

Oxidation of Pyrite and Marcasite by *Thiobacillus ferrooxidans* Bacteria

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Abstract

This paper reports results of studies on the influence of the crystallographic mineral structure on the process of pyrite and marcasite leaching.

Kinetic studies show that the crystallographic structure of minerals like FeS_2 type does not influence the efficiency of the process.

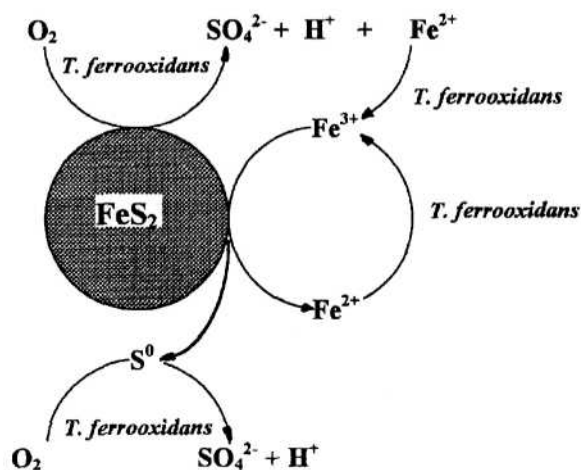
Keywords: *Thiobacillus ferrooxidans*, pyrite, marcasite, bioleaching

Introduction

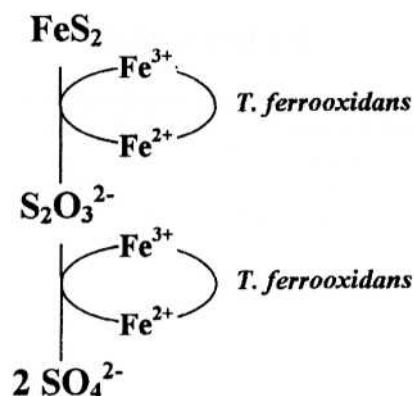
The process of metal leaching from ores with the help of bacteria depends on many physical, chemical and biological factors [1]. Its efficiency is affected by environmental conditions but also on bacteria activity and the structure of metal-bearing minerals. According to one approach explaining the role of bacteria in the process of metal leaching, the mineral molecules with the adsorbed bacteria cells form an electrochemical system in which the electrons from the cathode surface of the mineral move to the final electron acceptor being the atmospheric oxygen [2]. The adsorption of bacteria on the metal surface is possible thanks to organic polymers produced by their cells [3]. The adsorption sites are first of all cation deficits, which are also the sites of occurrence of elemental sulphur, which is dissolved in phospholipides of the cell membrane and then transported inside the cell (following the concentration gradient) and enzymatically oxidized to sulphates. At the sites from which sulphur was washed out, secondary cation deficits appear stimulating diffusion of sulphur from deeper layers of the mineral crystal lattice onto the mineral surface where it is subjected to another attack of bacteria. The process can be illustrated as beside.

Biooxidation leads to the formation of sulfuric acid, which initiates subsequent stages of the process involving iron ions (II), which after oxidation to iron (III) ions are

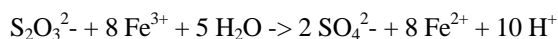
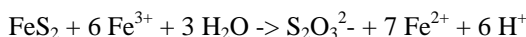
responsible for chemical oxidation of sulphides [4]. As yet the mechanism of metal bioextraction has not been unambiguously determined; some authors concentrate on the direct process involving microorganisms [5], while others consider mainly the chemical (indirect) mechanism [6]. Recent works by Schippers et al. [7] prove that the process is dominated by the chemical mechanism. As follows from their results, pyrite oxidation by iron ions



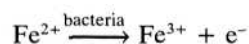
(III) in the absence of bacteria (only chemical leaching is observed), leads to the formation of sulphates according to the mechanism involving thiosulphate formation. The same products were obtained with the use of the *T. ferrooxidans* bacteria, which suggests that the role of bacteria is to maintain a desired concentration of iron ions and the mechanism of metal leaching can be depicted as follows:



It was also found that the crystallographic form of the minerals influences the kind of products formed as a result of microbiological oxidation [8], so it must also affect the mechanisms of the processes. The sulphides insoluble in acids (FeS_2 , MoS_2 , WS_2) are susceptible for the oxidation attack of iron ions (III), which leads to the formation of thiosulphides as the main intermediate products oxidized further according to the scheme:



The iron (II) ions are oxidized by the bacteria:



As follows from the above, mineral leaching may occur mainly by chemical processes, and the role of bacteria is reduced to

(i) production of biogenic sulfuric acid used for the hydrolytic attack (if a given mineral is susceptible for it) and to

(ii) maintaining iron ions (III) in the oxidized form (Fe^{3+}) ready for the oxidation attack.

The same conclusions were drawn by T.A. Flower *et al.* [6], who reported that leaching of ZnS in the presence of bacteria as well as in the sterile samples, in the conditions of a constant redox potential (constant concentration of iron (II) and iron (III) ions) gives the same products.

This paper reports results of study on the influence of the crystal structure of minerals on the efficiency of bacteria-aided metal leaching. The minerals chosen were chemically identical iron sulfides: pyrite of the regular structure and marcasite of the rhombohedral structure.

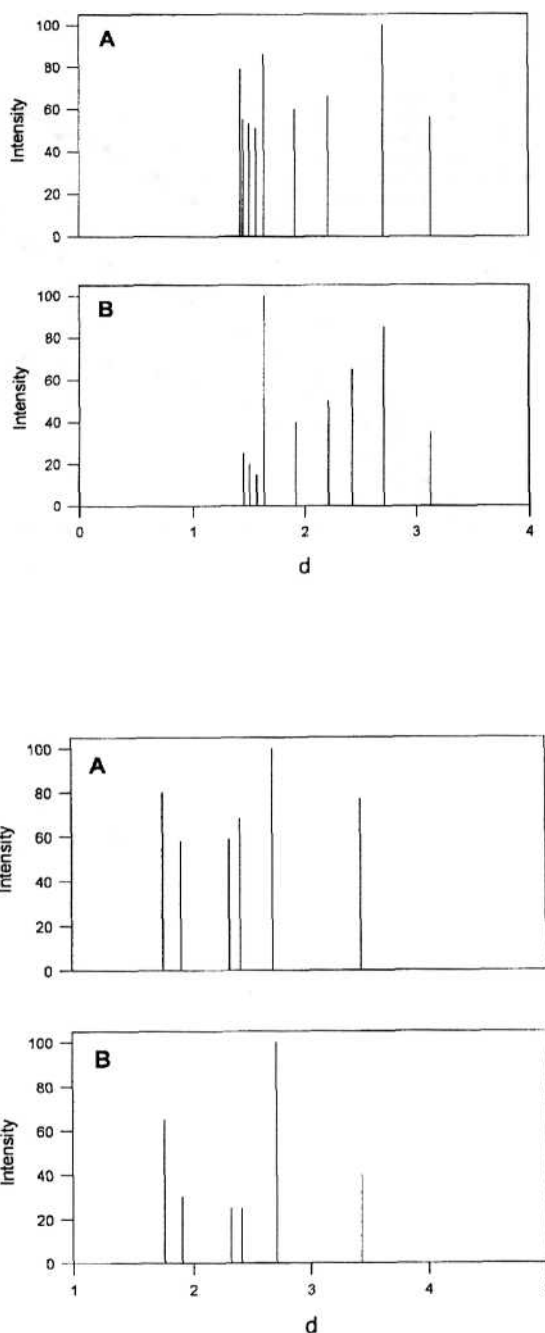


Fig. 2. Powder diffractogram of marcasite (A - examined, B - standard).

Materials and Methods

The *Thiobacillus ferrooxidans* bacteria were isolated from the mine waters from the Siersza colliery. Standard growth was conducted on Silverman 9K medium in 50 ml Erlenmayer flasks kept in thermostated shakers. The process was run at 37°C at the initial pH of the medium of 2.20. The inoculum made 10% (wt/vol). Experiments were performed for the chemically identical iron sulphides (FeS_2) pyrite and marcasite. Their chemical composition was established from quantitative analyses - pyrite contained 46.5% Fe and 53.4% S, while marcasite 45.9% Fe and 53.5% S.

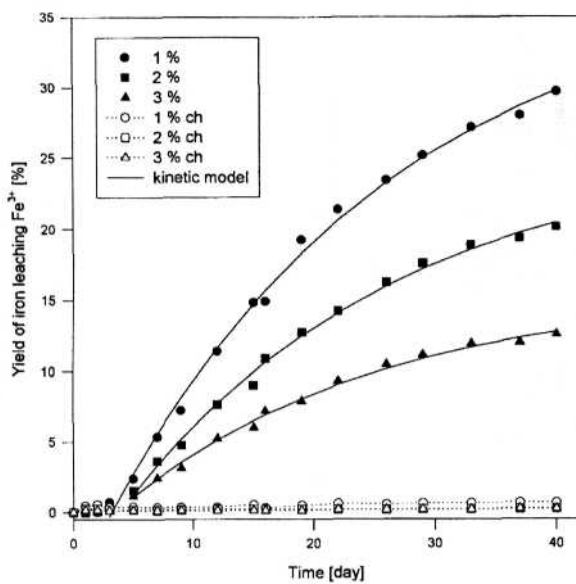
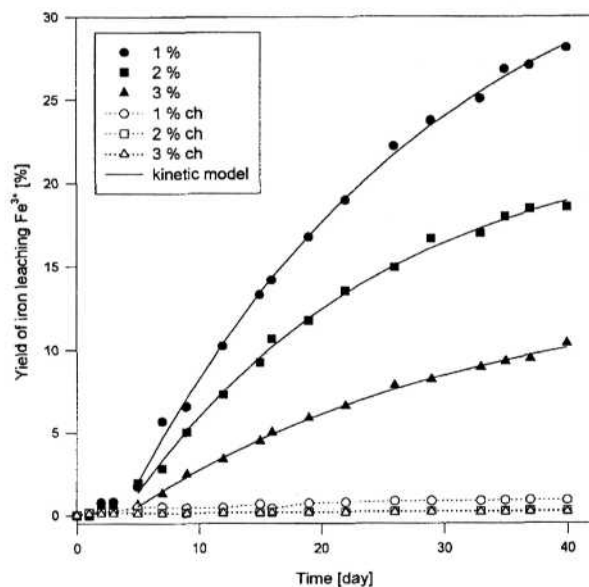


Fig. 3. The effect of pyrite content in the medium [%] on the yield of iron leaching (temp. 37°C, pH - 2.2, mineral grain size below 0.125 mm, ch - chemical leaching).

Fig. 4. The effect of marcasite content in the medium [%] on the



yield of iron leaching (temp. 37°C, pH - 2.2, mineral grain size below 0.125 mm, ch - chemical leaching).

The crystalline structure of the minerals was determined on the basis of X-ray diffraction measurements by the powder method for the angles 2-30 Θ . The concentration of iron (III) ions was measured by the rhodanate method [9] on a Beckman DU 640 spectrophotometer. The process of the mineral leaching was run in 350 ml Erlenmeyer flasks containing iron-free Silverman medium with 10% of the inoculum and 1.2 and 3% (wt/vol) of pyrite or marcasite. The process was monitored by measurements of changes in the concentration of iron (III) ions in the solution. The reference samples (chemi-

cal leaching) were inoculated by boiled inoculum and moreover to each reactor 1500 ppm of HgI_2 , as a bacteriostatic agent, was added.

The kinetic data were processed by the program Scientist for Windows. The fit of the model curves to experimental data was performed by linear regression using the least square method.

Results and Discussion

The Kinetic Model

The process was best described by the first order reaction against the substrate, inhibited by the product Fe^{3+} , the sum of the squares of deviations did not exceed 0.02, and the correlation coefficient was 0.998 in almost all cases. The reaction could be described by the following equation:

$$-\frac{dx}{dt} = k_1x - k_2(x_0 - x)$$

from which

$$x = \frac{x_0}{k_1 + k_2 [k_2 + k_1 e^{(k_1 + k_2)(t - t_0)}]}$$

where:

x_0 and x - are the initial and current concentration of the substrate,

k_1 - is the rate constant of leaching,

k_2 - the rate constant of inhibition,

t_0 - induction period,

t - time.

The parameters found from this equation were: k_1 , k_2 and t_0 .

As follows from the kinetic curves of pyrite and marcasite oxidation by *Thiobacillus ferrooxidans* bacteria, the processes of inhibition take place during leaching (Figs. 3 and 4). With increasing concentrations of the mineral in the system the rate constant of the reaction decreases while the rate of inhibition increases. The efficiency of the iron extraction decreased also with an increasing amount of the mineral in the substrate.

A comparison of the kinetic curves of marcasite and pyrite leaching shows that the rate of pyrite oxidation is greater (Table 1). The increase of the percent contribution of pyrite from 1 to 3% resulted in a twofold decrease in the reaction rate, while the same increase in marcasite contribution - a threefold increase in the reaction rate. The rate constants of the inhibition of pyrite and marcasite oxidation are similar, the only exception was noted in the variant when 3% (wt/vol) of marcasite was applied - then the rate constant of inhibition was lower than that for pyrite by 9.0/24 h. No influence of the mineral concentration on the induction period of the reaction was observed - it was the same for all variants.

The above results indicate that the efficiency of microbiological leaching of iron from pyrite is somewhat greater than that from marcasite. In all laboratory experiments, the efficiency of iron leaching was about 2%

Table 1. Kinetic parameters of the process of pyrite and marcasite oxidation with the use of *Thiobacillus ferrooxidans* bacteria (temp. 37°C, pH - 2.2, mineral grain size below 0.125 mm, ironless Silverman medium 9K, k_1 - leaching rate constant, k_2 - inhibition constant, t_0 - induction period)

FeS ₂ content in the medium [%]	Yield of iron leaching [%]		$k_1 \cdot 10^{-3}$ [day ⁻¹]		$k_2 \cdot 10^{-3}$ [day ⁻¹]		t_0 [day]	
	pyrite	marcasite	pyrite	marcasite	pyrite	marcasite	pyrite	marcasite
1.0	29.7	28.1	15.8 ± 0.8	14.5 ± 0.6	25.8 ± 3.2	24.1 ± 2.6	3.2 ± 0.3	3.6 ± 0.3
2.0	20.1	18.5	11.3 ± 0.6	10.9 ± 0.6	32.9 ± 3.9	36.7 ± 3.7	3.9 ± 0.3	3.7 ± 0.3
3.0	12.6	10.4	7.3 ± 0.4	5.0 ± 0.2	39.6 ± 3.9	30.6 ± 2.9	3.5 ± 0.3	3.8 ± 0.3

greater in media containing pyrite of the regular structure. Unfortunately, the results of the kinetic studies of the process of iron leaching from pyrite and marcasite, do not allow an unambiguous verification of the relation between the process efficiency and the mineral structure suggested in literature. It seems that as far as pyrite and marcasite are concerned, such a relation should not be expected.

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