Mechanism of pyrite catalysis of As(III) oxidation in bioleaching solutions at 30 °C and 70 °C

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Abstract

Arsenic, present as impurity in many sulfide ores, dissolves during the bioleaching process and the resulting high As(III) concentration can inhibit bacterial activity, compromising the whole process. Oxidation of As(III) to As(V) and its further precipitation as ferric arsenate is probably the most accurate way to face the problem. Thermodynamically, As(III) should be easily oxidized by Fe (III), but the reaction is very slow and only in the presence of pyrite, significant oxidation of As(III) to As(V) takes place. In the present study, the catalysis mechanism of arsenic oxidation on pyrite surface and the role of *Acidithiobacillus ferrooxidans* at 30 °C and *Sulfolobus metallicus* at 70 °C were analysed. Anaerobic experiments demonstrated that ferric ions participate as electron acceptors during the oxidation of As(III) to As(V) but that electron transfer only takes place at the pyrite surface. As(III) oxidation is only observed at high oxidoreduction potential (Eh>450 mV vs. Ag/AgCl). At lower potential, As(V) is reduced to As(III), oxidising the pyrite. The role of microorganisms is mainly to maintain a high potential. Ferric ions produced by bacterial oxidation are reduced at the pyrite surface, oxidising both pyrite and As(III). Only a small fraction of electrons transferred comes from As(III).

Keywords: Arsenic; Pyrite; Catalysis; Biooxydation

1. Introduction

Arsenic is a major impurity present in most sulfide ores. It is mainly present as arsenopyrite (FeAsS) in gold sulfide ores and concentrates and as enargite (Cu_3AsS_4) and tennantite ($(Cu, Fe)_{12}As_4S_{13}$) in copper ores and concentrates. It can also be present as realgar (AsS) and orpiment (As_2S_3) or included as minor element in other metal sulfides as pyrite.

During the leaching and bioleaching of copper ores and concentrates and the biooxidation of refractory gold concentrates, arsenic bearing sulfides are oxidized and the increasing dissolved arsenic concentration in the leaching solution can produce serious metallurgical and environmental problems. On the one hand, dissolved arsenic interferes with the leaching and all the downstream processes and could contaminate the final product, in particular in the case of copper metallurgy. In the bioleaching and biooxidation, the high toxicity of dissolved arsenic compounds can inhibit the microorganisms and completely stop the process [1]. On the other hand, the high mobility of dissolved arsenic compounds could derive in the release of arsenic into the environment and the pollution of surface and underground waters. An efficient process to remove and stabilize arsenic is then necessary.

Arsenic compounds have been used as poison during centuries. Arsine gas is the most toxic arsenic compound followed by As(III) compounds which are more than 10 times more toxic than As(V) compounds. Toxicity of

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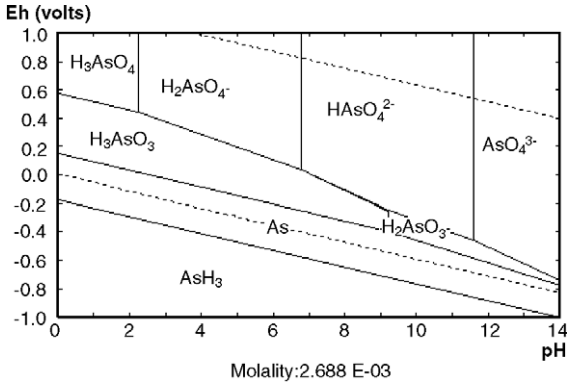

Fig. 1. Pourbaix diagram (Eh–pH) of arsenic species in aqueous solutions at 25 °C and 1 atm.

arsenic compounds in bioleaching processes is well known and well documented [2–4]. As(V) in the presence of ferric ions can precipitate as ferric arsenate, which in its crystallized form of scorodite ($FeAsO_4 \cdot 2H_2O$) is very stable and almost insoluble.

Then, the strategy to face the problem of dissolved arsenic in bioleaching and biooxidation solutions would be first the oxidation of As(III) to As(V) and then the precipitation of ferric arsenate, preferably as scorodite.

Speciation of dissolved arsenic can be represented in an Eh–pH diagram (Pourbaix diagram). Fig. 1 shows the predominant As(III) and As(V) dissolved ions as a function of Eh and pH. Thermodynamically, at low pH, As(III) present as H_3AsO_3 should be easily oxidized to As(V) as H_3AsO_4 by ferric ions:

$$H_3AsO_3 + Fe^{3+} + H_2O \rightarrow H_3AsO_4 + Fe^{2+} + 2H^+$$

But, as reported by several authors, in most cases, the kinetics of the reaction is very slow and almost no oxidation of As(III) is observed. However, in the presence of pyrite, significant oxidation of arsenic is observed. Oxidation takes place in the presence of ferric ions and microorganisms. The catalytic effect of pyrite has been reported by several authors [5,6], but the mechanisms involved have not yet been completely elucidated.

The aim of the present study was to analyse the catalysis mechanism of arsenic oxidation on pyrite surface and the role of *Acidithiobacillus ferrooxidans* at 30 °C and *Sulfolobus metallicus* at 70 °C.

2. Materials and methods

2.1. Microorganisms

Microorganisms used in this study were a strain of the mesophilic bacteria *A. ferrooxidans* (ATCC 19859) and a strain of the thermophilic archea *S. metallicus*, provided by Dr. Antonio Ballester, Universidad Complutense de Madrid. *A. ferrooxidans*, previously adapted to increasing concentration of arsenic (up to 0.5 g/L As^{3+}), was grown in shake flasks at 30 °C and 100 rpm in MC medium (0.4 g/L $(NH_4)_2SO_4$, 0.4 g/L $MgSO_4 \cdot 7H_2O$ and 0.056 g/L $K_2HPO_4 \cdot 3H_2O$) at pH 1.6 in the presence of 3.0 g/L of Fe^{2+} as energy source and 0.5 g/L As^{3+} to maintain bacterial adaptation. *S. metallicus*, also adapted to increasing concentration of arsenic (up to 0.5 g/L As^{3+}), was grown in shake flasks at 70 °C and 150 rpm in Norris medium (0.4 g/L $(NH_4)_2SO_4$, 0.5 g/L $MgSO_4 \cdot 7H_2O$ and 0.2 g/L KH_2PO_4) at pH 1.8 in the presence of 1% pyrite as energy source and 0.5 g/L As^{3+} to maintain bacterial adaptation. For use in the experiments, microorganisms were filtered on 0.22 μm membrane and resuspended in basal medium.

2.2. Pyrite

Museum pyrite sample was ground and separated in granulometric fractions. The granulometric fraction used in this study, between 75 and 104 μm (>#270, <#150), was analysed, showing the following composition: 41.85% Fe, 47.95% S and 0.0245% As.

2.3. Experimental methods

Anaerobic experiments were performed in 125 mL Erlenmeyer hermetically closed flasks filled with 50 mL medium and previously desoxigenated with nitrogen. Aerobic experiments were performed in.250 mL Erlenmeyer flasks with 100 mL medium. Ferric ion was added as ferric sulfate ($Fe_2(SO_4)_3 \cdot xH_2O$) and As(III) as As_2O_3. 5 mL samples were withdrawn periodically and analysed for pH, Eh, [Fe_{tot}], [Fe(III)], [As_{tot}], [As(III)] and microorganism concentration. In all experiment at 30 °C, MC medium at initial pH 1.6 was used. At 70 °C, the medium used was Norris medium at initial pH 1.8.

2.4. Analytical methods

Total dissolved arsenic concentration ([As_{tot}]) was determined by atomic absorption spectrometry. As(III) concentration was determined by differential pulse polarography [7]. As(V) concentration was determined by difference between [As_{tot}] and [As(III)]. Total and ferric iron concentrations were determined by spectrophotometry using the sulfosalicilic acid method [8]. Concentration of microorganisms was determined by microscopy counting using a Petroff Hausser chamber.

Solid precipitates samples were analysed by X-ray diffraction.

3. Results and discussion

3.1. Anaerobic chemical oxidation

Fig. 2 shows changes in Fe(III) and As(III) concentrations in anaerobic experiments at 70 °C under different conditions. Experiment a corresponds to a solution of 0.5 g/L Fe(III) with 0.5 g/L arsenic (0.4 g/L As(III) and 0.1 g/L As(V)), experiment b to a solution of 0.5 g/L Fe(III) with 1% pyrite and experiment c to a solution of 0.5 g/L Fe(III) with 0.5 g/L arsenic (0.4 g/L As(III) and 0.1 g/L As(V)) with 1% pyrite.

The results show that, under anaerobic conditions and without pyrite (experiment a), both Fe(III) and As (III) concentrations remain constant during the whole experiment (120 h). In the presence of pyrite, a rapid reduction of ferric to ferrous iron was observed, both in the presence and absence of As(III) (experiments b and c). A slight increase of total iron concentration was observed (data not shown), indicating that ferric reduction corresponds to the oxidation of pyrite. In the oxidation of pyrite, 14 ferric ions are reduced for each mole of pyrite dissolved, according to the following reaction:

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

However, in the presence of As(III) and pyrite, part of the Fe(III) initially reduced corresponds to the oxidation of As(III). As(III) concentration decreased from 0.50 g/L to 0.28 g/L during the first 40 h, while As (V) concentration increases from 0.01 g/L to 0.20 g/L.

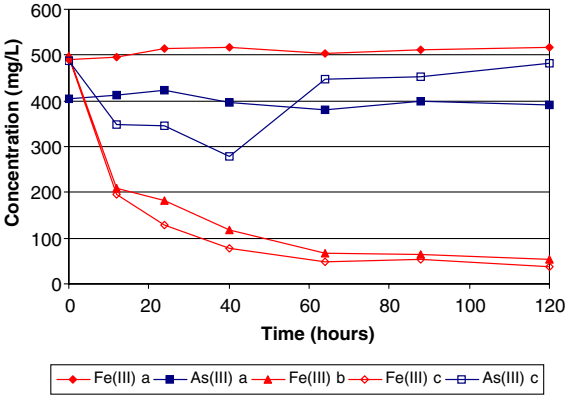

Fig. 2. Anaerobic experiments at 70 °C: (a) Fe(III)+As(III), (b) F(III)+pyrite, (c) Fe(III)+As(III)+pyrite.

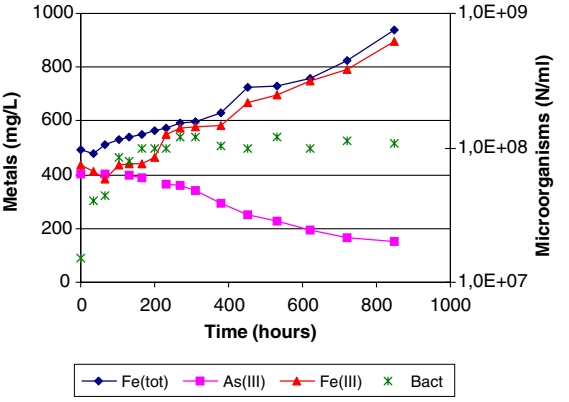

Fig. 3. Biooxidation of pyrite at 30 °C with *Acidithiobacillus ferrooxidans*, Fe(III) and As(III).

After 40 h, 80% of initial ferric ion is reduced to ferrous iron and a significant decrease of Eh from 546 to 410 mV vs. Ag/AgCl was observed. A further increase of As(III) concentration is then observed that corresponds to the reduction of As(V) on the pyrite.

A similar behaviour was observed in experiments at 30 °C, but the rate of ferric ion reduction at the pyrite surface was much lower. In the presence of pyrite and As(III), after 88 h, the ferric ion concentration had decreased from 0.50 g/L to 0.20 g/L. At the same time, As(III) concentration had decreased from 0.43 g/L to 0.26 g/L.

The results suggest that, at high Eh potential, the electrons transferred to ferric iron come from both anodic oxidation of pyrite and oxidation of As(III) to As (V). At lower Eh potential (<420 mV vs. Ag/AgCl), the cathodic reduction of As(V) also takes place at the pyrite surface and As(V) acts as oxidizing agent in the electrochemical pyrite dissolution.

3.2. Bacterial oxidation

Fig. 3 shows the results of aerobic bacterial oxidation of pyrite in the presence of Fe(III) and As(III) at 30 °C.

During the first 200 h, the concentration of free bacteria increases exponentially from an initial value of $1.5 \cdot 10^7$ bact/mL to $1.0 \cdot 10^8$ bact/mL. At the same time, total iron concentration increases as a result of pyrite dissolution, but ferric iron only represents 80% of total iron, which suggests that the reduction of ferric ion at the pyrite surface is quicker than the bacterial oxidation of ferrous iron. During these initial 200 h, As(III) concentration decreases very slowly from 0.41 g/L to 0.38 g/L. Then, the increasing bacterial oxidation of ferrous ion results in an increase of Eh potential (almost 95% of dissolved iron is present as ferric ion) and the

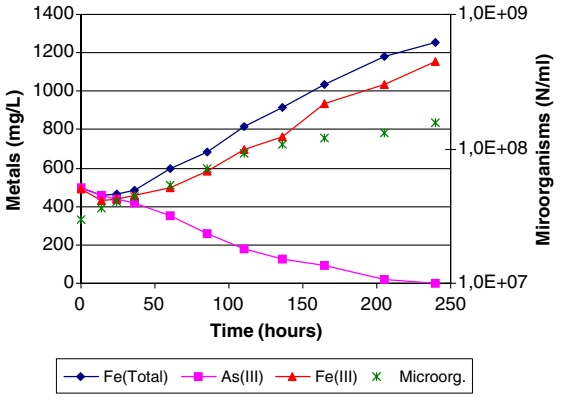

Fig. 4. Biooxidation of pyrite at 70 °C with *Sulfolobus metallicus*, Fe (III) and As(III).

rates of As(III) oxidation as well as pyrite dissolution increase. However, from 400 h to the end of the experiment, a progressive decrease of the rate of As(III) was observed which can be interpreted as the dependency of the oxidation rate with the concentration of As (III). An analysis of the reaction rate between 200 and 850 h shows that, at high Eh potential, the rate is first order with respect to the As(III) concentration. There is no significant change in total arsenic concentration and almost no precipitation was observed.

Fig. 4 shows the results of a similar experiment of pyrite bioleaching performed at 70 °C with *S. metallicus* in the presence of Fe(III) and As(III). The results are similar to those obtain at 30 °C with the difference that, in this case, even at the beginning, most of the iron is present as ferric iron. The rates of pyrite dissolution and As(III) oxidation are much higher than at 30 °C. The rate of pyrite dissolution is more than five times greater. Again, there is a decrease of As(III) oxidation rate when the concentration of As(III) decreases. It should be noted that, in this case, there is an important decrease of total arsenic concentration due to the precipitation of As (V). X-ray diffraction analysis of the solid precipitated indicates the presence of scorodite ($FeSO_4{\cdot}2H_2O$). As (V) precipitates as scorodite in the presence of ferric sulfate according to the following reaction:

$$Fe_2(SO_4)_3 + 2H_3AsO_4 + 2H_2O \rightarrow 2FeAsO_4 \cdot 2H_2O + 3H_2SO_4$$

The amount of scorodite precipitated was calculated from the decrease of total arsenic concentration. The corresponding amount of precipitated iron is then calculated and added to the increase of total dissolved iron to estimate the amount of total dissolved pyrite.

From the determination of pyrite dissolution and arsenic oxidation, the ratio of moles of FeS_2 and H_3AsO_4 oxidized can be calculated. At 70 °C with *S. metallicus*, for each mole of H_2AsO_3 oxidized there are 3.0 mol of pyrite oxidized. In other words, this means that, according to electrons transferred from both anodic reactions, there are 21 electrons transferred from pyrite dissolution for every electron transferred from As(III) oxidation. At 30 °C with *A. ferrooxidans*, the ratio is higher with 4.2 mol of pyrite oxidized for each mole of H_2AsO_3 oxidized or 29.5 electrons transferred from pyrite for each electron transferred from As(III).

3.3. Mechanisms of arsenic oxidation

The results of the present study suggest that the oxidation of As(III) in bioleaching solution can be explain as an electrochemical reaction that takes place at the surface of pyrite. At high Eh potential (>420 mV vs. Ag/AgCl), the semi reactions involved are the following:

- anodic reactions:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$$
$$H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2e^-$$

- cathodic reaction:

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

Fig. 5 shows the different reactions involved in the process. At 30 °C, for each mole of H_3AsO_3 oxidized, 4.2 mol of pyrite are dissolved while at 70 °C, the ratio is 3.0 mol of pyrite per mole of H_3AsO_3.

The role of microorganisms is mainly to maintain the high potential and a high concentration of ferric ion in the solution, catalysing the reoxidation of ferrous ion

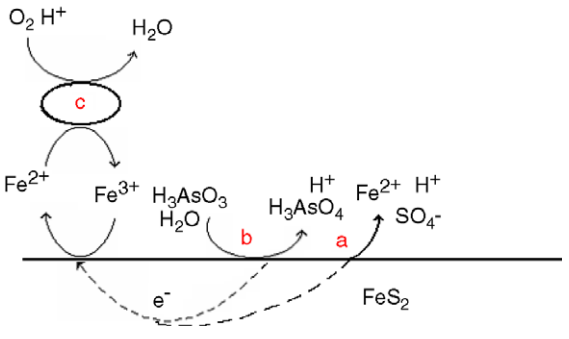

Fig. 5. Mechanisms involved in As(III) oxidation in the presence of pyrite and microorganisms: (a) anodic pyrite dissolution, (b) As(III) oxidation, (c) bacterial ferrous oxidation.

(see c on Fig. 5). Microorganisms may also be involved in both anodic and cathodic reactions, catalysing the transport of electrons at the solid surface.

At lower potential (Eh<450 mV vs. Ag/AgCl), pyrite dissolution is the only remaining anodic reaction while Fe(III) and As(V) are reduced cathodically.

4. Conclusions

Chemical oxidation of As(III) by ferric ion, although thermodynamically possible, is a very slow reaction. However, in the presence of pyrite, an electrochemical reaction takes place. On the cathodic side, ferric ion is readily reduced while on the anodic part, two reactions are involved: pyrite oxidation and As(III) oxidation. In the absence of bacteria, ferric ion concentration decreases and at lower Eh potential (<450 mV vs. Ag/AgCl), As(V) is reduced cathodically, while pyrite dissolution is the only remaining anodic reaction.

In aerobic conditions and in the presence of microorganisms, ferrous ion is readily reoxidized and conditions of high potential are maintained. Microorganisms may also be involved in both anodic and cathodic reactions, catalysing the transport of electrons at the solid surface. Under these conditions, both pyrite and As(III) are oxidized.

The rate of pyrite oxidation is more than five times greater at 70 °C in the presence of *Sulfolobus metallicas* than at 30 °C in the presence of *A. ferrooxidans*. At 70 °C, As(III) is readily oxidized and As(V) produced is partially precipitated as scorodite.

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