Effect of SO₂ & Air Sparging In Electrowinning of Copper

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Electrodeposition of copper was carried out in an acidic medium with compressed air and SO, in an electrolytic cell with continuous solution flow. The effect of copper, sulfuric acid and ferrous iron concentrations in the electrolyte on the nature of the deposit, current efficiency, and cell voltage were investigated. Copper concentration was varied from 5 to 50 g/L, sulfuric acid, 0 to 200 g/L and ferrous iron from 0 to 10 g/L. Current density was varied from 100 to 300 A/m². Cell voltage was reduced by about 0.2 V in the case of copper variation and about 1.0 V in the case of sulfuric acid variation. With increase of current density from 100 to 300 A/m², cell voltage increased by 0.4 V. With increase of ferrous iron, however, there was scarcely any change in cell voltage up to 5 g/L, but marked difference was observed at 10 g/L. At a current density of 300 A/m², the reduction in cell voltage was 0.25 V because of the presence of sulfur dioxide and air. The deposit morphology is compared on the basis of SEM photographs.

Current interest in hydrometallurgy has resulted in renewed interest in electrowinning, especially of copper. Conventional copper electrowinning involves decomposition of water at the anode and the cell potential is approximately two volts. If the anodic reaction is changed to involve the oxidation of sulfur dioxide, the cell voltage can be reduced, and this change can reduce the overall energy consumption of the electrowinning process. Apart from saving energy, this reaction produces additional sulfuric acid that will be useful in the overall process flowsheet.

The reactions involved in copper electrowinning are as follows:¹

At the cathode:

 $Cu^{+2} + 2e^{-} \rightarrow Cu^{0} \quad E^{0} = 0.345 \text{ V}$ (1)

At the anode:

 $Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e^-$ (2)

 $H_2O \rightarrow {}^{1}\!/_2O_2 + 2H^+ + 2e^- E^0 = 1.230 V$

Solution :

 $2\mathrm{H}^{+} + \mathrm{SO}_{4}^{-2} \to \mathrm{H}_{2}\mathrm{SO}_{4} \tag{4}$

Overall cell reaction:

$$Cu^{+2} + SO_4^{-2} + H_2O \rightarrow Cu^0 + H_2SO_4 + \frac{1}{2}O_2 \quad E^0 = 0.885 \text{ V}$$
 (5)

Cathode overvoltage = 0.050 VAnode overvoltage = 0.600 VSolution overvoltage = 0.465 VTotal cell voltage = 2.0 V

Reactions for SO_2 - Copper electrowinning in the presence of iron:

$$Cu^{+2} + SO_4^{-2} + 2e^- \rightarrow Cu^0 + SO_4^{-2}$$
 $E_0 = +0.345 V$

Anode reaction:

$$2 \operatorname{Fe}^{+2} + 2\operatorname{SO}_{4}^{-2} \to 2\operatorname{Fe}^{+3} + 2\operatorname{SO}_{4}^{-2} + 2\operatorname{e}^{-1} \operatorname{E}_{0}^{-1} = +0.770 \operatorname{V} (6)$$

Solution reactions:

$$2 \operatorname{Fe}^{+3} + 3\operatorname{SO}_{4}^{-2} + \operatorname{SO}_{2} + \operatorname{H}_{2}O \rightarrow 2 \operatorname{Fe}^{+2} + 2\operatorname{SO}_{4}^{-2} + \operatorname{SO}_{3} + 2\operatorname{H}^{+} + \operatorname{SO}_{4}^{-2}$$
(7)
$$\operatorname{SO}_{3} + \operatorname{H}_{2}O \rightarrow \operatorname{H}_{2}\operatorname{SO}_{4}$$

$$\operatorname{SO}_{4}^{-2} + 2\operatorname{H}^{+} \rightarrow \operatorname{H}_{2}\operatorname{SO}_{4}$$

Overall cell reaction:

Overall cell reaction:

(3)

$$Cu^{+2} + SO_4^{-2} + SO_2 + 2H_2O \rightarrow Cu + 2H_2SO_4 E_0 = 0.425 V$$
 (8)

Anode overvoltage = 0.060 VCathode overvoltage = 0.050 VSolution overvoltage = 0.465 VE = 1.000 V

Cooper and Mishra used SO₂ sparging² and found the nature of the copper electrodeposition in the presence of ferrous iron. They concluded that good quality, bright copper deposits can be obtained by the ferrous oxidation/SO₂ sparging process. In the presence of SO₂, there was a tendency to form a pyramidal surface morphology. D.J. Robinson¹ used SO₂ in copper electrowinning for reducing energy consumption and concluded that hydrometallurgical processes would be competitive with the pyrometallurgical alternative if the energy consumption were decreased. K.A. Spring and J.W. Evans³ tried sulfite ion oxidation as an alternative anodic reaction in fluidized bed electrowinning and other high-rate electrolytic cells. Electro-oxidation of SO2 in sulfuric acid solution on smooth platinum electrodes has been studied by Sportintz et al.4 Cook et al.5-7 also studied the reduction of ferric iron, using reducing agents such as SO₂ and Cu(I) sulfide and coal. These studies are directed toward the mass transfer kinetics.

In this paper, an attempt is made to see the effect of electrolyte composition and current density in the presence of SO_2 and air on the anode potential, overall cell voltage,

Table 1 Effect of Copper Concentration

| Sample No. | Cu Conc. g/L | Wt of Metal g | An Pote Initial | ode ential I Final | Cat Pote Initial | hode ntial I Final | Current Efficiency % | C Vol Initial | ell tage I Fina | Nature of I Deposit |
|---------------|--------------------|---------------------|-----------------------|--------------------------|------------------------|--------------------------|----------------------------|---------------------|-----------------------|---------------------------------------|
| | | | V | V | V | V | | V | V | |
| 1. | 5 | 1.25 | 1.67 | 1.376 | -0.251 | -0.228 | 100 | 2.0 | 1.7 | Smooth, adherent little black at top |
| 2. | 10 | 1.19 | 1.70 | 1.453 | -0.150 | -0.143 | 95.6 | 1.7 | 1.5 | Smooth, yellowish |
| 3. | 30 | 1.23 | 1.641 | 1.406 | -0.141 | -0.137 | 98.87 | 1.7 | 1.5 | Smooth, adherent black spot at top |
| 4. | 50 | 1.70 | 1.736 | 1.402 | -0.171 | -0.150 | 100 | 1.8 | 1.5 | Smooth, adherent |

Conditions: H₂SO₄ 100 g/L; Ag 10 ppm; Fe 5 g/L; current density 200 A/m²; SO₂ flow rate 200 mL/min; Air flow rate 400 mL/min; circulation rate 80 mL/min.

| Table 2 Effect of Sulfuric Acid Concentration | | | | | | | | | | |
|--|--|---------------------|----------------------|--------------------------|------------------------|--------------------------|----------------------------|---------------------|----------------------|------------------------------|
| Sample No. | H ₂ SO ₄ Conc. g/L | Wt of Metal g | An Pote Initia | ode ential I Final | Cat Pote Initial | hode ntial Final | Current Efficiency % | C Vol Initial | ell tage Final | Nature of Deposit |
| | | | V | V | V | V | | V | V | |
| 1. | 50 | 1.69 | 1.658 | 1.300 | -0.385 | -0.275 | 100 | 2.0 | 1.5 | Uniform, smooth, adherent |
| 2. | 100 | 1.70 | 1.730 | 1.430 | -0.345 | -0.197 | 100 | 2.0 | 1.5 | Non-uniform |
| 3. | 150 | 1.70 | 1.700 | 1.500 | -0.180 | -0.106 | 100 | 1.9 | 1.5 | Uniform, smooth |
| 4. | 200 | 1.67 | 1.750 | 1.422 | -0.230 | -0.134 | 100 | 2.0 | 1.7 | Uniform, smooth |
| 5. | 0 | 1.40 | 1.742 | 1.318 | -1.300 | -0.921 | 84.36 | 2.8 | 2.5 | Uniform, smooth |
| | | | | | | | | | | adherent |

Conditions: Cu 35 g/L; Ag 10 ppm; Fe 5 g/L; current density 200 A/m²; SO₂ flow rate 200 mL/min; Air flow rate 400 mL/min; circulation rate 80 mL/min.

current efficiency and nature of the deposit during electrodeposition of copper.

Experimental Procedure

Materials

Copper sulfate, sulfuric acid and ferrous sulfate were analytical reagent grade. SO_2 was obtained from industrial gas cylinders. The electrolyte was prepared by dissolving cupric sulfate, ferrous sulfate, and sulfuric acid in distilled water.

Apparatus

The electrolytic cell was a perspex vessel having dimensions of length 10.0 cm, width 6.0 cm, and depth 10.0 cm. The cell is provided with an inlet and outlet, each having a 0.6 cm dia. and placed at heights of 2.0 cm and 8.0 cm, respectively. A lead-antimony anode of length 9.2 cm, width 5.2 cm and thickness 0.3 cm was placed in the cell. The cathode was 316 stainless steel and has the same dimensions as the anode. A metering pump was used for circulating the electrolyte in the cell. SO₂ gas was sparged through a perforated glass tube kept near the anode and between anode and cathode. A copper electrode immersed in the same copper sulfate electrolyte as in the cell was used as reference electrode.

The anode potential, cathode potential and cell voltage were measured by precision voltmeter. Flow rates of the air and sulfur dioxide were measured with calibrated rotameters. The temperature of the electrolyte was kept at 30 ± 1 °C. Copper electrodeposits were analyzed for purity of the metal by atomic absorption spectrophotometer. The electrodeposits were examined by scanning electron microscope.

Electrolysis

Electrolysis was carried out at room temperature of 30 °C. Copper was deposited from a solution containing copper sulfate, ferrous sulfate, and sulfuric acid. During electrolysis, the electrolyte was circulated though the cell at the desired rate and SO₂ gas was sparged continuously for two hr. After the electrolysis, the cathode was removed, thoroughly washed with water, dried with acetone and weighed, then stripped and analyzed for purity of the copper deposit.

Results & Discussion

The effect of copper, sulfuric acid and ferrous iron concentration and current density on electrowinning of copper in SO_2 and-air mixture sparging is shown in Tables 1-5. The tables show anode potential, cathode potential, current efficiency and cell voltage, as well as the nature of the deposit by visual and by microscopic examination.

Table 1 lists the effect of copper concentration. SO_2 sparging near the anode makes the anode potential decrease by 0.25 V. The current efficiency varies from 95.6 to 100 percent. Smooth and bright deposits are obtained even in the presence of SO_2 .

Table 2 shows the effect of sulfuric acid concentration during electrodeposition of copper. The sulfuric acid concentration varies from 0 to 200 g/L. In the absence of sulfuric acid, the cell voltage is high and current efficiency is low. Smooth and bright deposits are obtained with increase of sulfuric acid concentration, even in the presence of sulfur dioxide in the electrolyte.

Table 3 Effect of Current Density

| Sample No. | Current Density A/m ² | Wt of Metal g | Anode Potential Initial Final | | Catl Pote Initial | hode ntial I Final | Current Efficiency % | Cell Voltage Initial Fina | | Nature of I Deposit |
|---------------|--|---------------------|-------------------------------------|-------|-------------------------|--------------------------|----------------------------|---------------------------------|--------------|---------------------------|
| | | | V | V | V | V | | V | \mathbf{V} | |
| 1. | 100 | 0.81 | 1.763 | 1.410 | -0.082 | -0.041 | 97.61 | 1.5 | 1.2 | Uniform, smooth, adherent |
| 2. | 150 | 1.26 | 1.612 | 1.384 | | 0.088 | 100 | 1.4 | 1.3 | Uneven, smooth, adherent |
| 3. | 200 | 1.7 | 1.694 | 1.410 | -0.310 | -0.139 | 100 | 2.0 | 1.6 | Uneven, smooth, adherent |
| 4. | 250 | 2.07 | 1.721 | 1.452 | -0.235 | -0.140 | 99.78 | 1.8 | 1.6 | Smooth |
| 5. | 300 | 2.41 | 1.702 | 1.420 | -0.190 | -0.189 | 96.81 | 1.8 | 1.6 | Smooth |
| 6. | 300 | 2.43 | 1.742 | 1.629 | -0.286 | -0.315 | 97.61 | 2.0 | 1.8 | Smooth |
| | (No air $+$ SO ₂) | | | | | | | | | |
| 7. | 300 (No SO ₂ | 2.41 + air) | 1.718 | 1.613 | -0.466 | 0.373 | 96.81 | 2.0 | 2.0 | Smooth |

Conditions: Cu 35 g/L; Ag 10 ppm; Fe 5 g/L; current density 200 A/m²; SO₂ flow rate 200 mL/min; Air flow rate 400 mL/min; circulation rate 80 mL/min.

| Table 4 Effect of IronVariation | | | | | | | | | | |
|------------------------------------|----------------------|---------------------|----------------------|--------------------------|-------------------------|--------------------------|----------------------------|--------------------|-----------------------|----------------------------|
| Sample No. | Iron Conc. g/L | Wt of Metal g | An Pote Initia | ode ential I Final | Catl Pote Initial | hode ntial I Final | Current Efficiency % | C Vol Initia | ell tage l Fina | Nature of I Deposit |
| | | Ū. | V | V | V | V | | \mathbf{V} | V | - |
| 1. | 0 | 1.79 | 1.587 | 1.392 | -0.205 | -0.092 | 100 | 1.7 | 1.6 | Smooth at bottom, adherent |
| 2. | 1 | 1.74 | 1.908 | 1.393 | -0.398 | -0.152 | 100 | 1.8 | 1.5 | Smooth at bottom, adherent |
| 3. | 2 | 1.73 | 1.598 | 1.406 | -0.195 | -0.117 | 100 | 1.6 | 1.5 | Smooth |
| 4. | 5 | 2.86 | 1.680 | 1.498 | -0.335 | -0.031 | 98.87 | 1.6 | 1.5 | Smooth |
| 5. | 10 | 1.64 | 1.630 | 1.388 | -0.370 | -0.079 | 91.9 | 1.6 | 1.5 | Smooth |



Table 3 lists the effect of current density on electrodeposition of copper in SO₂ sparging at a flow rate of 200 mL/min and an air flow rate of 400 mL/min. The quality of deposition is good at current densities of 100 to 300 A/m². There is no appreciable change in the anode potential because of increase of current density. In either the absence of air circulation or SO₂ sparging, the decrease in the final anode potential is only about 0.12 V. At higher current density of 300 A/m² and with SO₂ sparging, however, but in the absence of air agitation, it shows a rise in anode potential around 0.2 V. With air agitation but no SO₂ sparging, and at the same higher current density, it shows an increase of anode potential to about 0.2 V. The current efficiency in all the cases is found to be nearly 100 percent, but the cell voltage is found to increase with increase in current density. At highest current density, the cell voltage is greater, regardless of air and SO₂ sparging in the electrolytic cell.

The figure shows the quality of the deposit produced during copper electrowinning in the presence and absence of SO₂. It can be seen that a smooth, compact deposit is obtained.

Éccause ferrous iron is a very good anode depolarizer and better than SO₂, it is worthwhile to study the effect of Fe⁺² ion along with SO₂ sparging during electrowinning of Cu. As revealed by Eq. (6), the ferrous iron is oxidized to ferric iron. Consequently, in the utilization of the ferrous iron oxidation anode reaction, attention must be paid to the regeneration of the ferrous iron, inasmuch as the reduction of ferric iron at the cathode reduces the current efficiency in the electrowinning process. Table 4 embodies the results obtained during variation of ferrous iron in electrowinning of Cu^{+2} during SO_2 sparging. The use of the SO_2 + air mixture as a sparging gas seems to enhance the mass transport in the solution and to reduce the ferric iron to ferrous iron, according to the following reaction, and improves the deposit morphology.

$$2Fe^{+3} + SO_2 + 2H_2O \rightarrow 2Fe^{+2} + H_2SO_4 + 2H^+$$
 (9)

At 5 g/L ferrous iron concentration, Table 4 shows better current efficiency, with electrowinning taking place at low cell voltage. At high ferrous iron concentration of 10 g/L, there is a decrease in current efficiency of about eight percent.

Table 5 shows the effect of sulfur dioxide in the electrolyte. It is observed that with increase of SO_2 concentration in the electrolyte, the cell voltage is reduced considerably; the cell voltage can be reduced up to 0.86 V when the sulfur dioxide concentration in the electrolyte is maintained at a level of 14.05 g/L.



SEM photos showing effect on copper deposition of higher current density: (a) in the absence of SO₂. 200X; (b) with SO₂ + air sparging. 200X. Bath composition: (a) H₂SO₄100 g/L; Cu 5 g/L; Ag 10 ppm; Current density 300 A/m²; Air flow rate 400 mL/min; circulation rate 80 mL/min; (b) H₂SO₄ 100 g/L; Cu 35 g/L; Fe 5 g/L; Ag 10 ppm; current density 300 A/m²; SO₂ flow rate 200 mL/min; air flow rate 400 mL/min; circulation rate 80 mL/min.

Conclusions

The following conclusions can be drawn from this study:

- 1. Anode potential is reduced by SO₂ sparging.
- 2. Fe⁺² ion works as a better anodic depolarizer up to a concentration of 5 g/L.
- 3. The sulfuric acid concentration of 150 g/L may be a recommendable concentration level during electrowinning of copper in an electrolytic cell in the presence of sulfur dioxide.
- 4. Smooth copper deposits with higher current efficiency are observed at high copper concentration, even in the presence of SO₂.
- 5. Increase of sulfuric acid increases the smoothness of the deposit and in the absence of sulfuric acid, the deposit adheres to the cathode because of the presence of SO₂.
- 6. Cell voltage is reduced considerably with increase of sulfur dioxide concentration in the electrolyte when using a graphite anode.

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Table 5 Effect of Sulfur Dioxide on Electrolyte with Graphite Anode

| Sample No. | Concentration of SO, in the electrolyte, g/L | Cell Voltage V |
|---------------|---|-------------------|
| 1. | | 1.790 |
| 2. | 3.71 | 1.620 |
| 3. | 7.00 | 1.000 |
| 4. | 10.27 | 0.870 |
| 5. | 14.05 | 0.860 |
| | | |

Conditions: Cu 40 g/L; H₂SO₄ 150 g/L; current density 200 A/dm².





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of battery-grade nickel hydroxide, and electroplating of different metals.

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