Copper Leaching from Chalcopyrite: Mechanochemical Approach

Matej TEŠINSKÝ[1)], Peter BALÁŽ[2)]

[1)] Ing., Ph.D.; Institute of Geotechnics of SAS, Watsonova 45, 04353 Košice, Slovak Republic, email: tesinsky@saske.sk
[2)] Prof. RNDr., DrSc.; Institute of Geotechnics of SAS, Watsonova 45, 04353 Košice, Slovak Republic; email: balaz@saske.sk

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Abstract

In the presented work, possibilities of intensification of copper leaching from chalcopyrite $CuFeS_2$ induced by mechanical activation was studied. In this article, the influence of mechanical activation time on copper leaching efficiency is compared. This study also shows how mechanical activation time influences selectivity of copper and iron leaching. For mechanical activation, planetary mill Fritsch Pulverisette 6 at 400 rpm and room temperature was used. Grinding chamber (250 cm³ in volume) and 50 balls (10 mm in diameter) made of tungsten carbide were used. Specifically, the effect of mechanical activation time (4, 20, 30 minutes), the effect of temperature (40, 60, 80°C) on the copper recovery by leaching and the effect of the leaching atmosphere (air, argon) were examined. The results showed that the highest possible recovery of copper from chalcopyrite was obtained after 20 minutes of milling and leached in hydrochloric acid at 80°C, with air atmosphere without any oxidizing reagents.

Keywords: milling, mechanical activation, leaching, chalcopyrite

Introduction

The mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes such a degree of disordering that the thermal activation may be omitted entirely. The mineral activation leads to a positive influence on the leaching reaction kinetics, to an increase in the measured surface area and to further phenomena, especially the potential mitigation of environmental pollutants which is becoming increasingly important with the time. At present, it is not known whether the kinetics of heterogeneous reactions are determined by the contact area, the structure of the mineral, or both. The required modification of the structure can be achieved by mechanical activation of the mineral, typically by high-energy milling. The breaking of bonds in the crystalline lattice of the mineral brings about a decrease in activation energy and an increase in the rate of leaching (1).

Chalcopyrite is the most abundant copper-bearing mineral containing nearly equal parts of copper, iron, and sulfur. Chalcopyrite can be readily floated from finely ground disseminated ores. Flotation concentrate containing at least 90% of the mineral is usually obtained and the remaining 10% contains other sulfide minerals, gangue and moisture. Depending on deposit, an approximate analysis of an industrial flotation concentrate is 30% Cu, 30% Fe and 30% S (2). Chalcopyrite covers 70% of the world copper sources (3) (4). The extraction of copper from minerals may be conducted using two different processes: the pyrometallurgical and the hydrometallurgical. The pyrometallurgical process has dominated the copper industry since the late nineteenth century (5).

Production of copper by pyrometallurgical method is energy intensive and environmentally unfriendly because a lot of solid and gaseous wastes are created (2) (6). Sulfur removal is carried out in several steps and sulfur in the final form occurs as sulfur dioxide. If the sulfur content in the ore is converted directly into the elemental form it can at least eliminate the urgent problem of air pollution by smelter gases and at the same time, produce a by-product that can be readily stored or shipped. This can be achieved by hydrometallurgical methods. Producing hydrogen sulfide from chalcopyrite is more convenient than producing sulfur dioxide because hydrogen sulfide can be oxidized to elemental sulfur at low energy levels, while the reduction of sulfur dioxide to elemental sulfur involves high energy. The problem of iron is not as urgent as that of sulfur (2).

Production of copper by hydrometallurgical method has also some disadvantages. Processing cannot be provided without the addition of oxidizing reagents and the elevated pressures and temperatures are frequently required (7). This is due to the fact that copper sulfides are relatively refractory (resistant to degradation), which is due to the nature of the crystal structure. However, processing with the oxidizing reagents make the whole process economically unstable, which results into the overcharge of pyrometallurgy, despite the fact the hydrometallurgical treatment is an environmentally more friendly method (7) (8). This is the reason why the hydrometallurgical treatment is not used as a major method. Current efforts and innovative trends in the leaching of sulfides are using chemicals, physical-chemical, physical and other specific methods

Tab. 1 Chemical composition of chalcopyrite from Slovinky

Tab. 1. Skład chemiczny chalkopirytu ze złoża Slvinky

Component	Cu	Fe	S	SiO_2	Insoluble residuum
[%]	31,55	31,44	32,54	4,11	0,24

Tab. 2 Specific surface area of mechanically activated $CuFeS_2$

Tab. 2. Powierzchnia właściwa CuFeS2 po aktywacji mechanicznej

Milling time [min]	**Specific surface area** [$m^2.g^{-1}$]
0	0.28
4	2.67
20	2.7
30	2.63

(7) (9) (10). The intensification of chalcopyrite leaching can also be provided with mechanical pretreatment (mechanical activation) which means, that the mineral is submitted to high energy milling (11).

It is well known that chalcopyrite leaching in hydrochloric acid, without the addition of oxidizing reagents, at low temperatures and pressures can be described by the equation (1)

$$CuFeS_2 + 4HCl \rightarrow CuCl_2 + FeCl_2 + 2H_2S \quad (1)$$

However, without oxidants and high temperatures and pressures, the recovery of metals into leach is very low (12).

The aim of this work is to assess the possibility of performing chalcopyrite leaching according to the previously mentioned equation (1) at ambient pressure and temperature and thus enhance the metals recovery. As the main tool mechanical activation $CuFeS_2$ will be applied.

Materials and Methods

Chalcopyrite preparation

Chalcopyrite from Slovakia (deposit Slovinky) was used for all experiments. The chalcopyrite applied for mechanical activation has been obtained by sieving to particle size 170 μm. The mechanical activation was performed in a planetary mill Fritsch Pulverisette 6 at 400 rpm in an argon and air atmosphere for different milling times: 4, 20, 30 minutes. Milling chamber (250 cm^3 in volume) and 50 balls (10 mm in diameter) made of tungsten carbide were used. X-ray diffraction (XRD) quantitative analysis indicated that the sample contained chalcopyrite ($CuFeS_2$) and (SiO_2). The chemical analysis of the used sample is shown in tab.1.

Leaching procedure

Leaching was performed in a 1000 ml leaching reactor which was immersed in a thermostated water bath under atmospheric pressure. The temperature of the bath was: 40, 60, and 80°C. The leaching solution was added to the reactor when the required temperature was reached. Copper and iron in the solution was determined by atomic absorption spectrometry method (AAS).

Results and discussion

The values of specific surface area are listed in Table 2. After 4 minutes of mechanical activation specific surface area was stable as a consequence of mechanochemical equilibrium.

Mechanically activated samples were treated by leaching and the dependence of efficiency copper and iron leaching on the time of mechanical activation is presented in Figs. 1. These plots show that with increasing mechanical activation, the efficiency of copper and iron leaching also increase. After 20 minutes of mechanical activation, decreasing efficiency of leaching copper is observed, which can be caused by structural changes after a longer time of mechanical activation. Specific surface area has no impact on leaching efficiency due to fact that after 4 minutes of mechanical activation, there are no significant changes. In this case the reaction (1) is structure sensitive. The effect was also observed in (13) for chalcopyrite leaching by $Fe_2(SO_4)_3$.

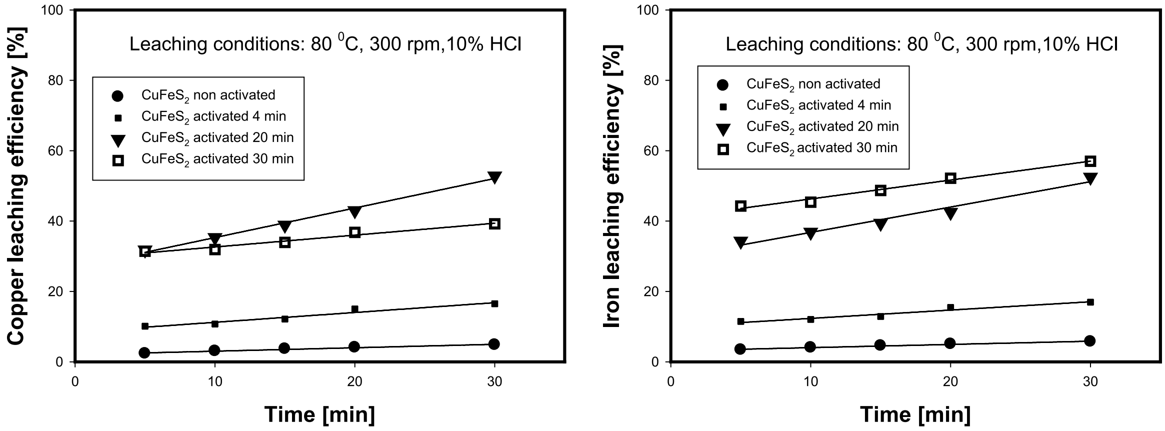

Fig. 1 Efficiency of copper and iron leaching in dependance on time of mechanical activation

Rys. 1 Efektywność ługowania miedzi i żelaza w zależności od czasu aktywacji mechanicznej

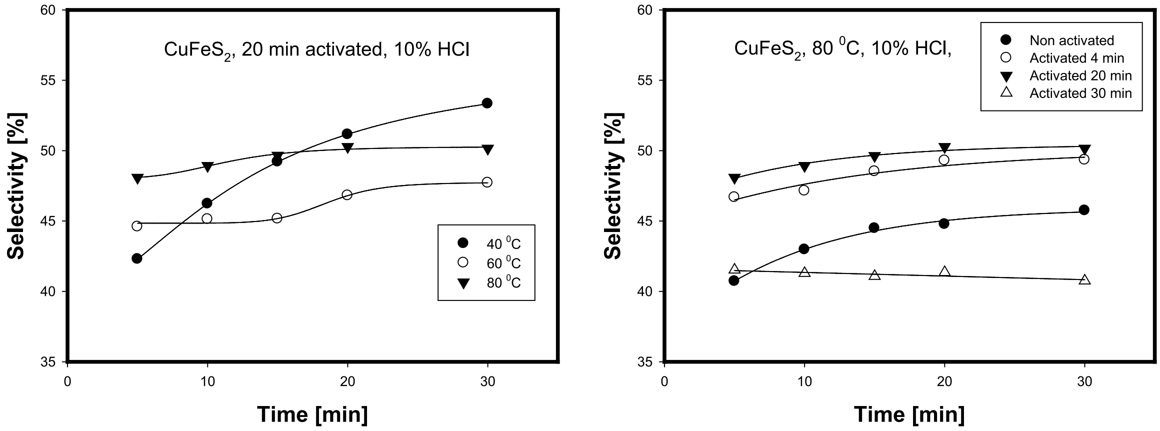

Fig. 2 Selectivity of copper leaching in dependance on temperature (right) and time of mechanical activation (left)

Rys. 2 Selektywność ługowania miedzi w zależności od temperatury (po prawej) i czasu aktywacji mechanicznej (po lewej)

In Figs. 2 the selectivity of the leaching of iron and copper, depending on temperature and time of mechanical activation is shown. Depending on temperature the highest selectivity was obtained during leaching at 40°C, but efficiency of copper leaching at this temperature was not the highest possible. Depending on the mechanical activation time, it is observed that after 20 minutes the selectivity has a decreasing trend. It can by caused also by the primary leaching of iron. Selectivity (S) of copper leaching can be described to equation (2)

$$S = \frac{Cu\,recovery}{Cu\,recovery + Fe\,recovery} * 100\ (\%) \qquad (2)$$

Plots on Fig. 3 shows the efficiency of leaching copper from a chalcopyrite sample under different conditions. Results show that leaching of copper in an argon atmosphere has a negative effect on the efficiency of leaching compared to air atmosphere. The highest efficiency was achieved with the sample which was leached under air atmosphere. For elucidation of this experimental fact, further experiments are needed in order to describe the surface chemical composition of leached chalcopyrite.

Conclusion

Impact of mechanical activation on copper leaching and selectivity of copper and iron leaching was observed in this paper. Nowadays, it is still important to continue improving the copper extraction process from chalcopyrite by the hydrometallurgical way. This is because hydrometallurgy seems to be more environmentally friendly then pyrometallurgy, due to reasons mentioned above in this article. The mechanical activation method offers a great advantage in commercial utilization of the copper recovery, by leaching from chalcopyrite in the more environmental way in comparison to other intensification possibilities. This is due to fact that mechanical activation pretreatment can raise recovery of copper during leaching process without any oxidizing additions, which means there is no need using

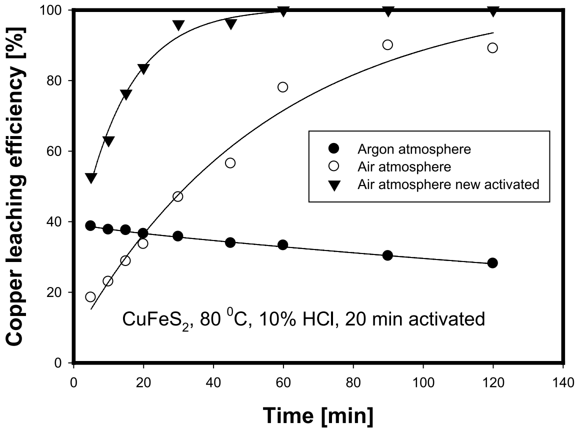

Fig. 3 Efficiency of copper leaching in different leaching atmospheres

Rys. 3 Efektywność ługowania w różnych atmosferach

of oxidizing reagents. This very promising intensification method can in the future lead to improvements in the copper recovery process from minerals. Specifically, the lowering of costs can be observed in the whole copper processing by using hydrometallurgy.

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Ługowanie miedz z chalkopirytu – aspekt mechaniczny i chemiczny

W artykule przedstawiono możliwości intensyfikacji procesu ługowania miedzi z chalkopirytu $CuFeS_2$ za pomocą aktywacji mechanizcnej. Zbadano wpływ czasu aktywacji mechanicznej na efektywność ługowania miedzi. Wyniki badań pokazały również wpływ czasu na selektywnośc rozdziału miedzi i żelaza. Do aktywacji mechanicznej wykorzystani młyn planetarny Fritsch Pulverisette 6, aktywację prowadzono przy obrotach 400 rpm, w temperaturze pokojowej. Do badan wykorzystano komorę mielenia o objetości 250 cm^3 i 50 kul o średnicy 10 mm wykonanych z węglika wolframu. Określono wpływ czasu aktywacji mechanicznej (4, 20, 30 minut), wpływ temperatury (40, 60, 80°C) na odzyskmiedzi w procesie lugowania w atmosferze powietrza i argonu. Wyniki wskazują, że najwyższy możliwy odzysk miedzi z chalkopirytu uzyskano po 20 minutach mielenia i ługowaniu w kwasie solnym w temperaturze 80°C, w atmosferze powietrza, bez jakichkolwiek czynników utleniających.

Słowa kluczowe: mielenie, aktywacja mechaniczna, lugowanie, chalkopiryt