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ELECTRODEPOSITION OF METALS IN AGITATED BED PARTICLE ELECTRODES*

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Polarization phenomena associated with the use of an agitated bed of particles as an electrode for metal deposition were studied. The concentration polarization of this type of electrode is much smaller than that occurring at a fixed or moving electrode surface. Agitated particle electrodes can be used to electrowin copper from solutions over a wide range of concentration and at current density up to 1,000 A/ft^2 of bed cross section.

INTRODUCTION

Electrolytic reduction of metals from aqueous salt solutions is one of the most attractive methods of abtaining the final product in a hydrometallurgical process. A number of suggestions have been made to improve the design of cells used for electrowinning and electrorefining metals.

Most of these designs have been aimed at increasing the current density used in order to increase the cell capacity. The limit imposed on the current density (either the actual upper limit imposed by nature or a lower value selected to provide good deposits at moderate power costs) has the important consequence that a large amount of electrode surface area is needed for a typical metal electrowinning plant.

Figures for the electrowining plant for the Cyprus Bagdad copper plant are as follows [1]: There are 42 cells producing finished cathodes, each cell contains 48 cathodes and 49 anodes which are slabs approximately 3 – 5 ft. In addition there are six cells producing starter sheets each with 48 cathodes 49 anodes. This means about 40,000 square feet of cathode surface area for a plant with quite a modest production rate (22 tons of copper/day).

The high capital cost is associated with fairly high labour costs since much expenditure is entailed in removing finished cathodes, inserting fresh starter sheets and eliminating short circuits caused by warping of electrodes or growth of dendrites. Furthermore, the conventional cell suffers from the disadvantage that oxygen bubbles (formed at the anode) burst at the electrolyte surface ejecting electrolyte droplets and forming "acid mist" over the cell.

For these reasons there is considerable incentive to improve the electrowinning operation. Improvements in the electrolyte flow distribution in conventional cells has resulted in a decrease in the concentration polarization and an improvement in the physical nature of the deposited metal [2]. Other cell designs based on a moving electrode, usually a rotating disc, are aimed at producing electrodeposited metals in a continuous manner.

An alternative approach to lowering the capital cost of an electrowinning plant is to make equipment more "compact" by increasing the electrode surface area per unit volume of plant. This can be achieved by using a porous or particulate electrode. A bed of fixed graphite particles has been used [3] to electrowin copper from solution down to 0.01 g/l. However the need to periodically break down and replace the bed would be a disadvantage in a commercial operation. Fluidized beds for the electrowinning of metals have been under investigation for some time (e.g. ref. [4]. Electrodes consisting of a bed of electrically conducting spherical particles fluidized by electrolyte flow have been described by Backhurst [5] and it has been demonstrated that the charge is dispersed throughout the bed such that the electrochemical reaction takes place at the particulate surface. The applications of fluidized beds in electrochemistry has been discussed by Le Goff [6].

It appears that fluidized bed electrodes are not suitable for metal deposition reactions in which the size of the particles is increasing.

This paper examines the properties of a bed of agitated conducting particles when used as an electrode system for metal deposition from aqueous solutions and suggests

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that the system has a number of advantage over the conventional electrode systems. These advantages include:

1. The low concentration polarization associated with the electrode allows metal to be deposited at high current densities even from solutions containing a low concentraion of metal ion, and.
2. The continuous electrolytic production of metals in the form of approximately spherical particles of controlled size and hence the elimination of the need to prepare "starter sheets" and stripping of metal from cathodes.

THEORITICAL CONSIDERATIONS

It can be shown [6] that the maximum current density (i.e. production rate per unit area of cathode) is given by the limiting diffussion current:

$$i_L = \frac{DZFC}{S}$$

Where i_L is the limiting diffusion current density; D, is the diffusion coefficient of the metal ion being discharged; Z, is the ionic charge; F, is Farady's Number; C, is the concentration of the metal ion in solution; and S, is the equivalent boundry layer thickness.

The limiting current for metal ion discharge can only be increased by increasing the ion diffusivity, the bulk concentration, or by decreasing the diffusion layer thickness. High ion concentration, higher temperatures, and increased electrolyte agitation lead to higher limiting currents.

With simple electrolytes and high current densities the physical nature of the deposit is unsatisfactory. Dendritic growth leads to localized high current density areas and eventual shorting of the electrolytic cell. This effect may limit the operating current density in a commercial cell to values much lower than the limiting diffusion current.

As the cell current density is increased, the cell voltage also increases because of the polarization effects and of the ohmic resistance of the elctrolyte. This latter potential varies approximately linearly with cell current density and is a factor in determining the economic current density used in practice. The resistance losses in a cell are minimized by operating with solutions having high conductivity at an elevated temperature and by maintaining as close an anode cathode spacing as possible.

A bed consisting of a large number of small conducting particles has an inherently large surface area and if the bed is agitated it should behave as an electrode exhibiting low polarization.

EXPERIMENTAL

Measurement of the polarization phenomena using an agitated bed of particle as an electrode system were made using a cell described by Harris [7] and is shown diagrammatically in Fig. 1. The unit consisted of a glass cell (A) having a stainless steel plate (B) sealed to the bottom by means of a neoprene ring gasket. The stainless steel plate acted as the electrical contact to the bed of particles (C) comprising the cathode. This bed was initially made up of minus 100 mesh copper powder produced by the cementation of a copper sulphate solution with zinc. A glass agitator (D), situated close to the bottom of the bed, was rotated by a variable speed motor. Solution entered the cell near the bottom of the bed, through a small tube (E) and left from the cell through a tube (F) connected to a constant level device to maintain the level of the solution in the cell at the position (G). The solution was returned to a reservoir and pumped back to the cell. A copper anode (H) was situated so that particles falling from it did not enter the cathode bed but were collected in the bulk solution reservoir.

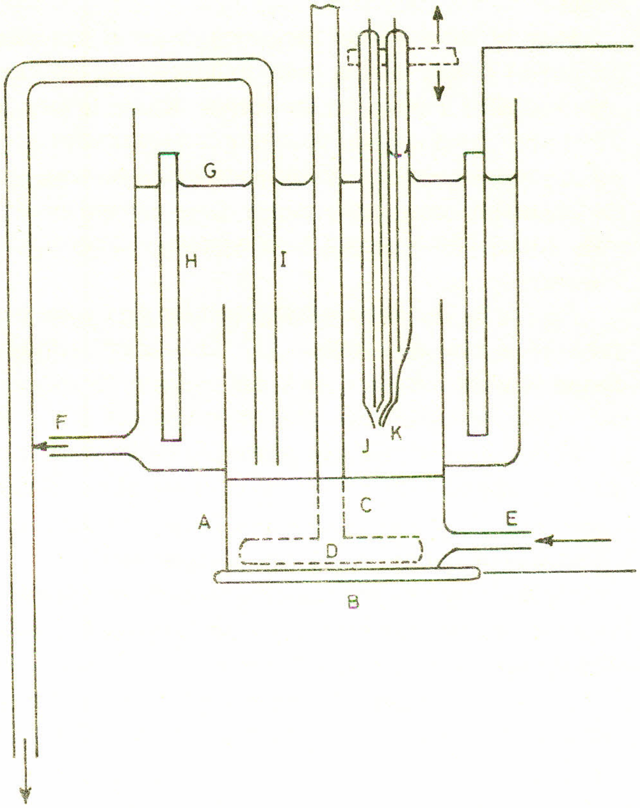

Fig. 1. Diagram of electrochemical cell. (A): Glass cell (B) Stainless steel plate. (C). Bed of particles. (D). Glass agitator. (E). Solution inlet. (F). Solution outlet. (G). Solution level. (H). Copper anode. (I). Siphon. (J). Copper probe. (K). Copper reference electrode.

The bed was operated under constant volume conditions by having a siphon (1) as indicated. As the particle size increased the excess material was *siphoned* off to a collector thus maintaining the bed height close to the bottom of the *siphon* inlet. The cell design was not aimed at producing an electrochemical cell having a high power efficiency.

The stainless steel cathode connection acts only as electrical contact to the particles comprising the bed and very little copper is deposited on it even after many hours of cell operation at high current density.

All measurements, reported in this paper, were made using an electrolyte containing copper sulphate and 100 g/l sulphuric acid. A.R. grade chemicals were used.

The effect of a number of variables on the polarization behaviour of the electrode system was studied. The variables included:

1. Current density. 2. Copper ion concentration.

RESULTS

The copper particles were found to grow to form approximately spherical shapes under a wide range of conditions. As the particles "grew" at the same rate all the particles in the bed were approximately the same size at any time. The growth occurred, at high current efficiencies, in solutions ranging in copper concentration from less than 1 g/l to greater than 50 g/l and for the higher solution concentrations, up to current densities of 1.000 A/sq. ft. The nature of the product was substantially the same for any of these conditions.

Fig. 2 shows the variation of the polarization as a function of current density for two values of the copper ion concentration.

DISCUSSION

The difference in potential between the copper electrode and the copper reference electrode is a measure of the polarization at that position in the bed. This is because the copper electrode when immersed in the bed, is measuring the potential of the copper particles which it is contacting while the copper reference electrode is measuring the solution potential adjacent to these particles. This polarization is a measure of the metal deposition rate at this position in the bed although the rate is not a linear function of the polarization. The potential change (as measured by the copper electrode) was taken as a measure of the maximum polarization occurring within the cell with a given set of conditions.

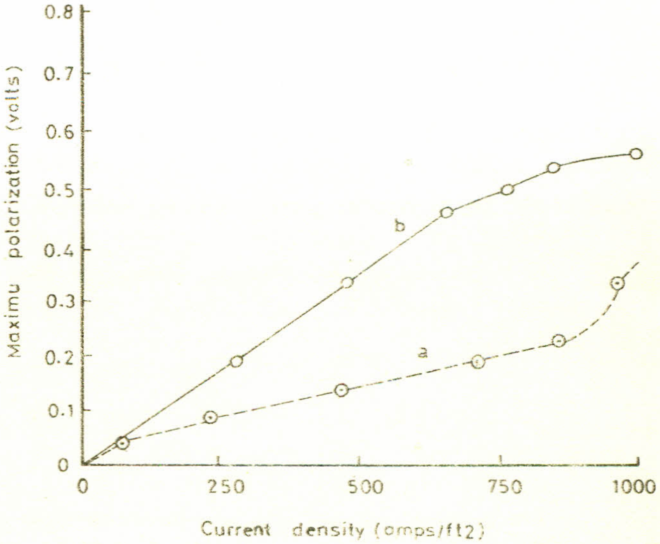

Fig. 2. Palarization curve for solution containing: (a). 10 g/l Cu^{2+}. (b). 1 g/l Cu^{2+}

The polarization of an agitated electrode, as shown in Fig. 2, is small compared to that measured at stationary electrode. This low polarization can be attributed to: 1. the large surface area per unit volume of electrode; 2. the degree of agitation which involves both the particles relative to the solution and changing contacts between particles themselves causing an enhanced rate of transport of ions to the surface.

CONCLUSIONS

It appears that the use of an agitated bed of particles as an electrode system for metal deposition has a number of advantages over other electrode systems. The main advantages are:

1. The continuous production of metals electrolytically; 2. The recovery of metals from solution containing a low concentration of metal ion; 3. The production of metal in the form of approximately spherical particles of controlled size, and 4. Bridging and shorting of the cell does not occur because of the physical nature of the metal deposit produced.

The disadvantages of such a system are:

1. The additional power required to agitate the bed; 2. The additional complexity and cost of the cell, and 3. The increased cell voltage required to operate the cell at its maximum current density.

These factors are of an economic nature and the process will need to be evaluated before its introduction as a commercial process is considered.

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