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# *Enhanced mass transfer at the rotating cylinder electrode. II. Development of roughness for solutions of decreasing concentration*

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The development of roughness at a rotating cylinder electrode has been investigated in the context of a metal recovery system – the ECO-CELL – where the solution concentration necessarily falls with time under batch processing. Roughness has been quantified using knurled cylinders and the use of thiourea as an additive has been considered. The development of a rough surface allows a reactor to recover metal at enhanced rates and the exploitation of this feature is discussed.

## 1. Introduction

In Part I [1] it was shown that the smooth rotating cylinder electrode assembly designed both to obtain definitive mass transfer data and to simulate a commercial ECO-CELL plant could be characterized according to classical equations. It was also shown that during prolonged electrodeposition in solutions of constant copper concentration, rough powdery deposits formed at apparently enhanced rates of mass transfer. This enhancement can be expressed empirically by a power law, first proposed by Holland [2–4]:

$$I_0 = KCU^x \qquad (1)$$

where $x \simeq 0.7$ for a smooth surface and $x \simeq 0.9$ for a surface of saturated roughness. $I_0$, termed the 'useful' current by Holland [2–4], may be identified with the limiting current under mass transport controlled deposition of metal. The ECO-CELL reactor is designed to recover metal as powder from waste liquors and effluent, either by batch processing or continuous recycling. In this mode of operation, there is a gradual decrease in the concentration of metal ions in solution. Furthermore, with potentiostatic control, clean separation of metals in solution can be achieved [5, 6] in certain cases. This investigation is concerned with an overall assessment of the analytical approach to the rough electrode surfaces developed in these circumstances.

## 2. Experimental details

The apparatus used and the procedure were comparable to those previously described [1]. As the present studies involved catholyte concentration depletion, however, insoluble anodes were utilized in a divided cell in all cases.

## 3. Results

In Part I [1] it was shown how potentiodynamic polarization data can be used to characterize the RCE and obtain mass transfer data. It was also demonstrated that, monitoring current at a constant high overpotential, the increase in surface roughness could be equated with an increase in surface area. Several trials were undertaken to examine mass transfer to previously roughened surfaces, the surfaces being grown under controlled conditions of solution concentration, potential, rotational speed and for various process times. The overall shape of the polarization curves

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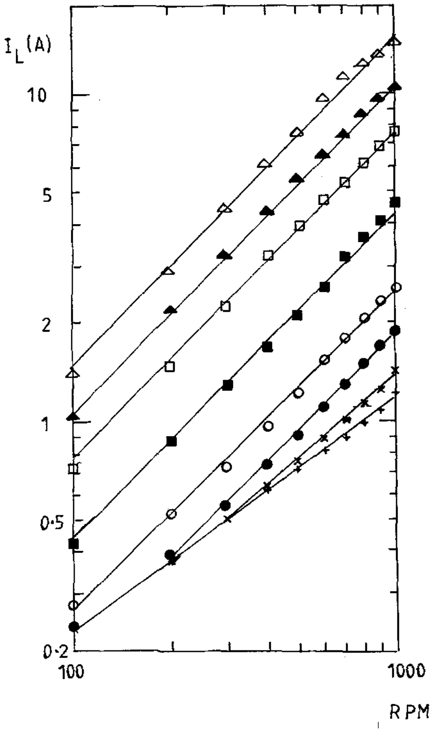

Fig. 1. Limiting current as a function of rotation speed for rough deposits grown at $-1.0$ V (SSE/1 M $Na_2SO_4$) for various times. 0.014 M $CuSO_4$ + 1.5 M $H_2SO_4$; 22° C, 340 r.p.m. ($U = 112.2$ cm s$^{-1}$); cylinder: 6.3 cm diameter, 4.3 cm active length. Values for time (min): △ 100; ▲ 80; □ 60; ■ 40; ○ 30; ● 15; x 10; + 0.5.

for roughened electrodes was comparable to that shown for their smooth counterparts (see Part 1, Fig. 3).

Limiting current data was obtained for various degrees of developing roughness and at ten rotation rates within the range 100–1000 r.p.m.; the pseudo-mass transfer plot is shown in Fig. 1. It may be seen that for low times ≈ 5 min the line has a slope of 0.74 indicative of a substantially smooth electrode. At greater times the slope rises and then at $t > 30$ min (i.e. for a sufficiently large surface roughness) the slope approaches unity; at times in excess of 100 min there was no further increase in slope. The effect of abruptly removing a rough deposit is illustrated in Fig. 2 when a full length Tufnol wiper blade was used to remove all the rough deposit; the current dropped sharply to a value slightly in excess of the original value.

It is clear that roughness as produced by a growing electrodeposit is difficult to characterize, is somewhat random and has a varying degree and distribution of protuberances. It was therefore decided to produce surfaces having a deliberately machined roughness, e.g. by knurling, so as to facilitate the characterization of the roughness. In the first case, 1.5 cm diameter cylinders were

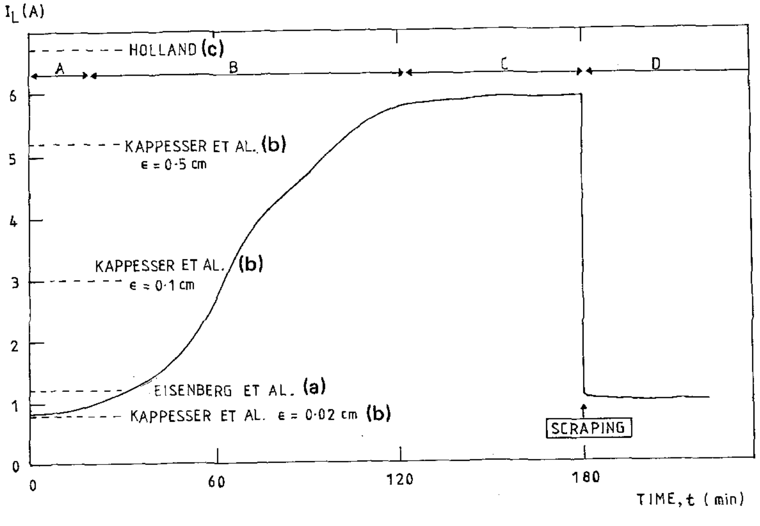

Fig. 2. Effect of abrupt and complete deposit removal on mass transport. Solution as in Fig. 1 but at 360 r.p.m. (113 cm s$^{-1}$); cylinder active length: 6.3 cm ($A = 119$ cm$^2$). Deposition is onto an initially smooth cylinder; broken lines indicate comparisons with $I_L$ values calculated from literature correlations: (a) Eisenberg *et al.* [11, 12]: $j'_D = St\, Sc^{0.644} = 0.079\, Re^{-0.30}$ for a hydrodynamically smooth cylinder; (b) Kappesser *et al.* [10]: $j'_D = St \cdot Sc^{0.644} = [1.25 + 5.76 \log (d/e)]^{-2}$ for a knurled cylinder of saturated roughness; (c) Holland [4]: $j'_D = St \cdot Sc^{0.644} = 0.0791\, Re^{p}$ (a $p$-value of $-0.10$ has been chosen) for a cylinder having a rough metal deposit. The zones correspond to conditions at the cylinder surface: (A) substantially smooth; (B) developing roughness; (C) tendency to a 'saturated' roughness; (D) complete deposit removal to re-expose a substantially smooth electrode.

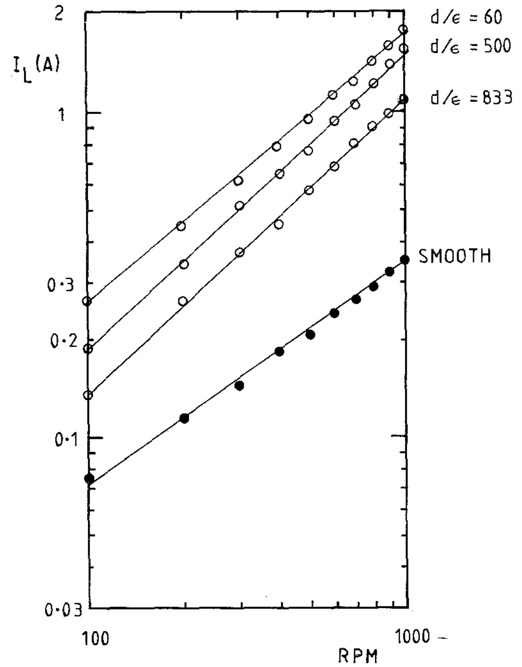

Fig. 3. Limiting current as a function of rotation speed for knurled cylinders. Solution as in Fig. 1 but for cylinder diameter of 1.5 cm.

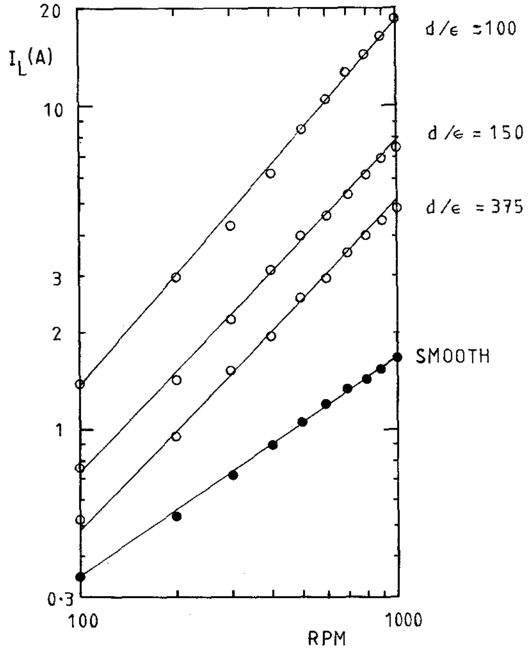

Fig. 4. Limiting current as a function of rotation speed for knurled cylinders. Solution as in Fig. 1 but for cylinder diameter of 6.0 cm.

knurled to give peak to valley roughnesses of 0.0018, 0.003 and 0.025 cm when compared to a smooth electrode; the mass transfer data is given in Fig. 3. In the second case, 6 cm diameter cylinders of knurled roughnesses 0.016, 0.040 and 0.060 cm were used (Fig. 4). Both cases show that the empirical relation $I_L \propto U^x$ is obeyed and that for smooth surfaces $x \simeq 0.7$ while for rough surfaces $x \rightarrow 1.0$; the mass transport increases with increasing roughness at a given rotational speed.

When the RCE was operated in a simulated electrowinning mode, solution concentration was monitored continuously by both atomic absorption spectrophotometry and by the use of an ion-selective electrode device [7]. Under such conditions, a concentration decay was observed which

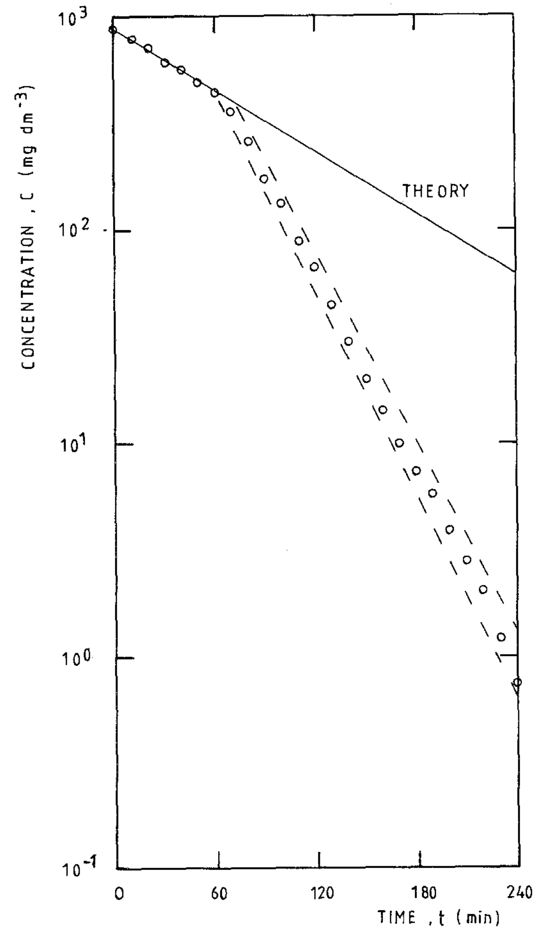

Fig. 5. Concentration decay in a batch RCE reactor. Conditions as in Fig. 1. The solid line shows the predicted behaviour expected from a hydrodynamically smooth cylinder. —— Theoretical; – – – reproducibility limits; o experimental data.

at short times follows the exponential law as might be anticipated. However, after a short period the concentration actually falls faster than the exponential behaviour predicts (Fig. 5) and a substantially lower concentration results after 120 min; this effect is associated with the onset of significant roughness. Further experiments for electrodes prepared by various chemical or electropolishing techniques did not significantly alter this behaviour. Attempts were made to monitor the current during such an exercise and took the form illustrated in Fig. 6 in which the predicted current for a continuously smooth surface is shown as a full line. The initial increase in current is associated with powder development and the succeeding rapid fall with enhanced metal depletion. At lower metal concentrations it is no longer appropriate to assume a cathode current efficiency of 100%, hydrogen evolution playing an increasing role with copper dilution.

All the above data were obtained at high overpotential. Clearly, if lower overpotentials are used roughness develops less rapidly and the consequent enhancement of reactor performance is lower. This can be illustrated in two ways: firstly, by various degrees of enhanced concentration decay on a semi-logarithmic plot (Fig. 7), or by the use of various rotation rates (Fig. 8). This data shows that the first order rate of decay increases after a certain critical time whose value decreases with increased velocity of rotation.

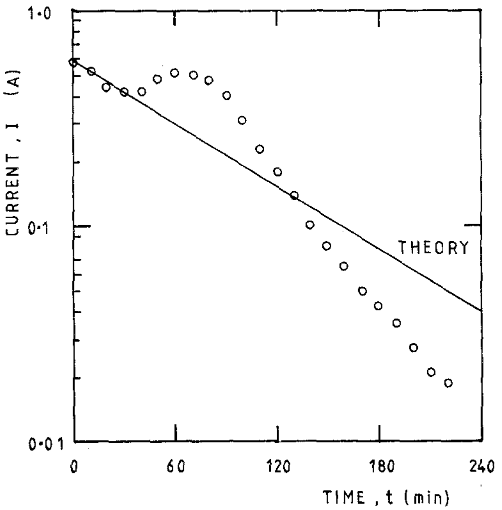

Fig. 6. Current decay in a batch RCE reactor. Data corresponding to Fig. 5.

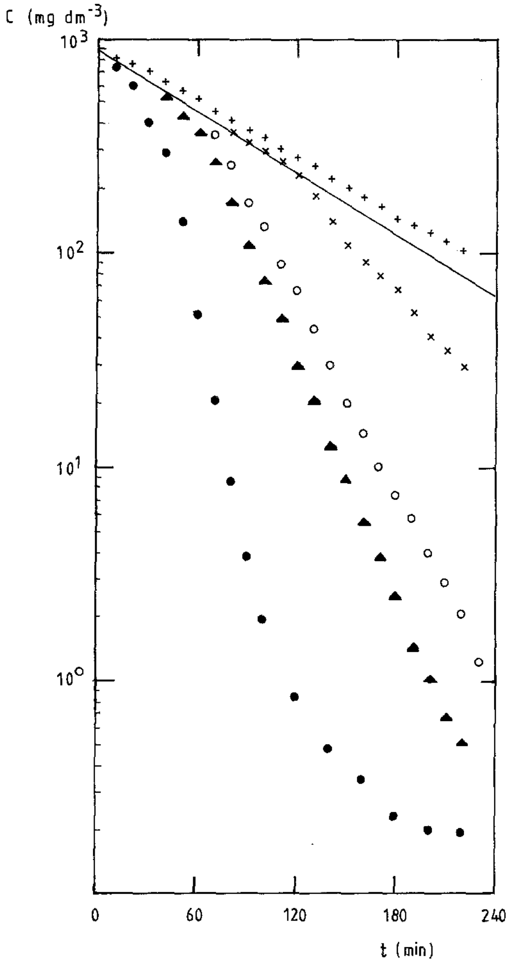

Fig. 7. Concentration decay in a batch RCE reactor. Conditions as in Fig. 5; potentials vs SSE/1 M Na$_2$SO$_4$ electrode. The solid line indicates the predicted behaviour for a smooth electrode under limiting current conditions. $E$ (mv) values: + −850; x −910; ○ −1000; ▲ −1070; ● −1150.

In electrowinning processes it is common to use addition agents to suppress powdery growth and improve levelling. Thiourea is such an additive and is known to be effective at levels in the order of $10^{-3}$ M, higher concentrations lead to darkened deposits. It has a marked effect on cathodic polarization and the rest potential (Fig. 9), but the pattern is somewhat irregular. In terms of concentration decay, marked changes were observed (Fig. 10): at $10^{-3}$ M the deposit is apparently maintained smooth; at concentrations $< 10^{-3}$ M enhanced depletion occurred but after longer times; at concentrations $> 10^{-3}$ M a much reduced rate of decay was observed due to the whole

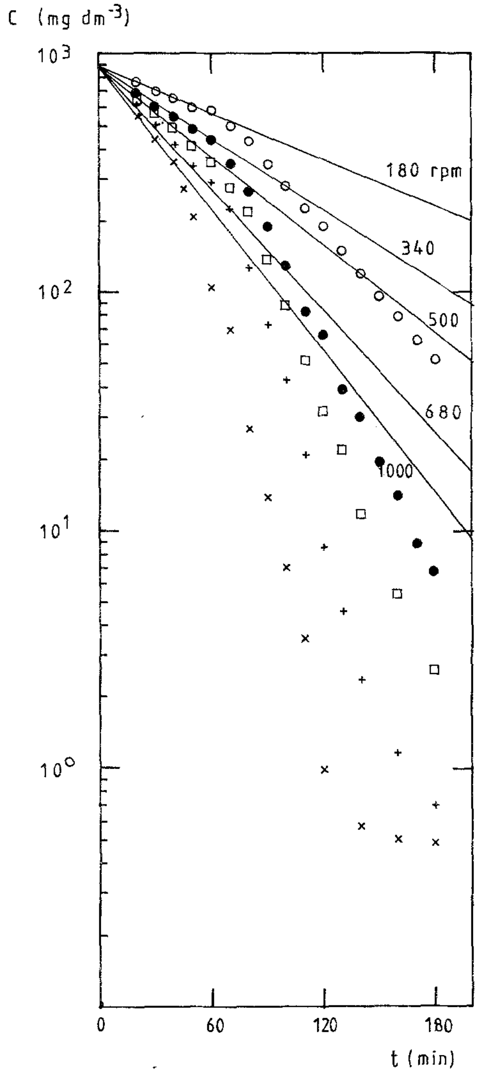

Fig. 8. Concentration decay in a batch RCE reactor showing effect of rotation rate. – 1.0 V (SSE/1 M $Na_2SO_4$). Solid lines show predicted behaviour for smooth electrodes. Other conditions as for Fig. 5. RPM: ○ 180; ● 340; □ 500; + 680; x 1000.

cathode deposition reaction being inhibited. A concentration of approximately $10^{-3}$ M is clearly an optimum for levelling.

## 4. Discussion

The experimental results presented here and in Part I show clearly the association of roughness with enhanced mass transfer (and consequently enhanced rates of metal deposition) is well-founded. Two aspects of this behaviour, together

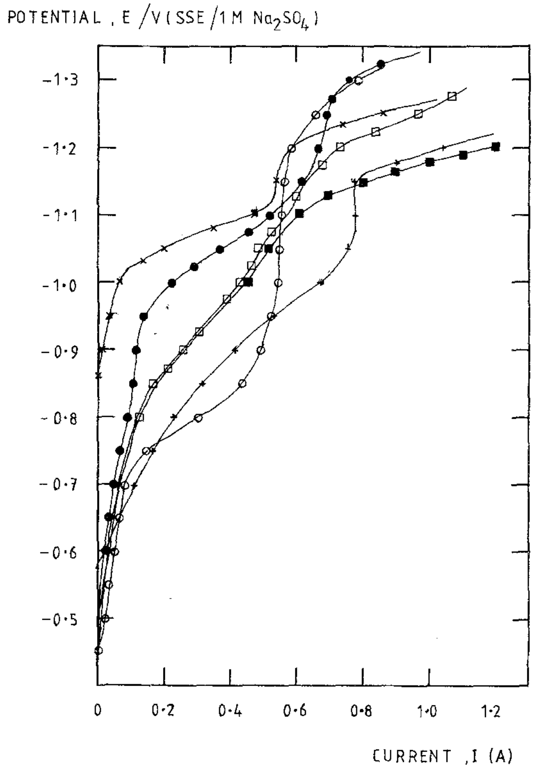

Fig. 9. Cathode polarization curves in the presence of thiourea. Conditions otherwise as in Fig. 1. Thiourea concentration (M): ○ 0; ● $10^{-5}$; □ $10^{-4}$; ■ $10^{-3}$; + $10^{-2}$; x $10^{-1}$.

with the implications for successful exploitation, require discussion. Firstly, the practical consequences for the optimum operation of a metal-recovering reactor must be considered. Secondly, it should be decided whether a fundamental description of the enhanced mass transfer by surface roughening is feasible.

When the RCE is used as a batch reactor in a solution whose concentration is not replenished by means of a soluble anode and which is operated under mass transfer control, the concentration falls exponentially according to the simple rate law:

$$C_t = C_0 \exp(-kt) \qquad (2)$$

where $k$ is the apparent first order rate constant and is given by $k = (K_L A/V_R)$ where $A$ is the active electrode area, $V_R$ is the effective reactor volume and $K_L$ is the mass transfer coefficient. In the case of deposition at potentials such that the current is mass transport limited, the development of roughness means an increase in the rate of decay

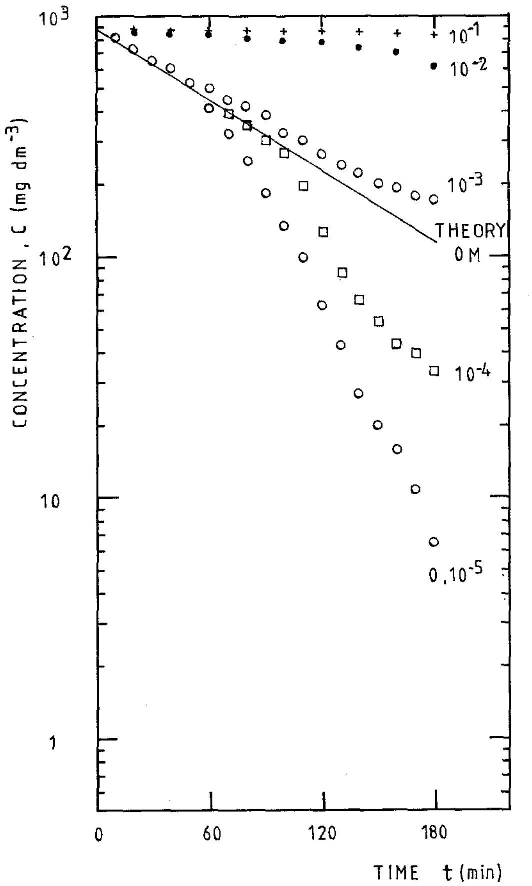

Fig. 10. Copper concentration decay in the presence of thiourea (0, $10^{-5}$, $10^{-4}$, $10^{-3}$, $10^{-2}$, $10^{-1}$ M). Conditions otherwise as in Fig. 1 but at — 1.00 V (SSE scale).

(see Fig. 5) caused by an increase in the value of $k$. $K_L$ may be determined from an auxiliary polarization curve for a smooth electrode surface where

$$K_L = \frac{I_L}{AzFC} \qquad (3)$$

After some 60 min the copper concentration departs from the predicted line (see Fig. 5) indicating increased reactor performance. Reproducibility was poor unless preplating of the electrode surface was carried out so excluding randomness of nucleation from the data; such preplating also stabilized the open circuit, or rest potential. Superior preparation of a smooth electrode surface by mechanical, chemical or electropolishing did not significantly change the reproducibility and this verifies other workers views, typically those of Ibl *et al.* [8].

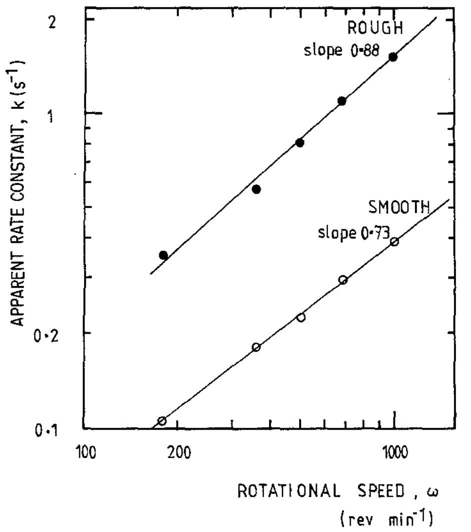

Fig. 11. Apparent rate constant as a function of rotation rate. Data obtained by subjecting sample in Fig. 5 to further electrolysis under identical conditions.

Information on roughness development was also provided by current decay during a batch treatment (see Fig. 6) when the analogous current equation is:

$$I_{L,t} = I_{L,o} \exp(-kt) \qquad (4)$$

The initial current, $I_{L,o}$ is close to that recorded on a polarization curve, but after 30 min the current increases passing through a maximum after about 60 min. At longer times, it falls rapidly. This pattern of behaviour is the result of competing effects: a declining concentration of metal in solution leading to smaller currents but an increasing roughness encouraging a larger effective mass transfer coefficient. This effect is also affected by the initial solution concentration because below about 650 ppm the initial rise is negligible due to concentration decay occurring so fast that roughness development is insufficiently rapid to offset the decline. The actual mass transfer coefficient for longer times and rough deposits may be calculated from the concentration decay curve as $6.7 \times 10^{-3}$ cm s$^{-1}$ and is considerably greater than the initial value at short times of $2.2 \times 10^{-3}$ cm s$^{-1}$. The latter value is very similar to that for a smooth electrode surface of $2.3 \times 10^{-2}$ cm s$^{-1}$.

The effect of potential can also be seen (see Fig. 7) when the low values given a wholly linear behaviour and total enhancement, over the whole time interval, only occurs above a certain critical value. However, at potentials more negative than $-1050$ mV (SSE/1 M $Na_2SO_4$) significant hydrogen evolution was noted. This acts as a source of electrolyte agitation and induces a further increase in performance. Thus, a certain amount of current inefficiency could be tolerated if the evolved gas provides additional agitation. It should be noted that very low residual concentrations could be achieved in batch operations ($< 1$ ppm in some cases) but reproducibility is necessarily poor at this level.

Rotation speed is also an important parameter, as it increases both the early and late decay slopes and decreases the transition time (see Fig. 8). Apparent rate constants may be calculated and related to rotation rate (Fig. 11): the early results prior to transition display a slope of 0.73 typical of a smooth electrode surface while later results on a roughened electrode give a slope of 0.88 and appreciably higher mass transport values. This is an important parameter in further raising the mass transport efficiency, thereby inducing early transitions and enhanced recovery for as wide an operating time span as possible. Separate studies have shown that this enhancement can be combined with controlled potential separation from a mixed metal electrolyte [6], thereby giving a very powerful tool for metal recovery.

It was pointed out, in Part I [1], that because of the difficulty of separating microturbulence caused by surface roughness, the power law represented a simple, but empirical, means of describing enhancement. Using the relationship:

$$I_L = \text{constant} \cdot U^x \qquad (5)$$

(where $x \simeq 0.74$ for a smooth cylinder electrode and $x \simeq 0.90$ for a rough surface) it has been shown that use of apparent mass transfer coefficients or rate constants (see Fig. 11) may be an alternative way of illustrating enhancement. The data obtained here cannot enable a definitive analysis to be made but can provide insight into the optimum method of operating a commercial reactor of the ECO-CELL type where the product of continuous operation is metal powder. Powder may be removed by random centrifugal action or by deliberate scraping of the rotated cylinder surface using an inert scraper or 'doctor blade'. The effect of using a full length, flat blade scraper is illustrated in Fig. 2, where, in the absence of scraping, the current progressively developed from a smooth cylinder value ($x \simeq 0.74$) to a saturated condition of roughness ($x \simeq 0.90$) after some 120 min when the current tended to stabilize. After 180 min the scraper blade was applied, the powder was almost completely removed leaving a substantially smooth electrode surface and the current rapidly fell to a value only just in excess of the original value for the smooth cylinder. Because enhanced mass transport is dependent upon maintaining surface roughness, this full blade scraping is deleterious; it is therefore preferable to use a reciprocating point scraper scanning the surface slowly and scraping not more than 5% of the total area. Under these circumstances the reactor performance is maintained at $> 95\%$ of the maximum for those particular conditions while maintaining a continuous stream of metal powder product. Other options exist and the ultimate choice is dependent upon design considerations and the rate of metal/solution throughput required [9]. It should be noted that such roughness is always superior to using a knurled cylinder because such knurling only increases mass transfer marginally over that for a smooth cylinder and of course scraping may become less easy for a knurled surface.

An analysis of the knurled surfaces can be made from the experimental data of Figs. 3 and 4. Using a power law $x \simeq 1.0$ for such surfaces but by using the modified Chilton–Colburn $j'_D$ factor, some systematic behaviour can be discerned (Fig. 12).

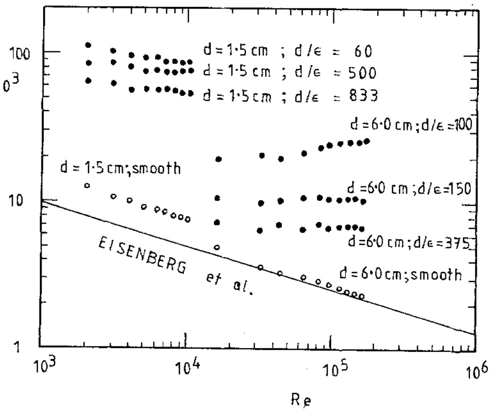

Fig. 12. Mass transfer to knurled rotating cylinders. Plot of modified Chilton–Colburn factor $j'_D$, against Reynolds number, $Re$, $j'_D = 0.079\,Re^{-0.30} = St\,Sc^{0.644}$.

*Table 1. Mass transport to knurled rotating cylinder electrodes*

| *Roughness,* $\epsilon$ *(cm)* | *Diameter,* d *(cm)* | *Relative roughness* $d/\epsilon$ | *Limiting current* $I_L$/A* | | $j'_D \times 10^3$* | | *Predicted* $Re_{crit}$ |
|---|---|---|---|---|---|---|---|
| | | | *Predicted*† | *Observed* | *Predicted*† | *Observed* | |
| $< 5 \times 10^{-5}$ | 1.5 | $> 3 \times 10^4$ | 0.222 | | 4.95 | | Large |
| 0.0018 | 1.5 | 833 | 0.137 | 1.11 | 3.06 | 55.2 | 51 448 |
| 0.003 | 1.5 | 500 | 0.159 | 1.57 | 3.55 | 78.1 | 28 158 |
| 0.025 | 1.5 | 60 | 0.340 | 1.78 | 7.57 | 88.5 | 2307 |
| $< 5 \times 10^{-5}$ | 6.0 | $> 12 \times 10^4$ | 1.52 | | 2.15 | | Large |
| 0.016 | 6.0 | 375 | 2.74 | 4.90 | 3.87 | 6.8 | 20 053 |
| 0.040 | 6.0 | 150 | 3.72 | 7.45 | 5.26 | 10.4 | 6802 |
| 0.060 | 6.0 | 100 | 4.34 | 19.0 | 6.13 | 26.5 | 4215 |

* At 1000 r.p.m.

† By Equation $j'_D = [1.25 + 5.76 \log (d/\epsilon)]^{-2}$.

$$j'_D = 0.079\, Re^{-0.30} \tag{6}$$

This data show that, for a given value of relative roughness, $d/\epsilon$, the mass transport is appreciably higher than that predicted by the generalized equation of Kappesser *et al.* [10]:

$$j'_D = [1.25 + 5.76 \log (d/\epsilon)]^{-2} \tag{7}$$

which was originally reported for cathodic reduction of dissolved oxygen at a model RCE. The data are presented fully in Table 1 for comparison. It may be surprising that all knurled surfaces appear to act as hydrodynamically rough surfaces because Kappesser *et al.* [10] suggest that it may be true only if $Re = Ud/\nu > Re_{crit}$, where

$$Re_{crit} = (11.8\, d/\epsilon)^{1.18} \tag{8}$$

In this study, $d = 1.5$ cm and $d/\epsilon = 833$ and 500 when cylinders should have behaved as 'smooth' surfaces. However, it is important to appreciate that the present results concern very specific conditions, i.e. one concentration and rotation rate variations of less than an order of magnitude.

## References

[1] D. R. Gabe and F. C. Walsh, *J. Appl. Electrochem.* 14 (1984) 555.

[2] F. S. Holland, British Patent 1 505 736 (1978).

[3] *Idem,* US Patent 4 028 199 (1977).

[4] *Idem, Chem. Ind.* (1978) 453.

[5] D. R. Gabe and F. C. Walsh, Proceedings of Interfinish '80, Kyoto, Japan (1980) p. 486.

[6] *Idem, Surf. Technol.* 12 (1981) 25.

[7] *Idem, J. Appl. Electrochem.* **11** (1981) 117.

[8] N. Ibl, P. Javet and F. Stahel, *Electrochim. Acta* **17** (1972) 733.

[9] F. S. Holland and F. C. Walsh, British Patent Application 81-04 624 (1981).

[10] R. Kappesser, I. Cornet and R. Greif, *J. Electrochem. Soc.* **118** (1971) 1957.

[11] M. Eisenberg, C. W. Tobias and C. R. Wilke, *Chem. Eng. Prog. Symp. Ser.* **51** (1955) 1.

[12] *Idem, J. Electrochem. Soc.* **101** (1954) 306.