

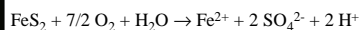
# Pyrite dissolution in acidic media

DESCOSTES M.<sup>1\*</sup>, VITORGE P.<sup>2</sup> and BEUCAIRE C.<sup>1,3</sup>

<sup>1</sup>: CEA DPC SECR Laboratoire de Mesure et Modélisation de la Migration des Radionucléides (L3MR) CEA Saclay, F-91191 Gif-sur-Yvette Cedex  
<sup>2</sup>: CEA DPC SECR Laboratoire de Spéciation des Radionucléides et des Molécules, Gif sur Yvette, France  
<sup>3</sup>: Actual address: IRSN/DEI SARG Laboratoire d'Etude des Transferts dans les Sols et Sous-sols (LETSS), Fontenay aux Roses, France.  
 \*michael.descostes@cea.fr

## 1. Introduction

Pyrite (FeS<sub>2</sub>) oxidation by oxygen leads to the release of two moles of H<sup>+</sup> per mole of oxidized pyrite:



FeS<sub>2</sub> oxidative dissolution has been studied using most techniques available (electrochemistry, solution chemistry, spectroscopic and other techniques) but despite all these efforts, **no consensus has yet emerged on a single and well-established oxidation mechanism.**

Recent literature focuses on acidic dissolution and observed by spectroscopic techniques a sulphur-rich layer on a pyrite surface. A **non-stoichiometric oxidation of pyrite, with preferential dissolution of iron** is then proposed.

To resolve this issue, **both pyrite surface chemistry and aqueous chemistry of iron and sulphur** have to be taken into account to thoroughly interpret any experimental data on pyrite oxidation. We propose to focus on the **ratio R = [S]<sub>tot</sub>/[Fe]<sub>tot</sub>** measured in batch dissolution experiments at pH ≈ 2, in addition to solid characterization methods. A value of R = 2 corresponds to a stoichiometric dissolution.

## 2. Method: Batch experiments

### Sample characterisation and preparation

Pyrite samples (Logroño) were prepared under anoxic and anhydrous glove-box (both P<sub>O2</sub> and P<sub>H2O</sub> < 1 ppm). Control by XPS and others techniques<sup>1</sup> showed no oxidation products at the pyrite surface.

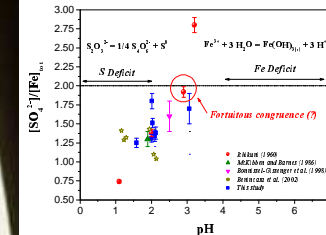
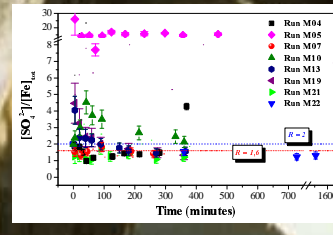
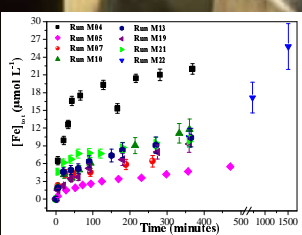
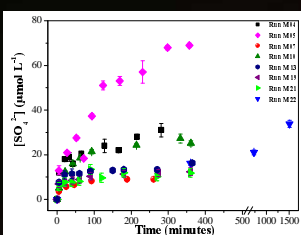
### Dissolution experiments

Batch experiments were run in glass electrochemistry cells, thermostated at 25.0 ± 0.1°C in contact with air. The water to solid ratio was 150 mL g<sup>-1</sup>. Experiments were carried out in HCl and HClO<sub>4</sub> media at pH values around 2 and 3. Aliquots were immediately analysed for sulphur and iron. The final solid samples were analysed by XPS.

### Analysis in solutions

Sulphur aqueous speciation and analysis were performed by both IC and CE<sup>2</sup>. [Fe]<sub>tot</sub> were determined by FAAS. Oxidation state of iron was investigated by spectrophotometry. Electrochemical parameters (pH and Eh) were also followed.

## 3. Results



Sulphur only under SO<sub>4</sub><sup>2-</sup> form

Fe majority divalent (95%)

After a short period, the ratio R = [S]<sub>tot</sub>/[Fe]<sub>tot</sub> stabilized from 1.25 to 1.6 at pH = 1.5 to 3

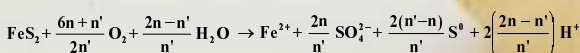
R values consistent with previously published measurements

Same initial conditions lead to different rate dissolution (presence of chemical impurities<sup>4</sup> in FeS<sub>2</sub>)

## 4. Reaction mechanism at pH < 3

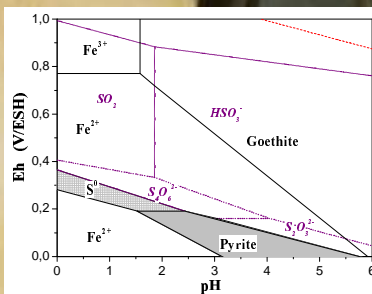
The comparison of the different sets of experiments show that [Fe]<sub>tot</sub> is comparable for similar reaction periods, while [SO<sub>4</sub><sup>2-</sup>] can reach very low values in run M21 ([HCl]=10<sup>-1.5</sup> mol L<sup>-1</sup>). In this last case, R = 1.25 is the lowest value recorded for all experiments, likely **indicating a deficit in aqueous sulfur.**

We propose disproportionation of a sulfur intermediary species in acidic medium: First, FeS<sub>2</sub> dissolves, with release of an aqueous sulfur species S<sup>(n)</sup>, which should then disproportionate into another sulfur species S<sup>(n')</sup> with an oxidation number n' (0 < n' < n ≤ 6), and S<sup>0</sup>, which would not be further oxidized for thermodynamic or kinetic reasons. Finally, S<sup>(n')</sup> species would be oxidized into SO<sub>4</sub><sup>2-</sup>. The overall FeS<sub>2</sub> oxidation reaction can be written as:



and R = [SO<sub>4</sub><sup>2-</sup>]/[Fe]<sub>tot</sub> can be easily expressed as

$$R = \frac{2n}{n'}$$

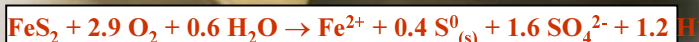


Eh-pH diagram for S-Fe-H<sub>2</sub>O system at 25°C, considering only sulfur species less oxidized than sulfate ions ([S<sup>0</sup>] = 2 × 10<sup>-3</sup> mol/L<sup>3</sup>).

Several (S<sup>(n)</sup>, S<sup>(n')</sup>) couples can theoretically generate R ≤ 2. Among them, the (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>; S<sub>4</sub>O<sub>6</sub><sup>2-</sup>) couple is plausible for several reasons.

The observed variation of R as a function of pH can be explained by the stability domains of FeS<sub>2</sub>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sup>0</sup> and S<sub>4</sub>O<sub>6</sub><sup>2-</sup>. S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is unstable in acidic medium from pH = 3. It disproportionates into S<sup>0</sup> and S<sub>4</sub>O<sub>6</sub><sup>2-</sup>. S<sub>4</sub>O<sub>6</sub><sup>2-</sup> would then be rapidly oxidized into SO<sub>4</sub><sup>2-</sup>. As pH decreases, the proportion of S<sup>0</sup> increases. The R ratio then decreases.

A reaction mechanism is proposed assuming that thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) is the first sulfoxyanion released in solution. It disproportionates into S<sup>(0)</sup> and S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, which in turn is oxidized into the sulfate anion according to the overall reaction



$$R = 2n/n' = 4/2.5 = 1.6$$

In summary, disproportionation of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> into S<sup>0</sup> and S<sub>4</sub>O<sub>6</sub><sup>2-</sup> is consistent with thermodynamic considerations and mechanisms proposed elsewhere<sup>5</sup>.

**Thus, there is no need to assume preferential Fe dissolution in acidic media.**

- References:
- Mottelier S. and Descostes M. (2001) *Journal of Chromatography A* 907, 329-335.
  - Descostes M. (2001) Ph.D. Thesis, Université Denis Diderot Paris VII.
  - Descostes M., Mercier F., Beaucaire C., Zaddas P. and Trocellier P. (2001) *Nuclear Inst. and Methods in Phys. Research B* 181, 603-609.
  - Descostes M., Vitorge P. and Beaucaire C. (2004) Accepted in *Geochimica et Cosmochimica Acta*.
  - Rimstidt J.D. and Vaughan D.J. (2003) *Geochimica et Cosmochimica Acta* 67, 873-880.