

*Peter BALAZ**

*Daniel KUPKA**

*Jaroslav BRANCIN***

*Tomas HAVLIK****

*Milan SKROBIAN****

BACTERIAL LEACHING OF THE MECHANICALLY ACTIVATED PYRITE

The interaction of *Thiobacillus ferrooxidans* with mechanically activated pyrite was studied. Mechanical activation produces changes in specific surface area as well as in crystallographic order of the mineral. The evoked changes have influence on the course of bacterial leaching and confirm importance of solid state properties of minerals in biohydrometallurgical operations.

Introduction

In the presence of thiobacteria - some oxidation processes take place in deposits of sulphidic ores accessible to oxygen. In these processes, the sulphidic forms of metals undergo a transformation into water-soluble form and are leached from the ores [1,2]. The water circulating in these oxidation zones contains rather great amounts of sulfuric acid and metal sulfates among which ferric sulfate [3] is the most aggressive with respect to sulphides. Its reaction with sulphides can be described by the following equation:



Pyrite belongs among frequent accessory minerals of nonferrous metal deposits. This mineral was known as early as in the age of ancient Greece [4]. In Middle ages it was used till 19th century for producing sulfuric acid. At present, sulfuric acid and pyrite is exploited mainly because of its frequent association with gold. Flotation is used for preparing the pyrite concentrate which is ground and gold is obtained by cyanidation.

*Mining Institute, Slovak Academy of Sciences, Košice, ČSFR

**Institute of Experimental Metallurgy, Slovak Academy of Sciences, Košice, ČSFR

***Dept. of Non-ferrous Metallurgy, Technical University, Košice, ČSFR

2. Bacterial leaching

In accordance with eqn. (3), the reaction of pyrite with bacteria *Thiobacillus ferrooxidans* involves the transfer of the Fe^{2+} ions into solution and the decrease in pH-value of the leach.

The plot in Fig. 4 expresses the dependence of iron concentration C_{Fe} on the time of bacterial leaching t_{BL} for the pyrite mechanically activated for different periods of time. It results from these plots that the bacterial decomposition of pyrite is accelerated for the times of mechanical activation t_{PM} equal to 450, 900 and 1 800 s.

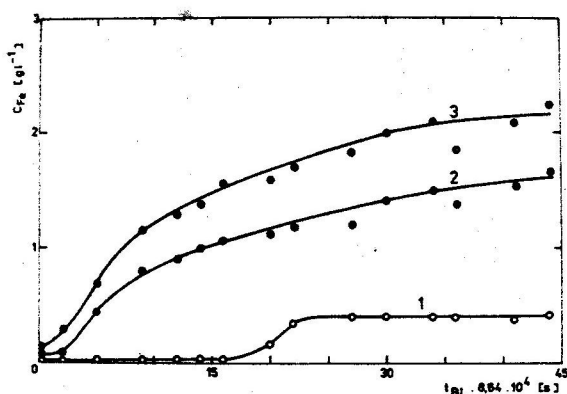


Fig. 4. The dependence of iron concentration C_{Fe} on the time of bacterial leaching t_{BL} .

Grinding time t_g : 450 s, 900 s, 1 800 s.

These curves exhibit a character analogous to that of the growth curve of bacteria while the maximum rate of bacterial leaching in that t_{PM} interval increases and the values of t_{INFL} shift to lower values (Fig. 5). It ensues from this figure that the process of bacterial leaching is retarded provided the specific surface of samples $S_A > 0.5 \cdot 10^3 \text{ m}^2 \text{ kg}^{-1}$ (it corresponds to $t_{\text{PM}} > 1\,800 \text{ s}$) which is also confined by the course of the values of v_{max} and t_{INFL} . In this region, small pH - values of the leach varying at about pH 1.5 can also be observed (Fig. 6, curve 1). It is stated in literature that the pH-value optimum for the mentioned kind of bacteria is in the region pH 2.0 - 3.0 [12]. It results from the course of the values of iron concentration in the leach (Fig. 6, curve 2) that the process of leaching practically comes to a standstill.

The retardation of bacterial oxidation can be explained from the view-point of the mechanism of leaching (eqn. 2 - 5) as well as from the view-point of the violation of pyrite structure produced by mechanical activation.

A coating of elemental sulphur on the surface of fine pyrite particles arises in the course of bacterial chemical oxidation (eqn. 4) and simultaneously pH decreases mainly because of reaction (5). The high concentration of sulfuric acid has inhibiting influence on the oxidizing ability of bacteria. The equilibrium in reaction (5) shifts to the left under these conditions owing to which the reaction is retarded.

The disordering of pyrite structure increases on account of mechanical activation. Besides the increase in overall surface, new boundaries and cracks which are accompanied by the formation of lattice defects and imperfections on a submicroscopic scale come into existence. According to Shewmon [13] diffusion of sulfur atoms through pure crystal line solids is usually of the order $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ while diffusivities along dislocations and grain boundaries are of the order $10^{-12} \text{ cm}^2 \text{ s}^{-1}$. From the energetic point of view a sufficient supply of sulfur on these spots produces increased metabolic activity of bacteria which manifests

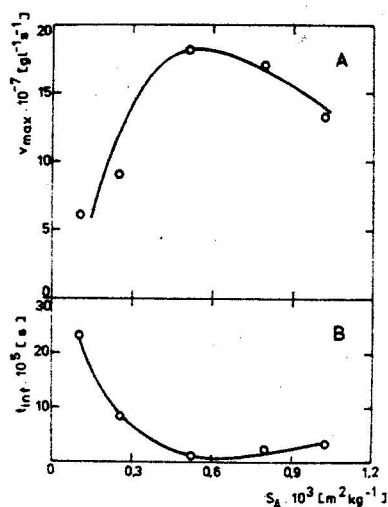


Fig. 5. Changes in maximum rate of bacterial leaching v_{max} (A) and value of t_{inf} (B) with the specific surface area S_A of pyrite samples

Results and discussion

1. Changes in surface and amorphization of pyrite structure

The mechanical activation of pyrite gives rise to significant changes in specific surface S_A and amorphisation of structure A of this mineral (Fig. 1). The increase in quantity A is monotonous (curve 2) and lessens with grinding time t_{PM} . The course of S_A (Fig. 1) exhibits sigmoid character. The sensitivity of these quantities to grinding time is expressed by the ratio S_A/t_{PM} or A/t_{PM} in Fig. 2. The maximum on curve 1 indicates

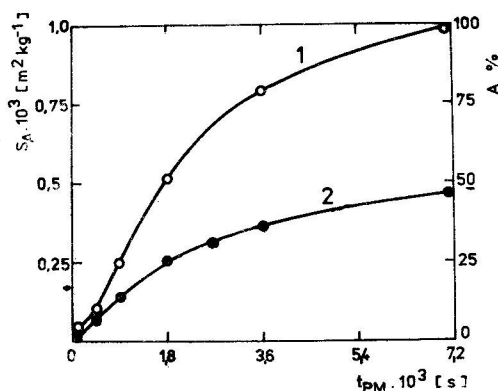


Fig. 1.

The influence of grinding time t_{PM} of pyrite on the specific surface area S_A (1) and amorphisation A (2)

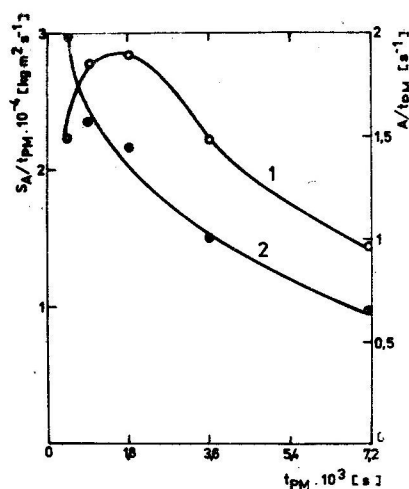


Fig. 2.

Changes in ratio S_A/t_{PM} (1) and A/t_{PM} (2) with grinding time t_{PM}

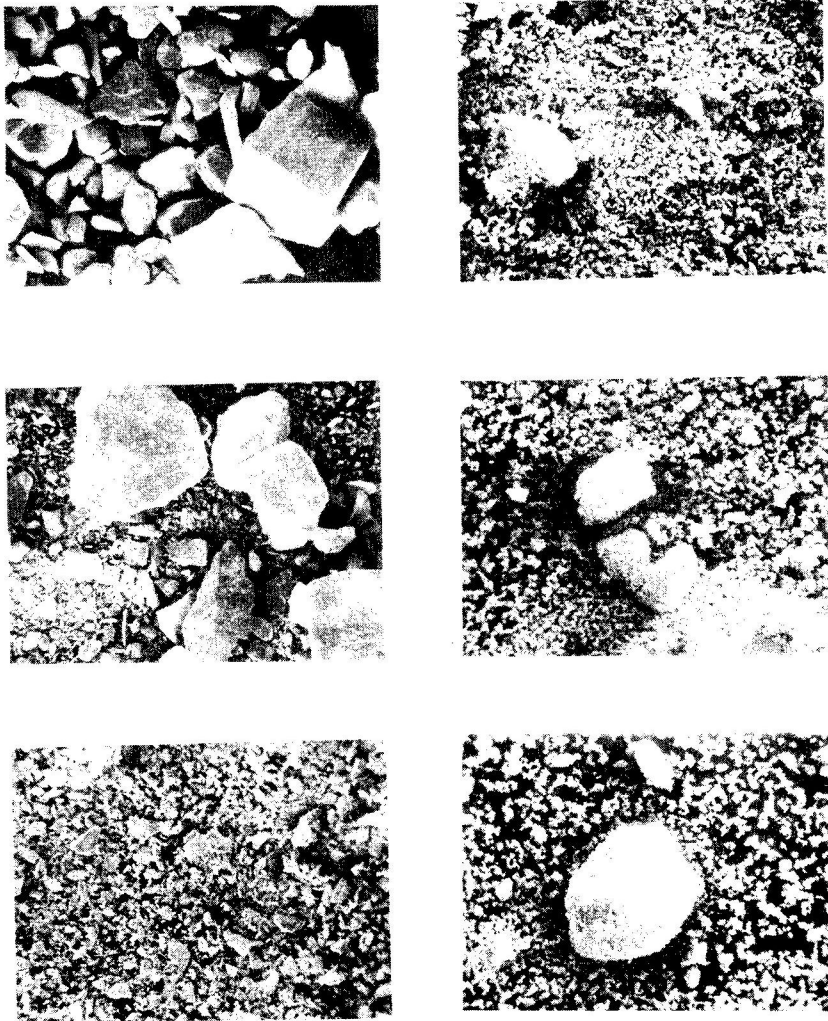


Fig.3. Scanning electron micrographs of pyrite:

A non ground sample (1000-40 μ m), B-F grinding time,

t_G : B - 450 s, C - 900 s, D - 1 800 s, E - 3 600 s,

F - 7 200 s

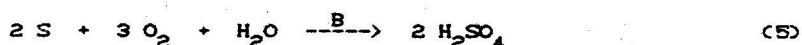
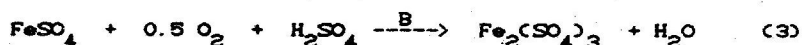
that the maximum increase in specific surface is reached in the region $t_{PM} = 450 - 900$ s. The decrease in quantity S_A/t_{PM} at higher values of t_{PM} is a consequence of agglomeration of the ground particles and is documented by SEM pictures in Fig. 3.

In ore deposits gold occurs dispersed in cracks and deformations of the lattice of pyrite. Its isolation necessitates violation of the crystalline lattice owing to which the gold becomes accessible to leaching agent.

The aim of this study has been to point out the possibility of attacking the lattice of pyrite by the effect of bacteria *Thiobacillus ferrooxidans* and simultaneously to use our present knowledge of the influence of mechanical activation on the violation of structure and on the rate of leaching of sulphides [5-8].

Chemism of leaching

The products of bacterial oxidation of pyrite are sulfuric acid and ferric sulfate. The overall course of decomposition may be described in agreement with literature [9] as follows:



(B - bacterial leaching, Ch - chemical leaching)

Besides the direct oxidation of pyrite by the bacteria adsorbed on the surface of this mineral (eqn. 2) a bacterial regeneration of the Fe^{3+} ions also takes place in the solution (eqn. 3). The generated ferric sulfate is a strong oxidation agent which leaches the pyrite according to eqn. 4. The formed elemental sulfur is bacterially oxidized according to eqn. 5.

Materials and methods

The pyrite found in the locality Smolník (East Slovakia) containing 50.90 % Fe and 43.88 % S was used for investigation. The accompanying mineral was quartz.

Mechanical activation: The samples were activated by grinding in a ball mill Pulverisette 4 (Fritsch, FRG). The weighed amounts of sample were equal to 15 g, the input granularity being 1 000 - 40 μm . Material of grinding chamber and balls : agate; volume of grinding chamber: 350 ml;

grinding medium: benzene (100 mL); filling of grinding chamber: 25 balls $\varnothing = 5$ mm and two balls $\varnothing = 25$ mm; relative acceleration of the mill: b/g = 10.3; grinding time = 450 - 7 200 s.

Specific surface: S_A was determined from the adsorption of benzene vapour by the BET method [10].

Amorphization of structure: A was calculated from the content of crystalline phase X by using formula

$$A = 100 - X \quad (6)$$

where the value of X was estimated from the ratio of relative intensities of the peaks of a mechanically activated (210) FeS_2 sample and of the standard (granularity $\sim 40 \mu\text{m}$). The measurement was performed by the method of X-ray diffractometry on an instrument DRON 2.0 (USSR) under these conditions: Fe - anode ($U=25$ kV, $I = 10$ mA), counting tube shift $2^\circ/\text{min}$, paper speed 40 mm/min, sensitivity 4 000 impulses/s, slits 1 and 0.5.

Bacterial leaching: A culture *Thiobacillus ferrooxidans* isolated from the mine water in the locality Smolnik was used as leaching medium. The leaching was carried out at 30°C by using spherical 250 mL flasks put in a laboratory rotating shaker (type ELPAN, Poland), the amplitude and frequency of rotation being 5 mm/s and 3 revolutions/s. The liquid phase consisted of the nutritive medium 9 K [11] (90 mL) adjusted to pH 2.5 without iron and of inoculum (10 mL) - bacterial suspension grown in the complete medium containing iron.

Chemical analysis and evaluation of results: The concentration of iron in the leach was determined on an instrument Spectr. AA-30 (Varian, Australia) by using the AAS method. The pH-value of the sampled leach was also measured.

The dependence of iron concentration in the leach C_{BL} on the time of bacterial leaching t_{BL} was evaluated by using the following regression equation

$$C_{Fe} = p_1 (1 - e^{-p_2 t^{p_3}}) \quad (7)$$

where p_1 , p_2 and p_3 are parameters. The maximum rate of leaching v_{max} was ascertained from the first derivate of function (7) in its point of inflection t_{inf} .

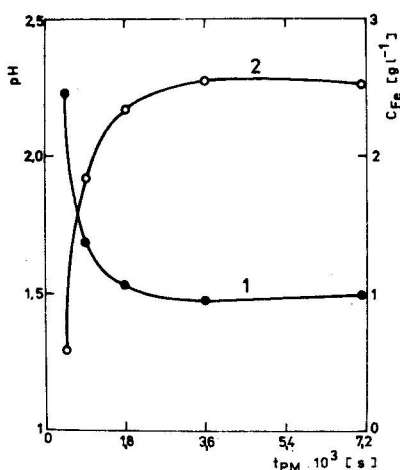


Fig. 6. Changes in pH value (1) and iron concentration C_{Fe} (2) with the grinding time t_{PM} after 14 days of bacterial leaching

itself by pitting on the surface of pyrite [14]. Such explanation is of good use for the samples mechanically activated not longer than 1 800 s. In this case, the rate of bacterial leaching increases with grinding time (Fig. 5). At higher time of activation ($t_{PM} > 1\ 800\ s$), the favourable effect of defects is suppressed by reassemblage of the particles of pyrite which form agglomerates (Fig. 3). Though the specific surface and the amorphization of structure do not decrease (Fig. 1), the accessibility of defect spots for bacteria is worse. For this reason, the metabolic activity of bacteria is smaller which manifests itself by a decrease in the rate of leaching.

Conclusions

1. Mechanical activation produces changes in specific surface as well as in crystallographic order of pyrite
2. The surface - structural changes have influences on the oxidation of pyrite by bacteria *Thiobacillus ferrooxidans*. It results from the course of bacterial leaching that this process may be divided in two stages:
 - a) if the time of mechanical activation is shorter than 1 800 sec, the surface - structural changes in mineral have positive influence on the rate of bacterial leaching
 - b) if the time of mechanical activation exceeds 1 800 s, the bacterial leaching is reduced, probably as a consequence of agglomerate

formation, in spite of further increase in specific surface and in disordering of the structure of pyrite.

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Streszczenie

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