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Metal recovery using a moving-bed electrode

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This paper describes an experimental study of a moving bed of solid metal particles which can be used for the electrolytic recovery of metals from aqueous solutions. A cell with rectangular geometry is used to deposit copper, tin, zinc, cobalt and manganese metals on copper particles. Current efficiencies and energy consumptions are obtained at various current densities and concentrations. A cell with cylindrical geometry is also used to deposit copper from acidified aqueous solutions. The use of a finned cathode feeder is briefly investigated.

1. Introduction

Three-dimensional particulate electrodes have been investigated extensively over the past decade or so in areas such as electrowinning [1], effluent treatment [2, 3], fuel cells and batteries [4, 5] and organic electrosynthesis [6, 7]. These electrodes, either in the form of packed, slurry or fluidized beds, have been considered because of their high specific surface areas and mass transfer rates, which make them attractive systems for a number of electrochemical processes, especially those with very low operating current densities. In particular, fluidized bed electrodes (FBE) and packed (or porous) bed electrodes have been extensively investigated in applications such as extractive metallurgy and metal-ion removal from dilute solutions [2, 8–11].

Packed or porous electrodes have shown an ability to remove metal ions from aqueous solutions to very low levels [12]. However, these electrodes are limited in operating life because the structure finally agglomerates into a solid mass. Fluidized bed electrodes avoid this problem, and can theoretically be used for the continuous electrolytic recovery of metals, by the removal of grown particles and the addition of particles of the original bed size.

Recently, it has been observed that there are regions within fluidized bed electrodes which are bipolar [13, 14], perhaps due to single or groups of particles becoming electronically isolated from their neighbours in the potential field. Problems could therefore be encountered in their use when product or reactant species are susceptible to reaction at the oppositely polarized electrode, and in applications such as metal deposition when spontaneous dissolution is likely. In fact, attempts to electrowin metals such as manganese and zinc from simulated industrial solutions using the FBE have proved unsuccessful [15].

This paper is concerned with the performance of a new particulate electrochemical reactor, the moving-bed electrode (MBE) [16]. The MBE may be suitable for the continuous electrowinning of metals which are inherently difficult to deposit, e.g. manganese, and also for effluent treatment and battery applications. The present work looks at these applications using the deposition of metals such as copper, zinc, manganese and tin. Emphasis is placed on determination of current efficiencies and energy consumptions.

Briefly, the MBE consists of a bed of relatively small conducting particles approximately spherical in shape. The bed resembles a packed bed, in that electronic contact is maintained between individual particles, but it moves continuously either countercurrent or concurrent to a flowing electrolyte stream. The configuration of the MBE is such that the bed moves vertically between two electrodes, one of which is separated from the bed by a diaphragm. Electrolyte flow and current path are therefore perpendicular and hence residence time (or electrode size) can be arranged to be independent of reaction distribution.

The design of MBE used in this work employs

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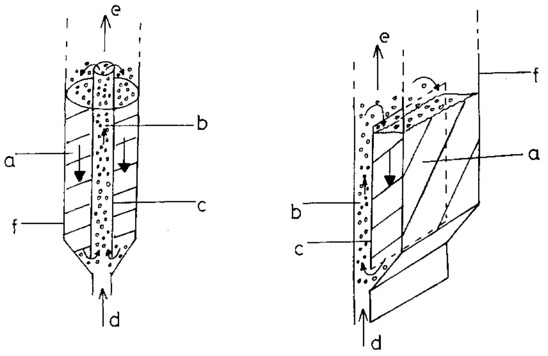

Fig. 1. Moving-bed electrode geometries (counter electrode and diaphragm not shown). (a) Moving-bed, (b) conveying section, (c) feeder electrode, (d) electrolyte inlet, (e) electrolyte outlet, (f) cell housing.

countercurrent movement (under the influence of gravity) of the bed and electrolyte in both rectangular and cyclindrical geometries (Fig. 1). Particles emerge at the downstream end of the moving bed and are recirculated to the top, upstream end in the conveying section. In this way a continuous movement of the bed is maintained allowing removal and replenishment of particles as required.

2. Experimental

2.1. *Cells*

Two cell designs are used in this work, one with a rectangular geometry, the other with a cylindrical geometry.

2.1.1. Rectangular geometry. The cell, made from three Perspex sections, is shown in Fig. 2. The first section holds a stainless steel cathode feeder, behind which is a channel 0.5 cm wide in which particles are coveyed to the top of the moving bed. The bed moves in a U-shaped cathode compartment 2 cm thick and 8 cm wide. One of two materials is used to separate the bed from the anode: an ion-exchange membrane or a plastic gauze.

The ion-exchange membrane is supported by a thin (2 mm) Perspex sheet with a series of slots cut out to give an effective diaphragm area of 100 cm^2. This membrane separates the bed from a platinized titanium anode and an aqueous solution of sulphuric acid (1 M) which circulates continuously through the anolyte compartment.

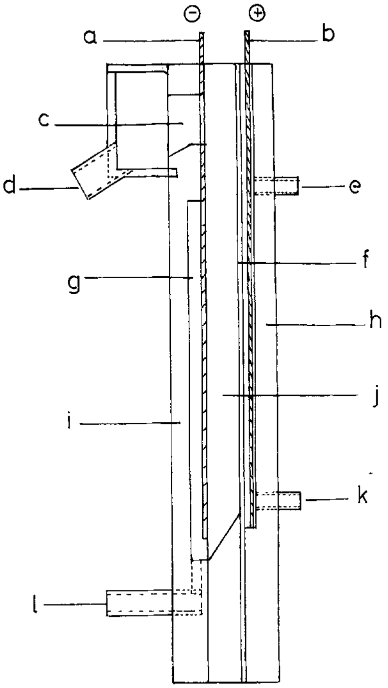

Fig. 2. The rectangular cell. (a) Cathode feeder, (b) anode, (c) weir, (d) catholyte outlet, (e) anolyte outlet, (f) diaphragm support plate, (g) conveying section, (h) anolyte section, (i) cathode section, (j) moving-bed region, (k) anolyte inlet, (l) catholyte inlet.

The plastic gauze separator is of woven Terylene with a 95 mm aperture. It covers a sheet anode (area 100 cm^2) set flush into the surface of a Perspex rectangular block. This block is positioned next to the U-shaped cathode compartment so that only one electrolyte is used. The anode material is either platinized titanium or nickel.

2.1.2. Cylindrical geometry. The cell shown in Fig. 3 is made from QVF glass fittings with an internal diameter of 8 cm. The cathode current feeder is a stainless steel cylinder 2.5 cm in diameter and 25 cm long, located centrally in the cell. The moving bed is external to the cylinder and particles are transported inside. Three platinized titanium anodes in the form of thin sheets 2.5 cm wide are located in the cell on a 5.5 cm diameter circle in a triangular pitch. The anodes of total active area of 180 cm^2 are exposed to electrolysis on the side facing the cathode feeder and are covered by a plastic gauze to separate them from the bed. Only one electrolyte is circulated through the cell.

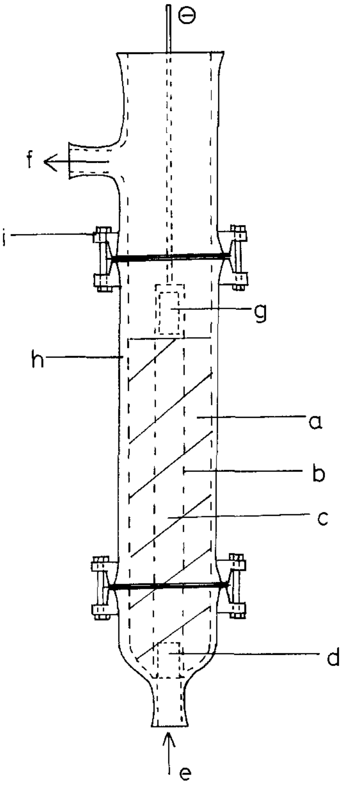

Fig. 3. The circular cell (anode and membrane not shown). (a) Moving-bed region, (b) cathode feeder, (c) conveying section, (d) particle outlet from moving bed. (e) electrolyte inlet, (f) electrolyte outlet, (g) particle outlet from conveying section, (i) flange.

2.2. *Flow circuit and power source*

Electrolyte solutions are circulated through the cell from PVC reservoirs by circulating pumps. Glass coil heat exchangers are used to maintain a constant electrolysis temperature. All pipework, valves and fittings are made of PVC. Catholyte flow rates are sufficient to give a moving-bed velocity (as measured visually at the outside of the bed) of about 0.5 to 1 cm s^{-1}.

Power to the cell is supplied by rectification of a three-phase supply, using a General Electric Company silicon rectifier, transformer rated at 200 A, 50 V. The quantity of current passed is monitored using a suitable shunt and a Time Electronics TS100A digital integrator.

2.3. *Materials*

The particulate bed material was made of approximately spherical, solid copper particles (supplied by Powder Metallurgy Ltd, Stratford) which were cleaned in dilute sulphuric acid to remove surface oxides and rinsed in distilled water. The particle size in most experiments was 500–700 μm (sieved), except in one case where particles in the size range 1–2 mm (sieved) were used.

Electrolyte solutions were made from technical-grade chemicals and distilled water. Metal-ion concentrations were measured either by volumetric titration with EDTA solution or by atomic absorption spectrophotometry. The cation-exchange (MC-3470) and anion-exchange (MA-3475) membranes were supplied by Ionac Chemical Corporation, New Jersey, USA.

2.4. *Experiments*

The principal experiments were designed to establish current efficiencies and energy consumptions of a number of electrodepositions. The effect of current density was also considered in most experiments and to a lesser extent the effect of metal-ion concentration, particle size and separator type.

All experiments were performed using batch circulation of a known volume of catholyte (between 4 and 10 dm^3) from a reservoir through the cell, and catholyte samples, taken at intervals, were analysed to determine metal-ion concentrations. Cell voltages were measured throughout each experiment. All current densities referred to in this paper are based on the diaphragm area available for electrolysis.

2.5. *Hydrodynamic aspects of the moving bed*

As designed, the moving-bed electrode operates with countercurrent flow of electrolyte and particles. The flow of electrolyte through the bed tends to oppose the downward motion of the bed such that its velocity will be less than that for hindered settling of a loosely packed bed. During electrolysis, when particles grow in size, there will be a tendency for the bed velocity to change and therefore the mass transfer rates and the fraction of total electrolyte which flows through the moving-bed section will vary.

A fraction of the total electrolyte which is required to convey the particles is not electrolyzed. The lower limit on this fraction is governed by requirements to achieve hydraulic or fluidized bed conveying and is a function of particle size and density, solid concentration and circulation rate and cell geometry. Therefore, in a single pass of liquid through the cell only a fraction of it will be electrolyzed. Hence the continuous treatment of an electrolyte stream is not possible in single or parallel arranged units when large conversion per pass are required. Either series connection of cells, electrolyte recycling or batch circulation will be necessary.

From theoretical considerations of the hydrodynamics of the system it can be shown that the fraction of fluid flowing through the bed is small. Therefore the moving bed may need to be restricted in length so that problems of reactant depletion do not produce a detrimental effect on performance. Alternatively, cells may be designed so that the spacer between the conveying and moving-bed regions, i.e. the cathode feeder in the preferred cell design, is of expanded metal or mesh to induce electrolyte (and particle) mixing between the regions. This effect is also achieved with the finned cathode feeder.

3. Results and discussion

3.1. *Preliminary performance*

The deposition of copper from aqueous solutions containing 2 g dm^{-3} copper in sulphuric acid (1 M) was used to investigate the operation of the moving-bed electrode. A rectangular cell similar to that described in Section 2.1 was used except that the conveying section and moving-bed were operated side by side as viewed in the direction of current flow. The length and width of the bed were half that of the cell in Section 2.1 and the active area of the diaphragm was 40 cm^2. The bed was separated from the anode by a cation-exchange membrane.

In the first few electrolyses it was apparent that to deposit metal on to the moving-bed without particle agglomeration and deposition on the diaphragm, a continuous movement of the bed was required in all active regions. It is therefore beneficial to ensure that the diaphragm is smooth and flat and that retaining walls are designed such that particles do not lodge in the structure and hence grow *in situ*. Sluggish area of movement of the bed should also be avoided and therefore it is recommended that the conveying section and moving-bed be arranged as described in Section 2.1. This is because when greater bed widths are used in the 'side by side' arrangement there will be a tendency for stationary areas of the bed to occur, due to the converging nature of the particle flow at the base. Alternatively a multiplicity of these side by side units may be used.

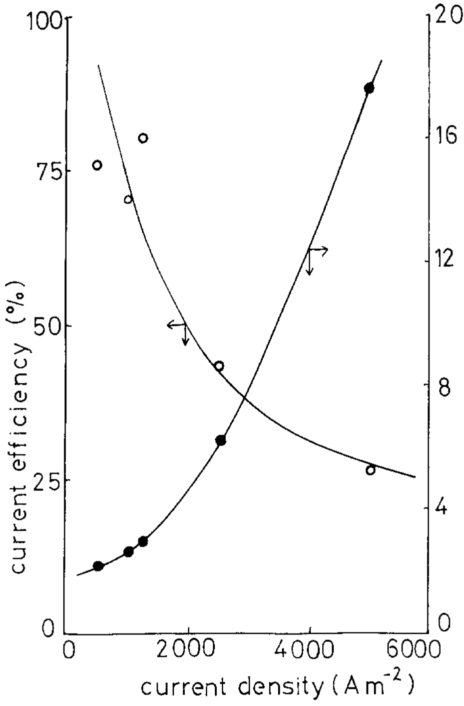

Fig. 4. Current efficiencies and energy consumptions for copper deposition (copper concentration: initial, 2 g dm^{-3}; final, 0.3 g dm^{-3}; temperature 20° C). ○, current efficiency; ●, energy consumption.

Fig. 4 shows current efficiencies and energy consumptions (kW h of electrical energy used per kg of copper deposited) as a function of current density. As expected, current efficiency decreases with increase in current density due to an increase in the rate of the secondary reaction (hydrogen evolution). Correspondingly the energy consumption increases with current density, typical values of which at current densities of 2500 A m^{-2} and below are comparable with those obtained with fluidized bed electrodes [1, 8]. Potential probing of the bed during operation showed it to be of uniform potential and hence analagous in behaviour to a packed bed cell.

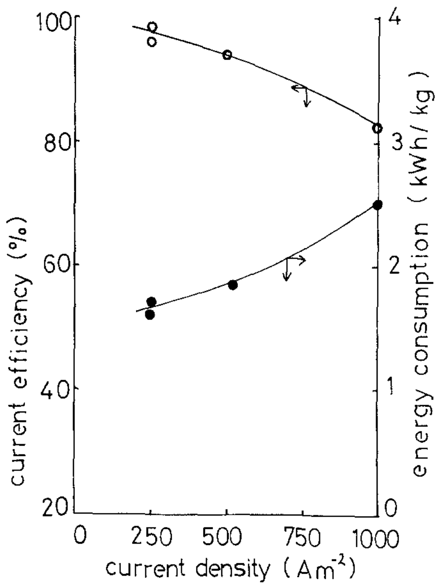

Fig. 5. Variation of current efficiency and energy consumption with current density for copper deposition (copper concentration: initial, 1 g dm^{-3}; final, 0.1 g dm^{-3}; temperature 20° C).

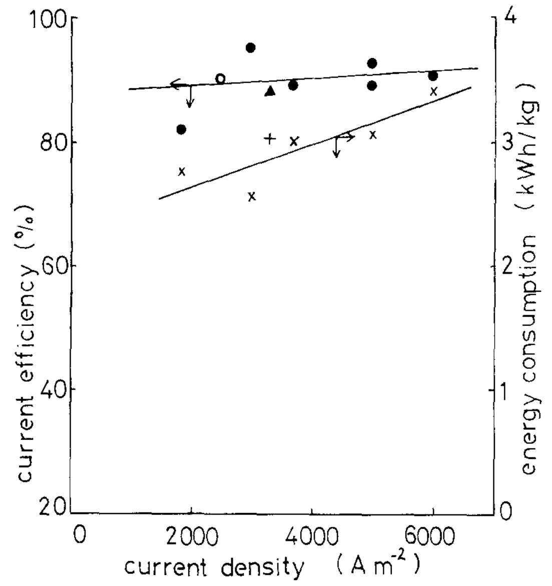

Fig. 6. Zinc deposition from alkaline electrolyte. 6.0 M KOH, temperature 20° C, plastic mesh bed separator. Zinc concentration 20 to 25 g dm^{-3}: ●, current efficiency; ×, energy consumption. Zinc concentration 3.4 to 2.0 g dm^{-3}: ▲, current efficiency; +, energy consumption; ○, current efficiency (cation-exchange membrane).

The production of hydrogen gas during electrolysis did not effect the downward movement of the bed, although on scale-up the likelihood of formation of large bubbles or gas pockets may well inhibit solid flow and should therefore be minimized.

3.2. *Metal recovery and various parameters*

Experience gained from the preliminary tests led to modifications being incorporated into the cell design as shown in Fig. 2. This design is amenable to unlimited scale-up in both horizontal and vertical directions perpendicular to the direction of current flow.

3.2.1. Diaphragm material. In the operation of the moving-bed electrode, the anode must not contact the bed otherwise electronic shorting will occur. This is achieved by using some form of separator, such as an ion-exchange membrane or porous diaphragm, which separates catholyte and anolyte streams, or a plastic mesh which simply prevents contact when only one electrolyte stream is used.

Fig. 5 shows the variation of current efficiency and energy consumption with current density for copper deposition using a plastic mesh as the bed separator. Results are similar to those in Fig. 4 (with a cation-exchange membrane) and current efficiencies are noticeably high, greater than 80%, in the range of current densities investigated. Energy consumptions are about 10% to 15% lower using this type of separator, which is to be expected in the absence of an anolyte and an ion-exchange membrane. The movement of the bed is not noticeably impaired by oxygen evolution at the anode and no deposition of metal occurs on the separator.

3.2.2. Alkaline zinc deposition. The deposition of zinc from alkaline electrolyte is of interest because it forms the charging mode of zinc–alkaline batteries. One criteria of upmost importance in this application is energy consumption. Fig. 6 shows the variation of energy consumption and current efficiency with current density and it can be seen that current efficiencies are typically greater than 80% and energy consumptions are in the range of 2.5 to 3.4 kW h kg^{-1}. These energy consumptions are comparable to those achieved with fluidized bed cells operating without diaphragms [17]. The effect of zinc concentrations down to 2 g dm^{-3} is shown not to significantly affect the performance

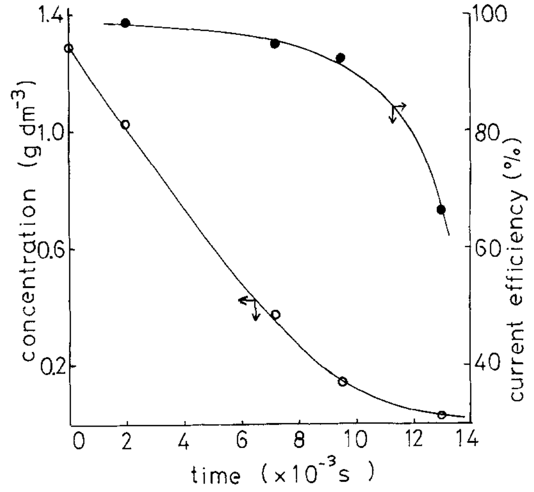

Fig. 7. Variation of copper concentration and current efficiency with electrolysis time. (Current density 600 A m^{-2}, temperature 20° C, 1 M H_2SO_4 supporting electrolyte).

of the system (Fig. 6). However, as expected, using a cation-exchange membrane increases the energy consumption of the deposition.

3.2.3. Metal-ion concentration. The typical effect of metal-ion concentration can be seen in results for the deposition of copper (Fig. 7). As expected, current efficiency falls with length of electrolysis and correspondingly the rate of depletion of copper concentration also decreases. Similar results are also obtained in the electrolytic recovery of tin, described below.

3.2.4. Electrolytic recovery of tin. One approach to the electrolytic recovery of tin in the metal-finishing industry is the use of an 'integrated system' [18]. Here, tin at concentrations of 1.0 g dm^{-3} in aqueous alkaline sulphate or fluoborate electrolyte is recovered at current densities of 20 to 50 A m^{-2} with current efficiencies of 50%.

Tin can be recovered from stannous sulphate solutions using the moving-bed electrode at current efficiencies approaching 100% if the current density is of the order of 300 to 1200 A m^{-2} (Table 1). During a batch recovery of tin the rate of change of tin concentration and current efficiency both decrease with time (Fig. 8). Typically, on reducing tin concentration levels from 1000 to 660 ppm to about 1.0 ppm, current efficiency falls from 100% to about 50%.

3.2.5. Particle size. Experiments with particles of size 1000–2000 μm (sieved) (tin recovery) and 500–700 μm demonstrated that the cell can operate successfully over quite a large range of particle size and with a wide size distribution.

3.2.6. Metal winning applications. Cobalt and zinc can be deposited on the moving-bed electrode using an anion-exchange membrane to separate anolyte from catholyte and maintain a reasonably constant pH (Table 2). In most cases high current densities are used and current efficiencies of at least 50% can be achieved.

The deposition of manganese and zinc from acid electrolyte occurs in potential regions where

Table 1. The electrolytic recovery of tin (rectangular cell, cation-exchange membrane, molar sulphuric acid supporting electrolyte, 30° C)

Current density (A m^{-2})	*Average cell voltage* (V)	*Stannous ion concentration* (ppm)	*Current efficiency cumulative* (%)	*Energy consumption* (kW h kg^{-1})
1200	2.5	950		
		562	100	
		283	86	1.36
600	2.2	660		
		275	100	
		147	78	
		1.0	45	2.29
300	2.15	1150		
		679	100	
		135	100	1.0

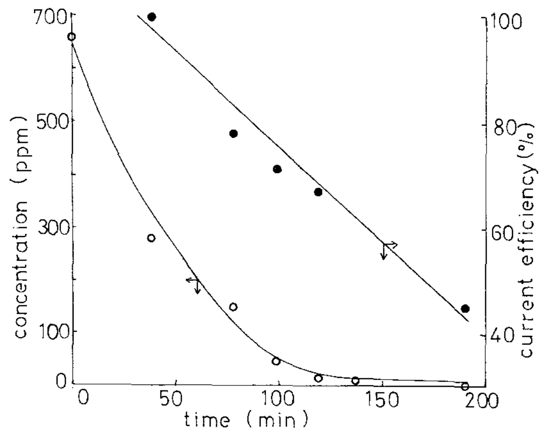

Fig. 8. Variation of concentration and current efficiency with electrolysis time. (Current density 600 A m^{-2}, temperature 30° C, 1 M H_2SO_4 supporting electrolyte).

Table 3. Copper deposition in the cylindrical cell (temperature 20°C, 1.0 mol dm^{-3} H_2SO_4 supporting electrolyte)

Current (A)	*Copper concentration change* (g dm^{-3})	*Current efficiency* (%)
10	0.8 to 0.3	62
20	0.8 to 0.3	84
30	0.8 to 0.3	81
40	0.8 to 0.3	84

hydrogen gassing is likely and therefore difficulty is expected when using electrode systems which may exhibit non-uniform potential distribution, such as the MBE. In the case of manganese a few electrolyses (of solutions containing 45 g dm^{-3} Mn in 140 g dm^{-3} ammonium sulphate, pH 7.5 to 8.5) showed that it will deposit on to the moving bed, although current efficiencies are not high, which is probably due to uneven potential distributions and regions in the cell where dissolution occurs. However this partial success with manganese in what were basically one-off experiments could be improved by re-designing the MBE to:

(a) produce a more uniform current and potential distribution, by using a thinner bed or larger particles;

(b) ensure all regions of the moving bed are in the potential field;

(c) cathodically protect the conveying region of the cell. This could be done by using either a finned cathode feeder or a cathode feeder duct(s) surrounding the conveying region(s) or by initiating fluidized bed conveying.

The deposition of zinc from a solution containing 30 g dm^{-3} of zinc in 1.0 M sulphuric acid is not possible in the cell described in this paper due to an uneven potential distribution and dissolution. During operation, however, the zinc metal is deposited on to the particles in the region next to the diaphragm, but once these particles move from this region the deposit dissolves.

3.2.7. The cylindrical cell. Table 3 shows results of copper deposition in the form of current efficiencies obtained with the cylindrical cell. Over the range of currents used efficiencies are reasonably high, greater than 60%, although they are slightly inferior to those obtained with the rectangular cell. This is probably due to dissolution of the copper, resulting from saturation of the electrolyte with oxygen from the anodic reaction, the large mass of bed (3 kg) used and inactive regions of the bed. Even allowing for this, current efficiencies of 50% and greater are obtained on reducing copper concentrations to 20 ppm and less.

Table 2. Electrowinning of cobalt and zinc

Metal	*Temperature* (° C)	*Electrolyte*	*pH*	*Metal ion concentration* (g dm^{-3})	*Current density* (A m^{-2})	*Current efficiency* (%)
Cobalt + 1 g dm^{-3}	60	Sulphate	2–4	48–46	5700	55
	60	Sulphate	2–4	38–33	5700	50
	60	Sulphate	2–4	46–43	4850	51
Zinc	60	Sulphate	2–4	50–45	7000	61
				50–45	8500	60
Zinc	20	Chloride	2–4	32–29	2000	65

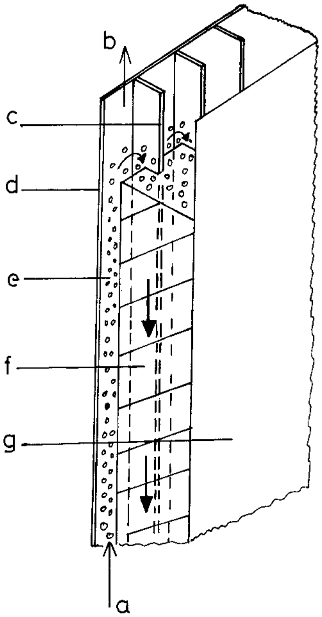

Fig. 9. Finned cathode feeder. (a) Electrolyte inlet, (b) electrolyte outlet, (c) fin, (d) cathode feeder, (e) conveying section, (f) moving bed, (g) diaphragm.

3.2.8. Finned cathode feeder. In this arrangement (Fig. 9) the particles are conveyed in front of the cathode feeder and vertical fins project through this region into the moving bed. Copper has been deposited on to the moving bed with this feeder arrangement. A typical run produced a current efficiency of 68% at a current density of 1400 $\mathrm{A\,m^{-2}}$, for a change in copper concentration of 1.4 to 0.16 $\mathrm{g\,dm^{-3}}$. The energy consumption is 3.1 $\mathrm{kWh\,kg^{-1}}$.

4. Conclusions

It has been shown that the moving-bed electrode can be used to recover metals such as copper, tin, cobalt and zinc from aqueous solutions in applications such as electrowinning and effluent treatment. Operating at relatively high current densities, concentration of a few ppm of metal are attainable with low energy consumptions. The MBE offers a combination of characteristics of the fluidized bed electrode, i.e. continuous operation, and of the packed bed electrode. Metals which are difficult to deposit such as manganese may now be electrowon continuously.

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