Pyrite dissolution in acidic media

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ABSTRACT: Oxydation of pyrite (initially free from oxidation products) by atmospheric oxygen (20%) in acidic media was studied at 25°C using short-term batch experiments. Fe^{2+} and SO_4^{2-} were the only dissolved Fe and S species detected in these solutions. After a short period, $R = [S]_{tot}/[Fe]_{tot}$ stabilized from 1.25 at pH = 1.5 to 1.6 at pH = 3. These R values were found to be consistent with previously published measurements. This corresponds to a non stoichiometric dissolution (R < 2) resulting from a deficit in aqueous sulphur. A reactional mechanism is proposed assuming that thiosulfate ($S_2O_3^{2-}$) is the first sulfoxyanion released in solution. It disproportionates into $S^0_{(s)}$ and $S_4O_6^{2-}$ which in term is oxidized into sulfate according to the overall reaction

$$FeS_2 + 2.9\ O_2 + 0.6\ H_2O \rightarrow Fe^{2+} + 0.4\ S^0_{(s)} + 1.6\ SO_4^{2-} + 1.2\ H^+.$$
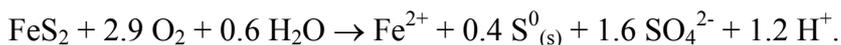
1 INTRODUCTION

The overall reaction of pyrite (FeS_2) oxydation by oxygen is usually expressed by reaction (1):

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$
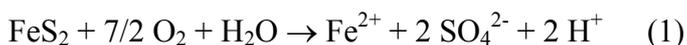
Recent literature focuses on acidic dissolution observed by spectroscopic techniques. Sasaki *et al.* (1995) observed a sulphur rich layer on FeS_2 surface oxidized in acidic medium (pH = 2) during 72 hours. These authors concluded to a non-stoichiometric oxidation of FeS_2 with a preferential dissolution of iron, as also commonly accepted in literature. Nevertheless, Luther (1997) argued against this interpretation, based on his mechanism proposed earlier from electronic orbital considerations (Luther, 1987) and sulphur aqueous chemistry. Luther (1997) proposed that the sulphur rich layer on FeS_2 surface is not a direct oxidation product, but should stem from the disproportion of thiosulphate ($S_2O_3^{2-}$), the actual oxidation product of FeS_2, into elementary sulphur (S_8 or S^0) and hydrogenosulphite (HSO_3^-) according to:

$$8\ S_2O_3^{2-} + 8\ H^+ \rightarrow S_8 + 8\ HSO_3^- \qquad (2)$$
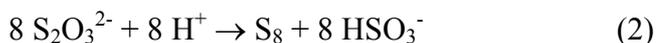
The sulphur superficial enrichment of the oxidized FeS_2 surface analysed by Sasaki *et al.* (1995) would therefore result not from non-stoichiometric dissolution with iron preferential dissolution, but from precipitation of elementary sulphur (see also Rimstidt and Vaughan, 2003). To resolve this issue, both surface and aqueous chemistry of iron and sulphur have to be taken into account to thoroughly interpret any experimental data on FeS_2 oxidation.

Ichikuni (1960) focused on the ratio $R = [S]_{tot}/[Fe]_{tot}$ to interpret his experimental data for the dissolution of FeS_2 in aqueous solutions at pH ranging from 1.1 to 3.2. A value of R = 2 corresponds to a stochiometric dissolution. Although parameter R can be used to directly compare dissolution experiments in different chemical and physical conditions, there is no other occurrence of this experimental parameter, to our knowledge. We decided to use similar treatment of experimental data, *i.e.* using the $R = [S]_{tot}/[Fe]_{tot}$ aqueous ratio measured in batch dissolution experiments at pH $\cong$ 2 in addition to solid characterization methods. FeS_2 surfaces free of any oxidation products were dissolved in acidic media to avoid iron hydrolysis and precipitation, and sulphur and iron aqueous speciations were monitored. With these controlled chemical conditions, we were able to verify experimentally the hypothesis of Luther (1987 and 1997).

2 MATERIALS AND METHODS

Dissolution experiments carried out in acidic media ($HClO_4$ and HCl), sample preparation and analysis are documented elsewhere (see Descostes *et al.* 2001a, b; Descostes *et al.* 2002; Descostes, 2001 and Motellier and Descostes, 2001).

3 RESULTS AND INTERPRETATION

Trends of $[SO_4^{2-}]$ and $[Fe]_{tot}$ in function of time are different from a run to another for a same medium, indicating different dissolution rates. Dissolved iron is mainly divalent (up to 95 % of $[Fe]_{tot}$). Dissolved sulphur is exclusively under SO_4^{2-} form. No dissolved sulphoxyanion was detected. Furthermore, oxidation of samples by H_2O_2 did not show any difference between $[S]_{tot}$ and $[SO_4^{2-}]$. The great disparity in time in rates of $[SO_4^{2-}]$ and $[Fe]_{tot}$ increase can be traced to the presence of chemical impurities in FeS_2 (Cruz *et al.*, 2001). Therefore, release rates are not convenient parameters to lay the foundations for a reactional mechanism of FeS_2 dissolution.

Table 1. Ratios $R = [SO_4^{2-}]/[Fe]_{tot}$ calculated in this study and from data taken from Ichikuni (1960) [1], McKibben and Barnes (1986) [2] and Bonnissel-Gissinger *et al.* (1998) [3].

Run	Media	R	Reference
M02	$HClO_4$ 10^{-2} mol L^{-1}	1.38 ± 0.08	
M04	$HClO_4$ 10^{-2} mol L^{-1}	1.34 ± 0.07	
M07	$HClO_4$ 10^{-2} mol L^{-1}	1.51 ± 0.06	
M13	HCl 10^{-2} mol L^{-1}	1.8 ± 0.1	
M19	$HClO_4$ 10^{-3} mol L^{-1}	1.7 ± 0.2	
M21	HCl $10^{-1.5}$ mol L^{-1}	1.25 ± 0.06	
M22	$HClO_4$ 10^{-2} mol L^{-1}	1.31 ± 0.05	
	HCl 10^{-1} mol L^{-1} (pH=1.1)	0.74 ± 0.02	[1]
	$HCl + H_2O_2$ (pH=1.89)	1.3 ± 0.1	[2]
	HCl 10^{-2} mol L^{-1} (pH=2)	1.38 ± 0.05	[1]
	HNO_3 (pH=2.5)	1.6 ± 0.2	[3]
	HCl 10^{-3} mol L^{-1} (pH=2.9)	1.92 ± 0.07	[1]
	H_2O (pH=3.2)	2.8 ± 0.1	[1]

Whatever the variations of $[Fe]_{tot}$ and $[SO_4^{2-}]$, R ratios ($= [SO_4^{2-}]/[Fe]_{tot}$, as $[S]_{tot} = [SO_4^{2-}]$) eventually converge toward a value of $R = 1.6$, and down to 1.25 for run M21. Furthermore, the dispersion in R values is smaller than in $[Fe]_{tot}$ and $[SO_4^{2-}]$. R seems therefore a more convenient experimental parameter. Such R values are also observed for long duration experiments (see for example run M22, 1500 min).

4 DISCUSSION

4.1 Comparison with bibliography

To achieve consistency and unearth a plausible mechanism of FeS_2 dissolution in acidic media, it is desirable to discuss our results with those of previously published studies. However, most FeS_2 oxidation studies do not provide values of dissolved concentrations of iron and sulphur, not to mention R ratios. Only Ichikuni (1960), McKibben and Barnes (1986) and Bonnissel-Gissinger *et al.* (1998) studies could be used to estimate R values. Data gathered in table 1 are extrapolated from kinetic curves published by these authors. When R ratios obtained in this study are compared to those from literature, three pH fields can be distinguished (figure 2). First, $R < 2$ in very acidic to moderately acidic media (pH ≤ 2). Results from our study are in good agreement with those from McKibben and Barnes (1986), Ichikuni (1960) and Bonnissel-Gissinger *et al.* (1998). Second, at pH = 3, R = 2 (maybe fortuitously) which is in agreement with the solid stoichiometry ratio of FeS_2. Third, at pH > 3, R > 2, traducing iron precipitation by hydrolysis.
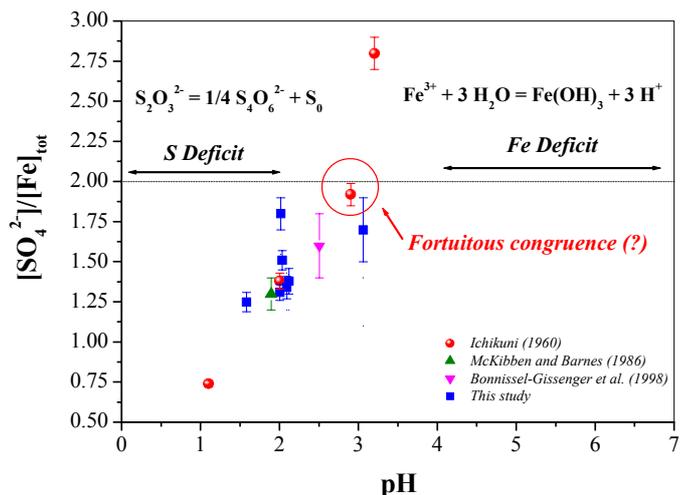
Figure 1: Comparison of ratios $R = [SO_4^{2-}]/[Fe]_{tot}$ calculated in this study and from data taken from literature.

4.2 Reaction mechanism at pH < 3

Non stoichiometric dissolution with $R < 2$ can result either from an excess release of iron, leaving a sulphur-enriched layer at the FeS_2 surface, or from FeS_2 congruent dissolution followed by removal of dissolved sulphur species. The comparison of the different sets of experiments show that $[Fe]_{tot}$ are comparable for similar reaction periods, while $[SO_4^{2-}]$ can reach very low values in run M21 ($[HCl] = 10^{-1.5}$ mol L^{-1}). In this last case, R = 1.25 is the lowest value recorded for all experiments, likely indicating deficit in aqueous sulphur. Therefore, FeS_2 dissolution in acidic media is not congruent. The only possible explanation for the observed non-stoichiometry in FeS_2 dissolution is that sulphur is

removed from the solution, either as a solid, or as a gas. In both case, this removal indicates that sulphur species other than S_2^{2-} and SO_4^{2-}, the stable sulphur species, are present in the solution. This species could be one of the products of an intermediary disproportionation step, while the other(s) product(s) of the disproportionation would be soluble and further oxidized to S(VI). Metastable sulphur species must form upon FeS_2 oxidation, and consequently the oxidation of FeS_2 into Fe^{2+} and SO_4^{2-} cannot be described by a single elementary step.

According to a thermodynamic approach, we have privileged the hypothesis of a disproportion of a sulphur specie in acidic medium with an oxidation number lying between S^0 and SO_4^{2-}. First, FeS_2 dissolves, with release of an aqueous sulphur species $S^{(n)}$ which should then disproportionate into another sulphur specie $S^{(n')}$ with an oxidation number n' ($0 < n < n' \le 6$), and metastable S^0 (which would not be oxidized for thermodynamic or kinetic reasons). Finally, $S^{(n')}$ specie would be oxidized into SO_4^{2-}. The overall FeS_2 oxidation reaction can be written as

$$FeS_2 + \frac{6n+n'}{2n'}O_2 + \frac{2n-n'}{n'}H_2O \rightarrow Fe^{2+} + \frac{2n}{n'}SO_4^{2-} + \frac{2(n'-n)}{n'}S^0 + 2\left(\frac{2n-n'}{n'}\right)H^+$$ (3)
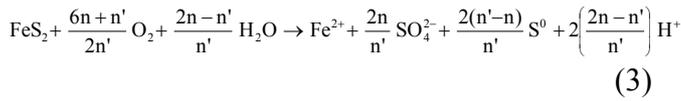
and R = $[SO_4^{2-}]/[Fe]_{tot}$ can be easily expressed as

$$R = \frac{2n}{n'}$$ (4)

Several ($S^{(n)}$, $S^{(n')}$) couples can theoretically generate R $\le$ 2. Among them, the ($S_2O_3^{2-}$; $S_4O_6^{2-}$) couple is plausible for several reasons. $S_2O_3^{2-}$ has already been detected in such dissolution experiments in carbonated media (Descostes *et al.*, 2002). $S_2O_3^{2-}$ has a mean number of oxidation equal to 2 and is thought to be the first aqueous sulphur specie released from FeS_2 surface (see Luther, 1987; Descostes *et al.*, 2001; Rimstidt and Vaughan, 2003). Its oxidation into $S_4O_6^{2-}$ is possible in only one elementary reaction since the number of transferred electrons is inferior to 2 (Basolo and Pearson, 1958). $S_2O_3^{2-}$ and $S_4O_6^{2-}$ are expected to be metastable before the formation of SO_4^{2-} in our experimental conditions (figure 2). The observed variation of R in function of pH can be explained by the stability domains of FeS_2, $S_2O_3^{2-}$, S^0 and $S_4O_6^{2-}$. Thiosulphate ion is unstable in acidic medium from pH = 3. It disproportionates into S^0 and $S_4O_6^{2-}$. $S_4O_6^{2-}$ would then be rapidly oxidized into SO_4^{2-}. As pH decreases, the proportion of S^0 increases. $[SO_4^{2-}]/[Fe]_{tot}$ ratio then decreases. However, as we will discuss below, this trend can also be assigned to exsolution of SO_2.

The proposed FeS_2 oxidation in acidic medium can be summarized by the following reactional sequence. Corresponding ΔG_R (see Descostes (2001) for thermodynamic data) are also given.

$$FeS_2 + 3/2O_{2(g)} \rightarrow Fe^{2+} + S_2O_3^{2-}$$ (5)
ΔG_R = -445.9 kJ mol^{-1}

$$S_2O_3^{2-} + 6/5H^+ \rightarrow 2/5S^0 + 2/5S_4O_6^{2-} + 3/5H_2O$$ (6)
ΔG_R = -36.0 kJ mol^{-1}

$$S_4O_6^{2-} + 7/2O_{2(g)} + 3H_2O \rightarrow 4SO_4^{2-} + 6H^+$$ (7)
ΔG_R = -1224.0 kJ.mol^{-1}
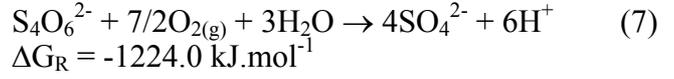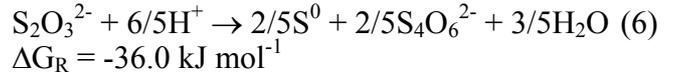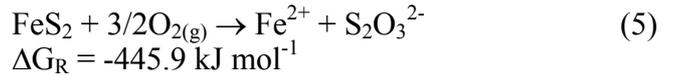
Reaction (7) can tentatively be divided in to two other intermediary steps with the production of sulphite (SO_3^{2-}) in order to respect the rule of the limited electron number transferred and its observation in alkaline media (Descostes *et al.*, 2002) according to:

$$S_4O_6^{2-} + 3/2O_{2(g)} + 3H_2O \rightarrow 4SO_3^{2-} + 6H^+$$ (8)
ΔG_R = -193.5 kJ mol^{-1}
and
$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$$ (9)
ΔG_R = -257.6 kJ mol^{-1}
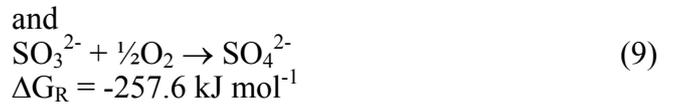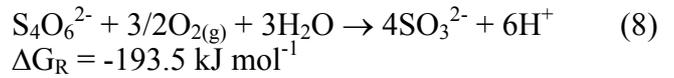
Hence, the overall reaction (*i.e.* reaction 3 when R = 1.6) is
$$FeS_2 + 2.9O_{2(g)} + 0.6H_2O \rightarrow Fe^{2+} + 0.4S^0 + 1.6SO_4^{2-} + 1.2H^+.$$ (10)
ΔG_R = -971,5 kJ mol^{-1}
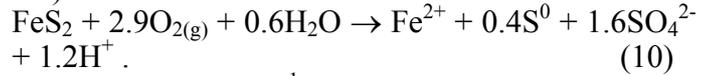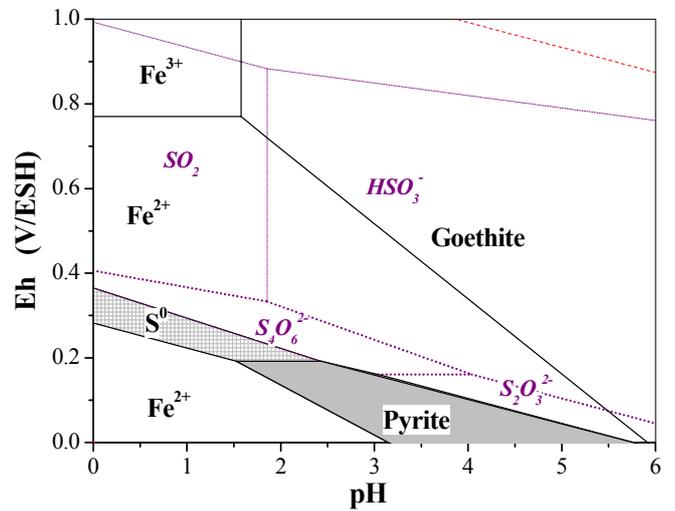
Figure 2. Eh-pH diagram for S - Fe – H_2O system at 25°C, considering only sulphur species with an oxidation number inferior to sulphate ($[\Sigma S] = 2 \times [\Sigma Fe] = 2.10^{-5}$ mol L^{-1}).

S^0 precipitation, as a consequence of $S_2O_3^{2-}$ disproportion is enough to explain the sulphur deficit observed in solution (figure 2). However the expected R = 1.6 is greater than experimental R values under more acidic conditions. Therefore reaction (3) might not be complete or another step of disproportion should be considered from, *e.g.* sulphite (SO_3^{2-}). In the first case, a ratio equal to

1.20 is expected. We assign ratios inferior to 1.6 to SO_3^{2-}. Moreover, SO_3^{2-} in acidic conditions is stable under SO_2 form (figure 2). If $S_2O_3^{2-}$ is considered as the first aqueous specie, then SO_2 formation in acidic conditions leads to the following net reaction:

$$FeS_2 + 2.1O_2 + 2H^+ \rightarrow Fe^{2+} + 0.4S^0 + 1.6SO_{2(g)} + H_2O, \tag{11}$$
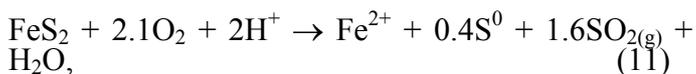
and the R ratio calculated is then equal to 1.00. Hence, it is not out of the question that a partial exsolution of SO_2 occurs in that case, which would tend to increase the aqueous sulphur deficit and leading to ratios between 1.6 and 1.00, depending on pH.

In conclusion, assuming disproportion of $S_2O_3^{2-}$ into S^0 and $S_4O_6^{2-}$ is consistent with thermodynamic considerations (figure 2) and mechanisms proposed by Luther (1997), Kelsall *et al.* (1999) and Rimstidt and Vaughan (2003). There is no need to assume Fe preferential dissolution in acidic media.

5 CONCLUSION

Mechanisms of FeS_2 oxidation in acidic medium were investigated by batch experiments at 25.0°C in contact with atmosphere at pH 2 and 3, and by reevaluation of previously published data. A particular effort was made to obtain a pristine FeS_2 surface without any oxidation products by preparation under anoxic atmosphere. Using the parameter $R = [S]_{tot}/[Fe]_{tot}$ was central to understanding the evolution of the dissolution stoichiometry as a function of pH. R values below the S/Fe stoichiometric ratio in FeS_2 (*i.e.*, S/Fe = 2) can be traced to an aqueous deficit in S according to multi-step mechanisms.

The first step sees the production of a $S_2O_3^{2-}$. This specie would disproportionate into $S_4O_6^{2-}$ and another S specie that would disappear from solution, probably as a solid compound (typically S^0). $S_4O_6^{2-}$ would finally be oxidized into SO_4^{2-}. Experimental $R = [SO_4^{2-}]/[Fe]_{tot} = 1.6$ can then be smartly predicted and is equal to the double of the ratio of the numbers of oxidation of each intermediate sulphoxyanion considered. In more acidic conditions, SO_2 formation followed by an exsolution is consistent with lower experimental values for R (R = 1.25). These mechanisms, according to a simple thermodynamic approach, are in good agreement with most experimental published data. $S_2O_3^{2-}$ disproportion alone can explain the observed aqueous sulphur deficit. It is therefore not needed to assume iron preferential dissolution in acidic media. Further experiments are needed to detect and characterize the sulphur precipitate.

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