Electrochemical removal of cadmium using a batch undivided reactor with a rotating cylinder electrode

Javier M Grau and José M Bisang*

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química (UNL), Santiago del Estero 2829, 3000 Santa Fe, Argentina

Abstract: The performance of an undivided electrochemical batch reactor with a rotating cylinder electrode under potentiostatic control is examined for the removal of cadmium from a sodium sulfate solution containing 500 ppm Cd(II) at pH $\cong$ 7. The effect of hydrogen evolution as a side cathodic reaction on the figures of merit of the reactor is analysed. The best results were obtained for a cathode potential of -0.9 V against the saturated calomel electrode. With an angular velocity of 1500 rpm the space time yield and the normalized space velocity were 0.66 mol m^{-3} s^{-1} and 3.9 h^{-1} respectively, while the fractional conversion was 67.3% with a current efficiency of 66.7%. The surface morphology of the deposits as a function of the applied potential is also reported.
© 2001 Society of Chemical Industry

NOTATION

a_e	Specific surface area (m^{-1})
A	Electrode surface area (m^2)
C	Concentration (mol m^{-3})
E_s	Specific energy consumption (Ws mol^{-1} or kWh mol^{-1})
E_{SCE}	Cathode potential referred to saturated calomel electrode (V)
F	Faraday constant (C mol^{-1})
i	Current density (A m^{-2})
I	Total current (A)
k	Mass transfer coefficient (m s^{-1})
n	Ratio between the passed charge and the stoichiometric value
Q	Stoichiometric charge (As)
s_n	Normalized space velocity (s^{-1} or h^{-1})
t	Time (min or s)
U	Cell voltage (V)
V	Effective electrolyte volume within the reactor (m^3)
V_R	Reactor volume (m^3)
x	Fractional conversion
β	Current efficiency
v_e	Charge number of the electrode reaction
ρ_{mean}	Space time yield (mol m^{-3} s^{-1})
ω	Angular velocity (rpm)

1 INTRODUCTION

The cadmium electroplating industry is under pressure from environmental regulatory agencies to minimize hazardous waste and effluent discharge from its operations. However, cadmium coatings offer exceptional corrosion resistance in marine environments, superior lubricity and high electrical conductivity. These conflicting issues in cadmium plating can be resolved by controlling the cadmium concentration in effluents. Thus, cadmium removal methods have received growing attention in recent years, in particular some electrochemical reactors have been proposed. Firstly, the cadmium concentration in effluents is controlled by associating the first wash tank of the electroplating line with a Chemelec cell,[1] which consists of a series of expanded metal electrodes immersed in a fluidized bed of inert glass beads. The Chemelec cell prevents the build-up of cadmium concentration and allows effective operation in the concentration range 50–150 ppm. Likewise, cadmium is recovered because the Chemelec cathodes are used as anodes in the plating bath. The removal of cadmium at very low levels can be performed with three-dimensional electrodes. Thus, Kreysa and Reynvaan[2] reported the use of a packed bed electrode of graphite particles. Carbon felt[3] was also reported to be efficient electrode material. Small cadmium concentrations

were also achieved by using a fluidized bed electrode.[4] However, in an earlier work from this laboratory[5] it was demonstrated that the cadmium deposition takes place at limiting current conditions over a narrow range of potentials, lower than 0.1 V, because of the onset of hydrogen evolution. Taking into account the importance of the potential distribution in the electrode so that the entire cathode operates at the limiting current density, the electrode thickness parallel to the current flow must be small, which restricts the use of three-dimensional electrodes and it is necessary to consider another set-up to give a high value of the product between the mass-transfer coefficient and the active electrode area. In this manner, the rotating cylinder electrode performs as a successful reactor for the cathodic removal of metals,[6] which presents high mass-transfer conditions at a two-dimensional cathode whose surface area is increased by the metal deposition and additionally, under an appropriate design, is able to achieve continuous product extraction. Thus, Gabe and Walsh[7] reported the removal of cadmium from a zinc calcine liquor by means of a divided electrochemical reactor with a rotating cylinder electrode.

The purpose of the work reported here is to analyse the behaviour of an undivided electrochemical reactor with a rotating cylinder electrode for the removal of cadmium and to perform a systematic study of the process variables. Special attention is paid to the effect of hydrogen evolution, which occurs as a side cathodic reaction, on the performance of the reactor in depositing cadmium.

2 EXPERIMENTAL SET-UP AND PROCEDURE

The experiments were performed in an undivided batch reactor, 95 mm internal diameter and 140 mm high. The reactor was thermostatted by a heating jacket. Figure 1 depicts schematically the complete experimental arrangement. The working electrode was a rotating cylinder made of 316 stainless steel, which consists of an active electrode area, 37.9 mm diameter and 30.5 mm long, bounded by Teflon sleeves, 39 mm diameter and 30 mm long. The sleeves protrude by a small distance from the cathode and form a right angle with it, thereby preventing a sharp increase of the current density near the edges, which may lead to a localized dendritic growth of the electrodeposit. Likewise, the recess depth of the cathode is small in order to minimize hydrodynamic edge effects produced by the insulator sleeves.[8] The upper end of the cylinder is attached to the motor shaft. As counterelectrode three platinum wires, 1 mm diameter and 90 mm long, placed symmetrically were used. The working electrode and the counterelectrode were concentric, thereby ensuring a uniform primary current distribution. The interelectrode gap was 11 mm. A saturated calomel electrode was used as reference and the potentials are referred to this electrode. To minimize the error due to the initial surface roughness, the
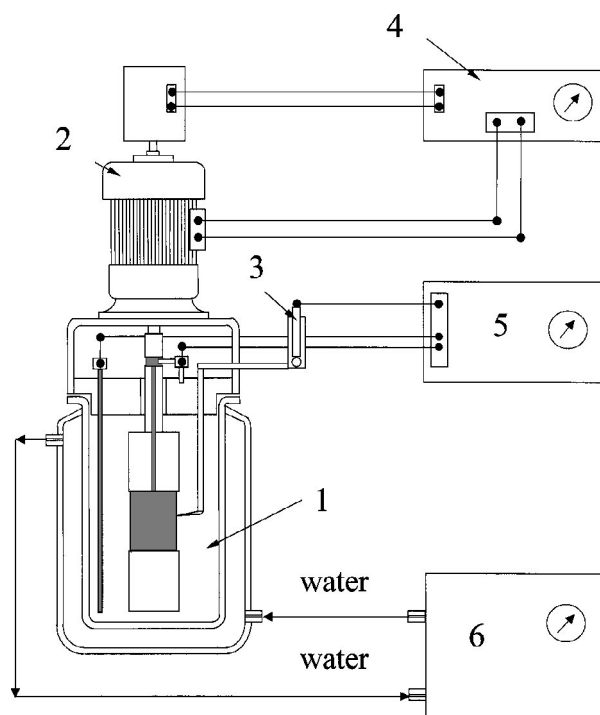

Figure 1. Experimental apparatus: (1) electrochemical reactor, (2) motor, (3) reference electrode, (4) velocity controller, (5) potentiostat, (6) thermostat.

surface of the working electrode was carefully polished with emery paper 600; it was washed with tap water followed by distilled water. All experiments were performed at 30 °C under potentiostatic control up to a charge of nQ was passed, where Q is the theoretical electrical charge necessary to deposit the initial cadmium, termed the stoichiometric charge, and n is 0.5, 1, 2 or 3. The theoretical charge was calculated according to Faraday's Law assuming 100% current efficiency. The supporting electrolyte was 1 M Na_2SO_4 at pH $\cong$ 7 with an initial cadmium concentration of approximately 500 ppm. The solution volume in each experiment was 0.5 dm^3. The anodic reaction was oxygen evolution:
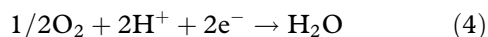
$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \tag{1}$$
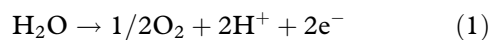
The main cathodic reaction was:

$$Cd^{+2} + 2e^- \rightarrow Cd \tag{2}$$
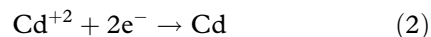
and the side reactions were the hydrogen evolution:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$
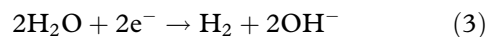
and the reduction of oxygen:

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{4}$$

Reaction (4) can be considered negligible because of the low value of the oxygen concentration.

Cadmium hydroxide precipitates at pH $\cong$ 8.7 for a cadmium concentration in solution of 500 ppm, and the precipitation occurs at higher pH as the cadmium concentration decreases. For the experiments an undivided reactor was adopted taking into account

mainly two aspects. On one hand for cadmium removal from waste waters it is unnecessary to use a divided reactor, which shows complex constructive features and requires higher cell voltage for a given current. On the other hand the cathodic side reaction increases the pH of the solution, but in an undivided reactor the evolution of oxygen from the anodic reaction decreases the pH value. Thus, when the current is connected the pH decreases with time because the generation of hydrogen ions by the anodic reaction is higher than the production of hydroxyl ions by the side reaction (3) and cadmium hydroxide precipitation is hindered.

During the experiment, samples of solution were taken from the reactor in order to determine the cadmium concentration by complexometry.[9]

3 REACTOR PERFORMANCE

In order to analyse the performance of the rotating cylinder electrode and to compare the experimental results with previous studies of cadmium deposition or with other cells for metal ion removal some 'figures of merit' will be introduced.

The space time yield is the amount of product which can be produced within a unit volume reactor per unit time. For a batch reactor the mean value of the space time yield during the time t of the experiment is given by

$$\rho_{\text{mean}} = \frac{V[C(0) - C(t)]}{V_{\text{R}} t} \qquad (5)$$

Equation (5) expressed in terms of the fractional conversion and assuming $V = V_{\text{R}}$ is

$$\rho_{\text{mean}} = \frac{C(0)x(t)}{t} \qquad (6)$$

The normalized space velocity, s_{n}, is a figure of merit frequently used to compare electrochemical reactors for the treatment of waste waters. s_{n} is the volume of waste water in which the reactant concentration is reduced by 90% in a unit volume reactor per unit time. However, the calculation of s_{n} requires the adoption of a mathematical model to represent the electrochemical reactor. For a rotating cylinder electrode the electrolyte is assumed to be well-mixed at all times. In a batch reactor where the cadmium deposition takes place simultaneously with the hydrogen evolution the change of the cadmium concentration with time under potentiostatic control is given by:

$$\frac{dC(t)}{dt} = -\frac{i(t)\beta(t)A(t)}{v_{\text{e}}FV} \qquad (7)$$

In eqn (7) A is a function of time because the cadmium deposition alters the electrode surface area. According to a previous work from this laboratory[5] for potentials more negative than $-0.85\,\text{V}$ the cadmium deposition on a cadmium cathode is mass-transfer controlled,

thus

$$i(t)\beta(t) = v_{\text{e}}Fk(t)C(t) \qquad (8)$$

where for the calculation of the mass-transfer coefficient a combined effect of the forced convection, due to the angular velocity, and of the bubble-induced convection, due to the hydrogen evolution, must be taken into account. Likewise, it must be recognized that when the electrode surface is covered with cadmium the hydrogen evolution is inhibited and it is expected that the bubble-induced convection component of the mass-transfer coefficient changes with time. Combining eqns (7) and (8) yields

$$\frac{dC(t)}{dt} = -\frac{k(t)a_{\text{e}}(t)C(t)V_{\text{R}}}{V} \qquad (9)$$

Equation (9) reveals the complex nature of the present electrochemical reactor due to the fact that both reactions that take place at the cathode are highly coupled. On one hand the hydrogen evolution promotes the mass-transfer of Cd(II) ions to the cathode, increasing the cadmium deposition rate and modifying the electrode surface area and on the other hand when the stainless steel electrode is covered with cadmium the hydrogen evolution is inhibited. Therefore, the high coupling between both cathodic reactions makes the rigorous mathematical model of the reactor difficult. However, for short times of the experiment it may be assumed that ka_{e} is not a function of time and the conventional theory of simple batch reactor can be applied. Thus, for $V = V_{\text{R}}$ is

$$x(t) = 1 - \exp(-k\,a_{\text{e}}t) \qquad (10)$$

and

$$s_{\text{n}} = \frac{k\,a_{\text{e}}}{\ln 10} \qquad (11)$$

Combining eqns (10) and (11) yields

$$s_{\text{n}} = -\frac{\ln[1 - x(t)]}{t \ln 10} \qquad (12)$$

Likewise, the specific energy consumption during the time t of the experiment is given by

$$E_s = \frac{\int_0^t U(t)I(t)\,dt}{VC(0)x(t)} \qquad (13)$$

4 RESULTS AND DISCUSSION

Figure 2 shows the current as a function of time for three experiments performed at $-1.0\,\text{V}$. The thick full line represents the mean value of the current and typical bars of the standard error of the mean are also reported. Likewise, the standard error of the mean and the histogram are included as insets in Fig 2. The curves present small differences between them because of the roughness of the electrode produced by the cadmium deposition, nevertheless the reproducibility
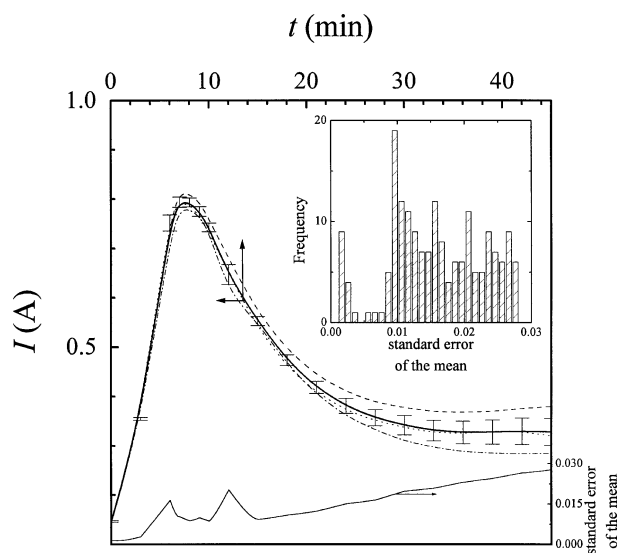
Figure 2. Reproducibility study of the current as a function of time. (---), (···) and (-·-): three different experiments performed at −1.0V. ω:1000rpm. Initial cadmium concentration $\cong$ 500ppm. Supporting electrolyte: 1 M Na$_2$SO$_4$ at pH $\cong$ 7. T=30°C. Thick full line: mean value of the current. Bars: typical values of standard error of the mean. Insets: histogram of the standard error of the mean and thin full line: standard error of the mean.

of the experiments is acceptable. The mean value of the standard error of the mean is 0.01574 A with a standard deviation of 0.00704 A. Likewise, the curves of Fig 2 show a maximum, which is the consequence of two opposite effects. On one hand the cadmium deposition increases, by the increase in the roughness, the electrode surface area and thus the total current. On the other hand, in a batch reactor the cadmium concentration decreases with time. The second factor predominates over the first at high times and the current shows a maximum.

Figure 3 shows typical responses of the temporal behaviour in current at different applied potentials. Curves of the same shape were obtained indepen-
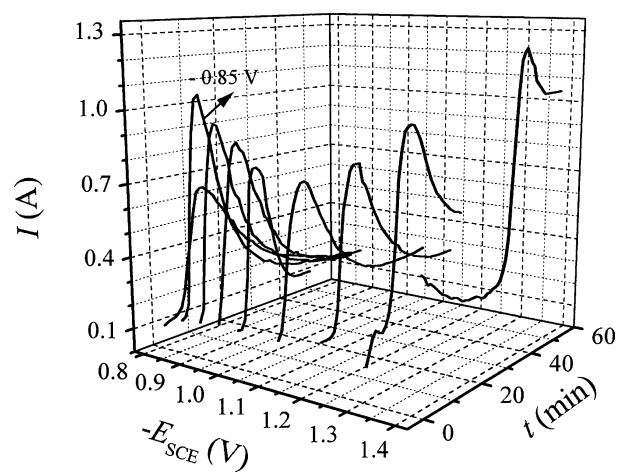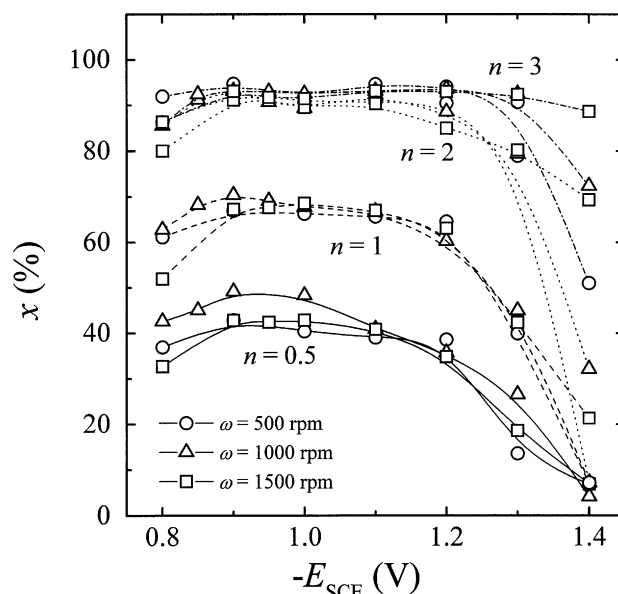
Figure 3. Current as a function of time at different applied potential. ω:1000rpm. Initial cadmium concentration $\cong$ 500ppm. Supporting electrolyte: 1 M Na$_2$SO$_4$ at pH $\cong$ 7. T=30°C.
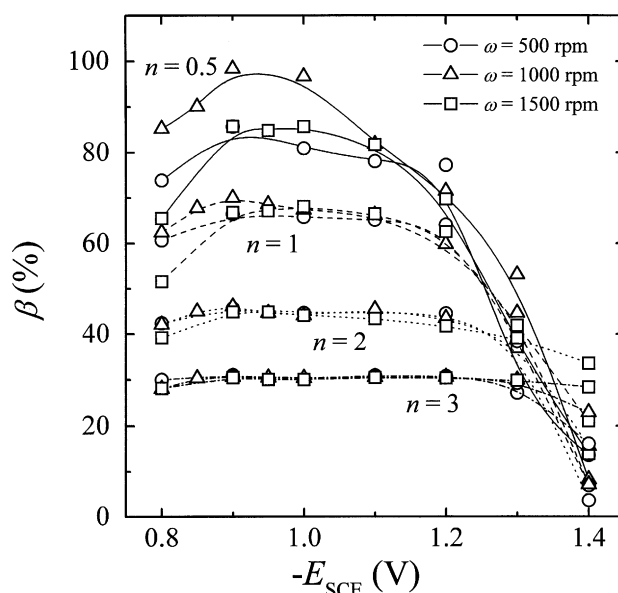
Figure 4. Current efficiency as a function of the applied potential at different values of the charge passed in the reactor. Initial cadmium concentration $\cong$ 500ppm. Supporting electrolyte: 1 M Na$_2$SO$_4$ at pH $\cong$ 7. T=30°C.

dently of the angular velocity. It can be observed that the position of the maximum and its numerical value depend on the applied potential to the cathode. With the exception of the curve obtained at −0.8V, the position of the maximum shifts towards higher times when the applied potential becomes more negative. Likewise, the numerical value of the maximum decreases when the potential decreases from −0.85V to −1.1V and increases for potentials lower than −1.2V.

Figures 4 and 5 respectively show the current

Figure 5. Fractional conversion as a function of the applied potential at different values of the charge passed in the reactor. Initial cadmium concentration $\cong$ 500ppm. Supporting electrolyte: 1 M Na$_2$SO$_4$ at pH $\cong$ 7. T=30°C.
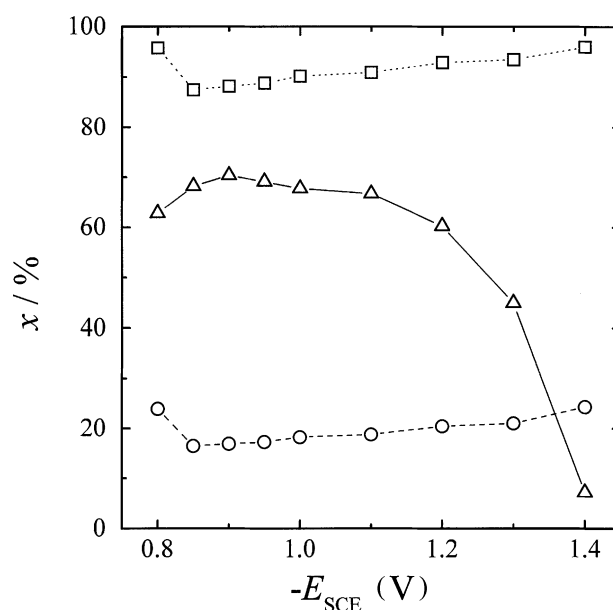
efficiency and the fractional conversion as a function of potential at different angular velocities and for different values of the charge passed in the reactor. The curves show a maximum, which is more pronounced at low values of the charge. This behaviour may be explained by taking into account that for all potentials at a stainless steel cathode the cadmium deposition takes place simultaneously with the hydrogen evolution and both reactions are highly coupled. Thus, hydrogen evolution promotes localized turbulence near the electrode surface, enhancing the mass transfer of Cd(II) to the electrode. However, when the electrode surface is covered with cadmium the hydrogen evolution is inhibited. At high potentials, for example −0.8V, the cadmium deposition is low and the required time to cover the electrode with cadmium is large. Thus, the hydrogen evolution predominates and the current efficiency and the fractional conversion are low. When the potential is more negative the rate of cadmium deposition increases, becomes mass-transfer controlled and may be influenced by the turbulence promoting action of the hydrogen evolution, also termed bubbled-induced convection. Thus, the time to cover the electrode surface area with cadmium is reduced, the hydrogen evolution is inhibited earlier and both the current efficiency and the fractional conversion increase. This behaviour is sharper when the passed charge is low. At very negative potentials the hydrogen evolution predominates and low values of current efficiency and fractional conversion are measured. It must be recognized that the values of current efficiency for cadmium deposition reported by Gabe and Walsh[7] lay in the range of 50–80%. Figure 5 also shows that in the potential range from −0.8V to −1.2V the fractional conversion approaches 90% when the charge passed in the reactor duplicates the stoichiometric value.

From a practical point of view, the analysis of the experimental data for high values of the charge passed in the reactor is interesting for the production of thick spongy deposits, where it can be observed that the effect of the angular velocity on the current efficiency and fractional conversion is negligible. The analysis for the small values of the passed charge shows a different behaviour. On one hand the current efficiency and the fractional conversion are influenced by the angular velocity and on the other hand represent a similar situation to that presented for the production of cadmium powder with continuous separation of the metal from the electrode. Thus, a surface area of stainless steel or partially covered with cadmium is offered. Taking into account Figs 4 and 5 it can be observed that an applied potential near −0.9V is a promising value to produce cadmium powder, due to the fact that the current efficiency and the fractional conversion are high with a maximum value of the total current.

In order to explain the influence of the angular velocity on the current efficiency and on the fractional conversion it must be recognized that for potentials

more negative than −0.85V the cadmium deposition is under limiting current conditions[5] and the mass-transfer coefficient presents a combined effect of the forced convection, due to the angular velocity, and the bubble-induced convection, due to the hydrogen evolution. On one hand, for a given applied potential an increase in the angular velocity increases the current of the cadmium deposition because the convective mass-transfer coefficient is higher. On the other hand when the current of the cadmium deposition increases the bubble-induced convection coefficient decreases due to the fact that hydrogen evolution is inhibited. When the passed charge is low, the maximum in the current efficiency and in the fractional conversion is a consequence of these two opposite effects as the angular velocity increases. When the passed charge is high the current efficiency and the fractional conversion are not influenced by the angular velocity due to the fact that the increase of the convective mass-transfer coefficient is counterbalanced by the faster depletion of the cadmium concentration in the solution.

Figure 6 compares the experimental data of fractional conversion for $\omega = 1000$ rpm and $n = 1$ with the theoretical values given by eqn (10). For the calculations the experimental time values to pass the stoichiometric charge for each potential were used and the mass-transfer coefficient was calculated according to the correlations of Eisenberg *et al*,[10] valid for smooth electrodes and represented by the dashed line, and Holland,[11] valid for metal powder deposition and represented by the dotted line. It is observed that the theoretical prediction according to the dashed line is lower than the experimental values of fractional

Figure 6. Comparison of the experimental fractional conversion with theoretical predictions. Full line: experimental values. Dashed line: eqn (10) with a mass-transfer coefficient according to Eisenberg *et al*[10] correlation. Dotted line: eqn (10) with a mass-transfer coefficient according to Holland expression.[11] Initial cadmium concentration $\cong$ 500 ppm. Supporting electrolyte: 1 M Na_2SO_4 at pH $\cong$ 7. T = 30 °C. $n = 1$. $\omega = 1000$ rpm.
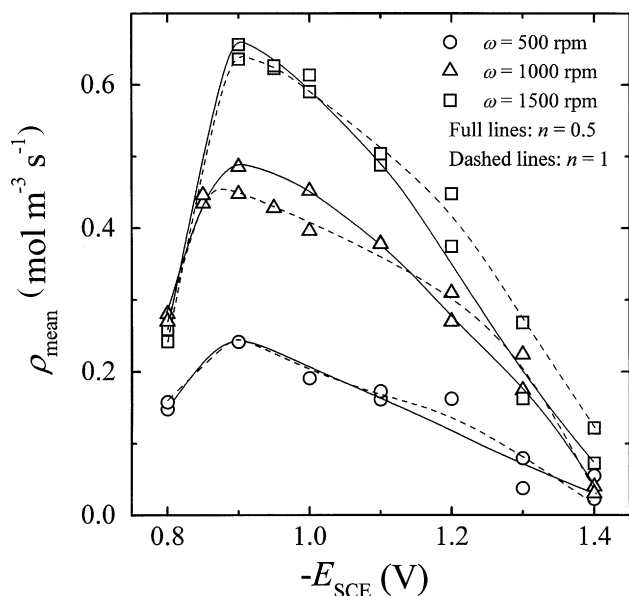
Figure 7. Mean value of the space time yield as a function of the applied potential for the smaller values of charge passed in the reactor. Initial cadmium concentration $\cong$ 500 ppm. Supporting electrolyte: 1 M Na_2SO_4 at pH $\cong$ 7. T=30 °C.
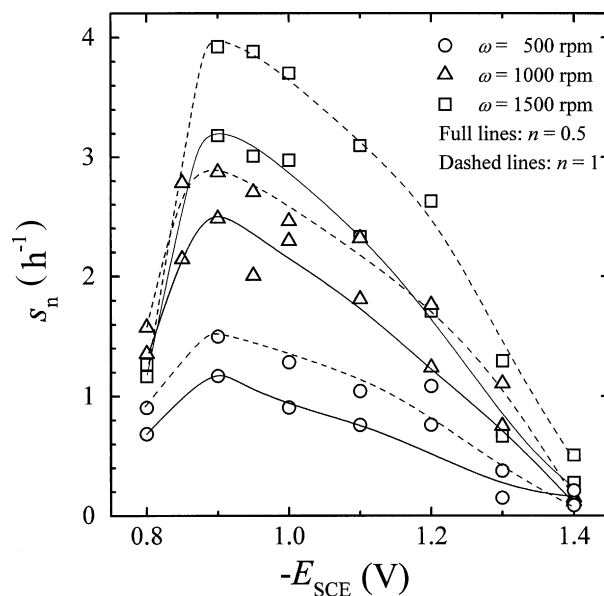

Figure 9. Normalized space velocity as a function of the applied potential for the smaller values of charge passed in the reactor. Initial cadmium concentration $\cong$ 500 ppm. Supporting electrolyte: 1 M Na_2SO_4 at pH $\cong$ 7. T=30 °C.

conversion due to the fact that the cadmium deposition increases the electrode surface area. Likewise, the dotted line, which takes into account a mass-transfer coefficient for metal powder production, gives theoretical values higher than the experimental ones, because of the cadmium deposition takes place simultaneously with the hydrogen evolution, which consumes a portion of charge during the time of the experiment.
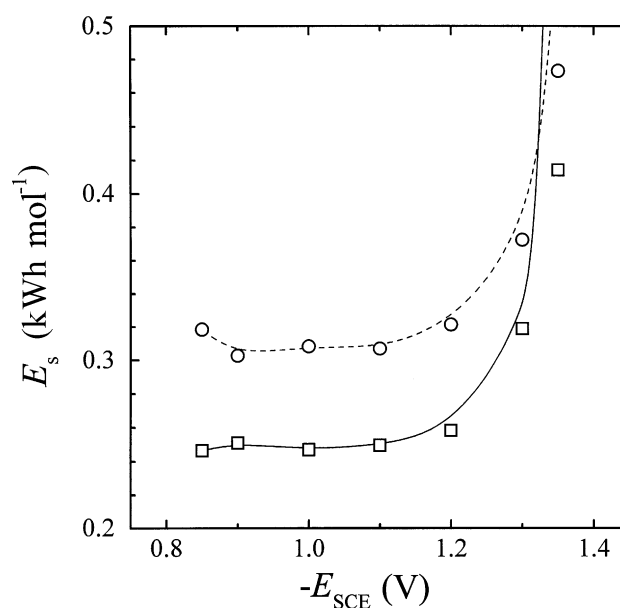
Figure 7 shows some results of the mean value of space time yield, calculated with eqn (6), as a function of potential at different angular velocities and for the smaller values of the charge passed in the reactor.

Figure 7 confirms the finding from the previous figures, the space time yield shows a maximum when the potential is approximately -0.9 V and increases when the angular velocity increases.
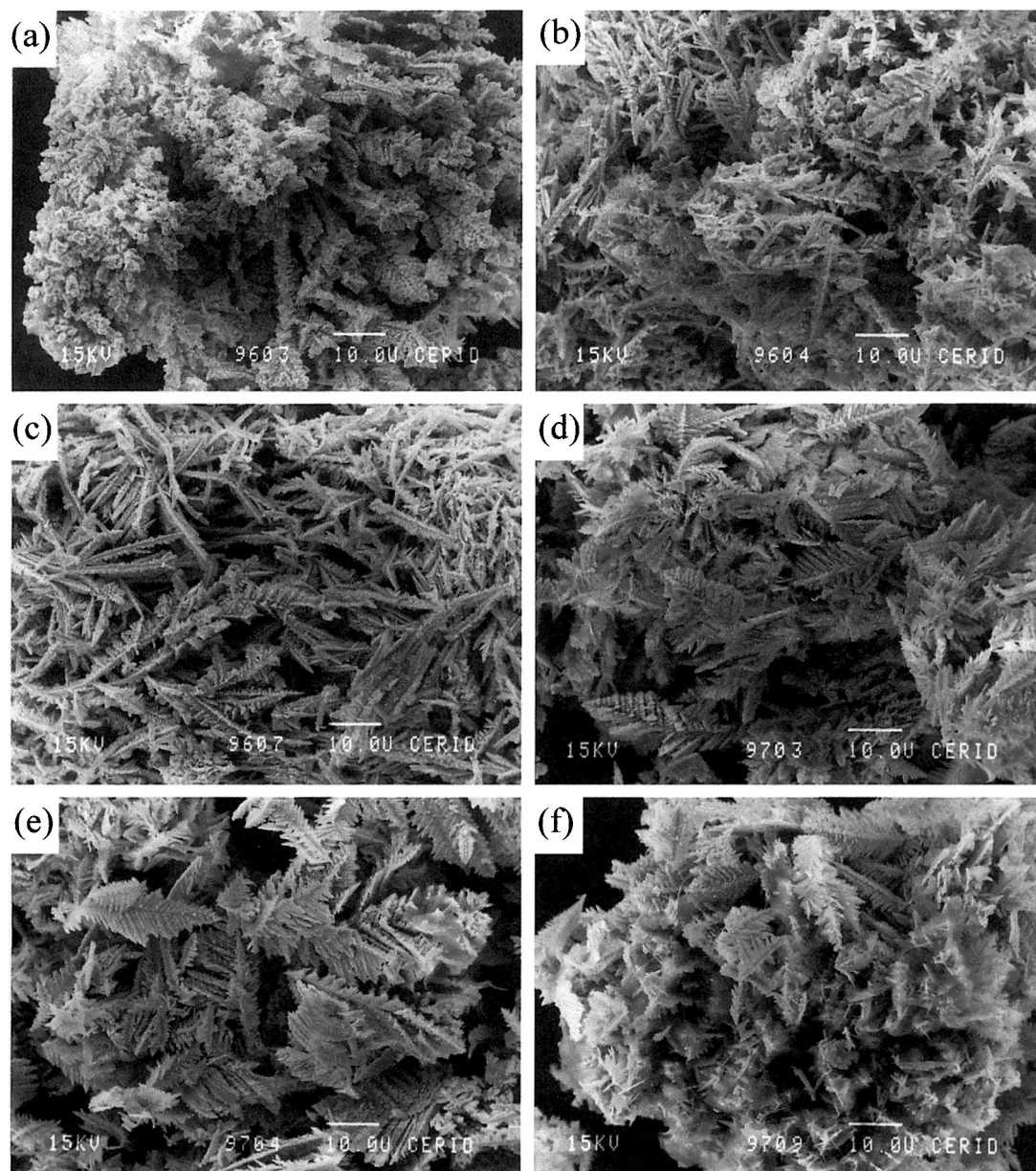
In order to explain the maximum in the space time yield, Fig 8 shows some typical curves of the required time to pass different charges as a function of potential. It can be observed that the required time to pass a given charge decreases at high potential, as expected, and increases when the potential becomes more negative due to the fact that the cadmium deposition has inhibited hydrogen evolution. This
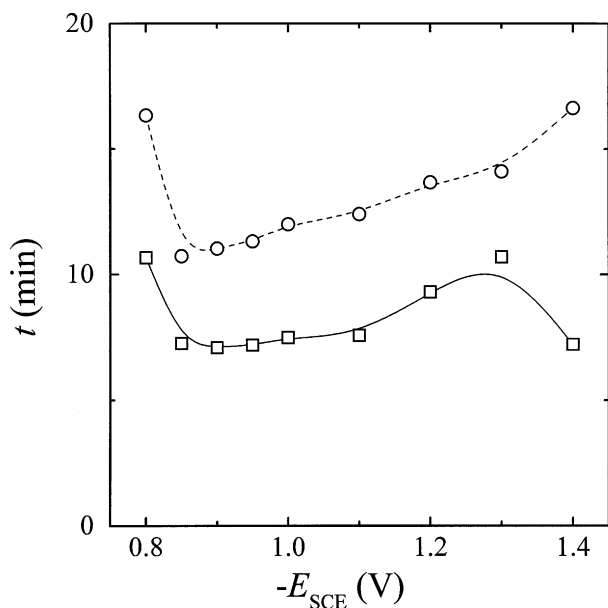
Figure 8. Time required to pass the specified charge as a function of applied potential. Initial cadmium concentration $\cong$ 500 ppm. Supporting electrolyte: 1 M Na_2SO_4 at pH $\cong$ 7. T=30 °C. ω=1000 rpm. Full line: n=0.5. Dashed line: n=1.

Figure 10. Specific energy consumption as a function of the applied potential. Initial cadmium concentration $\cong$ 500 ppm. Supporting electrolyte: 1 M Na_2SO_4 at pH $\cong$ 7. T=30 °C. ω=1000 rpm. Full line: n=0.5. Dashed line: n=1.

Figure 11. Scanning-electron micrographs of cadmium powders at different potentials. (a) $-0.85\,V$, (b) $-0.9\,V$, (c) $-1.0\,V$, (d) $-1.2\,V$, (e) $-1.3\,V$, (f) $-1.4\,V$, Cadmium concentration $\cong 500\,ppm$. Supporting electrolyte: $1\,M$ Na_2SO_4 at pH $\cong 7$. T $= 30\,°C$. $\omega = 1000\,rpm$. $n = 1$. Magnification: $\times 1200$.

behaviour is opposite to the behaviour reported in a previous work,[12] where iron(II) oxidation and oxygen evolution were analysed simultaneously. It must be recognized that in the present work the main reaction is highly coupled with the side reaction while in the previous work both reactions were independent.

Figure 9 shows some results of the normalized space velocity, calculated with eqn (12), as a function of the applied potential at different angular velocities and for the smaller values of the charge passed in the reactor. The curves of s_n exhibit the same shape as the curves of space time yield with a maximum at $-0.9\,V$. The normalized space velocity increases with the angular velocity because of the increase of the convective mass-transfer coefficient. The maximum s_n value is approximately $4\,h^{-1}$, which is near the values reported by Walsh[13] ($4.2 < s_n/h^{-1} < 4.8$) obtained on a pilot-scale rotating cylinder electrode reactor for the single pass

mode of operation using copper deposition as test reaction. From the data of Gabe and Walsh[7] a higher value, $15.6\,h^{-1}$, of the normalized space velocity for cadmium removal is calculated, which is a consequence of the high value given for a_e. However, these s_n values are lower than those reported for electrochemical reactors with three-dimensional electrodes, which present higher specific surface area.

The effect of the applied potential on the specific energy consumption is shown in Fig 10. At potentials more positive than $-1.2\,V$ and for the stoichiometric value of the charge passed in the reactor E_s is near $0.3\,kWh\,mol^{-1}$, which is in accordance with the value reported by Ibl[14] for the electrochemical production of copper powder but is slightly lower than the value reported by Gabe and Walsh[7] for cadmium removal using a divided electrochemical reactor. When the potential is more negative than $-1.2\,V$ a sharp increase

in E_s is observed because the hydrogen evolution decreases the current efficiency of cadmium deposition.

The surface morphology of the electrodeposited cadmium powders at different applied potentials, obtained at 1000 rpm and for the stoichiometric charge, was examined by scanning electron microscopy (SEM) and the results are shown in Fig 11. The highly dendritic nature of the cadmium deposits is revealed. As expected, in the potential range from -1 V to -1.4 V, the deposits showed similar surface morphology, due to the fact that the deposition process takes place at limiting current, but the cadmium dendrites increase the feather-like appearance as the potential is lowered. Calusaru[15] reported the same surface morphology for cadmium deposits obtained from more concentrated solutions. However, it can be observed that the deposits at -0.85 V and -0.9 V are also highly dendritic but with a slightly different morphology.

5 CONCLUSIONS

The following conclusions may be drawn:

(i) It was demonstrated that the cadmium removal from dilute aqueous solution could be performed in an efficient manner in an electrochemical reactor with a rotating cylinder electrode. Therefore, from Figs 4 and 5 it can be seen that in the potential range from -0.85 V to -1.1 V the current efficiency and the fractional conversion are similar and are also independent of the angular velocity for higher values of the passed charge. Therefore, it is possible to define a large range of potentials where thick spongy deposits of cadmium can be produced.

(ii) Taking into account Figs 7 and 9 it can be concluded that for the lower values of the passed charge the maximum values of space time yield and normalized space velocity are achieved when the potential is approximately -0.9 V. This value may be considered as an optimum for the applied potential to the cathode in order to produce cadmium powder.

(iii) The side reactions cannot be considered *a priori* as detrimental for the performance of electrochemical reactors, in many important industrial cases the side reactions can be beneficial, such as the case in the present study where the turbulence promoted by the side reaction increases the current of the main reaction.

REFERENCES
1 Tyson AG, An electrochemical cell for cadmium recovery and recycling. *Plat Surf Finish* **71**:44–47 (1984).
2 Kreysa G and Reynvann G, Optimal design of packed bed cells for high conversion. *J Appl Electrochem* **12**:241–251 (1982).
3 Pletcher D, Metal ion removal from effluents. *Watts New* (Newsletter from the Electrosynthesis Company, Inc) **2**:No 3 (1996).
4 van der Heiden G, Raats CMS and Boon HF, Fluidised bed electrolysis for removal or recovery of metals from dilute solutions. *Chem and Ind* (London) **July**:465–468 (1978).
5 Grau JM and Bisang JM, Cadmium removal from aqueous sulphate solutions by treatment with iron felts. *J Chem Technol Biotechnol* **73**:398–404 (1998).
6 Walsh FC, The role of the rotating cylinder electrode reactor in metal ion removal, in *Electrochemistry for a Cleaner Environment*, Ed by Genders D and Weinberg N, The Electrosynthesis Company Inc, New York. pp 101–159 (1992).
7 Gabe DR and Walsh FC, Removal of cadmium from a zinc calcine liquor by means of a rotating cylinder electrode reactor. *Proc Reinhardt-Schuhmann, Symp Ser Met Soc (AIME)*: 775–794 (1987).
8 Dinam TE, Matlosz M and Landolt D, Experimental investigation of the current distribution on a recessed rotating disk electrode. *J Electrochem Soc* **138**:2947–2951 (1991).
9 Merck AG, Cadmio, in *Métodos Complexométricos de Valoración con Titriplex*, 3rd edn, Ed by Merck AG, Darmstadt. pp 23–24.
10 Eisenberg M, Tobias CW and Wilke CR, Ionic mass transfer and concentration polarization at rotating electrodes. *J Electrochem Soc* **101**:306–319 (1954).
11 Holland FS, The development of the Eco-Cell process. *Chem and Ind* (London) **July**:453–458 (1978).
12 Bisang JM, Electrochemical treatment of waste solutions containing ferrous sulfate by anodic oxidation using an undivided reactor. *J Appl Electrochem* **30**:399–404 (2000).
13 Walsh FC, Determination of the normalised space velocity for continuous stirred tank electrochemical reactors. *Electrochim Acta* **38**:465–468 (1993).
14 Ibl N, Applications of mass transfer theory: the formation of powdered metal deposits, in *Advances in Electrochemistry and Electrochemical Engineering*, Ed by Delahay P and Tobias CW, Interscience Publishers, New York. Vol 2, p 55 (1962).
15 Calusaru A, *Electrodeposition of Metal Powders*, Elsevier Science Publishers, Amsterdam. p 255 (1979).