

The Use of *Thiobacillus Ferrooxidans* Bacteria in the Process of Chalcopyrite Leaching

K. Nowaczyk, A. Juszczak, F. Domka, J. Siepak

Department of Kinetics and Catalysis, Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznan, Poland

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Abstract

The use of *Thiobacillus ferrooxidans* bacteria in the process of copper and iron leaching from chalcopyrite coming from Kotlina Ktodzka was investigated. The influence of the mineral content in the leaching solution the pH value and refinement of chalcopyrite on the subsequent stages of leaching was established. The process was described by the 1st order reaction inhibited by one of the products (Cu^{2+}). Assuming this model, the kinetic parameters of leaching were determined.

Keywords: *Thiobacillus ferrooxidans*, chalcopyrite, biological leaching of copper and iron

Introduction

Biological leaching of metals (the basis of biohydrometallurgy), is justified not only by economical but also ecological reasons. Increasing demand of industry for metals leads to a quick exhaustion of the best or the easiest accessible resources, which stimulates the search for new environment-friendly solutions enabling exploitation of poor deposits or recovery of metals from industrial wastes. A promising solution seems to be a well recognised process of biological leaching of sulphide ores. Biohydrometallurgy should be considered whenever the conventional methods fail because of too much energy consumption, a deposit structure or low metal content [1].

Konnect Copper Corporation has been a leading concern in biohydrometallurgy since patenting biooxidation of ferrous to ferric ions in 1958. Up to today 4 billion tons of copper-bearing low-grade ores in the USA, Spain, Chile and Peru have been treated, producing 1500 tons of copper every month.

ENAMI Corporation recovers 300 tons of copper per year by in situ leaching of porphyritic copper deposits in Andacollo (Chile). Total cost of 1 ton of copper recovery is approximately \$ 1300. Additionally, ENAMI Corporation, Dayton Development Corporation and Anacondo Corporation are also involved in copper recovery by bioleaching techniques [2].

Thiobacillus ferrooxidans bacteria, which grow on a wide spectrum of substrates including the reduced forms of metals (Fe^{2+} , Sn^{2+} , Sb^{3+} , U^{4+}) or reduced forms of inorganic sulphur (S^0 , S^{2-} , $\text{S}_2\text{O}_3^{2-}$), permit to select the mutants of specific biochemical properties [3, 4]. They have become an attractive material of possible applications in different industrial processes. Recently, it has been found that their metabolism can be used in the technology of desulphurization of fuels and industrial gasses [5, 6, 7]. The efficiency of this process is competitive with the traditional methods of desulphurization and the side products are sulphur, sulphuric acid or gypsum.

Economical balance of biological exploitation of metal deposits should take into account the position of the deposit, its chemicals composition, kinds of contamination, composition of the leaching solution, and the activity of the selected strain of bacteria. The classification of the latter has been based so far on morphological features and ecological distribution. In our recent studies we have selected a strain showing significant activity in the process of coal desulfurization [8] which has prompted us to consider the possibility of its use in the process of metal leaching from different sulphide ores.

This paper reports the results of a study of the effect of chalcopyrite refinement, pulp density and pH of the leaching solution on the degree of copper and iron leaching and on the kinetic parameters of this process.

Materials and Methods

Microorganisms

The laboratory strain of *Thobacillus ferrooxidans* was isolated from the waters in the Siersza colliery. Standard cultures were grown in reactors of 50 cm³ in volume containing 20 cm³ of Silverman 9K medium [9] placed in Elpan 357 thermostated shakers. The process was conducted at 37°C and the initial pH of the medium of 2.2. Inoculum used for leaching was collected after 48 hours of growth (the logarithmic phase), and filtered and tested for the presence of Fe (III) in order to ensure the same initial conditions for all series. The media were inoculated with 10% volume of the medium.

Chalcopyrite

Studies were performed on chalcopyrite from Kotlina Kłodzka containing 33.9% Cu, 30.4% Fe and 34.0% S. The mineral was ground and divided into 3 fractions of 0.16-0.125, 0.125-0.06 and below 0.06 mm grain size. The samples were subjected to chemical analysis and observations under a scanning electron microscope (Philips SEN 515) before and after the process.

Kinetic Studies

Studies were carried out in glass flasks of 20 or 50 cm³ in volume, containing ironless Silverman medium with 10% volume of inoculum, and chalcopyrite in the amounts of 1.0, 1.7, 3.3 and 5% w/vol of the leaching solution. After the first stage of leaching the mineral was washed with hot 3M HCl, tested for the contents of copper and iron, and put back into the flask containing a new portion of the leaching solution with the active inoculum. The procedure was repeated in the third stage of leaching when using the mineral after the second stage washed with hot 3M HCl. In all three stages the amount of the mineral made 5% w/vol of the leaching solution. The reference samples contained the same amounts of the components but prior to addition the inoculum was boiled and 1500 ppm of HgCl₂ was introduced to inhibit the process of biological leaching [10].

Kinetic parameters of copper and iron leaching from chalcopyrite were calculated, assuming that the process is a 1 st order reaction inhibited by one of the products (Cu²⁺) [11]. This assumption was made on the basis of a good correlation between the experimental and calculated data. The parameters calculated were: rate constant of leaching reaction (k_1), inhibition rate constant (k_2), and induction time of the reaction (t_0).

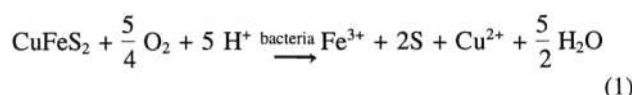
Analytical Studies

The process of leaching was monitored by measuring the time changes in concentrations of Fe³⁺, Cu²⁺ ions and pH of the system. The concentration of Fe³⁺ was measured by the thiocyanate method [12] (using a Beckman DU 640 spectrophotometer) and the results were correlated with results of atomic absorption spectrophotometry (Unicam SP 90 A). The total amount of Fe³⁺ ions washed out from the mineral was a sum of those determined in the solution and in the precipitates after their dissolution in hot 3M HCl.

The concentration of Cu²⁺ was determined by the cuprisone method [12] (Beckman DU 640 spectrophotometer) and correlated with the results of atomic absorption spectrophotometry (Unicam SP 90 A). The content of copper was determined both in the leaching solution and in the precipitates after their dissolution in hot 3M HCl. The initial pH of the medium in which the leaching was conducted was 1.1, 1.7, 2.0, 2.4 and 2.8.

Results and Discussion

In general, the leaching of metals from chalcopyrite occurs according to the reaction [13]:



As follows from the studies, this process can be described as a 1 st order reaction inhibited by the product, by the following equation:

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

where: x_0 and x are the initial and current concentration of the substrate, respectively;
therefore:

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

From the latter equation the kinetic parameters of the reaction were calculated: the rate constant of leaching (k_1), the inhibition rate constant (k_2) and the induction period (t_0). Correlations of the experimental data with the results of the calculations are illustrated in Fig. 1.

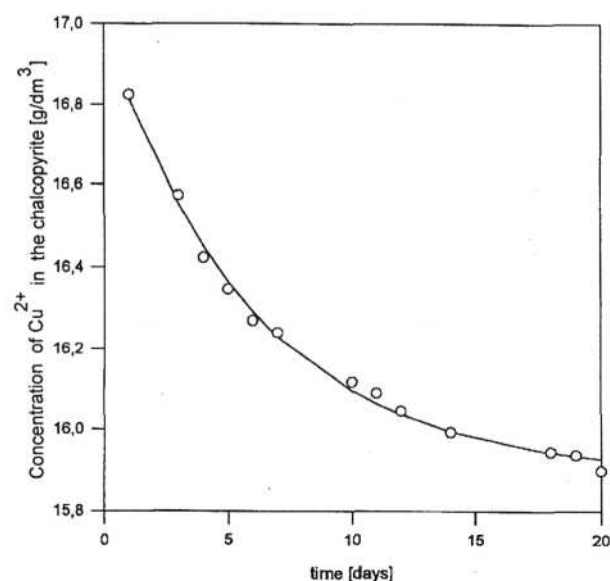


Fig. 1. Correlation between experimental data (circles) and theoretical model predictions (solid line).

Table 1. Kinetic parameters of the process and contents of copper and iron in the medium after leaching of chalcopyrite with the use of *Thiobacillus ferrooxidans* bacteria. (Temp. 37°C, pH = 2.2, mineral grain size below 0.06 mm, ironless Silverman medium, k_1 - leaching rate constant, k_2 - inhibition constant, t_0 - induction period).

CuFeS ₂ content in the medium (%)	Yield of leaching (%)	Final concentration in the medium (g/dm ³)	k_1 (dm ³ · g ⁻¹ · h ⁻¹)	k_2 (dm ³ · g ⁻¹ · h ⁻¹)	t_0 (h)
Cu					
1.0	21.8	0.78	0.063 ± 0.002	0.216 ± 0.009	2.54 ± 0.04
1.7	18.2	1.08	0.071 ± 0.002	0.308 ± 0.009	2.13 ± 0.04
3.3	15.0	1.78	0.048 ± 0.005	0.263 ± 0.04	1.36 ± 0.02
5.0	13.8	2.48	0.028 ± 0.005	0.147 ± 0.038	1.38 ± 0.44
Fe					
1.0	28.8	0.78	0.034 ± 0.003	0.216 ± 0.009	2.54 ± 0.04
1.7	20.5	1.00	0.053 ± 0.014	0.308 ± 0.009	2.13 ± 0.04
3.3	16.4	1.60	0.031 ± 0.003	0.263 ± 0.04	1.36 ± 0.02
5.0	12.6	1.84	0.029 ± 0.005	0.147 ± 0.038	1.38 ± 0.44

The relative error not exceeding 0.18% confirms that the process studied can be well described by the kinetic model assumed.

Results of the studies on the effect of the chalcopyrite content in the leaching solution on the yield of leaching occurring with the use of *Thiobacillus ferrooxidans* bacteria are collected in Table 1 and illustrated in Fig. 2 and Fig. 3.

As follows from the results (Table 1), the yield of copper and iron leaching from the chalcopyrite tested decreases with increasing content of the mineral in the leaching solution, from 21.8% Cu²⁺ and 28.8% Fe³⁺ for 1% concentration of chalcopyrite in the medium, to 13.8% Cu²⁺ and 12.6% Fe³⁺ for 5% of chalcopyrite concentration in the

medium. This decrease is accompanied by a reduction of the rate constant of leaching (k_1), increase of the inhibition rate constant (k_2), and shortening of the induction period of the reaction (t_0). However, a hard-to-explain exception to this rule is the situation for the CuFeS₂ content in the medium of 1.7% (w/vol), Table 1. In general, the higher the content of chalcopyrite in the medium, the higher the final concentration of copper (an increase from 0.78 to 2.48 g/dm³) and iron (an increase from 0.78 to 1.84 g/dm³). As increasing concentration of copper (II) ions inhibits the process of bacteria growth, the observed decrease of the leaching rate constant (k_1) and increase of the inhibition rate constant (k_2) seem obvious. The shortening of the

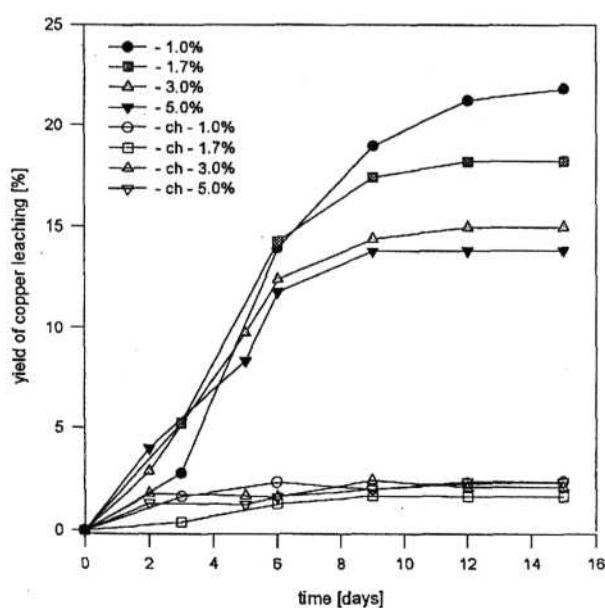


Fig. 2. The effect of chalcopyrite content in the medium [%] on the yield of copper leaching (temp. 37°C, pH 2.2, mineral grain size < 0.06 mm; ch - chemical leaching)

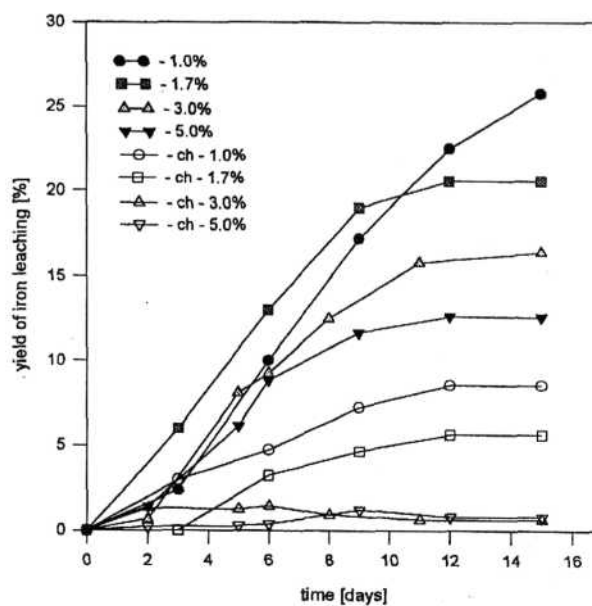


Fig. 3. The effect of chalcopyrite content in the medium [%] on the yield of iron leaching (temp. 37°C, pH 2.2, mineral grain size < 0.06 mm; ch - chemical leaching)

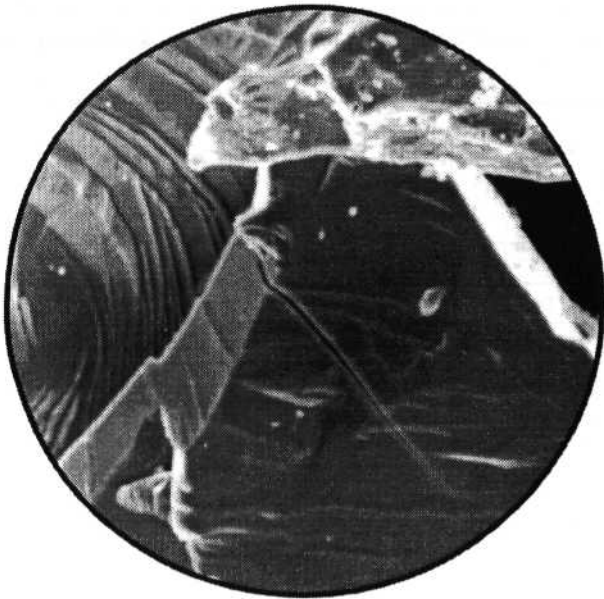


Photo 1. Chalcopyrite (0.16-0.12 mm grain size) before leaching

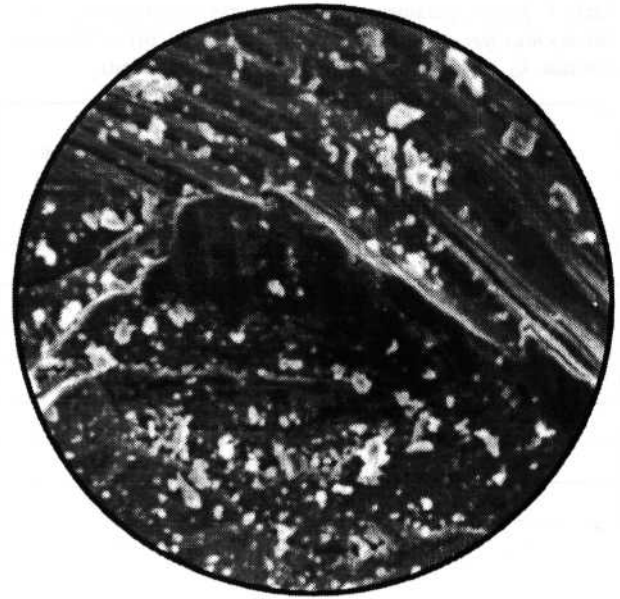


Photo 3. Chalcopyrite (0.12-0.06 mm grain size) before leaching



Photo 2. Chalcopyrite (0.16-0.12 mm grain size) after leaching

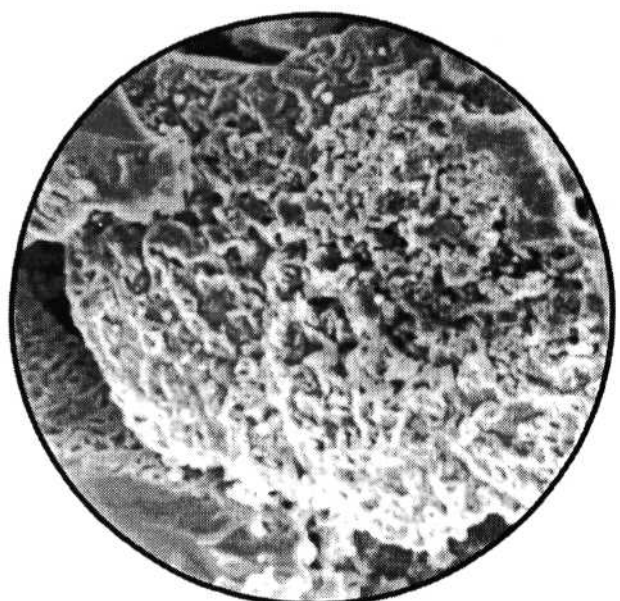


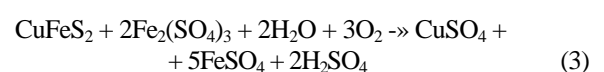
Photo 4. Chalcopyrite (0.12-0.06 mm grain size) after leaching

induction period with increasing chalcopyrite content may be attributed to the increased area of the mineral accessible to the microorganisms. Changes in the mineral surface caused by the bacteria are illustrated in the electron-microscope photographs (photos 1-4) taken before and after leaching. The photographs show that the initial crystals of sharp edges are transformed into irregular fine grain aggregations. The changes in CuFeS_2 texture are greater the more refined the initial mineral.

From the kinetic point of view, the most advantageous is the process in which the mineral makes 1 % of the leaching mixture; however, more economic would be use of the highest possible concentrations of the mineral. An optimum choice seems to be the case when the mineral makes 5% (w/vol) of the leaching mixture; as despite a lower

efficiency of the reaction, the final concentration of copper and iron in the leaching solution is over 3 times greater.

As it has been established, leaching of copper and iron from chalcopyrite takes place by both direct enzymatic oxidation of iron and sulphur (reaction 1 and 2) and indirect chemical dissolution of copper (reaction 3) according to the following reaction [13]:



The *Thiobacillus ferrooxidans* bacteria live on the energy from the process of oxidation of Fe (II) to Fe (III) and the sulphide sulphur to sulphate sulphur. The formed Fe (III) ions are strong chemical oxidants involved in the che-

Table 2. The influence of the initial pH of the medium on the yield of leaching of copper and iron with the use of *Thiobacillus ferrooxidans* bacteria. (Temp. 37°C, mineral grain size below 0.06 mm, 1 % (w/vol) chalcopyrite in the medium)

Initial pH of the medium	Yield of leaching (%)		Final concentration in the medium (g/dm ³)	
	Cu (II)	Fe (III)	Cu (II)	Fe (III)
1.1	0.95	8.81	0.03	0.26
1.7	4.11	22.10	0.15	0.65
2.0 - 2.4	21.8	25.80	0.80	0.78
2.8	1.05	7.80	0.04	0.23

mical leaching of chalcopyrite (reaction 3). In this way the cycle of transformation of Fe (II) to Fe (III) is closed, and the formed H₂SO₄ increases the solubility of the mineral. The chemical leaching of iron occurs with a yield from 8% (1% mineral in the medium) to 5% (1.7% mineral in the medium), while the chemical leaching of copper yields about 2.5%, irrespective of the concentration of chalcopyrite in the mixture (Fig. 3).

In a subsequent series of experiments, the effect of the initial pH of the leaching solution on the efficiency of the process was studied. The results are given in Table 2 and illustrated in Figs. 4 and 5.

When the process was run at pH 1.1, only chemical leaching of copper and iron was observed, after 20 days the efficiency was 1% and 9% of leached copper and iron, respectively. The contribution of biological leaching was observed starting from pH 1.7, and then the yield of the leached copper increased slightly - up to 4%, while that of iron leaching increased significantly - up to 22%. When pH of the leaching solution was increased to 2.0-2.4, the yield of copper leaching increased to 22.6%, but the yield of iron

Table 3. The influence of the chalcopyrite grain size on the yield of subsequent stages of microbiological leaching of copper and iron.

Chalcopyrite grain size	Yield of leaching (%)					
	1 st stage		2 nd stage		3 rd stage	
	Cu (II)	Fe (III)	Cu (II)	Fe (III)	Cu (II)	Fe (III)
0.16-0.125 mm	4.67	4.93	0.43	2.72	0.29	1.10
0.125-0.06 mm	7.42	6.10	0.73	3.65	0.41	3.47
< 0.06 mm	18.03	9.95	4.17	7.40	3.34	6.73

leaching increased only by 4%, reaching 26%. These results indicate that efficient leaching of iron takes place already at pH of about 1.7, while that of copper at pH of about 2.0. Further increase of the medium pH to 2.8 inhibits biological leaching. Consequently, the greatest yield of the process can be achieved for pH of the leaching solution from 2.0 to 2.4, see Table 2.

As the next step of the studies, the effect of chalcopyrite refinement on subsequent stages of leaching was checked. Results of this series of experiments are given in Table 3 and Fig. 6.

In general, the yield of leaching of both copper and iron increases with refinement of the mineral and the effect is more pronounced for copper. Subjecting the mineral to repeated leaching, in case of copper, seems to be justified only for the mineral of the greatest refinement - grain size below 0.06 mm. The leaching of copper from chalcopyrite of greater grain size, in subsequent stages of the process, brings insignificant yield increase from 0.43 to 0.29%. The situation is different for iron, in subsequent stages, for the mineral of all grain sizes used the yield of iron leaching was significant, but the greatest for the most refined mineral.

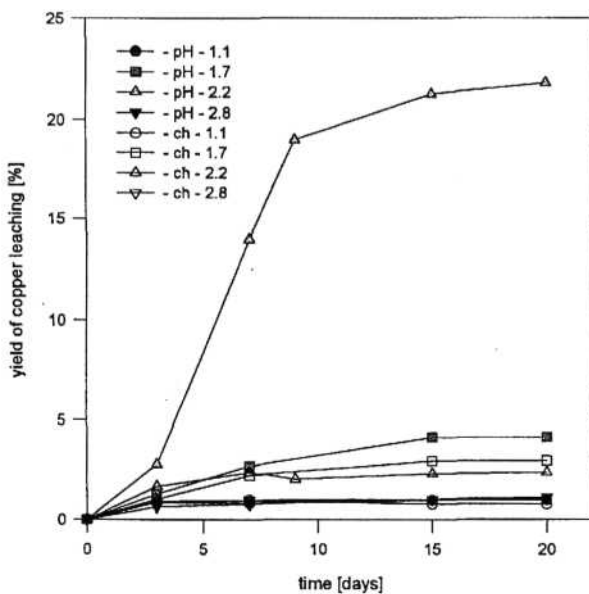


Fig. 4. The influence of initial pH of the medium on the yield of copper leaching from chalcopyrite (temp. 37°C, 1% (w/vol) of chalcopyrite, mineral grain size < 0.06 mm, ch - chemical leaching)

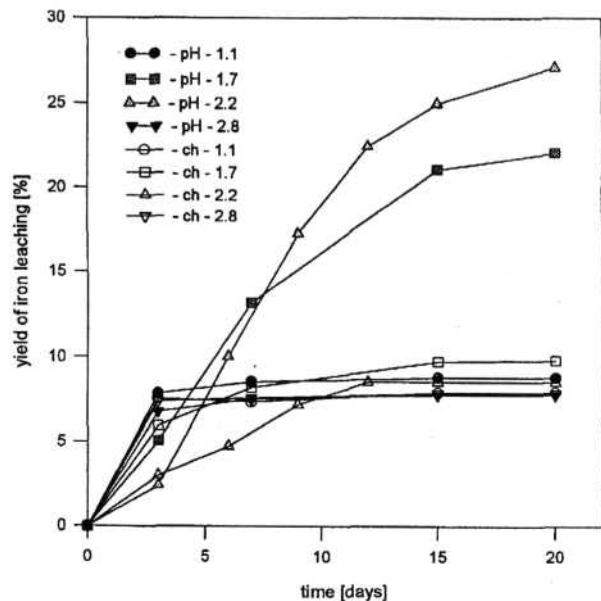


Fig. 5. The influence of initial pH of the medium on the yield of iron leaching from chalcopyrite (temp. 37°C, 1% (w/vol) of chalcopyrite, mineral grain size < 0.06 mm, ch - chemical leaching)

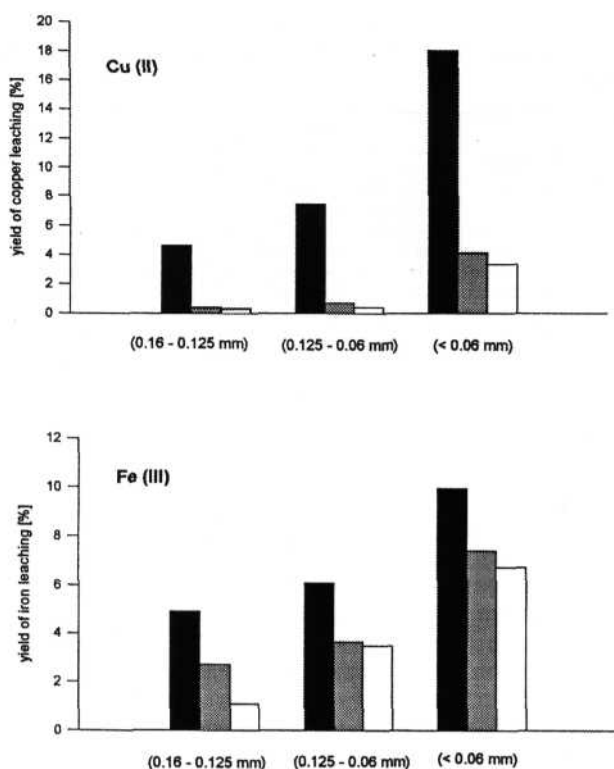


Fig. 6. The influence of chalcopyrite refinement on the yield of copper and iron leaching in subsequent stages of the process
Leaching stages: ■ - 1 ▒ - 2 □ - 3

Conclusions

The results obtained in this study allow a conclusion that the proposed kinetic model can be used for optimisation of the parameters of the process of copper and iron leaching from chalcopyrite with the use of *Thiobacillus ferrooxidans* bacteria. The efficiency of this process can be increased by using the leaching mixture of appropriate pH, the optimum mineral refinement and the optimum percent contribution of chalcopyrite in the leaching solution.

It should be emphasised that although the copper leaching yield was only of 22%, the final concentration of this metal in the leaching solution was of 2.5 g/dm^3 , which is 10 times more than that achieved with current technology [2]. The yield of this process is also expected to increase when it is run in a continuous way. The biohydrometallurgical methods have great chances to become increasingly popular in the future not only for economical but ecological

reasons. However, the biochemical mechanism of chalcopyrite leaching has not been fully recognized (taking into account the complex character of its deposits and variety of microorganisms which can be used) and requires further study.

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