Abstract: Arsenopyrite oxidative dissolution is a process that supplies arsenic in waters. The effects that environmental factors (e.g., variation of pH, concentration of iron and sulfate, and surface reactivity) exert on the arsenopyrite (AsFeS) decomposition rate are studied by means of flow-through experiments. Preliminary results suggest that the arsenopyrite decomposition rate is not affected by pH in very acidic conditions. Arsenic in the output solutions is present as As(III) and As(V) and the respective amount depends on the O₂ availability during the arsenopyrite oxidation.

Keywords: arsenic, arsenopyrite, water contamination, dissolution kinetics

Introduction
Arsenic contamination in waters can be associated with sulphide mine activity. The disposal of sulphide mine tailings generates water pollution caused by oxidation of metal-sulphur phases making up the tailings (FeAsS, FeS₂, CuFeS₂, PbS, ZnS, etc), producing acid mine drainage (AMD). Sulphide oxidation occurs as sulphides interact with oxygen (atmospheric or dissolved in water). Presence of aqueous As is a severe environmental problem mainly due to As(III) toxicity. Oxidative dissolution of arsenopyrite is a process responsible of arsenic release to waters. There exist several factors that affect the oxidation process of arsenopyrite: oxygen availability, preproducing of iron and bacteria, ionic strength, pH. In this communication, preliminary results of the arsenopyrite decomposition are presented.

Oxygen availability
Arsenopyrite decomposition can be expressed with the following reactions

\[ \text{FeAsS} + 3.5\text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{AsO}_4^- \]

\[ \text{FeAsS} + 7\text{H}_2\text{O} = \text{Fe}^{2+} + \text{H}_3\text{AsO}_3 + 11\text{H}^+ + 11\text{e}^- + \text{SO}_4^{2-} \]

showing that arsenopyrite decomposition can occur in the presence or absence of oxygen (eqs. (1) and (2), respectively). Therefore, the oxygen availability plays an important role in the arsenopyrite solubility.
Walker and Schreiber (2003) are currently studying the arsenopyrite oxidation as a function of dissolved oxygen concentrations (e.g., log Rate vs. $P_{O_2}$). The rate of arsenopyrite decomposition may depend on the oxygen content as it is observed for other sulphides’ disintegration (Acero et al., 2004, Domènech et al., 2002; Lengke and Tempel, 2001, 2002).

Under anoxic conditions (reducing media) release of As is observed. Salzauler et al. (2004) observe that an increase of reducing conditions in depth in a residue pile, whose primary sulphide composition is 45-50 % arsenopyrite, 10-15 % pyrrothite and 5 % pyrite, increases the Ar concentration in solution. Lazareva et al. (2004) observe that As concentration increases in pond waters ($6.6 < \text{pH} < 9$) and pore solutions during storage of tailing impoundment. Gómez et al (2004) determine the As concentration (0.024 to 2.8 mgL$^{-1}$) in groundwaters (Eh ~ -250 mV and pH from 6.8 to 8) of a U mine where arsenopyrite is distributed in fracture fillings and in the granite.

**Bacteria and iron content**

Presence of *Thiobacillus ferrooxidans* increases the rate of arsenopyrite oxidation in mine tailing piles catalyzing the iron oxidation

$$2Fe^{2+} + 0.5O_2 + 2H^+ = 2Fe^{3+} + H_2O$$

Then, the presence of iron(III) in solution favours the arsenopyrite oxidation

$$FeAsS + 13Fe^{3+} + 8H_2O = 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_2AsO_4^{-}(aq)$$

where some of the Fe(III) can react with the dissolved arsenate to precipitate scorodite (FeAsO$_4 \times 2H_2O$). Rimstidt et al. (1994) determined that at pH 2, the rate of reduction of Fe(III) to Fe(II) (mmol m$^{-2}$ s$^{-1}$) according to eq. (4) is expressed as

$$R_{Fe^{3+}} = k[Fe^{3+}]^{0.98}$$

**Arsenate/Arsenite**

Redox condition in the contaminated waters controls the aqueous arsenic speciation (As(III) or As(V)), which is a major concern since arsenic toxicity increases with the presence of aqueous As(III).

Recently, Yunmei et al. (2004) determined that during arsenopyrite dissolution at pH 2 and anoxic conditions (Eh ~ 525 mV) the arsenic released to solution is present dominantly as aqueous As(III). Only small amounts of As(V) were released due to previous arsenopyrite surface oxidation.
Aim of the paper
The main purpose of our study is the obtainment of an arsenopyrite oxidative dissolution rate law, which is necessary to estimate As release in pore waters and groundwaters of an aquifer, soil, mine tailing, etc. Knowing such a rate law allows predicting arsenic mobility and arsenic pollution extent in areas that are distinctly affected by presence of arsenopyrite.

Different environmental variables, e.g., pH, concentration of sulphate and iron, oxygen dissolved, and surface reactivity, are varied in the experiments carried out at the laboratory scale. Two types of experiments are used: (1) flow-through experiments, which allow obtainment of the bulk arsenopyrite dissolution and (2) in-situ Atomic Force Microscope (AFM) experiments, by which a nanoscale identification of sulphide surface mechanisms involved in the oxidation reaction can be made.

Materials and methods
The arsenopyrite sample is from Cerdanya County (Pyrenees range). Sample is ground to a fraction ranging from 10 to 100 μm. SEM images of the sample powder show the prismatic habit of the particles (Fig. 1). Based on electron microprobe analysis (EMP) the arsenopyrite (FeAsS) atomic composition is Fe 33.5 ± 0.1 %, As 32.1 ± 0.3 % and S 34.4 ± 0.3 %. Total iron, arsenic and sulphur are measured by means of ICP-AES. Analysis of arsenic speciation is carried out by means of LC-HG-AFS.

![Figure 1. SEM image of the arsenopyrite grains that show a prismatic habit. Attached microparticles on cleavage surfaces are observed.](image)

Results and discussion
Currently, we are studying the arsenopyrite oxidative dissolution rate using flow-through experiments under acidic pH (1 to 3), varying the concentrations of SO₄²⁻, Fe and oxygen
dissolved (from 4.5 to 20 %) at room temperature (24 ± 2 °C). The details of the experimental set-up and flow-through description are reported in Acero and Cama (2004).

In the flow-through experiments, once the steady state is attained, the dissolution rate, $R$, (mol m$^{-2}$ s$^{-1}$) is calculated based on the release of metal (As and Fe) and S according to the expression (Nagy et al., 1991)

$$ v_j R = \frac{q}{A} (C_{j,\text{out}} - C_{j,\text{inp}}) $$

where $C_{j,\text{inp}}$ and $C_{j,\text{out}}$ are the concentrations of component $j$ (metal or S) in the input and the output solutions, respectively (mol m$^{-3}$), $v_j$ is the stoichiometry coefficient of $j$ in the dissolution reaction, $t$ is time (s), $A$ is the reactive surface area (m$^2$) and $q$ is the fluid volume flux through the system (m$^3$ s$^{-1}$). Figure 2 shows the variation of total arsenic and total iron with time in a flow-through experiment carried out at pH 1. At the onset of the experiment a high release of As and Fe is observed. Afterwards, the concentration diminishes to reach steady state. Based on As and Fe release, normalized to final mass, the dissolution rate is $4.2 \pm 0.6 \times 10^{-11}$ mol g$^{-1}$ s$^{-1}$.

![Figure 2](image)

Figure 2. Variation of total As (a) and total Fe (b) with time in a flow-through experiment at pH 1 ($H_2SO_4$) and 20 % O$_2$ at room temperature. Empty symbols denote steady state.
The stoichiometric ratio between Fe and As is defined as the ratio between total Fe output concentration and the total arsenic output concentration ([Fe]_{out}/[As]_{out}). Variation of this stoichiometric ratio with time is depicted in Fig. 3. It is observed that during the first 100 h the Fe release is favoured since the Fe/As ratio is higher than the molar ratio of the arsenopyrite sample used (1.04 ± 0.01). Afterwards, the Fe/As ratio decreases to reach a value of 1.1±0.07, which is in very good agreement with the molar ratio. This suggests that in the start of the experiment the dissolution may be controlled by fast dissolution of highly reactive microparticles. As these ultra fine particles dissolve, the arsenopyrite dissolution is stoichiometric.

![Figure 3. Variation of the Fe/As ratio with time in a flow-through experiment at pH 1 (H_2SO_4) and 20 %O_2 at room temperature. The empty symbols denote steady state.](image)

Speciation analysis of total arsenic output concentrations shows the existence of As(III) and As(V) in solution. The amount of As(III) increases by decreasing atmospheric O_2 during arsenopyrite oxidative dissolution. Figure 4 depicts the arsenic speciation variability that is observed in the chromatograms with the peaks of As(III) and As(V) of two output samples.

![Figure 4. The chromatograms show distinct amount of As(III) and As(V): in (a) the oxygen concentration was 4.5 % and 20 % in (b).](image)
In summary, the preliminary results suggest that:

1. Arsenopyrite oxidative dissolution rate is pH independent at very acidic conditions.
2. Arsenopyrite dissolves stoichiometrically since the Fe/As ratio is similar to the molar ratio.
3. The amount of As(III) and As(V) in solution may depend on the O$_2$ content during the oxidation reaction.
4. Further experiments (flow-through and in-situ AFM) are warranted to decipher the role of distinct environmental factors involved in the arsenopyrite oxidative dissolution kinetics.

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References


