

Microwave Leaching of Chalcopyrite - Possible Improvement in Hydrometallurgy

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The leaching characteristics of chalcopyrite concentrate pre-treated by a new method and leached in water were investigated in this study. In the pre-treatment phase the chalcopyrite concentrate was mixed with acidified FeCl_3 solution and exposed to a microwave field. The dry paste of chalcopyrite with $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ was exposed to the microwave field for 15 minutes. The originated intermediate product was leached in ordinary cold water during 5 minutes. The copper leaching efficiency achieved was 55.2 %. The duration of the microwave pretreatment, intermediate product leaching time in water, chalcopyrite / FeCl_3 mixture ratio, water addition into dry mixture as well as HCl addition into mixture were investigated in this case. The optimum conditions for this new pre-treatment method in laboratory scale were defined.

The most common raw materials for copper hydrometallurgical treatment are chalcopyrite concentrates. Unfortunately, these are also considerably resistant against leaching processes. Although at present the pyrometallurgy of copper is predominant, the hydrometallurgical and biometallurgical methods for chalcopyrite treatment have become more common. The main reason for the increasing interest in hydrometallurgical processes lies probably in the variable raw material quality as well as in the ecological legislation, which is becoming more stringent. Fig. 1 shows the tendency of copper hydrometallurgical production [1, 2]. Our previous works have been focused on finding effective methods of chalcopyrite leaching in comparison to classical leaching methods, which use acidified ferric chloride or ferric sulphate leaching solutions [3, 4].

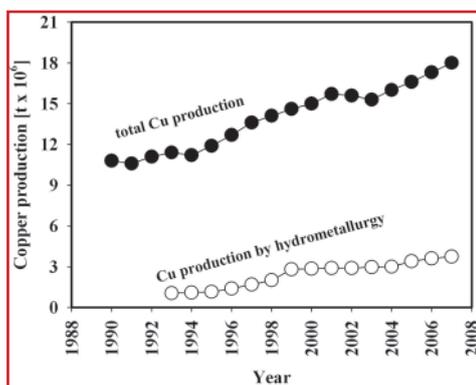


Fig. 1: Tendency of copper production [1, 2]

When ferric sulphate [5, 6] was used as a leaching medium within the temperature range 20 - 99 °C, the chalcopyrite leaching resulted in a change of the leaching mechanism. At temperatures 20 - 40 °C the apparent activation energy was $E_A = 12 \text{ kJ/mol}$. The rate-controlling step was the leaching agent diffusion onto the leaching surface. At higher temperatures the apparent activation energy $E_A = 69 \text{ kJ/mol}$ was detected. The rate-controlling step was the chemical reaction kinetics on the leaching surface. The mineral surface was covered by solid reaction product, e.g. elemental sulphur.

Within the temperature range 3.5 - 95 °C the leaching curves for chalcopyrite exhibited the parabolic character with apparent activation energy $E_A = 55 \text{ kJ/mol}$ in ferric chloride medium [7-10]. The overall reaction rate was controlled by chemical kinetics, probably by the generation of an elemental sulphur layer on the leached mineral surface.

Carbon tetrachloride, CCl_4 , was used as a solvent for the elemental sulphur produced during the chalcopyrite leaching by ferric chloride [11]. These tests showed also a higher extraction for copper. The activation energy value of 31.2 kJ/mol in the temperature range 45 - 80 °C indicated a diffusion-controlled process. Also the sulphur dissolution in carbon tetrachloride had some role in this leaching process.

When gas atmosphere containing ozone in the sulphuric acid medium

[12-14] was used, the more effective leaching of chalcopyrite was gained. The copper yield was higher than with all the methods described above. The highest efficiency is achieved at ca. 20 °C defined by the solubility of ozone in the aqueous solutions. The advantage of these media is that they do not require any regeneration.

Because of the temperature dependencies of the ozone solubility in the aqueous solutions, it was impossible to determine the activation energy value for the ozone leaching.

However, the experimental results revealed that the chemical reaction on the leached mineral surface is rate controlling.

The leaching of chalcopyrite in the sulphuric acid in the presence of ozone atmosphere does not depend on the acid concentrations. Sulphuric acid is needed only to avoid iron hydrolysis. The process is accelerated with the increasing ozone concentration in the working atmosphere.

Chalcopyrite has also been leached in the high - frequency field [15]. Likewise above, no activation energy value could be determined. That is because when using high - frequency energy, only process leaching temperatures near the boiling point of solution are possible.

The heating rate was extremely high and the leaching efficiency higher than with the methods described above. Not only increasing ferric ion concentration, but also arising acidity had a positive influence on the extraction. These factors do not apply in classical leaching methods.

When chalcopyrite was leached in the microwave field [16, 17], the experimental arrangement was principally the same as in the previous case; however, microwave energy was used. The heating rate was again very high as well as the achieved leaching efficiency. The existence of commercial microwave equipment was an additional advan-

Material	Leaching medium	E _A [kJ/mol]	t [°C]	Cu efficiency (120 min leaching)	Mechanism	Feature
CuFeS ₂	Fe ₂ (SO ₄) ₃ + H ₂ SO ₄	12	20 - 40	0.36 / 40 °C	mass transfer	elemental sulfur origination
	Fe ₂ (SO ₄) ₃ + H ₂ SO ₄	69	40 - 95	7.99 / 95 °C	chemical reaction	elemental sulfur origination
	FeCl ₃ + HCl	55	3.5 - 95	14.85 / 95 °C	chemical reaction	elemental sulfur origination
	FeCl ₃ + HCl + CCl ₄	31.2	45 - 80	16.57 / 80 °C	mass transfer, sulfur dissolution in CCl ₄	no elemental sulfur observed on interface
	H ₂ SO ₄ + O ₃		22	23.4 / 22 °C	chemical reaction	no elemental sulfur observed on interface
	FeCl ₃ VHF heating		104	27.4 / 104 °C	parabolic kinetics mass transfer	reaction in solid state
	FeCl ₃ microwave heating		104	33.2 / 104 °C	parabolic kinetics mass transfer	900 W

Tab 1: Chalcopyrite leaching kinetics and mechanism results [5]

tage. Both high-frequency and microwave field have the advantage that the perfect pulp stirring is achieved by boiling, without any mechanical facility. An excellent overview of microwave leaching was given by Al-Harahsheh [18]. In this paper a new method of microwave leaching is described. This method is based on the pre-treatment in which a mixture of chalcopyrite and ferric chloride is prepared and heated for a short time in the microwave field. Also a small amount of water or HCl is added in the mixture. By the solid-state chemical reactions, easily soluble compounds can be produced, and these can be transferred into the solution after a short time leaching in ordinary water. The achieved copper extraction efficiencies are much better than in all the cases described above (Tab. 1, Fig. 2).

Experimental part

The experiments were carried out with chalcopyrite concentrate from Cuba with the chemical composition of 32.3 % Cu, 28.4 % Fe, 31.9 % S and 5.61 % of insoluble oxides determined by AAS method. The fraction -80 +60 μm was separated by screening and used for leaching in most of experiments. The X-ray phase analysis of the concentrate revealed that the sample contains

mainly chalcopyrite CuFeS₂ (JCPDS-ICDD index 9-423), a small amount of quartz SiO₂ (index 5-490) and sillimanite Al₂SiO₅ (index 10-369). To carry out these experiments, a microwave oven with an adjustable power (up to 900 W) and microwave frequency of 2450 MHz adapted with special devices for heating and leaching was used. Fig. 3 shows the scheme of the experimental apparatus.

Results

Microwave action influence

Initially, 2 g of chalcopyrite, an equimolar amount of ferric chloride (6.5 g) and 5 ml water were used in the experiments. This mixture was exposed to the microwave field for 1, 5, 10, 15, 20, 45 or 60 min. No temperature was measured during the experiment. The originated intermediate product was leached immediately after the heating using cold water (normally 200 ml). Fig. 4 shows the copper dissolution efficiency as a function of time of the microwave action and the influence of both water and HCl used in the charge.

Fifteen minutes of microwave action was observed to be the best time for the heating of chalcopyrite - ferric chloride mixture. As shown in Fig. 5, all cop-

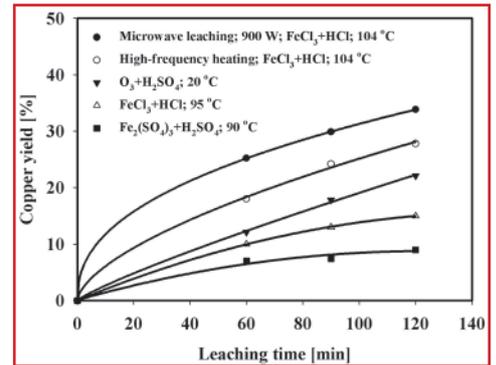


Fig 2: Comparison of various kinetic chalcopyrite-leaching curves

per available was dissolved practically immediately, and no more copper was dissolved even after 24 hours. For that reason a five minute leaching period was defined as the standard leaching time in the following experiments.

Influence of the leaching water amount

Fig. 6 shows the influence of the leaching water amount on copper efficiency. It can be clearly seen that 200 ml is an optimum amount of leaching water for the defined charge amount. The bigger volumes uselessly dilute the leachate.

Influence of the ferric chloride amount in charge

Fig. 7 shows the copper leaching efficiency as a function of the ferric chlo-

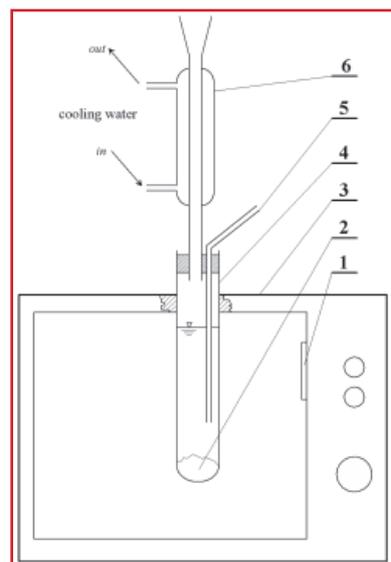


Fig. 3: Scheme of apparatus for microwave leaching

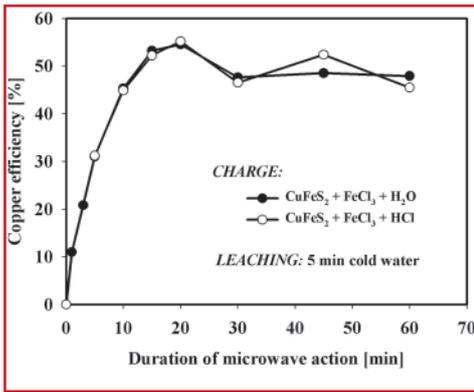


Fig. 4: Influence of leaching time on copper efficiency at various time periods of microwave action.

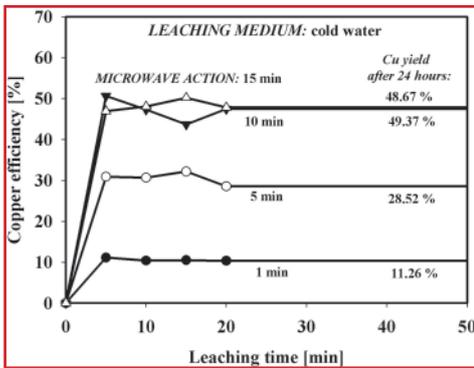


Fig. 5: Copper efficiency vs. leaching time dependence at various time periods of microwave action

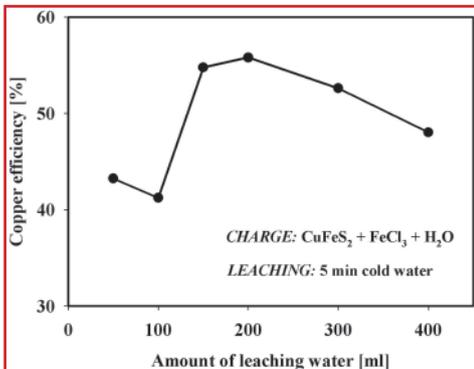


Fig. 6: Copper efficiency vs. leaching water amount dependence

ride amount in charge. It can be seen that the optimum amount of ferric chloride in the charge is the stoichiometric amount of salt.

Influence of the water amount in charge

Fig. 8 shows the influence of water amount in charge on copper efficiency.

Five millilitres of water for a defined charge (2 g CuFeS₂) give the optimum copper dissolution efficiency. The increase of water amount causes the situation according to which the relative part of microwave radiation will be absorbed in water, and that is why it will not influence the solid state chemical reaction. The additional increase of water amount causes the pulp creation instead of paste, like in the classical leaching cases. In such case the chemical reaction will take place in the liquid-solid state and not in the solid-solid state.

Influence of HCl in charge

Fig. 4 shows the similarity in the leaching curves, when water or HCl is used in charge. The copper efficiency in both cases is practically the same. However, the experiments with various concentrations of HCl added in the charge were carried out. The results are shown in Fig. 9.

Although the copper efficiency is higher at HCl concentrations in the range 0.25 - 0.5 M/L, using pure water, better or at least similar results can be achieved. The reason could be again in partial consumption of the microwave energy for the interaction with HCl. The comparison of the results achieved by leaching of chalcopyrite pulp in the microwave field and the results achieved by the heating of chalcopyrite and ferric chloride dry mixture followed by leaching in cold water reveals that the latter is a more effective method, as shown in Fig. 10. Moreover, by this new method not only higher copper efficiency is achieved, but the efficiency is practically achieved immediately after starting the leaching experiment.

Stability of leached metals in the solution

By heating of chalcopyrite-ferric chloride mixture the solid state reaction takes place according to $CuFeS_2 + 4 FeCl_3 \rightarrow CuCl_2 + 5 FeCl_2 + 2 S$ $\Delta G_{100}^0 = -167.365 \text{ kJ/mol}$ (1)

The reaction takes place on the solid-liquid phase interface, and because

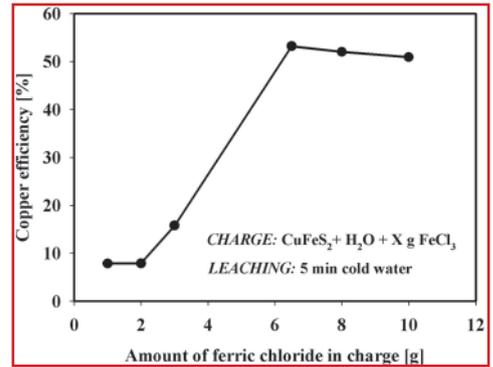


Fig. 7: Copper efficiency vs. ferric chloride amount in charge

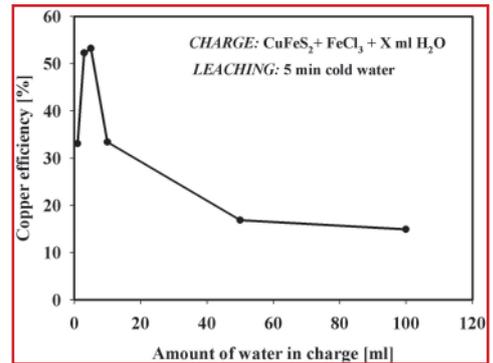


Fig. 8: Copper efficiency vs. water amount in charge

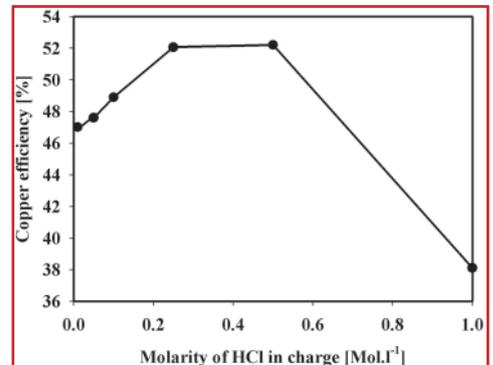


Fig. 9: Copper efficiency vs. HCl concentration in charge

of a relatively small interface area its progress is also relatively slow. Both soluble copper and iron ions are transferred into solution. As follows from eq. (1), the presence of the acid is not necessary for the reaction, but the acid medium (pH < ~ 2) is necessary to avoid hydrolytic precipitation of iron from the solution. However, in the next step of solution treatment iron causes technological troubles, which increases the price of the entire process.

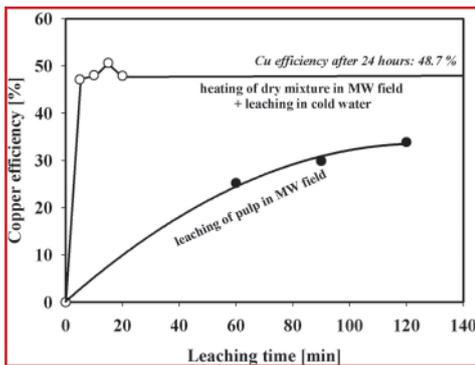


Fig. 10: Leaching of chalcopryrite pulp in the microwave field compared to the pre-treated chalcopryrite - ferric chloride mixture leaching in cold water

A big amount of energy is coming to the system by the microwave heating of chalcopryrite-ferric chloride mixture. The reaction (1) takes place in solid state and whole charge volume, not only on the surface like in the previous case. Both cupric and ferrous chlorides are well soluble in water. That is why placing both of them in cold water is sufficient for their total dissolution. Due to the absence of acid in the system, or presence of a very small amount of acid, the pH of the solution is stabilized at a higher value ($\text{pH} \approx 4$). This one does not ensure the stability area of soluble iron ions in the solution. Iron starts gradually precipitate by hydrolysis, and only copper remains in the solution. This is a very significant advantage of this method, because the automatic separation of metals in the solution occurs. The precipitated iron in the goethite form can be filtered out. Fig. 11 shows the goethite precipitation from samples being under microwave radiation for various time periods within the range from 1 to 60 minutes followed by the leaching in water for five minutes.



Fig. 11: Hydrolytic precipitation of goethite from lixiviant

Conclusions

The advantage of this new pre-treatment method combined with the leaching in cold water is as follows:

- simple process;
- reactions take place under normal pressure;
- extremely short reaction and leaching time;
- cheap and neutral leaching medium - water;
- copper leaching efficiency is the highest among the methods which have been investigated;
- ecological advantage - no acid in the leaching process;
- the availability of commercial microwave equipment for this pre-treatment.

Microwave leaching of chalcopryrite seems to be a new promising method for copper extraction. A comparison of the chalcopryrite leaching results in various leaching solutions with several leaching methods reveals that the microwave leaching is a very effective leaching method, giving the best copper extraction of the methods studied.

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