



## THE ELECTROCHEMICAL BEHAVIOUR OF CHALCOPYRITE IN SULFURIC ACID IN THE PRESENCE OF CYSTEINE

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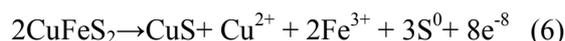
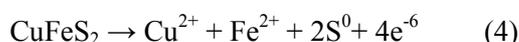
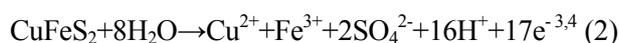
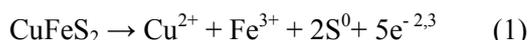
In this paper the effects of different concentrations of cysteine in  $10^{-2}$  mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> on dissolution of chalcopyrite are studied. The cyclic voltammograms at the scan rate values of 1 mV s<sup>-1</sup>, 5 mV s<sup>-1</sup>, 10 mV s<sup>-1</sup> and 20 mV s<sup>-1</sup> are observed. After cyclic voltammetry, the analysis of dissolved metals and sulfur in the solutions was done. The results show that the highest concentrations of the Fe and Cu are obtained at the scan rate 1 mV s<sup>-1</sup>. With increasing scan rate only fast reactions can be realized. The low scan rates are associated with slow reactions. Therefore, a molar ratio of Cu/Fe is the largest at the scan rate of 1 mV s<sup>-1</sup> and concentration of  $10^{-2}$  mol L<sup>-1</sup> Cys.

High scan rate  $\xrightarrow{\text{rapid reaction}}$  Cu(I)-Cys complex  
is formed which reduces  
dissolution of Cu

Low scan rate  $\xrightarrow{\text{rapid reaction}}$  Cu(I)-Cys complex  
is formed which reduces  
dissolution of Cu  $\xrightarrow{\text{slow reaction}}$  Cu(I)-Cys complex  
is dissolved and  
concentration of Cu  
in solution is  
increased

### INTRODUCTION

Copper has been found wide application in industry. It is usually obtained from sulphide copper minerals as chalcopyrite (CuFeS<sub>2</sub>). More than 70% of the copper reserves are situated in chalcopyrite.<sup>1</sup> The recovery of copper is realized by pyrometallurgical, hydrometallurgical and biohydrometallurgical processes. Due to the ecological reasons the chemical leaching and biochemical processes are preferable. Electrochemical methods are suitable for investigating the process of leaching. During the electrochemical oxidation and oxidative leaching following dissolution reactions of chalcopyrite can occur:



The generation of elemental sulphur,<sup>9-11</sup> jarosite<sup>12</sup> and different intermediate sulphide species<sup>8,11-14</sup> is considered responsible for surface passivation of chalcopyrite and slow dissolution of copper. Therefore, the permanent research efforts to find new assets with increasing efficiency of dissolution of minerals are desirable. Various studies have shown that amino acids in different environments can be either green inhibitors of corrosion<sup>15-25</sup> or activators of corrosion<sup>16,19,26,27</sup> of metals, their alloys and minerals.

The most of studies consider the effect of cysteine (Figure 1) on corrosion. Studies have shown that cysteine can be a good inhibitor of corrosion of copper in: 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>,<sup>15</sup> 1 mol L<sup>-1</sup> HNO<sub>3</sub>,<sup>16</sup> 8 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>,<sup>17</sup> 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub><sup>18</sup> and 0.5 mol L<sup>-1</sup> HCl.<sup>19</sup> It also inhibits the dissolution of iron in 1 mol L<sup>-1</sup> HCl<sup>20</sup> and mild steel in

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$0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ,<sup>25</sup> but enhances dissolution of 304L stainless steel in  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ <sup>26</sup> and pyrite ( $\text{FeS}_2$ ) in Tuovinen buffer.<sup>27</sup>

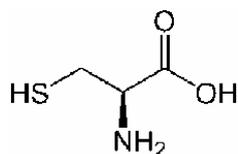


Fig. 1 – The molecular structure of the cysteine.

Investigations presented in this paper examine the impact of different concentrations of cysteine in  $10^{-2} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  on dissolution of chalcopyrite.

## RESULTS

### Cyclic voltammetry

Results of cyclic voltammetry are presented in Figure 2. At a scan rate of  $1 \text{ mV s}^{-1}$  and  $5 \text{ mV s}^{-1}$  (Figure 2a et Figure 2b) the current values are up to certain potential values greater than, or equal to the current value of  $10^{-2} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  for all concentrations of Cys. After that all of the current values for all concentrations of Cys are less than current values from the  $10^{-2} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ . Expressed anode peaks occur by increasing the scan rate for concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$ . The highest anodic peak current occur at a scan rate of  $1 \text{ mV s}^{-1}$  for concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$ . At a scan rate of  $20 \text{ mV s}^{-1}$  and concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$  in anodic part of the curve the area of passivation is not emphasized, while at a scan rates of  $5 \text{ mV s}^{-1}$  and  $10 \text{ mV s}^{-1}$  area of the passivation is in the range from 350 to 450 mV. At the scan rate of  $20 \text{ mV s}^{-1}$  area of passivation is moved to within the limits between 450-550 mV.

In Figure 3 cyclic voltammogram for  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$  for different scan rates is shown. From Figure 3 can be seen that the anodic peak current moves a bit in a positive direction with the increase of the scan rate. This indicates that either the character of process changes from quasi-reversible to irreversible one<sup>28,29</sup> or that an uncompensated ohmic drop occurs.<sup>30</sup> The absence of increase in  $\Delta E_p$  with increases of scan rate shows that uncompensated ohmic drop is not reason for moving of anodic peak current.

The dependence of the anodic peak current of scan rate, for concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$  is presented in Figure 4. This dependence is linear (see Figure 4) which indicates a diffusion controlled dissolution.<sup>29</sup>

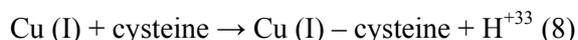
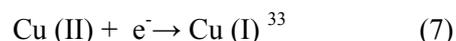
### Chemical analysis of solutions after cyclic voltammetry

Results of the chemical analysis of the solutions after cyclic voltammetry are presented in Figure 5-6. They show that the highest concentrations of Cu and Fe are obtained at a scan rate of  $1 \text{ mV s}^{-1}$  (Figure 5). At a scan rate of  $1 \text{ mV s}^{-1}$  and concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$ , the concentration of Cu is higher than the concentration of Fe, while at other scan rates is opposite (Figure 6). From table 1 it can be seen that the largest molar ratio Cu/Fe is obtained at a scan rate of  $1 \text{ mV s}^{-1}$  and concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$ . For concentration  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$  the molar ratio Cu/Fe decreases with increasing scan rate, while for other concentrations of cysteine the molar ratio Cu/Fe increases with increasing scan rate.

## DISCUSSION

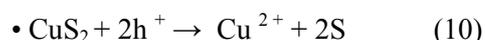
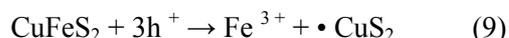
In the presence of the ligands, ligand-promoted dissolution occurs, which consists of rapid adsorption of the ligand, the slow release of the metal-ligand complex and rapid regeneration of the surface.<sup>31</sup> Oguzie *et al.* found that cysteine at low concentrations ( $0.1\text{--}0.5 \text{ mmol L}^{-1}$ ) is promoted, whereas at higher concentrations ( $1.0\text{--}5.0 \text{ mmol L}^{-1}$ ) was inhibited corrosion process of low carbon steel in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ .<sup>32</sup> El-Deab assumed that the formation of Cu (I) – Cys complex (Eqs 7 and 8) is a reason for improving the corrosion inhibition efficiency of iron in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  in the presence of copper ions.<sup>33</sup>

According to Matos *et al.*, the formation of Cu (I) - Cys complex inhibits corrosion of copper at concentrations  $10^{-2} \text{ mol L}^{-1} \text{ Cys}$  and  $10^{-3} \text{ mol L}^{-1} \text{ Cys}$  in  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ .<sup>15</sup>



Cysteine via FeS-R i Fe-S- S- R bridges favours dissolution of pyrite. Result is formation of iron-sulphur-cysteine complex.<sup>27</sup>

From Fig. 2 it can be seen that  $10^{-2} \text{ mol L}^{-1}$  of cysteine is enough to increase the dissolution of chalcopyrite. According to Crundwell, firstly the Fe-S bond is broken and then the Cu-S bond is broken in chalcopyrite.<sup>34</sup>



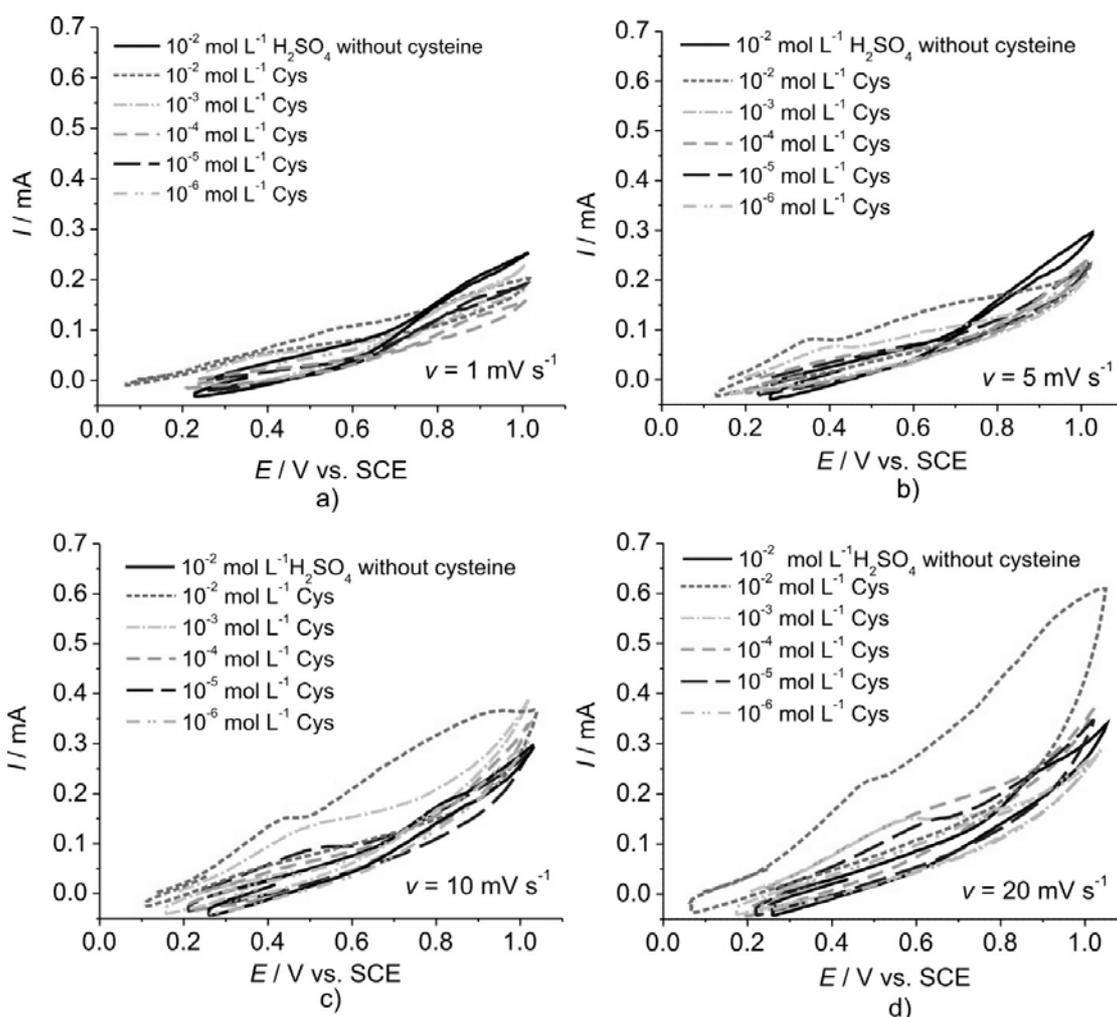


Fig. 2 – Cyclic voltammograms for  $10^{-2} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and different concentrations of cysteine in  $10^{-2} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at scan rate: a)  $1 \text{ mV s}^{-1}$ , b)  $5 \text{ mV s}^{-1}$ , c)  $10 \text{ mV s}^{-1}$ , d)  $20 \text{ mV s}^{-1}$ .

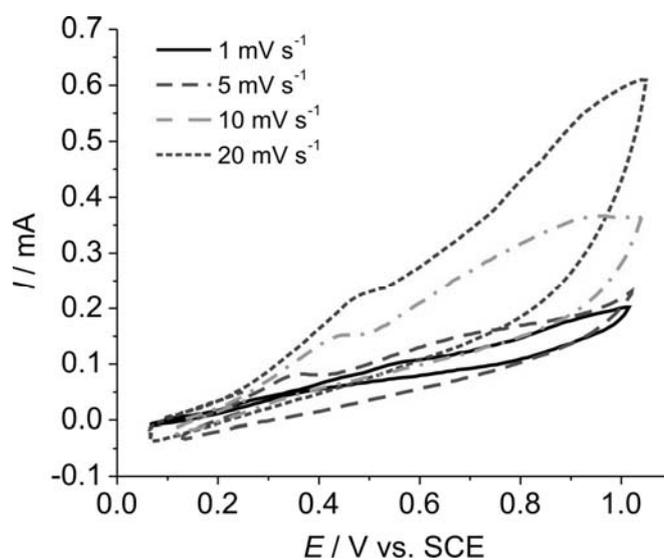


Fig. 3 – Cyclic voltammogram for  $10^{-2} \text{ mol L}^{-1}$  Cys for different scan rates.

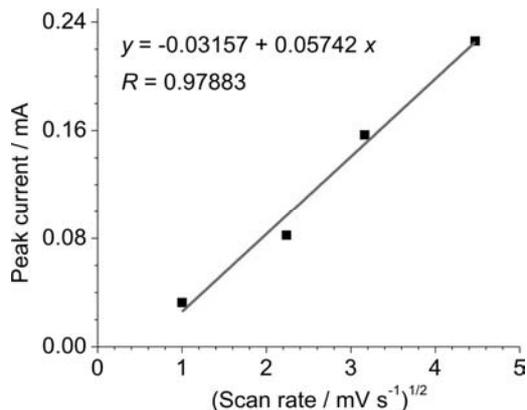


Fig. 4 – Peak current against the square root of scan rate for chalcopyrite in  $10^{-2}$  mol L $^{-1}$  Cys.

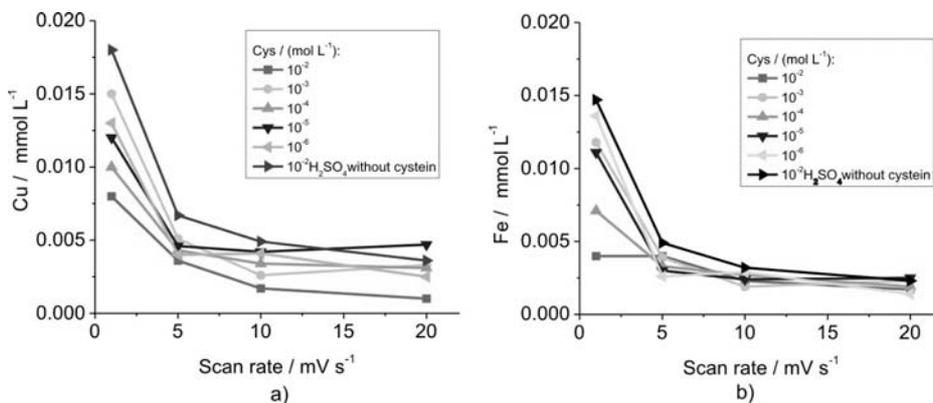


Fig. 5 – Concentrations of Cu and Fe in the solutions of cysteine after cyclic voltammetry at different scan rates.

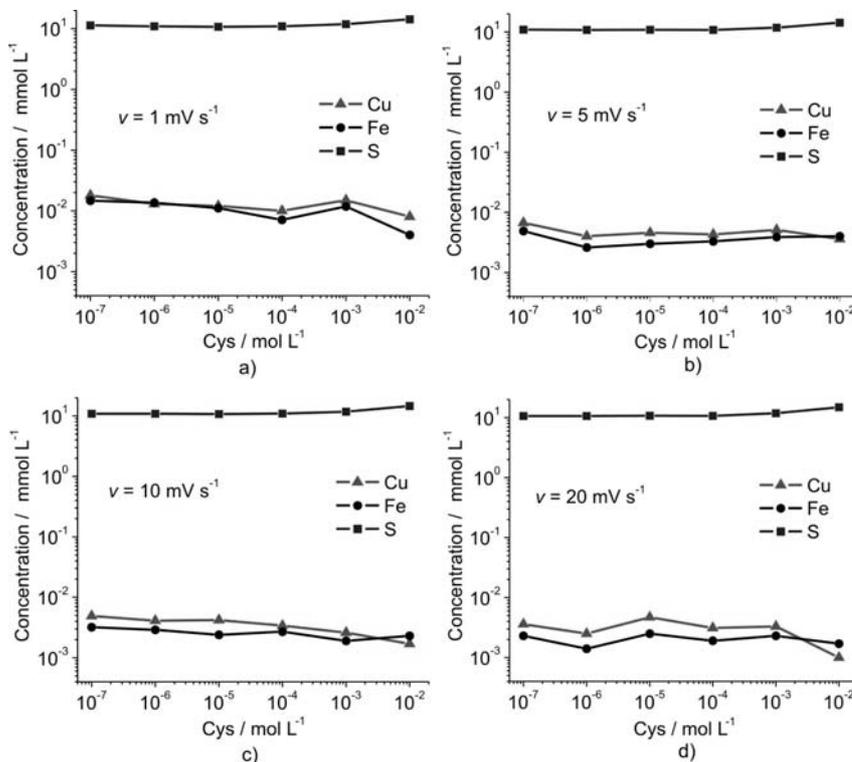


Fig. 6 – Concentrations of Fe, Cu and S in the solutions of cysteine after cyclic voltammetry for scan rate: a) 1mV s $^{-1}$ , b) 5mV s $^{-1}$ , c) 10mV s $^{-1}$ , d) 20mV s $^{-1}$ .

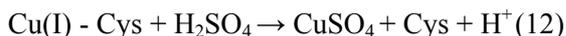
Table 1

Change of molar ratio Cu/Fe in the solutions after cyclic voltammetry at different scan rates and concentrations of cysteine

$C_{\text{Cys}}$ (mol L <sup>-1</sup> )	Cu/Fe			
	1 (mV s <sup>-1</sup> )	5 (mV s <sup>-1</sup> )	10 (mV s <sup>-1</sup> )	20 (mV s <sup>-1</sup> )
10 <sup>-2</sup>	2	0.9	0.74	0.59
10 <sup>-3</sup>	1.27	1.30	1.37	1.44
10 <sup>-4</sup>	1.40	1.30	1.26	1.63
10 <sup>-5</sup>	1.08	1.53	1.75	1.88
10 <sup>-6</sup>	0.95	1.54	1.41	1.78
-	1.22	1.37	1.53	1.56

For higher scan rate and concentrations of cysteine, the breaking of Fe - S bonds, dissolution of Fe and formation of iron-sulphur-cysteine complex is probably done via FeS -R i FeS - S- R bridges<sup>27</sup>. In this manner the dissolution of chalcopyrite accelerates with respect to the case without cysteine in 10<sup>-2</sup> mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Copper ions from dissolved chalcopyrite form Cu (I) - cysteine complex (Eqs 7 and 8). The Cu (I)-Cys complex reduces dissolution of Cu<sup>15</sup>, because of which concentration of Cu ions is smaller than the concentration of Fe ions in solution with concentration of 10<sup>-2</sup> mol L<sup>-1</sup> Cys and scan rate 20mV s<sup>-1</sup> (Fig 6d).

Figs 2a and 2b show that at a lower scan rate and high concentrations of the cysteine the dissolution of chalcopyrite is better at lower potentials, while at high potentials this process is inhibited with respect to the case with 10<sup>-2</sup> mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> without cysteine. At a lower scan rate and high concentrations of the cysteine slow reaction have enough time to occur after rapid reaction. The slow reaction is a reaction of the sulfuric acid with ions of copper from complex Cu (I) - Cys:



It is possible that at high potentials some insoluble compounds of Fe can be formed. This may be reason for higher concentrations of Cu ions with respect to Fe ions in solution with the concentration of 10<sup>-2</sup> mol L<sup>-1</sup> Cys and scan rate of 1mV s<sup>-1</sup> (Fig 6a).

All mentioned previously in this section causes that the molar ratio of Cu/Fe is the largest at a scan rate of 1mV s<sup>-1</sup> and concentration of 10<sup>-2</sup> mol L<sup>-1</sup> Cys (Tab.1). These results can be significant for electrochemical dissolution of chalcopyrite.

## EXPERIMENTAL

### Materials

A sample of chalcopyrite is obtained from the Bor deposits in Serbia. A piece of chalcopyrite from a naturally occurring mineral is a metallographically polished by

comprising grinding on paper, rinsing with water and alcohol. Polished sample then is coupled with silver wick is adhesive for copper wire, and then sealed with the material on the basis of methyl-methacrylate.

Working surface of electrode of 1 cm<sup>2</sup> is firstly mechanically polished with silicon carbide paper and alumina (Al<sub>2</sub>O<sub>3</sub>), and then the electrode is washed with distilled water and dried.

Cysteine (Merck) directly is added to 10<sup>-2</sup> mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> to obtain the 10<sup>-2</sup> mol L<sup>-1</sup> solution which is later used to obtain a series of solutions with concentrations of 10<sup>-3</sup> mol L<sup>-1</sup> Cys, 10<sup>-4</sup> mol L<sup>-1</sup> Cys, 10<sup>-5</sup> mol L<sup>-1</sup> Cys, 10<sup>-6</sup> mol L<sup>-1</sup> Cys.

### Electrochemical measurements

Electrochemical measurements were performed in a system with three electrodes: working electrode made of natural chalcopyrite, reference saturated calomel electrode and auxiliary electrodes made of platinum.

Apparatus for measuring is made up of potentiostat and polarographic analyzer directly connected to the computer via the AD card.

We applied the following electrochemical methods: open circuit potential and cyclic voltammetry. Open circuit potential is measured 15 min, then the cyclic voltammograms were determined from open circuit potential up to 1 V (SCE) in the anodic direction. Measurements were performed at scan rates of 1 mV s<sup>-1</sup>, 5 mV s<sup>-1</sup>, 10 mV s<sup>-1</sup> and 20 mV s<sup>-1</sup>, at room temperature in naturally aerated solutions.

### ICP measurements

After cyclic voltammetry, analysis of dissolved metals and sulfur in the solutions has been carried out by simultaneous atomic emission spectrometry with inductively coupled plasma (ICP AES), model Spectro ciros vision.

## CONCLUSION

Analysis of the solutions after the cyclic voltammetry has been shown that the highest concentrations of Cu and Fe are obtained at the scan rate of 1mV s<sup>-1</sup>. This happens due to the long polarization time. At scan rate 1mV s<sup>-1</sup> and concentration of 10<sup>-2</sup> mol L<sup>-1</sup> Cys in 10<sup>-2</sup> mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> the concentration of Cu is higher than the concentration of Fe, while at the other values of the scan rate the situation is opposite. Molar ratio Cu/Fe is the largest at the scan rate of 1mV s<sup>-1</sup> and concentration of 10<sup>-2</sup> mol L<sup>-1</sup> Cys. This is probably

a consequence that at higher scan rate only reaction of rapidly forming Cu (I)- cysteine complex can be realized, and that at slow scan rate have enough time to dissolve Cu (I)- cysteine complex which increasing the concentration of Cu in solution. The dissolution process of chalcopyrite is diffusion controlled at  $10^{-2}$  mol L<sup>-1</sup> Cys concentration. All these findings can be important for electrochemical leaching.

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