

## Leaching of djurleite in $\text{Cu}^{2+}/\text{Cl}^-$ media

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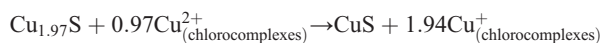
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### Abstract

A study of leaching kinetics of djurleite ( $\text{Cu}_{1.97}\text{S}$ ) using  $\text{Cu}(\text{II})$  solutions in a chloride medium was carried out. Copper sulfate and sodium chloride in an acid solution were reacted in order to obtain the aqueous solution medium for the study. Leaching of djurleite occurs as:



Where the conditions were: copper concentration = 0.02–0.23 M, chloride concentration = 0.6–1.3 M, temperature = 20–80 °C. At room temperature, a complex solid-phase transformation with formation of intermediate  $\text{Cu}_{1.97-x}\text{S}$  phases is observed.

Different variables such as total chloride and total copper concentrations, temperature, and particle size were used for obtaining kinetic data. The concentration of cupric chlorocomplexes using thermodynamic data available in the literature was calculated. The kinetics is governed by chemical reaction control, with activation energy of 35 kJ/mol (8.4 kcal/mol). The apparent reaction orders with respect to the total  $\text{Cu}(\text{II})$  and total  $\text{Cl}^-$  were 0.23 and 0.53, respectively.

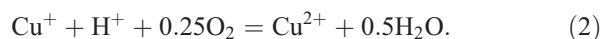
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**Keywords:** Leaching; Copper; Chloride; Djurleite

### 1. Introduction

Leaching of some species of the type  $\text{Cu}_{2-x}\text{S}$ , existing in low-grade copper ores or copper concentrates, has been studied in high concentration chloride media (Herreros et al., 2004). However, leaching characteristics of some recently recognized important species, such as djurleite ( $\text{Cu}_{1.97}\text{S}$ ) and roxbyite ( $\text{Cu}_{1.75}\text{S}$ ) are not well known. Studies on this technique

have been made by Hwang et al. (2002) who leached chalcocite ( $\text{Cu}_2\text{S}$ ) using  $\text{CuCl}_2$  solutions (0 to 0.25 M) and NaCl (0.4 M) under the influence of microwaves at 135 °C and an oxygen pressure of 45 psi. These authors assumed that leaching occurred as:



In a laboratory system, Herreros et al. (1999) leached chalcocite and white metal using chlorine generated from mixtures of sodium hypochlorite with sulfuric and/or hydrochloric acid (0.001–0.005 [M]  $\text{Cl}_2$  and 0.17–

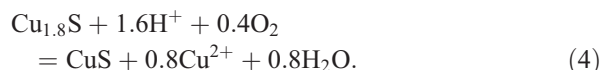
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0.24 [M]  $\text{Cl}^-$ ). They found that the kinetics was governed by mass transfer in the fluid film. In the case of chalcocite, it was determined that the reaction proceeded as:

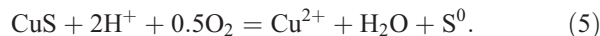


Ruiz et al. (1998) determined that leaching of digenite ( $\text{Cu}_{1.8}\text{S}$ ) concentrate, by means of oxygenated solutions of  $\text{CuCl}_2\text{--HCl--NaCl}$ , was quite rapid. Leaching of digenite concentrate using  $\text{HCl--NaCl--O}_2$  in the range of 50 to 90 °C was achieved in two sequential steps. First, the digenite was transformed to covellite ( $\text{CuS}$ ):



In the first step, the fraction of copper extracted increased over time, following a rate law of type  $\alpha = kt$ , where  $\alpha$  is the fraction reacted in this step and  $k$  is the rate constant. An activation energy of 15.8 kJ/mol was obtained.

In the second step, covellite was dissolved to  $\text{Cu}^{2+}$  and elemental sulfur:



Following a rate law of the type  $1 - 2/3\alpha_{\text{CV}} - (1 - \alpha_{\text{CV}})^{2/3} = k_{\text{CV}}t$ , where  $\alpha_{\text{CV}}$  is the covellite fraction reacted and  $k_{\text{CV}}$  is the second step rate constant. The activation energy for this second step was 84.0 kJ/mol.

Cheng and Lawson (1991a,b) leached similar samples of synthetic chalcocite and covellite. In both cases, leaching occurred in two steps: for the chalcocite, the first step was rapid dissolution where the cuprous ions became scattered through the solid layer and were oxidized to  $\text{Cu(II)}$  through the limiting layer of the liquid with activation energy of 33.5 kJ/mol. The second step, which developed in parallel with the first, was much slower, where leaching may be described in terms of the shrinking core, in which the nucleus is unreacted covellite, covered by a thick layer of elemental sulfur. The apparent activation energy of the second step was 69.0 kJ/mol, which is characteristic of a reaction that occurs under mixed control, or under the control of a chemical reaction. More than 97% of the copper of the chalcocite dissolved at 85 °C in a solution of 0.5 M  $\text{H}_2\text{SO}_4$ /0.5 M  $\text{NaCl}$  with oxygenation for 3 h.

On the other hand, leaching processes for copper concentrates in chloride media have recently been proposed [Intec Process, Moyes and Houllis (2002);

CESL Process, Barr et al. (2000); CUPREX Process, Dalton et al. (1991) and HydroCopper Process, Hyvarinen et al. (2002)].

Noteworthy among processes is the Cuprochlor (Chilean Patent, 2001) which leach secondary sulfide copper ores, mainly of the chalcocite type. This process is competitive with bacterial leaching, which is currently the main hydrometallurgical process commercially applied for the treatment of these minerals. The new process is highly similar to heap leaching traditional, sharing the same steps, including: crushing, agglomeration, leaching, solvent extraction, and electrowinning. The original concept can be summarized as follows. Dissolved calcium chloride is added in addition to the water and sulfuric acid (Vracar et al., 2000). The  $\text{CaCl}_2$  immediately reacts with the acid to produce calcium sulfate which acts to agglomerate the mineral particles, notably improving the permeability and resistance of the agglomerate. In addition, a high concentration of chloride ions is obtained in the wet phase of the agglomerate. This high concentration of chloride permits high cuprous ion concentration in solution. These solutions, being easily oxidized by air, produce a highly oxidant  $\text{Cu(II)}$  chlorocomplexes which facilitates the dissolution of copper sulfides. The agglomerate, forming a heap, is allowed to stand for 24 to 48 h. Leaching is then begun using an irrigating solution containing high concentrations of chloride (90 g/L) and copper (5 g/L) in order to reproduce conditions occurring during the agglomeration phase. Leaching, obtaining metallurgical recoveries of about 90% of the total Cu, occur over irrigation times of about 100 days, providing an additional advantage over bacterial leaching whose irrigation times often exceed 500 days.

The objective of the present study is to evaluate the effects of the concentrations of total copper, total chloride, temperature, and particle size on the leaching of djurleite, using  $\text{Cu(II)}$  chloride solutions to determine the kinetic control step for the process and propose the chemical reactions involved.

Table 1  
 $K_{\text{exp}}$  as a function of the calculated chlorocomplex concentrations (20 °C, 350 rpm,  $C_{\text{Cl}} = 1.29$  [M],  $\text{pH} = 1.04$ )

$C_{\text{Cu}}$ [M]	$\text{Cu}^{2+}$ [M]	$\text{Cl}^-$ [M]	$\text{CuCl}^+$ [M]	$\text{CuCl}_2(\text{aq})$ [M]	$\text{CuCl}_3^-$ [M]	$K_{\text{exp}}$
0.019	0.0029	1.2725	0.0111	0.0010	0.00003	0.0008
0.038	0.0059	1.2595	0.0222	0.0019	0.00006	0.0009
0.078	0.0125	1.2315	0.0460	0.0039	0.00012	0.0011
0.156	0.0261	1.1785	0.0917	0.0074	0.00022	0.0013
0.234	0.0408	1.1268	0.1369	0.0105	0.00030	0.0014

Table 2

$K_{\text{exp}}$  as a function of the calculated concentrations of chlorocomplexes (20 °C, 350 rpm,  $C_{\text{Cu}}=0.078$  [M], pH=1.04)

$C_{\text{Cl}}$ [M]	$\text{Cu}^{2+}$ [M]	$\text{Cl}^-$ [M]	$\text{CuCl}^+$ [M]	$\text{CuCl}_2(\text{aq})$ [M]	$\text{CuCl}_3^-$ [M]	$K_{\text{exp}}$
0.570	0.0246	0.5296	0.0389	0.0014	0.00002	0.0007
1.000	0.0157	0.9496	0.0444	0.0029	0.00007	0.0009
1.286	0.0125	1.2315	0.0460	0.0039	0.00012	0.0011

### 1.1. Kinetic model used

The kinetic model used is that of the shrinking core: chemical controlling reaction (Levenspiel, 1979; Sohn and Wadsworth, 1986):

$$1-(1-\alpha)^{1/3} = K_{\text{exp}} t \quad (6)$$

with

$$K_{\text{exp}} = b k_q [A]^n / \rho_B r_0. \quad (7)$$

Where:  $b$ =stoichiometric coefficient (mol djurleite/mol leaching agent),  $k_q$ =chemical rate constant,  $[A]$ =concentration of the leaching reagent (mol/cm<sup>3</sup>),  $\rho_B$ =molar density of the djurleite (mol djurleite/cm<sup>3</sup>),  $r_0$ =particle radius (cm).

The leaching model was consistent with the effects of particle size, Cu(II) concentration and temperature.

### 1.2. Distribution of chloride species

When chloride ion and cupric ion occur within the same aqueous system, the composition of the resulting

solution is governed by the following equilibria (Duby, 1977; HSC Outokumpu, 1999):

Reaction	Duby	HSC
$\text{Cu}^{2+} + \text{Cl}^- \rightarrow \text{CuCl}^+$	$K_1 = 10^{0.46}$	$10^{0.474}$ (8)
$\text{CuCl}^+ + \text{Cl}^- \rightarrow \text{CuCl}_2(\text{aq})$	$K_2 = 10^{-0.27}$	$10^{-1.165}$ (9)
$\text{CuCl}_2(\text{aq}) + \text{Cl}^- \rightarrow \text{CuCl}_3^-$	$K_3 = 10^{-2.48}$	$10^{-1.599}$ (10)
$\text{CuCl}_3^- + \text{Cl}^- \rightarrow \text{CuCl}_4^{2-}$	$K_4 = 10^{-2.30}$	$10^{-2.30}$ (11)

All the thermodynamic results and those of the species distribution given below are in the HSC software database.

In order to calculate the concentrations of the different species of cupric chlorocomplexes in solution, the following material balance is proposed:

$$C_{\text{Cl}} = [\text{Cl}^-] + [\text{CuCl}^+] + 2[\text{CuCl}_2] + 3[\text{CuCl}_3^-] + 4[\text{CuCl}_4^{2-}] \quad (12)$$

and

$$C_{\text{Cl}} = C_{\text{NaCl}} \quad (13)$$

$$C_{\text{Cu}} = [\text{Cu}^{2+}] + [\text{CuCl}^+] + [\text{CuCl}_2] + [\text{CuCl}_3^-] + [\text{CuCl}_4^{2-}] \quad (14)$$

where  $C_{\text{Cl}}$ ,  $C_{\text{NaCl}}$  and  $C_{\text{Cu}}$  are the total concentrations, and  $[i]$  the concentrations of the different species (mol/L). If  $C_{\text{Cl}}$  and  $C_{\text{Cu}}$  are known, the concentrations of the different species remain defined if it is assumed that the activity coefficients are near unity.

According to the values of the formation constants of the chlorocomplexes, the predominant species in the

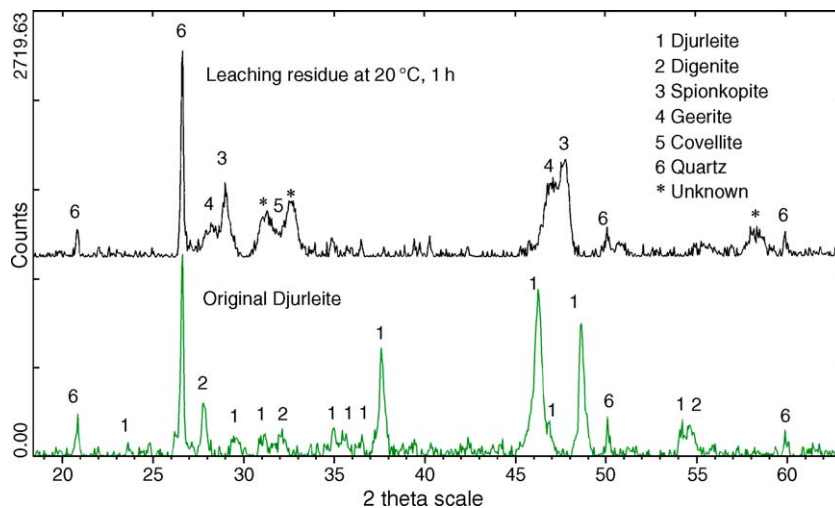


Fig. 1. Diffractogram of the residue leached at 20 °C (1 h,  $r_0=0.124$  mm) and of the original djurleite.

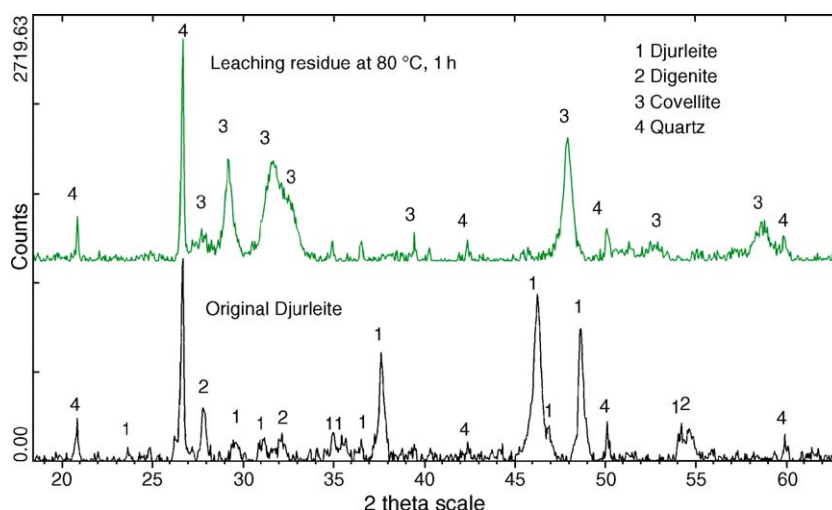


Fig. 2. Diffractogram of the residue leached at 80 °C (1 h,  $r_0=0.124$  mm) and that of the original djurleite.

$\text{Cu}^{2+}/\text{Cl}^-$  system in the interval studied (Tables 1 and 2) are  $\text{Cu}^{2+}$  and  $\text{CuCl}^+$ .

## 2. Materials and experimental procedures

### 2.1. Materials

The mineral employed in the kinetic tests originated from the Minera Escondida, Antofagasta, Chile. Uniformly sized particles were used, obtained by crushing and selective screening of the mineral sample. In all experiments except for those testing the effects of variation in particle size, the trials were carried out with a mean particle size diameter of 0.247 mm, and an elemental composition of 58.11% Cu and 14.80% S. Examination using X-ray diffraction showed that the mineral was primarily djurleite ( $\text{Cu}_{1.97}\text{S}$ ) with small amounts of digenite ( $\text{Cu}_{1.80}\text{S}$ ). The samples also contained an appreciable quantity of quartz and some mica. No other copper phases were detected. The

mineralogical composition was therefore: 73% djurleite (+minor digenite) and 27% quartz (+minor mica).

### 2.2. Reactor

Conventional leaching equipment was used under sealed conditions, including a 1200-ml round-bottom glass reactor, fitted with a 5.5 cm helical Teflon stirrer sealed through an acrylic stopper. The system was also fitted with electrodes which were used to measure the potential in the system ( $\text{Ag}/\text{AgCl}$ ,  $E^0=220$  mV) as well as pH. A small volume of air ( $\sim 50$  cm<sup>3</sup>) remained over the liquid in the system (1.000 cm<sup>3</sup>).

### 2.3. Experimental development

Solutions used in the experiments were prepared by introducing known volumes of copper sulfate into the

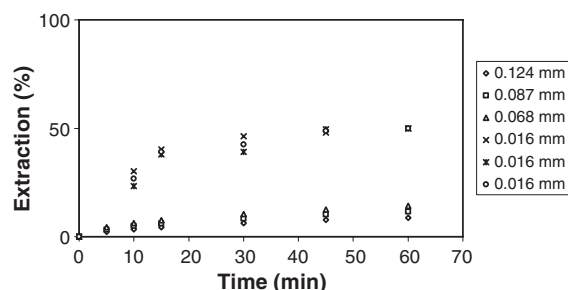


Fig. 3. Copper extraction vs. time as a function of particle size (20 °C, 350 rpm,  $C_{\text{Cl}}=1.29$  [M],  $C_{\text{Cu}}=0.156$  [M], pH=1.04).

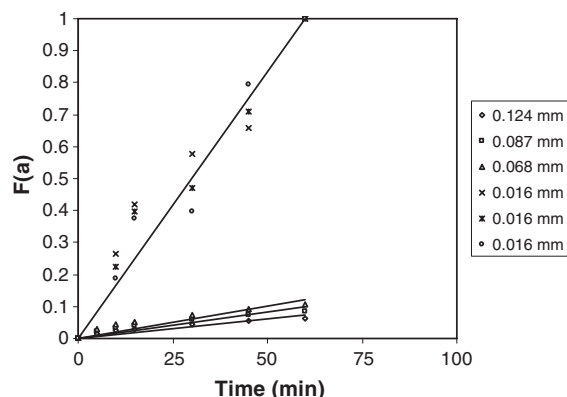


Fig. 4. Kinetic model vs. time as a function of particle size (20 °C, 350 rpm,  $C_{\text{Cl}}=1.29$  [M],  $C_{\text{Cu}}=0.156$  [M], pH=1.04).

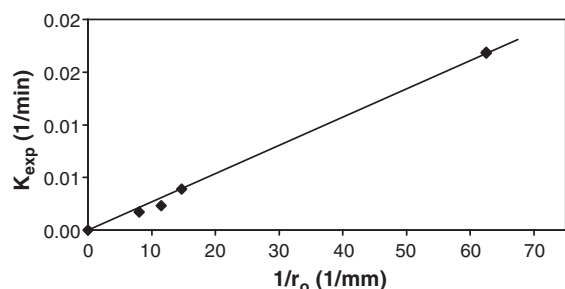


Fig. 5. Plot of rate constant vs. inverse of particle radius (20 °C, 350 rpm,  $C_{Cl}=1.29$  [M],  $C_{Cu}=0.156$  [M], pH=1.04).

reaction flask; sodium chloride was added according to the concentration desired, and then a determinate volume sulfuric acid was added in order to adjust the pH. The solution was finally made to 1000 ml using distilled water. All the reagents used to prepare the leaching solutions were of analytical grade.

Two grams of sample were then added and the progress of the leaching was determined by taking 10 ml samples of the liquid, with subsequent copper analysis by atomic absorption spectrometry. The fraction of copper extracted was determined as the relation of the copper concentration at time  $t$  to the copper concentration in the original sample. Conversions,  $\alpha(t)$ , were computed according the reaction involved.

### 3. Results and discussion

#### 3.1. Nature of the reactions

In examination of the types of reactions associated with the leaching of the djurleite, preliminary experiments were carried out at 20 and 80 °C, and the residues were analyzed using X-ray diffraction. At 20 °C (1 h,  $r_o=0.124$  mm), no patterns were observed representing djurleite or digenite. Wide bands were observed which suggested a complex change in the structure of the djurleite ( $Cu_{1.97}S$ ) with loss of copper and formation of

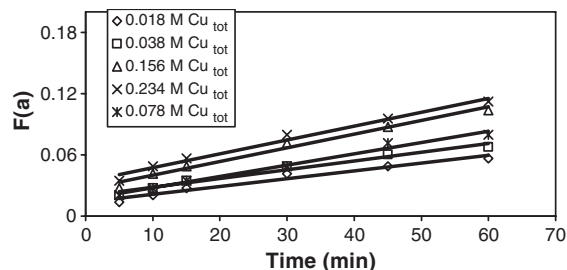


Fig. 6. Effect of the total copper concentration (20 °C, 350 rpm,  $C_{Cl}=1.29$  [M], pH=1.04,  $r_o=0.124$  mm).

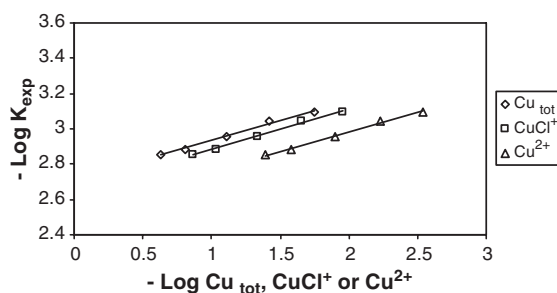


Fig. 7. Logarithmic plot of the rate constants vs. the concentrations of total copper,  $CuCl^+$  and  $Cu^{2+}$  (20 °C, 350 rpm,  $C_{Cl}=1.29$  [M], pH=1.04,  $r_o=0.124$  mm).

$Cu_{1.97-x}S$  phases, among which was detected the possible formation of spionkopite ( $Cu_{1.40}S$ ) and perhaps minor amounts of geerite ( $Cu_{1.60}S$ ). If, in simplified terms, we consider the conversion of djurleite to spionkopite,  $x$  would be situated near 0.57, with which the theoretical extraction of copper would be near 30%, which was somewhat less than the experimentally observed, up to near 40%, and which also suggested some transformation to covellite ( $CuS$ ). Covellite, however, is not easily detected in X-ray diffraction at 20 °C since its main peak remains within a wide band which is difficult to pinpoint using the files of the DIFRAC-AT databank.

Based on the preceding results, it is probable that at 20 °C the main reaction types are:

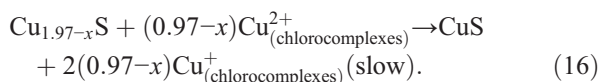
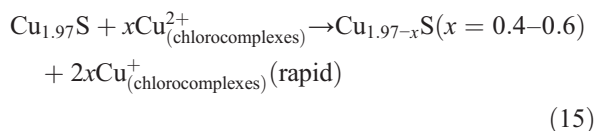


Fig. 1 shows the diffractogram of the original djurleite and the residue from leaching at 20 °C.

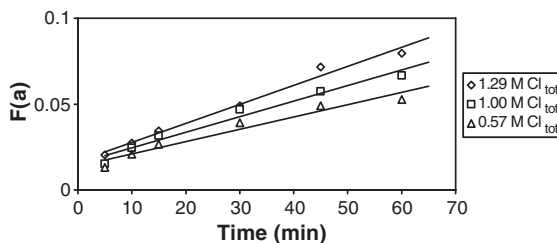


Fig. 8. Kinetic model vs. time, as a function of  $C_{Cl}$  (20 °C, 350 rpm,  $C_{Cu}=0.078$  [M], pH=1.04,  $r_o=0.124$  mm).

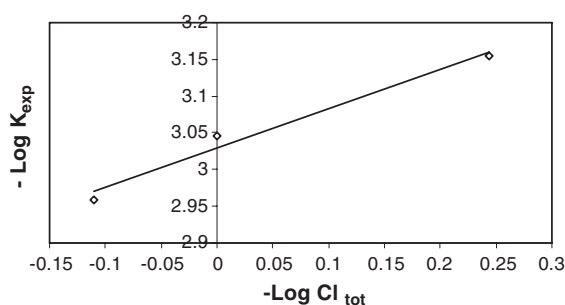
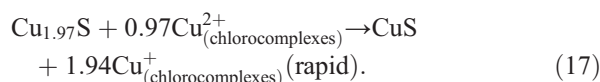


Fig. 9. Logarithmic plot of  $K_{\text{exp}}$  as a function of the concentration of total chloride (20 °C, 350 rpm,  $C_{\text{Cu}}=0.078$  [M],  $\text{pH}=1.04$ ,  $r_0=0.124$  mm).

At 80 °C peaks reflecting the original djurleite (and digenite) were again absent, with the clear detection of covellite as the reaction product. This agrees with the recovery obtained of exactly 50% of the copper under these conditions. The overall main reaction was therefore:



Nevertheless, it is also possible that the reaction to covellite occurred through quick passages to the sulfides  $\text{Cu}_{1.97-x}\text{S}$  and a similar quick passage at 80 °C from  $\text{Cu}_{1.97-x}\text{S}$  to  $\text{CuS}$ .

The final oxidation (leaching) of covellite to obtain total copper recovery does not appear feasible in this medium in this range of  $\text{Cu}^{2+}/\text{Cl}^{-}$  concentrations. Fig. 2 shows the diffractogram of the original djurleite and the leach residue at 80 °C.

### 3.2. Effect of particle size

Experiments were carried out using different granulometric size fractions, stirring at 350 rpm, with 2 g of mineral,  $C_{\text{Cu}}=0.156$  [M] and  $C_{\text{Cl}}=1.29$  [M]. The results on copper extraction are shown in Fig. 3.

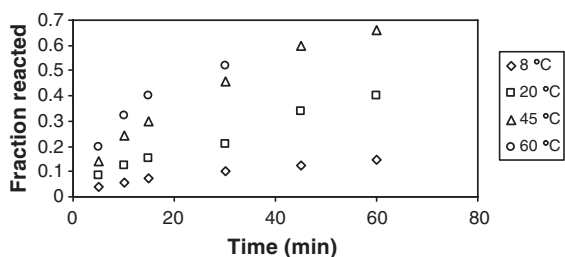


Fig. 10. Fraction reacted vs. time as a function of temperature (350 rpm,  $C_{\text{Cl}}=1.29$  [M],  $C_{\text{Cu}}=0.156$  [M],  $\text{pH}=1.04$ ,  $r_0=0.124$  mm).

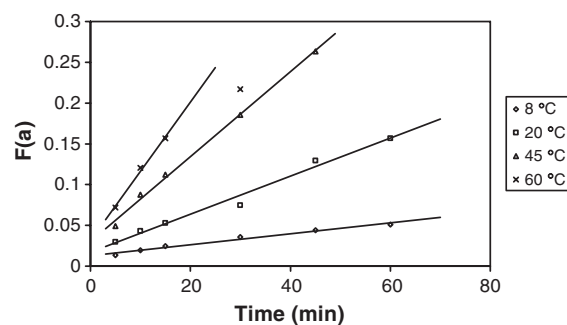


Fig. 11. Kinetic model vs. time as a function of temperature (350 rpm,  $C_{\text{Cl}}=1.29$  [M],  $C_{\text{Cu}}=0.156$  [M],  $\text{pH}=1.04$ ,  $r_0=0.124$  mm).

Copper extraction was very sensitive to the particle size effect. However, maximum extraction in very fine particles practically stopped at 50%, in accordance with the preliminary experiments. Consequently, the data on fraction reacted were computed according to the global reaction of the formation of covellite (Eq. (17)).

Application of the kinetic model ( $F(a)=1-(1-\alpha)^{1/3}$ ) is plotted in Fig. 4.

Fig. 5 shows the experimental rate constants plotted against the inverse of the particle radius. Intersection of the plotted line in Fig. 5 with the origin confirmed kinetic control exercised by chemical reaction.

### 3.3. Effect of the total copper concentration ( $C_{\text{Cu}}$ )

Data on the effect of the total copper concentration in the system were first obtained on the dissolution of the copper contained in the djurleite. Leaching was carried out at room temperature (20 °C), stirring at 350 rpm,  $C_{\text{Cl}}=1.29$  [M],  $r_0=0.124$  mm with 2 g of the mineral. Results on the leaching model are plotted in Fig. 6. As it can be seen, straight lines were obtained in spite of the lines do not intersect exactly at the origin. The

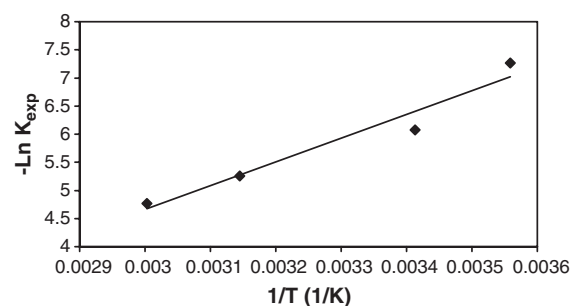


Fig. 12.  $\text{Ln}K_{\text{exp}}$  as a function of the reciprocal of the temperature (Arrhenius plot).



aforementioned was attributed to a small oxidized fraction ( $\sim 0.03$ ) containing fast-soluble copper.

Reaction rate increases quickly directly proportional to the total copper concentration with an apparent reaction order of 0.23 (Fig. 7). This fractional order also suggests chemical reaction control because it is not consistent with a process controlled by solid layer diffusion.

Table 1 includes the calculated concentrations of the chlorocomplexes generated under the experimental conditions. Under these conditions, the predominant copper species were  $\text{CuCl}^+$  and  $\text{Cu}^{2+}$ . However, the increase of the total copper concentration tends to raise the concentration of both species. So, the apparent reaction was nearly identical to that obtained with respect to total copper(II) concentration.

### 3.4. Effect of total chloride concentration ( $C_{\text{Cl}}$ )

Data on the effect of the total chloride concentration in the system was then obtained on the dissolution of the copper contained in the djurleite. The experiments were carried out at room temperature ( $20^\circ\text{C}$ ), stirring at 350 rpm,  $C_{\text{Cu}}=0.078$  [M],  $r_0=0.124$  mm with 2 g of mineral. Leaching results are shown in Fig. 8.

Leaching rate increases directly proportional to the total chloride concentration. Fig. 9 is a plot of the rate constants regarding this concentration. An apparent order of 0.53 was obtained.

Table 2 shows the experimental constants  $K_{\text{exp}}$  and the calculated concentrations of the species generated under the experimental conditions. On increasing  $C_{\text{Cl}}$ ,  $\text{Cu}^{2+}$  decreases significantly. So it seems reasonable that  $\text{Cu}^{2+}$  does not contribute to leaching. On the contrary, the increase of the concentrations on Cu(II) chlorocomplexes, particularly of the predominant  $\text{CuCl}^+$ , suggests that these are the active species in the leaching reaction:



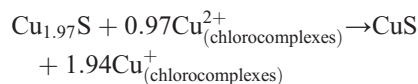
### 3.5. Temperature effect

Data was further obtained on the effect of temperature on the dissolution of copper contained in the djurleite. Experiments were carried out at temperatures of 8, 20, 40 and  $60^\circ\text{C}$ , with stirring at 350 rpm, using 2 g of mineral,  $C_{\text{Cu}}=0.156$  [M],  $C_{\text{Cl}}=1.29$  [M] and  $r_0=0.124$  mm. Results of these tests are plotted in Figs. 10 and 11.

The Arrhenius plot of the experimental rate constants are presented in Fig. 12. Activation energy of 35 kJ/mol (8.4 kcal/mol) is obtained, confirming a chemical reaction control.

## 4. Conclusions

1. In the ranges  $C_{\text{Cu}}=0.02\text{--}0.23$  M,  $C_{\text{Cl}}=0.6\text{--}1.3$  M,  $20\text{--}80^\circ\text{C}$ , the leaching of djurleite occurs as:



The subsequent leaching of covellite is not produced under these conditions.

2. During leaching at room temperature, a complex solid-phase transformation occurs with formation of intermediate  $\text{Cu}_{1.97-x}\text{S}$  phases, such as spionkopite ( $\text{Cu}_{1.40}\text{S}$ ) and perhaps minor amounts of geerite ( $\text{Cu}_{1.60}\text{S}$ ).
3. The kinetics of djurleite in a  $\text{Cu}^{2+}/\text{Cl}^-$  system is governed by chemical reaction control, with activation energy of 35 kJ/mol (8.4 kcal/mol). The apparent reaction orders with respect to the total Cu(II) and total chloride were 0.23 and 0.53, respectively.

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## References

- Barr, G., Defreyne, J., Jones, D., Moore, R., 2000. The CESL process – successful refinery of a low grade copper concentrate. Proc. ALTA Copper 2000, Adelaide, Australia.
- Cheng, Yong Chu, Lawson, F., 1991a. The kinetics of leaching chalcocite in acidic oxygenated sulphate–chloride solutions. Hydrometallurgy 27, 249–268.
- Cheng, Yong Chu, Lawson, F., 1991b. The kinetics of leaching covellite in acidic oxygenated sulphate–chloride solutions. Hydrometallurgy 27, 269–284.
- Dalton, R.F., Díaz, G., Price, R., Zunkel, A.D., 1991. The CUPREX metal extraction process – recovering copper from sulfide ores. JOM 51–56.
- Duby, P., 1977. Incra Monograph IV, The Metallurgy of Copper, Library of Congress, Catalogue Card number 77-71709. National Bureau of Standards, USA, pp. 30–31.
- Herreros, O., Quiroz, R., Viñals, J., 1999. Dissolution kinetics of copper, white metal and natural chalcocite in  $\text{Cl}_2/\text{Cl}^-$  media. Hydrometallurgy 51, 345–357.

- Herreros, O., Quiroz, R., Fuentes, G., Salazar, C., Viñals, J., 2004. Review respecto a la lixiviación de especies sulfuradas y concentrados de cobre con cloruros. *Innovación* 16 (1 y 2), 49–61.
- Hwang, J.-Y., Shi, S., Xu, Z., Huang, X., 2002. Oxygenated leaching of copper sulfide mineral under microwave hydrothermal conditions. *J. Min. Mater. Charact. Eng.* 1, 111–119.
- Hyvarinen, O., Hamalainen, M., Leimala, R., 2002. Outokumpu hydrocopper process – a novel concept in copper production. In: Peek, E., Van Weert, G. (Eds.), *Proc., Chloride Metallurgy 2002*, Montreal, Quebec, Canada. The Metallurgical Soc. CIM.
- Levenspiel, O., 1979. *Ingeniería de las Reacciones Químicas*. Editorial Reverté, Barcelona.
- Moyes, J., Houllis, F., 2002. Intec base metal processes – releasing the potential of chloride metallurgy technical update and commercialization status. In: Peek, E., Van Weert, G. (Eds.), *Proc., Chloride Metallurgy 2002*, Montreal, Quebec, Canada. The Metallurgical Soc. CIM.
- Patente Chilena No 40891, 2001.
- Ruiz, M.C., Honores, S., Padilla, R., 1998. Leaching kinetics of digenite concentrate in oxygenated chloride media at ambient pressure. *Metallurgical and Materials Transactions. B, Process Metallurgy and Materials Processing Science* 29B, 961–969.
- Software HSC Chemistry, ver 1.12 copyright Outokumpu Research Oy, Pori, Finland, 2001.
- Sohn, H.Y., Wadsworth, M.E., 1986. *Cinética de los Procesos de la Metalurgia Extractiva*. Trillas, México D.F.
- Vracar, R.Z., Paresanovic, I.S., Cerovic, K.P., 2000. Leaching of copper(I) sulfide in calcium chloride solution. *Hydrometallurgy* 58, 261–267.