ACID PRODUCTION FROM THE LEACHING OF PYRITE AND CHALCOPYRITE[1]

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Abstract. Pyrite and chalcopyrite samples were subjected to wet and dry cycles to mimic natural weathering. Eh and pH were measured directly after drainage. The pH (<2.5) of the effluent from the pyrite was consistent with predicted solution speciation. The oxidation rate of solution sulfide containing species is dependent on the solution Fe concentration. We propose that the pyrite effluent was at equilibrium at the time of Eh measurement whereas the chalcopyrite effluent was not. In the latter case the low solution concentration of Fe, due to precipitation results in the slow oxidation of the solution S species. Hence the pH of the chalcopyrite effluent (>5) is considerably higher than predicted on the basis of the measured Eh and solution S assay.

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Introduction

Complete dissolution and hydrolysis of pyrite (FeS_2) can be expressed as:

$$FeS_2 + 2.5H_2O + (7.5/2)O_2 \rightarrow FeOOH_{(ppt)} + 2\ SO_4^{-2} + 4H^+ \qquad \textbf{(1)}$$

with the production of two H^+ per SO_4^{-2-} dissolved. The complete oxidation of chalcopyrite ($CuFeS_2$) also results in two moles of H^+ for each mole of SO_4^{-2} produced:

$$CuFeS_{2(s)} + 3.5H_2O + (8.5/2)O_2 \rightarrow FeOOH_{(ppt)} + Cu(OH)_{2(ppt)} + 2\ SO_4^{-2} + 4H^+ \qquad \textbf{(2)}$$

According to Equations (1) and (2) it may be expected that the acid leach behavior of FeS_2 and $CuFeS_2$ are similar. The total acid produced can be affected by the final Eh, pH, solution concentrations and the nature of any leach residues or secondary mineralization. We have sought to establish, through the application of wet and dry cycles, to mimic the conditions experienced in the field, whether Equations (1) and (2) adequately describe the leach behavior of these minerals.

Methodology

FeS_2 (Huanzala, Peru, 44.7 wt.% Fe, 51.3 wt.% S, 1.4 wt.% Si, 0.27 wt.% Pb with Cu and Zn at lower concentrations, equivalent to 96 wt.% FeS_2), $CuFeS_2$ (Kennecott Operations, Rio Tinto, USA, 32.0 wt. % S, 29.3 wt. % Cu, 27.6 wt. % Fe, 2.6 wt. % Si, 0.6 wt. % Mo, 0.6 wt.% Mg, 0.5 wt.% Al, 0.4 wt.% Ca, 0.3 wt.% Pb, 0.3 wt. % Zn, 0.3 wt.% As, 0.1 wt.% Ti, equivalent to 86 wt.% chalcopyrite) and high-purity quartz were ground separately, as required, using a tungsten mill and wet-sieved to obtain a 38 – 90 μm size fraction. The surface area of the $CuFeS_2$ and FeS_2 (determined using BET Kr gas adsorption) were 0.4 m^2g^{-1} and 0.5 m^2g^{-1} respectively. The materials were used in an as is state with no washing or autoclaving.

The experiments were carried out in cylinders 2.5 cm in diameter and 1 cm high. These experiments contained 0.125 M of S corresponding to 7.5 g of FeS_2 (Py, Table 1) and 11.5 g of $CuFeS_2$ (Cp, Table 1). Py and Cp were watered with 2 ml per week in weeks one to three and 10 ml in the fourth week. Flushing with pure water (pH 6) is not indicative of a field situation but does enable reproducibility. To aid the drying cycle, the experiments were grouped so that all were exposed to the heat from a 100 W lamp, which was turned off at watering and left off for three days and then turned on for the remainder of the week. The temperature of the experiments thus varied between 40 and 25°C. The columns were free draining in all instances and the leachate was sampled on drainage (approximately 20 minutes after watering) every fourth week.

Speciation modeling was carried out using the computer program PHREEQC (Parkhurst and Appelo, 1999). It was assumed that all solution S was present as SO_4^{-2}. The solution concentrations used are given in Table 1. No precipitation was allowed during the course of the modeling, both Eh and pH were held constant and the simulations were carried out for 25°C.

Table 1. Average solution conditions are initial period of high S release to solution. The standard deviations are given in ( ). The minimum detectable concentration of Fe is 0.009 mM. The very high concentration standard deviations for Cp is indicative of the low solution concentrations.

	Py	**Cp**
Time period (weeks)	12 - 58	8 – 58
Eh (mV)	700 (30)	610 (60)
pH	2.9 (0.2)	5.5 (0.5)
Cu (mM L^{-1})	NA	0.02 (0.01)
Fe (mM L^{-1})	1.4 (0.2)	below detection limit
S (mM L^{-1})	3.1 (0.4)	0.5 (0.2)
Total Fe(II) calculated (mM)	0.6	0.009 (using the detection limit)
Total Fe(III) calculated (mM)	0.8	0.000

Results

The solution concentrations for Py (Table 1) indicate near stoichiometric dissolution. For Cp there is considerably less Cu and Fe present in solution than anticipated on the basis of the S solution concentration and stoichiometric dissolution, indicating precipitation of both Cu and Fe-containing species. In total (based on the solution S assays) 35 % of the Py was leached whereas only 6 % of the Cp.

Figure 1 shows the pH of the effluent over the duration of the experiments. The pH of Cp remained at five or above for the duration of the experiment. The pH calculated on the basis of measured solution S concentrations, assuming all S is present as SO_4^{-2} and assuming Equations 1 and 2 are representative of the overall processes occurring, is also shown in Fig. 1. For both columns the predicted pH values are less than the measured pH values. The discrepancy between calculated pH and observed pH is much greater for Cp than for Py.

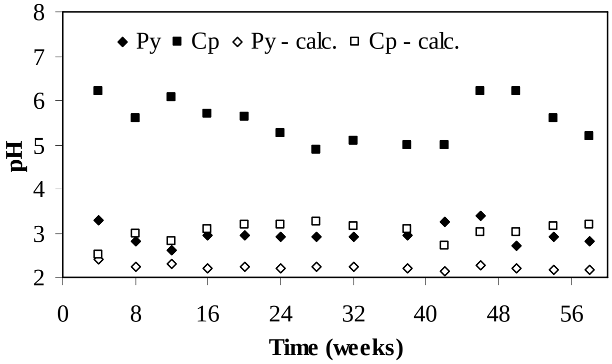

Figure 1. Measured and calculated pH (from Equations (1) and (2), both as function of leach time.

Using the solution conditions given in Table 1 for Py, Fe^{+2} and $FeSO_4^+$ were calculated to be the dominant Fe-containing species (both 0.5 mM) followed by $FeOH^{2+}$ (0.2 mM) and $FeSO_4$ (0.1 mM). The reaction to form Fe^{+2} results in the production of one H^+ per SO_4^{-2} (Equation (3)) in solution whereas the reaction to form $FeSO_4^+$ results in the production of only half an H^+ per SO_4^{-2} in solution (Equation (4)).

$$FeS_2 + H_2O + (7/2)O_2 \rightarrow Fe^{+2} + 2\ SO_4^{-2} + 2H^+ \tag{3}$$

$$FeS_2 + (1/2)H_2O + (7.5/2)O_2 \rightarrow FeSO_4^+ + SO_4^{-2} + H^+ \tag{4}$$

The pH observed (taking into account only Fe^{+2} and $FeSO_4^+$) would therefore be expected to be in the region of 2.9 on the basis that only 0.375 of the H^+ would be produced as compared to Equation (1). If complexation of H^+ with SO_4^{-2} is taken into account using the concentration of HSO_4^- (0.2 mM provided by PHREEQC) the pH would increase to 3.0. Both values are in excellent agreement with the average experimental value (Table 1). The speciation calculation for Py (and Cp) indicated that the solution was supersaturated with respect to both goethite and hematite.

The cation speciation calculated for Cp is almost entirely comprised of $Fe(OH)_2^+$ (0.008 mM) and Cu^{+2} (0.02 mM). This speciation would result in only one quarter as much H^+ produced per SO_4^{-2} dissolved (Equation (5)) as compared to Equation (2). However, (assuming both Cu and Fe are present in solution at 0.02 mM) 92 % of the cations are not accounted for in the solution assays, *i.e.* precipitation may be occurring via Equation (1). Taking these two possible reaction mechanisms into account, pro-rata, has little effect, with a calculated pH of 3.0.

$$CuFeS_{2(s)} + (3/2)H_2O + (8.5/2)O_2 \rightarrow Fe(OH)_2^+ + Cu^{+2} + 2\ SO_4^{-2} + H^+ \tag{5}$$

X-ray photoelectron spectroscopic analysis of the leach residue from Cp confirms that the non-stoichiometry in solution must be, at least in part, due to precipitation with 98 % of the surface Fe present as Fe(III)-O-OH. This is in contrast to Py where only 17 % of the surface Fe was present as Fe(III)-O-OH (Fig. 2(a)). Additionally for Cp, 73 % of the surface Cu is present as Cu(II)-OH. The very low concentrations of metal cations in solution and the high surface concentration of metal hydroxyl species preclude the possibility that the discrepancy in acid concentration between the calculated and observed data for Cp is substantially due to incomplete metal hydrolysis.

S 2p X-ray photoelectron spectra indicate a considerable fraction of polysulfide and elemental sulfur on the leach residue from both Py and Cp (Fig. 2(b), 16 % of all S for Py and 17 % for Cp). The oxidation process to form elemental sulfur (S^0) (Equation (6)) and polysulfides (S_n^{-2}) is acid consuming. However, if stoichiometric release of cations occurs on leaching of $CuFeS_2$ and these are then fully hydroxylated, on formation of surface S^0, a net neutral reaction results (Equation (7)). Therefore the occurrence of these S surface polymerization reactions cannot adequately explain the relatively high pH observed, as compared to that calculated on the basis of solution S concentration and Equation (2).

$$S^{-2}_{(s)} + 2H^+ + (1/2)O_2 \rightarrow S^0 + H_2O \tag{6}$$

$$CuFeS_{2(s)} + 1.5H_2O + (2.5/2)O_2 \rightarrow FeOOH_{(ppt)} + Cu(OH)_{2(ppt)} + 2S^0 \tag{7}$$

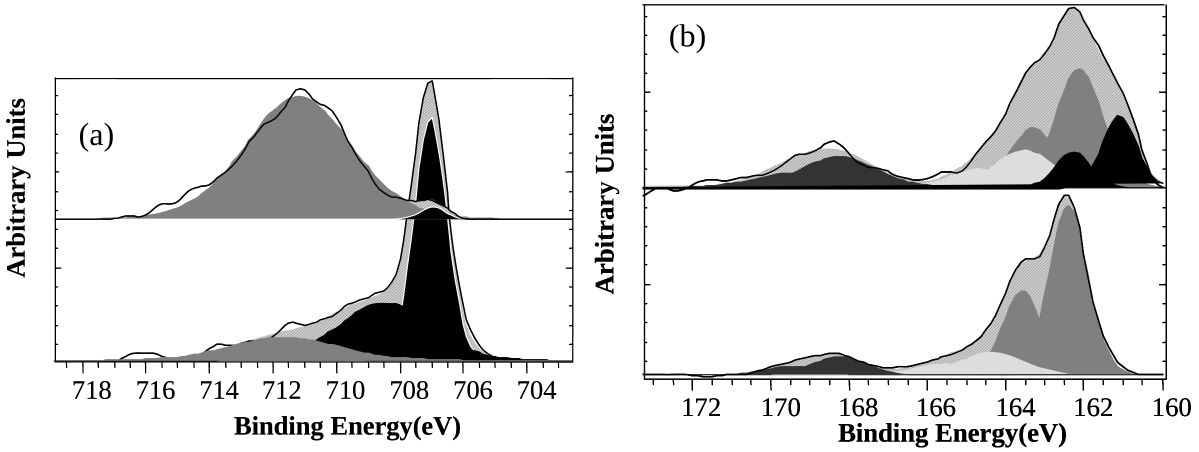

Figure 2. **(a)** Fe 2p XPS spectra for the residues from Py (bottom) and Cp (top). The black component represents Fe(II) and the grey Fe(III). The diagonal black lines indicate the sum of all the contributions and the solid black line indicates the experimental data. **(b)** S 2p XPS spectra for the residues from Py (bottom) and Cp (top). The black doublet represents S^{-2} (S $2p_{3/2}$ at approximately 161 eV), the medium grey doublet S_2^{-2} (at approximately 162.4 eV), the light grey doublet S_n^{-2} and S^0 combined (at approximately 164.8 eV) and the medium grey doublet SO_4^{-2} (at approximately 168.3 eV). The diagonal black lines indicate the sum of all the contributions and the solid black line depicts the experimental data.

Non-equilibrium of all redox couples in solution has been demonstrated to be the rule rather than the exception for temperatures below 100 °C (Nordstrum and Alpers, 1999). It has been proposed (Rimstidt et al., 1994) that S^0 species may be formed via precipitation and oxidation of aqueous S containing species, for instance HS^-. If this is the case then it is possible that H_2S (and HS^-) may form the majority of the initial S species in solution on leaching.

On examination of the possible rate of oxidation of $H_2S_{(aq)}$ using the rate expression developed by Zhang and Millero (1994) and the ratio of Fe^{+2} to Fe^{+3} (Table 1) as predicted by PHREEQC we find that at the relatively high Fe concentrations observed for Py conversion of $H_2S_{(aq)}$ to SO_4^{-2} is mostly complete (97 %) after 5 minutes. Where considerably less Fe is present in solution, particularly where it is predominantly as Fe^{+3}, the oxidation rate of $H_2S_{(aq)}$ is much slower. For Cp only 8 % oxidation of $H_2S_{(aq)}$ to SO_4^{-2} would occur after 30 minutes assuming a solution Fe^{+3} concentration of 0.009 mM (*i.e.* the detection limit).

The formation of H_2S, $Fe(OH)_3$ and $Cu(OH)_2$ on dissolution of $CuFeS_2$ does not result in the production of H^+ (Equation 8).

$$CuFeS_{2(s)} + 4.5H_2O + 0.5O_2 \rightarrow FeOOH_{3(ppt)} + Cu(OH)_{2(ppt)} + 2H_2S \qquad \textbf{(8)}$$

The observed average pH for Cp is 5.5 whereas the pH calculated from Equation 2 is 3.0, a difference in H^+ concentration of 1.0 mM. This equates to the dissolution via Equation (2) of 0.5 mM S, *i.e.* very close to the average solution S assay. It would appear therefore that a very slow oxidation rate of H_2S to SO_4^{-2} may be a plausible explanation for the high observed solution pH for Cp.

Conclusion

Equation 1 appears to be a good overall descriptor of the pyrite dissolution process for the conditions examined. The dissolution is nearly stoichiometric and the acid produced by the dissolution process as measured and calculated (based on solution S concentrations and solution speciation modeling) are in good agreement.

Equation 2, however, is not a good descriptor for the chalcopyrite dissolution process. The resulting pH is considerably higher than predicted (based again on solution S concentrations and solution speciation modeling). Far more S is present in solution than expected as compared to Fe and Cu, based on stoichiometric dissolution than Fe or Cu. Surface analysis revealed the presence of a high surface concentration of oxidized cations (Fe(III)-OH and Cu(II)-OH) suggesting widespread precipitation, as suggested by Equation (2). The formation of polysulfide is an acid consuming reaction. However, the concentration of polysulfide on the surfaces of Cp and Py are similar and cannot be used to explain the high solution pH in the case of Cp.

We conclude therefore that the solution speciation of the effluent from the pyrite leach solutions was near to equilibrium and that the chalcopyrite solutions were not. The rate of oxidation of $H_2S_{(aq)}$ to SO_4^{-2} is dependent on the Fe concentration in solution and increases as the component of Fe(II) increases. Calculations using the oxidation rate laws developed by Zhang and Millero (1994) demonstrate that at the low pH conditions of Py dissolution the oxidation rate of $H_2S_{(aq)}$ and is almost complete after 5 minutes. For the high pH, low Fe concentration conditions of Cp dissolution the oxidation rate is extremely slow. As the dissolution of $CuFeS_2$ to give FeOOH, $Cu(OH)_2$ and H_2S does not result in acid production this may account for the high observed pH (as compared to the calculated pH values).

It appears that the pH measured is a balance between the rate of dissolution of the $CuFeS_2$ and the rate of precipitation of the Fe species. If the rate of the leaching is relatively high then the solution Fe concentration would increase as would the rate of $H_2S_{(aq)}$ oxidation. The decrease in solution pH would therefore be rapid. Where the rate of leaching is comparable or slower than the rate of precipitation of the Fe species the rate of oxidation of $H_2S_{(aq)}$ will remain low and the solution pH high for longer.

Although the experiments and conclusions drawn here are for single mineral systems flushed with clean water the results are relevant to site investigations. It appears from these measurements that on initial solution sampling the pH of the sample may not be indicative of the acidity inherent within the sample and that the pH may continue to decrease during equilibration. It is therefore important, that on assessing site acid mine drainage, that the pH of the solution is registered over a period of time to enable the correct assessment of the behavior of the drainage waters.

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