



# Dissolution kinetics of metallic copper with $\text{CuSO}_4\text{--NaCl--HCl}$

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## Abstract

A study was made on the dissolution kinetics of metallic copper flat packs using solutions of Cu(II) in a chloride medium which was obtained via reaction between copper sulfate and sodium chloride. The effect of stirring, chloride and Cu(II) concentrations, distribution of Cu(II) chlorocomplexes and temperature were investigated.

The leaching data showed the reaction to be under chemical kinetics control, with an activation energy of 28 kJ/mol (7 kcal/mol). Leaching occurred at an apparent order of  $-1$  with respect to the total chloride concentration and an apparent first order with respect to the total copper concentration. The Cu(II) ion was the main active species based on calculation of copper species distribution and the solution kinetics may be interpreted as  $\text{rate} = k[\text{Cu}^{2+}]$ . For ratios of  $C_{\text{Cl}}/C_{\text{Cu}}^{2+}$  of less than about 8, a layer of  $\text{CuCl}_{(s)}$  formed which impeded the solubilization process.

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## 1. Introduction

Processes for the leaching of metallic copper in chloride media have been based primarily on the action of cupric copper in the presence of sodium chloride. Important references on this topic include the studies of Lin et al. (1992) and Tolley et al. (1977), which report on the thermodynamics of the equilibrium involved as well as on kinetic data in the Cu/

$\text{Cl}^-$  system. Lin et al. report a copper leaching rate consistent with the following expression:

$$\text{rate} = k[\text{Cu}^{2+}]^{1/2}[\text{Cl}^-]^2 \quad (1)$$

The order of this in reference to  $[\text{Cu}^{2+}]$  is 0.5, which is in agreement with that reported by Tolley et al. (1977), who leached copper beads with  $\text{CuCl}_2$  in a stirred reactor.

The study carried out by Herreros et al. (1999) on the dissolution of copper flat packs by aqueous  $\text{Cl}_2/\text{Cl}^-$  media ( $0.5 \times 10^{-2}$ – $1.9 \times 10^{-2}$  M  $\text{Cl}_2$ , 0.5–1.4 M  $\text{Cl}_{\text{tot}}$ ), reported that the most significant effects

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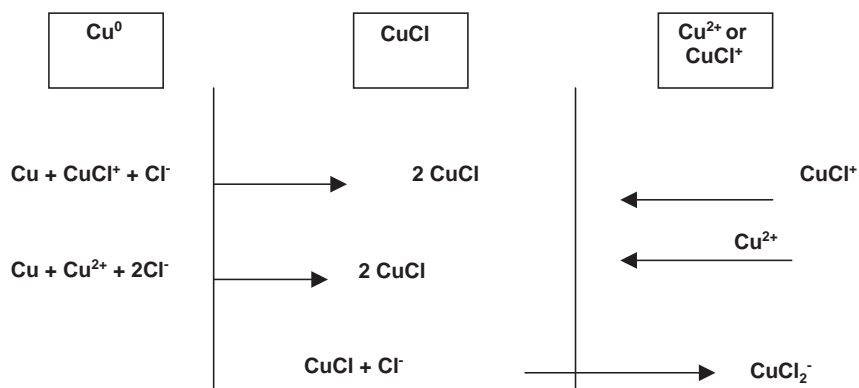


Fig. 1. Scheme of the possible steps in the leaching of metallic copper with Cu(II) in chloride media.

were those related to the concentrations of chlorine and chloride, and that the aqueous chlorine was the reagent that made possible the dissolution of the copper, with chloride contributing a negative effect. The chloride inhibited the dissolution, probably due to the formation of a superficial layer of CuCl. When working with excess chlorine, however, the dissolution of this solid CuCl was increased. In this case the kinetic control was affected by the transfer of mass in the film, with activation energy of 18 kJ/mol (4.3 kcal/mol). The apparent order of reaction with respect to chlorine was 1.0 and  $-0.17$  for the chloride.

On the other hand, the literature describes a process for copper recovery from bronze scrap in which leaching is obtained using 0.28 M  $\text{CuCl}_2$  and 4.8 M NaCl at a temperature of 75 °C (Langer et al., 1977). The CLEAR process, dating from the 1970s (Copper Leach, Electrolysis and Regeneration) also uses cupric chloride together with a solution of 4.4 M NaCl and 2.4 M KCl, although in this case, the objective was the leaching of chalcopyrite (Atwood and Livingston, 1980).

In contrast with results from the preceding brief literature review, the objective of the present research was to study the dissolution of metallic copper with cupric chlorocomplexes generated in situ by reacting copper sulfate with sodium chloride in a hydrochloric acid medium, and then determining if the  $\text{CuCl}^+$  complex is the main active species in the leaching of the metallic copper by having a sufficiently oxidative potential for obtaining the solubilization. This kinetic study may be applicable

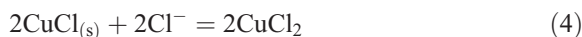
in the leaching of copper precipitates, which in Chile have varying degrees of surface oxidation, as well as in treatment of discarded cathodes from the electro-winning process.

Our study determined the effects of the stirring, temperature, as well as the concentrations of total Cu(II), total chloride, and copper chlorocomplexes for postulating the possible controlling stage or stages of the dissolution, and modeling a kinetic expression for the leaching rate.

### 1.1. Criteria for the application of kinetic models

It is broadly recognized in the literature that in the case of dissolution of pure species without formation of insoluble products in surface layers, the only controlling steps can be the mass transfer through the fluid film and the specific chemical reaction (Levenspiel, 1979; Sohn and Wadsworth, 1986). In the case of leaching of Cu with Cu(II) in a  $\text{Cl}^-$  medium, competition may exist between a “solid” intermediate formed on the surface of the metallic copper, probably CuCl, which would tend to dissolve, whereupon the leaching reagent would advance to the reaction surface.

A diagram of the possible steps is presented as Fig. 1. The reactions of this process would be



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