

Electrolytic recovery of copper from dilute solutions considering environmental measures

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The electrolytic recovery of copper is one of the methods of preventing the formation of sludges generated by conventional treatments. Electrolysis of metal ions in dilute solutions using vertical electrodes results in low recovery. Therefore, a design consisting of a rotating tubular bed reactor with extended cathode surfaces was developed to improve the mass transfer in the cell. The electrolytic conditions were fixed in a Hull cell prior to the actual electrolysis in the reactor. Two types of copper solution obtained from actual industrial sites were used. This process allowed the copper concentrations in the solutions to be reduced to low levels. More importantly, a combination of electrolytic and ion exchange treatments further reduced the copper content below the p.p.m. levels. This technique not only recovers more copper but also protects the environment with additional economic savings.

1. Introduction

Over the last few decades, environmental protection measures have been intensified in the Western countries particularly in the USA. The American Environmental Protection Agency, for example, has ordered a zero discharge of toxic materials in drainage [1]. Waste solutions generated by the mining, mineral processing and metallurgical industries alone in the USA produce large quantities of metal ions [2, 3]. These waste solutions have to be treated for recovery of metals to control environmental pollution using various hydro-metallurgical and electrochemical processes such as cementation, precipitation, ion exchange, solvent extraction, reverse osmosis and electrolysis.

The conventional treatment of metal ions in dilute solutions generally requires various processing steps such as chemical neutralization, precipitation of metals as hydroxide sludges and filtration followed by transportation and dumping. This treatment causes a loss of a few hundred tons of metals per annum and also contributes to environmental problems [4, 5].

Unlike the above processes the electrochemical methods consist of only one step for the direct recovery of metals and thus provide great economic benefits. In the electrolytic processes mass transfer takes place by natural or turbulent convection, migration and diffusion. However in dilute solutions mass transfer of the electrolytic processing is mainly controlled by diffusion [6]. Electrolytic recovery of metals from dilute solutions with a high space-time yield can be accomplished either by increasing the surface area of the cathode or by minimizing the thickness of the boundary layer. This can be achieved by circulation of the electrolyte and movement of the electrodes.

On the basis of the above principles, different types

of cells for the electrolysis of dilute solutions have been developed in the last few years. However only some of these have found industrial application [7–17]. Whilst fixed bed and extended surface electrolysis cells are used to produce concentrated solutions from dilute effluents [9–12], the Chemelec cell is suited for metal deposition on vertical mesh electrodes [7, 13]. In the ECO-cell the metal is deposited as powder on a rotating cylindrical cathode [14, 15]. On the other hand, the fluidized bed cell employs metal particles as cathode [16, 17].

Despite its advantages, the fluidized bed system exhibits several technical problems in industrial applications [18, 19]. Therefore, an alternative electrolytic reactor was developed to investigate the possibility of recovering metals from dilute solutions.

2. Experimental details

Two types of copper solution, acidic dilute copper solution ($2.4 \text{ g l}^{-1} \text{ Cu}$) and alkaline cyanide solution ($1.8 \text{ g l}^{-1} \text{ Cu}$), from industrial sites were used. Prior to the actual electrolysis in the reactor, the electrolytic parameters such as copper concentration, cell current, pH and temperature were fixed in a Hull cell [20].

Fig. 1 shows a schematic representation of the rotating tubular bed reactor used in this study. The reactor was made of two perforated concentric non-conductive plastic tubes. The internal and external tubes of the reactor had a wide extended perforation with a square opening of 4 mm^2 . In order to achieve a good agitation the space between the tubes was filled with copper particles of 10 mm in diameter and surface area of 40 dm^2 as cathode occupying four fifths of its internal volume. The mechanical agitation of the particles together with circulation of the electrolyte led to

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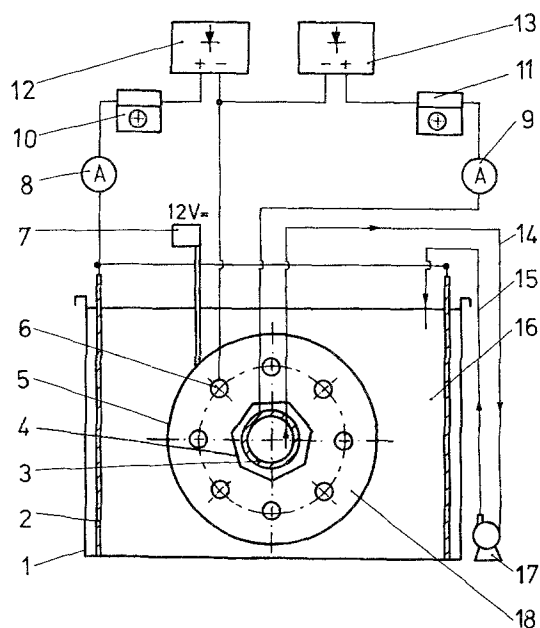


Fig. 1. Schematic representation of the rotating tubular bed reactor for the recovery of copper from dilute solutions:

- | | |
|-------------------------------------|-----------------------------|
| 1. Electrolytic tank | 7. DC driving motor |
| 2. External anodes | 8, 9. Ammeters |
| 3. Internal anode | 10, 11. Ampere hour meters |
| 4. Internal perforated plastic tube | 12, 13. Regulators |
| 5. External perforated plastic tube | 14. Draw-off pipe |
| 6. Metal rods as feeder electrodes | 15. Feed back pipe |
| | 16. Electrolyte |
| | 17. Circulation pump |
| | 18. Particulate bed cathode |

improved mass transfer. Agitated and extended cathode surfaces were surrounded by an internal tube anode and two external anode sheets. The external anodes consisted of lead sheets for acidic solutions and platinum coated titanium mesh for alkaline cyanide solutions. The optimum rotational velocity of the reactor was found to be 8 r.p.m. At this speed the particles were observed to cataract periodically. Agitation of the bed electrode increased the effective surface of the metallic particles. The electrolyte was circulated through the particles in the radial direction of the

reactor by means of a pump. In this case, turbulent convection and improved deposition kinetics could be established [21].

3. Results

Fig. 2 shows the copper concentration in acidic dilute solutions as a function of quantity of electricity. As the current decreases the concentration of copper approaches closer to the theoretical deposition line calculated using Faraday's law. Current efficiency as a function of copper concentration is illustrated in Fig. 3. It is evident that electrolysis of copper with a current of 4 A produces a current efficiency of more than 80% at a copper concentration of 500 mg l^{-1} . Beyond this level of copper the current efficiency remains approximately constant. Also, increasing the current from 4 A to 15 A reduces the current efficiency. The copper concentration was reduced from 2400 mg l^{-1} to 1 mg l^{-1} of copper during 84 Ah of plating and 60 g of copper was recovered. The energy consumption was 6.3 kWh kg^{-1} copper, as shown in Table 1.

In alkaline cyanide solutions copper is found in the form of a stable cyanocuprate complex [22]. Therefore, electrolysis of cyanide solutions in the absence of oxidizers leads to lower copper recoveries. The electrolytic treatment of copper cyanide solutions was carried out first without additives. The results were unsatisfactory. Therefore, NaCl was introduced in the electrolyte, to form both chloride and hypochlorite and concurrently to destroy the cyanide. While the copper concentration of 1800 mg l^{-1} in copper cyanide solutions without additive could be reduced to 670 mg l^{-1} of copper during 120 Ah of plating, only 28.3 g of copper was recovered. Addition of 50 g l^{-1} NaCl, however, reduced the same initial copper concentration to 75 mg l^{-1} with a copper deposition of 43 g during 120 Ah of electrolysis. Combination of oxidizer and complexing agent, namely NaOCl and NH_4Cl not only reduced the copper concentration to 4 mg l^{-1} with a copper deposition of 44.9 g as shown in Fig. 4, but

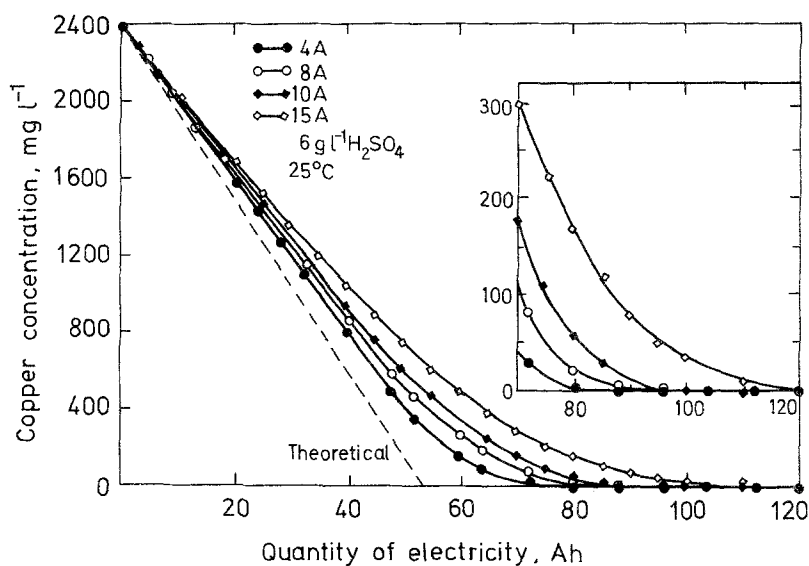


Fig. 2. Copper concentration as a function of the quantity of electricity in acidic copper solutions.

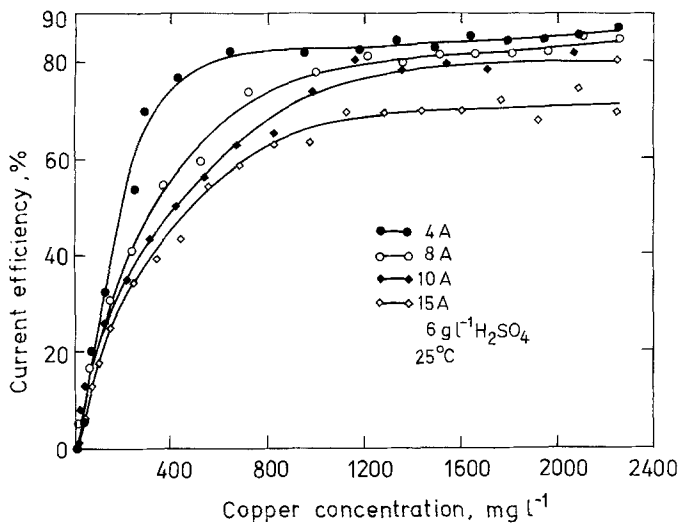


Fig. 3. Current efficiency as a function of copper concentration in acidic copper solutions.

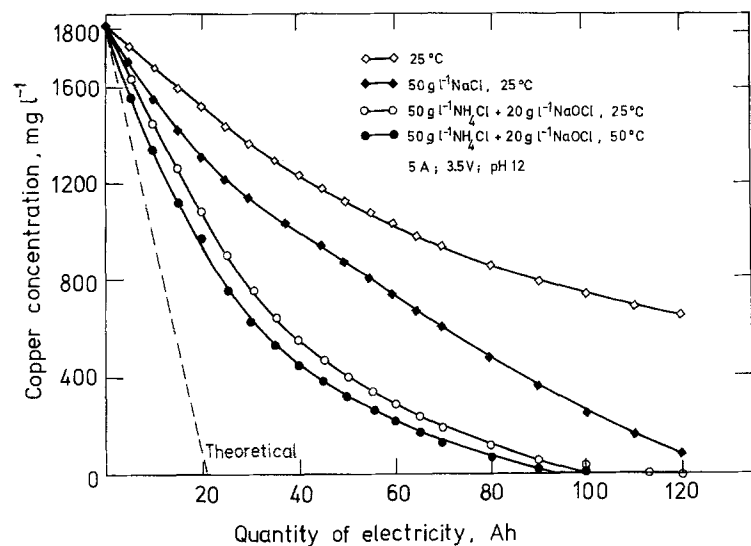


Fig. 4. Copper concentration as a function of the quantity of electricity in copper cyanide solutions.

also improved the oxidation of cyanide. The energy consumption by the electrolysis of the solutions without additive was 15 kWh kg^{-1} copper, whereas in the presence of oxidizer and complexing agent this value could be reduced to 9.3 kWh kg^{-1} copper. Furthermore, increasing the temperature from 25 to 50°C led to enhanced copper removal.

4. Discussion

Comparison of the current efficiencies obtained using acidic and alkaline cyanide solutions reveals that the former yields much higher recoveries. An explanation of this effect can be offered in the following manner. Addition of sodium hypochlorite increases the oxi-

Table 1. Performance data for the rotating tubular bed reactor

Cell parameters	Acidic	With cyanide		
		without additive	50 g l^{-1} NaCl	$50 \text{ g l}^{-1} \text{ NH}_4\text{Cl} + 20 \text{ g l}^{-1} \text{ NaOCl}$
Copper concentration				
initial, mg l^{-1}	2400	1800	1800	1800
final, mg l^{-1}	1	670	75	4
cell current, A	4	5	5	5
cell voltage, V	4.5	3.5	3.5	3.5
current density, A m^{-2}	10	12.5	12.5	12.5
quantity of electricity, Ah	84	120	120	120
mass transfer coefficient, $\text{ms}^{-1} \times 10^{-3}$	2.06	0.096	0.87	0.92
mass transfer rate, $\text{g Cu } 251^{-1} \text{ electrolyte}$	60	28.3	43	44.9
energy consumption, $\text{kWh kg}^{-1} \text{ Cu}$	6.3	15	9.8	9.3

Table 2. Costs for electrolytic and conventional treatment of copper effluents

ELECTROLYTIC	Energy demand:	[DM]
	Electrolysis, 30 kWh	
	Driving motor, 5 kWh	
	Total (35 kWh; 0.15 DM kWh ⁻¹)	5
	Neutralization of acid	4
	Regeneration of ion exchange resins (6 l)	5
Draining of treated waste water	1	
Total cost	15	
CONVENTIONAL	Value of metal (2.4 kg Cu; 3.5 DM kg ⁻¹ Cu)	8
	Neutralization and precipitation	6
	Filtration of sludge	2
	Transportation of sludge	1
	Dumping cost	2
	Draining of treated waste water	1
	Total cost	20

Acidic effluents, 1 m³Copper content, 2.4 g l⁻¹ CuFree sulphuric acid, 6 g l⁻¹ H₂SO₄

dation rate of cyanide whereas that of ammonium chloride leads to less stable cyanoammincopper (II) complexes [23]; this in turn prevents the precipitation of copper ions in alkaline solutions. Fig 5 presents the current efficiency obtained in the electrolysis of alkaline cyanide solutions as a function of copper concentration. It is seen that the presence of oxidizer and complexing agent again improves the current efficiency considerably. While addition of NaCl increases the mass transfer rate about 52%, introduction of oxidizer and complexing agent enhances the deposition rate up to 60% compared to copper deposition without any additive.

The final part of the curves given in Figs 2 and 4 can be utilized to estimate the mass transfer coefficient. Table 1 presents the calculated mass transfer coefficients under various conditions. The data reveal that the mass transfer coefficient is the largest in the case of dilute acidic copper solutions ($2.06 \times 10^{-3} \text{ ms}^{-1}$). In the presence of cyanide, a combination of oxidizer and complexing agent increases the mass transfer coefficient considerably.

In the electrolytic treatment, an optimum deposition rate of copper can be achieved only to a certain level of copper removal. Further recovery of copper can be obtained through ion exchange processes [24–26]. Thus a combination of electrolytic treatment followed by ion exchange is feasible to recover copper concentrations as low as 0.01 p.p.m. Moreover, the eluates of the ion exchanger resins will be returned to the electrolytic cell [27].

Table 2 presents a comparison of costs incurred by the electrolytic and chemical treatments. Interestingly, the electrolytic treatment is approximately 5 DM cheaper for each m³ of effluent compared to the chemical treatment. In the calculations investment, capital and labour costs were not included because they vary to a large extent.

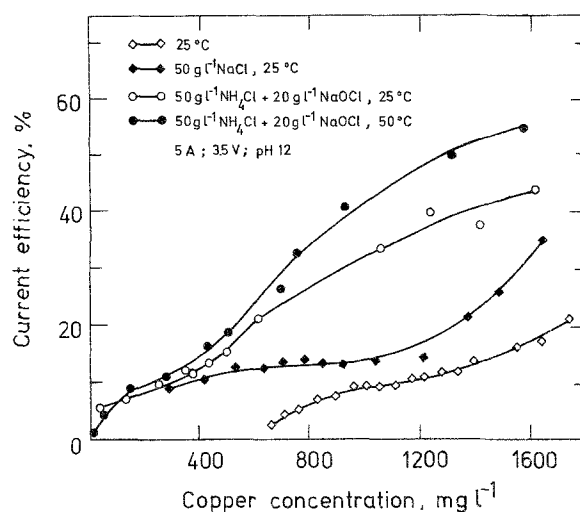


Fig. 5. Current efficiency as a function of copper concentration in copper cyanide solutions.

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