JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 745–750

An electrochemical hydrocyclone cell for the treatment of dilute solutions: approximate plug-flow model for electrodeposition kinetics

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Received 20 July 1992; revised 27 September 1993

The mass transfer conditions in a hydrocyclone cell have been analysed and an approximate plug-flow model has been developed to describe metal ion depletion during batch recycle operation. The resulting concentration–time relationship and reaction rate equation has been shown to describe satisfactorily the experimental data obtained for the electrodeposition of copper and silver from dilute solutions. Moreover, these relationships have enabled the evaluation of mass transfer coefficients in the hydrocyclone cell.

List of symbols

a_1, a_2, b	numerical exponents
C	concentration (mol dm^{-3})
C_o	initial bath concentration (mol dm^{-3})
$C(0)$	cell inlet concentration (mol dm^{-3})
$C(\mathrm{L})$	cell outlet concentration (mol dm^{-3})
k	rate constant (h^{-1})
K	mass transfer coefficient (m s^{-1})
K_L	volumetric mass transfer coefficient $= 2\pi RLK$ (m^3 s^{-1})
L	'active' length of the cylindrical cathode (m)
Q	volumetric flow rate (m^3 s^{-1})
r	inside radius of the conical part of the cell
r_A	reaction rate of component A (mol dm^{-3} h^{-1})
R	inside radius of the cylindrical part of the cell (m)
t	time
u	vertical (axial) velocity in the annulus
U	cell voltage (V)
v_t	horizontal (tangential) velocity in the annulus
V_B	volume of the reservoir/bath
V_R	volume of the cell/reactor
τ_B	residence of time of the reservoir

1. Introduction

The hydrocyclone is an effective item of industrial equipment, well known for its simple modular design, without moving parts, and its high throughput per unit volume. Based on its principal feature of helical downward accelerated flow (Fig. 1) [1, 2], and considering the advantages regarding industrial application, a novel electrochemical reactor has been developed as the hydrocyclone cell (HCC). This has been recently used in metal recovery from dilute solutions [3].

The present work analyses mass transfer conditions in the HCC and develops an approximate model for describing the kinetics of electrodeposition.

2. Apparatus

The HCC and the schematic arrangement of the experimental setup are shown in Fig. 2. The stainless steel hydrocyclone wall (a) serves as cathode. As depicted, the standardized cyclone of 78 mm diameter [4–6] is modified: in the central exit a graphite/stainless steel block, as an anode (b), is situated concentrically and is surrounded by a cation-exchange membrane (c), type Thomapor 50382, which acts as 'vortex finder' (Fig. 1). Two reservoirs, coupled with the cell via a sliding-vane type rotary pump, enable either batch recycle or single-pass mode experiments to be performed. The reservoirs are considered to be well mixed. Redissolution of the metal deposit can be achieved by polarity reversal.

The HCC is characterized by a helical downward accelerated flow along the cathode surface (due to the conical shape of the cathodic compartment). This plays an important role in metal recovery since higher mass transfer coefficients occur towards the apex, i.e. in the region with lower metal content [3].

3. Mass-transfer conditions in HCC

The accelerated helical flow in the HCC is different to that observed in rotating disc [7], cylinder [8, 9, 10] or cone [11] electrodes, and even to that observed in cells with helical/swirling flow [12–20]. Because of the paucity of data for mass transfer in the hydrocyclone geometry, it is relevant to discuss the case of the rotating cylinder electrode with axial flow [13]. For this case the mass transfer coefficient may be written as

$$K \sim u^{a_1} v_t^{a_2} \tag{1}$$

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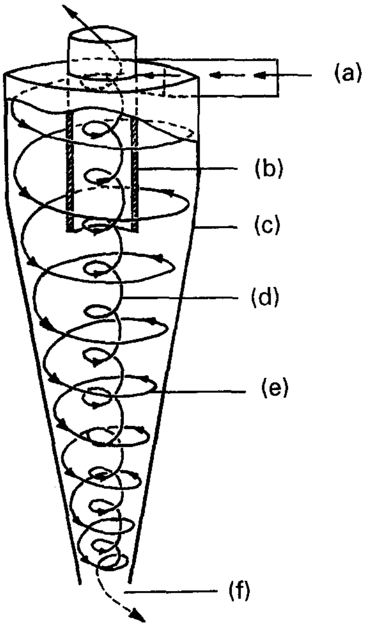


Fig. 1. Schematic representation of the spiral-within-spiral flow pattern in the hydrocyclone. (a) Inlet, (b) vortex finder, (c) hydrocyclone wall, (d) helical upward flow, (e) helical downward flow, (f) apex-opening.

where u is the axial velocity, v_t is the tangential velocity and a_1 and a_2 are two exponents which, in the turbulent regime, may be considered as 0.33 and 0.4, respectively [13].

In the cylindrical part of the hydrocyclone (Fig. 3(a))

$$u \sim Q \tag{2}$$

and, according to Kelsall [21],

$$v_t \sim Q^{1.12} \tag{3}$$

where Q represents the volumetric flow rate. For the conical part we can write

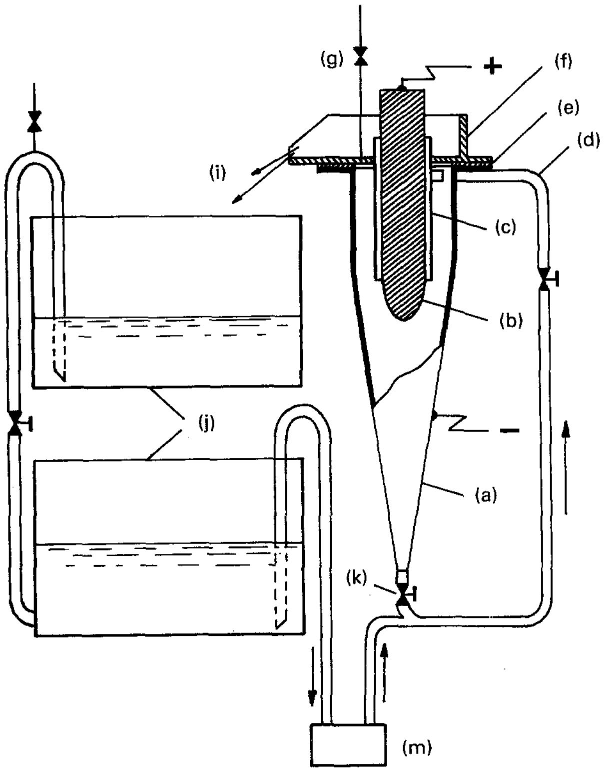
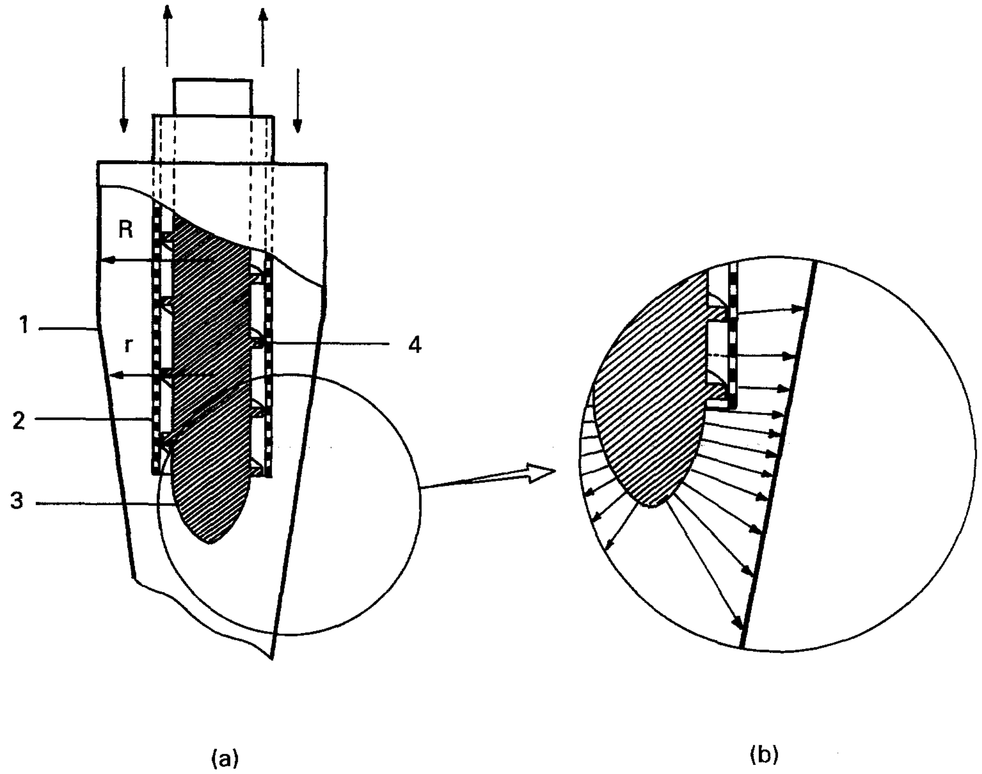


Fig. 2. Schematic arrangement of HCC-system. (a) Cathode, (b) anode, (c) cation exchange membrane, (d) electrolyte inlet, (e) Teflon-gasket, (f) transparent Perspex cell top, (g) vent, (i) electrolyte outlet, (j) electrolyte reservoirs, (k) apex valve, (m) recirculating pump.

$$u \sim Q/r^2 \tag{4}$$

and referring to the data of Kelsall [21, fig. 6]

$$v_t \sim Q^{1.12}/r^{5/9} \tag{5}$$



(a) (b)

Fig. 3. Schematic representation of (a) HCC-concept and (b) electrical field configuration near the bottom of vortex-finder. (1) Cathode (hydrocyclone wall), (2) cation exchange membrane (vortex-finder), (3) anode, (4) helical wings.

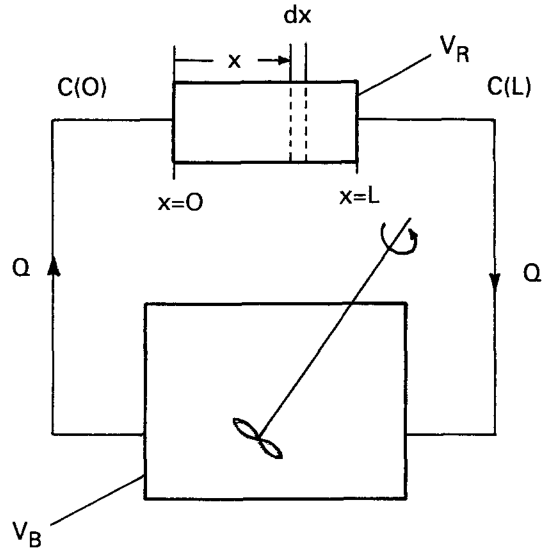


Fig. 4. Electrochemical cell in batch recycle mode of operation.

Taking into account the above mentioned numerical values for a_1 and a_2, substitution of u and v_t into Equation 1 leads to the following expressions:
for the cylindrical part

$$K \sim Q^{7/9} \tag{6}$$

for the conical part

$$K \sim Q^{7/9}/r \tag{7}$$

In other words, the product of the mass transfer coefficient with the wall surface is almost independent of r. Thus, the whole cell can be considered cylindrical with the following mass transfer coefficient

$$K \sim Q^{b} \tag{8}$$

where b has a numerical value of $\sim 7/9$.

Furthermore, due to the geometry of the HCC, the interelectrode gap at the bottom of the vortex finder (Fig. 3(b)) varies and the electrical field becomes less uniform. Consequently the cathode activity is strongly influenced by the cell voltage.

4. Theory

Consider the HCC in the batch recycle mode of operation shown in Fig. 4. Following the analysis described elsewhere [22–24] and taking into account that in the present experiments the initial metal concentrations varied from 60 to 110 p.p.m. and the ratios V_B/V_R from 45 to 90 [3], the assumptions involved in the present work are as follows:

(a) The spiral movement of the electrolyte through the cathodic compartment may be approximated to plug-flow.

(b) The concentration of the metal ion is very low and hence the electrochemical reaction is mass transfer controlled.

(c) The reservoir is a perfectly stirred tank.

(d) The volume of the cell is very small compared with that of the reservoir and hence the change in metal concentration with time is negligible as compared to its change with length.

According to (d), the differential mass balance over a cylindrical element of length dx (Fig. 4) yields

$$\frac{\mathrm{d}C}{\mathrm{d}x} = -\left(\frac{2\pi RK}{Q}\right)C \tag{9}$$

which, after integration, leads to

$$C(\mathrm{L}) = C(0)\exp\left(\frac{-2\pi RLK}{Q}\right) \tag{10}$$

Since it is difficult to separate the contribution of the volumetric flow rate on mass transfer coefficient from that of the cell voltage on the cathode activity, it is convenient to use a volumetric mass transfer coefficient

$$K_{\mathrm{L}} = 2\pi RLK \tag{11}$$

Thus the outlet concentration is

$$C(\mathrm{L}) = C(0)\exp\left(\frac{-K_{\mathrm{L}}}{Q}\right) \tag{12}$$

The mass balance for the reservoir may be written as

$$V_{\mathrm{B}}\frac{\mathrm{d}C(0)}{\mathrm{d}t} = Q[C(\mathrm{L}) - C(0)] \tag{13}$$

Substitution of Equation 12 into Equation 13 and integration leads to the following expression for the concentration–time dependence:

$$C(0) = C_{\mathrm{o}}\exp\left\{-\frac{t}{\tau_{\mathrm{B}}}\left[1 - \exp\left(\frac{-K_{\mathrm{L}}}{Q}\right)\right]\right\} \tag{14}$$

Solving the last equation with respect to K_{L} gives

$$K_{\mathrm{L}} = -Q\ln\left[1 + \frac{\tau_{\mathrm{B}}}{t}\ln\left(\frac{C(0)}{C_{\mathrm{o}}}\right)\right] \tag{15}$$

From Equation 14 the following expression may be derived for the reaction rate of component A (metal ion):

$$-r_{\mathrm{A}} = -\frac{\mathrm{d}C(0)}{\mathrm{d}t} = \frac{1}{\tau_{\mathrm{B}}}\left[1 - \exp\left(-\frac{K_{\mathrm{L}}}{Q}\right)\right]C(0) \tag{16}$$

which confirms a first order reaction

$$-r_{\mathrm{A}} = kC(0) \tag{17}$$

with the following rate constant

$$k = \frac{1}{\tau_{\mathrm{B}}}\left[1 - \exp\left(-\frac{K_{\mathrm{L}}}{Q}\right)\right] \tag{18}$$

5. Experimental details

Copper recovery from dilute acidified sulphate solutions containing 0.25 M Na_2SO_4 as supporting electrolyte (pH $\sim$ 1.6) and silver recovery from dilute alkaline electroplating rinsewaters containing $K[Ag(CN)_2]$, K_2CO_3, KCN and additives (pH $\sim$ 11.4) were chosen to check the validity of the above model.

The experiments were performed at room temperature (17–23° C) and in the batch recycle mode of operation. The apex valve (Fig. 2) was kept closed and the solution entered the cell tangentially and left

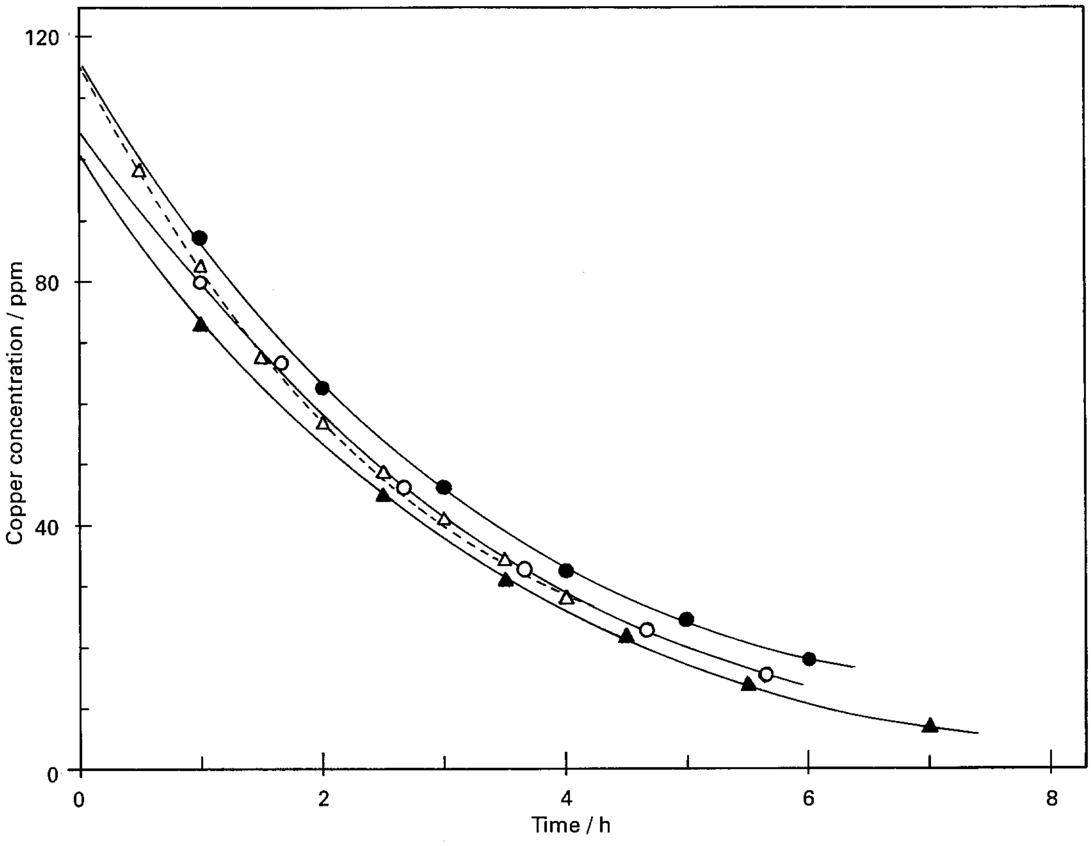


Fig. 5. Variation of copper concentration with time. Graphite anode (cell voltage/V, flow rate/dm^3 min^{-1}): (△) 3.15, 12; (●) 2.5, 12; stainless steel anode (cell voltage/V, flow rate/dm^3 min^{-1}): (○) 2.5, 12; (▲) 2.5, 15.

it flowing upwards via the helical channel between the anode and the membrane due to the helical wings on the anode surface (Fig. 3). At certain intervals samples were taken from the lower reservoir. The metal ion concentrations in the samples were determined by atomic absorption spectrophotometry.

In the case of copper, the initial metal concentration was varied between 100 and 116 p.p.m. and the volume of solution in each run was ~ 70 dm^3. Both

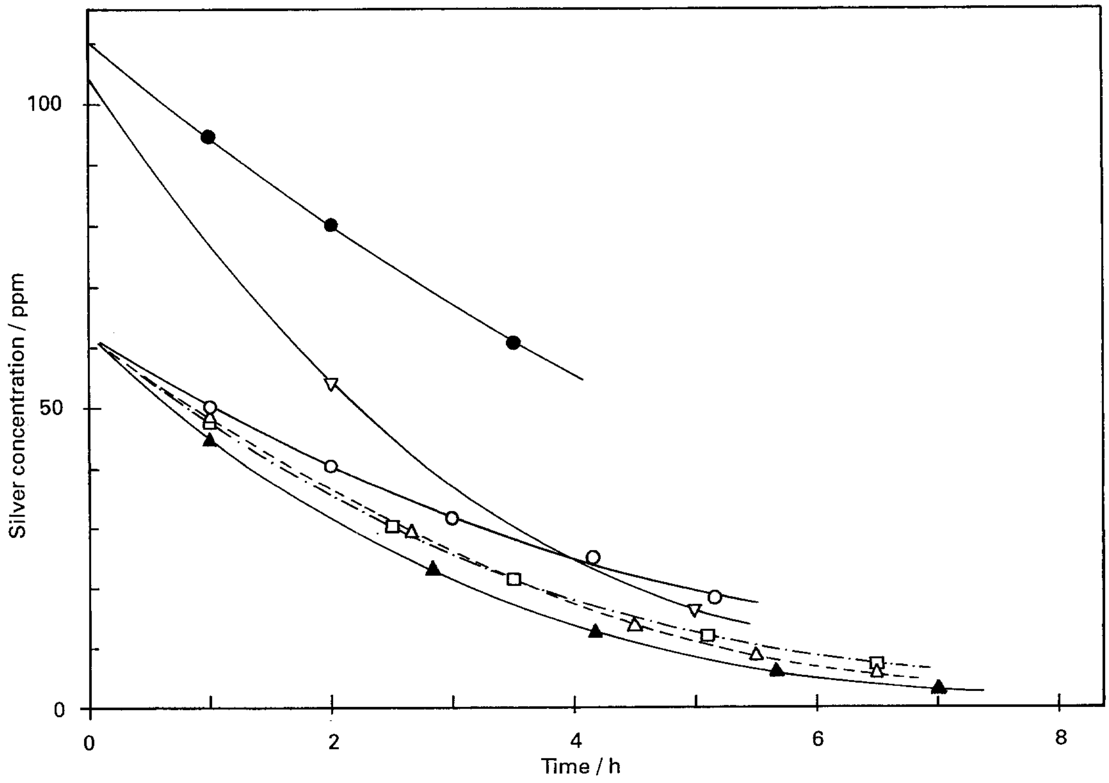


Fig. 6. Variation of silver concentration with time. Cell voltage/V, flow rate/dm^3 min^{-1}: (□) 1.8, 17; (●) 1.9, 7; (▽) 1.9, 17; (△) 2.0, 17; (○) 2.2, 10; (▲) 2.2, 17.

Table 1. Operating conditions, mass transfer coefficient and rate constant in the case of copper recovery

Operating conditions							*Values of k/h^{-1}*		
Anode	*Q* /dm^3 min^{-1}	*U* /V	*τ_B* /min	*Conc. range* /p.p.m.	*$K_L \times 10^6$* /m^3 s^{-1}	*$K \times 10^4$* /m s^{-1}	*Derived from correlation* (Equation 17)	*Calculated by means of Equation 18*	*Discrepancy/* /%
Graphite	12	3.15	5.83	116/28	6.89	1.73*	0.353	0.348	−1.4
	12	2.5	5.83	115/18	5.97	1.50*	0.307	0.302	−1.6
Stainless	12	2.5	5.75	104/15	5.89	1.48*	0.285	0.303	+6.3
steel	15	2.5	4.60	100/6.9	6.47	1.63*	0.321	0.342	+6.5

* Calculated by means of Equation 11, taking as 'active' area of the cathode the surface covered with metal.

graphite and stainless steel were used as anode material.

In the case of silver, the initial metal concentration was varied between 60 and 100 p.p.m. and the volume of solution in each run was $\sim 35\,\mathrm{dm}^3$. Graphite was used as anode material.

6. Results and discussion

Figures 5 and 6 show copper and silver depletion with time at various cell voltages and volumetric flow rates. From these experimental concentration–time curves the coefficient K_L and the reaction rates r_A were determined.

The plot of ln $[C(0)/C_0]$ against t (Equation 14) gave K_L from the slope of the straight line; this resulted in very good agreement with the experimental points.

The reaction rates were determined by graphical differentiation of the concentration–time curves. They were thereafter correlated to the experimental values of $C(0)$ to determine, according to Equation 17, the rate constant k.

Table 1 summarizes the data obtained in the case of copper recovery. An attempt was made to calculate the HCC mass transfer coefficients, taking as cathode 'active' area only the surface covered with metal. It may be seen that HCC gives lower mass transfer coefficients when compared with the pump cell [26], but higher than those reported for other cells under similar conditions [27–29].

In the case of silver recovery, the correlation (according to the Branton strategy) of the coefficient K_L with the flow rate and the cell voltage led to the following empirical equation:

$$K_L = 0.0022\,Q^{0.9} \exp(0.4\,U) \qquad (19)$$

where $1.2 \times 10^{-4}\,\mathrm{m^3\,s^{-1}} < Q < 2.8 \times 10^{-4}\,m^3\,s^{-1}$ and $1.8\,\mathrm{V} < U < 2.2\,\mathrm{V}$. Equation 19 results in good agreement with Equation 8 as regards the exponent of the volumetric flow rate. In this case the coefficient K varied between 0.43×10^{-4} and $1.06 \times 10^{-4}\,\mathrm{m\,s^{-1}}$.

Table 2 summarises the operating conditions and the data obtained in the case of silver recovery.

The small discrepancies enable prediction of the rate constant by means of Equation 18, taking into account the values for K_L calculated by means of Equation 15 or those obtained in this work (see Table 1 in the case of copper recovery or empirical Equation 19 in the case of silver recovery).

7. Conclusions

The approximate plug flow model involved in the derivation of the concentration–time relationship during batch recycle operation of the hydrocyclone cell led to a first order reaction for metal recovery from dilute solutions and has been shown to describe satisfactorily the electrodeposition of copper and silver. The data obtained in this work, Table 1 and Equation 19, may be used to predict the reaction rates under similar operating conditions. The approach enabled evaluation of mass transfer coefficients for the HCC.

Acknowledgements

The research was initiated under a grant from the Alexander von Humboldt–Stiftung which is very gratefully acknowledged. The author also wishes to thank Prof. Dr-Ing. R. Kammel Institut für

Table 2. Operating conditions and rate constant in the case of silver recovery

Operating conditions				*Values of k/h^{-1}*		
U /V	Q /dm^3 min^{-1}	τ_B /min	Conc. range /p.p.m.	Derived from *correlation [Eqn 17]*	Calculated *by means of Eqn 18*	Discrepancy /%
1.8	17	1.94	61.6 → 7.24	0.314	0.308	−1.9
1.9	17	2.06	104 → 0.26	0.342	0.345	+0.9
1.9	7	4.58	110 → 60.7	0.151	0.158	+4.6
2.0	17	1.94	60.4 → 5.81	0.341	0.342	+0.3
2.2	17	1.94	62.1 → 3.07	0.370	0.403	+8.9
2.2	10	3.30	62.3 → 18	0.229	0.225	−1.7

Metallurgie-Metallhüttenkunde, Berlin, for helpful discussions and the facilities offered.

References

[1] D. Bradley, 'The Hydrocyclone', Pergamon Press, Oxford (1965) pp. 9–20.
[2] R. W. Day, *Chem. Engng. Prog.* **69** (1973) 67.
[3] N. Dhamo and R. Kammel, *Metall* **46** (9), (1992) 912.
[4] D. Bradley, *op. cit.* [1], pp. 107–122.
[5] R. H. Perry, D. W. Green and J.O. Maloney, 'Perry's Chemical Engineers' Handbook' 6th edn. McGraw-Hill, New York (1984) section 20 (82).
[6] D. S. Azbel, N. P. Cheremisinoff, 'Fluid Mechanics and Unit Operations', Ann Arbor Science Publications (1983) pp. 608–612.
[7] R. E. W. Jansson, *Electrochim. Acta* **23** (1978) 1345.
[8] D. R. Gabe, *J. Appl. Electrochem.* **4** (1974) 91.
[9] N. A. Pakryvailo, E. B. Kaberdina and M. I. Syrkin, *ibid.* **21** (1991) 1077.
[10] D. R. Gabe and D. J. Robinson, *Electrochim. Acta* **17** (1972) 1121.
[11] A. F. S. Afshar and D. R. Gabe, *J. Appl. Electrochem.* **21** (1991) 32.
[12] L. J. J. Janssen and J. G. Wijers, *ibid.* **19** (1989) 823.
[13] J. Legrand, P. Legentilhomme and H. Aouabed, Electrochim. Acta **25** (1980) 669.
[14] J. C. Cox, *US Patent 4 372 829* (1983).
[15] K. R. Houseman, *US Patent 4 439 300* (1984).
[16] S. M. Zuwala and L. D. Cass, *US Patent 4 530 748* (1985).
[17] F. C. Walsh and G. Wilson, *Trans. Inst. Met. Finish.* **64** (1986) 55.
[18] R. J. Herbst and R. R. Renk, *PCT Int. Appl. WO 88 09 772* (1988).
[19] P. Legentilhomme and J. Legrand, *J. Appl. Electrochem.* **20** (1990) 216.
[20] J. Legrand, P. Dumargue and F. Coeuret, J. Appl. Electrochem. **21** (1991) 1063.
[21] D. F. Kelsall, *Trans. Instn. Chem. Engrs.* **30** (1952) 87.
[22] A. T. S. Walker and A. A. Wragg, *Electrochim. Acta* **22** (1977) 1129.
[23] L. H. Mustoe and A. A. Wragg, *J. Appl. Electrochem.* **8** (1978) 467.
[24] D. J. Pickett, *Electrochim. Acta* **18** (1973) 835.
[25] O. Levenspiel, 'Chemical Reactor Engineering', 2nd edn John Wiley & Sons, New York (1972) p. 67.
[26] R. E. W. Jansson and G.A. Ashworth, *Electrochim. Acta* **22** (1977) 1301.
[27] T. Sasaki and T. Tshikawa, *Electrochim. Acta* **31** (1986) 745.
[28] V. A. Ettel, B. V. Tilak and A. S. Gendron, J Electrochem. Soc. **121** (1974) 867.
[29] S. Ehdaie, M. Fleischmann and R. E. W. Jansson, J. Appl. Electrochem. **12** (1982) 59.