

THE INFLUENCE OF MECHANICAL ACTIVATION OF CHALCOPYRITE ON THE SELECTIVE LEACHING OF COPPER BY SULPHURIC ACID

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In this paper chalcopyrite, CuFeS_2 , has been selective leached by H_2SO_4 as leaching agent (170 g/dm^3) in procedure of hydrometallurgical production of copper. Mechanical activation of the chalcopyrite resulted in mechanochemical surface oxidation as well as in the mineral surface and bulk disordering. Furthermore, the formation of agglomerates during grinding was also occurred. Surface changes of the samples using infrared spectroscopy and scanning electron microscopy methods were investigated before and after leaching. The leaching rate, specific surface area, structural disorder as well as copper extraction increased with the mechanical activation of mineral.

Key words: *chalcopyrite, mechanical activation, sulphuric acid leaching, selectivity*

Utjecaj mehaničke aktivacije halkopirita na selektivno izluživanje bakra sumpornom kiselinom. U ovom je radu halkopirit, CuFeS_2 , selektivno izluživan sumpornom kiselinom (170 g/dm^3) u postupku hidrometalurške proizvodnje bakra. Mehanička aktivacija halkopirita rezultirala je mehanokemijskom oksidacijom površine te nepravilnošću površine i unutrašnjosti minerala. Nadalje, također se događalo stvaranje nakupina tijekom mljevenja. Površinske promjene uzorka istraživane su prije i poslije izluživanja uporabom infracrvene spektroskopije i metodom pretražne elektronske mikroskopije. Za karakterizaciju čvrstog ostatka poslije izluživanja korištena je rentgenska difrakcijska analiza. Brzina izluživanja, specifična površina, strukturna nepravilnost i izdvajanje bakra povećavaju se s mehaničkom aktivacijom minerala.

Ključne riječi: *halkopirit, mehanička aktivacija, izluživanje sumpornom kiselinom, selektivnost*

INTRODUCTION

Base metal sulphides are an important source of various metals. They are typically intergrowth and due to the complex nature of their ores, the hydrometallurgical technique is the very convenient way of extracting the desired component. If it is possible to extract the metal from an ore selectively, the subsequent processing steps become less complicated.

Mechanical activation seems to be a favourable pre-treatment process for the processing of sulphides prior to the leaching with significantly enhanced metal recoveries reported [1]. This increase in leachability may well be due to a combination of mechanically induced structural defects and chemical reactions involving the mineral and the local environment. Senna [2] analysed the effect of surface area and the structural disordering on the leachability of mechani-

cally activated minerals. The rate of leaching may be sensitive or insensitive to structural changes. The differences in reactivity of the mineral components of ore, as well as the differences in solubility of the reaction products, can be used for selective leaching of metals from minerals [3 - 6].

The aim of this paper is to analyze the influence of mechanical activation of chalcopyrite CuFeS_2 on the selective leaching of copper in sulphuric acid medium.

EXPERIMENTAL

Material

The investigations of selective leaching of copper were carried out with chalcopyrite CuFeS_2 (deposit Slovinky, Slovakia).

The specimens contained admixtures of pyrite and quartz. The chemical composition was: 31,55% Cu, 31,44% Fe, 32,54% S, 4,11% SiO_2 and 0,24% insoluble residuum. The particle size of applied CuFeS_2 before mechanical activation and leaching tests has been under $170 \mu\text{m}$.

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Mechanical activation

Mechanical activation of the mineral under study was performed in a planetary mill Pulverisette 4 (Fritsch, Germany) under the following conditions: weight of mineral - 20 g, grinding means - 25 pieces of balls with diameter 15 mm and 5 pieces of balls with diameter 25 mm, material of grinding means and chambers - tungsten carbide, grinding time 5-30 min, relative acceleration of the mill - $b/g = 10.3$. The planetary mill has been applied as a model milling equipment in order to perform the effective chalcopirite surface and bulk disordering.

Leaching

The leaching was performed in a 500 cm³ glass reactor into which 400 cm³ of leaching solution (170 g/cm³ H₂SO₄) and 0,5 g of chalcopirite was added. The low slurry density has been used in order to contribute for elucidation of leaching mechanism. The leaching was performed for 120 min at 90 °C with a stirring rate of 8,33 s⁻¹, atmospheric pressure and in absence of oxidizing agent. Only atmospheric oxygen was present in glass reactor. Aliquots (1 cm³) of the solution were withdrawn at appropriate time intervals for determination of the contents of the dissolved copper and iron by AAS.

Infrared spectroscopy

Measurements of infrared spectra were performed using an infrared spectrometer SPECORD IR 75 (Carl Zeiss, Germany) by using KBr disc technique (Kössler,

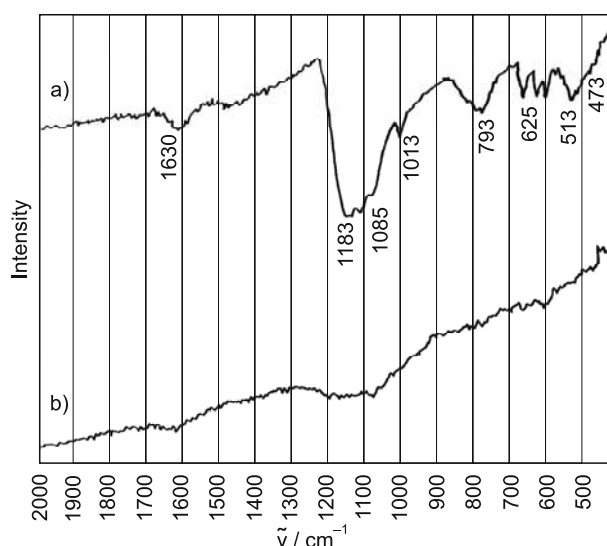


Figure 1. Infrared spectrum of chalcopirite CuFeS₂, mechanically activated 30 min: a) before leaching, b) after leaching
Slika 1. Infracrveni spektar mehanički aktiviranog halkopirita, CuFeS₂, u trajanju 30 minuta: a) prije izluživanja, b) poslije izluživanja

1976). The infrared spectra of standard probes of sulphates (CuSO₄·5H₂O, FeSO₄·7H₂O, Fe₂(SO₄)₃·9H₂O) were taken in order to compare the standard data with the patterns for products of surface mechanochemical oxidation of studied chalcopirite under study.

XRD analysis

The X-ray diffraction measurement were carried out using a diffractometer X'Pert (Philips, Netherland) working in the 2 θ geometry with CuK_α radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards.

Scanning electron microscopy

Scanning electron micrographs were obtained on a BS 300 scanning electron microscope (Tesla, Czech Republic).

RESULTS AND DISCUSSION

Surface mechanochemical oxidation

The surface properties were studied using infrared spectroscopy. This method enables the identification of new compounds formed on the sulphide surface as a result of mechanical activation. Due to a low bond strength of the sulphides, they become instable. In some cases the bonds broke and thus during mechanical activation in air, the appearance of oxidic compounds like oxides, sulphates and oxysulphates can be expected. Their characteristic peaks occur in the range of 700 - 2000 cm⁻¹ [8, 9].

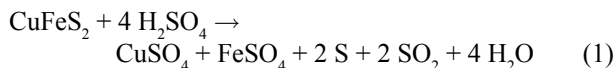
The infrared spectrum of CuFeS₂ on Figure 1.a shows that the mechanical activation resulted in mechanochemical surface oxidation of the mineral. The appearing sulphates are characterised by peaks at 1085, 625 and 473 cm⁻¹. The rest of the peaks belong to admixture of quartz (1183, 1013, 793 and 513 cm⁻¹) and water in the KBr tablet (1630 cm⁻¹). In literature [10, 11] it is stated that on the surface of mechanically activated CuFeS₂ both copper sulphate (CuSO₄) and iron sulphate (FeSO₄) are formed. Moreover, the appearance of Fe(OH)₃ or Fe(O)(OH) is also possible due to the atmospheric oxidation of fresh surface of crystals of natural CuFeS₂ [12].

Acid leaching

The rate of leaching of sulphide minerals is usually low, especially in the case of H₂SO₄ application at atmospheric pressure without oxidant addition. When oxidant is added the leaching is usually enhanced [13 - 15]. Only few sulphides, e.g. ZnS, NiS, CoS and FeS are soluble in dilute H₂SO₄ solutions [16]. Sulphuric acid is a cheap and plentiful material emergent consequently from the sulphide

values of the ores being processed [17]. The rate of sulphide leaching can be enhanced by process of mechanical activation [1].

Leaching of chalcopyrite in concentrated H_2SO_4 solutions takes place at a reasonable rate between 150 - 250 °C. In this temperature interval there is a formation of elemental sulphur, copper and iron sulphates. The overall reaction is:



The process has the advantage of forming elemental sulphur, but the disadvantage of solubilizing iron and the necessity of regenerating H_2SO_4 by decomposing the ferrous sulphate. However, below 150 °C there is no reaction [18].

We have tried to achieve relative good recoveries of copper and iron metals by using H_2SO_4 acid leaching at 90 °C and at atmospheric pressure. The selected results for mechanically inactivated as well as for mechanically activated $CuFeS_2$ during 30 minutes are given in Figure 2.

There is a very small efficiency in Cu and Fe metals extraction for mechanically activated $CuFeS_2$ (Figure 2.a). In this case the recoveries are not higher than 6%. However, the maximum recovery of 36% Cu and 24% Fe has been obtained for $CuFeS_2$ mechanically activated during

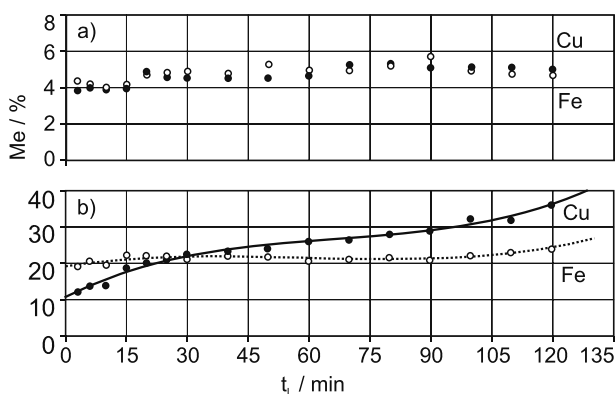


Figure 2. Recovery of metals into the solution, Me vs. leaching time t_l for $CuFeS_2$: a) mechanically inactivated, b) mechanically activated 30 min

Slika 2. Izdvajanje metala u otopinu, metal nasuprot vremenu izluživanja t_l za $CuFeS_2$: a) mehanički neaktiviran, b) mehanički aktiviran

30 minutes (Figure 2.b). This is in agreement with infrared spectra on Figure 1.b from which it follows that an acid leaching of mechanically activated chalcopyrite resulted in a nearly complete disappearance of peaks characteristic for Fe and Cu sulphates. However the absorbance curve is not flat as a consequence of admixed SiO_2 (quartz). Quartz is refractory in H_2SO_4 medium and that is why is still present in the infrared spectrum after leaching.

In the course of reaction the leaching agent attacks the plastically deformed cores of $CuFeS_2$ particles, the def-

ectiveness of which increases with the time of mechanical activation. The iron content in the leachate is practically constant and only copper is preferentially leached. Tkáčová et al. [19] found the same tendency for a series of mechanically activated $CuFeS_2$ leached out in HCl.

The deeper insight into the bulk behaviour of the mechanically activated and leached chalcopyrite is illustrated by the XRD patterns in Figure 3. There is an evidence of small amounts of crystalline copper sulphate $CuSO_4 \cdot 5 H_2O$ in mechanically inactivated samples of $CuFeS_2$ which is consequence of mineral aging in the air environment (Figure 3.a). The bulk sample of $CuFeS_2$ is strongly amorphized as can be deduced from the pattern changes (Figure 3.b). Moreover, the copper sulphate peaks are no more visible

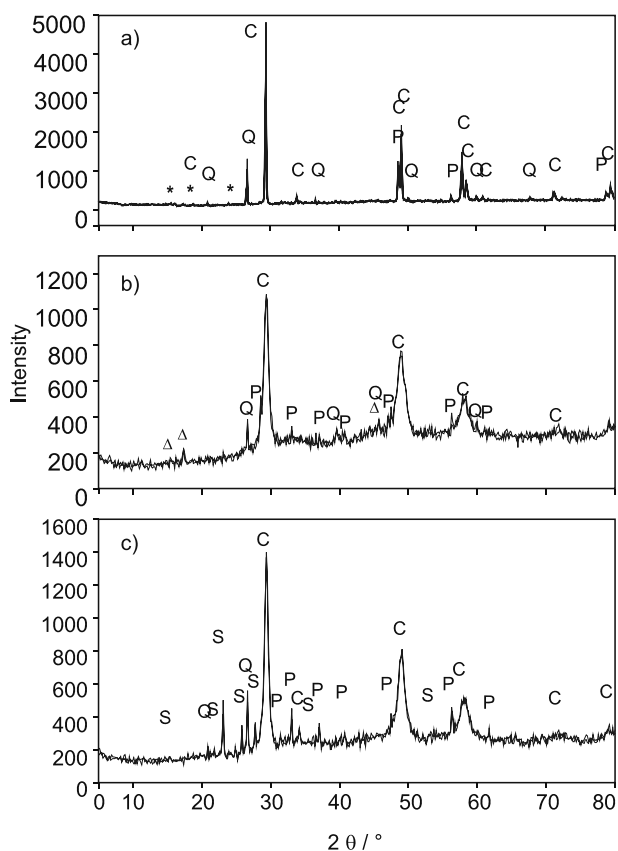


Figure 3. X-ray diffractometry of $CuFeS_2$: a) mechanically inactivated; b) mechanically activated 30 min; c) sample b) after leaching in H_2SO_4 C - chalcopyrite $CuFeS_2$ (JCPDS 35-0752), Q - quartz SiO_2 (JCPDS 33-1161), P - pyrite FeS_2 (JCPDS 06-0710), S - sulphur S (JCPDS 08-0247), * - chalcantite $CuSO_4 \cdot 5H_2O$ (JCPDS 11-0646), Δ - iron sulphate hydrate $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$ (JCPDS 18-0644)

Slika 3. Rentgenska difrakcijska slika $CuFeS_2$: a) mehanički neaktiviran; b) mehanički aktiviran u trajanju 30 minuta; c) uzorak b) poslije izluživanja u H_2SO_4 C - halkopirit, $CuFeS_2$ (JCPDS 35-0752), Q - kremen, SiO_2 (JCPDS 33-1161), P - pirit, FeS_2 (JCPDS 06-0710), S - sumpor, S (JCPDS 08-0247), * = halkantit, $CuSO_4 \cdot 5H_2O$ (JCPDS 11-0646), Δ - željezov sulfat dihidrat $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$ (JCPDS 18-0644)

which is consequence of its strong amorphization. However, the iron sulphate hydrate $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2 \text{H}_2\text{O}$ has been detected. The same mechanically activated sample has been leached out in H_2SO_4 medium and also X-ray examined (Figure 3.c). The presence of elemental sulphur as the only solid phase is in a good agreement with the reaction (2) and scanning electron micrograph in Figure 4.d. There is no evidence of some new copper and iron sulphide phases as a consequence of chalcopyrite phase transformation during mechanical activation.

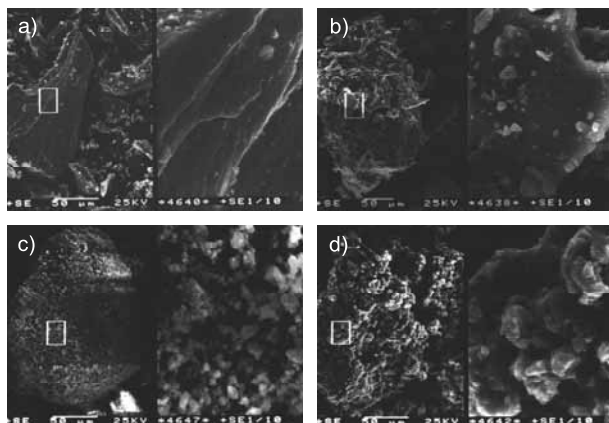


Figure 4. Scanning electron micrographs of chalcopyrite CuFeS_2 : a), b) mechanically inactivated (170 μm); c), d) - mechanically activated (20 min); a), c) before leaching; b), d) - after leaching
Slika 4. Pretražna elektronska mikrofografija halkopirita, CuFeS_2 : a), b) - mehanički neaktiviran, ispod 170 μm ; c), d) - mehanički aktiviran 20 minuta; a), c) - prije izluživanja; b), d) - poslije izluživanja

The promotion of leaching by mechanical activation is a phenomenon common for many minerals [1, 4, 20]. However, the selective effect of the grinding upon one part of the crystal lattice is a characteristic feature for minerals with close - packed structural units [21].

Figure 4.a shows the grains of chalcopyrite before leaching. The surface of the leached chalcopyrite (Fig 4.b) is more rough and small particles are stuck to the bigger ones. The small number of sulphur particles can be seen in right side of this picture. The mechanical activation of CuFeS_2 results in a greater portion of finer particles and the formation of agglomerates which may have dimensions comparable to those of non-activated particles (Figure 4.c). The sample after leaching (Figure 4.d) have much more roughed surface in comparison with Figure 4.b and it seems the small grains are more compacted probably by coating with elemental sulphur as observed by Dutrizac [22].

CONCLUSIONS

On basis of the obtained results it is possible to conclude that mechanical activation affects the selectivity of leaching

of chalcopyrite CuFeS_2 . Mechanical activation resulted in an increased specific surface area, structure disorder and in the appearance of sulphates on the surface of CuFeS_2 . The products of mechanochemical surface oxidation are easily soluble and thus in the initial step of leaching positively affect the rate of copper and iron extraction. With the increase of mechanical activation in time, the number of structural defects of the mineral increases together with an increase of specific surface area. It has been shown that increase of copper leaching apart from the leaching of iron is influenced by mechanical activation of the mineral.

REFERENCES

- [1] P. Baláž, Extractive Metallurgy of Activated Minerals, Elsevier, Amsterdam, 2000, pp. 270.
- [2] M. Senna, Part. Part. Charact. 6 (1989), 163 - 167.
- [3] K. Tkáčová, P. Baláž, B. Mišura, V. Vigdergauz, V. V. Chanturiya, Hydrometallurgy 33 (1993), 291 - 300.
- [4] N. J. Welham, CIM Bulletin 90 (1997), 64 - 68.
- [5] N. J. Welham, D. J. Llewellyn, Miner. Engn. 11 (1998), 827 - 841.
- [6] M. Achimovičová, Acta Montanistica Slovaca 3 (1998), 172 - 176 (in Slovak).
- [7] I. Kössler, Quantitative Infrared Spectroscopy, SNTL, Prague, 1970 (in Czech).
- [8] A. I. Boldyrev, Infrared Spectra of Minerals, Nedra, Moscow, 1976 (in Russian).
- [9] V. C. Farmer, (Ed.), The Infrared Spectra of Minerals, Monograph 4, Mineralogical Society, London, 1974.
- [10] D. Brion, Applications on Surface Science 5 (1980), 133 - 152.
- [11] E. Godočiková, P. Baláž, Z. Bastl, L. Brabec, Applied Surface Science 200 (2002), 36 - 47.
- [12] A. N. Buckley, R. Woods, Proceedings, International Symposium on Electrochemistry in Mineral and Metallurgical Processing, New York, 1984, P.E. Richardson, S. Srinivasan, R. Woods (eds.), The Electrochem. Soc., Pennington, 1984, pp. 286 - 301.
- [13] M. M. Antonijevic, Z. D. Jankovic, M. Dimitrijevic, Hydrometallurgy 35 (1994), 187 - 201.
- [14] M. M. Antonijevic, Z. D. Jankovic, M. D. Dimitrijevic, Hydrometallurgy 71 (2004), 329 - 334.
- [15] M. M. Antonijevic, G. D. Bogdanovic, Hydrometallurgy 73 (2004), 245 - 256.
- [16] F. Habashi, A Textbook of Hydrometallurgy, Metallurgie Extractive Quebec, Quebec, 1993.
- [17] F. Habashi, Sulphur 140 (1979), 37 - 42.
- [18] F. Habashi, Chalcopyrite its Chemistry and Metallurgy, McGraw Hill, New York, 1978.
- [19] K. Tkáčová, V. V. Boldyrev, J. T. Pavljuchin, E. G. Avvakumov, R. Š. Sadykov, P. Baláž, Mössbauer investigations of structural changes in the mechanically and thermally activated chalcopyrite, Izvestija sibirskogo otdelenija akademii nauk SSSR, serija chimičeskich nauk, 2 (1984), 9 - 13 (in Russian).
- [20] K. Tkáčová, Mechanical Activation of Minerals, Elsevier, Amsterdam, 1989.
- [21] K. Tkáčová, P. Baláž, Int. Journal of Miner. Proc. 44 - 45 (1996), 197 - 208.
- [22] J. E. Dutrizac, Can. Met. Quart. 28 (1989), 337 - 344.

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