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Mass transfer study of the electropolishing of vertical cylinders with active ends under natural convection conditions

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Rates of electropolishing of vertical copper cylinders with active ends in H_3PO_4 were studied by measuring the limiting current under natural convection. Variables studied were H_3PO_4 concentration, cylinder diameter and aspect ratio. The rate of polishing of the whole cylinder was represented by the mass transfer equation

$$Sh = 0.33(Sc\ Gr)^{0.32}$$

for the range $1.17 \times 10^{10} < Sc\ Gr < 5.11 \times 10^{11}$. Rates of mass transfer were measured also at vertical cylinder with insulated ends, and the upward facing surface (disc). Data for the vertical cylindrical surface were represented for the range $8.75 \times 10^9 < Sc\ Gr < 1.1 \times 10^{12}$ by the equation

$$Sh = 1.206(Sc\ Gr)^{0.255}$$

while data at the upward facing disc were correlated for the range $0.11 \times 10^{10} < Sc\ Gr < 46 \times 10^{10}$ by the equation

$$Sh = 0.17Sc^{0.396}(Sc\ Gr)^{0.146}$$

A comparison between the measured rate of mass transfer at the whole cylinder and the value calculated by adding the rates of mass transfer at the separate surfaces of the cylinder shows that the measured value deviates from the calculated value, the degree of deviation increases with increasing $Sc \times Gr$. Deviation was attributed to flow interaction at the different cylinder surfaces.

List of symbols

A	anode area
C	concentration of Cu^{2+}
C_S	saturation solubility of copper phosphate (as Cu^{2+}) in H_3PO_4
C_H	concentration of H^+
C_A	concentration of anion $H_2PO_4^-$
D	diffusivity of Cu^{2+}
D_H	diffusivity of H^+
D_A	diffusivity of $H_2PO_4^-$
d	cylinder diameter
E	potential
F	Faraday constant
g	acceleration due to gravity
I	limiting current
i	limiting current density
K	mass transfer coefficient
L	cylinder height
L_c	characteristic length calculated from Equation 10
N_{Cu}	flux of Cu^{2+}
N_H	flux of H^+
N_A	flux of $H_2PO_4^-$
R	gas constant
T	absolute temperature
X	distance from the electrode surface
Z	number of electrons involved in the reaction
Gr	Grashof number $(gL_c^3(\rho_i - \rho_b)/\nu_{av}^2\rho_i$
Sc	Schmidt number, ν/D
Sh	Sherwood number, KL_c/D
ρ_i	interfacial density of the solution
ρ_b	bulk density of the solution
ν_{av}	average kinematic viscosity
δ	diffusion layer thickness

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1. Introduction

Previous studies aimed at quantifying the process of electropolishing in terms of the rate of mass transfer have dealt with simple geometries such as vertical plates, vertical discs, horizontal downward facing discs, horizontal cylinders with insulated ends and vertical tubes. Recently, there has been a growing interest in studying rates of polishing and etching of workpieces of complex geometry such as open cavities and enclosures [1–6], in view of their practical importance. In line with this trend the present work aims at studying the rate of polishing of vertical cylinders with active ends to test the possibility of predicting the polishing current of the whole cylinder from the rate of mass transfer obtained by summing the individual rates at the separate surfaces of the cylinder. Krysa and Wragg [7] studied the natural convection mass transfer behaviour of vertical cylinders with active ends by measuring the limiting current of the cathodic deposition of copper from acidified $CuSO_4$ solutions. The equation obtained by Krysa and Wragg [7] cannot be used to predict the polishing currents at vertical cylinders with active ends because of the possible contribution of migration to the rate of mass transfer in the case of electropolishing as revealed by previous studies [6, 8] especially under laminar flow conditions [9]. The present study was carried out by measuring the limiting current for the anodic dissolution of whole vertical copper cylinders of different aspect ratios in phosphoric acid. For the purpose of comparison between the experimental rate of mass transfer and that predicted by adding rates of mass transfer at separate surfaces, rates of mass transfer at a vertical cylinder with insulated ends, and the upward facing surface were also studied. Rates of mass transfer during the electropolishing of downward facing horizontal disc were studied by Sedahmed *et al.* [10], the data were represented for the conditions $1.1 \times 10^9 < Sc\,Gr < 2.46 \times 10^{11}$ by the equation

$$Sh = 0.18(Sc\,Gr)^{0.33} \tag{1}$$

2. Theory of the possible role of electrical migration in the rate of electropolishing

During electropolishing of copper in phosphoric acid the diffusion layer contains mainly the ions Cu^{2+}, H^+ and $H_2PO_4^-$ whose concentrations will be denoted by C, C_H and C_A, respectively. Neglecting convection in the diffusion layer, these ions are transferred across the diffusion layer by electrical migration and diffusion according to the Nernst–Planck equation as follows:

$$N_H = 0 = -D_H\left[\frac{dC_H}{dx} + \frac{C_H ZF}{RT}\frac{dE}{dx}\right] \tag{2}$$

$$N_{Cu} = \frac{i}{2F} = -D\left[\frac{dC}{dx} + \frac{CZF}{RT}\frac{dE}{dx}\right] \tag{3}$$

$$N_A = 0 = -D_A\left[\frac{dC_A}{dx} + \frac{C_A ZF}{RT}\frac{dE}{dX}\right] \tag{4}$$

The assumption of electroneutrality across the diffusion layer requires that

$$2C + C_H = C_A \tag{5}$$

Glarum and Marshall [11], and Kontturi and Schiffrin [8] independently solved the above equations to correlate the limiting current to the saturation solubility of copper phosphate, C_S, and the concentration of H^+ by the equation

$$i = \frac{2FD}{\delta}\left[C_S + 2(C_S^2 + C_H^2)^{1/2} - 2C_H\right] \tag{6}$$

Two limiting cases can be considered. When the H^+ concentration is much higher than the saturation solubility of copper phosphate, the limiting current density is given by

$$i = \frac{2FD}{\delta} C_S \tag{7}$$

On the other hand when the H^+ concentration is much less than the saturation solubility of copper phosphate Equation 6 leads to

$$i = \frac{6FD}{\delta} C_S \tag{8}$$

The above equation shows that the limiting current density becomes thrice the diffusion value, i.e., electrical migration can increase the limiting current by an amount ranging from 0 to 200% depending on the ratio between Cu^{2+} and H^+ concentrations in the diffusion layer during electropolishing. This is consistent with the finding of Newman [12]. In the presence of convection it is expected that the contribution of migration will decrease owing to the faster rate of mass transfer of H^+ and Cu^{2+} to and away from the anode surface, respectively.

To shed some light on the extent of contribution of electrical migration to the rate of mass transfer under the present conditions, C_H was calculated for each H_3PO_4 concentration. The values of the primary, secondary, and tertiary ionization constants of the acid are, respectively, 7.5×10^{-3}, 6.2×10^{-8} and 5.0×10^{-13} [13]. In view of the relatively small values of the secondary and the tertiary ionization constants, H^+ produced by secondary and tertiary ionization was neglected for these calculations. For 8, 10 and 12 M H_3PO_4, C_H was found to be 0.245, 0.274 and 0.300 M, respectively. The saturation solubility values of copper phosphate (C_S) in 8, 10 and 12 M H_3PO_4 are 1.076, 0.9384 and 0.780 M, respectively [10]. Substituting for C_H and C_S in Equation 6 it was found that electrical migration increases the rate of mass transfer by about 179.3%, 134.6% and 85% in 8, 10 and 12 M H_3PO_4, respectively.

3. Experimental technique

Figure 1 shows the cell and electrical circuit used. The cell consisted of a two litre glass container of 12 cm

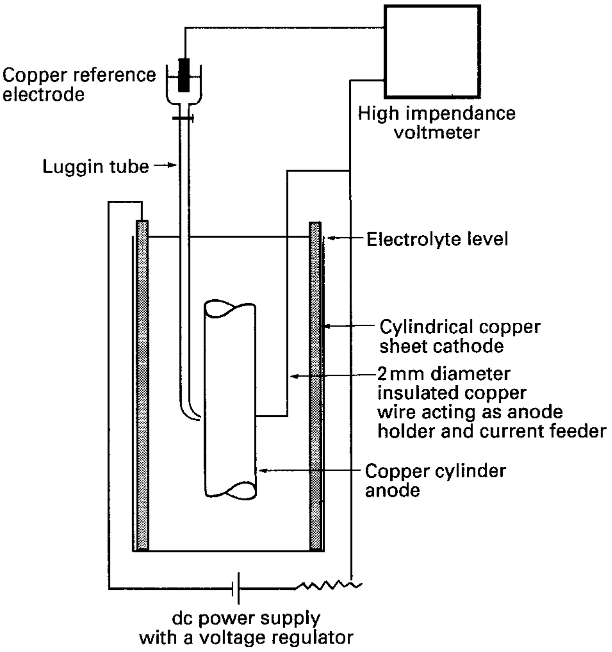

Fig. 1. The apparatus.

diameter and 19 cm height. The vertical copper cylinder anode was placed in the centre of the container midway between the top and the bottom of the container which was filled with H_3PO_4. The anode was held in position by 2 mm diameter insulated copper wire threaded to the cylinder. The copper wire acted also as anode current feeder. The anode was surrounded by a cylindrical copper cathode of 11.8 cm diameter and 19 cm height. Anode dimensions are shown in Table 1. The circuit used consisted of a d.c. power supply with a voltage regulator and a multirange ammeter connected in series with the cell. Limiting current was obtained from polarization curves which were constructed by increasing the current stepwise and measuring the steady state anode potential, by means of a high impedance voltameter, against a copper reference electrode placed in the cup of a Luggin tube filled with the cell solution. The tip of the Luggin tube was placed 0.5–1 mm from the anode surface. All anodes were far enough from the upper solution layer where cathodically evolved hydrogen caused some turbulence. Three H_3PO_4 concentrations were used, namely 8, 10 and 12 M. All solutions were prepared from AR grade chemicals and demineralized water. Temperature was kept at 22 ± 0.5° C. Each run was repeated twice. The mass transfer coefficient was obtained from the limiting current using the equation

$$K = \frac{I_L}{ZFC_S A} \tag{9}$$

To measure the limiting current at vertical cylinders with insulated ends and at the upward facing disc, the undesired parts of the cylinder were isolated by epoxy resin. The presence of small current oscillations did not affect the precision with which the limiting current was determined.

Table 1. Dimensions of the active-ended vertical cylinders used in obtaining Equation 11

Cylinder diameter, *d*/cm	*Cylinder height,* *L*/cm	*Characteristic length,* L_c/cm	*Aspect ratio,* *L*/*d*
2.2	6.65	7.75	3.02
2.2	5.5	6.6	2.5
2.2	4.45	5.55	2.02
2.2	3.3	4.4	1.5
2.2	2.2	3.25	1
2.2	1.1	2.2	0.5
1	2	2.5	2
3.15	3.15	4.675	1
4.4	4.4	6.6	1
5.1	5.1	7.55	1
7.4	3	6.7	0.405

4. Results and discussion

4.1. *Mass transfer at a vertical cylinder with active ends*

Figure 2 shows the effect of cylinder height ($d = 2.2$ cm) on the mass transfer coefficient of the whole cylinder for three H_3PO_4 concentrations. The mass transfer coefficient is almost independent of cylinder height. This suggests that the overall mass transfer coefficient of the whole cylinder is dominated by the turbulent flow resulting from the interaction of the flow coming from the top surface with the flow at the vertical part along with turbulent flow at the downward facing disc [10]. Mass transfer data at the whole active cylinder were correlated using the dimensionless groups *Sh*, *Sc* and *Gr*. Physical properties used in correlating the data (ρ, μ, D) were taken from the literature [10] and corrected for the change in temperature whenever necessary. Following Weber *et al.* [14], the characteristic length used to calculate *Sh* and *Gr* was obtained from the equation

$$L_c = \frac{\text{surface area of the whole cylinder}}{\text{perimeter projected on a horizontal plane}} \tag{10}$$

Figure 3 shows that the mass transfer data at the whole cylinder for the range $1.17 \times 10^{10} < Sc\,Gr < 5.11 \times 10^{11}$, $0.8128 \times 10^5 < Sc < 3.59 \times 10^5$ can

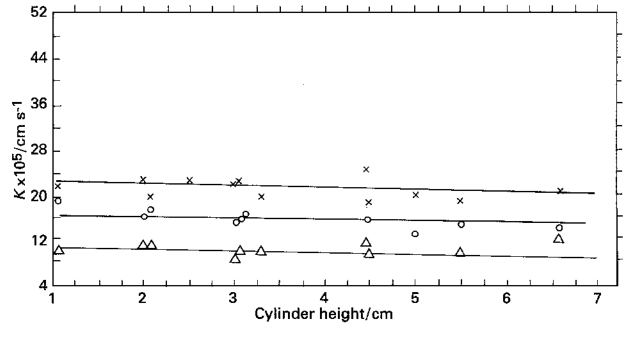

Fig. 2. Effect of cylinder height on the mass transfer coefficient at the active-ended cylinder. H_3PO_4 concentration: (×) 8, (○) 10 and (△) 12 M.

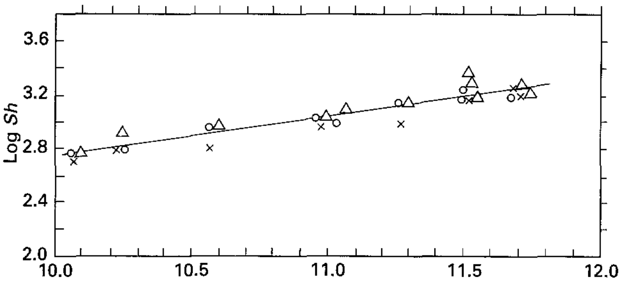

Fig. 3. The overall mass transfer correlation at the active-ended cylinder. H_3PO_4 concentration: (×) 8 ($Sc = 0.8128 \times 10^5$); (○) 10 ($Sc = 1.68 \times 10^5$); (△) 12 M ($Sc = 3.59 \times 10^5$).

be correlated by the equation

$$Sh = 0.33(Sc\ Gr)^{0.32} \tag{11}$$

with an average deviation of ±7.57. The correlation coefficient was found to be 0.954. The exponent 0.32 confirms the dominance of turbulent flow under the present conditions.

4.2. *Mass transfer at a vertical cylinder with insulated ends*

Figure 4 shows the effect of height of a vertical cylinder with insulated ends on the mass transfer coefficient. Cylinders of diameter 2.2 cm and heights of respectively 2, 4, 6, 8 and 10 cm were used in this part of study. The decrease in the mass transfer coefficient with cylinder height as shown in Fig. 4 suggests a laminar flow mechanism. Figure 5 shows that the mass transfer data for a vertical cylinder with inactive ends can be correlated for the range $8.75 \times 10^9 < Sc\ Gr < 1.1 \times 10^{12}$, $0.8128 \times 10^5 < Sc < 3.59 \times 10^5$ by the equation

$$Sh = 1.206(Sc\ Gr)^{0.255} \tag{12}$$

with an average deviation of ±3.7%. The correlation coefficient was found to be 0.9947. Cylinder height was used as a characteristic length in the above equation. The exponent 0.255 in the above equation agrees with the prediction of boundary layer theory and agrees also with the experimentally obtained equation for vertical plates [15]. However, the coefficient 1.206 of Equation 12 is higher than the established value for vertical plates (0.67). The discrepancy between the coefficient 1.206 and the value of 0.67 may be attributed in part to the possibility of copper ion transfer from the anode surface to the solution bulk by electrical migration in addition to diffusion and natural convection. Migration is favoured because (i) the concentration of H_3PO_4 supporting electrolyte in the diffusion layer is insufficient to eliminate the transfer of Cu^{2+} by migration at the limiting current where part of H_3PO_4 is converted to copper phosphate, (ii) the dissolved Cu^{2+} consumes part of the available solvent water (34.3, 27.6 and 21 M H_2O in, respectively, 8, 10 and 12 M H_3PO_4) to form hexaquo ions [11], which decreases the amount of water available as a solvent for the remaining H_3PO_4 with a consequent decrease in the degree of acid ionization, and (iii) the increase in the solution viscosity inside the diffusion layer as a result of the formation of solvated Cu^{2+} [11] which may slow down diffusion and natural convection in favour of migration. The high coefficient of Equation 12 is consistent with the result of the theoretical part that electrical migration could increase the rate of mass transfer of a divalent ion by an amount depending on the ratio between the concentration of the supporting electrolyte and that of the electroactive ion.

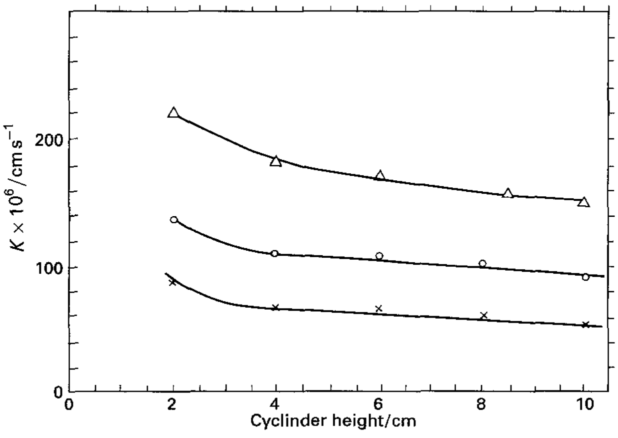

Fig. 4. Effect of cylinder height on the mass transfer coefficient of the inactive-ended cylinder. H_3PO_4 concentration: (△) 8, (○) 10 and (×) 12 M.

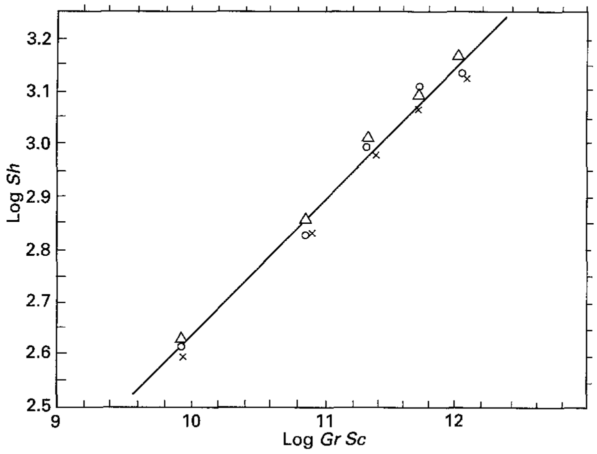

Fig. 5. The overall mass transfer correlation at inactive-ended cylinder. H_3PO_4 concentration: (△) 8, ($Sc = 0.8128 \times 10^5$); (○) 10 ($Sc = 1.68 \times 10^5$); (×) 12 M ($Sc = 3.59 \times 10^5$).

4.3. *Mass transfer at the upward facing surface*

Figure 6 shows the effect of upward facing surface diameter on the mass transfer coefficient at the upward facing disc (other parts being insulated). The decrease in the mass transfer coefficient with increasing disc diameter suggests the presence of a laminar hydrodynamic boundary layer which moves radially on the disc. Figure 7 shows that mass transfer data at the upward facing surface for the range $0.11 \times 10^{10} < Sc\ Gr < 46 \times 10^{10}$, $0.8128 \times 10^5 < Sc < 3.59 \times 10^5$ can be correlated by

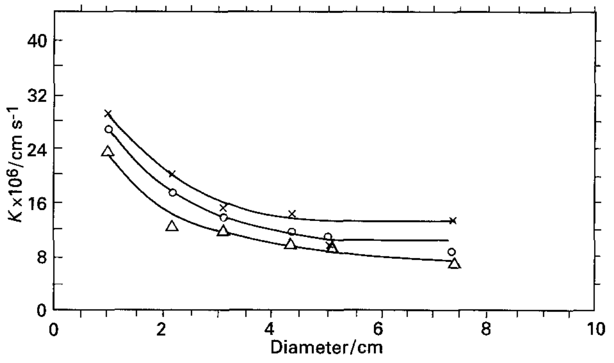

Fig. 6. Plot of mass transfer coefficient against diameter of the upward-facing end. H_3PO_4 concentration: (×) 8, (○) 10 and (△) 12 M.

the equation

$$Sh = 0.17 Sc^{0.396} (Sc\ Gr)^{0.146} \qquad (13)$$

with an average deviation of ±5.7%. The correlation coefficient was found to be 0.991. Disc diameter was used as a characteristic length in obtaining Equation 13. Attempts to correlate the data without separating *Sc* from *Gr* failed to give a satisfactory correlation. It seems that transfer by electrical migration is more pronounced at the upward facing disc than elsewhere on the cylinder owing to the slow rate of removal of copper phosphate from the diffusion layer by the weak laminar flow prevailing at the disc surface as denoted by the exponent 0.146.

4.4. *Comparison between the experimental and the calculated rates of mass transfer*

To test the possibility of obtaining the rate of mass transfer at the whole cylinder from the separate rates of mass transfer at the two flat ends and the vertical curved part, the rate of mass transfer was calculated for each surface using the equation

$$\text{rate of mass transfer} = KAC \qquad (14)$$

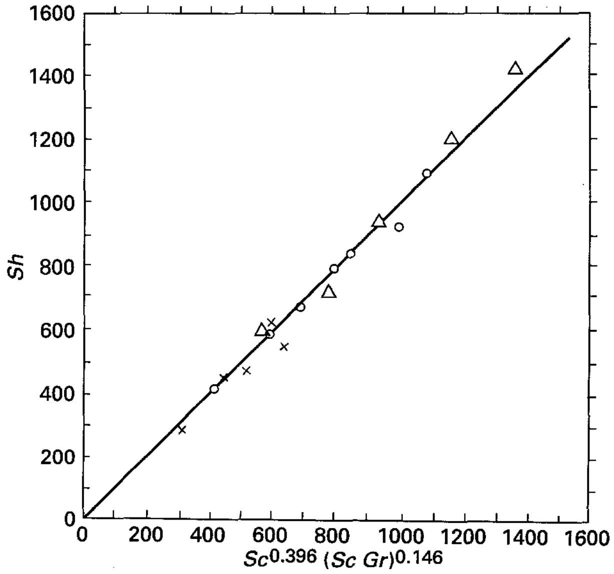

Fig. 7. Plot of Sherwood number against $Sc^{0.396}(Sc\ Gr)^{0.146}$ for the upward-facing disc. H_3PO_4 concentration: (×) 8 ($Sc = 0.8128 \times 10^5$); (○) 10 ($Sc = 1.68 \times 10^5$); (△) 12 M ($Sc = 3.59 \times 10^5$).

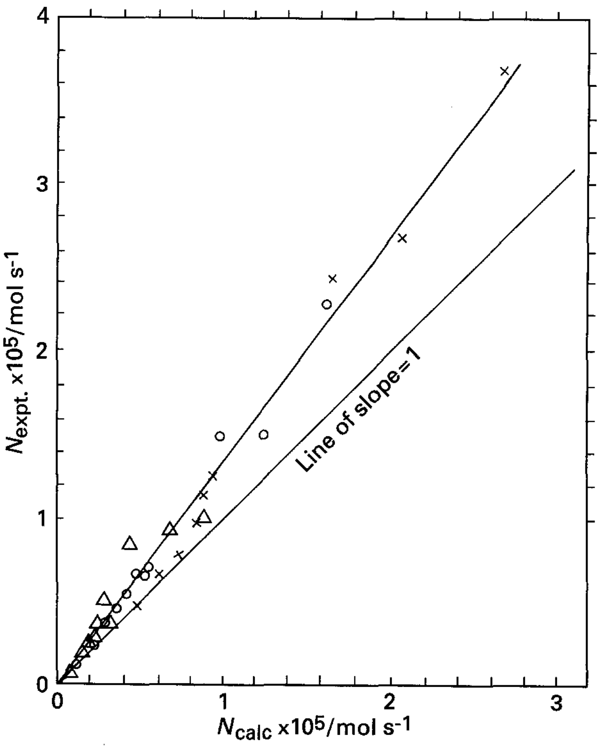

Fig. 8. Comparison between the experimental and the calculated rates of mass transfer at the active-ended cylinder. H_3PO_4 concentration: (×) 8, (○) 10 and (△) 12 M.

The total rate of mass transfer at the whole cylinder was obtained by adding the rates of mass transfer at the three surfaces. The experimental rate of mass transfer at the whole cylinder was calculated using Equation 14 with the experimentally determined *K*. Figure 8 shows that the experimental rate of mass transfer deviates from the calculated value by an amount ranging from 10–45% depending on the value of *Sc Gr*. The high value of the experimental rate of mass transfer compared to the calculated value at high *Sc Gr* suggests that the negative interaction between the solution falling from the upward facing disc which is depleted in H_3PO_4 and the downward flowing solution along the vertical cylinder is negligible. The enhancing interaction may be attributed to the fact that at relatively high *Sc Gr* the downward falling boundary layer undergoes separation with eddy formation at the lower edge of the cylinder, thus enhancing the rate of mass transfer at the periphery area of the lower disc. According to Wragg [16] who studied flow patterns at downward facing disc during electropolishing, for relatively small disc diameters, for example 25 mm, the flow at the downward facing disc tends to be radial at the periphery area before it develops into a turbulent plume at a distance from the periphery of the disc. The present result is at variance with the results obtained by Krysa and Wragg [7], and Selman and Tavakoli-Attar [17] who found that the measured rate of mass transfer at the active ended cylinder is less than the summed rate of mass transfer at the separate surface. This was explained by the upward escape of light solution, depleted in $CuSO_4$ around the edge of the cylinder bottom to the vertical surface of the cylinder. This leads to decreasing the rate of mass transfer at the vertical surface and the upward facing surface. The discrepancy between the present finding and the results of those who used the Cu–$CuSO_4$ system [7, 17] suggests that natural convection results obtained using the Cu–$CuSO_4$ system should be applied cautiously to anodic processes.

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