitates can evidence their presence, even from airborne imagery (Swayze et al. 2000; Williams et al. 2002). Because of their relation to mineralogy, the colours can also serve as indicators of the conditions under which the precipitates were formed (Murad and Rojík 2003).
Case studies: environmental implications of mine drainage precipitates in the Sokolov district, Czech Republic

In the Sokolov area of the western Czech Republic, mining of lignite for combustion is documented since 1793. Initially mined surface-near deposits were extremely rich in pyrite and marcasite, the dried coal locally containing over 5 wt. % sulfur. Firing of this material led to high atmospheric concentrations of sulfur dioxide and caused severe environmental problems. Presently mined lignite stems from the Antonín seam in the lower part of the Sokolov Basin and has a sulfur concentration of \( \leq 1 \% \) (Fraus 1999), which has led to a significant reduction of sulfur dioxide emission.

In the following section we describe selected mine drainage precipitate assemblages from this district and the genetic inferences that can be gathered from the precipitate mineralogy.

**Active ferrihydrite and ferrihydrite-goethite precipitation under near-neutral conditions**

The lower levels of the Družba open pit, in which the Antonín seam is mined, are traversed by a series of ditches that contain light brown (Munsell 7YR 6/5) to orange-coloured (Munsell 5YR 5/6) precipitates. The effluents are generally neutral with pH-values ranging between 6.3 and 7.7. X-ray diffraction showed the mineralogy of three sampled precipitates to be dominated by ferrihydrite; goethite (MCL\(_{110} \approx 12 \text{ nm}\)) was present in two of these precipitates, and one sample contained a lepidocrocite of very poor crystallinity. Kaolinite, that is a constituent of some of the precipitates, is of detrital origin.

The ca. 30-m thick Antonín seam is intensely penetrated by a network of vertical joints and horizontal bedding planes. The underlying ca. 120-m thick volcanic beds are strongly argillized and hydrogeologically insulating, whereas the overlying, ca. 160 m thick Cypris Formation, which consists of consolidated carbonaceous claystones, is penetrated by fissures in a manner similar to the Antonín coal seam. The joints, which are in part a result of desiccation and diagenesis, but mostly due to tectonic stress after deposition of the Tertiary sediments, form prevalently regular systems. This jointing allows waters to readily move between both units, and therefore to deposit precipitates characteristic of alkaline environments on the coal.

The Podkrušnohorská dump NW of the Lomnice pit is made up mainly of the mentioned claystones of the Cypris Formation. Water with a pH of 6.5 flowing out of a drill hole that taps this dump precipitates large quantities of an orange (Munsell 6YR 6/6) ochre into a ditch. Numerous mounds of reddish-brown (4YR 5/5) material have been deposited to both sides of the ditch.

X-ray diffraction showed the precipitate in the immediate vicinity of the water outlet to consist of 2-peak ferrihydrite and a poorly crystalline (MCL\(_{110} \approx 9 \text{ nm}\)) goethite. Material from the mounds was made up of the same minerals but had a higher ferrihydrite/goethite ratio, hence their redder colour (Table 1).

**Iron oxide coatings on lignite**

Lignites from upper levels of the Družba mine are partly coated by thin layers of a reddish-brown (4 YR 4/4) precipitate. Waters percolating through the lignite that probably deposited the coatings were moderately alkaline with a pH of 8.1. The hue is indicative of either lepidocrocite (\( \gamma \)-FeOOH) or ferrihydrite, whereas minor admixtures of lignite may have caused the rather low Munsell value by masking the true colour.

X-ray diffraction showed the coatings to be dominated by kaolinite, 6-peak ferrihydrite and lepidocrocite in proportions, which vary widely between samples (Figure 3). Both ferrihydrite and lepidocrocite typically form by rapid oxidation of Fe\(^{2+}\)-bearing solutions, but the presence of lepidocrocite, which is less common in mine drainage environments, and the absence of goethite indicate the crusts to have formed in an environment that is low in CO\(_2\) (Schwertmann 1985). Relatively narrow XRD peaks indicating a \( b \) particle dimension of about 60 nm are in line with the better crystallinity of lepidocrocite when formed in alkaline than in acid environments (Schwertmann and Fitzpatrick 1977).

Infrared spectra of the coatings measured in transmittance were relatively similar. The OH-stretching region was dominated by broad bands at \( \sim 3410 \text{ cm}^{-1} \) that can be attributed to ferrihydrite and lignite material and minor but well-defined narrow bands at 3696 and 3618 cm\(^{-1}\) ensuing from kaolinite.
Relatively prominent OH-bending vibrations at 1625 cm\(^{-1}\) also relate to ferrihydrite and lignite, whereas mainly lattice vibrations of kaolinite superimposed upon broad ferrihydrite bands are developed at lower frequencies (Figure 4).

The “contradictory” mineralogy of iron oxide coatings characteristic of alkaline environments on “acid” coal thus – in analogy to the precipitates in the lower levels of the Družba mine described above – is an outcome of the local hydrogeological conditions.

Influence of pH on precipitate mineralogy

The abandoned Lomnice pit is located in the marginal part of the lignite-bearing basin. At this locality the previously mined Antonín seam has a mean sulfur content of 5.6 %, leading to the formation of a variety of secondary mine drainage minerals. Precipitates in a ditch draining the lignite seam at the western pit wall show a striking change in colour following an influx of slightly alkaline (pH 8.3) water that raises the pH of the effluent from 3.7 to 7.3. Prior to the confluence the precipitate has a bright orange colour, whereas following the confluence the colour has changed to reddish-brown (in Figure 5 the ferrihydrite precipitate has a significantly darker colour than schwertmannite).

X-ray diffraction (Figure 6) showed the orange precipitate to consist of schwertmannite with a minor admixture of poorly-crystalline (MCL\(_{110} \approx 6\) nm) goethite, whereas the reddish-brown precipitate showed only a 2-peak ferrihydrite. Minor mounts of admixed kaolinite, illite and quartz are of detrital origin. Infrared spectra taken in transmittance confirm the X-ray data (Murad and Rojík 2003).

Chemical analyses carried out in the field showed the effluent to have a dissolved Fe\(^{2+}\) content of about 100 ppm. Rapid mixing of this effluent with the (iron-free) alkaline waters at the confluence leads to conditions that are essentially the same as those for ferrihydrite synthesis in the laboratory, resulting in an almost immediate precipitation of this mineral rather than goethite or another Fe\(^{3+}\) oxyhydroxide (Schwertmann and Cornell 2000). The precipitate mineralogy at this location thus is a sensitive indicator...
of the environment in which the precipitates were formed, and factors such as colour can serve as indicators of the depositional milieu.

Figure 5. View of ditch on the western wall of the Lomnice pit. The original schwertmannite-bearing effluent is visible at the top, the (marked) alkaline water inflow at the center and the ferrihydrite precipitate below the confluence at the bottom. See Murad and Rojík 2003 and Earth Science Picture of the Day for 21.11.2003 (http://www.epod.usra.edu).

Figure 6. X-ray diffraction patterns of the Lomnice precipitates showing schwertmannite with a minor goethite admixture (“Gt”) at the top and ferrihydrite at the bottom. Not to scale; contributions of detrital minerals have been removed by subtracting diffraction data of the residue after selective dissolution of the precipitate minerals.

Following a hot and extremely dry summer in 2003, the alkaline influx had run dry. The reduced supply of water also resulted in an increasing acidity of the effluent; thus in November 2003 the pH had fallen from 3.7 to 3.0 and the precipitate consisted throughout of pure schwertmannite (Figure 7). In July 2004 the pH had again risen slightly to 3.3, and X-ray diffraction data of several precipitates that had been sampled at different locations in the ditch once more showed, besides the eight peaks of schwertmannite, weak and broad goethite 110 peaks (MCL_{110} \approx 5 \text{ nm}). The observed temporal changes in genetic conditions thus are reflected in the precipitate mineralogy, formation of schwertmannite being increasingly favoured as the environment becomes more acidic.

Conclusions
The described examples of mine drainage precipitates from the Sokolov mining district and selected examples from the literature show that a precise knowledge of the mineralogy of the solid products of acid mine drainage is an indispensable prerequisite for the comprehension of the stabilities of these precipitates and their reactions, and consequently for an assessment of the environmental impact that they may have.

The mineralogy of mine drainage precipitates can disclose the conditions under which these were formed. Precipitate mineralogy may furthermore have a dominant effect on the environmental impact of the leftovers of mining. Examples include adsorption/desorption reactions on secondary mineral surfaces and the incorporation and release of a plethora of – often toxic – elements into and from the structures of the
weathering products of sulfides, all of which depend as much – if not more – on mineralogy as on extraneous conditions.

The small particle sizes and consequently large surface areas of many of the secondary mine drainage minerals (see Table 1) are supportive of adsorption/desorption processes, and countless publications have focussed on such reactions. As an example of the effects that such adsorption reactions may have on the quality of acid mine waters, Fukushi et al. (2003) showed dissolved As\(^{5+}\) liberated by weathering of realgar (AsS\(_2\)) in an abandoned arsenic mine to be selectively adsorbed on schwertmannite formed in the course of concurrent pyrite weathering, thereby removing the arsenic from the effluent. A further positive side-effect observed by the authors was the retardation of the transformation of schwertmannite to goethite as a result of arsenic adsorption. It should be noted that the cause of arsenic depletion would have been completely missed, had this study addressed only water and precipitate chemistry and the precipitate mineralogy been ignored.

Figure 7. X-ray diffraction diagrams of precipitates from the abandoned Lomnice mine sampled over a period of two years. All samples consist predominantly of schwertmannite. Samples collected during May 2002 and July 2004 display minor but distinct goethite 110 peaks (top and bottom), whereas goethite is absent in the sample taken during November 2003, when the effluent pH (3.0) was at a minimum.

A persuasive example of the influence that secondary minerals can exert on the chemistry of mine drainage effluents was given by Alpers et al. (1994) in a study of an exceedingly acidic mine drainage environment. Here the preferential incorporation of copper relative to zinc in melanterite appears to be the cause of cyclic variations of zinc/copper ratios in the effluents that can be related to the precipitation and dissolution of this mineral during dry and wet seasons, respectively. The eventual transformation of schwertmannite formed under more moderately acid environments (e.g. to goethite) will lead to the release of substantial quantities of sulfate, and thus also have a profound effect on effluent chemistry.
References


