JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 124–129

An investigation of the spouted bed electrode cell for the electrowinning of metal from dilute solutions

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Received 21 February 1990; revised 20 June 1990

The depletion process of copper ions from dilute solutions has been used as a model system to investigate the spouted bed cell with a three-dimensional electrode of conducting particles. Experiments under potentiostatic and galvanostatic conditions have been carried out. Results obtained indicate that the spouted bed cell has several favourable characteristics for application in metal recovery. The potentiostatic mode of operation appears to be superior to the galvanostatic mode for electrowinning.

1. Introduction

Three-dimensional electrode cells have been investigated extensively over the past two decades and have been shown to be suited to applications in different areas such as electrowinning, effluent treatment and electroorganic synthesis. The extremely high specific surface area of these 'new generation' cells makes them attractive systems for numerous electrochemical processes which can only be successfully carried out with low current densities. The early research in three-dimensional electrodes was focused on the fixed and fluidized bed, especially on the latter. The main purpose of these investigations was application of the cell for the winning of heavy metals from very dilute solutions [1–3]. Despite early optimism the fluidized bed electrode (FBE) cell has manifested many limitations in later investigations such as: poor conductivity of the dispersed phase at higher bed expansion, deposition of metal on the feeder electrode and diaphragm, channelling through the bed in scaled up cells, bipolar characteristics with large interelectrode distances, relatively short lifetime of the diaphragm etc. [1, 4, 5]. Some of these shortcomings have seriously limited the viability of the FBE cell for metal reclamation. The disadvantages prompted the appearance of some new types of cell, derived from the FBE cell, such as the inclined FBE cell [6], the moving bed cell [7], the vortex bed cell [8] and the spouted bed cell [4, 5, 9].

The spouted bed electrode (SBE) cell attracted greater attention than the other types of cells, and there is a greater wealth of published data. Thus, Coeuret *et al.* [4] have measured the potential distribution across the inclined half column SBE cell. Scott [5] has also investigated the half column SBE cell, also making a comparison between different kinds of three-dimensional cells. Hadžismailović *et al.* [9] have investigated a cylindrical diaphragmless SBE cell with a counter electrode outside the bed with particular attention to the quality of the deposited copper on the metal particles.

Based on Scott's results [5] it may be concluded that the SBE cell is a promising electrochemical reactor with better characteristics than the FBE cell.

The objective of the present work is to investigate the performance of an SBE cell of larger dimension than previously used, as well as with different electrode configuration.

2. Particle motion in the spouted bed

A spouted bed is a bed of particles situated in a vertical column of cylindrical or rectangular geometry with a conical bottom, into which a fluid is introduced as a jet through a nozzle or a slot. Such introduction of the fluid into the column forms two regions in the bed, as shown in Fig. 1:

- a spout in the central part in which particles are transported upwards by the fluid jet and where the bed porosity is very high;
- an annular region with a slow downwards dense flow of particles between the wall and the spout and where the bed porosity is close to that in the fixed bed.

At the bottom of the column, particles from the annulus are entrained into the spout by the fluid flow.

It should also be noted that there is a radial transfer of particles from the annulus to the spout. The fluid stream passes mainly through the spout but a part of it percolates through the annulus.

3. Experimental details

3.1. *Cell design and electrodes*

The SBE cell was made of plexiglass and is schematically shown in Fig. 2. The dimensions of the cell were 50 mm × 50 mm × 200 mm in height. The slot width was 2 mm and the apex angle of the lower part was 45°. Plastic mesh served to prevent particles falling into the lower part of the cell.

Two copper sheets located on the opposite walls

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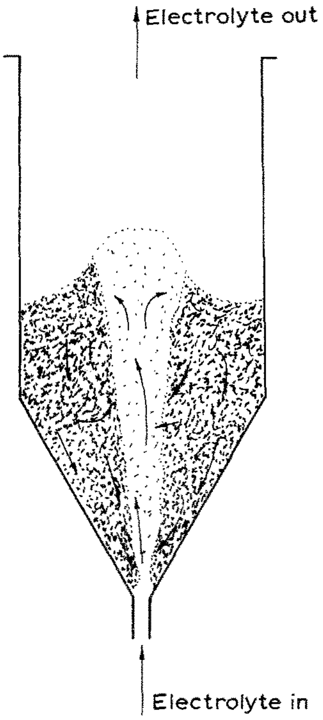

Fig. 1. Schematic view of particle circulation within the spouted bed.

served as current feeders whilst the lead counter electrode was placed in the middle of the cell as shown in Fig. 2. The interelectrode distance was 2 cm. To prevent physical contact between particles and the counter electrode, the latter was covered by a plastic cleat.

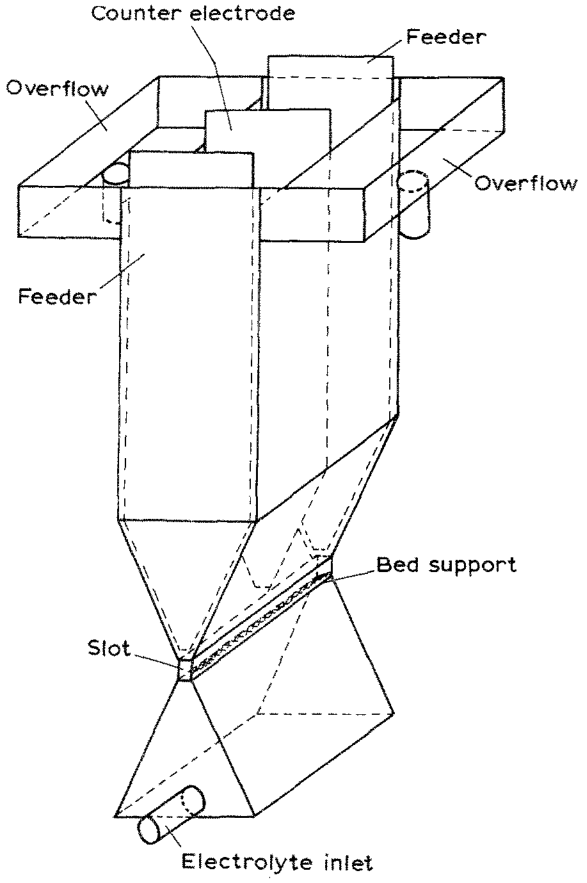

Fig. 2. Schematic view of the spouted bed cell and electrodes arrangement.

The particulate bed consisted of spherical copper grains in the size range 0.5 to 0.8 mm and these served as the three-dimensional cathode. The volume of particles was the same in all experiments and as 100 cm^3.

3.2. *Electrolyte*

To investigate the performance of the SBE cell, the electroreduction of Cu^{2+} ions, from acidified copper sulphate solution, was used. The initial concentration of Cu^{2+} ions was 1 g dm^{-3} in all experiments, while as a supporting electrolyte sulphuric acid was used at a concentration of 0.5 M. The volume of electrolyte was 4 dm^3 in most experiments. It is noteworthy that there was only one electrolyte circuit. Since the experiments were performed in a batch recirculating mode of operation, the decrease of Cu^{2+} ion concentration was periodically monitored using a Perkin-Elmer atomic absorption spectrophotometer.

3.3. *Other experimental details*

An Amel potentiostat–galvanostat (10 to 20 V) served as a power supply. The charge passed through the cell was measured by means of an Amel coulometer with an integrator.

Experiments were carried out at ambient temperature.

3.4. *Operating modes*

Two series of Cu^{2+} ion depletion experiments were carried out: (a) under potentiostatic conditions, and (b) under galvanostatic conditions.

In the first set of experiments the feeders were maintained at constant potential referred to SCE. During each experiment the cell voltage and the current were measured as well as the charge passing through the cell. Periodic sampling of electrolyte was performed to obtain the decrease of reacting ions with time. From these data the current efficiency and the specific energy consumption were derived. The average current was obtained from the amount of electric charge passed over a given process time.

In the second series of experiments, under galvanostatic conditions, the removal of copper ions from electrolyte was carried out at chosen constant operating currents. The cell voltage was monitored and the concentration of Cu^{2+} ions was again periodically determined.

The influence of the electrolyte flow rate on the cell voltage and the rate of depletion was investigated only under galvanostatic conditions.

4. Results and discussion

4.1. *Galvanostatic conditions*

The concentration decrease of Cu^{2+} ions with time was determined over a wide range of applied current densities and the results are presented in Fig. 3, as dimensionless concentration against time.

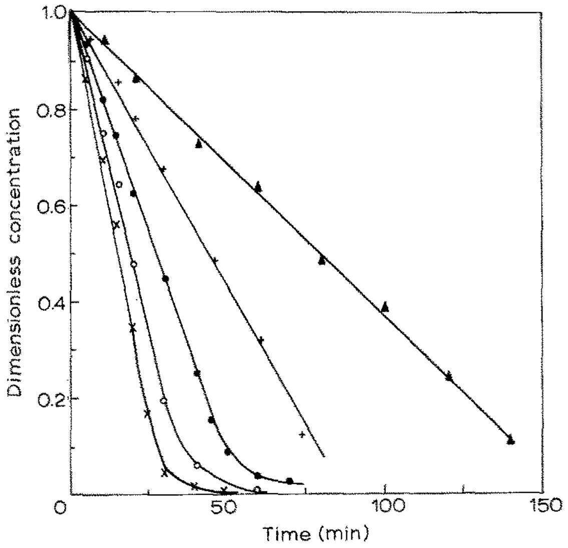

Fig. 3. Concentration–time relationship for galvanostatic mode of operation. Effect of current density (▲) 800; (+) 1200; (●) 1600; (○) 2400; (x) 300 Am^{-2}.

Dimensionless concentration is here defined as the ratio of actual concentration at a given time and initial concentration, i.e. C/C_0.

Variation of C/C_0 is a linear function of time until it reaches a certain value (depending on applied current density), after which nonlinearity begins.

Departure from linearity corresponds to the appearance of hydrogen evolution in the cell. When the operating current reaches the value of the limiting current for given experimental conditions, an exponential form of the concentration–time curve begins. It is obvious that curves are getting nearer with increasing current densities approaching a curve which could be obtained for a limiting current density for given experimental conditions.

The change of current efficiency with decrease of dimensionless concentration is given in Fig. 4. It may be seen that the current efficiency does not change significantly with the C/C_0 ratio in the range investigated. The applied current density has more influence on the current efficiency, as is shown in Fig. 5. The relatively low current efficiency, which is obtained at lower current densities (see Figs 4 and 5), is probably a consequence of the existence of anodic zones in some parts of the bed and the consequent dissolution of deposited copper [4].

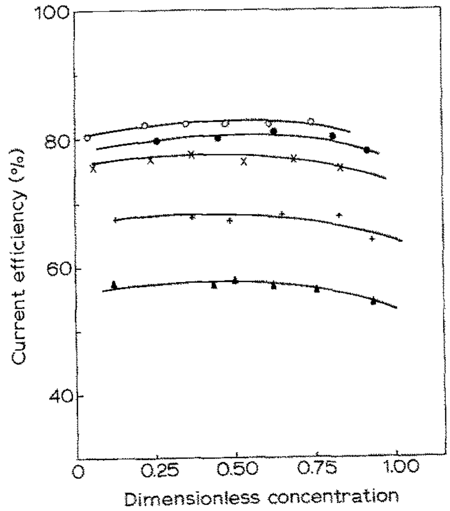

Fig. 4. Variation of current efficiency with dimensionless concentration for galvanostatic mode of operation. Current densities: (▲) 800; (+) 1200; (x) 1600; (○) 2400; (●) 3000 Am^{-2}.

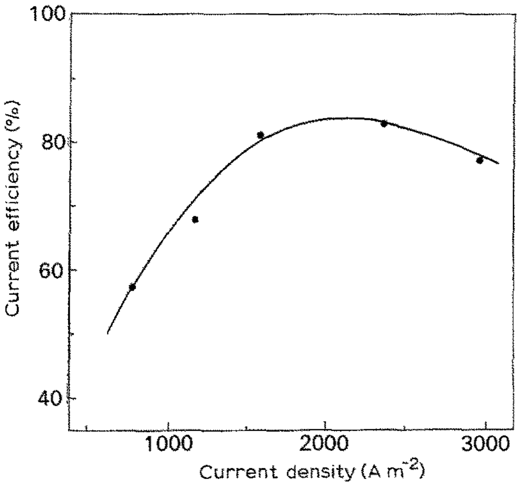

Fig. 5. Current efficiency against current density for galvanostatic mode of operation.

These zones disappear at higher current densities, so that the current efficiency increases and passes through a maximum as shown in Fig. 5. The decrease in current efficiency after the maximum is caused by hydrogen evolution in the cell. Similar current efficiency behaviour has been observed in work of Scott [5], and Stanković and Wragg [8].

The variation in cell voltage with time for different current densities is given in Fig. 6. At the beginning of the electrowinning process, the cell voltage falls slightly. After this initial period, the cell voltage remains constant over a longer period and then it starts to increase. The period of constancy of the cell voltage is shorter for higher current densities [10]. The small decrease of the cell voltage at the beginning of the process may be a consequence of the deposition of fresh metal onto the partly oxidised particles thus

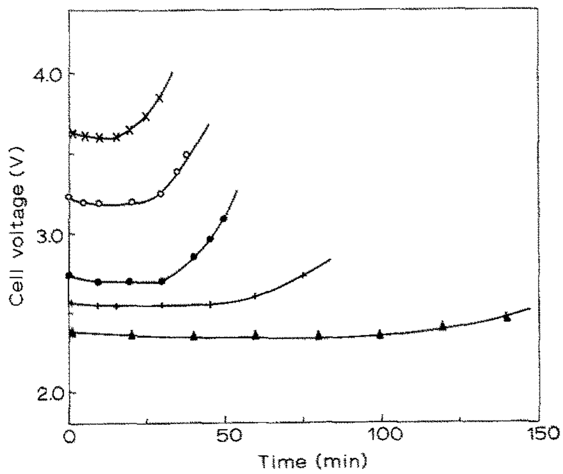

Fig. 6. Variation of cell voltage with time for galvanostatic mode of operation. Effect of current density: (▲) 800; (+) 1200; (●) 1600; (○) 2400; (x) 3000 Am^{-2}.

decreasing the bed resistance. A similar effect has been observed by Wilkinson and Haines [1]. The increase in cell voltage corresponds approximately to the departure of the dimensionless concentration from its linear relationship with time and is due to the appearance of the hydrogen evolution reaction and its associated overpotential [10]. A further effect may be the existence of gas bubbles inside the three-dimensional electrode causing a decrease in its conductivity [8, 10].

4.2. *Potentiostatic mode of experiments*

In the investigations under potentiostatic conditions, it is assumed that the feeders are kept at constant potential during the experiment. It is known [10] that, for a batch recirculating system operated under constant electrode potential, the limiting current may be maintained throughout the process, the continuous depletion of input concentration to the cell results in both applied current and cell voltage decreasing with time. In such a way, it is possible to carry out the process with a sufficiently high electrode potential corresponding to an initial operating current close to the limiting current for given experimental conditions and with avoidance of hydrogen evolution during the process, thus keeping the current efficiency at a high level. Furthermore, decreased applied current and cell voltage result in decreased process energy.

Figure 7 represents the effect of the applied feeder overpotential on the dimensionless concentration with time. The values of overpotential were deduced from the measured feeder potential and the equilibrium potential. Increase of the overpotential to more negative values, causes a rapid increase in the rate of depletion, tending to approach to a limiting value corresponding to limiting initial current.

The behaviour of the current density with time for different applied overvoltages is presented in Fig. 8. Depending on the feeder overpotentials, two operating regions are seen to exist. At lower overpotentials lower initial operating currents are obtained which remain unchanged with time in the first part of the process. When the operating current reaches the value of the limiting current for a given concentration of reacting ions, the second period starts up in which the current falls more or less slowly depending on the applied overpotential. The period of constant initial current becomes shorter and shorter tending to zero for an initial current equal to the limiting current for given experimental conditions.

The current efficiency was determined by measurement of the electric charge passed through the cell as registered on the integrating coulometer and the amount of the copper extracted for a given process time. In Fig. 9 the variation of the current efficiency with dimensionless concentration is presented for different overpotentials.

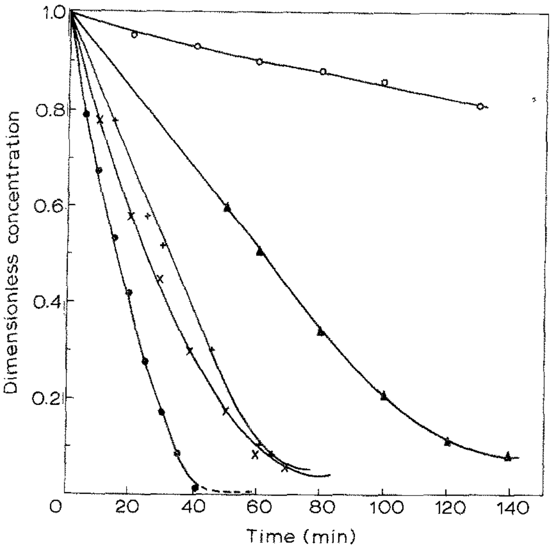

Fig. 7. Concentration–time relationship for potentiostatic mode of operation. Effect of feeder overpotential: (○) 110; (▲) 150; (+) 200; (x) 250; (●) 300 mV.

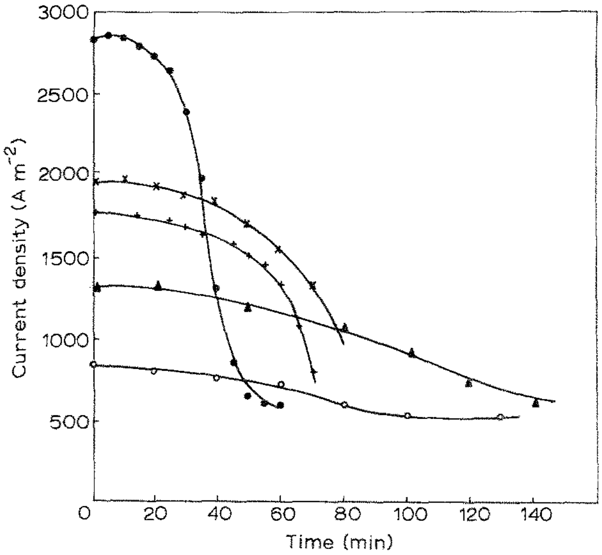

Fig. 8. Variation of current density with time for potentiostatic operational mode at different feeder overpotentials: (○) 110; (▲) 150; (+) 200; (x) 250; (●) 300 mV.

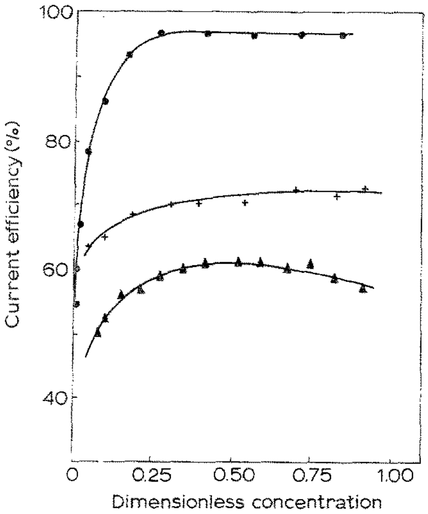

Fig. 9. Variation of current efficiency with dimensionless concentration for potentiostatic mode of operation at different feeder overpotentials: (▲) 110; (+) 200; (●) 300 mV.

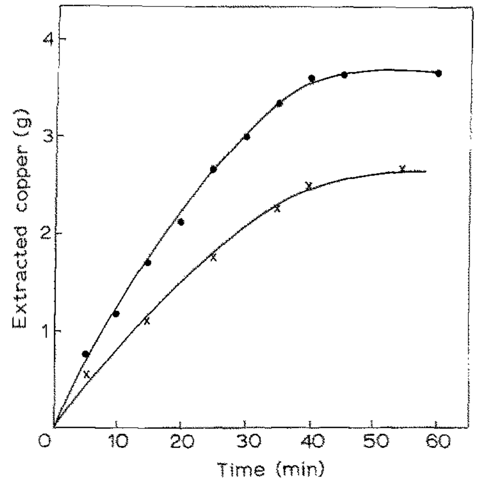

Fig. 10. Mass of deposited copper against time: (x) galvanostatic mode of operation; I = 5.53 A and (●) potentiostatic mode of operation; I_{av} = 5.53 A.

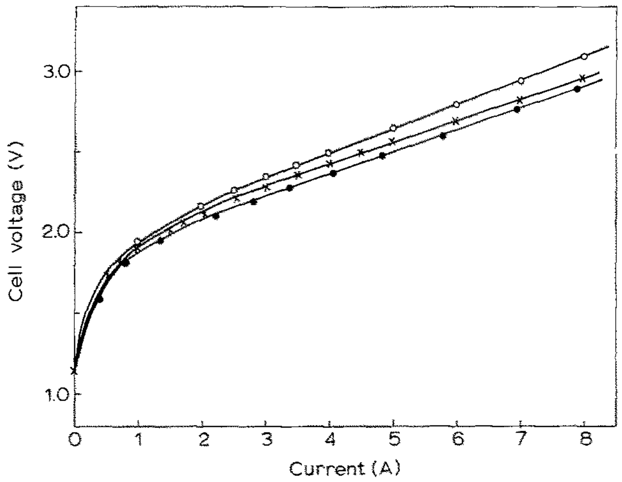

Fig. 11. Cell voltage against applied current. Effect of electrolyte flow rate: (●) 2.5; (x) 3.75; (○) 6.0 dm^3 min^{-1}.

At lower feeder potentials, i.e. lower initial and average currents, the current efficiency was unsatisfactorily low. The reason may be the same as for the case of galvanostatic operation; i.e. an anodic zone exists inside the SBE cell. At higher potentials, current efficiency increased significantly reaching values in excess of 90%. At low concentrations the current efficiency declined sharply corresponding to the low currents observed towards the end (see Fig. 8). In this period chemical dissolution of deposited copper takes place. The cell voltage behaves in a similar manner to that of the current with time, i.e. after a certain period of constant cell voltage, this starts to decrease slowly before reaching a constant value.

To compare the potentiostatic and galvanostatic modes of operation an experiment under constant overpotential was first carried out. This was followed by an experiment under galvanostatic conditions with the same total electrical charge passed. The amounts of extracted copper against time in these experiments are presented in Fig. 10. It is clear from this figure that the potentiostatic process is more efficient than the galvanostatic. At the beginning of the potentiostatic process, higher currents were observed, for a given overpotential, so that the process of depletion is faster in this initial period.

This is caused by the behaviour of the applied current with time in both galvanostatic and potentiostatic cases. Namely, the galvanostatic process current remains constant during the whole of the metal winning time and in the part of the process while the current is less than limiting current the process occurs with constant rate. When the current exceeds the limiting current copper electrowinning is accompanied by H_2 evolution and current efficiency decreases.

In the potentiostatic process the operating current changes with time in the above mentioned manner and therefore at the beginning of the process higher current is observed for given overpotential so that the process is faster in this initial period. In the latter stage of the process current decreases with time, and the process occurs slower but hydrogen evolution is avoided.

4.3. *Effect of electrolyte flow rate*

The influence of the electrolyte flow rate on the SBE cell characteristics was investigated under galvanostatic conditions. The change in cell voltage and the rate of depletion of copper ions with electrolyte velocity through the cell were measured. The spouted bed is characterized by a faster circulation of particles with increasing fluid velocity while the bed expansion is negligible in comparison with the fluidized bed expansion for similar hydrodynamic conditions. For this reason, only a small increase in the cell voltage with the electrolyte flow rate is expected. This can be seen in Fig. 11. The slight increases in cell voltage with flow rate are a consequence of the small expansion of the bed and the corresponding increase of the resistance of the dispersed phase.

4.4. *Specific energy consumption*

Current efficiency is an important parameter for any electrochemical process. But specific energy consumption (energy expended per unit reaction product), gives a better indication of the efficiency of the cell and the process. This data makes possible a comparison between different kinds of cell working under similar conditions as well as a comparison of operational modes applied to the same cell.

In this case, the determination of specific energy consumption for galvanostatic and potentiostatic modes should enable us (together with data about rate of the process), to derive another important cell characteristic. The specific energy consumption as a function of applied current density is given in Fig. 12 for the same amount of metal removed. It may be seen that the energy consumption increases slowly with increasing current density. But the potentiostatic mode of operation gives lower specific energy, for the

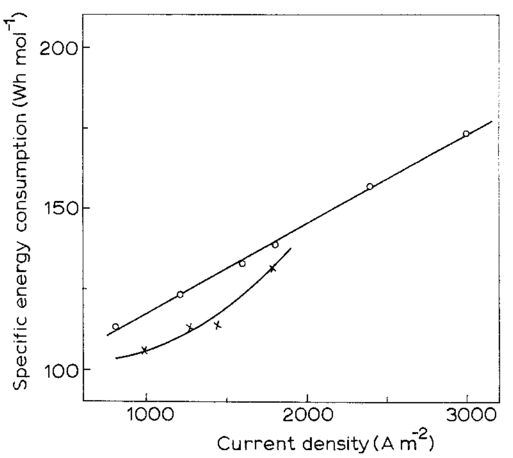

Fig. 12. Specific energy consumption against current density for 90% degree of conversion: (○) galvanostatic mode of operation and (x) potentiostatic mode of operation.

investigated model system and in the range of depletion presented. Bearing in mind that the rate of the process is faster under potentiostatic conditions, as shown in Fig. 10, this mode is favourable for technological application. However, further investigations of this operational mode will be carried out in the future.

5. Conclusions

The SBE cell considered in this work showed some good performance characteristics for the recovery of metals from dilute solutions with a satisfactory high current efficiency and process rate.

The potentiostatic mode of operation gave better results for both electrowinning rate and energy consumption. Higher electrode potentials provide higher current efficiencies.

No agglomeration of the particles or deposition of metal on the feeder surface was observed.

Acknowledgement

The authors are very grateful to Dr A. A. Wragg (Exeter) and Mrs D. Radisavljević (RTB Bor) for their help in preparing this paper.

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