The Effect of Temperature on the Electrowinning of Copper

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Abstract

In this paper, a brief overview of the effect of temperature on the electrowinning of copper was provided. Furthermore, experimental data for the influence of temperature on current efficiency, energy consumption, rate, and morphology of Cu deposition in the electrowinning of copper from a synthetic copper sulfate solution were also presented. Temperature is an important parameter for copper electrowinning process. In general, earlier experimental studies emphasized that an increase in temperature may increase current density, rate of copper deposition. Albeit, the type of deposition reaction and composition of electrolyte (i.e. Cu²⁺ concentration in electrolyte) are temperature independent.

The resistance of electrolyte solution and cell is reduced with the rise in temperature leading to an increased rate of electrodeposition of copper. In addition, the temperature of the electrolyte positively affects the quality of cathode copper. In the experiments conducted under constant concentration and current density (30 g/L Cu, 250 A/m²), increasing temperature was shown to improve the kinetics of the process and reduce the cell potential by approximately 0.09 V with a concomitant ~10% reduction in energy consumption. The reduction of energy consumption was identified to be the most important effect of increasing temperature.

1. Introduction

Electrowinning is extensively used for recovery of copper from pregnant leach solutions (PLS). In the electrowinning of copper the pure copper metal at the cathode, oxygen gas at the anode and regenerated sulfuric acid in the electrolyte solution are produced. In the electrowinning of copper the cathode (1), anode (2) and overall reactions (3) are as follows [1]–[3]:

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad (E^0 = +0.34 \, \text{V}) \quad (1) \]

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- (E^0 = -1.23 \, \text{V}) \quad (2) \]

\[ \text{Cu}^{2+} + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \quad (3) \]

In general, copper electrowinning is performed under a wide temperature range between 25-65 °C in industry. Thus, there is no ideal temperature for this process and the optimum temperature is determined by other operating parameters specific to each plant. Temperature as one of the most influential parameters for copper electrowinning can be used to control the production and quality of copper cathode [1], [4], [5].

Temperature affects notably the psycho-chemical properties of the electrolyte solution and the mass transfer parameters in copper electrowinning and ultimately, the efficiency of electrochemical process. According to Casas et al. [6], temperature affects the electrolyte speciation with the concentration of \( \text{H}^+ \) and \( \text{Fe}^{3+} \) decreasing with increasing temperature due to the formation of complex species. Moreover, increasing temperature reduces viscosity of electrolyte, which facilitates mass transfer and improves current efficiency (i.e. the ratio between the actual amount of metal deposited or dissolved, \( \text{Ma} \), to that calculated theoretically \( \text{Mt} \)) [7], [8].

\[ W_l = \frac{M(Cu) \times I(A) \times t}{n \times F} \quad (4) \]

\[ CE = \frac{W_d}{W_l} \times 100 \quad (5) \]

Where, \( M (\text{Cu}) \) is the molecular weight of Cu, \( I (\text{A}) \) is current passed in amperes, \( t \) is the time in sec, \( n \) is number of transferred electrons (in this case =2) and \( F \) represents Faraday’s constant (96500 C/mol).

In another study Anderson et al [9] shows that an increase in temperature contributes significantly to an increase in limiting current density. In addition, the diffusion coefficient of ions in the solution increases by increasing temperature [8]. Thus, the current efficiency can be improved by increasing the temperature of the
electrolyte with high Cu concentration and low concentration of impurity ions, especially Fe$^{3+}$. However, in an electrolyte containing high Fe$^{3+}$ concentration, increasing temperature cause to increase in the Fe$^{3+}$ diffusion coefficient and as a result of this phenomenon it decreases the current efficiency. In this case, with rising the temperature from 30 to 60°C current efficiency decreased [7], [8].

In another study, Alfantazi and Valic [10] demonstrated the occurrence of interactions between temperature, Cu concentration and current density with no Fe$^{3+}$ impurity in the electrolyte. They have found that, in the absence of Fe$^{3+}$, at high Cu concentration (i.e. 65 g/L), increasing temperature (from 40 to 60°C) has a negative effect on current efficiency. However, at low Cu concentrations (i.e. 25 g/L) increasing temperature results in an increase in current efficiency. In accordance with their model developed in their study, they concluded that high temperatures in addition to high Cu concentration in electrolyte and high current densities tend to improve current efficiency.

Mishra and Cooper [11] reported that changing the electrolyte temperature under the same operating parameters (Cu 10-20 g/L; Fe$^{3+}$ 1 g/L; H$_2$SO$_4$ 20 g/L) influences the quality of Cu cathode deposit and its structure. Pradhan et al. [12] also reported the effect of temperature on the nature of deposit. With increasing temperature from 30 to 60°C in presence of 100 mg/L Cl$^-$, the surface roughness of cathode became more pronounced. According to O’Keefe and Hurst [13] lacy (discontinued) Cu deposition is obtained at 65 °C.

In the present work, the effects of temperature on current efficiency, energy consumption, the rate and morphology of Cu deposition in the electrowinning of copper from a synthetic copper sulfate solution were also examined.

2. Experimental Procedure

Details of experimental apparatus and procedures can be found in our previous studies [3], [14]. The electrolytic cell used in this study was a 400-ml pyrex beaker in which Ti (mixed metal oxide coated) anode and copper sheets as the cathode were used. Anode and cathode were connected to a DC source (model: Hyelec HY3005F) and PHYWE Cobra 3 basic unit device to monitor the average voltage and hence energy consumption. The interelectrode space was fixed at 2.5 cm.

The electrolyte solution was prepared from sulphuric acid (98% H$_2$SO$_4$, Merck), reagent grade copper sulphate (CuSO$_4$.5H$_2$O, Merck), 4 mg/L gelatine, 3 mg/L thiourea, and deionized-distilled water. All the electrowinning experiments were carried out using synthetic electrolytes (Cu$^{2+}$ 30 g/L; H$_2$SO$_4$ 1.2 M; 4 mg/L gelatine; 3 mg/L thiourea) for 20 hours. The current density was held constant at 250 A/m$^2$. The effect of temperature was studied in the range from 20 to 50±2°C. These levels of temperature were selected based on previous studies and industrial applications. In order to control the temperature all the experiments conducted in water bath. During the electrolysis, the cell was sampled at predetermined intervals (0-2-4-6-8-20. hours) to monitor the electrodeposition of Cu.

The concentration of copper was determined by the iodometric titration due to the high concentration of copper (i.e. 30 g/L Cu$^{2+}$) in the electrolyte [15]. An atomic absorption spectrophotometer (AAS, Perkin Elmer Analyst 400) was also used to analyse low levels of Cu at the end of the experiment.

The rate of copper deposition was determined using Equation (6) based on the slope of linear trend-line for the first 8 h of electrowinning experiments due to the apparent deviation of trend in the reaction rate, accompanying with the depletion of copper (Figure 1) [14].

$$\text{Deposition Rate } \left( \frac{g}{L} \right) = \text{Slope } \left( \frac{g}{L . h} \right) . \text{ V (L) }$$

**Figure 1.** A typical kinetic trend-line for Cu electrowinning of copper from sulphate solutions [14].

The macroscopic surface analyses of the cathodes were carried out using a Leica microscope equipped with high resolution camera. Surface roughness of cathodes was also determined by Mahr surf PS1 device, which measures Ra (arithmetic mean surface roughness) and Rz (mean peak-to-valley height, Japanese Industrial Standard (JIS)) based on the five highest peaks and lowest valleys over the entire sampling length, in micrometer ($\mu$m) units.
3. Results and Discussion

3.1. Effect of temperature on copper electrowinning

Figure 2 illustrates effect of temperature (20-50°C) on the rate of Cu deposition (g/h). With increasing the temperature the rate of copper deposition increased. The beneficial effect of temperature could be attributed to the improved diffusion of Cu ions at cathode [5], [8].

![Figure 2. Effect of Temperature on the rate of copper deposition.](image)

Energy consumption is one of the main issues in all fields of industry, especially mineral and metallurgy. Compared with electrorefining, electrowinning of copper is an energy intensive process. The electrical potential needed for electrowinning is ~2.0 V, as compared to ~0.3 V for electrorefining. In practice, the energy requirement for electrowinning is ~2.2 kWh/t. The required energy for electrowinning of copper is calculated by Equation (7) [1], [2], [16].

\[ E = V \times I \times t \]  
\[ \text{(7)} \]

Where, V is calculated average voltage in volts, I is constant current (0.31 A), and t is time in seconds.

It was observed that with increasing temperature (from 20 °C to 50 °C), energy consumption was reduced by about 10% (from 1.94 to 1.69 kWh/kg Cu) (Figure 3). These findings were concomitant with the decrease (by approximately 0.09 V) observed in cell potential. This was consistent with the earlier reports in literature [10].

![Figure 3. Effect of temperature on energy Consumption](image)

Figure 4 also show the effect of temperature on current efficiency, which is regarded as an important parameter in electrowinning processes. It significantly affects the energy consumption and efficiency of the electrowinning processes [1], [4]. The current efficiency of the copper electrowinning process was determined to increase with rising the temperature in the rage tested. A ~2% increase in the current efficiency was recorded with increasing the temperature from 20 to 50°C.

![Figure 4. Effect of temperature on current efficiency (%)](image)

Effect of temperature on the morphology of copper deposits was also examined through the determination of surface roughness. As illustrated in Figure 5 and presented in Table 1, the surface roughness of the cathode tended to increase with increasing the temperature as also reported by Pradhan et al. [12].

The surface roughness of cathodes as represented by Ra (arithmetic mean roughness) and Rz (mean peak-to-valley height) values. The increasing of temperature from 20 to 50°C increased the Ra and Rz values of the deposit from 2.30 and 15.92 µm to 12.31 and 49.79 µm, respectively.

One consistent explanation is that the electrochemical reaction and diffusion rate of ions are accelerated with increasing the temperature. Thus, there is not enough time to develop the crystal structure. In other words, the rough cathode surface (along with dendritic structure) is often associated with high rate of nucleation and crystal growth accompanying with increasing of the temperature [17], [18].
**Acknowledgements**

The authors greatly appreciate the financial support from TUBITAK (Project No: 109M111) and Mr. Fatih Erdemir (Metallurgical and Materials Engineering, KTU) for his help during microscopic examination of cathodes.

**References**


