AMD generation from dissolution of secondary metal sulphates

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Abstract Melanterite ($Fe^{2+}SO_4{\cdot}7H_2O$) is one of the most common oxidation products of pyrite. Field observations in mine sites indicate that melanterite is associated with acidic waters. However, simple dissolution of melanterite, without oxidation of Fe^{2+} to Fe^{3+}, can not generate AMD because the hydrolysis of Fe^{2+} is not able to significantly lower the water pH. Laboratory dissolution experiments modelled with PHREEQC have shown that trace amounts of Fe^{3+} contained in melanterite in the range of 0.16—0.20 wt.% are sufficient to significantly lower the pH of very dilute interacting waters as a consequence of Fe^{3+} hydrolysis. In the field, the rapid dissolution of Fe^{3+}-bearing melanterite by rain water may thus generate AMD and also provide a supply of Fe^{3+} for subsequent sulphide oxidation. These results should be taken into account when evaluating the impact of AMD on the environment and planning its treatment.

Key Words sulphides oxidation, secondary metal sulphates, melanterite, dissolution, AMD generation

Introduction

The environmental significance of secondary sulphate minerals deriving from oxidation of metal sulphides in abandoned and active mines is well known (Alpers *et al.* 1994, Bigham and Nordstrom 2000, Cravotta III 1994, Frau 2000, Hammarstrom *et al.* 2005, Jambor *et al.* 2000, Jerz and Rimstidt 2003). However, the main processes generating acid mine drainage (AMD) are generally considered to be the oxidation of metal sulphides, in particular pyrite, by oxygen or Fe^{3+} and the precipitation of metal hydroxides, in particular those of Fe^{3+} and Al, according to the following reactions taken as an example:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (3)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (4)$$

The role of secondary metal sulphates as potential producers of acidity is generally overlooked and undervalued, although they often represent the intermediate step between the contaminant-bearing primary minerals (i.e. metal sulphides) and the release of contaminants to the environment. Many metal-sulphate salts occur as efflorescences, are characterized by high solubility, are ephemeral and strongly affected by climatic conditions (i.e. temperature, relative humidity, rainfall). Therefore, these phases are able to transiently store metals in a solid form during dry periods and, successively, to become a (quasi)instantaneous, conspicuous source of contamination upon more or less fast and often complete dissolution during wet periods (Frau and Marescotti 2011, and references therein).

With regard to their possibility of storing acidity along with metals, Frau (2000) pointed out by means of laboratory experiments that the simple dissolution of melanterite ($Fe^{2+}SO_4{\cdot}7H_2O$) is an acidity-generating process affecting the chemistry of interacting water and, indirectly, contributing to the supply of Fe^{3+} required for the aqueous oxidation of pyrite and other sulphides under acidic conditions. The mechanism responsible for acid production suggested by Frau (2000) was Fe^{2+} hydrolysis. Jerz and Rimstidt (2003) showed that the dissolution of fibroferrite ($Fe^{3+}SO_4(OH){\cdot}5H_2O$) has the highest acid producing potential, followed by copiapite ($Fe^{2+}Fe^{3+}{}_4(SO_4)_6(OH)_2{\cdot}20H_2O$), halotrichite ($Fe^{2+}Al_2(SO_4)_4{\cdot}22H_2O$) and melanterite. These authors stressed the release of most acid upon dissolution of phases bearing trivalent cations (i.e. Fe^{3+} and Al^{3+}) as due to their extensive hydrolysis compared to divalent cations (i.e. Fe^{2+}). The difference between the acid producing potential was most marked in very dilute solutions, while in moderately concentrated solutions (about 10 g/L) the pH of leachate solutions converged to 3.0 or less for all aforesaid minerals. Hammarstrom *et al.* (2005) performed dissolution experiments on composite metal-sulphate salt samples and observed a rapid decrease in pH of leachate solutions from 6.9 to < 3.7. Hurowitz *et al.* (2009) conducted a combined experimental and modeling study to evaluate the mechanism of rapid production of acidity during dissolution of Fe^{2+}-sulphate minerals by dilute waters, and indicated the hydrolysis of Fe^{3+}, occurring as a trace contaminant in Fe^{2+}-sulphate, as the cause of acid production.

The aim of this paper is to review and model with PHREEQC (Parkhurst and Appelo 1999) the experiments of melanterite dissolution previously conducted by Frau (2000) in order to identify the real mechanism responsible for water acidification. The results obtained will be useful when investigating the source of acidity in mine sites that is a fundamental information to prevent or minimize the impact of AMD on the environment and possibly plan its treatment.

Methods

Laboratory experiments on melanterite dissolution were carried out using both natural melanterite from the abandoned Genna Luas mine site (Sardinia, Italy) and commercial granular melanterite (Carlo Erba RPH code n. 344957, CAS n. 7782—63—0), Milli-Q® water (Millipore; 18 MΩ·cm), an Orion pH-meter (model 920A) interfaced to an IBM PC for continuous pH measurements, and an Orion Ross® combination pH electrode (code n. 8103) calibrated with commercial buffers at pH 7.0, 4.0 and 1.0. Dissolved ferrous iron and total iron were measured spectrophotometrically using the colorimetric 2,2'-Bipyridine method (Aquamerck® 8023 Iron test), while dissolved sulphate was determined by ionic chromatography (Dionex).

The catalogue of the manufacturer (Carlo Erba) of the commercial melanterite used in the experiments indicates that synthetic melanterite may contain up to 0.5 wt.% of Fe^{3+}. Since melanterite tends to oxidize when exposed to air, the amount of Fe^{3+} could increase with time. However, melanterite oxidation is not so fast, often prevailing dehydration to rozenite ($FeSO_4{\cdot}4H_2O$) and szomolnokite ($FeSO_4{\cdot}H_2O$) (Frau 2000). Moreover, the bottle of commercial melanterite was opened just the time sufficient to pick up the amount of salt needed for the experiments, the melanterite was visually inspected for possible color changes attributable to oxidation, and experiments were immediately conducted without leaving melanterite exposed to air. Another piece of information reported by the manufacturer is that the pH of a 5 % melanterite solution (50 g/L melanterite) ranges from 3.0 to 4.0.

Different amounts of melanterite (0.08, 0.4, 2, 5, 10, 20, 40, 80 g) were dissolved at room temperature (about 20 °C) within a glass beaker with 200 mL Milli-Q water continuously stirred at a low rate (3 on a scale from 0 to 10) with a Teflon coated magnetic bar. An automated determination of water pH (a measurement each minute) was carried out. The measured pH of the batch solutions before adding melanterite was in the range of 5.66—5.69. In the experiments with melanterite loadings of 2, 25, 100 and 200 g/L, a 15 mL aliquot of water was collected from the reactor beaker after three minutes from the start of the experiment for the determination of dissolved iron and sulphate.

The dissolution experiments were simulated with PHREEQC Interactive (ver. 2.15.0) with the included 'llnl.dat' thermodynamic database, which corresponds to the 'thermo.com.V8.R6.230' database prepared at the Lawrence Livermore National Laboratory (California, USA) and contains the 'B-dot' aqueous model parameters for calculating activity coefficients in solutions with ionic strength up to 1 molal. According to the experimental observations by Frau (2000) and Hurowitz *et al.* (2009), which ruled out oxidation of Fe^{2+} to Fe^{3+} during the time span of the complete dissolution of melanterite, the kinetic mode was not used and dissolved oxygen was set at zero to prevent Fe^{2+} oxidation in the simulation. Pure water at 20 °C in equilibrium with atmospheric CO_2 (log fugacity = -3.5) was considered as initial batch solution, resulting in an initial pH of 5.64 for all simulations that matches very well with measured pH values. Dissolution of melanterite was not simulated as a function of time but as if all the melanterite dissolved instantly. As schwertmannite is the mineral most likely to precipitate under the experimental conditions, the following equilibrium reaction for schwertmannite from Majzlan *et al.* (2004) was included in the database:

$$\mathrm{FeO(OH)_{0.75}(SO_4)_{0.125} + 2.75H^+ = Fe^{3+} + 0.125SO_4^{2-} + 1.75H_2O} \qquad \log K = 1.2 \quad (5).$$

Simulations were performed for (i) pure melanterite, (ii) melanterite containing 0.5 wt.% Fe^{3+} (the maximum amount indicated by the manufacturer of the commercial melanterite used in the experiments), (iii) melanterite containing the amount of Fe^{3+} needed to reach the observed pH, and (iv) melanterite containing the amount of Fe^{3+} needed to reach the observed pH with schwertmannite precipitation allowed. The generic phase $Fe_2(SO_4)_3$ was chosen as the Fe^{3+}-bearing contaminant of melanterite.

Results

Figure 1a shows that the decrease in water pH occurs as soon as melanterite is put into the reaction beaker, and is greater as the melanterite loading increases. A dissolution experiment with natural melanterite from Genna Luas (40 g as a single block in 200 mL Milli-Q water) provided results very close to those obtained with the same amount of commercial melanterite as 1 mm grains. Figure 1b shows the variation of water pH during and after melanterite dissolution: the pH drops sharply and instantly with melanterite loading, then decreases slightly until complete dissolution of melanterite; a slight increase in pH can be sometimes observed when Fe^{2+} oxidizes to Fe^{3+} consuming H^+, then turbidity appears and flocculation of a Fe^{3+} colloidal phase occurs causing a further drop in pH; the appearance of an ochreous precipitate is followed by a flat pH.

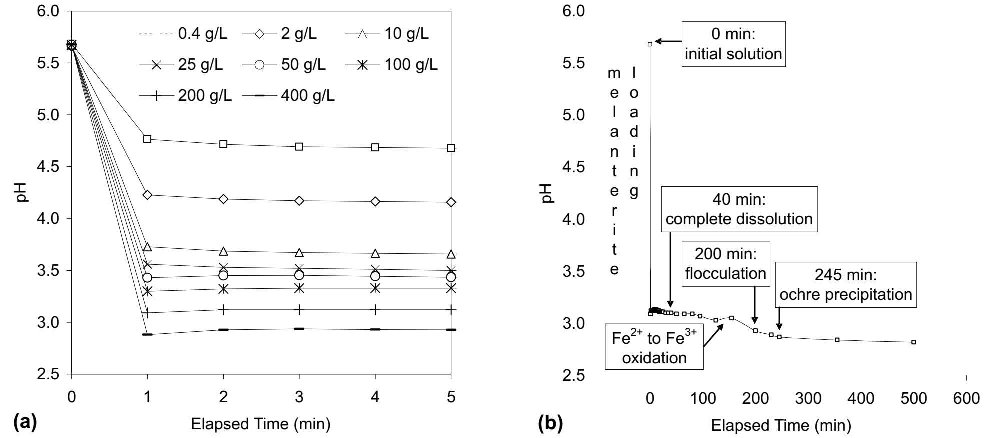

Figure 1 *(a) Decrease in water pH in the first five minutes upon dissolution of different amounts of melanterite; (b) Variation of water pH upon dissolution of 200 g/L melanterite.*

The plot of Figure 2a shows that the dissolution time increases with melanterite loading according to a power function. The rate law for melanterite dissolution can be written as follows: $r = kC^n$ (Fig. 2b), where r ($gL^{-1}s^{-1}$) is the dissolution rate, $k = 0.0043\ s^{-1}$ is the rate constant, C (gL^{-1}) is the concentration of melanterite dissolved, and n = 0.707 is the order of reaction. The plot 'pH vs. melanterite loading' of Figure 2c shows that, according to the following equation: $pH = 4.355C^{-0.066}$, the decrease in pH is very steep at low melanterite concentrations, then declines almost asymptotically for high melanterite concentrations when is limited by the solubility of melanterite.

The plots 'pH vs. elapsed time' of Figure 3 show the results of PHREEQC simulations for different amounts of dissolved melanterite (0.4, 2, 10 and 25 g/L). According with Hurowitz *et al.* (2009), dissolution of pure melanterite results in an insignificant decrease in pH (from 5.64 to 5.43 as maximum decrease). On the other hand, dissolution of melanterite containing 0.5 wt.% Fe^{3+} always generates a decrease in pH greater than that experimentally observed. The amount of Fe^{3+} needed to reach the observed pH varies between 0.16 and 0.20 wt.%. Except for simulations with pure melanterite, batch solutions resulted to be oversaturated with respect to schwertmannite (saturation index from 2.6 to 2.9) and, thus, when precipitation of schwertmannite is allowed, a further decrease in pH is obtained (2.75 moles H^+ generated for 1 mole schwertmannite precipitated). However, batch solutions remained clear during the time span for complete melanterite dissolution so that precipitation of schwertmannite or other Fe^{3+}-bearing phases can be discounted.

Discussion

Melanterite ($Fe^{2+}SO_4{\cdot}7H_2O$) is one of the most common oxidation products of pyrite and its presence has been recently hypothesized in the evap-

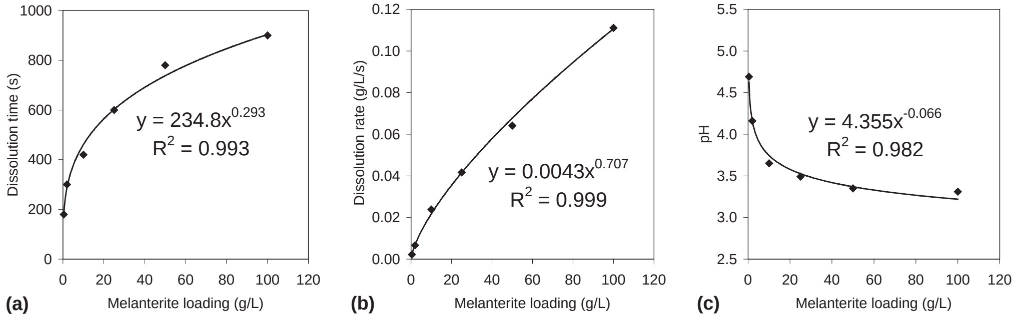

Figure 2 *(a) Time for complete melanterite dissolution as a function of loading; (b) Dissolution rate as a function of loading; (c) Correlation between water pH at complete melanterite dissolution and loading.*

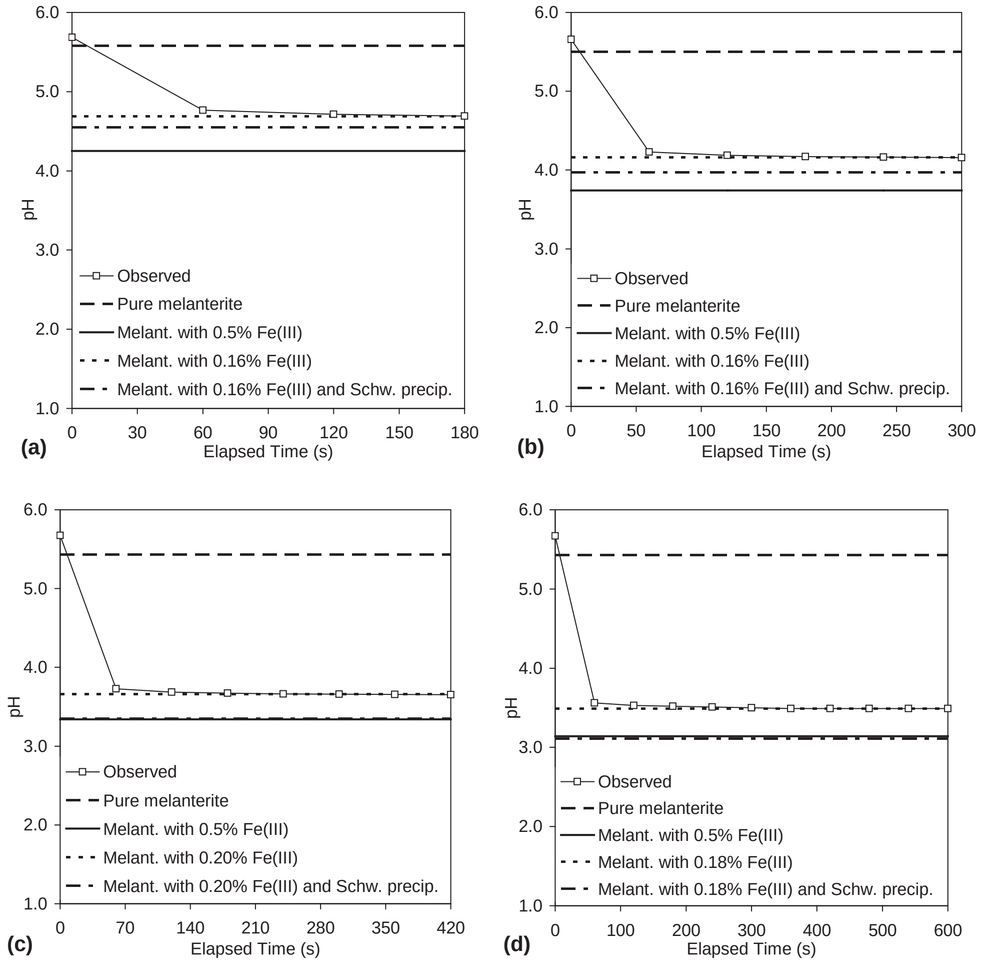

Figure 3 *pH variation as a function of time for experimental data and PHREEQC simulations of melanterite dissolution. Different melanterite loadings were used: (a) 0.4 g/L; (b) 2 g/L; (c) 10 g/L; (d) 25 g/L. Each plot reports (i) the experimental observation, (ii) the simulation with pure melanterite, (iii) the simulation with melanterite containing the maximum* Fe^{3+} *concentration (0.5 wt.% as indicated by the manufacturer of the commercial melanterite used), (iv) the simulation with melanterite containing the amount of* Fe^{3+} *needed to fit the observed pH, and (v) the latter simulation with schwertmannite precipitation allowed. The elapsed time is different in each plot and corresponds to the time for complete melanterite dissolution.*

orites on the surface of Mars (Tosca *et al.* 2005). Alteration of pyrite to melanterite, according to the following reaction:

$$FeS_2 + 3.5O_2 + 8H_2O \rightarrow FeSO_4 \cdot 7H_2O + H_2SO_4 \quad (6),$$

indicates that the formation of melanterite is associated with very acidic conditions, while its simple dissolution, according to the following equilibrium reaction:

$$FeSO_4 \cdot 7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O \qquad \log K = -2.35 \ (7),$$

apparently does not affect the water pH. Also considering the hydrolysis of Fe^{2+}:

$$Fe^{2+} + H_2O = FeOH^+ + H^+ \quad \log K = -9.50 \qquad (8),$$

the equilibrium constant is too low to significantly lower the water pH. Moreover, the aqueous speciation of ferrous iron calculated with PHREEQC for dissolution of pure melanterite always indicates Fe^{2+} and $FeSO_4°$ as the dominant species, while $FeOH^+$ is lower of 4—5 orders of magnitude. On the contrary, the aqueous speciation of ferric iron for dissolution of melanterite containing the amount of $Fe_2(SO_4)_3$ needed to fit the observed pH indicates $FeOH^{2+}$ and $Fe(OH)_2{}^+$ as the dominant species, according to the following hydrolysis reactions:

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \quad \log K = -2.19 \qquad (9)$$

$$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+ \quad \log K = -5.67 \quad (10).$$

Summarizing, even trace amounts of Fe^{3+} are capable to acidify dilute interacting waters, such as rain water, and the rapidity of acidification is a function of mineral solubility. In the case of Fe^{3+}-bearing melanterite, its very high solubility leads to an instantaneous decrease in pH as soon as melanterite comes into contact with water and Fe^{3+} is dissolved along with melanterite. This finding is also confirmed by the analysis of dissolved iron and sulphate in the batch solutions after 3 minutes from the start of the dissolution experiments. As an example, for a melanterite loading of 25 g/L, about 67% of melanterite (i.e. 17 g/L) was already dissolved after 3 minutes and another 7 minutes were needed for the complete dissolution. The observed change in pH from 5.67 to 3.52 ($\Delta pH = 2.15$) after 3 minutes is in very good agreement with the calculated change in pH from 5.64 to 3.56 ($\Delta pH = 2.08$) obtained by simulating with PHREEQC the dissolution of 17 g/L melanterite containing 0.18 wt.% Fe^{3+}. Therefore, although a role of melanterite surface as H^+ donor or OH^- acceptor can not be completely ruled out, the high solubility of melanterite suggests that the rapid decrease in pH can be simply explained by dissolution of melanterite containing trace amounts of Fe^{3+}.

Conclusions

Oxidation of metal sulphides, in particular pyrite, by oxygen or Fe^{3+} is considered the main process generating AMD. However, secondary minerals from sulphide oxidation can significantly contribute to AMD generation. Secondary metal sulphates are common phases in sulphide ore mines and their formation-dissolution cycle is often influenced by climatic conditions. Melanterite, the heptahydrated ferrous sulphate, is one of the most diffuse oxidation products of pyrite. Moreover, its presence has been recently hypothesized in the evaporites on the surface of Mars. Field observations in mine sites show that melanterite is associated with acidic waters and laboratory experiments confirm this finding. However, simple dissolution of melanterite, without oxidation of Fe^{2+} to Fe^{3+}, can not generate AMD because the hydrolysis of Fe^{2+} is not able to significantly lower the water pH. Both commercial and natural melanterites always contain small amounts of Fe^{3+}, probably as a ferric sulphate of some sort. Modelling of laboratory batch experiments with PHREEQC has shown that Fe^{3+} concentrations in melanterite in the range of 0.16—0.20 wt.% are sufficient to significantly lower the pH of very dilute interacting waters as a consequence of Fe^{3+} hydrolysis. Since melanterite is very soluble, its rapid acid-generating dissolution can occur without invoking oxidation of Fe^{2+} to Fe^{3+} that is slow under acidic conditions, as well as without involving the acidity-generating precipitation of a Fe^{3+} phase. In the field, the fast dissolution of Fe^{3+}-bearing melanterite by rain water may thus generate acidity and also provide an important supply of dissolved Fe^{3+} for subsequent oxidation of pyrite and other sulphides. This finding should be considered when investigating the source of AMD in mine sites in order to prevent its impact on the environment and plan its treatment.

Acknowledgements

The authors thank the anonymous reviewer for his/her comments to this paper.

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