

Chemical metathesis of chalcopyrite in acidic solutions

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Abstract

The chemical metathesis of chalcopyrite in the presence of cupric ions was studied in sulphuric acid solutions. The effects of stirring, Cu(II) concentration, temperature and annealing were investigated by leaching and kinetic experiments. The primary reaction involved in the chemical metathesis leads to the formation of covellite, which is followed by an oxidation–reduction couple, with digenite production. This second step was found to be very slow requiring sub-sieve size particles for extensive reaction. The reaction was insensitive to the copper ion concentrations, and practically insensitive to stirring speed. The strain induced by stirred ball milling enhanced the reaction rate markedly due to the recrystallisation process which provides easy paths for diffusion along dislocation and grain boundaries. The kinetics were well correlated with a two-stage product layer diffusion model, with apparent activation energies less than 30 kJ mol^{−1}, and ferrous ion was found to be the rate determining diffusion species through the covellite phase (first stage) and covellite and digenite phase (second stage).

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1. Introduction

In recent years, there has been an increasing interest in the development of new copper hydrometallurgical processes to minimise air pollution problems due to low grade SO₂ emissions from conventional smelters. Copper has been produced almost exclusively by smelting and converting methods which achieve high recoveries of copper and precious metals (Davenport et al., 2002). Although hydrometallurgical processes do not provide clear-cut advantages over existing pyrometallurgical processes, they do offer several possible alternative means for producing copper from sulphide minerals without producing gaseous SO₂ (Burkin, 2001).

Among copper bearing minerals, most research has been conducted with chalcopyrite since it is the most abundant and most refractory of all copper sulphides. A few copper hydro-

metallurgical processes have been developed and carried to pilot and full scale operation such as the Arbiter process, the CLEAR process, the Cymet process and the Sherritt–Cominco process. Apart from the leaching, conversion of chalcopyrite into a more leachable form may play an important role for these processes. Among several processes, this conversion could be performed by simple heat treatment such as activation with elemental sulphur (Subramanian and Kanduth, 1973) or roasting (Prasad and Pandey, 1998) in the temperature range of 400–550 °C to produce covellite or bornite, respectively. The purpose of this study was to investigate the kinetics of the chemical conversion of chalcopyrite into copper sulphide in the presence of cupric ions in sulphuric acid media. The effect of Cu(II) on the decomposition of chalcopyrite in sulphuric acid has been well documented (Elsherief, 2002; Lundström et al., 2005; McDonald et al., 1984).

2. Experimental

The chalcopyrite mineral fractions used in this study were obtained from Pima flotation concentrate. The chemical and

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Table 1
Analysis of Pima concentrate

| Chemical analysis | | Mineralogical analysis | |
|-------------------|------|--------------------------------|------|
| Element | % | Mineral | % |
| Cu | 27.2 | CuFeS ₂ | 80 |
| Fe | 29.2 | FeS ₂ | 5 |
| S | 30.8 | SiO ₂ | 5 |
| Sb | 0.60 | Al ₂ O ₃ | 0.93 |
| Zn | 0.50 | CaO | 0.52 |
| Mo | 0.14 | Talc and chlorite | 8 |
| Pb | 0.07 | | |
| As | 0.02 | | |

mineralogical analysis of chalcopyrite concentrate, as received, using ICP and XRD and verified by the Rietveld method (O'Connor et al., 1992) is shown in Table 1.

Fine mono-size particles, 2.5 × 5 μm, 5 × 10 μm and 10 × 20 μm were prepared with an Accucut Model B air classifier. Stirred ball milling was carried out in a one gallon tank Model 1-S Union Process Attritor Mill using 15.25 kg of 0.63 cm diameter stainless steel balls. The mill was operated at 340 rpm at a pulp density of 60%. Particle size distribution measurements were performed with a Micrometrics Sedigraph 5000D Particle Size Analyser and are shown in Fig. 1.

The attritor ground chalcopyrite was strained as evidenced by the broad peaks present in the X-ray diffraction pattern. Heat treatment of the strained product at 500 °C in an evacuated sealed Pyrex tube for 2 h completely relieved the residual stress and restored the original XRD pattern (Fig. 2).

Leaching tests were run in a baffled 1 L glass reaction kettle fitted with a Friedrichs condenser, nitrogen dispersing glass frit and glass impeller (20 mm vertical profile and a 75 mm diameter). The entire reaction assembly was heated in an oil bath.

Approximately 5 g of chalcopyrite was used for leaching tests and ~5 ml samples were taken through a fritted glass sampling device for iron and copper analysis by AAS (Perkin-Elmer Model 305A). Deionised water and reagent grade

chemicals were used to prepare all aqueous solutions. Solid samples and residues were examined by XRD before and after annealing and before and after leaching.

3. Results and discussion

The chemical conversion of chalcopyrite into copper sulphide with cupric ion under a nitrogen atmosphere can be expressed as:



followed by oxidation–reduction couple,



Preliminary tests showed that the conversion of 90 × 75 μm particles was around 4% at 90 °C after 100 h. One of the factors most likely to increase the reaction rate is to decrease the particle size. The “activation leach” step in the Sherritt–Cominco process, high temperature autoclave system (>150 °C), was carried out with 80% <15 μm particle size to achieve high removal of iron. According to Habashi (1978), reaction (1) is limited by diffusion in the solid phase. The “activation leach” step is less effective for high pyrite–chalcopyrite concentrates and its major effectiveness was apparent for concentrates like

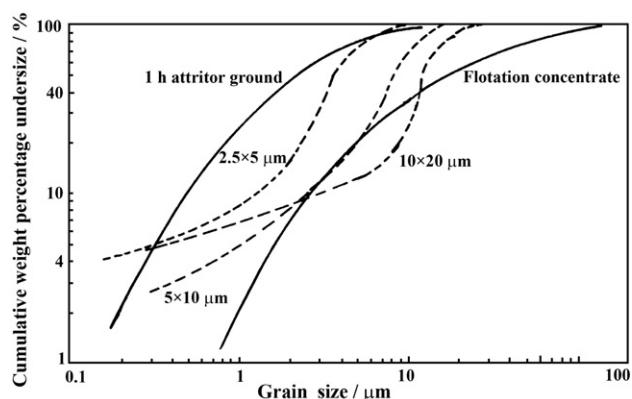


Fig. 1. Grain-size distribution of mineral samples for leaching tests.

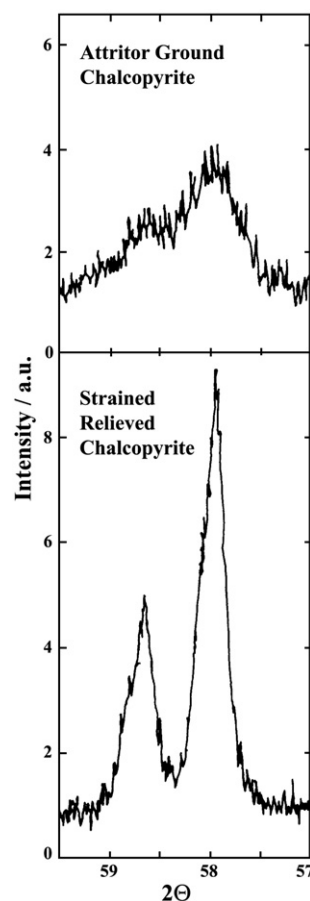


Fig. 2. X-ray diffraction of the attritor ground and strain-relieved chalcopyrite.

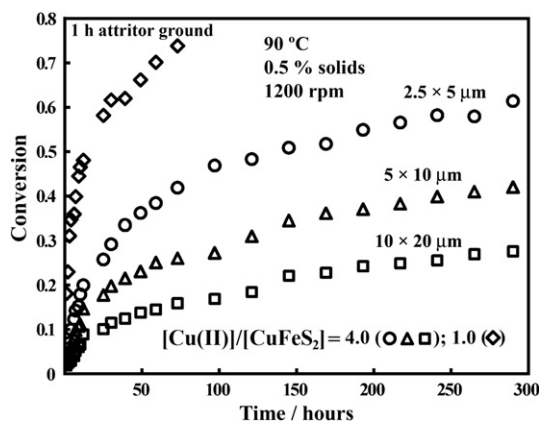


Fig. 3. Fraction of iron released for four particle sizes as a function of time.

bornite (Cu_5FeS_4). Fig. 3 illustrates the comparative conversion curves for three different fine mono-sizes ($2.5 \times 5 \mu\text{m}$, $5 \times 10 \mu\text{m}$ and $10 \times 20 \mu\text{m}$) and one hour attritor ground chalcopyrite at 90°C and 1200 rpm, measured in this study. The rate data are expressed in terms of the fraction of Fe(II) released into solution based upon Eq. (1) and “conversion” of chalcopyrite to covellite.

3.1. Effect of stirring speed

Experiments were run for three different stirring speeds with one hour attritor ground chalcopyrite, 0.5% solids, molar ratio $\text{Cu(II)}/\text{CuFeS}_2 = 1.0$, ambient nitrogen atmosphere and 70°C (Fig. 4). Leaching rate was independent for 600, 1200 and 1800 rpm, and all other experiments reported here were performed at 1200 rpm.

3.2. Effect of copper ion addition

The effect of copper(II) concentration on the reaction rate is presented in Fig. 5. When one-half of the stoichiometric amount of Cu(II) was added, the conversion was influenced

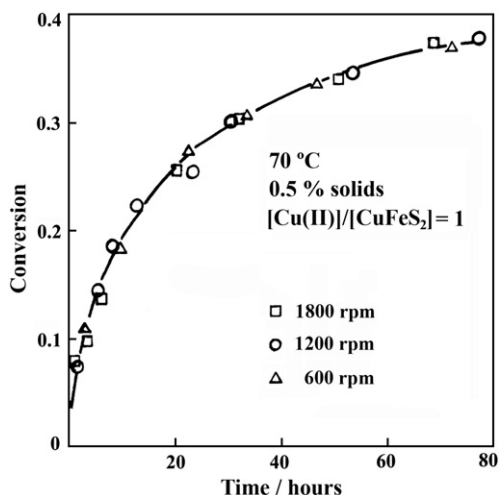


Fig. 4. Effect of stirring speed on the iron released into solution as a function of time.

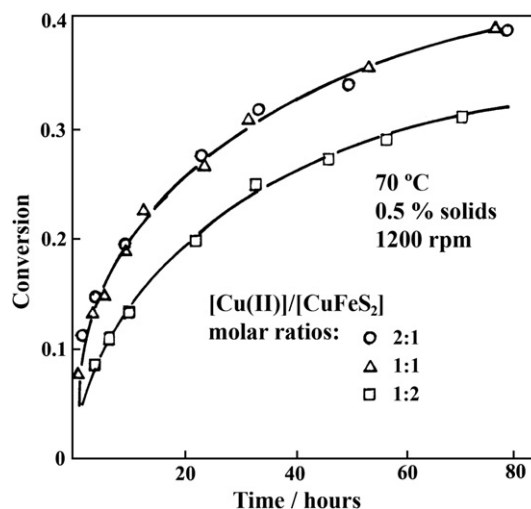


Fig. 5. Plot of conversion vs. time at various copper sulphate concentrations.

markedly by the depletion of copper ions in solution. Above the stoichiometric amount of Cu(II), the concentration of Cu(II) had little effect on the leaching rate.

3.3. Effect of temperature and annealing

Several tests were performed in order to determine the effect of temperature on the reaction rate for both strained and annealed chalcopyrite (Fig. 6).

As previously mentioned, the attritor ground particles were strained (as evidenced by XRD, Fig. 2), but this stored energy was released and restored upon annealing. As the chalcopyrite may form a solid aggregate during annealing, it was stirred in an ultrasonic field to obtain good dispersion just before the leaching experiments. As shown in Fig. 6, annealing had a significant effect on the iron extracted from one hour attritor ground chalcopyrite, contrary to the oxidation of chalcopyrite with Fe (III) (Beckstead et al., 1976) where there was no difference on the leaching rate between strained and annealed particles.

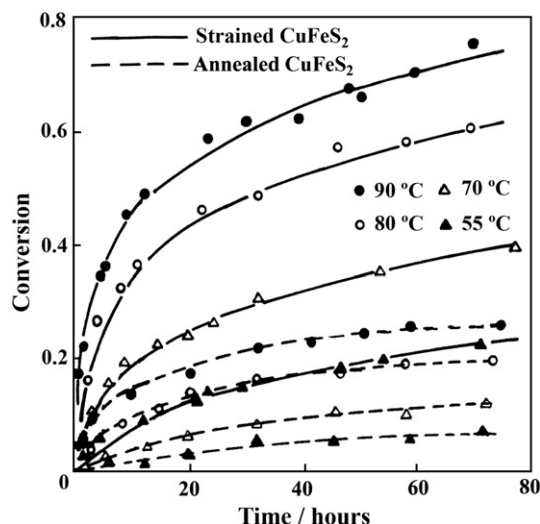


Fig. 6. Plot of conversion vs. time at various temperatures, for strained and annealed chalcopyrite.

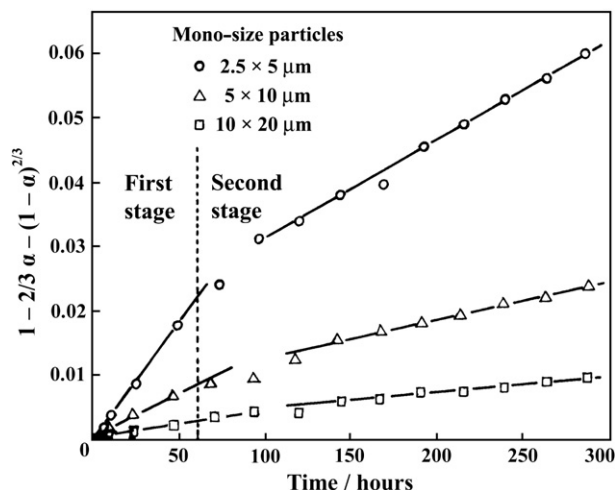


Fig. 7. Plot of product layer model fitting of conversion vs. time at 90 °C, based on Fig. 3.

These mechanical activation processes increase the chemical reactivity as well as diffusivity (Baláz, 2000; Wadsworth, 1985a). The diffusion coefficient measured in a strained system induced by plastic deformation may be expected to be enhanced. Generally, two possible mechanisms would account for increasing the diffusivity (Wadsworth, 1985b; Zhu et al., 1994):

- Straining generates vacant lattice sites, raising their mean concentration above that corresponding to thermal equilibrium. When diffusion is by a vacancy mechanism, this increase will lead to a corresponding increase in diffusivity.
- Dislocations and grain boundaries produced during plastic deformation and recrystallisation provide easy paths for diffusion.

If the crystal distortion due to strain introduced by stirred ball milling accounts for the enhanced reaction rate observed in this study, then it also has to increase the reaction rate for the case of ferric ion leaching of chalcopryrite studied by Beckstead et al. (1976), where there was no difference in reaction rate. Also, the increase in vacancy concentration cannot explain the enhanced rate since the reaction products (covellite, CuS, and digenite, Cu_{1.8}S) did not show any strain from XRD examination. We propose that dislocations and grain boundaries produced during recrystallisation provide easy paths for diffusion since the reaction is controlled by diffusion through the product layer. A further analysis of the temperature effect on the kinetics of the reaction is presented in the following section, showing that the system is controlled by a transport process (parabolic leaching), whether in the product layer or a boundary fluid film (Dreisinger and Abed, 2002).

4. Dissolution kinetics

The leaching response of 2.5 × 5 μm, 5 × 10 μm and 10 × 20 μm mono-size chalcopryrite particles is presented in

Fig. 3, as a fraction of iron released. The rapid decrease in rate is due to the formation of the product layers on the surface of chalcopryrite according to reactions (1) and (2) thus providing a diffusion barrier.

For spherical particles, in which the reaction rate is controlled by transport through a product layer, the following relationship between fraction reacted and time can be obtained for a batch system (Levenspiel, 1972). The total flux may be represented by the equation:

$$dn/dt = -4\pi\gamma r^2 D dC/dr \quad (3)$$

where n is the number of moles of chalcopryrite in a particle at time t , r is the radius of the particle at any time t , D is the effective diffusion coefficient for transport through the product layer, C is the concentration of diffusing species, and γ is the stoichiometric factor. Eq. (3) can be integrated under steady-state conditions in which the flux is constant for all values of r between r and r_0 resulting in the equation,

$$dn/dt = -4\pi\gamma r r_0 D \Delta C (r_0 - r)^{-1} \quad (4)$$

where r_0 is the initial particle radius, ΔC is the concentration difference between reaction interface and bulk phase. Also, the number of moles can be expressed as,

$$n = 4\pi r^3 (3v)^{-1} \quad (5)$$

where v is the molar volume of reacting solid. Upon differentiation of Eq. (5) and combining with Eq. (4), gives

$$dr/dt = -v\gamma D \Delta C r^{-1} (r_0 - r)^{-1} \quad (6)$$

the fraction reacted, α , is related with r as

$$\alpha = 1 - (r/r_0)^3 \quad (7)$$

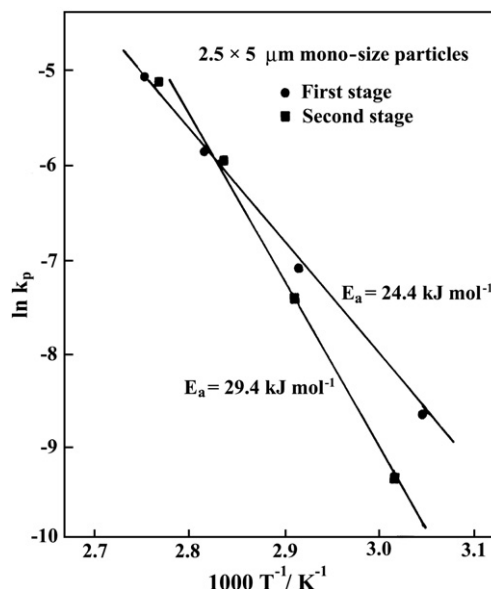


Fig. 8. Plot of parabolic leaching rate constants vs. inverse of temperature (Arrhenius plot) for the first and second stage, based on Fig. 6.

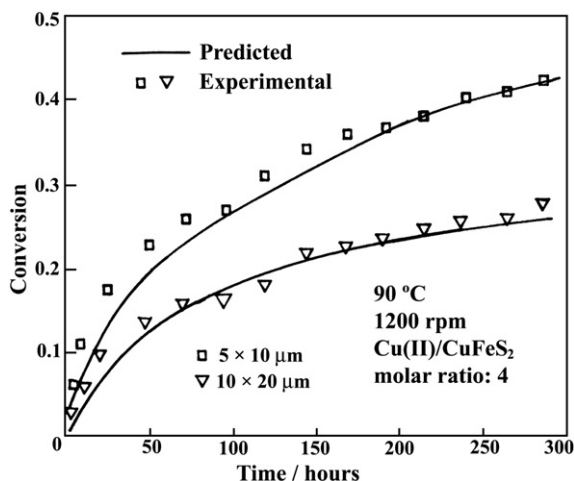


Fig. 9. Predicted and experimental leaching responses based on Eq. (10), using the k_p values for $2.5 \times 5 \mu\text{m}$ mono-size particles, and on Fig. 3.

which upon differentiation with respect to time becomes

$$d\alpha/dt = -3r^2 r_0^{-3} dr/dt \quad (8)$$

Combining Eqs. (6), (7) and (8) gives

$$d\alpha/dt = 3v\gamma D \Delta C r_0^{-2} (1 - \alpha)^{1/3} \left[1 - (1 - \alpha)^{1/3} \right]^{-1} \quad (9)$$

Integration for the boundary conditions $\alpha=0$ and when $t=0$ results in the expression

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = k_p t \quad (10)$$

where $k_p = 2\gamma v D \Delta C r_0^{-2}$

According to Eq. (10), a plot of $1 - 2/3\alpha - (1 - \alpha)^{2/3}$ versus time is linear.

This plot is shown in Fig. 7 for three different mono-sizes chalcopyrite where two distinct linear relationships are observed. The first portion of the linear region goes up to approximately 60 h which corresponds to the same thickness of product layer, approximately $0.28 \mu\text{m}$. Only covellite was observed as a reaction product during the first stage. The transition region corresponds to the initial formation of digenite ($\text{Cu}_{1.8}\text{S}$) formed according to reaction (2). The second linear region is rate limited by the combined diffusional resistance of covellite and digenite (Furer et al., 1975, 1977).

As seen from the integrated equation for diffusion, Eq. (10), the parabolic rate constant k_p , will have a first order dependence on copper concentration if Cu(II) is the rate controlling diffusing species. However, Fig. 5 shows that the rate is essentially independent of the copper ion concentration above the stoichiometric amount. In view of this observation, the ferrous ion appears to be the diffusing species which controls the reaction rate.

Arrhenius plots based on the data presented in Fig. 6 for strained chalcopyrite are shown in Fig. 8 which gives the activation energy of 24.4 kJ mol^{-1} for the first stage and 29.4 kJ mol^{-1} for the second stage. The parabolic rate constants were obtained from fitted values for each stage. Such high activation energy indicates that the ferrous ion diffusion is a solid state diffusion through the product layer rather than pore diffusion.

In order to test the validity of a two-stage product layer diffusion model, the leaching responses of $5 \times 10 \mu\text{m}$ and $10 \times 20 \mu\text{m}$ particle size are predicted with the parabolic rate constants determined from $2.5 \times 5 \mu\text{m}$ mono-size. The parabolic rate constants obtained for each stage are $5.69 \times 10^{-6} \text{ min}^{-1}$ for the first stage up to a product thickness of $0.28 \mu\text{m}$ and $2.57 \times 10^{-6} \text{ min}^{-1}$ for the second stage where both covellite and digenite provide the diffusion barrier, respectively. The results from this computation are presented in Fig. 9 which compares favourably with the experimental data.

Quantitative XRD (Rietveld) studies gave additional proof of the formation of covellite and digenite resulting from the metathesis of chalcopyrite. Actually, covellite (CuS , JCPDS 6-464) was identified for shorter leaching times ($<60 \text{ h}$), and digenite ($\text{Cu}_{1.8}\text{S}$, JCPDS 47-1748) and some covellite phases were identified for longer leaching times ($>150 \text{ h}$). However, it was not possible to establish a clear parallel between the estimated relative amounts of digenite and covellite and the experimental kinetic data obtained for the reductive decomposition of chalcopyrite/conversion of covellite into digenite. Given the aforementioned difficulty, it was more acceptable to draw conclusions on the basis of the kinetic work.

5. Conclusions

Under the conditions of this study it was found that a fine grind of sub-sieve particle size was required for extensive reaction. The following conclusions can be drawn:

1. The initial chemical reaction was the simple metathesis reaction,

$$\text{CuFeS}_2 + \text{CuSO}_4 = 2\text{CuS} + \text{FeSO}_4$$
 followed by the oxidation–reduction couple,

$$6\text{CuS} + 3\text{CuSO}_4 + 4\text{H}_2\text{O} = 5\text{Cu}_{1.8}\text{S} + 4\text{H}_2\text{SO}_4$$
2. The reaction rate was independent of stirring speed and was not controlled by diffusion in the liquid phase.
3. The reaction rate was insensitive to Cu(II) concentration when excess was added.
4. The strain induced by stirred ball milling enhanced the reaction rate markedly due to the recrystallisation process which provides easy paths for diffusion along dislocations and grain boundaries.
5. The kinetics were well correlated with the two-stage product layer diffusion model with ferrous ion the rate determining diffusing species through the first stage covellite and second stage digenite phases.

References

- Baláz, P., 2000. Extractive Metallurgy of Activated Minerals. Elsevier, Amsterdam.
- Beckstead, L.W., Munoz, P.B., Sepulveda, J.L., Herbst, J.A., Miller, J.D., Olson, F.A., Wadsworth, M.E., 1976. Acid ferric sulphate leaching of attritor-ground chalcopyrite concentrates. Extractive Metallurgy of Copper, vol. II. Metallurgical Society of AIME, New York, pp. 611–632.
- Burkin, A.R., 2001. Chemical Hydrometallurgy: Theory and Principles. Imperial College Press, London.

- Davenport, W.G.L., King, M., Schlesinger, M., Biswas, A.K., 2002. *Extractive Metallurgy of Copper*, 4th ed. Pergamon, London.
- Dreisinger, D., Abed, N., 2002. A fundamental study of the reductive leaching of chalcopyrite using metallic iron. Part I: kinetic analysis. *Hydrometallurgy* 66, 37–57.
- Elsherief, A.E., 2002. The influence of cathodic reduction, Fe^{2+} and Cu^{2+} ions on the electrochemical dissolution of chalcopyrite in acidic solution. *Miner. Eng.* 15, 215–223.
- Furer, J., Lambertin, M., Colson, J.C., 1975. Kinetic and morphological study of digenite sulphidation into covellite. *Mater. Res. Bull.* 10, 1047–1054.
- Furer, J., Lambertin, M., Colson, J.C., 1977. Morphological and kinetic study of copper corrosion when covered with digenite sulphide layer, in sulphur, under covellite formation conditions. *Corros. Sci.* 17, 625–632.
- Habashi, F., 1978. *Chalcopyrite, Its Chemistry and Metallurgy*. McGraw-Hill, London.
- Levenspiel, O., 1972. *Chemical Reaction Engineering*, 2nd ed. Wiley, New York.
- Lundström, M., Aromaa, J., Forsén, D., Hyvärinen, O., Barker, M.H., 2005. Leaching of chalcopyrite in cupric chloride solution. *Hydrometallurgy* 77, 89–95.
- McDonald, G.W., Udovic, T.J., Dumas, J.A., Langer, S.H., 1984. Equilibria associated with cupric chloride leaching of chalcopyrite concentrate. *Hydrometallurgy* 13, 125–135.
- O'Connor, D.J., Sexton, B.A., Smart, R.S.C. (Eds.), 1992. *Surface Analysis Methods in Materials Science*. Springer-Verlag, Berlin.
- Prasad, S., Pandey, B.D., 1998. Alternative processes for treatment of chalcopyrite — a review. *Miner. Eng.* 11, 763–781.
- Subramanian, K.W., Kanduth, H., 1973. Activation and leaching of chalcopyrite concentrate. *CIM Bull.* 66, 88–91.
- Wadsworth, M.E., 1985a. Sulfide and metal leaching reactions. *Min. Eng.* 37, 557–562.
- Wadsworth, M.E., 1985b. Separation and recovery of metals from dilute solids and aqueous phases. *Sep. Sci. Technol.* 22, 711–730.
- Zhu, X., Li, J., Wadsworth, M.E., 1994. Characterization of surface layers formed during pyrite oxidation. *Colloids Surf., A* 93, 201–210.