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Leaching of djurleite in Cu^{2+}/Cl^- media

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Abstract

A study of leaching kinetics of djurleite ($Cu_{1.97}S$) using Cu(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:

$$Cu_{1.97}S + 0.97Cu^{2+}_{(\text{chlorocomplexes})} \rightarrow CuS + 1.94Cu^{+}_{(\text{chlorocomplexes})}$$

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 $Cu_{1.97-x}S$ 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 Cu(II) and total Cl^- were 0.23 and 0.53, respectively.

Keywords: Leaching; Copper; Chloride; Djurleite

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1. Introduction

Leaching of some species of the type $Cu_{2-x}S$, 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 ($Cu_{1.97}S$) and roxbyite ($Cu_{1.75}S$) are not well known. Studies on this technique have been made by Hwang et al. (2002) who leached chalcocite (Cu_2S) using $CuCl_2$ 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:

$$Cu_2S + 2Cu^{2+} = 4Cu^{+} + S \tag{1}$$

$$Cu^{+} + H^{+} + 0.25O_2 = Cu^{2+} + 0.5H_2O. \tag{2}$$

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] Cl_2 and 0.17–

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0.24 [M] 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:

$$\begin{aligned}&Cu_2S + 5Cl_2(g) + 4H_2O\\&\quad = 2CuCl_2 + 6HCl + H_2SO_4.\end{aligned} \tag{3}$$

Ruiz et al. (1998) determined that leaching of digenite ($Cu_{1.8}S$) concentrate, by means of oxygenated solutions of $CuCl_2$–HCl–NaCl, was quite rapid. Leaching of digenite concentrate using 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 (CuS):

$$\begin{aligned}&Cu_{1.8}S + 1.6H^+ + 0.4O_2\\&\quad = CuS + 0.8Cu^{2+} + 0.8H_2O.\end{aligned} \tag{4}$$

In the first step, the fraction of copper extracted increased over time, following a rate law of type $\alpha = kt$, where α 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 Cu^{2+} and elemental sulfur:

$$CuS + 2H^+ + 0.5O_2 = Cu^{2+} + H_2O + S^0. \tag{5}$$

Following a rate law of the type $1 - 2/3\alpha_{CV} - (1 - \alpha_{CV})^{2/3} = k_{CV}t$, where α_{CV} is the covellite fraction reacted and k_{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 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 H_2SO_4/0.5 M 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 $CaCl_2$ 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 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 Cu(II) chloride solutions to determine the kinetic control step for the process and propose the chemical reactions involved.

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

C_{Cu} [M]	Cu^{2+} [M]	Cl^- [M]	$CuCl^+$ [M]	$CuCl_{2(aq)}$ [M]	$CuCl_3^-$ [M]	K_{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