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Experimental study of copper deposition in a fluidized bed electrode

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This paper deals with an experimental study of copper deposition in fluidized bed electrodes from acidified aqueous solutions containing copper. Overpotential distributions are determined and the amount of copper deposited at various levels within the electrodes is also measured. Experiments with long duration times allow the variations of current efficiency for recovery to be obtained as a function of current density and fixed bed thickness. These variations could be explained by the existence of dissolution zones within the electrodes.

1. Introduction

Although the concept of the fluidized bed electrode (FBE) is relatively new [1, 2], this electrode has been studied experimentally [3–20], theoretically [21, 22] and some reviews have been published [23–25]. Applications have been considered in fuel cells [9, 11] but its main use would seem to be in extractive metallurgy [15–18, 20, 26]. Indeed the FBE is attractive for the extraction of metals from dilute solutions because it has a high specific electrode area and allows continuous metal deposition on the fluidized particles without any clogging such as is encountered in fixed bed electrodes [27].

Most experimental papers have dealt with the metal–solution potential distribution within the FBE [3, 5–8, 13, 19, 20]. Such studies are obviously necessary to understand the behaviour of the system because the local electrochemical activity depends on the above-mentioned distribution which changes with bed expansion.

The work of Wilkinson [26] is particularly important because he examined the economic aspects of copper electrowinning and electrorefining in cells with fluidized bed electrodes whose dimensions are of industrial interest. Recently the effects of certain variables – such as temperature and the presence of iron in the electrolyte – on the current efficiency and power consumption in a small FBE electrowinning cell have been reported [18]. The results of this latter study are presented as discouraging for future applications but it seems to us that they have been generalized too rapidly. For example, coppered glass spheres were used and not copper particles, only one bed expansion was investigated and the current feeder to the FBE was located arbitrarily with respect to the bed support. Also it has to be emphasized that this work has been criticized in the literature [28].

In a more recent paper Germain and Goodridge [20] investigated the local behaviour of a FBE for the case of copper electrowinning in a cell in which electrolyte flow direction is normal to current flow. Their work deals with important aspects of the problem such as metal–solution potential distributions, current distributions and current efficiencies.

The present paper reports results of an experimental study analogous to [20] except that the cell geometry is different and would not be used for applications. It also concerns copper electrowinning in an FBE of copper particles and deals with the overpotential distributions, the distributions of the weight of metal deposited at different levels within the FBE and the current efficiencies. The copper concentration, the electro-

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lyte acidity and the current densities are chosen to be similar to industrial values and the influence of fluidization parameters is investigated.

2. Experimental

2.1. *Cell and current feeders*

The cell (Fig. 1) is made of altuglass; it is cylindrical with an internal diameter of 40 mm and is composed of separate elements to allow easy dismantling. The cathodic current feeder is a copper grid held above a polyethylene porous distributor and the anode is a perforated circular copper disc which has a central hole to allow a composite probe for electrode potential measurement to be moved along the column axis. This composite probe which is similar to that previously described [29] includes a copper ring as the sensing element and is associated with a saturated K_2SO_4 reference electrode. The electrolyte enters the column through a calming section and recirculates successively through a tank, a centrigugal pump and a rotameter. The temperature is maintained at 30° C by control and heating in the tank itself.

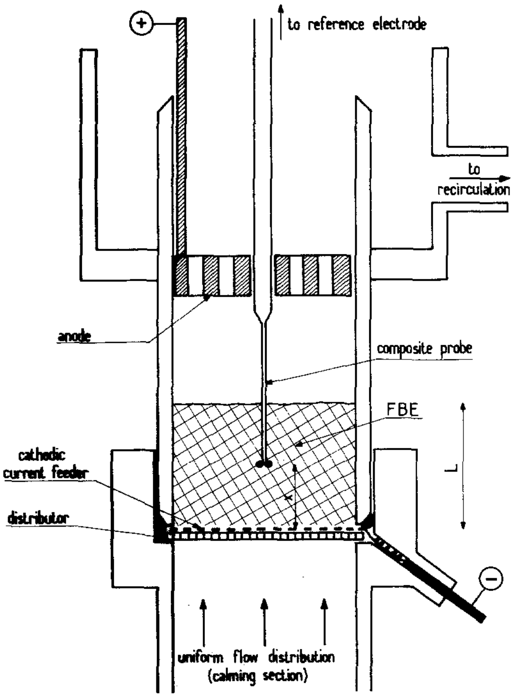

Fig. 1. The cell including the FBE and the composite probe.

2.2. *Fluidized particles and electrolytes*

Only cylindrical copper particles (diameter 1 mm; length 1·2 mm) were used; they were obtained by automatic machine sectioning of electrical copper wire. Fixed bed heights L_0 were varied between 7 and 35 mm, the bed porosities ϵ and the corresponding bed expansions investigated being given in Table 1.

Table 1.

ϵ	*Bed expansion* (%)
0·43	0
0·50	14
0·53	21
0·57	32

Three electrolytes were used with the following characteristics: electrolyte 1: Cu 5, H_2SO_4 10; electrolyte 2: Cu 25, H_2SO_4 100; electrolyte 3: Cu 40, H_2SO_4 100 $g\,l^{-1}$ (respectively).

They were made from reagent grade chemicals and deionized water. The copper concentration was determined by gravimetric titration (electrochemical deposition on platinum basket). The height of the anode above the different FBE was maintained equal to 3 cm for all the experiments.

2.3. *Power source and electrical measurements*

The electrolytic cell is fed at constant current using a TACUSSEL PRT 10-20 potentiostat working amperostatically. Cell currents range from 0·5 to 4 A and correspondingly current densities (c.d.) from 400 to 3200 $A\,m^{-2}$ relative to column cross-sectional area. The local FBE potentials $E(x)$ from the composite probe were measured using a five digit SCHLUMBERGER digital voltmeter.

3. Results

3.1. *Overpotential distributions*

The local overpotential $\eta(x)$ within the FBE at the height x above the current feeder is calculated from $E(x)$ as follows:

$$\eta(x) = E(x) - E_{eq}$$

where $E(x)$ is the metal–solution potential at the sensing element of the composite probe and E_{eq} the equilibrium potential. E_{eq} is the same at every point within the FBE owing to the negligible variation of the copper concentration across the bed and also over the whole hydraulic circuit during a determination of the complete distribution $E(x)$ which needs only a few minutes.

Figs. 2–4 give typical results. Fig. 2 presents the influence of the height L of the FBE on the overpotential distribution, the bed porosity and the c.d. being maintained constant. One can see that a thin FBE behaves cathodically at every point including the current feeder but that the local electrochemical activity increases rapidly with the distance above the current feeder. For higher bed heights positive values of the overpotential which may characterize anodic behaviour appear in the distributions. The extent of this positive overpotential range increases with L but in every case, as indicated in Fig. 2, it occupies about 80% of the bed depth.

Fig. 3 shows how the bed porosity ϵ influences the distribution $\eta(x)$ for given fixed bed height (i.e. given amount of particles in the bed) and c.d. It is observed that for $\epsilon = 0{\cdot}43$ (fixed bed situation), the bed behaves cathodically over a small depth near its top whereas the lower parts are at equilibrium ($\eta = 0$) which agrees with previous studies of fixed bed flow-through electrodes [29, 30] where the concept of effectiveness or overpotential penetration depth was discussed. When the beds were fluidized the overpotential distributions show again that η is positive over a fraction of the bed thickness and that this fraction increases with increasing ϵ (Fig. 3). It may also be noted that for sufficiently high ϵ values the cathodic current feeder works as a cathode ($\eta < 0$) whereas it seems to be at equilibrium for low bed expansions.

Finally Fig. 4 which gives the influence of c.d. shows that the positive part of the overpotential distribution becomes more and more obvious with increasing c.d. Here also it occupies about 80% of

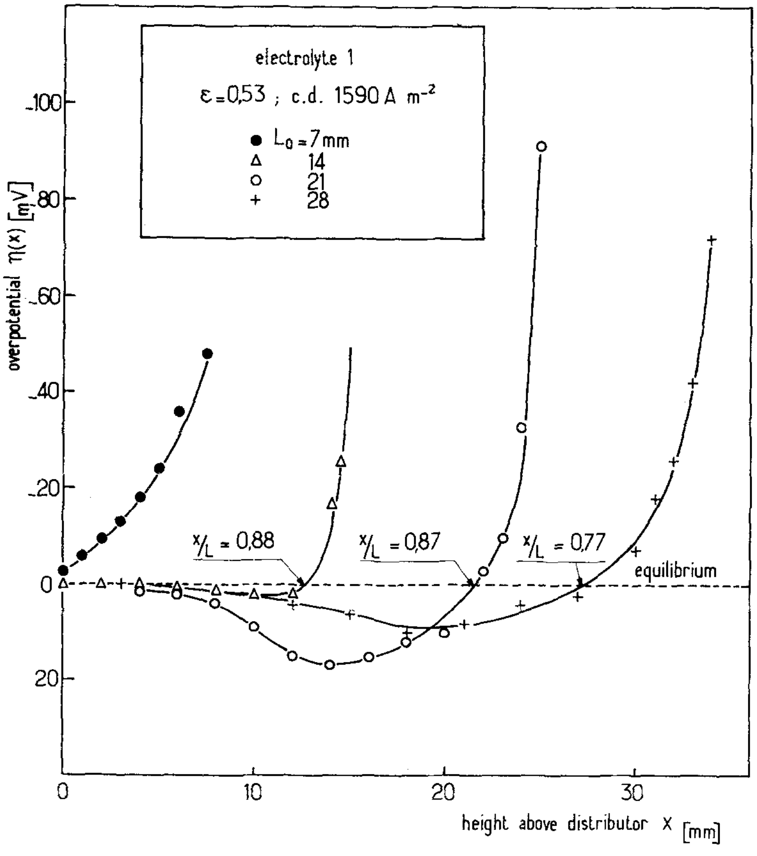

Fig. 2. Vertical overpotential distributions showing the influence of the FBE height.

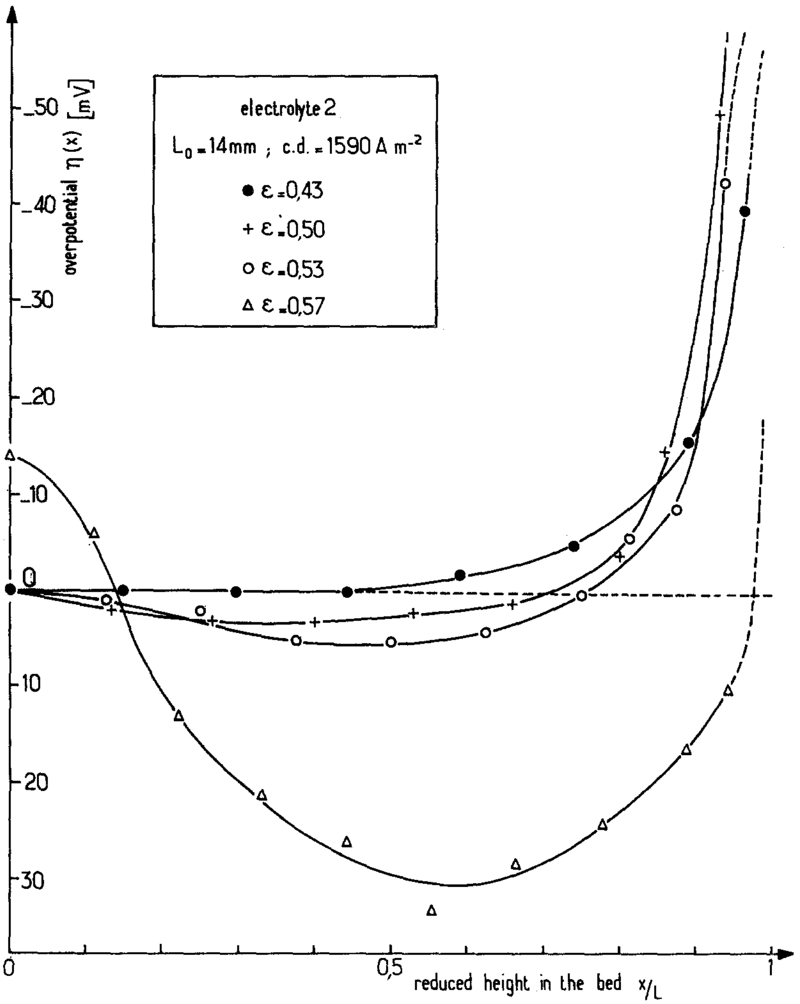

Fig. 3. Vertical overpotential distributions showing the influence of bed porosity.

the bed thickness, the overpotential being negative only within the layers near the top of the bed i.e. within 20% of the bed height.

3.2. *Copper deposition at different levels*

In order to obtain the variation of copper recovery at different levels in the FBE, a simple method consists in simulating fluidized particles by stationary sections of copper wire and to measure the weight variation of these sections after each experiment. Fig. 5 shows schematically the method used to make such determinations: a PVC cylindrical rod carries small sections (diameter: 1 mm; length 11 mm) of copper wire planted in holes 1 mm deep disposed at intervals of 5 mm along the rod. The variation in weight Δm of each piece of wire allows the distribution $\Delta m(x)$, which is synonymous with the reaction current distribution along the FBE height, to be obtained.

Such determinations have to be sufficiently long in order to be able to measure Δm accurately using a laboratory balance having a precision of 0·1 mg but not so long as to modify the hydrodynamic behaviour of the FBE by copper deposition. The duration was 1 h for the determination of $\Delta m(x)$ only and up to 5 h for the simultaneous determination of $\Delta m(x)$ and of current efficiencies (see Section 3.3).

Fig. 6, given as an example, reports an experimental distribution $\Delta m(x)$ in a FBE, the conditions of the experiment being summarized in the figure. It is representative of results corresponding to other runs. It can be seen that there is no copper deposition at $x = 0$ i.e. on the current feeder (as confirmed by weighing before and after

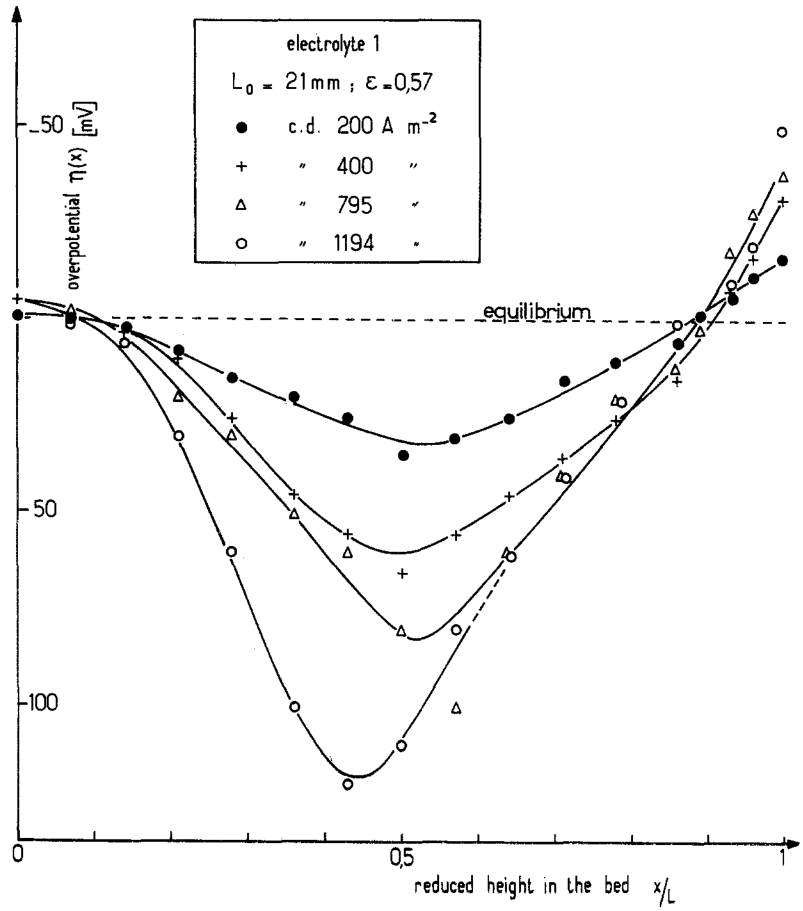

Fig. 4. Vertical overpotential distributions showing the influence of c.d.

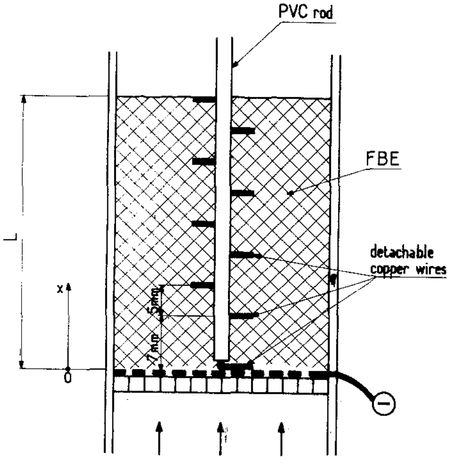

Fig. 5. Schematic view of the system for local deposition measurements.

the experiment) and that the lowest 85% of the bed height corresponds to a dissolution zone. By considering the results for all runs, it can be concluded that:

(a) For given fixed bed height and c.d., the dissolution zone is more pronounced when the FBE porosity is increased.

(b) For given ϵ and c.d. the extension of the dissolution zone increases with increasing bed height.

(c) In a given FBE the dissolution zone remains present and still occupies about the lowest 85% of the bed thickness when the c.d. is increased.

However if the experiments give a demonstration of the presence of a dissolution zone and allow its extent to be measured, they give no significant information on the deposition zone which exists at the top of the bed. Indeed, this deposition zone is confined in too thin a slice for the method of Fig. 5 to be adequate. This is probably due to the small particle size.

3.3. *Current efficiency*

For experiments with a long duration time, the

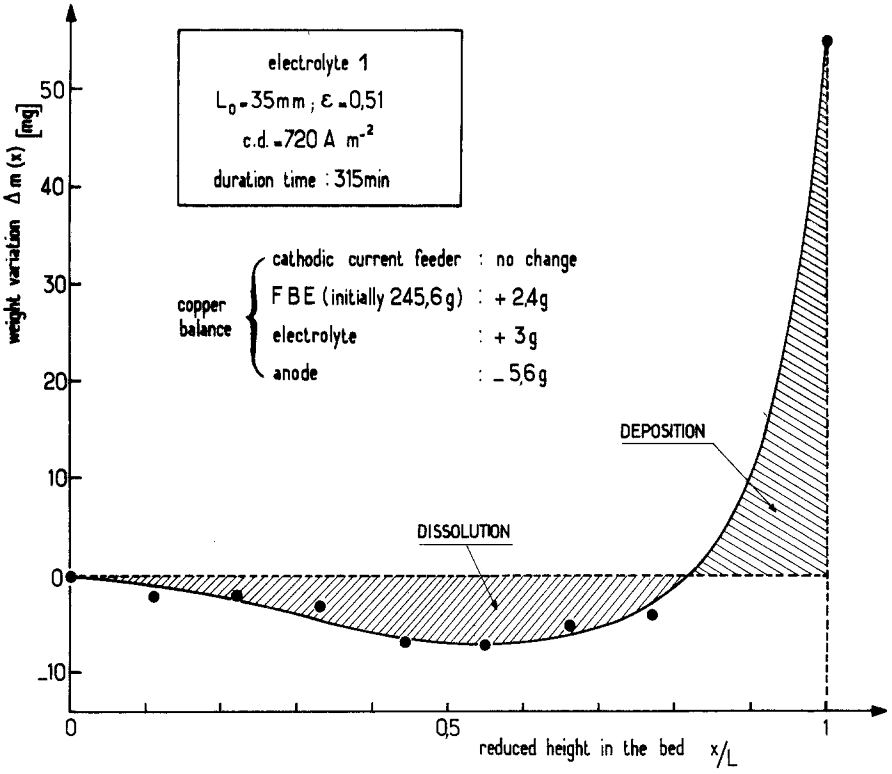

Fig. 6. Example of an experimental distribution $\Delta m(x)$ along the axis of a FBE.

complete copper mass balance can be performed in the system. It requires various weighings (bed, cathodic current feeder, anode) and copper titration before and after the experiment. An example of such a balance is tabulated in Fig. 6; it can be seen that it is almost satisfied, the difference being due to the amount of copper which is taken out of the circuit for the titration. It has been verified for all runs that the amount of copper dissolved at the anode always satisfies Faraday's law.

Current efficiencies for deposition on the FBE at given c.d. are plotted in Fig. 7 as a function of the fixed bed height L_0 for three fluidized bed porosities. Also in the same figure is reported the change of copper concentration in the electrolyte for runs with $\epsilon = 0{\cdot}53$. It can be seen that:

(a) At given ϵ the current efficiency decreases with increasing L_0 which corresponds to the fact that the extent of the dissolution zone also increases. At the same time the copper concentration is improved. At zero fixed bed height (i.e. cathodic current feeder alone) the results of Fig. 7 seem to indicate that current efficiency would be near 1.

(b) At given fixed bed height, the current efficiency increases with decreasing ϵ, i.e. when the fixed bed situation is approached. This observation agrees with the results of Fig. 3.

For a FBE with $\epsilon = 0{\cdot}53$ the influence of c.d. on the current efficiency is shown in Fig. 8: current efficiency increases with increasing c.d. and reaches 83% as a maximum value for a c.d. of about 3000 A m^{-2}. From Fig. 7 it can be deduced that lower ϵ values would lead to higher maximum current efficiencies than in Fig. 8. Here also the experiments indicate that an increase in current efficiency corresponds to a decrease in the change in copper concentration; this means that when c.d. is increased the dissolution zone has comparatively less influence than the deposition zone.

The results so far presented in this section were for electrolyte 1. Only 3 runs were made with electrolyte 3. The results corresponding to a FBE with

Table 2.

c.d. (A m^{-2})	*Current efficiency (%)*
1590	68
2390	83
3183	82

$\epsilon = 0{\cdot}53$ are given in Table 2. The results in Table 2 agree with values plotted in Fig. 8 for soluble anode experiments (curve 1).

4. Discussion

The recent work of Germain and Goodridge [20] for a FBE cell and current flow normal to the electrolyte flow also reported values of current efficiency as a function of c.d. for copper deposition. The results of Fig. 8 are similar and of the same order as those in [20] although the influence of ϵ was not brought out in that paper. However, as in [20], it is shown here that, contrary to expectations, current efficiency decreases with decrease in c.d. and that this phenomenon is explained by the fact that part of the bed is not cathodically protected.

Also Flett [16] mentioned that current efficiency for copper electrowinning in a FBE increases with increasing c.d. and only reaches 90% for sufficiently high c.d. On the other hand he reported current efficiencies higher than 100% for an electrorefining FBE. For fluidized cathodes he invoked the action of dissolved oxygen in the electrolyte to explain redissolution of the deposited copper.

The present paper shows that the variations of current efficiency with c.d., bed porosity and bed height can be explained by means of $\eta(x)$ and $\Delta m(x)$ distributions. Except for fixed beds and thin fluidized beds, an important part of the FBE is a definite dissolution zone in which overpotentials are positive as for anodic electrochemical reactions. The explanation of such observations will not be given here because it seems evident that

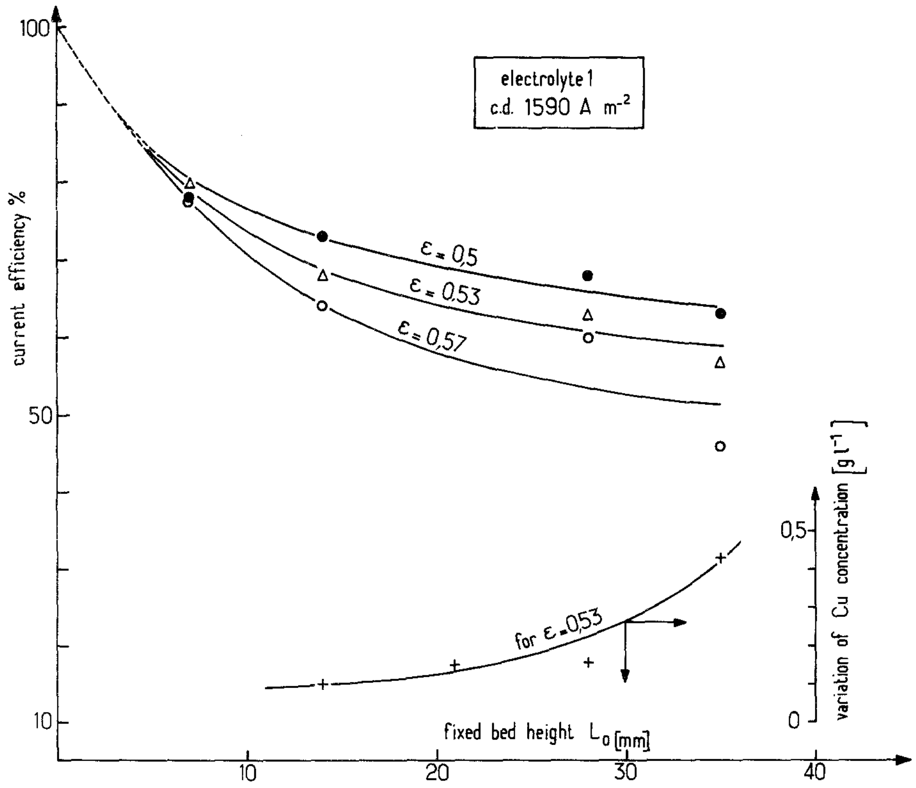

Fig. 7. Influence of bed porosity and bed height on the current efficiency.

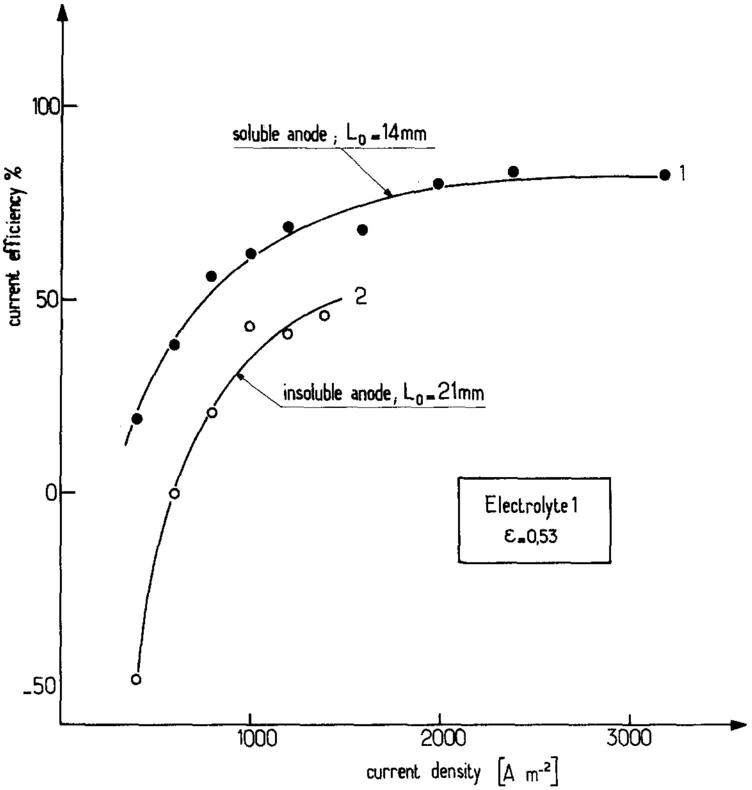

Fig. 8. Variations of current efficiency with c.d. for soluble and insoluble anodes.

further work is necessary. Our object is only to clear up the question of the dissolution zone through some complementary experiments which are summarized below.

Results presented in the previous sections of the paper were obtained in the cell of Fig. 1 which includes a soluble anode i.e. without anodic oxygen evolution. When an insoluble anode is used oxygen evolution occurs at this anode and the electrolyte becomes saturated in oxygen. Results obtained in these conditions are plotted in Fig. 8 (curve 2) and can be compared with those corresponding to soluble anode operations (curve 1). The variations of current efficiency with c.d. are similar in both cases but the high oxygen concentration strongly reduces the current efficiency. Curves 1 and 2 do not correspond to the same fixed bed height L_0 but as one can see from Fig. 7 the influence of L_0 for $\epsilon = 0{\cdot}53$ is too small to explain the deviations between the curves of Fig. 8. Furthermore curve 2 indicates, as in [20], that at low c.d. current efficiencies are negative which signifies that the dissolution zone is predominant.

The question is then to find out if the experimental results obtained with the soluble anode were influenced by dissolved oxygen. Three experiments were performed with a soluble anode and the following conditions (electrolyte 1; c.d. = 1590 A m^{-2}: $L_0 = 21$ mm; FBE porosity $\epsilon = 0{\cdot}53$) with continuous bubbling (O_2 or N_2) in the tank itself and without bubbling respectively. The following results were obtained: O_2 bubbling: current efficiency = 30%; N_2 bubbling: current efficiency = 70%; no bubbling: current efficiency = 63%.

These show that high oxygen concentration reduces the current efficiency but also that there is no significant difference between N_2 bubbling and no bubbling. This allows us to conclude that the results presented in Section 3.3 were apparently not influenced by dissolved oxygen in the electrolyte.

It may be considered that the presence of a grid as the bed support is responsible for the existence of grid jets of electrolyte which lead to very bad electric contact between that grid (cathodic current feeder) and the fluidized particles of the lowest layer. With such a hydrodynamic effect at the bed entrance, the FBE would behave as a bipolar porous electrode with an anodic zone and a cathodic zone as experimentally observed. However by replacing the copper grid of Fig. 1 by a flat spiral of copper wire set some millimeters above the distributor, a dissolution zone was again detected which refutes any influence of grid jets.

After experiments with long duration times, the aspect of the stationary wires of the method shown in Fig. 5 may suggest a bipolar behaviour of the independent fluidized particles. Some experiments were repeated replacing the pieces of copper wire by pieces of gold wire of the same dimensions. It was observed that except at the top of the bed the lower faces of the wire were never covered with copper whereas their upper faces became more and more coppered when the wire to distributor distance was increased. Such visual observations may confirm that the FBE behaviour could perhaps be explained by further investigation on the basis of a bipolar behaviour of the fluidized particles.

5. Conclusions

Under the conditions used, current efficiency for copper deposition in a FBE is improved by increasing c.d. and/or decreasing bed porosity, and bed thickness in the direction of current flow. Low current efficiencies seem to be due to the existence of a definite dissolution zone within the FBE.

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