# Electrolytic Treatment
# of Acidic Copper Effluents
# in Particulate Electrode Cells

## A.W. BRYSON, S.W. ORCHARD AND P.W.E. YOUNG
## [DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF THE WITWATERSRAND.]

## Abstract

Two types of particulate electrode cells are described for treating dilute acidic copper sulphate effluents. Experimental results indicate that both systems are economically feasible over the range of copper concentrations investigated. Although the fluidised bed electrode shows superior performance, the fixed porous electrode would be easier to operate in an industrial environment.

## Introduction

In the electroplating industry the main sources of pollution are the deliberate dumping of process solutions, accidental spillage and discharge of spent rinse water effluent (Funke, 1973). In a well-managed plant the first two can be largely controlled, whereas spent rinse water is generally run into the municipal sewer on a regular basis. While most sewage treatment plants can tolerate dilute solutions of metal ions, there is evidence that plating wastes containing copper and chromium can seriously interfere with the biological purification techniques employed (Moore, 1961; McDermott, 1963).

In this study an attempt is made to remove copper electrolytically from acidic rinse waters thereby recovering the metal and acid in reusable form. The purified water can then be recycled to the wash tank resulting in considerable saving of water. A further advantage of an electrolytic technique is that purification is accomplished without addition of chemical reagents which could themselves cause further pollution problems. The major disadvantage of using conventional electrolytic cells is their poor performance in solutions with low metal ion content. This is due to concentration polarisation at the cathode with consequent evolution of hydrogen instead of metal deposition. A particulate electrode on the other hand has a large surface area per unit volume, which effectively reduces the current density thereby enhancing copper precipitation.

## Fixed Porous Electrode

Figure 1 shows a diagram of a cell fitted with a randomly packed bed of lead cylinders which act as cathode. The anode is

a lead sheet separated from the cathode by an anion permeable membrane. Four such cells connected in series are used in this work. Dilute copper sulphate solution flows into both cathode and anode compartments. When a potential is applied to the cell, sulphate ions pass through the membrane forming sulphuric acid in the anode compartment while copper ions discharge on the surface of the lead cylinders. The catholyte is thus purified to a desired level and the anolyte containing sulphuric acid can be re-used in the electroplating bath.
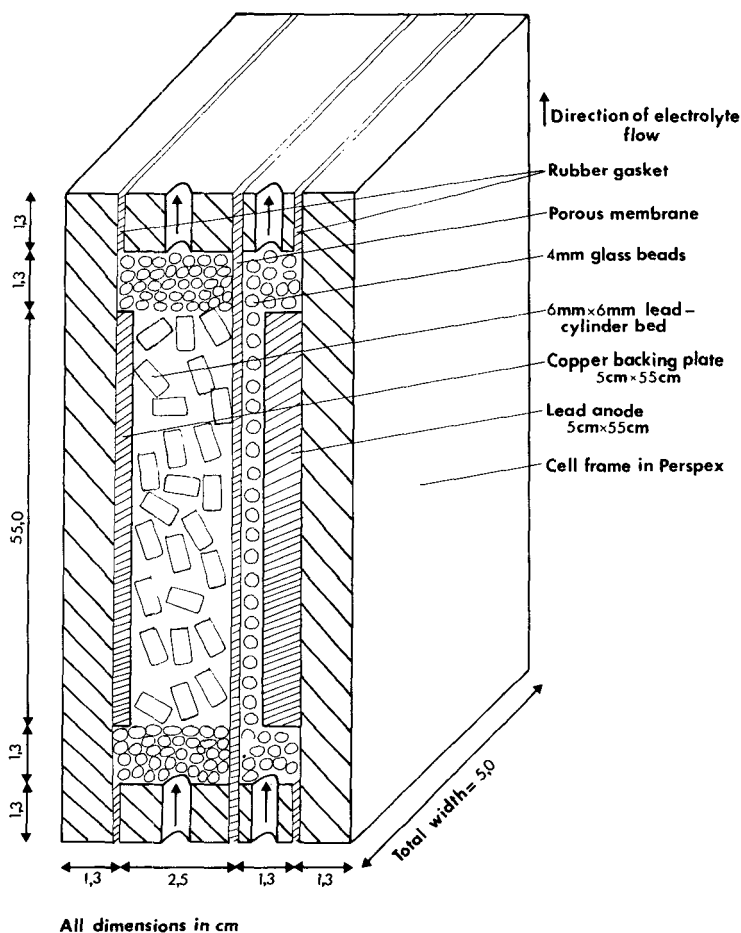


Direction of electrolyte flow
Rubber gasket
Porous membrane
4mm glass beads
6mmx6mm lead – cylinder bed
Copper backing plate 5cm×55cm
Lead anode 5cm×55cm
Cell frame in Perspex

All dimensions in cm
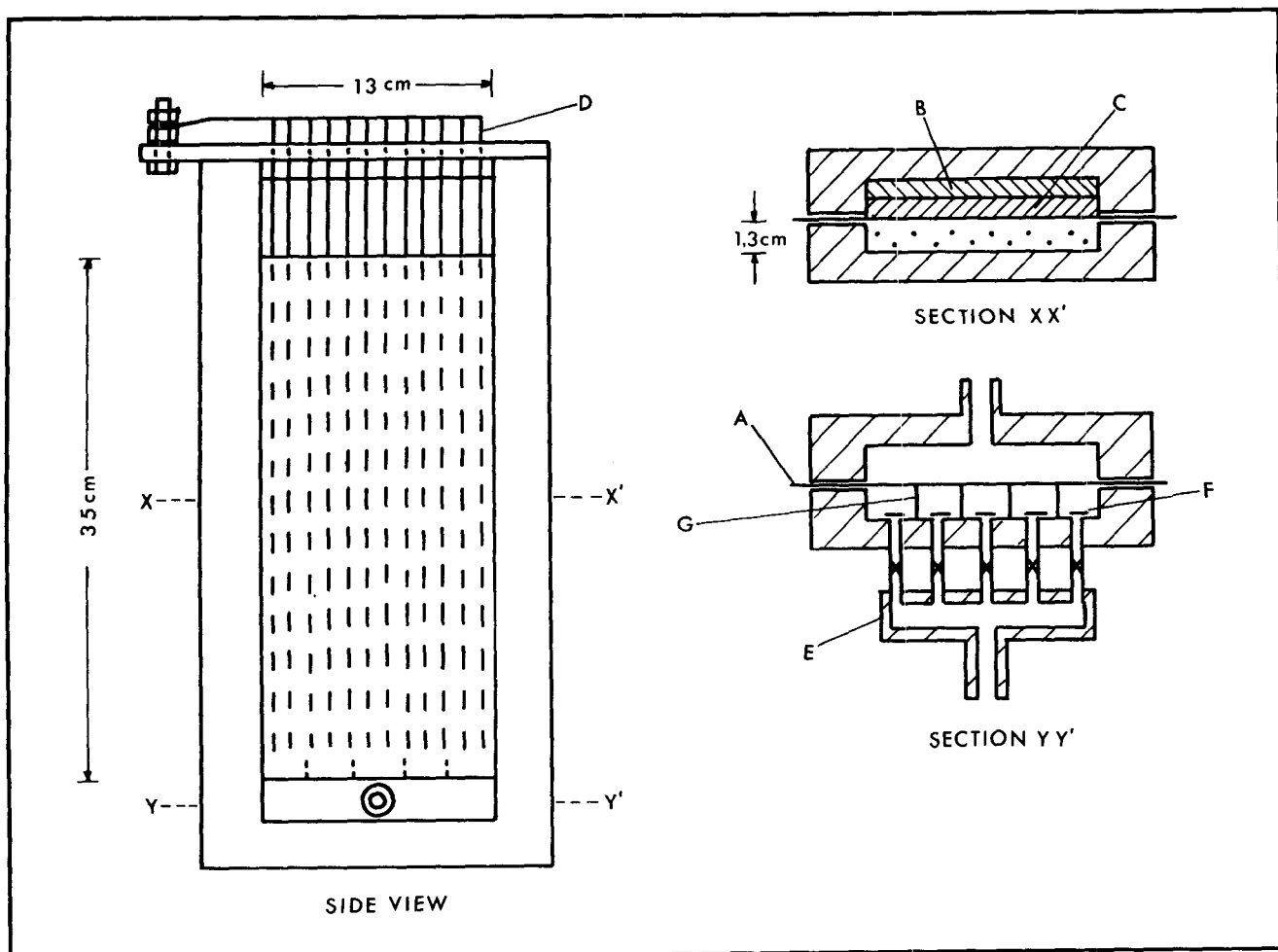
*Figure 1*
*Fixed porous electrode cell*

*Figure 2*
*Fluidised bed electrode cell*

A – Anion permeable membrane
B – Lead anode
C – PVC mesh support
D – Current feeders
E – Flow manifold
F – Non-return valves
G – Baffles

## Fluidised Bed Electrode

Figure 2 illustrates the arrangement which has been used in this study. The cathode consists of copper-coated glass spheres of 600 $\mu$m diameter and an anion permeable membrane and lead anode are again employed. The effluent solution to be treated flows upwards through the cathode compartment fluidising the spheres. Charge is transferred from the current feeders to the particles when contact is made between them and this is completely or partially shared with other particles through collisions in the bed (Goodridge, 1971). Part of the solution again flows through the anode compartment and as in the case of the fixed electrode sulphuric acid will be produced.

## Current Efficiency and Power Yield

In plating copper from dilute acidic sulphate solutions the following cathodic reactions are likely to occur:

$$Cu^{2+} + 2e \rightarrow Cu \qquad (a)$$
$$2H^+ + 2e \rightarrow H_2 \qquad (b)$$
$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad (c)$$

If $I_a$, $I_b$ and $I_c$ are the currents needed for reactions (a), (b) and (c) respectively, then the current efficiency of copper removal, $\xi$, can be defined as

$$\xi = I_a/I \qquad (1)$$
$$I = I_a + I_b + I_c \qquad (2)$$

From Faraday's second law, the mass of copper deposited per unit time is

$$\frac{m}{t} = \frac{wI_a}{2F} \qquad (3)$$

where m = mass of copper deposited
  t = plating time
  w = atomic weight of copper
  F = Faraday constant

In a continuous flow steady-state cell, the rate of copper deposition can be related to the inlet and outlet concentrations of copper ions in solution $C_i$ and $C_o$ respectively, i.e.

$$Q(C_i-C_o) = \frac{wI_a}{2F} \tag{4}$$

Q = volumetric flowrate of electrolyte

Combining equations (1) and (4)

$$\xi = \frac{2FQ(C_i-C_o)}{wI} \tag{5}$$

An important performance criterion for electrolytic cells is the power yield which may be defined as the mass of copper deposited per unit of power consumed. This quantity, which we will denote by the symbol $\phi$, will to a large extent determine whether the technique is economically feasible. We can evaluate $\phi$ from experimental measurements through the equation:

$$\phi = \frac{m}{I.E.t} = \frac{Q(C_i-C_o)}{I.E.} \tag{6}$$

where E is the cell voltage.

## Experimental Results

**TABLE 1**

| Cathode | Fixed Bed | | Fluidised Bed | |
|---|---|---|---|---|
| $C_i$ (mg/$\ell$) | 16,2 | 34,7 | 14,9 | 38,2 |
| $C_o$ (mg/$\ell$) | 6,8 | 15,7 | 8,2 | 14,6 |
| Q ($\ell$/min) | 1,93 | 1,93 | 0,93 | 0,93 |
| I (amps) | 4,00 | 4,00 | 1,00 | 2,00 |
| E (volts) | 3,88 | 3,58 | 2,26 | 2,70 |
| $\xi$ (dimensionless) | 0,23 | 0,47 | 0,31 | 0,55 |
| $\phi$ (gm/watt hr) | 0,07 | 0,16 | 0,16 | 0,24 |

Table 1 summarizes a typical set of results which were obtained with solutions in the range 10 to 40 mg/$\ell$ copper and 1 g/$\ell$ sulphuric acid. It can be seen that both current efficiency and power yield are markedly affected by the copper concentration. In fact, below 20 mg/$\ell$ we found that the current efficiency was approximately proportional to the mean copper concentration in the cells. Thus with a feed solution of 5 mg/$\ell$ and an effluent of about 1 mg/$\ell$ the current efficiency was 0,06 in the fluid bed cell. It is of interest to note that Mantell (1960) reports values

of 0,85 for $\xi$ and 0,5 for $\phi$ in a conventional copper electrowinning plant where the copper concentration is three orders of magnitude larger than the highest level used in this study.

## Conclusions

The power efficiencies for both the fixed and fluidised bed electrode cells are sufficiently high to make either system feasible as a pollution control device for spent rinse water. Although the fluidised bed is more efficient, it requires fairly tight control on flow rate and in addition the maximum height of the bed with existing membranes is limited to about one metre. If greater heights are needed the cell would have to be split into two or more beds which would require interstage pumping of the effluent. The cell must also be operated in the vertical position to obtain uniform fluidisation. The fixed porous electrode does not suffer from any of the above restrictions and could be the preferable system to use on a plating plant where skilled operating personnel are not available.

In practice problems could arise with the composition of the effluent which would be unlikely to contain sulphuric acid at concentrations as high as 1 g/$\ell$. Assuming a 500 to 1 dilution ratio in the washing operation, the spent solution would probably consist of about 100 mg/$\ell$ Cu and 100 mg/$\ell$ $H_2SO_4$. This would result in an electrolyte with very low conductivity, which would produce a high cell voltage. By mixing some of the anolyte exit stream with the incoming effluent it would be possible to raise the acid level to 1 g/$\ell$. This would necessitate a larger cell to handle the additional flow, but the saving in power would more than compensate for this increase in capital cost.

## Acknowledgement

## REFERENCES

FUNKE, J.W. and COOMBS, P. (1973): Water and Effluent Management in the Electroplating and Anodizing Industry. CSIR Technical Guide K29.
GOODRIDGE, F., HOLDEN, D.I., MURRAY, H.D. and PLIMLEY, R.F. (1971): A Mathematical Model of the Fluidised Bed Electrode. Trans. Instn. Chem. Engrs. 49, 128–136.
MANTELL, C.L. (1960): Electrochemical Engineering 4th Edition p.204. McGraw-Hill, New York.
MOORE, W.A., McDERMOTT, G.N., POST, M.A., MANDIA, J.W. and ETTINGER, M.B. (1961): Effects of Chromium on the Activated Sludge Process. J. Water Pollution Control Federation. 33, 54–72.
McDERMOTT, G.N., MOORE, W.A., POST, M.A. and ETTINGER, M.B. (1963): Effects of Copper on Aerobic Biological Sewage Treatment. J. Water Pollution Control Federation. 35, 227–241.