

Investigation of the leaching of chalcopyritic ore in acidic solutions

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Abstract

This work presents an investigation of the leaching of chalcopyrite ore using sulphuric acid. The influence of solid/liquid ratio, sulphuric acid concentration and iron(III) concentration on leaching process were examined. Investigations were carried out in PVC columns by percolation of leaching solution through the ore layer which consisted of 8 kg of 0–5 mm ore. It was established that the highest dissolution of minerals is at solid/liquid ratio of 4:1. An increase in the solution pH results in an insignificant increase in the chalcopyrite oxidation rate. Iron(III) concentration has no important influence on copper leaching rate. Open circuit potential was measured in leaching solutions. Chronoamperometric measurements showed that the chalcopyrite surface is passivated at lower potentials; this was confirmed by the small current densities observed using electrochemistry.

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1. Introduction

Around the world, there are a large number of tailings dumps from copper operations which are not economic to retreat to produce a concentrate, but still contain significant amounts of copper. These dumps have been weathered through time and comprise both oxide minerals and primary sulphides, mainly chalcopyrite. These old tailings dumps are now being retreated by in situ leaching, primarily using acid leaching (Auck and Wadsworth, 1973; Frenay and Dufresne, 1986) but an increasing fraction are using bioleaching (Brewis, 1995; Ahonen and Tuovinen, 1995; Casas et al.,

1998; Yuehua et al., 2002). However, if CuFeS_2 is the most common copper mineral in the dumps and heaps, the leaching rate is lower than for other minerals.

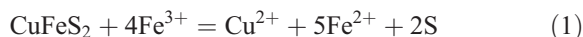
For the oxidation of chalcopyrite and other sulphides, various reagents are used. Iron(III) is most often applied (Dutrizac and MacDonald, 1973; Munoz et al., 1979; Dutrizac, 1981; Majima et al., 1985; Mateos et al., 1987; Hackl et al., 1995; Lu et al., 2000a,b; Klauber et al., 2001; Antonijević and Bogdanović, 2002). Besides iron(III) ions, several other oxidants have also been investigated including oxygen (Yu et al., 1973), ozone (Havlik and Skrobien, 1990), Cu(II) ions (Hiroyoshi et al., 2000, 2002), nitric acid (Habashi, 1978), electrochemical oxidation (Biegler and Swift, 1979; Warren et al., 1982; Parker et al., 1981; Gomez et al., 1996; Lu et al., 2000a,b), silver(I) ions (Mateos et al., 1987;

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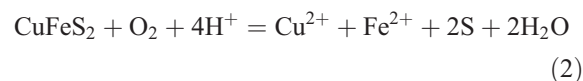
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Yuehua et al., 2002; Hiroyoshi et al., 2002) and chromium(VI) ions (Antonijević et al., 1994, Antonijević, 1995).

In general, the leaching of chalcopyrite by acid Fe(III) solution proceeds according to the following equation (Dutrizac and MacDonald, 1973; Munoz et al., 1979; Dutrizac, 1981; Mateos et al., 1987; Hackl et al., 1995; Lu et al., 2000a,b; Hiroyoshi et al., 2002)



Leaching solutions also contain oxygen that could oxidize the chalcopyrite per equation:



Electrochemical analyses are very important for obtaining the useful information on sulphide leaching. Process of anodic dissolution of chalcopyrite was studied by many researchers (Biegler and Swift, 1979; Parker et al., 1981; Warren et al., 1982; Gomez et al., 1996; Lu et al., 2000a,b) by the use of various auxiliary analytical methods for an identification of the reaction products. The cathodic reduction of chalcopyrite has also been investigated (Lazaro et al., 1995; Elsherief, 2002).

Parker et al. (1981) showed that oxidation dissolution of chalcopyrite is controlled by formation of unstable metal-deficient polysulphide film on chalcopyrite surface. Similar results were obtained by Lu et al. (2000a,b).

In this work, chalcopyrite oxidation of ore from the ore body Bor's river was analyzed in the sulphuric acid solutions where dissolved oxygen has a role of oxidant as well as formed iron(III) during leaching, and leaching was carried out with addition of iron(III) ions. The initial influence of pH values of sulphuric acid was investigated ($\text{pH}_0 = 0.5$, $\text{pH}_0 = 0.7$, $\text{pH}_0 = 1.0$, $\text{pH}_0 = 1.3$ and $\text{pH}_0 = 2.0$), concentrations of iron(III) ions (1, 5, 10, 15 and 20 g/dm³) as well as the influence of solid/liquid ratio on copper leaching rate from chalcopyrite ore. Investigations were carried out in columns by percolation of leaching solution through the ore layer. Besides copper, the contents of iron, silicon, magnesium and calcium were determined in output leaching solutions. The X-ray analysis of initial sample and

solid residues upon leaching was carried out. This work also presents the results of electrochemical behaviour of chalcopyrite in the sulphuric acid solutions and with presence of iron(III) ions. The open circuit potential was measured during experiments and the chronoamperometrical investigation was carried out.

2. Experimental

2.1. Material

Sample for laboratory investigations was taken from the ore body Bor's river, Bor, East Serbia. The sample was crushed to class -20 mm, and the samples for some investigations were selected by crushing and sieving. Fraction of $-5+0$ mm was used in this work, with the grain-size distribution presented in Fig. 1.

Chemical analysis of ore sample is presented in Table 1.

It was estimated, by the use of mineralogical and X-ray analysis of the samples, that the most present copper mineral is chalcopyrite, and pyrite from present sulphide mineral (chalcopyrite: pyrite = 1:3). Based on the obtained qualitative mineralogical analyses, the presence of magnetite, hematite, limonite, colusite, rutile, leucoxene and quartz was estimated, as well as the presence of chalcocite, covellite and

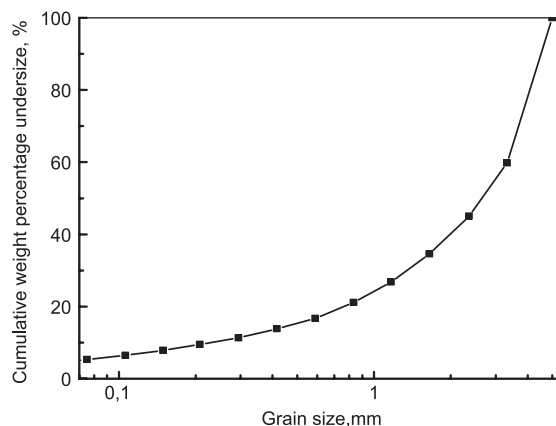


Fig. 1. Grain-size distribution of fraction ($-5.0+0.0$ mm) for column leaching.

Table 1
Chemical analysis of the ore sample

Content (%)	
Cu(total)	0.58
Cu(oxide)	0.010
Fe	3.92
CaO	6.3
MgO	1.69
SiO ₂	53.10
Al ₂ O ₃	12.97
S	5.57

bornite in traces from copper minerals. Background minerals are based on quartz–carbonate–silicate.

2.2. Experimental technique

2.2.1. Column leaching experiments

Dissolution of all samples was carried out in sulphuric acid solutions in columns of PVC material, diameter 110 mm and height 1000 mm. Eight kilograms of ore, grain size range $-5+0$ mm, was put into each column. Bed of silicon dioxide, thickness of about 1 cm, was put over ore for uniform distribution of solutions. Sulphuric acid solutions with the following pH value ($\text{pH}_0=0.5$, $\text{pH}_0=0.7$, $\text{pH}_0=1.0$, $\text{pH}_0=1.3$, $\text{pH}_0=2.0$) were used for dissolution. pH values were adjusted by addition of sodium hydroxide or sulphuric acid solution and output solutions were recirculated upon adjustment of pH value. In analyzing the influence of iron(III) in sulphuric acid solution with $\text{pH}_0=1.0$ (source of iron is iron(III) sulphate), concentrations of this oxidant were 1.0, 5.0, 10.0, 15.0 and 20.0 g/dm³. Influence of the ratio of solid/liquid was investigated at the following ratios of S/L (1:1, 2:1 and 4:1). At definite time intervals, 5 ml of solution was taken and transferred into measuring flask, the solutions made up to volume of 100 ml with distilled water, and then the contents of copper and iron were determined from those solutions by the use of atomic absorption spectrophotometry (AAS), and aluminium and silicon were determined by the use of atomic emission spectroscopy with plasma method (ICP-AES). Upon 90 days of leaching, the contents of Ca and Mg were determined in output leaching solutions by the use of atomic absorption spectrophotometry (AAS) method.

Liquid flow rate through columns was 3.3 cm³/min. All leaching experiments lasted for 3 months at atmospheric conditions.

2.2.2. Electrochemical studies

2.2.2.1. The leaching solutions. Electrochemical characterization of leaching solutions was carried out such as redox potentials were measured by the use of platinum electrode. During leaching process, solutions where redox potential was measured were sampled upon 15, 46 and 90 days.

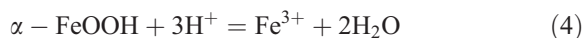
2.2.2.2. The crystal of chalcopyrite. Besides those studies, the electrochemical behaviour of natural chalcopyrite crystal from the Bor deposit was also studied. Electrochemical measurements were carried out in the sulphuric acid solutions ($\text{pH}=0.5$, $\text{pH}=0.7$, $\text{pH}=1.0$, $\text{pH}=1.5$, $\text{pH}=2.0$, $\text{pH}=2.5$ and $\text{pH}=3.0$) and iron(III) solution, concentration 10 g/dm³ Fe(III) ($\text{pH}=1.0$). Chalcopyrite in a form of quadrant was used as electrode material. Chalcopyrite electrode was made such as chalcopyrite crystal was polished on all sides by diamond paste, and then the best surface was selected as working surface of electrode. Copper wire was sealed on the opposite side by two-component glue, based on silver, which enabled the electrical contact of mineral with copper wire. Upon glue solidification, such prepared electrode was placed into a glass tube and it was cemented with the cold sealing mass based on methyl methacrylate. After solidification of mass, the glass tube was broken, and upon that the working surface of electrode was polished to the high glow. Electrode is then rinsed with distilled water and alcohol and dried in the air and it is ready for work. Working surface of electrode was 0.70 cm². The electrochemical experiments were carried out at room temperature and atmospheric pressure without mixing, using the potentiostat coupled to a personal computer. Data were acquired by an analogue board installed in PC. Electrochemical measurement was conducted using a conventional three-electrode system with chalcopyrite as working electrode; the reference was saturated calomel electrode and platinum was the counter electrode. The open circuit potential and chronoamperometry were used for the measurement.

3. Results and discussion

3.1. Influence of solid/liquid ratio

Influence of solid/liquid (S/L) ratio on leaching the ore of grain size range $-5+0$ mm with sulphuric acid (pH=1.0) at room temperature was investigated. In the experiments, S/L ratios of 1:1, 2:1 and 4:1 are used. The obtained results are presented in Fig. 2.

It is seen from Fig. 2 that the minerals are mostly dissolved during experiment where is used solid/liquid ratio of 4:1 (Fig. 2c). Iron and aluminium are mostly present in leaching output solutions. Iron could be released due to dissolution of its minerals:



From Fig. 2, it could be seen that iron concentration is in range from 0.67 to 2.09 g/dm³. It points out that iron, formed by dissolution of basic iron oxides, could present an agent for chalcopyrite oxidation (Eq. (1)). With decreased ration of S/L iron content in solution is increased, and by this also possibility of chalcopyrite oxidation. Besides this, from kinetic curves (Fig. 2) seen after approximately a month, on curves ($C_{\text{Fe}}=f(t)$) appearance of plateau points out that iron concentration in solution is unchangeable in solution. This appearance could be explained by the following: during time, concentration of iron(III) increases in solution which results in the appearance of iron hydroxide precipitation due to a fact that product of Fe^{3+} and OH^- concentrations has higher solubility product $P_{\text{Fe}(\text{OH})_3}$. Processes of iron oxide dissolution continue further, but iron content is not increased in solution because one part is precipitated. Precipitation of iron oxide on sulphide surface as well as in pores of ore grain could result in chalcopyrite passivation and decreased possible contact of leaching solution with mineral surface.

Ion concentrations of determined elements are increased as time increase. Concentration of copper(II) in those solutions, after 3 months of leaching, is low and it is in a range from 0.024 (for ratio S/L=1:1) to 0.092 g/dm³ in lower participation of liquid phase (S/L=4:1). This result is in accordance with

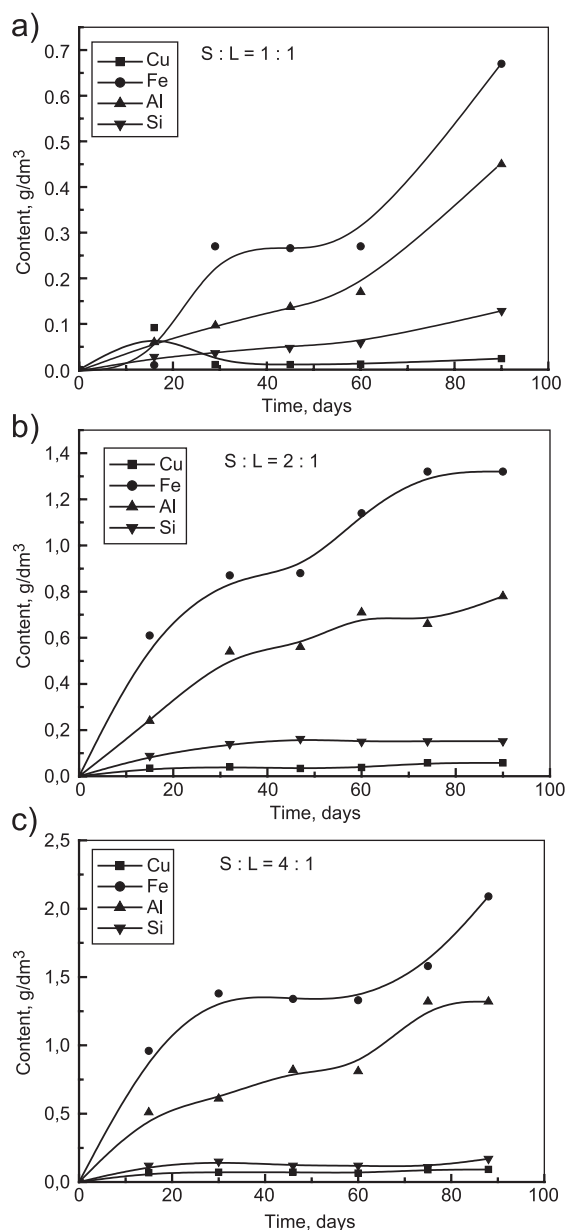


Fig. 2. Dependence of copper, iron, aluminium and silicon concentrations on time during copper ore leaching with sulphuric acid at various solid/liquid ratios: (a) S/L=1:1; (b) S/L=2:1; (c) S/L=4:1.

slow dissolution of chalcopyrite confirmed in the previous studies of chalcopyrite leaching at atmospheric conditions in sulphuric acid (Habashi, 1978). Aluminium concentration is in a range from 0.45 to

1.32 g/dm³ and silicon concentration from 0.12 to 0.15 g/dm³.

At S/L = 1:1 ratio, due to relatively high participation of liquid phase (8 dm³ of solution) such low concentrations of copper(II) are not surprising, until copper concentration increases with decrease of liquid phase participation as well as the other present elements in initial raw material. Further experiments were carried out at ratio of solid/liquid = 4:1.

3.2. Influence of initial pH solution of the sulphuric acid

Influence of initial pH solution ($\text{pH}_0=0.5$, $\text{pH}_0=0.7$, $\text{pH}_0=1.0$, $\text{pH}_0=1.3$ and $\text{pH}_0=2.0$) on leaching rate of copper, iron, silicon and aluminium from chalcopyrite ore with grain size range $-5+0\text{mm}$ was analyzed at ratio of S/L=4:1. The obtained results are presented in Figs. 3 and 4.

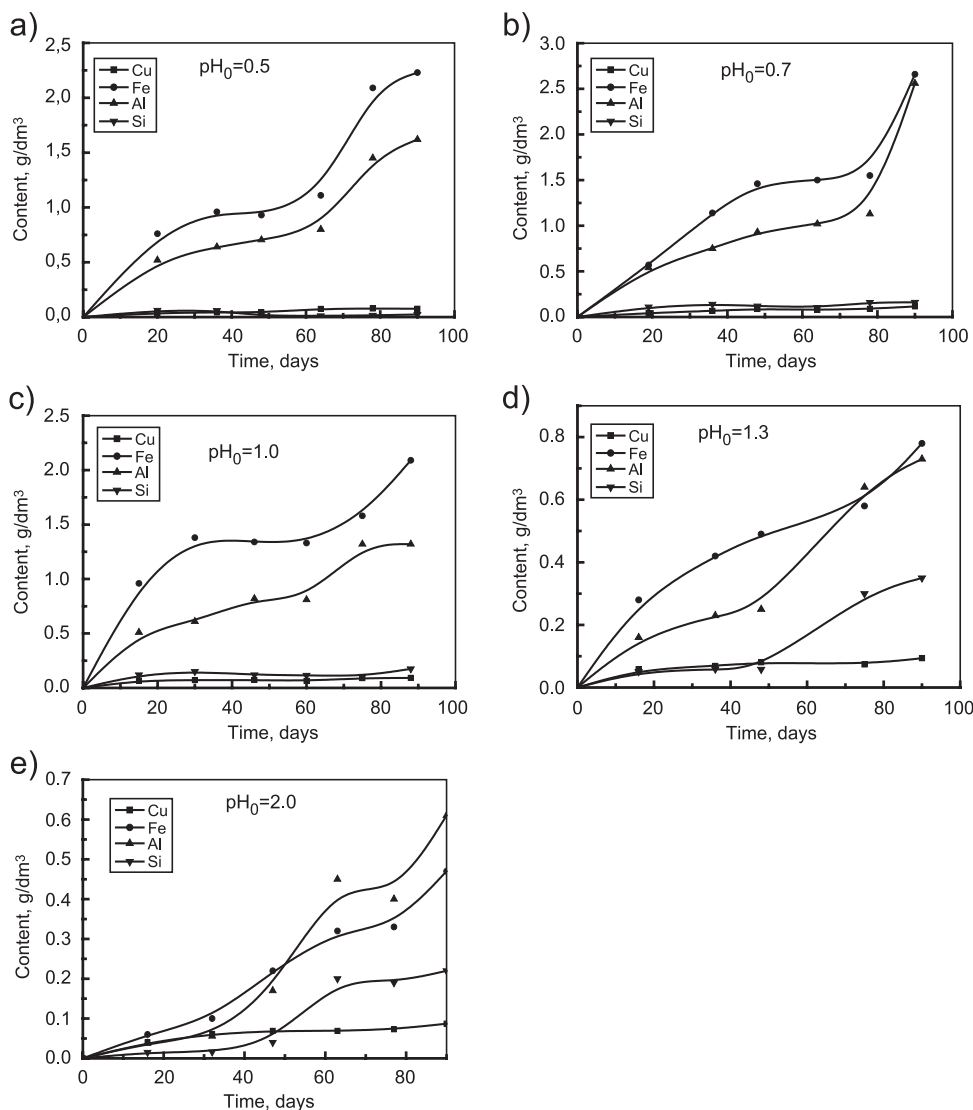


Fig. 3. Dependence of copper, iron, aluminium and silicon concentrations on time during copper ore leaching with sulphuric acid of various initial pH_0 values: (a) $\text{pH}_0=0.5$; (b) $\text{pH}_0=0.7$; (c) $\text{pH}_0=1.0$; (d) $\text{pH}_0=1.3$ and (e) $\text{pH}_0=2.0$ (S/L=4:1).

It is seen from Figs. 3 and 4 that increasing initial pH in range of 0.7–2.0, after 3 months of leaching, copper content in output solutions is in range 0.087–0.116 g/dm³. At pH=0.5, copper content is the lowest (0.076 g/dm³). It could be explained by a fact that chalcopyrite at this pH value could be in passive state where a layer of chalcopyrite deficient in iron is formed on the surface of this mineral (Lu et al., 2000a,b; Parker et al., 1981). Similar observations were also noticed in electrochemical investigations. It points out that chalcopyrite easily oxidizes at higher pH values with present oxygen in solutions. Acidity influence on dissolvability of treated ore is such that iron and aluminium are the most present in solution where their concentrations in solution are increased with an increase of leaching time. Concentrations of iron and aluminium are in limits of 0.47–2.66 and 0.61–2.56 g/dm³, respectively. Besides time, which was previously discussed, pH value has also an influence on iron precipitation process that could be seen from Fig. 4. It is seen that increased pH value results into decreased iron and aluminium concentrations due to precipitation of those metals hydroxides. Silicon content in output solutions is also low and it is in a range of 0.024–0.40 g/dm³. It could be seen from curves of dissolution that favourable ratio of concentration the elements, for eventual extraction of copper from the solutions, is realized by the use of low acid

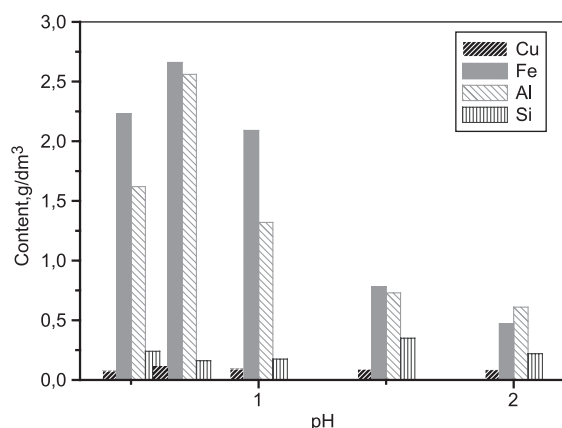


Fig. 4. Dependence of copper, iron, aluminium and silicon concentrations on pH values after 90 days of copper ore leaching with sulphuric acid (S/L = 4:1).

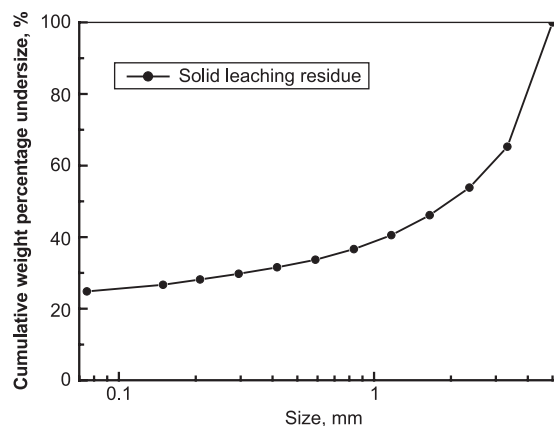


Fig. 5. Grain-size distribution of sample ($-5.00+0.00$ mm) and solid residue after leaching in 1 M H₂SO₄.

concentrations (pH=1.5 and pH=2.0). Concentrations of iron and aluminium ions increase at higher concentrations of sulphuric acid (pH=0.5 and pH=0.7) which will balk the process of copper extraction at possible use of those solutions.

Oxidation rate of chalcopyrite in the experimental conditions is low. Probably the reason for that is the impossibility of leaching solution contact and chalcopyrite particles, present inside ore grains. In the initial period of leaching, the chalcopyrite oxidation occurs on surface of ore grains. Due to a reaction between sulphuric acid and present minerals, the calcium ions are released that react with sulphate anion forming calcium sulphate as precipitate. Formation of the precipitate could occur on ore grain, where formation front will be moved to the ore grain interior by time. Due to the high volume of precipitate, small cracks will form in the grain which will enable to realize new chalcopyrite surfaces as well as conditions for further leaching. This phenomenon results into comminution of initial raw material during leaching which could be seen from the curve of grain-size distribution and the solid residue (Fig. 5).

It also results into the presence of calcium sulphate in solid leaching residues, which is confirmed by X-ray analysis (Fig. 6).

Open circuit potential was measured in the leaching solutions (Fig. 7).

It is seen from Fig. 7 that the potential is rapidly established on platinum electrode in leaching solu-

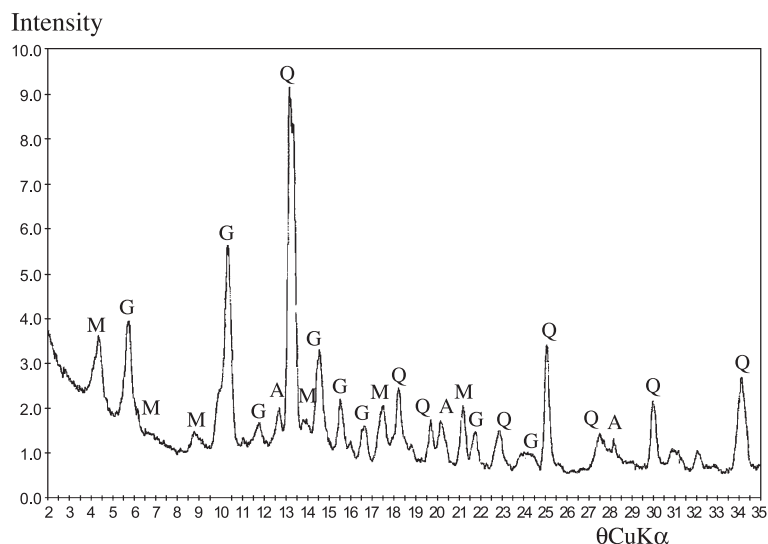


Fig. 6. X-ray diffraction of the residue after 90 days of leaching: gypsum (G), quartz (Q), anhydrite (A) and muscovite (M). Conditions: pH=1.0, S/L=4:1.

tions. Some negative potential values, after 46 days of leaching, were measured regarding the measured potential after 15 days. It could be explained by increased iron(II) concentration in solution. But, after 90 days of leaching, the potential is increased due to oxidation of iron(II) into iron(III). Values of potential and pH of medium ($E = 0.42\text{--}0.46$ V vs. SCE, pH=1) point out that Fe^{2+} is dominant in the obtained solutions regarding Fe^{3+} ion, which points out the mild oxidation conditions in the solution. It could be

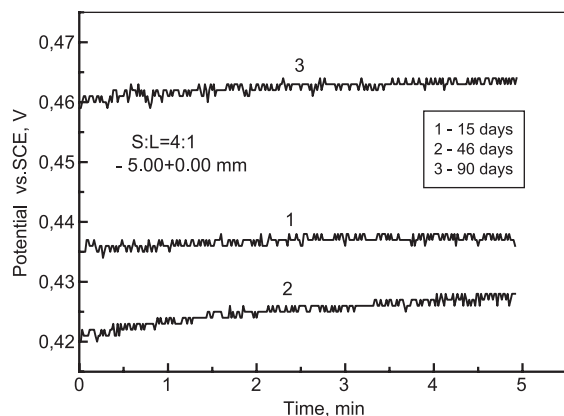


Fig. 7. Dependence of open circuit potential on time in output leaching solutions.

seen from diagram $E\text{--}pH$ for Cu–Fe–S– H_2O system (Pacović, 1980) that the oxidation process could occur on chalcopyrite surface under those conditions with formation of iron compounds, i.e. Fe_2O_3 , that could cover the chalcopyrite surface. Due to this, the reactions of chalcopyrite dissolution from the ore are slow, which results into low concentration of copper in outlet leaching solutions.

Chronoamperometric analyses in the solution of sulphuric acid (pH=1.0) at potentials 500, 550, 600, 650, 700, 800, 830, 850 and 900 mV vs. SCE were carried out for estimation of how dissolution rate of chalcopyrite is changed with time. Fig. 8 shows dependence of current densities, obtained after 60 s of chalcopyrite polarization, on potential in solution of H_2SO_4 (pH=1.0).

It is noticed from Fig. 8 that value of current density starts to increase from potential with value of about 700 mV which points out that more intensive decomposition of chalcopyrite starts from this potential. At lower potentials, chalcopyrite surface is passivated which also results in lower current densities. By studying the electrochemical oxidation of chalcopyrite, Lu et al. (2000a,b) showed that during initial leaching stages, chalcopyrite oxidation at low overpotential is slowed by formation of sulphide surface with low-grade metal, where oxidation of

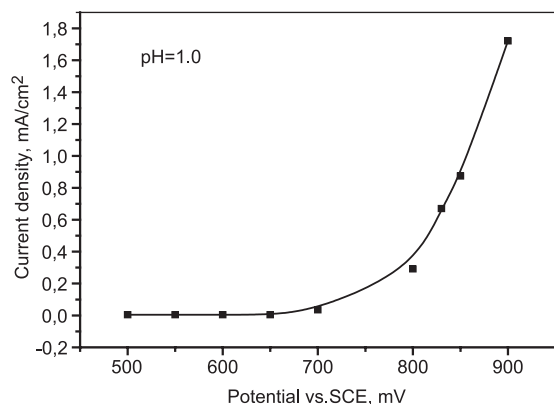
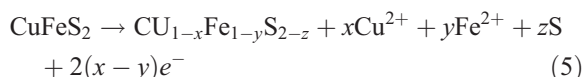


Fig. 8. Dependence of current density, obtained after 60 s polarization of chalcopyrite, on potential in the sulphuric acid solution (pH=1.0).

this mineral is developed per partial reaction, presented by Eq. (5), where $y > x$.



This suggests that there is release of iron from the chalcopyrite lattice during anodic dissolution. The structure $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$ is an intermediate product, which mixed with sulphur, forms a passive electron conducting layer on the mineral surface. Parker et al. (1981) referred to the product as a polysulphide, which has semiconducting properties.

Besides this, the chronoamperometrical analyses were carried out at various pH values in solution of sulphuric acid (pH=0.5, pH=0.7, pH=1.0, pH=1.5, pH=2.0, pH=2.5 and pH=3.0) at potential of 800 mV vs. SCE. Fig. 9 shows dependence of current density, obtained after 120 s polarization of chalcopyrite, on pH value at a potential of 800 mV.

Three regions could be seen from Fig. 9. In the first region (pH 0.5–1.5), there is a linear dependence between current densities and pH values with slope of 390 mA/pH. In the second region (pH 1.5–2.5), current density increases linearly with an increase of pH where slope is lower (90 mA/pH). Decrease of slope could be explained by formation of product layers on surface of chalcopyrite that have an influence on dissolution rate of the analyzed

mineral. At higher pH values (third region) the current density decreases, probably due to the formation of denser product layers that present a barrier on transport of electrons. Data from electrochemical studies (Parker et al., 1981; Warren et al., 1982; Gomez et al., 1996; Lu et al., 2000a,b) show that noticed rapid decrease of current density of chalcopyrite leaching was caused by formation of compact sulphide layer which is in accordance with the results in this work.

3.3. Influence of iron (III) concentration

Since iron (III) is a known oxidant, used for oxidation of various sulphide minerals, the influence of iron(III) concentration on chalcopyrite oxidation rate was analyzed. Investigations were carried out in the sulphuric acid solutions (pH=1.0) with various iron(III) concentrations. Influence of iron (III) concentrations (1, 5, 10, 15 and 20 g/dm³) on copper, iron, silicon, aluminium, calcium and magnesium leaching was analyzed at S/L ratio=4:1 with grain size range of $-5+0\text{mm}$. The obtained results are presented in Figs. 10–12.

Figs. 10 and 11 show that copper concentration in output solutions, after leaching for 3 months, is in a range of 0.085–0.100 g/dm³. Silicon content in output solutions is in a range of 0.073–0.31 g/dm³. Aluminium concentration is in the range of

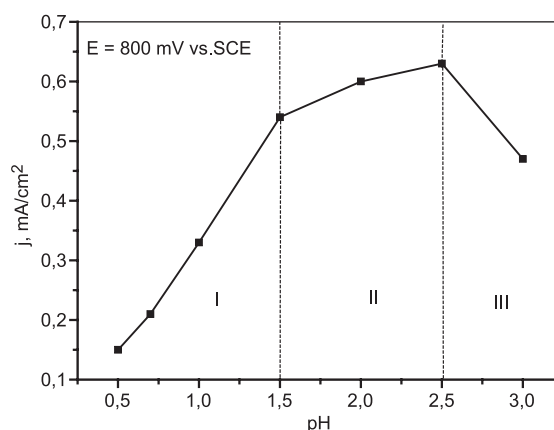


Fig. 9. Dependence of current density, obtained after 120 s polarization of chalcopyrite, on pH initial solution at potential of 800 mV.

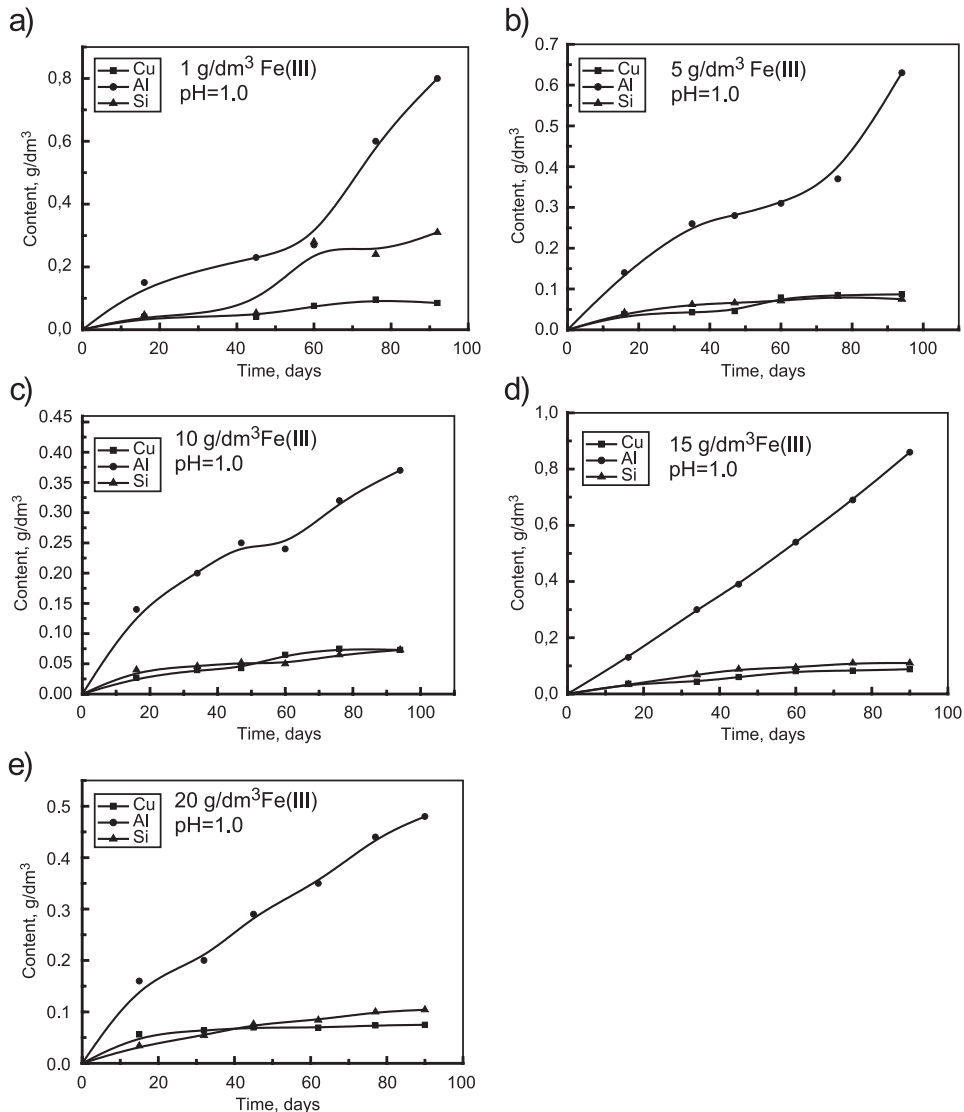


Fig. 10. Dependence of copper, aluminium and silicon concentrations on time during copper ore treatment with sulphuric acid solution (pH=1.0) with content of various iron (III) concentrations: (a) 1 g/dm³; (b) 5 g/dm³; (c) 10 g/dm³; (d) 15 g/dm³; (e) 20 g/dm³ (S/L=4:1).

0.63–0.86 g/dm³. Calcium content, after 90 days of leaching is low and it is about 0.018 g/dm³, and magnesium content is significantly higher than calcium content and it is in a range from 0.304 to 0.627 g/dm³. The analyses have shown out that iron(III) concentration (Fig. 11) has very small influence on copper concentration increase in solution. It points out that iron presence is enough, released during decomposition of oxidic iron minerals by acid, for

leaching of present sulphide copper minerals. This finding is very important because the addition of new iron source for hydrometallurgical ore treatment in Bor is unnecessary.

Regarding copper, this result is similar to the Dutrizac's (1981) findings. He confirmed that chalcopyrite oxidation rate was marginally dependent on the concentration of iron(III). Munoz et al. (1979) found similar results, too. They found out

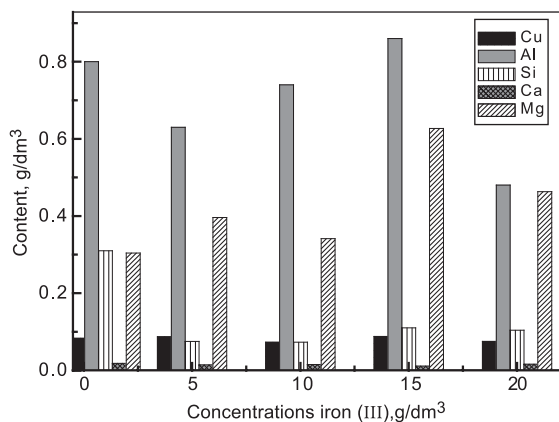


Fig. 11. Dependence of copper, aluminium, silicon, calcium and magnesium concentrations on concentration of iron(III) after 90 days of copper ore treatment with sulphuric acid solution (pH = 1.0).

that zero order reaction rate was related on iron(III) concentration.

Fig. 12 shows that concentration of calcium ions decrease with leaching time. This phenomenon can be interpreted as formation of calcium sulphate in a form of precipitate. It was confirmed by the use of X-ray analysis. It is seen that calcium concentration has minimum values upon 30–40 days of leaching, which is 0.018 g/dm^3 ($4.5 \times 10^{-4} \text{ mol/dm}^3$). Experiments were carried out at pH = 1.0, which is approximately equal to $0.1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$. Theoretical solubility of CaSO_4 in this media is $6.1 \times 10^{-4} \text{ mol/}$

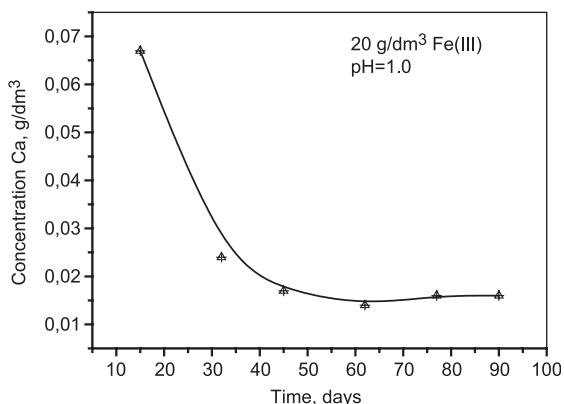


Fig. 12. Dependence of calcium concentrations on time after 90 days of copper ore treatment with iron(III) solution, concentration 20 g/dm^3 (pH = 1.0; S/L = 4:1).

dm^3 . Difference between found out of equilibric Ca^{2+} concentration and theoretical solubility could be explained by a fact that concentration of sulphate ions in leaching solution is increased by presence of entered iron sulphate, which leads to decreased solubility of calcium sulphate. It was already discussed that calcium sulphate could be deposited on mineral surfaces, and between them also chalcopryrite, and resulted into comminution of initial raw material. Besides, dissolution of carbonate background mineral influence on comminution, too. Better copper leaching from chalcopryrite would be expected due to these occurrences, but it is not specially noticed in experiments probably due to appearance of chalcopryrite passivation as a result of iron hydroxide deposition on surface. Passivation of chalcopryrite by iron(III) is observed from other authors (Dutrizac, 1978, 1989; Mateos et al., 1987; Hackl et al., 1995).

Chronoamperometric investigations of chalcopryrite mineral at various potentials at concentration of $10 \text{ g/dm}^3 \text{ Fe(III)}$ in sulphuric acid solution (pH = 1.0) were carried out, and the results are presented in Fig. 13. It was found from the chronoamperometric data that the current density values decrease rapidly with time in the initial period, where change of current densities were small with increase time at potentials of 700 and 750 mV vs. SCE. Values of current density on the potentials were low, which

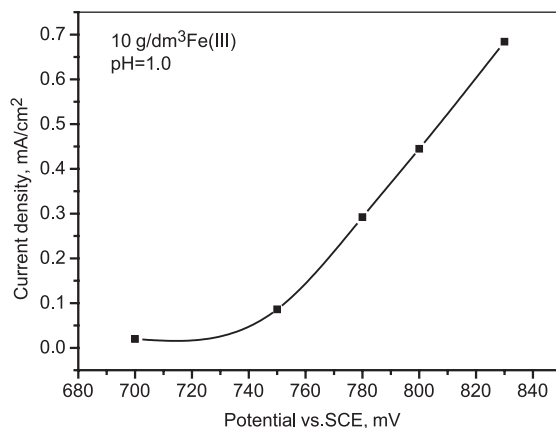


Fig. 13. Dependence of current density, obtained after 120 s of chalcopryrite polarization, on potential in solution of H_2SO_4 (pH = 1.0) with content of $10 \text{ g/dm}^3 \text{ Fe(III)}$.

suggests that chalcopyrite is passive state at the range of potential.

Fig. 13 presents dependence of current density, obtained upon 120 s of chalcopyrite polarization, on potential in solution of H_2SO_4 (pH = 1.0) with content of $10 \text{ g/dm}^3 \text{ Fe(III)}$.

It is seen from Fig. 13 that value of current density starts to increase from potential with value of 750 mV, which tells us that chalcopyrite at more positive potentials could be dissolved faster.

4. Conclusions

- It was found out that majority of present minerals are dissolved during leaching of chalcopyrite ore by the use of sulphuric acid solutions, which is shown by presence of various ion species in the obtained solutions (copper, silicon, aluminium, iron, calcium, magnesium and others).
- Dissolution of minerals is the highest at ratio of solid/liquid = 4:1.
- By studying the influence of pH value, it was found out that the change of pH value has small influence on dissolution rate of chalcopyrite. The lowest rate of chalcopyrite dissolution is at pH = 0.5. At higher pH values, chalcopyrite oxidizes easier by oxygen and iron(III) that are present in leaching solutions.
- It was found by X-ray analysis that during leaching calcium sulphate precipitates on mineral surfaces.
- Iron (III) concentration in investigated range has no important influence on chalcopyrite leaching rate. It points out that iron presence is enough, released during decomposition of oxidic iron minerals by acid, for leaching of present sulphide copper minerals.
- Open circuit potential in the analyzed leaching solutions is rapidly formed on platinum electrode and it is in range from 410 to 460 mV vs. SCE.
- By chronoamperometrical analyses, it was found out that increased pH value of acid (0.5–2.5), at potential of 800 mV, also increases the rate of anodic oxidation of chalcopyrite in sulphuric acid. Further increase of pH results into decrease of rate the anode oxidation of chalcopyrite.
- It was found out that in solution of H_2SO_4 (pH = 1.0) with content of $10 \text{ g/dm}^3 \text{ Fe(III)}$, more

intensive chalcopyrite decomposition starts from potential of 750 mV vs. SCE.

References

- Ahonen, L., Tuovinen, O.H., 1995. Bacterial leaching of complex sulfide ore samples in bench scale column reactors. *Hydrometallurgy* 37, 1–21.
- Antonijević, M.M., 1995. Investigation of chalcopyrite oxidation by sodium dichromate in perchloric acid. *Journal of the Serbian Chemical Society* 60, 233–240.
- Antonijević, M.M., Bogdanovic, G.D., 2002. Leaching of chalcopyrite ore with sulphuric acid solution. 34th IOC on Mining and Metallurgy, Bor Lake, Yugoslavia. Technical Faculty Bor, pp. 373–379.
- Antonijević, M.M., Jankovic, Z., Dimitrijevic, M., 1994. Investigation of the kinetics of chalcopyrite oxidation by potassium dichromate. *Hydrometallurgy* 35, 187–201.
- Auck, Y.T., Wadsworth, M.E., 1973. Physical and chemical factors in copper dump leaching. *International Symposium on Hydrometallurgy Chicago, Illinois, February 25–March 1. The American Institute on Mining and Metallurgical and Petroleum Engineers, Inc.*, pp. 645–700.
- Biegler, T., Swift, D.A., 1979. Anodic electrochemistry of chalcopyrite. *Journal of Applied Electrochemistry* 9, 545–554.
- Brewis, T., 1995. Metal extraction by bacterial oxidation. *Mining Magazine* 173, 5.
- Casas, J.M., Martinez, J., Moreno, L., Vargas, T., 1998. Bioleaching model of a copper-sulfide ore bed in heap and dump configurations. *Metallurgical Transactions. B, Process Metallurgy* 29, 899–909.
- Dutrizac, J.E., 1978. The kinetics of dissolution of chalcopyrite in ferric ion media. *Metallurgical Transactions. B, Process Metallurgy* 9, 431–439.
- Dutrizac, J.E., 1981. The dissolution of chalcopyrite in ferric sulfate and ferric chloride media. *Metallurgical Transactions. B, Process Metallurgy* 12, 371–378.
- Dutrizac, J.E., 1989. Elemental sulphur formation during the ferric sulphate leaching of chalcopyrite. *Canadian Metallurgical Quarterly* 28 (4), 337–344.
- Dutrizac, J.E., MacDonald, R.J.C., 1973. The effect of some impurities on the rate of chalcopyrite dissolution. *Canadian Metallurgical Quarterly* 12 (4), 409–420.
- Elsherief, A.E., 2002. The influence of cathodic reduction, Fe^{2+} and Cu^{2+} ions on the electrochemical dissolution of chalcopyrite in acidic solution. *Minerals Engineering* 15, 215–223.
- Frenay, J., Dufresne, P., 1986. Control conception in hydrometallurgy (laboratory scale). *Process Control in Metall.* May 13–14. Brussels, Belg. ATB Metallurgie (Acta Technica Belgica), vol. 26, n 4, pp. 147–152.
- Gomez, C., Figueroa, M., Munoz, J., Blazquez, M.L., Ballester, A., 1996. Electrochemistry of chalcopyrite. *Hydrometallurgy* 43, 331–344.
- Habashi, F., 1978. *Chalcopyrite, its Chemistry and Metallurgy*. McGraw-Hill, London.

- Hackl, R.P., Dreisinger, D.B., Peters, E., King, J.A., 1995. Passivation of chalcopyrite during oxidative leaching in sulphate media. *Hydrometallurgy* 39, 25–48.
- Havlik, T., Skrobjan, M., 1990. Acid leaching of chalcopyrite in the presence of ozone. *Canadian Metallurgical Quarterly* 29 (2), 133–139.
- Hiroyoshi, N., Miki, H., Hirajima, T., Tsunekawa, M., 2000. A model for ferrous-promoted chalcopyrite leaching. *Hydrometallurgy* 57, 31–38.
- Hiroyoshi, N., Arai, M., Miki, H., Tsunekawa, M., Hirajima, T., 2002. A new reaction model for the catalytic effect of silver ions on chalcopyrite leaching in sulfuric acid solutions. *Hydrometallurgy* 63, 257–267.
- Klauber, C., Parker, A., Bronswijk, W., Watling, H., 2001. Sulphur speciation of leached chalcopyrite surfaces as determined by X-ray photoelectron spectroscopy. *International Journal of Mineral Processing* 62, 65–94.
- Lazaro, I., Martinez-Medina, N., Rodriguez, I., Arce, E., Gonzales, I., 1995. The use of carbon paste electrodes with non-conducting binder for the study of minerals: chalcopyrite. *Hydrometallurgy* 38, 277–287.
- Lu, Z.Y., Jeffrey, M.I., Lawson, F., 2000a. An electrochemical study of the effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* 56, 145–155.
- Lu, Z.Y., Jeffrey, M.I., Lawson, F., 2000b. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* 56, 189–202.
- Majima, H., Awakura, Y., Hirato, T., Tanaka, T., 1985. Leaching of chalcopyrite in ferric sulphate solutions. *Canadian Metallurgical Quarterly* 24 (4), 283–291.
- Mateos, F.B., Perez, I.P., Mora, F.C., 1987. The passivation of chalcopyrite subjected to ferric sulfate leaching and its reactivation with metal sulfides. *Hydrometallurgy* 19, 159–167.
- Munoz, P.B., Miller, J.D., Wadsworth, M.E., 1979. Reaction mechanism for the acid ferric leaching of chalcopyrite. *Metallurgical Transactions. B, Process Metallurgy* 10, 149–158.
- Pacović, N.V., 1980. *Hidrometalurgija*. ŠRIF, Bor.
- Parker, A.J., Paul, R.L., Power, G.P., 1981. Electrochemistry of the oxidative leaching of copper from chalcopyrite. *Journal of Electroanalytical Chemistry* 118, 305–316.
- Warren, G.W., Wadsworth, M.E., El-Raghy, S.H., 1982. Passive and transpassive anodic behaviour of chalcopyrite in acid solutions. *Metallurgical Transactions. B, Process Metallurgy* 13, 571–579.
- Yu, P.H., Hansen, C.K., Wadsworth, M.E., 1973. A kinetic study of the leaching of chalcopyrite at elevated temperatures. *International Symposium on Hydrometallurgy Chicago, Illinois, February 25–March 1. The American Institute on Mining and Metallurgical and Petroleum Engineers, Inc.*, pp. 375–402.
- Yuehua, H., Guanzhou, Q., Jun, W., Dianzuo, W., 2002. The effect of silver-bearing catalysts on bioleaching of chalcopyrite. *Hydrometallurgy* 64, 81–88.