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## Dissolution kinetics of secondary covellite resulted from digenite dissolution in ferric/acid/chloride media

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**Abstract:** Dissolution kinetics of digenite ( $\text{Cu}_9\text{S}_5$ ) was studied in  $\text{Fe}^{3+}$ - $\text{H}_2\text{SO}_4$ - $\text{NaCl}$  media. The temperature range for the study was between 297 and 373 K (24 and 100°C), with a ferric concentration between 0.0100 and 0.0806 mol/dm<sup>3</sup>, a sulfuric acid concentration of 0.05 to 1.5 mol/dm<sup>3</sup> and a NaCl concentration of 1.5 to 5 mol/dm<sup>3</sup>. Agitation speed and particle size were also studied. Results indicate that the dissolution mechanisms of digenite occurs in two stages: i) generation of covellite ( $\text{CuS}$ ) with the formation of cupric ion ( $\text{Cu}^{2+}$ ) and ii) dissolution of covellite ( $\text{CuS}$ ) with copper production in the system, as well as amorphous sulfur ( $\text{S}^0$ ). The second stage occurred very slowly compared to the first stage, the above variables studied directly affected the second stage. Temperature,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{SO}_4$  concentration positively affected dissolution of covellite formed (second stage), while the presence of NaCl did not increase dissolution of  $\text{Cu}_9\text{S}_5$  or  $\text{CuS}$ . Results showed that stirring speed had an important role in the dissolution rate of  $\text{CuS}$ . Dissolution kinetics was analyzed using the model of diffusion through the porous layer. Covellite dissolution reaction order was 2.3 and 0.2 with respect to the concentration of ferric and sulfuric acid, respectively, and the rate was inversely proportional to particle size. The calculated activation energy was 36.1 kJ/mol, which is a typical value for a reaction controlled by diffusion in the porous layer at temperature between 297 and 373 K (24 and 100°C).

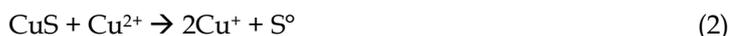
**Keywords:** dissolution kinetics, digenite, covellite, diffusion

### 1. Introduction

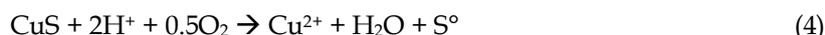
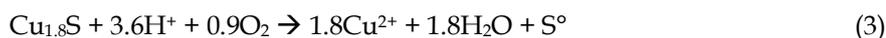
Currently there are significant resources of low-grade copper sulfide ores, which is a depletion sign of oxidized ore reserves. Environmental pollution produced by pyrometallurgical processes treating these copper concentrates is of great concern due to the production of large quantities of  $\text{SO}_2$  and  $\text{SO}_3$  in the environment, making it necessary to look for new treatment alternatives that are efficient and cost-effective for the recovery of copper from sulfides. In Chile, the Ministry of Finance has calculated that from 2017 to 2021 a total of US \$1.325 billion in funding will be obtained from green taxes, of which 1% will correspond to  $\text{SO}_x$  emissions. In other words, the approximate amount of tons annually from  $\text{SO}_x$  emissions would reach 26.5 million tons. An alternative way of treating these sulfides is hydrometallurgical processing (Domic, 2001). This type of processing is economically viable and environmentally friendly. Copper sulfide minerals commonly studied by aqueous processes are chalcopyrite ( $\text{CuFeS}_2$ ) (Lu et al., 2000; Hiroyoshi et al, 2001; Yoo et al., 2010; Padilla et al., 2015),

enargite ( $\text{Cu}_3\text{AsS}_4$ ) (Herrerros et al., 2002; Padilla et al., 2005, Riveros and Dutrizac, 2008; Tongamp et al., 2010), bornite ( $\text{Cu}_5\text{FeS}_4$ ) (Dutrizac et al., 1970; Pesic and Olson, 1983; Pesic and Olson, 1984; Lu and Dreinsinger, 2013), chalcocite ( $\text{Cu}_2\text{S}$ ) (Grizo et al., 1982; Fisher, 1994; Senanayake, 2007, Renman et al., 2010), digenite ( $\text{Cu}_9\text{S}_5$ ) (Ruiz et al., 1999, Miki et al., 2011), among others. From all the compounds mentioned, digenite is the sulfide less studied.

Ruiz et al. (1999) studied the dissolution of digenite in a  $\text{CuCl}_2$ -HCl-NaCl media, in an oxygenated and neutral (no oxygen) atmosphere. Dissolution mechanisms of  $\text{Cu}_9\text{S}_5$  and  $\text{CuS}$  in cupric chloride mediums under an inert atmosphere were represented by the following reactions:

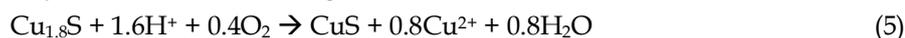


Furthermore, the digenite leaching mechanism in an oxygenated atmosphere was described as follows:



Ruiz concluded that the effect of oxygen was preponderant in the leaching of digenite, reaching values of 90% extraction, while extraction values only reached 50% in the neutral environment.

Unlike the previous investigation, Miki et al. (2011) studied the dissolution of synthetic digenite in chlorinated media at room temperature. For the above mentioned, the reactions described by Ruiz et al. (1999) were used as a basis for the case of digenite leached in a chlorinated media. Dissolution mechanisms were described by eq. 4 and the following one (Ruiz et al., 1999):



This investigation concluded that digenite leached under 550 mV became secondary covellite (intermediate species), and this can only be dissolved above 550 mV (Ruiz et al., 1999).

In brief, both studies present different reaction mechanisms of digenite dissolution (reaction 3 and 5), focused mainly on the formation of copper ions ( $\text{Cu}^{2+}$ ) and elemental sulfur ( $\text{S}^\circ$ ) for reaction 3 while covellite ( $\text{CuS}$ ) and copper ions are generated in reaction 5. It should be noted that the appearance of elemental sulfur is the cause (described as passivation), or generator of the main resistance to the flow of ions from the core of the solution to the surface of the particle, generating the passivation of the particle. In addition, for electrochemical dissolution processes (main mechanism for copper sulfides), passivation does not produce electron transfer because the sulfur is not conductive. Therefore, this research will evaluate dissolution rate of  $\text{Cu}_9\text{S}_5$  in an acidic media consisting of ferric ( $\text{Fe}^{3+}$ ) and chloride ( $\text{Cl}^-$ ), as well as dissolution kinetics of covellite.

## 2. Experimental procedure

Synthetic samples of digenite obtained from Sigma Aldrich were used for the experiments, consisting of a fine powder (under 45  $\mu\text{m}$ ) with a purity of 98%. The pelletizing method was used for experiments with different particle sizes, wherein the particles were bonded by controlled forces of pressure, obtaining different sized spheres (30, 45, 55 and 70  $\mu\text{m}$ ).

Isothermic batch-type leaching experiments were conducted in a 2  $\text{dm}^3$  glass reactor equipped with variable mechanical stirrers, a heating mantle, a thermocouple, a porous tube for liquid samples and a water cooled condenser to minimize medium loss by evaporation.

In a typical experiment, the reactor was charged with 1.0  $\text{dm}^3$  of ferric chloride leaching solution. The solution was then heated to the desired temperature, and solid samples of  $3 \cdot 10^{-3}$  kg (3.0 g) were added to the reactor. The reaction was allowed to proceed and then liquid samples were withdrawn at predetermined times for copper determination by atomic absorption spectroscopy (AAS). At the end of each experiment, solutions were filtered and residues were washed and dried to be sent to X-ray diffraction (XRD). The experimental tests were carried out in duplicate.

X-ray diffraction analysis of the original digenite sample is shown in Figure 1, and it can be seen that the diffraction lines correspond to a digenite sample with traces of covellite ( $\text{CuS}$ ), djurleite ( $\text{Cu}_{31}\text{S}_{16}$ ) and anilite ( $\text{Cu}_7\text{S}_4$ ). Mineralogical analysis of this materials showed that digenite was the principal copper compound present with 96.8 wt%.

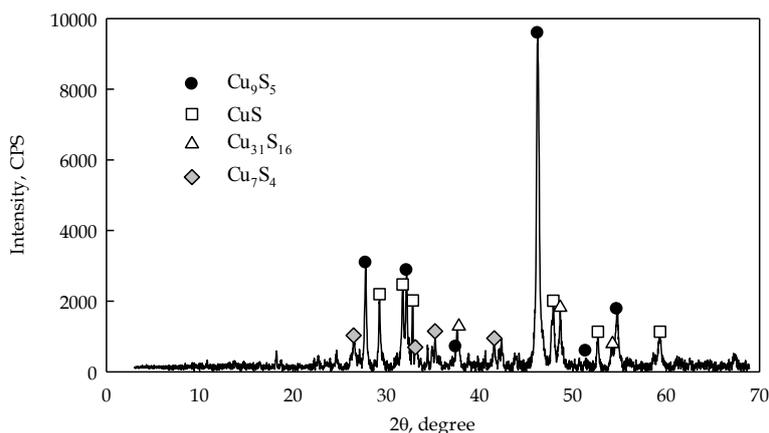


Fig. 1. XRD lines of the original digenite sample

### 3. Result and discussion

The studied variables that affect digenite dissolution were: agitation speed, temperature, ferric, acid and NaCl concentration, and particle size.

#### 3.1. Effect of agitation speed

Leaching experiments were conducted in the range from 250 to 750 rpm with 1 dm<sup>3</sup> of solution and wherein the concentration of Fe<sup>3+</sup>, H<sub>2</sub>SO<sub>4</sub> and NaCl were 0.027 mol/dm<sup>3</sup>, 0.5 mol/dm<sup>3</sup> and 1.5 mol/dm<sup>3</sup>, respectively. The results are shown in Figure 2.

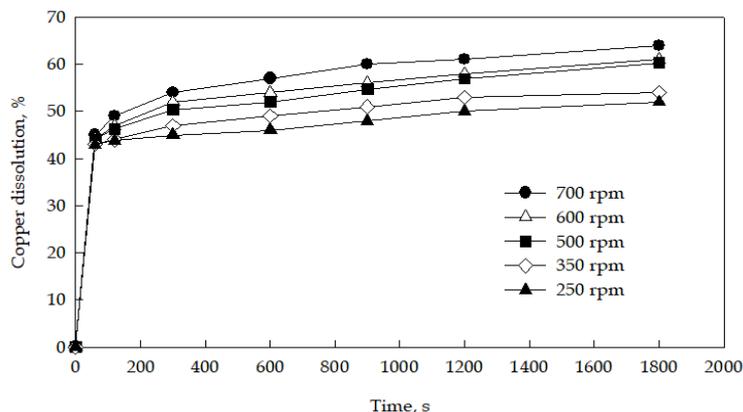


Fig. 2. Effect of agitation speed on the dissolution of digenite. Working conditions:  $T = 373 \text{ K}$ ,  $[\text{Fe}^{3+}] = 0.027 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol/dm}^3$ ,  $[\text{NaCl}] = 1.5 \text{ mol/dm}^3$ , particle size = 45  $\mu\text{m}$

The results show that agitation speed has an effect on the dissolution rate of digenite throughout the entire rpm range. These results indicate that mass transfer plays an important role in the dissolution rate of digenite. However, and based on the reactions shown above (eqs. 1 to 5), the velocity should not affect mainly due to the possible formation of elemental sulfur at the surface of the particle, i.e. the agitation cannot affect diffusion through a reaction product layer. However, these preliminary results show that the rate would be limited not by the sulfur layer but by another mechanism. This mechanism will be discussed later.

Furthermore, to maintain the solids in movement, the leaching solution was stirred at 500 rpm in all carried out experiments. No experiments were carried out at longer times (days) because of the difficulty of maintaining the leaching for a couple of days.

#### 3.2. Effect of NaCl concentration

Effect of NaCl on digenite dissolution rate was studied. The experiments were carried out varying the sodium chloride concentrations from 1.5 to 5.0 mol/dm<sup>3</sup>. Figure 3 shows digenite dissolution results

for an experimental time of 1800 s (30 min). As shown in the figure, presence of 1.5 mol/dm<sup>3</sup> NaCl in the medium positively affects digenite dissolution. NaCl concentrations between 1.5 and 5.0 mol/dm<sup>3</sup> did not affect copper dissolution predominantly.

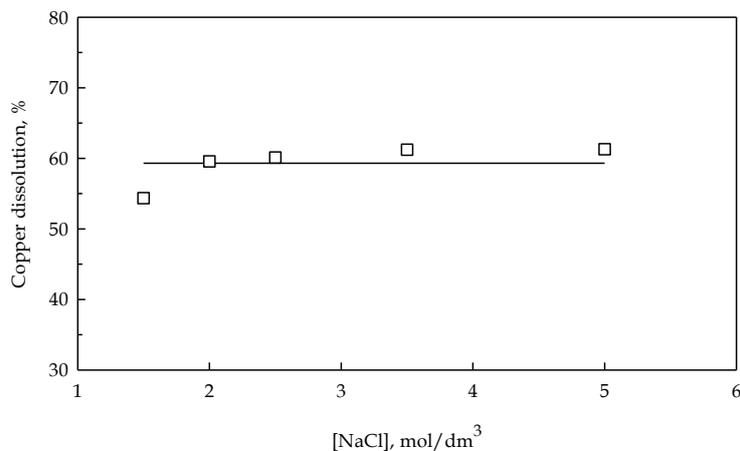


Fig. 3. Effect of NaCl concentration on the dissolution of digenite. Working conditions:  $T = 373$  K,  $[\text{Fe}^{3+}] = 0.0269$  mol/dm<sup>3</sup>,  $[\text{H}_2\text{SO}_4] = 0.5$  mol/dm<sup>3</sup>, particle size = 45  $\mu\text{m}$ , time period = 1800 s

Concentrations of NaCl lower than 1.5 mol/dm<sup>3</sup> were not taken into account because in this work the maximum dissolution of digenite was obtained. In this case, it was enough to use concentrations above 1.5 mol/dm<sup>3</sup> NaCl.

### 3.3. Effect of temperature

Experiments were carried out at temperature range from 297 to 373 K (24 to 100 °C). Results are shown in Figure 4, where it can be observed that digenite dissolution has two stages; first stage: very fast dissolution in the first few seconds and then, second stage: a gradual increase in the dissolution. Thus, at the temperature of 297 K, the dissolution of copper reaches 46.4% in 1800 s, while 60.3% dissolution is reached at a temperature of 373 K at the same time.

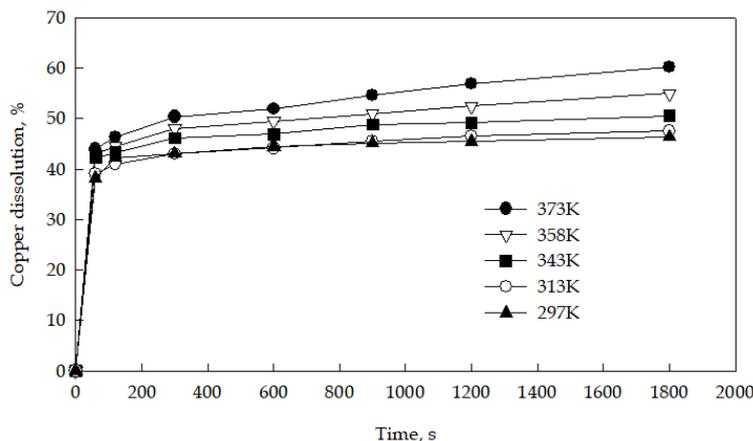
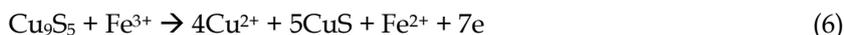
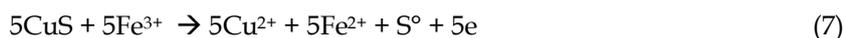


Fig. 4. Effect of temperature on the dissolution of  $\text{Cu}_9\text{S}_5$ . Working conditions:  $[\text{Fe}^{3+}] = 0.027$  mol/dm<sup>3</sup>,  $[\text{H}_2\text{SO}_4] = 0.5$  mol/dm<sup>3</sup>,  $[\text{NaCl}] = 1.5$  mol/dm<sup>3</sup>, particle size = 45  $\mu\text{m}$

Additional experiments carried out at various concentrations of  $\text{Fe}^{3+}$ ,  $\text{H}_2\text{SO}_4$  and NaCl showed similar behavior in the dissolution rate, as well as the amount of copper extracted. Based on the results generated by the dissolution behavior of digenite and on the characterization of the reaction products (shown later), the following two semi-reactions can be applied showing digenite dissolution, (reaction 6) and subsequent dissolution of covellite (reaction 7).





Copper ions would not play an important role in the leaching rate of digenite or covellite. In the presence of chloride ions, the copper ions were maintained in the solution as cupric chloride complexes, mainly as  $\text{CuCl}_2^-$  and  $\text{CuCl}_3^{2-}$ . This is accomplished normally by adding to the system sodium chloride or another chloride salt in high concentrations.

It was observed that the dissolution of digenite in the first stage reaches 47.9%. The theoretical extraction of digenite dissolution to pass over to covellite, according to reaction 6, is 44.4%. This suggests that in the temperature range studied, formation of CuS occurs directly from  $\text{Cu}_9\text{S}_5$  dissolution. In order to explain this behavior, an experimental test was performed under the same working conditions for 900 s. Solid residues produced in the experiment were analyzed by XRD to identify the products of the reaction. Figure 5 shows the diffraction lines for covellite (CuS), without the presence of digenite or other compounds of copper. Thus, the digenite dissolution mechanism is given by the formation of covellite and copper in the system, as shown in eqs. 6 and 7.

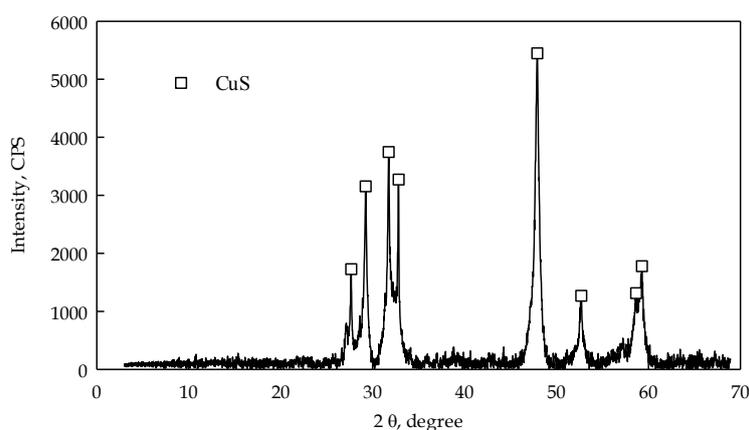


Fig. 5. XRD lines for digenite sample leached for 900 s

In addition, a small intensity of picks can be observed in the diffractogram. These picks (and in small intensities) can be due to the presence of amorphous sulfur in the particle. Taking the above into consideration, these XRD results would demonstrate the reactions postulated previously (reactions 6 and 7). That is to say, the digenite in a ferric/acid/chloride media, would proceed its dissolution towards the production of cupric ion and covelline, and then the CuS will be leached to produce copper in solution and elemental sulfur.

Then, the thin layer of elemental sulfur would cover the particles, however, with the presence of chloride ions, this layer becomes porous, thus, allowing the leaching solution to penetrate towards the surface of the particles (phenomenon widely analyzed in the literature (Ruiz et al. 1999; Padilla et al., 2005)). Therefore, the sulfur layer would not generate a resistance to covelline dissolution (see Figure 3). So, in summary, the chloride ions would have two important roles; complex formation of cupric ions and generation of a porous layer on the particles.

### 3.4. Effect of $\text{Fe}^{3+}$ concentration

The effect of ferric acid concentrations on the dissolution of digenite was studied. Results are shown in Figure 6. It can be clearly observed that in a low concentration of  $\text{Fe}^{3+}$  (0.0100 mol/dm<sup>3</sup>), digenite dissolution reaches a value of 51.0%. Increased concentrations of ferric acid strongly affect the dissolution rate of covellite. Thus, for  $\text{Fe}^{3+}$  concentration of 0.0125 mol/dm<sup>3</sup>, 54.0% dissolution is achieved, while increasing the  $\text{Fe}^{3+}$  concentration to 0.0806 mol/dm<sup>3</sup>, an almost complete dissolution (99.1%) of covellite is reached in the same experimental time of 1800 s.

### 3.5. Effect of $\text{H}_2\text{SO}_4$ concentration

Experiments were conducted for sulfuric acid concentration range from 0.05 to 1.5 mol/dm<sup>3</sup>. Dissolution of digenite results are shown in Figure 7. The positive effect of sulfuric acid on the

dissolution of covellite can be seen in this figure. The maximum copper extraction (64.3%) is obtained at 1800 s with 0.5 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>. However, increasing acid concentration (up 0.5 mol/dm<sup>3</sup>) the dissolution rate of covellite decreases. Thus, copper extraction with 1.5 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> reaches a value of 57.0%.

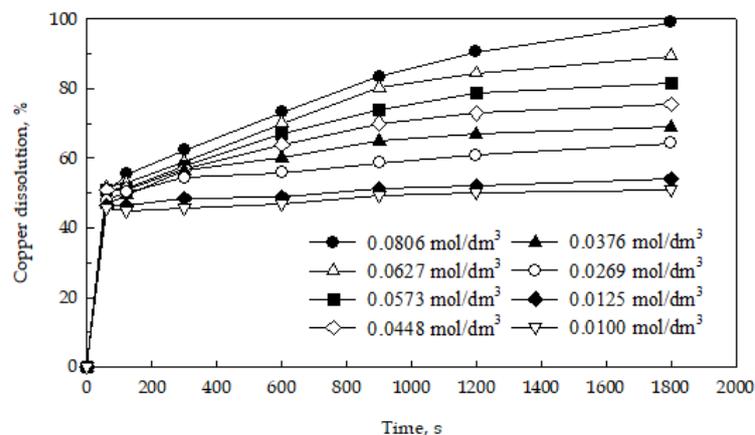


Fig. 6. Effect of Fe<sup>3+</sup> concentration on the dissolution of digenite. Working conditions:  $T = 373$  K,  $[\text{H}_2\text{SO}_4] = 0.5$  mol/dm<sup>3</sup>,  $[\text{NaCl}] = 1.5$  mol/dm<sup>3</sup>, particle size = 70  $\mu\text{m}$

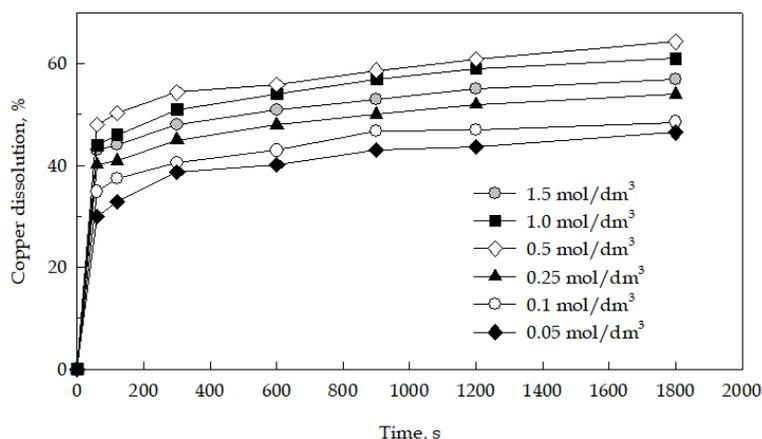


Fig. 7. Effect of H<sub>2</sub>SO<sub>4</sub> concentration on the dissolution of digenite. Working conditions:  $T = 373$  K,  $[\text{Fe}^{3+}] = 0.0269$  mol/dm<sup>3</sup>,  $[\text{NaCl}] = 1.5$  mol/dm<sup>3</sup>, particle size = 45  $\mu\text{m}$

This behavior is primarily due to the increase in the concentration of sulfate ions (HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) with increasing acid concentration. Antonijevic et al. (1997) found that an increase in the sulfate concentration negatively impacted iron recovery from pyrite and concluded that the sulfate ions competed with H<sub>2</sub>O<sub>2</sub> molecules (compound oxidizer) for adsorption sites on the surface of particles, leading to a decrease in the pyrite dissolution rate. Therefore, this behavior indicates that the decrease in the covellite dissolution rate at high H<sub>2</sub>SO<sub>4</sub> concentrations observed in this study could be due to the competitive adsorption of sulfate ions and Fe<sup>3+</sup> on the CuS surface.

### 3.6. Effect of particle size

Experiments were conducted using 0.027 mol/dm<sup>3</sup> Fe<sup>3+</sup>, 0.5 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> and 1.5 mol/dm<sup>3</sup> NaCl concentrations at 373 K for four different particle sizes: 30, 45, 55 and 70  $\mu\text{m}$ . Experimental results are shown in Figure 8. It can be observed that with increasing particle size, digenite dissolution with respect to dissolution speed, while the covellite dissolution rate decreases. Thus, 56.0% covellite dissolution is obtained at 30 s for particle size 30  $\mu\text{m}$ , while the same dissolution degree is obtained at 1500 s for particle size 70  $\mu\text{m}$ . Decreased dissolution rates for larger particles may be due to reduced interfacial reaction areas.

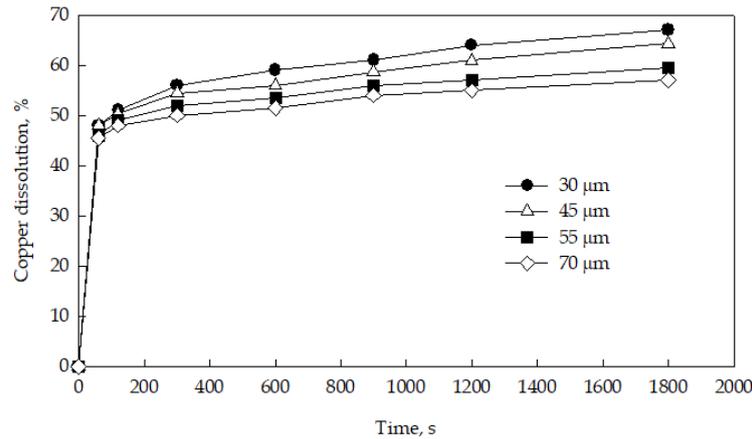


Fig. 8. Effect of particle size on dissolution of digenite. Working conditions:  $T = 373 \text{ K}$ ,  $[\text{Fe}^{3+}] = 0.027 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol/dm}^3$ ,  $[\text{NaCl}] = 1.5 \text{ mol/dm}^3$

### 3.7. Dissolution kinetics of covellite

As shown in Figure 4, the effect of temperature on the dissolution of copper from covellite was not significant. This behavior suggests that the process is controlled by diffusion through a porous layer of mineral. Therefore, taking control by diffusion through the porous layer, the rate equation for a recessive core model of diffusion through the porous layer with radius  $r_0$ , for a constant concentration of reactants, can be written as (Shon and Wadsworth, 1979):

$$1 - \left(\frac{2}{3}\right)\alpha - (1 - \alpha)^{\frac{2}{3}} = kt \quad (8)$$

where  $\alpha$  is the fraction of reacted covellite,  $t$  is the reaction time, and  $k$  is the apparent rate constant, given by the following general equation:

$$k = k_1 \frac{C_{\text{Fe}^{3+}}^p C_{\text{NaCl}}^m C_{\text{H}_2\text{SO}_4}^d}{r_0^2} \quad (9)$$

where  $k_1$  is the intrinsic rate constant,  $C_{\text{Fe}^{3+}}$ ,  $C_{\text{NaCl}}$  and  $C_{\text{H}_2\text{SO}_4}$  are the concentrations of ferric acid, sodium chloride and sulfuric acid in the system, respectively. Because the dissolution rate is independent of the sodium chloride concentration in the range used in this study ( $> 1.5 \text{ mol/dm}^3$ ), as shown in Figure 3, a zero reaction order can be assumed for the sodium chloride concentration. Therefore, the overall reaction rate constant can be expressed as:

$$k = k_1 \frac{C_{\text{Fe}^{3+}}^p C_{\text{H}_2\text{SO}_4}^d}{r_0^2} \quad (10)$$

The value of  $\alpha$  was 0.44 which considered the fraction of copper extracted when the digenite reacted completely. In this case,  $\alpha$  is represented as  $\alpha = (\alpha - 0.44)/0.56$ ,  $\alpha \geq 0.44$ . In addition, the leaching time for the formation of  $\text{Cu}^{2+}$  from the covellite (reaction 7) is given by  $t_{\text{Cu}^{2+}} = t - t_{\text{Cu}_9\text{S}_5}$ .

Figure 9 shows a graph of  $1 - \left(\frac{2}{3}\right)\alpha - (1 - \alpha)^{\frac{2}{3}}$  as a function of time for experimental data obtained from Figure 4, in the 297 to 373 K (24 to 100 °C) temperature range for digenite samples 45  $\mu\text{m}$  (particle size). Similar works were carried out for experimental results concerning the effect of  $\text{Fe}^{3+}$  and  $\text{H}_2\text{SO}_4$  concentrations. The results in Figure 9 show good linear adjustment of kinetic data with regression coefficients,  $R^2$ , from 0.93 to 0.98, for the entire temperature range, indicating the applicability of the equation (10). The values of apparent kinetic constants at various temperatures were obtained from the slopes of the straight lines and are shown in Table 1.

Furthermore, the reaction order  $p$  was calculated using kinetic data from the effect of ferric concentrations in the system. Figure 10 shows experimental data for various concentrations of  $\text{Fe}^{3+}$ , plotted according to the equation (8);  $k$  values were used to plot a graph of  $\ln k$  versus  $\ln C_{\text{Fe}^{3+}}$ , as shown in Figure 11. This figure shows a linear relationship with  $R^2$  equal to 0.99 and a slope which indicates that the reaction order is 2.3 with respect to the concentration of ferric.

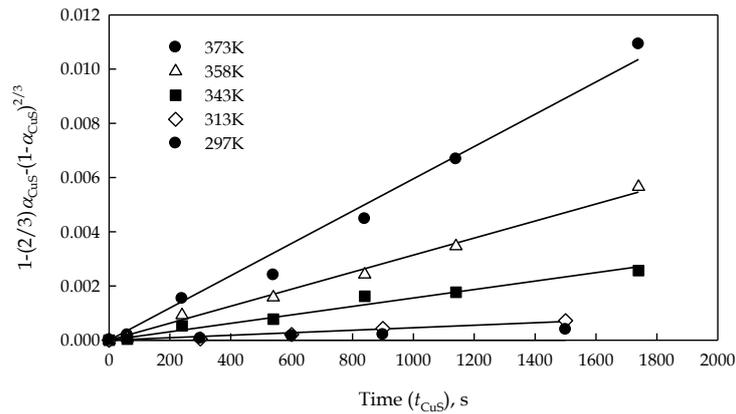


Fig. 9. Covellite dissolution kinetics for average particle size 45 μm in a Fe<sup>3+</sup>-NaCl-H<sub>2</sub>SO<sub>4</sub> media under conditions given in Figure 4

Table 1. Rate constants for the dissolution of covellite

T, °C (K)	1000/T (1/K)	k, 1/s	-ln k
24 (297)	3.367	0.3×10 <sup>-6</sup>	15.019
40 (313)	3.195	0.5×10 <sup>-6</sup>	14.509
70 (343)	2.915	1.6×10 <sup>-6</sup>	13.346
85 (358)	2.793	3.1×10 <sup>-6</sup>	12.684
100 (373)	2.680	6.0×10 <sup>-6</sup>	12.024

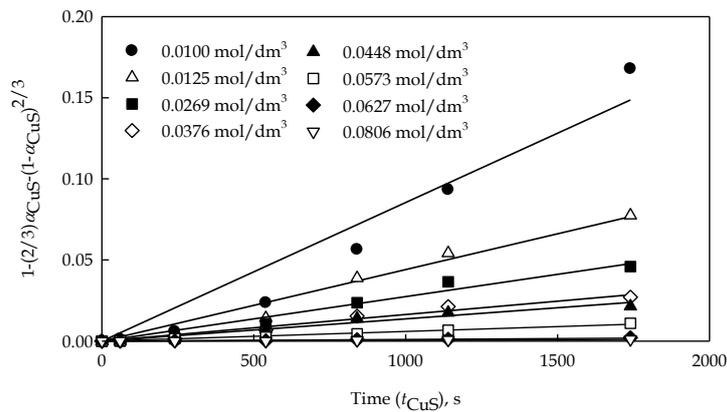


Fig. 10. Dissolution kinetics of digenite samples at various concentrations of Fe<sup>3+</sup> with an average particle size of 45 μm, under leaching conditions used in Figure 6

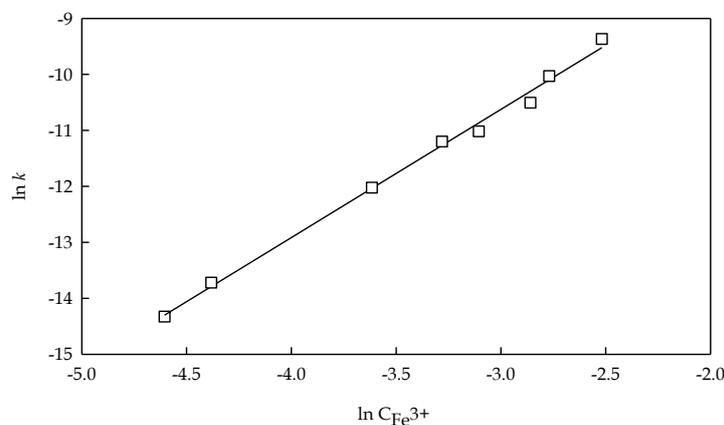


Fig. 11. Reaction order with respect to the concentration of ferric acid in media

Reaction order  $d$  calculations were developed using the kinetic data from Figure 7, which shows the effect of  $\text{H}_2\text{SO}_4$  concentration in the range between 0.05 and 0.5 mol/dm<sup>3</sup> on the dissolution of digenite. The same mathematical procedure was performed in relation to the ferric in solution, i.e. the experimental data in Figure 7 were used in equation (8) and then plotted (Figure 12). Subsequently, the values of the apparent kinetic constants were used to generate the graph of  $\ln k$  versus  $\ln C_{\text{H}_2\text{SO}_4}$  (Figure 13). The results of the trends shown in Figure 12 fit very well the diffusion model through the porous layer.

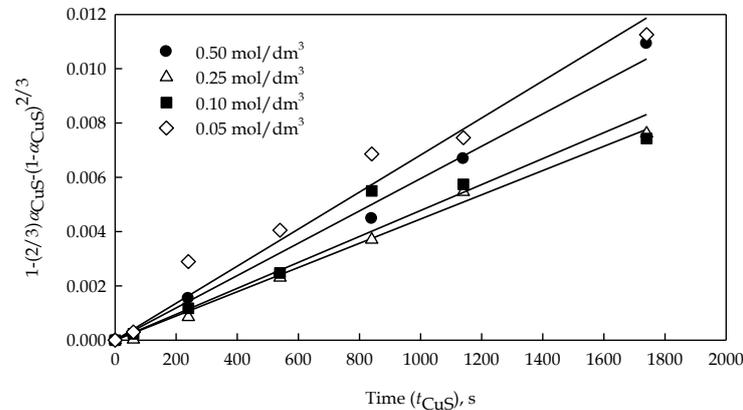


Fig. 12. Dissolution kinetics of digenite samples at various concentrations of  $\text{H}_2\text{SO}_4$ , with an average particle size of 45  $\mu\text{m}$ , under leaching conditions used in Figure 7

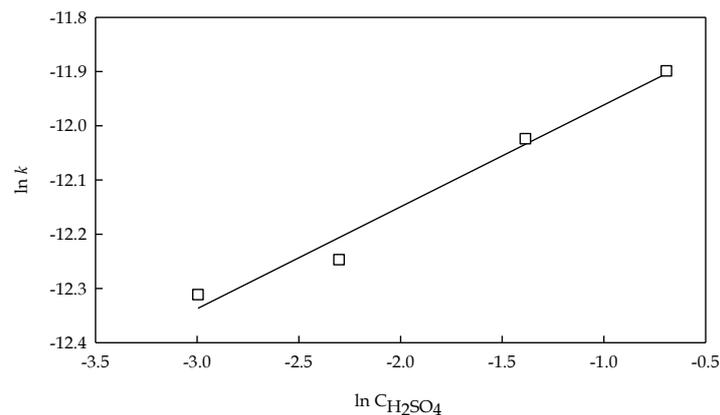


Fig. 13. Reaction order with respect to sulfuric acid concentrations

Figure 13 shows a linear relationship with  $R^2$  equal to 0.99 and a slope indicating the reaction order of 0.2 with respect to the concentration of sulfuric acid in the solution.

For kinetics controlled by diffusion through the porous layer,  $k_1$  should vary linearly with the inverse square of the initial particle radius, as shown in equation (10). To verify this dependence, data concerning particle size (Figure 8) was adjusted according to the equation (8) and results are shown in Figure 14.

The  $k$  values obtained from the slopes of the lines shown in Figure 14 were plotted in Figure 15 as a function of the inverse initial radius of the particle squared. Adequate linear dependence of the data shown in this figure ( $R^2 > 0.90$ ) supports the kinetic model used.

Consequently, the intrinsic oxidation rate constant,  $k_1$ , for different temperatures can be calculated using the apparent kinetics constant values obtained from Figure 9. The value of  $p$  is 2.4 and  $d$  is 0.2. Table 2 shows both apparent and intrinsic constants for the temperatures used in this study.

The values calculated for the intrinsic kinetics constant,  $k_1$ , were used to draw the Arrhenius plot shown in Figure 16. This figure shows a good linear fit ( $R^2 > 0.99$ ) for the apparent kinetics constant for each temperature. The equation of the straight line was  $-4.3466x + 12.424$ . The calculated activation

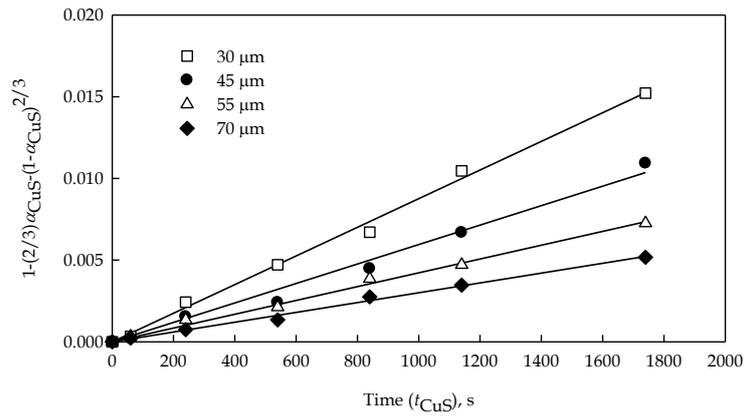


Fig. 14. Dissolution kinetics of digenite samples of various particle sizes, under leaching conditions used in Fig. 9

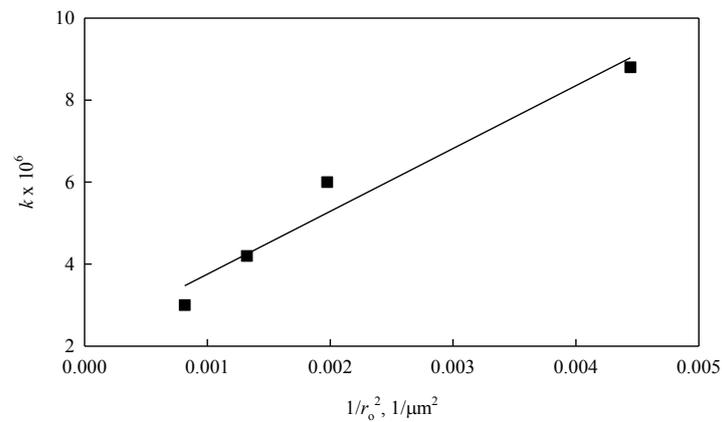


Fig. 15. Dependence of the constant rate of the inverse square of the initial particle size on covellite leaching

Table 2. Covellite dissolution rate constants in temperatures range of 297 to 373 K

$T, K$	$k, 1/s$	$k_1, (1/s) \mu m^2 (1/(mol/dm^3)^{2.3})$
297	$0.3 \times 10^{-6}$	0.1253
313	$0.5 \times 10^{-6}$	0.2088
343	$1.6 \times 10^{-6}$	0.6682
358	$3.1 \times 10^{-6}$	1.2947
373	$6.0 \times 10^{-6}$	2.5059

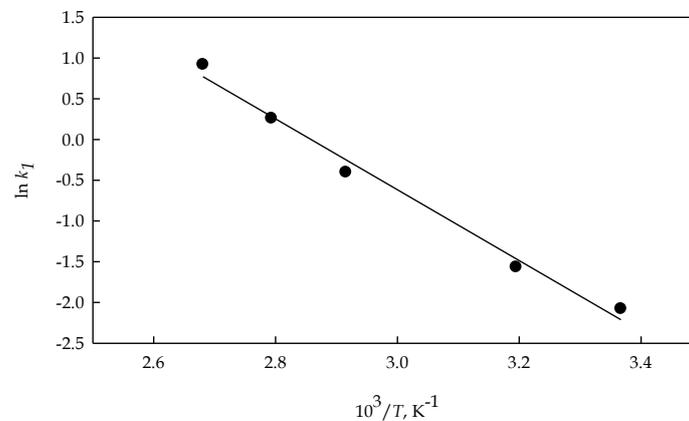


Fig. 16. Arrhenius plot for the dissolution of covellite in a  $Fe^{+3}$ - $H_2SO_4$ - $NaCl$  media

energy was 36.1 kJ/mol for temperature range from 297 to 373 K, which is a typical value for diffusional control through the porous layer (Domic, 2001).

Thus, the dissolution kinetics of covellite in a  $\text{Fe}^{3+}$ - $\text{H}_2\text{SO}_4$ -NaCl media can be represented by the following equation:

$$1 - \left(\frac{2}{3}\right)\alpha - (1 - \alpha)^{\frac{2}{3}} = \frac{2.49 \times 10^5 \cdot C_{\text{Fe}^{3+}}^{2.3} \cdot C_{\text{H}_2\text{SO}_4}^{0.2} \cdot \exp\left(-\frac{36,100}{RT}\right)}{r_0^2} t \quad (11)$$

where  $R$  is equal to  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $r_0$  is in microns,  $C_{\text{Fe}^{3+}}$  and  $C_{\text{H}_2\text{SO}_4}$  are in  $\text{mol/dm}^3$ ,  $t$  is in seconds, and  $k_1 = 2.49 \times 10^5 \text{ } \mu\text{m}^2 (\text{mol/dm}^3)^{2.3} (1/\text{s})$ .

#### 4. Conclusions

Results obtained in this research indicate the following:

- The dissolution mechanism of digenite in  $\text{Fe}^{3+}$ - $\text{H}_2\text{SO}_4$ -NaCl media is represented by two stages: i) covellite generation with cupric ion formation and ii) dissolution of covellite with copper production and anionic sulfur.
- In this study it was found that the dissolution of digenite is very fast compared to the dissolution of covellite.
- Variables such as concentration of sulfuric and ferric acids, greatly affected the covellite dissolution rate, while the temperature affected it to a lesser extent. The presence of NaCl did not produce significant effect.
- The kinetic equation representing the dissolution of covellite was for control by diffusion through the porous layer.
- Covellite dissolution (from digenite) depends on temperature, therefore, the linear kinetic model  $1 - \left(\frac{2}{3}\right)\alpha - (1 - \alpha)^{\frac{2}{3}} = kt$  represents copper dissolution very well. The calculated activation energy was 36.1 kJ/mol, which is a typical value for a reaction controlled by diffusion in the porous layer.
- The reaction orders in relation to the dissolution of the covellite were 2.3 and 0.2 with respect to the concentration of ferric and sulfuric acid, respectively, and was inversely proportional to the square of the particle size

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