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REVIEWS OF APPLIED ELECTROCHEMISTRY 3

The fluidized bed electrode for the continuous recovery of metals

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This review evaluates the work on the use of the fluidized bed electrode to recover metals from solution, since the appearance of this particular electrode in 1966.

1. Introduction

The fluidized bed electrode (FBE) concept seems to go back to the year 1966 when two patents, one in Great Britain [1], the other in France [2], were applied for almost simultaneously. Fourteen years have gone by since then and no industrial applications have been reported, although pilot size units have been tested. A recent process [3] has, however, revived interest for this type of electrode.

Since 1966, theoretical and experimental surveys have been relatively numerous [1–34]; three review articles were devoted to it [35–37] though only the last one takes into account results obtained in installations whose dimensions have an industrial significance. Several applications have been considered, for example fuel cells [10–12], hydrogen peroxide synthesis [31], ore flotation [32] and organic electrosynthesis [34], but it is especially in extraction metallurgy that the main applications are expected. Indeed, it is to the problem of metal recovery which most applied studies have been devoted. A bibliography concerning anodic electrodissolution of an FBE can be found in [33].

Thus it is timely to make a new evaluation of the knowledge acquired in the field of the application of the FBE to the continuous recovery of metals. This is the aim of the present article.

2. A brief history

The FBE concept is founded on two properties:

(a) The dispersed nature of the fluidized bed which presents a large specific surface area. This could, in principle, allow high specific productivities for electrochemical reactions which occur only at low current densities (i.e. processing dilute solutions).

(b) The 'unconsolidated' and 'mobile' character of the texture of the fluidised bed. This could allow the continuous recovery of metals in dilute solutions by the introduction of small particles at the top of the bed with extraction of grown particles at the bottom (see Fig. 1).

With these properties in mind, the FBE has been examined experimentally to determine the distribution of the metal–solution potential within the bed [4, 6–8, 14, 20]. Two extreme cases used in the laboratory are shown in Fig. 2. Fig. 2a shows the case where the electrolyte flow and the electric current run in the same direction. This situation is the one which has been commonly adopted for work on a small scale [4–6, 10–12, 14–16, 19, 22, 27]. Fig. 2b illustrates a practical situation which would allow the highest conversion of the liquid, and thus the highest recovery rate, per pass through the bed. Here the electrolyte flow and the electric current are perpendicular. There are several variants of this case where the

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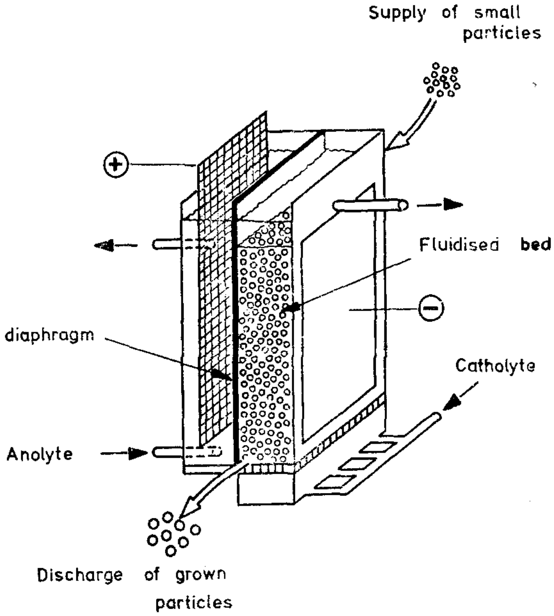


Fig. 1. Schematic view of a cell with a fluidized bed cathode for continuous metal deposition.

bed has a rectangular cross-section [18, 20, 26, 30, 31], occupies an annulus between cylinders [4, 7, 25], has a rectangular cross-section but is inserted between two anodic compartments [21] or, as in the AKSO process [3, 23] is placed round anodic compartments in a cylindrical column. In this latter case the electrolysis cell resembles a multitubular heat exchanger. In all the cases the current feeder to the fluidized bed is either an electrode at the plane $x = 0$ as in Fig. 2b, or is several rods immersed in the bed itself.

Besides these studies aiming to acquire some knowledge and control of the electrode potential distribution, the papers concerned with the electrolytic recovery of metals, especially copper, may be seen as belonging to two periods. In the first, roughly up to the years 1972–3, the motivation for the work with the FBE seems to have been the extraction of metals from solutions resulting from the leaching of ores. The concentrations of the solutions considered as treatable were over one gram per litre but below that where an admissible current density was obtained in classical electro-

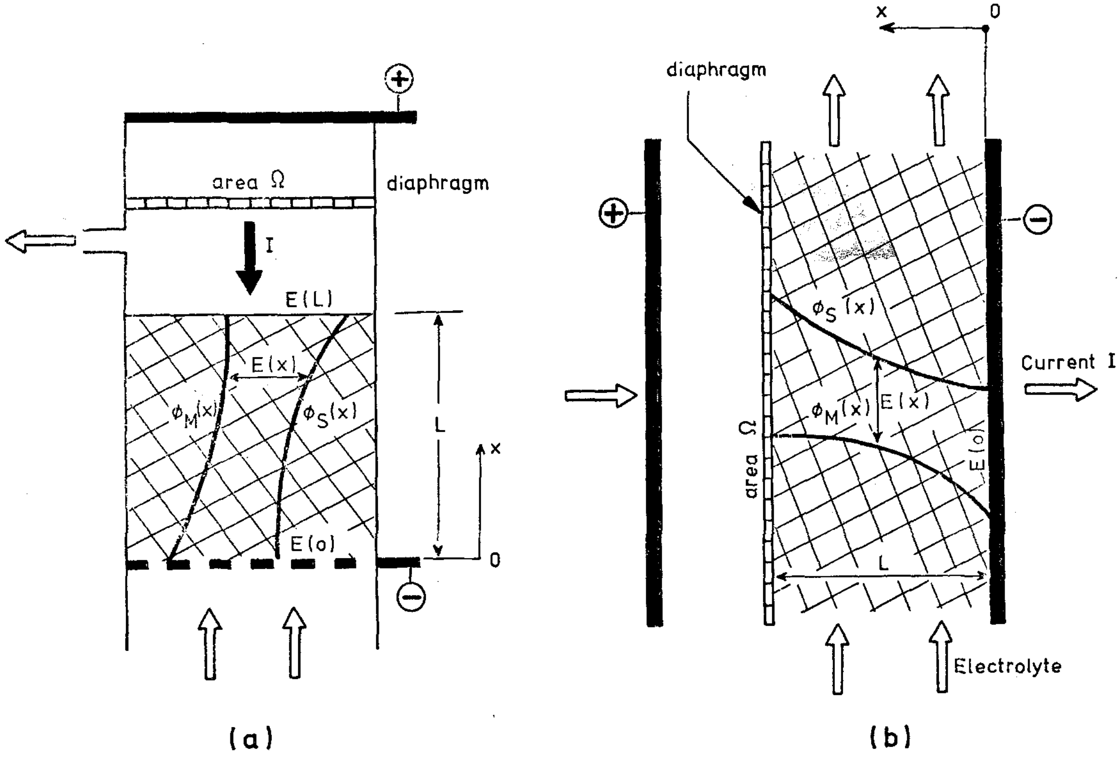


Fig. 2. Metal and solution potential distributions within fluidized bed cathodes: (a) parallel configuration, (b) perpendicular configuration.

lytic cells. The FBE seems not to have been feasible for such operations. In the second period the emphasis changed to the removal of heavy metals dissolved in liquid discharges. The metals to be eliminated are generally at low concentration (below 1 $\mathrm{g\,l^{-1}}$). The recent appearance of the AKSO process seems to have been motivated by such environmental applications.

3. Distribution of the electrode potential

One of the drawbacks of the FBE is common to all porous electrodes: it concerns the existence of a potential distribution within the electrode. This distribution is a function of the dimensions of the electrode (height L for Fig. 2a; thickness L for Fig. 2b). In particular, for the deposition of a metal in a cathodic FBE, it is important that:

(a) the potential $E(L)$ close to the separator between the two compartments (porous separator, anion exchange membrane) be sufficiently cathodic to allow efficiently the desired reaction but no other processes.

(b) the current feeder to the FBE (shown as the plane $x = 0$ in Fig. 2b), and perhaps a small depth of the bed immediately next to this current feeder, be at the equilibrium potential in order to avoid any deposit at this position.

The local electrode potential $E(x)$ (equal to $\phi_M(x) - \phi_s(x)$, the difference between the potential of the granular matrix of the bed $\phi_M(x)$ and the potential of the solution $\phi_s(x)$) evolves with x as shown in Fig. 2. The distribution curves for $\phi_M(x)$ and $\phi_s(x)$ can be obtained from a model of the FBE using two continuous media (see, for example, Euler and Nonnenmacher [38]). These media are (a) the continuous phase proper (the electrolyte) and (b) the particulate matrix of the electrode. The former is treated as a medium whose electric conductivity γ depends on the true electric conductivity γ_0 of the electrolyte and the tortuosity of the current lines round the elements of the electrode structure. γ can be determined experimentally if the matrix can be simulated by using a nonconducting structure identical to the particulate electrode; the relations known for the conductivity of a dispersed medium of grains [39] can also be applied. The latter, which is the granular matrix of the electrode, is considered as a pseudo-continuous medium characterized by an apparent global electronic conductivity σ lower than σ_0 of the electrode material and depending on its structure.

The theoretical approaches use, as Newman and Tobias [40] have for porous electrodes, Ohm's law in these two phases. If I is the global electrolysis current and Ω the area of the separator, then

$$I_M(x) = -\sigma\Omega \frac{d\phi_M(x)}{dx} \tag{1}$$

for the electrode matrix carrying the current $I_M(x)$, and

$$I_s(x) = -\gamma\Omega \frac{d\phi_s(x)}{dx} \tag{2}$$

for the electrolyte in which the current $I_s(x)$ flows. As electric charge is conserved

$$I = I_M(x) + I_s(x) \tag{3}$$

and the boundary conditions are,

$$\text{at } x = 0, \quad I_s = 0, \quad I_M = I$$

$$\text{at } x = L, \quad I_s = I, \quad I_M = 0.$$

Solving these equations leads to the curves for $\phi_M(x)$ and $\phi_s(x)$ in Figs. 2a and b.

Although various mathematical models have been proposed [5, 7, 28] and the agreement between model and experiment is at times satisfactory (see Fig. 3 given as an example), the potential distribution within an FBE is still not defined completely. There is uncertainty and difficulty in the measurement of the apparent global conductivity σ. Conduction mechanisms by grain bridges or by charge transfer can be envisaged. Conduction by charge transfer has been examined [41, 43] but the model is not good [6]. Moreover, the intergranular electric conductivity is very poor (σ is low) as soon as the conductive particles of the bed go into fluidization. In other studies it was shown that the liquid fluidized bed, often called the 'homogeneous fluidized bed', behaves like an expanded fixed bed, i.e. as if its particles were immobilized in their mean statistic positions [44]. Only a dense fluidized bed, i.e. one having a porosity very close to that of the fixed bed, could be sufficiently conductive.

To support these arguments it may be noted that the recent literature does not report any further calculations of $E(x)$. Only experimental

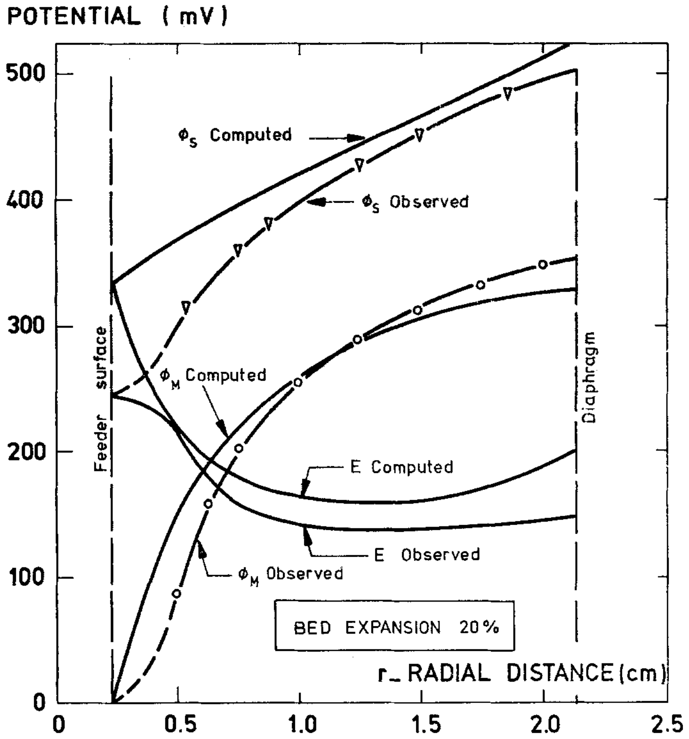


Fig. 3. Comparison of experimental and computed potential distributions. From [7].

distributions are still measured [20, 22, 26] in order to help the interpretation of global results. It must be emphasised that even if the mean local value of $\phi_s(x)$ can be obtained experimentally, it is not certain that in an FBE the sensing element (piece of wire, grain) of a probe gives the required information $\phi_M(x)$.

The last study to propose a mathematical model of an FBE was the one by Sabacky and Evans [24]; in the case of copper deposition from acidified aqueous solutions and in the presence of an oxidizing agent (ferric ion), they demonstrate the possible existence of an anodic zone. Fig. 4 reproduces the variations found for the local current density as a function of the distance to the diaphragm; zones where there would be oxidation are visible.

4. Global behaviour of the FBE for copper recovery

A number of authors have studied experimentally the recovery of copper in FBE systems. Table 1 extends that drawn up in [25] describing the experimental conditions. The studies which use pilot size plants with a design suited to industrial use are indicated by an asterisk.

4.1. *Current efficiency for copper deposition*

Flett [17] was probably the first to point out that the current efficiency increased with current density to reach a maximum value of 90%. This was confirmed [20, 22, 26]; Table 2 and Fig. 5 assemble the curves and results obtained and show that the current density can be high. Fig. 5 also shows that at low current density the current efficiency can be negative; this would be due to the existence of a parasitic redissolution caused by the presence of dissolved oxygen. The current density is defined relative to the surface area of the diaphragm. Although the types of cells were different (type of Fig. 2a or of Fig. 2b) the conclusions are similar and agree with Flett's observations [17]. The model developed in [24] also predicts such an influence of current density. The paper of Wilkinson and Haines [18] is the only one which presents a decrease in the efficiency when the current density increases.

At a given current density the current efficiency

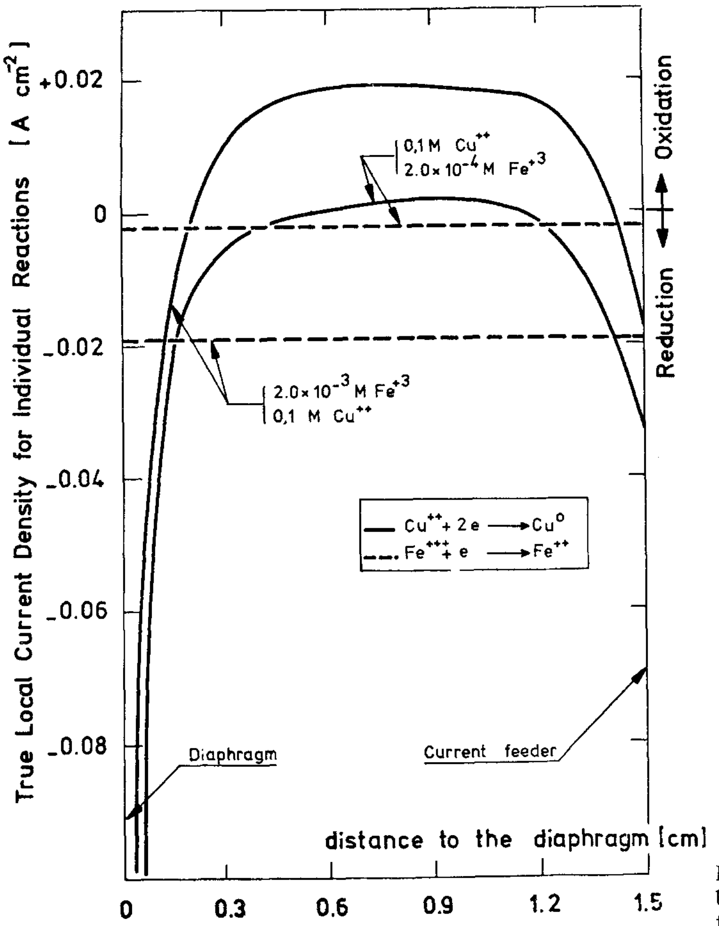


Fig. 4. Calculated local current density distribution in the direction of current flow when ferric ions are present. From [24].

Table 1. Papers on copper deposition in fluidized bed electrodes

Authors	*Type of cell*	*Electrolyte*	*Current density* ($A\,m^{-2}$)
Germain and Goodridge [20]	Fig. 2b (rectangular)	Cu 2 $g\,l^{-1}$ H_2SO_4 1 M	220–3000
Simpson [21]	Fig. 2b (rectangular)	Cu 2 $g\,l^{-1}$ H_2SO_4 1 M	540 and 1080
*Wilkinson and Haines [18]	Fig. 2b (rectangular)	Cu 2 $g\,l^{-1}$ H_2SO_4 1 M	1000–5000
Hutin and Coeuret [22]	Fig. 2a (cylindrical)	Cu 5–40 $g\,l^{-1}$ H_2SO_4 0.1–1 M	400–3200
Sabacky and Evans [25]	Fig. 2b (cylindrical)	Cu 20 $g\,l^{-1}$ H_2SO_4 1 M	2150–6450
*Goodridge and Vance [26]	Fig. 2b (rectangular)	Cu 3–5 $g\,l^{-1}$ H_2SO_4 1 M	250–5000
Flett [17]	Fig. 2b (rectangular)	Cu 2 $g\,l^{-1}$ H_2SO_4 1 M	–

* Pilot-size plants with a design suited to industrial use.

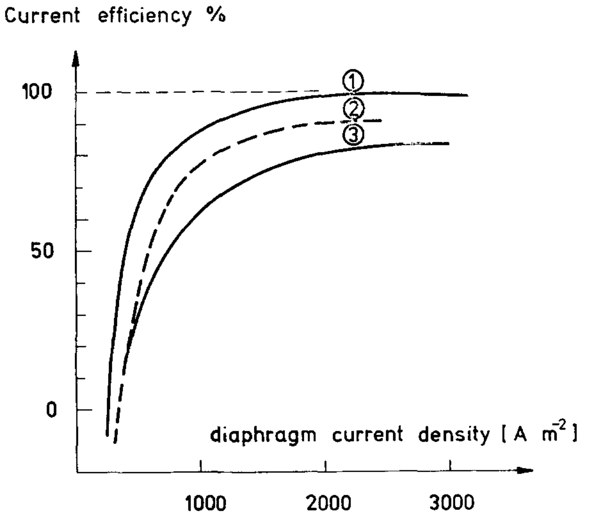


Fig. 5. Experimental variations of current efficiency for copper deposition with current density.

appears to be independent of the copper concentration and near 80 to 90%, except at low concentrations where it decreases quite rapidly. Fig. 6 compares results from various studies [21, 25, 26]. The drop in efficiency at low copper concentrations is due to the hydrogen evolution within the bed. The lower the concentration, the smaller the admissible current density which permits a good efficiency. Figs. 5 and 6 imply that it would not be possible to treat with a satisfactory efficiency solutions whose concentration were below about 100 mg l^{-1}. There have been no systematic studies at such low concentrations.

Strictly speaking, the comparison of results obtained by different groups of authors is uncertain. The experimental study [22] underlines the influence of other parameters such as the bed porosity and the bed dimension in the direction of the current. An increase in these two parameters has the effect of reducing the current efficiency; this would lead one to recommend the use of thin, dense beds. It will be seen however, a little further on, that such conditions do not allow reliable continuous operation. The particle size is probably a parameter to be considered too.

4.2. *Electric energy consumption*

Germain and Goodridge [20] show that the power efficiency (kg of Cu/kw h) presents a maximum value for current density in the 100 A m^{-2} region. Wilkinson and Haines [18] have also examined this problem and show that this economic parameter depends on several variables and in particular on the current density and the desired electrolyte conversion. In [25] the close relationship between this element of cost and the ohmic drop in the diaphragm, the anodic compartment and the electric resistivity of the electrolyte is emphasized.

4.3. *Feasibility studies*

Long-duration time studies on copper recovery from solutions with concentrations of over 1 g l^{-1} carried out in cells with compartments separated

Table 2. Experimental conditions and references for each of the curves in Fig. 5

Curve	*Reference*	*Type of cell*	*Electrolyte*		*Particle diameter*	*Bed expansion*	*Bed thickness*
			Cu (g l^{-1})	H_2SO_4 (M)	(μm)	(%)	(m)
1	[20]	Fig. 2b	2	1	500	20–50	0.025
2	[26]	Fig. 2b	3–5	1	500–700	40	0.025
3	[22]	Fig. 2a	5	1	1000–1200	20	0.017

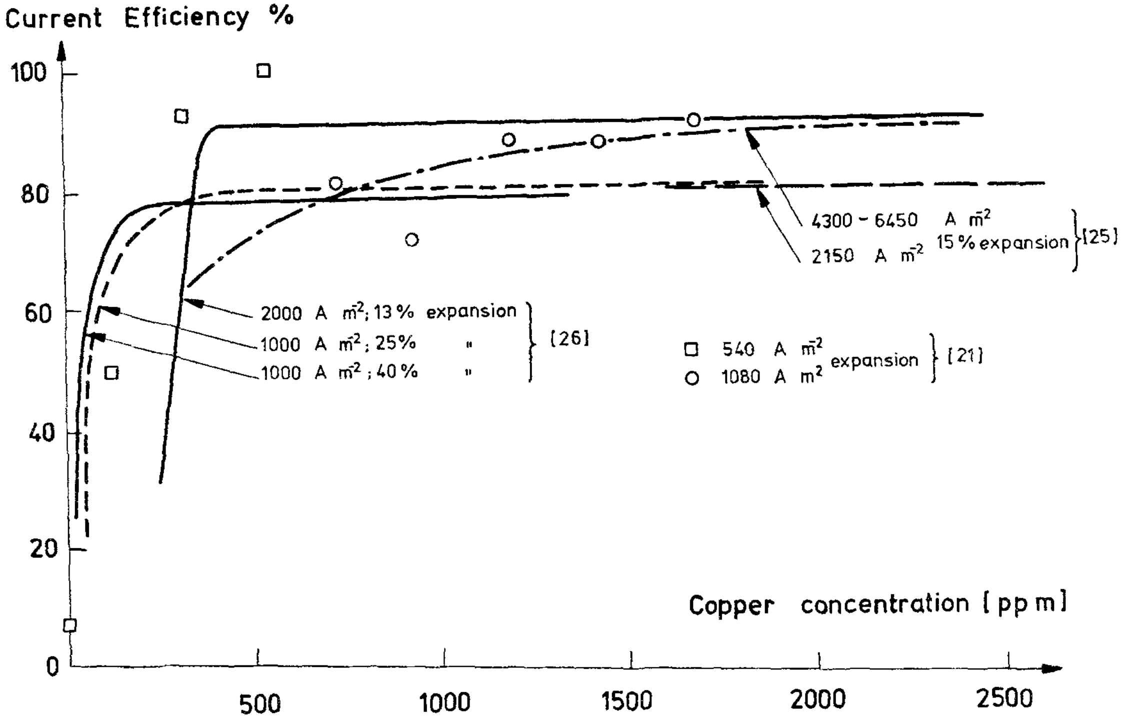


Fig. 6. Comparison of experimental variations of current efficiency with copper concentration

by a diaphragm or an ion-exchange membrane [18, 25] are unanimous in showing a number of difficulties:

(a) agglomeration of particles in those parts of the bed which cease to be mobile. These agglomerates can lead to the de-fluidization of the bed. Germain [45] emphasises this problem.

(b) preferential growths of deposits close to the separating membrane (formation of a sort of crust) resulting from blocking by more or less angular grains. It is, indeed, at the surface of the membrane that the cathodic potential is highest and hence the deposit formation greatest. The membrane can be torn.

(c) copper deposition on the current feeder to the bed seems inevitable and may initiate more or less rapidly the agglomeration of the bed.

It is possible that such difficulties may still take place in the case of dilute solutions (near 100 mg l^{-1}) but after a much longer period of time. The Akzo process seems to control these difficulties by paying special attention to the nature and the condition of the diaphragm surface as well as the technology (e.g. avoiding sharp angles). This process is reported to be workable and attractive for the treatment of solutions having metal concentrations lower than a few grams per litre [3, 23]. It has been tested on various solutions (copper and nickel, copper and cadmium, mercury) but the functioning time in continuous operation is only reported for the case of the recovery of mercury (in the form of an amalgam), which is an ideal situation since the electrolytic mercury deposit can be obtained without provoking bed-blocking.

The analyses [46, 47] of Leroy estimate the granulometric distribution of the particles of the bed and examine the influence of the operating mode on the variation with time of the current density. However such analyses assume the functioning of the FBE is perfectly reliable, which experiments do not confirm.

4.4. *Existence of noncathodically protected zones*

Flett [16] noted a re-dissolution of the copper: Germain [45] discussed this problem and indicated that the optimum conditions for limiting this re-dissolution would be to have low bed expansions and high current densities, conditions which also favour agglomeration. Also, as far as the recovery of copper is concerned, the presence of ferric ions in the electrolyte has been shown to decrease the current efficiency for deposition at the fluidized cathode [19, 24, 25]. In the papers [20, 22, 26] the existence of noncathodically protected zones in the bed was shown by experimental determination of the potential distributions in the direction of the current lines. It is in [22], where special precautions were purposely not taken to eliminate the dissolved oxygen, that the existence of an anodic zone is clearest: this zone is revealed both by the potential distribution and by the distribution of the weight variation of stationary copper elements disposed along the bed height. Fig. 7 reproduces experimental overpotential distributions and points out the influence of the fluidized bed depth in the direction of the current; in this figure ϵ is the bed porosity, L_0 the fixed bed height and electrolyte 1 signifies Cu $5\,\mathrm{g\,l^{-1}}$, H_2SO_4 $10\,\mathrm{g\,l^{-1}}$. A bed working cathodically in all its parts should not be very thick; indeed the increase in thickness results in the existence of an anodic zone whose height can occupy 85% of the total bed height but whose negative influence on the quantity of metal recovered overall diminishes when the current density increases. Unfortunately, a current density increase may cause the current feeder to be out of equilibrium and lead after a certain time to the agglomeration of the bed particles.

These zones called 'noncathodically protected' in [20, 26] and 'anodic' in [22] deserve perhaps some thought. Is their existence due to

(a) the presence of an oxidizing agent (oxygen, ferric ion)?

(b) the general form of the two distributions $\phi_M(x)$ and $\phi_s(x)$? Indeed, there is a minimum value for $E(x)$: if the current feeder was at equilibrium ($E(0) = E_{eq}$), such a minimum would mean the existence of a zone in which the overpotential would be positive.

(c) the homogeneous character of the liquid fluidization? This would cause the behaviour of the particles to be bipolar electrodes. In other words, the concept of a unipolar FBE may not be correct.

Anyway, the existence of a parasite dissolution

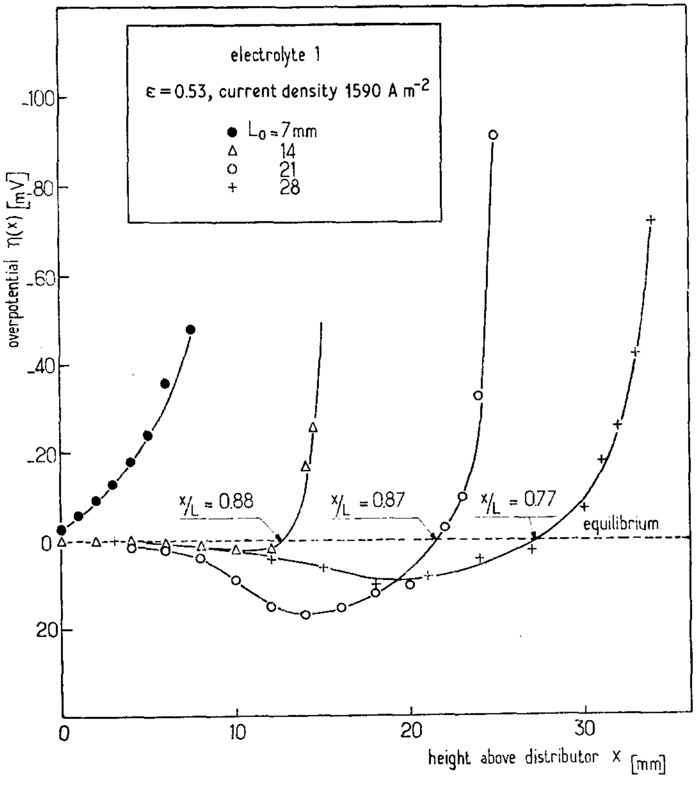


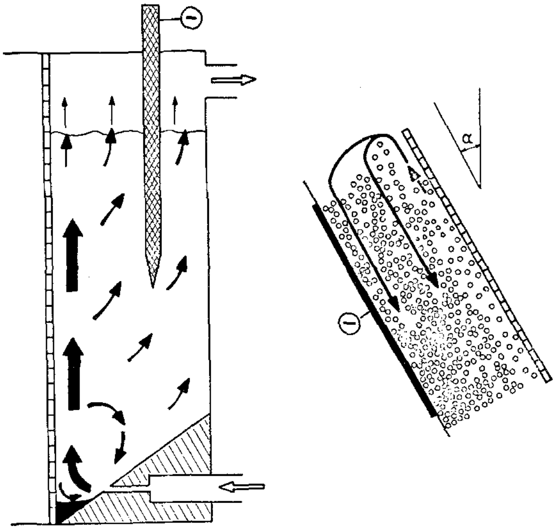
Fig. 7. Experimental overpotential distributions in the direction of current flow within cathodic fluidized beds of copper particles. From [22].

seems to be confirmed and allows a justification of the experimental variations of the current efficiency with current density.

5. Variants of the fluidized bed electrode

The bad electric conductivity of the granular matrix of the fluidized bed and the problems discussed above preventing the design of a reliable cell for copper recovery were no doubt at the origin of the search for variants. A concept used considers the use of a dense circulating bed allowing a very good intergranular electric conductivity and a continuous recovery on the grains.

In these variants, which make use of the spouted bed technique, the granular matrix of the electrode circulates as a rapidly ascending dilute phase and a slowly descending dense phase. This concept was considered in the cell of [48] whose cathodic compartment is represented in Fig. 8a. Fig. 8b shows schematically a cathodic compartment where the circulation of the solid would be obtained by tilting the cell [49]. Fig. 8a specifies the flow of the liquid whereas Fig. 8b shows the movement of the solid as an ascending dilute layer moving at high velocity (hydraulic transport) along the separator or diaphragm and a dense layer falling past the current feeder. Such a circulation of the dispersed phase can claim to have two favourable effects: there is no immobilization of grains on the diaphragm and thus no initiation of agglomeration, and metal deposition on the current feeder is avoided. The results obtained on the pilot-scate are not known.



(a) (b)

Fig. 8. Cell compartments using circulating beds: (a) from [48], (b) from [49].

In the case of copper recovery from a solution containing 1 g l^{-1} of Cu, [48] is oriented towards the demonstration that the electronic conduction in the dispersed phase is much better than when the bed is fluidized. Paper [50] uses the circulating bed for the recovery of zinc: the current efficiency increases with current density and reaches 80 to 90%; moreover, explorations of local electrode potential show that the metal deposition occurs essentially in a thin zone close to the diaphragm, whereas the remainder of the bed (essentially the falling phase) has an electrochemical activity virtually equal to zero. Similar results, though yet unpublished, have been obtained by the author in the case of copper. Although this idea of circulating the conducting matrix is original and may present a number of advantages, it is easy to imagine that the bed thickness, from an overall electric point of view, is equivalent to two resistances in series (the ascending dilute layer on the one hand, the descending dense layer on the other). The high porosity of the ascending layer involves a very low electric conductivity of the corresponding dispersed matrix; thus the corresponding resistance of this layer determines the potential profile.

6. Conclusions

This article has reviewed the application of the fluidized bed electrode to the recovery of metals and principally copper. The study of this topic has been going on for about ten years, and the objectives with regard to the concentration of the solutions to be treated have changed somewhat. The renewal of interest seems to result from environmental control and to concern more dilute solutions. In the case of copper, the problem of agglomeration and re-dissolution have been noted for solutions containing more than 1 g l^{-1} of Cu. Particle agglomeration is the problem which limits the operating duration time of an FBE for metal recovery (except mercury). In the case of copper, the existence, shown experimentally, of anodic or pseudo-anodic parts which do not exist when the bed is fixed leads one to consider the significance that should be given to the concept of the FBE. It could be that the bipolarity of the particles is the principal drawback, essentially due to the homogeneous character of the liquid–solid fluidization.

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