SHORT COMMUNICATION

Experiments on copper recovery in a pulsed granular fixed bed electrode

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1. Introduction

The periodic fluidization or pulsation of a cathodic granular fixed bed electrode for metal recovery from dilute solutions is one means of avoiding the progressive particle agglomeration, i.e. the blocking of the bed, which occurs with a fixed bed electrode [1]. The pulsation of the electrolyte flow-rate is capable of periodically putting the particles in suspension, thus allowing continuous metal recovery on the particles.

The present short paper reports previously unpublished results obtained several years ago [1] in a few experiments using the pulsation of a fixed bed electrode for copper recovery. The purpose of the work was to direct two flow-rates towards the electrode alternately: one, q, through the fixed bed electrode during the time interval t_1, and other $Q(>q)$ for the time interval t_2 such that the corresponding bed porosity, ε, corresponded to the fluidized state. Apart from the non-agglomeration of the bed, such a hybrid fixed fluidized bed electrode would show another practical advantage, at least with electrodes having the configuration shown in Fig. 1, in that the fluidization of the bed would classify the particles within the bed, the fine particles being situated at the top while the large ones being at the bottom. It is known that the potential distribution within a fixed bed cathode having the configuration of Fig. 1 is such that the cathodic potential decreases from the top to the bottom of the bed; the same situation occurs if the bed is fluidized at low expansions [2]. As the fine particles are located at the top of the bed, they will mainly recover copper and increase in size. Then the introduction of fine particles at the top and the extraction of large particles at the bottom of the bed is a possibility.

2. Experimental details

The pulsation of a granular fixed bed electrode was studied for copper removal from acid (H_2SO_4 50 g l^{-1}) $CuSO_4$ (between 3 and 5 g l^{-1}) copper containing solutions. The column (Fig. 1) containing the electrode was cylindrical and made of plexiglass; its internal diameter was 0.04 m and its lower part was filled with a fixed bed of glass beads (calming section). The particles of the bed were graphite spheres (diameter 0.003 m; density 1860 kg m^{-3}) which were electrolytically copper-plated before their experimental use, with a resulting density of 1970 kg m^{-3}. The particles, thus prepared, were kept in demineralized water. The bed support, formed of a circular screen of copper, was also used as the current feeder. The anode was a perforated circular disk of copper located as indicated in Fig. 1.

The flow-rate, q, was maintained at a fixed value of 10^{-5} m^3 s^{-1}, a value for which the particles formed a fixed bed. The supplementary flow-rate ($Q - q$) was directed towards the column, as necessary through an electrically activated valve controlled by a generator of rectangular pulses. The electrolytic cell was operated at room temperature (20° C) under batch recycle conditions, and at constant current. The copper concentration of the electrolyte was obtained by electrogravimetric titration.

The flow-rate Q, corresponding to the pulsed state of the bed, must be higher than the minimum fluidization flow-rate of the initial particles, and smaller than the minimum fluidization flow-rate of the particles to be produced. For a final particle diameter of 0.0035 m (overall density 3250 kg m^{-3}), the application of the fluidization equations led to values of Q between

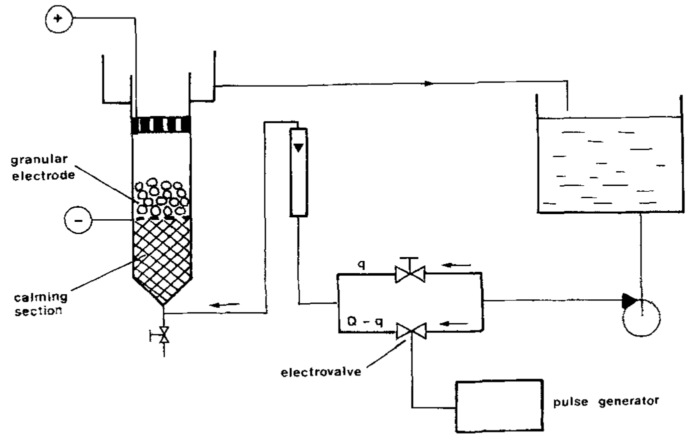

Fig. 1. Experimental circuit.

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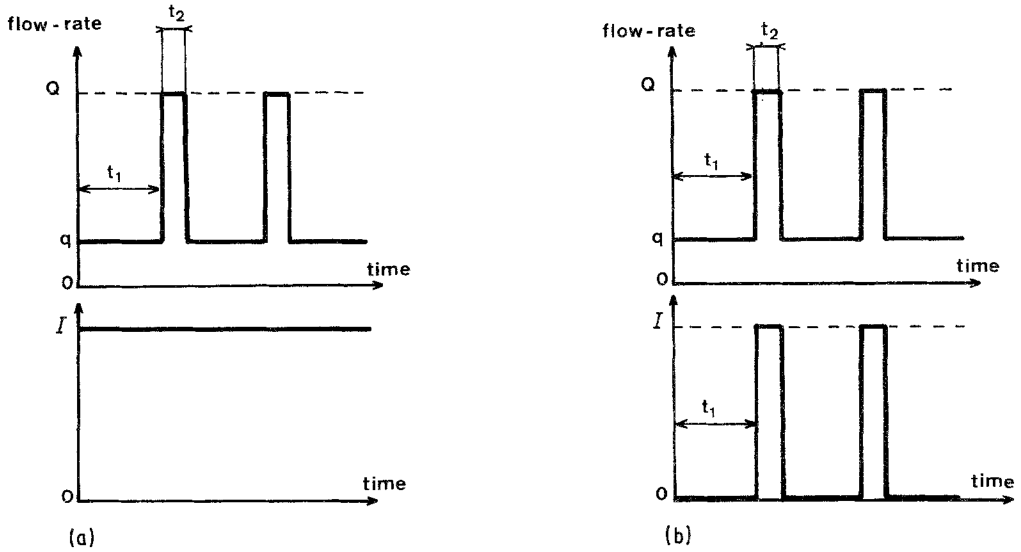

(a) (b)

Fig. 2. Models of operation. (a) Pulsed flow and constant current density; (b) pulsed flow and pulsed current.

$1.2 \times 10^{-5}\,m^3\,s^{-1}$ and $5.6 \times 10^{-5}\,m^3\,s^{-1}$ respectively. For the experiments the range $2.5 \times 10^{-5}\,m^3\,s^{-1}$ – $4 \times 10^{-5}\,m^3\,s^{-1}$ was adopted.

3. Results and discussion

3.1. *Pulsed flow-rate and constant current*

In this first part of the work, the electrolytic current, I, flowing through the cell was imposed continuously, i.e. during t_1 and t_2 as indicated in Fig. 2a. For given operating conditions (current I, flow-rate q, time intervals t_1 and t_2, initial copper concentration) Fig. 3 presents, as a function of the flow-rate Q, the weight change of the cathodic current feeder, the weight change of the anode, the weight of copper recovered on the particles and the copper concentration. Each experiment, corresponding to a given Q value, lasted 5 h. When Q (i.e. the overall bed porosity ε in the pulsed state of the bed) is increased:

the anode loses less copper;

the electrolyte copper concentration remains constant;

the cathodic current feeder loses copper at small Q values and recovers at high Q values;

the particles of the bed recover progressively less copper, but the quantity of the copper recovered is not known with precision owing to losses of copper during the handling of the particles.

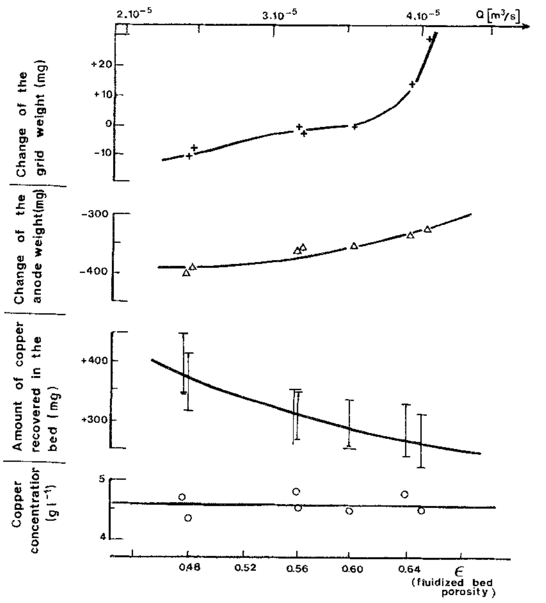

Fig. 3. Influence of the flow-rate for the electrode operating at constant current. *Operating conditions*: $I = 0.8\,A$; $q = 10^{-5}\,m^3\,s^{-1}$; $t_1 = 23\,s$; $t_2 = 2\,s$; initial copper concentration $= 46\,g\,Cu\,l^{-1}$.

The form of the curve showing the amount of copper recovered as a function of Q has to be compared with the variations of the cathodic efficiency with ε for copper recovery in fluidized bed electrodes of copper particles [2, 3]. In [2] the presence of a dissolution zone and of a deposition zone within the fluidized bed was demonstrated; this was possibly due to the bipolar behaviour of the particles and the decrease in the amount of copper recovered when the bed porosity was increased was explained by the growing contribution of the dissolution zone. For the fixed/pulsed system the electrochemical behaviour of the bed in the pulsed situation has a predominant influence in spite of the fact that the pulsation time interval t_2 is lower than t_1. In constant current operation, the overall current efficiency for the removal of copper is thus lowered by the behaviour of the bed in the pulsed situation. Also, at least for the case of Fig. 3, the cathodic current feeder recovers copper; thus, the continuity of the process is questionable.

3.2. *Pulsed flow-rate and pulsed current*

The specific problems arising from the flow of current during the pulsed state of the bed may be avoided if the current feed to the cell is switched off during the corresponding time interval t_2, a situation which corresponds to the use of a pulsed current (Fig. 2b). This was achieved by the simultaneous command of

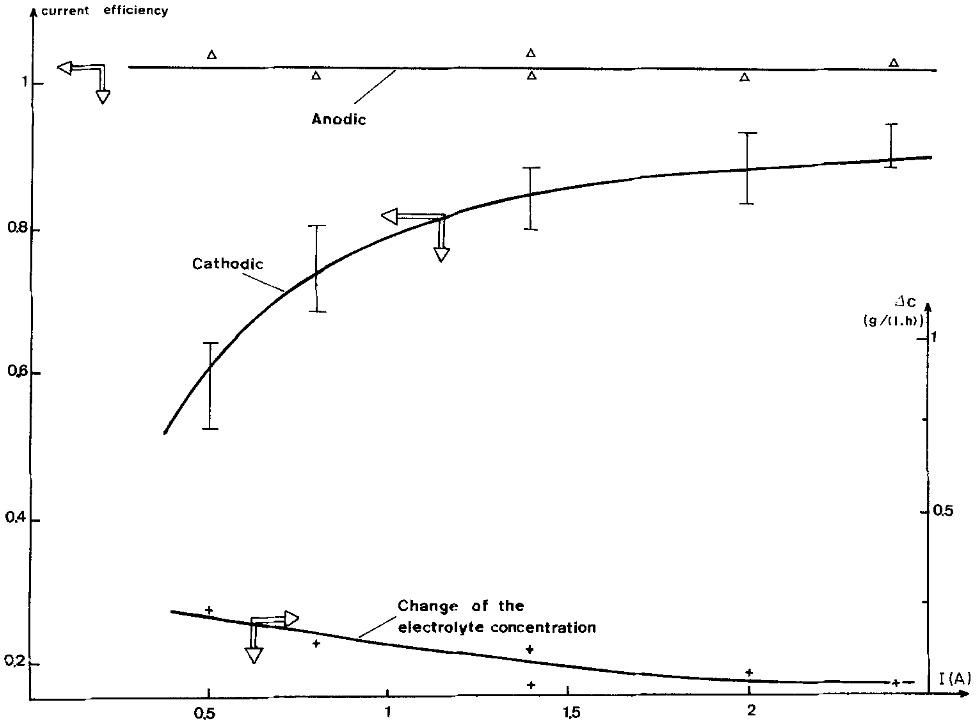

Fig. 4. Influence of the current in pulsed current operation. $L = 0.046\,\mathrm{m}$; $q = 10^{-5}\,\mathrm{m^3\,s^{-1}}$; $t_1 = 23\,\mathrm{s}$; $t_2 = \mathrm{s}$; initial copper concentration $= 4.3\,\mathrm{g\,Cu\,l^{-1}}$.

the electrovalve and of a switch in the electrical circuit. Then the pulsed/fixed electrode recovers copper only during the fixed bed situation. As the aim of the pulsation is now only to put the bed into suspension in order to avoid particle agglomeration, t_1 has to be made as high as possible while t_2 has to be very short. Using $t_1 = 23\,\mathrm{s}$ and $t_2 = 2\,\mathrm{s}$ it was possible to operate the cell for 27 h without any sign of blocking.

Fig. 4 shows the variations with I of the anodic and cathodic current efficiencies and of the change of the electrolyte concentration for 5 h experiments at different constant currents. While the anodic current efficiency is unchanged, the cathodic current efficiency increases with I and the final copper concentration diminishes.

Fig. 5 shows the influence of the fixed bed height, L, on the cathodic current efficiency, all the other parameters being maintained constant. As L is increased,

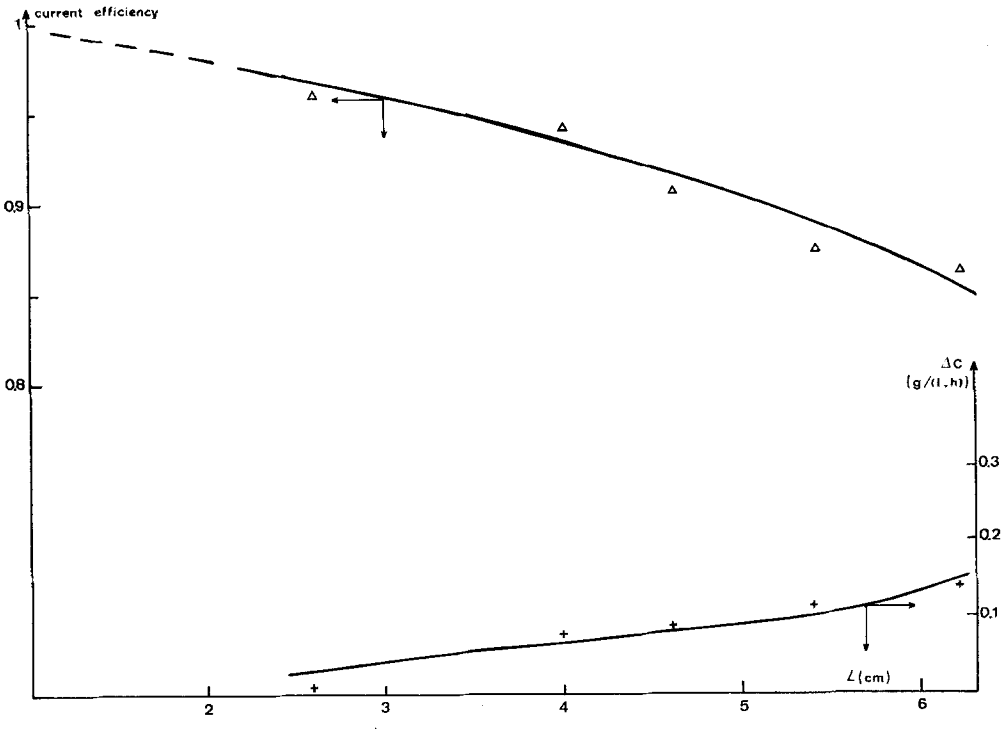

Fig. 5. Influence of the fixed bed height in pulsed current operation. $I = 1.4\,\mathrm{A}$; $q = 10^{-5}\,\mathrm{m^3\,s^{-1}}$; $t_1 = 23\,\mathrm{s}$; $t_2 = 2\,\mathrm{s}$; initial copper concentration $= 3.8\,\mathrm{g\,Cu\,l^{-1}}$; duration of each experiment = 5 h 30 min.

the current efficiency for the metal recovery decreases; the copper concentration increases slightly during each experiment. When L is increased for a given value of I, the local current density within the electrode decreases and thus, according to the results of Fig. 4, the cathodic current efficiency must decrease. Thus the results of Fig. 5 are consistent with those of Fig. 4.

4. Conclusion

The idea of the pulsed/fixed bed electrode for metal recovery from solutions without particle agglomeration is interesting but switching on the current only during the pulsation phase appears to be beneficial. The cathodic current efficiency is 25% higher than that obtained with a fluidized bed electrode [2] and may reach values very near to 100%. Further experimental work is necessary to clarify the behaviour of pulsed beds more fully.

References

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