ELSEVIER

Chemical Engineering Journal 79 (2000) 179–186

Chemical Engineering Journal

www.elsevier.com/locate/cej

Free convective mass transfer in open upward-facing cylindrical cavities

J. Krýsa [a,*], A.A. Wragg [b], D.M. Thomas [b], M.A. Patrick [b]

[a] *Department of Inorganic Technology, Institute of Chemical Technology, Technická 5, 16628 Prague 6, Czech Republic*
[b] *School of Engineering, University of Exeter, Exeter EX4 4QF, UK*

Received 4 November 1998; received in revised form 11 June 1999; accepted 9 July 1999

Abstract

Free convective mass transfer in open upward-facing cylindrical cavities was studied experimentally using the limiting diffusion current technique. The mass transfer rate for the total vertical cavity with all surfaces active is higher (except for the shallowest cavity) than for cavities with walls only active; this is due to the cavity base flow disturbing the more fully developed boundary layers on the longer vertical surfaces. The present correlation for vertical cavities based on characteristic length L_w (surface area/perimeter projected onto a horizontal plane)

$$Sh_{L_\mathrm{w}} = 0.559 Ra_{L_\mathrm{w}}^{0.265}$$

for Ra_{L_w} in the range from 2×10^7 to 1.2×10^{10} and $Sc \in \langle 2050, 2300 \rangle$ was found to be applicable for cavities with various height/diameter ratios (0.22–2.8). Re-evaluation of previous experimental data of Somerscales and Kassemi also gave excellent agreement with this equation. The flow development after sudden switch on of the limiting current potential was observed. The flow emerging from the mouth of vertical cavities with either active or inactive base was similar, showing a visible pulsing which was also noticed on the current transients. The current transients for deeper vertical cavities showed the slow build up of the steady state diffusion layer, whereas for shallow cavities an undershoot and overshoot, typical of up-facing horizontal surfaces, was observed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Free convective mass transfer; Limiting diffusion current technique; Open vertical cavities

---

1. Introduction

This study deals with free convective mass transfer in an open cylindrical cavity. The electrochemical technique of mass transfer measurement presents a quick and accurate method of determining the mass transfer coefficient. Mass transfer is directly analogous to heat transfer so that the electrochemical method constitutes an efficient method of cold modelling of heat transfer. The dimensionless mass transfer is represented by the Sherwood number (*Sh*) and the dimensionless heat transfer by the Nusselt number (*Nu*). The mass transfer results obtained with the electrochemical technique correspond to very high Schmidt numbers (≅2000) and must be applied with caution. On the other hand, in the case of heat transfer prediction with air ($Pr \cong 0.7$), the modelling of heat transfer in large cavities on a much smaller geometric scale is permitted.

Previous investigation of natural convection in cavities has been limited mainly to the heat transfer case. The relevant literature for vertical open cavities ($\theta = 0°$), horizontal open cavities ($\theta = 90°$) and for cavities at a number of angles between these two extremes was reviewed by Japikse [1,2] and also by Somerscales and Kassemi [3]. These authors suggest that heat and mass transfer in an open cavity depends on the dimensionless groups: (*Ra*, *Pr* or *Sc*), diameter to height ratio (*d*/*H*) and the inclination angle. The Rayleigh number, which is a dimensionless density difference, defines various flow regimes and, in the vertical cavity for $Ra_d \geq 4 \times 10^6$, the flow is usually taken to be turbulent. Martin [4] differentiated the fully mixed flow regime ($Ra_d \geq 1 \times 10^8$) from the so-called turbulent boundary layer regime using the criterion $4 \times 10^6 \leq Ra_d \leq 8 \times 10^7$.

Two studies are reported [3,4] where the electrochemical deposition of copper at the inner surface of a cathodically polarized open cavity immersed in acidified copper sulphate solution was used as the means of measurement.

Somerscales and Kassemi [3] measured free convective mass transfer in open cavities of different orientations. The data for inclined cavities were represented as an empirical relation in the form:

$$Sh_d = K_1(\theta) \left[\frac{d}{H}\right]^{K_2(\theta)} Sc^{0.056} Ra_d^{0.28} \qquad (1)$$

---

[*] Corresponding author. Tel.: +42-02-2435-4112;
fax: +42-02-311-4777.
E-mail address: krysaj@vscht.cz (J. Krýsa).

1385-8947/00/$ – see front matter
PII: S1385-8947(99)00105-9

Nomenclature

A	total surface area of cavity (m^2)
A_h	surface area of vertical walls of cavity (m^2)
c_b	bulk concentration of Cu^{2+} ions ($mol\,m^{-3}$)
$c_{H_2SO_4}$	bulk concentration of sulphuric acid ($mol\,m^{-3}$)
c_{CuSO_4}	bulk concentration of copper sulphate ($mol\,m^{-3}$)
C	pre-exponential coefficient, Eq. (A1)
d	diameter of cavity (m)
D	diffusion coefficient of Cu^{2+} ions ($m^2\,s^{-1}$)
F	Faraday constant = 96487 $A\,s\,mol^{-1}$
g	gravitational acceleration = 9.41 $m\,s^{-2}$
Gr	Grashof number, $Gr=\Delta\rho g L^3\rho/\mu^2$
Gr_{L_w}	Grashof number based on length defined by Eq. (2), $Gr_{L_w}=\Delta\rho g L_w^3\rho/\mu^2$
h	coefficient of heat transfer ($W\,m^{-2}\,K^{-1}$)
H	depth of cavity (m)
I_L	limiting diffusion current (A)
k	mass transfer coefficient ($m\,s^{-1}$)
K	thermal conductivity ($W\,m^{-1}\,K^{-1}$)
L	general characteristic length (m)
L_w	characteristic length defined by Eq. (2) (m)
n	charge number of cupric ion, 2
Nu	Nusselt number, $Nu=hL/K$
Pr	Prandtl number, $Pr=\mu/\rho k$
r	factor defined by Eq. (A2)
Ra	Rayleigh number, $Ra=Gr\,Sc$
Ra_{L_w}	Rayleigh number based on length defined by Eq. (2), $Ra_{L_w}=Gr_{L_w}Sc$
Sc	Schmidt number, $Sc=\mu/\rho D$
Sh	Sherwood number, $Sh=kL/D$
Sh_{L_w}	Sherwood number based on length defined by Eq. (2)
T	electrolyte temperature (K)

Greek symbols

κ	thermal diffusivity ($m^2\,s^{-1}$)
μ	dynamic viscosity ($kg\,m^{-1}\,s^{-1}$)
θ	inclination of cavity from the vertical (°)
ρ	density ($kg\,m^{-3}$)
$\Delta\rho$	density difference between bulk solution and interface ($kg\,m^{-3}$)
Ψ	correction factor, Eq. (A1)

where the coefficient K_1 and exponent K_2 are dependent on the angle of orientation, d/H is a diameter to depth ratio of the cavity and Sh_d and Ra_d are Sherwood and Rayleigh number based on the diameter of the cavity, respectively.

Recently, Sedahmed et al. [5] studied natural convection mass transfer inside cylindrical cavities of vertical (upward, downward) and horizontal orientation. The study was carried out using a cylindrical anode placed inside the cavity to improve current distribution. The characteristic length L_w used in calculating Sh and Gr was calculated from the equation proposed by Weber et al. [6]

$$L_w=\frac{\text{internal cavity area}}{\text{perimeter projected onto horizontal plane}}=H+\frac{d}{4}. \tag{2}$$

For up-facing vertical cavities the data were correlated by the equation

$$Sh=0.257\,(Gr\,Sc)^{0.33} \tag{3}$$

for $7\times10^7\leq Gr\,Sc\leq1\times10^{10}$.

Neither Somerscales and Kassemi [3] nor Sedahmed et al. [4] performed a flow visualisation. Furthermore, the proposed correlations are based on different characteristic lengths which complicates their comparison. The Eq. (1) of Somerscales and Kassemi was obtained only for H/d ratios 0.5, 1 and 2 for d equal to 0.0127, 0.0254 and 0.0381 m, respectively. Therefore the objectives of the present work were

1. to determine correlating equations for free convective mass transfer for vertical cavities with a large range of H/d ratio and compare it with literature correlations.
2. to observe and photograph the convection patterns emerging from the cavity openings for different H/d ratio, and varying ambient fluid concentration.

The present work has a number of practical applications in the design of both mass and heat transfer devices: for example, in the design of electronic circuit board enclosures where the components have cavities from which heat must be removed and where forced convection may be inappropriate. Applications in mass transfer are in the fields of electrodeposition, electroforming and electrochemical machining, where knowledge of current distribution is essential to the successful achievement of desired shape profiles.

2. Experimental

The mass transfer experiments were performed in a glass tank of rectangular cross-section. Copper sulphate concentrations were 0.04, 0.08 and 0.16 $mol\,dm^{-3}$ and each solution contained 1.5 $mol\,dm^{-3}$ aqueous sulphuric acid as supporting electrolyte. The electrolyte temperature always lay within the range 20–22°C, being constant to ±0.1°C during each individual experiment. The actual Cu^{2+} concentrations were determined before and after each experiment using spectrophotometry, the average value being used for determining physical properties.

Copper cavities of the type shown in Fig. 1 were made using a boring tool. The inner cavity surfaces were then polished using fine emery cloth. The inactive outer surface was coated with a lacquer, (Lacomit T 65411). The cavity was mounted in a holder in a standard Toepler–Schlieren optical system with a camera [7] (Fig. 1).

The usual electrical circuit for limiting current measurement was employed, consisting of a d.c. power supply with a

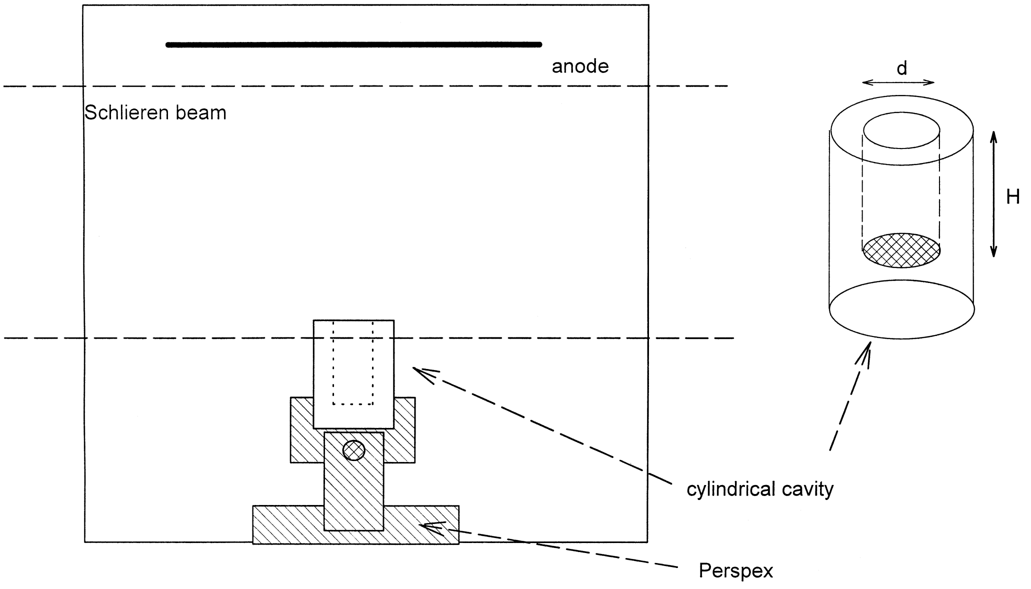

Fig. 1. Apparatus.

voltage regulator, a high impedance voltmeter, a multi-range ammeter and a chart recorder to measure the current transients. A copper sheet anode acted as a reference electrode in view of its high area compared to that of the cathode. Under such conditions polarisation is negligible at the anode and the cell current–voltage relationship depends only on the conditions prevailing at the cathode. Before each experiment the cavities were polished to a mirror finish using metal polish and then thoroughly washed. A polarisation curve for each cavity/solution combination was constructed so that the potential at which the limiting current occurred could be determined and the value of the limiting current identified. Before the experiment was commenced the electrolyte was stirred vigorously to eliminate any bulk thermal or concentration gradients. When the homogeneous stagnant state was achieved current transients were taken by suddenly applying the cathodic limiting current potential. As soon as convection from the mouth of the cavity was visible Schlieren photographs were taken at various stages of flow development.

Table 1 lists the geometric characteristics of the cavities used. This work considers a set of cavities of constant diameter d (1.35 cm) with varying heights of the vertical surface H (from 0.30 up to 3.81 cm). For experiments with side only active and base only active the surface required to be inactive was stopped off with lacquer.

Table 1
Cavity geometry

d (cm)	H (cm)	A_v (cm^2)	A (cm^2)	A_v/A_h	d/H	L_w (cm)
1.35	0	0	1.43	0	0	–
1.35	0.30	1.27	2.70	0.89	4.54	0.64
1.35	0.65	2.76	4.19	1.85	2.10	0.99
1.35	0.99	4.20	5.63	2.82	1.37	1.33
1.35	1.21	5.13	6.56	3.44	1.11	1.54
1.35	1.60	6.78	8.21	4.55	0.85	1.94
1.35	1.87	7.93	9.36	5.32	0.72	2.20
1.35	2.51	10.64	12.07	7.14	0.54	2.85
1.35	3.81	16.16	17.59	11.3	0.35	4.15

3. Result and discussion

3.1. Mass transfer data calculation

For each experiment the mass transfer coefficient was calculated from the measured limiting current using the equation:

$$k = \frac{I_L}{A\,n\,F\,c_b} \tag{4}$$

The area in this equation was the total internal area available for mass transfer for the particular experiment.

Sherwood and Rayleigh numbers for cavities were calculated using the characteristic dimension defined by Eq. (2)

$$Sh_{L_w} = \frac{kL_w}{D} \tag{5}$$

$$Ra_{L_w} = Gr_{L_w}\,Sc = \frac{g\,\Delta\rho\,L_w^3}{\mu D} \tag{6}$$

The diffusivity of the Cu^{2+} ions, and the density and viscosity of the electrolyte solution were calculated using data of Eisenberg et al. [8] for bulk concentration of Cu^{2+} ions. The $\Delta\rho$ terms were taken from Wilke et al. [9]. The effect of migration on the copper deposition rate is discussed in the Appendix A. In the present study it was considered negligible [10].

Table 2
Uncertainty of measured quantities

Quantity	Nominal value	Uncertainty	Error (%)
d	1.35 cm	0.01 cm	0.7
H	0.3 cm	0.01 cm	3.3
H	3.81 cm	0.01 cm	0.3
c_b	0.16 mol dm^{-3}	0.001 mol dm^{-3}	0.6
c_b	0.04 mol dm^{-3}	0.001 mol dm^{-3}	2.5
I_L	20 mA cm^{-2}	0.3 mA cm^{-2}	1.5

The experimental errors for measured quantities were expressed in Table 2. In addition, the uncertainty in the fluid properties D, μ and $\Delta\rho$ were taken as 0.5%. The uncertainty in the determination of the Sherwood number and Rayleigh number depends on the concentration of copper sulphate solution. For 0.04 mol dm^{-3} it was estimated as 2%, for 0.16 mol dm^{-3} as 1%.

3.2. Mass transfer measurement

The effect of cavity depth on mass transfer coefficient for vertical cavities for two copper sulphate concentrations is shown in Fig. 2. The mass transfer coefficient for a horizontal free standing disk of the same diameter as the cavity is shown as a point corresponding to zero cavity depth. It is apparent that the mass transfer rate for the entire cavity decreases with increasing cavity depth which is due to the dominant behaviour of flow at the inside vertical cylindrical wall where the mass transfer rate decreases with length [9,11].

The effect of the cavity depth on mass transfer coefficient for vertical cavities with total surface active, cylindrical wall only active and horizontal base only active, is shown in Fig. 3. The mass transfer coefficient to the horizontal base of the cavity (cylindrical wall inactive) is approximately constant for cavity depths in the range 1.9–0.65 cm but has a higher value when the cavity depth is zero. This implies that boundary conditions for mass transfer at the upward facing horizontal base surrounded by vertical walls are different from those for free discs. For a cavity depth of 0.3 cm the mass transfer coefficient for the cavity with an inactive base is higher than that for the entire cavity, whereas for cavity depths 0.7 up to 2.5 cm the mass transfer coefficient for the cavity with an inactive base is lower than that for the entire cavity. This suggests that for cavities of lower depths (up to 0.6 cm) the active base causes a decrease in the entire cavity mass transfer coefficient while for cavities with higher depths (0.7–2.5 cm) the active base increases the entire mass transfer coefficient due to the cavity base flow disturbing the more fully developed boundary layers on the longer surfaces.

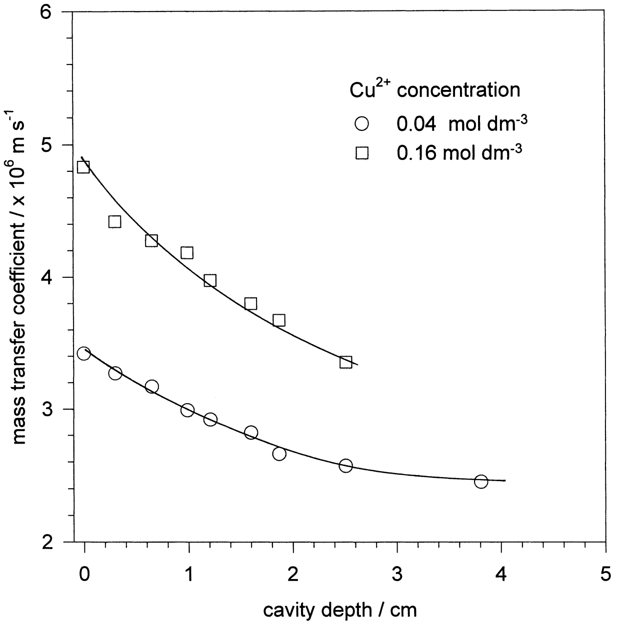

Fig. 2. Dependence of mass transfer coefficient on cavity depth for vertical upward-facing cavities for cupric ion concentrations 0.04 and 0.16 mol dm^{-3}.

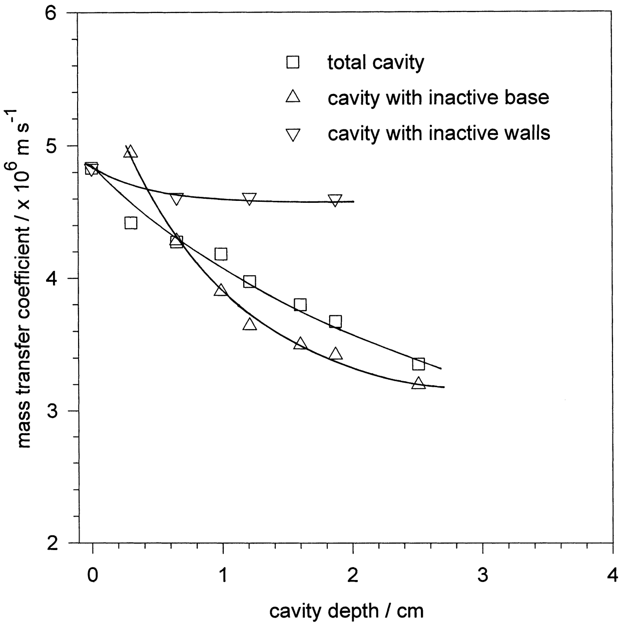

Fig. 3. Dependence of mass transfer coefficient on cavity depth for cavities with active and inactive base for a single cupric ion concentration of 0.16 mol dm^{-3}.

3.3. Mass transfer correlation

For correlation purposes various characteristic dimensions were investigated in this study. Using cavity depth as the characteristic dimension does not take into account the activity of the base. On the other hand using the cavity diameter as the characteristic dimension does not take into account the fact that the cylindrical walls are also active. The only single characteristic dimension which takes into account all the dimensions in question and can be satisfactorily used for cavities is that of Weber (L_w) [5,6] defined by Eq. (2). Thus, the Weber characteristic dimension was used here.

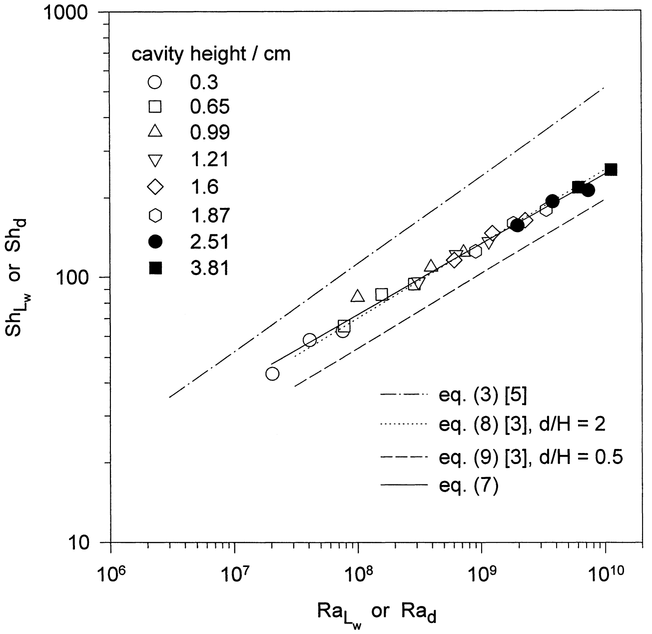

Fig. 4. Mass transfer correlation for vertical upward-facing cavity with characteristic dimension defined by Eq. (2).

The correlation of *Sh* against *Ra* for vertical cavities is shown in Fig. 4. A least squares analysis of 23 points gives the correlation

$$Sh_{L_w} = 0.559 Ra_{L_w}^{0.265} \tag{7}$$

for Ra_{L_w} in the range from 2×10^7 to 1.2×10^{10} and $Sc \in \langle 2050, 2300\rangle$. The coefficient 0.549 was reached with 95% confidence limits of 0.537–0.561. The coefficient of correlation, r^2, was 0.992.

For comparison the correlation for vertical cavities reported by Sedahmed et al. [5], who used the same characteristic length (defined by Eq. (2)), is also shown. A large discrepancy is evident between the correlating line of Sedahmed et al. [5] and the present data. A significant difference in the experimental arrangements was that in [5] an auxiliary anode was placed inside the cavity to improve current distribution. This inevitably leads to a different flow structure inside the cavity and to enhanced mass transfer. Sedahmed's work does not represent a true assessment of pure open cavity convective behaviour for mass or heat transfer.

Correlating equations based on Eq. (1) of Somerscales and Kassemi [3] for $Sc = 2000$ and d/H ratios of 2 and 0.5 reduce to

$$Sh_d = 0.404 Ra_d^{0.28} \quad \text{for } d/H = 2 \tag{8}$$

$$Sh_d = 0.311 Ra_d^{0.28} \quad \text{for } d/H = 0.5 \tag{9}$$

These equations are also shown in Fig. 4. The present data are in an excellent agreement with the correlating equation (8) for a d/H ratio of 2 while for a d/H ratio of 0.5 (deep cavities) the correlating equation (9) gives Sh_d values which are considerably lower. A further step was the correlation of the present data by equation (1) of Somerscales and Kassemi [3]. The characteristic dimension used in *Sh* and *Ra* was cavity diameter and this is the reason that *Ra* number values are practically constant for all cavities for a single copper concentration. The number of different *Ra* number values is therefore limited and use of this characteristic dimension is not very helpful.

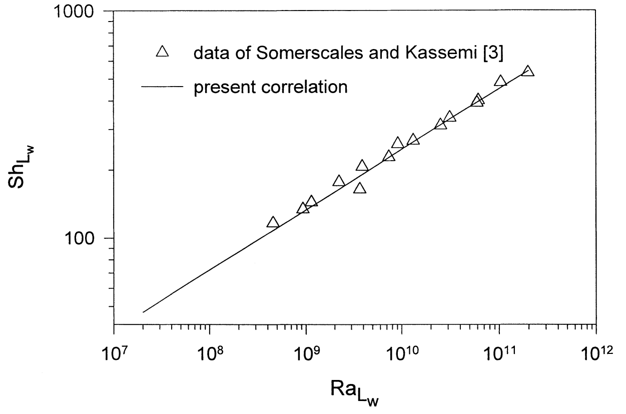

Fig. 5. Mass transfer correlation for vertical upward-facing cavity data of Somerscales and Kassemi [3] using the present approach with characteristic dimension defined by Eq. (2).

Data from vertical cavities reported by Somerscales and Kassemi (diameters 1.27, 2.54 and 3.81 cm, *H*/*d* ratios 0.5, 1.0 and 2.0) were replotted using the characteristic dimension defined by Eq. (2) and are shown together with the present correlation (Eq. (7)) in Fig. 5. There is very good agreement between the present correlation and the replotted Somerscales and Kassemi data. The correlating equation (7), which has a more convenient form, is therefore applicable for vertical cavities of not only constant diameter 1.35 cm but various diameters (from 1.27 to 3.8 cm) and *H*/*d* ratio in the range from 0.22 to 2.8 (Table 1).

The *Sh*–*Ra* correlation for the vertical cavity wall (inactive base) is shown in Fig. 6. Here the cavity depth, *H*, was taken as characteristic dimension in both *Ra* and *Sh*. A least

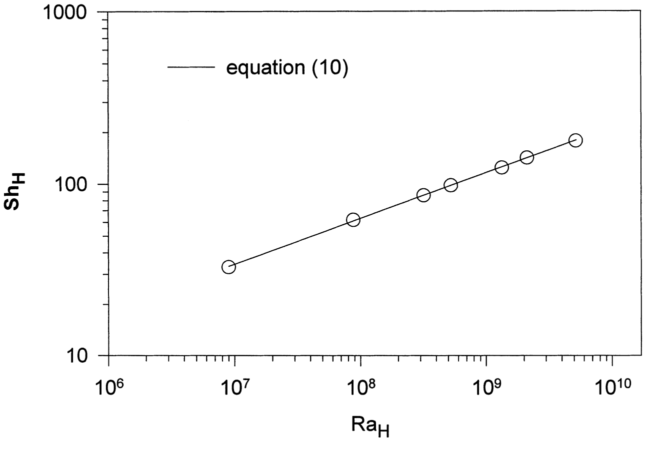

Fig. 6. Mass transfer correlation for vertical upward-facing cavities with inactive bases (cavity depth taken as characteristic dimension).

squares analysis gives the correlation

$$Sh_H = 0.480Ra_H^{0.265} \tag{10}$$

for Ra_H in the range from 2×10^7 to 1.2×10^{10}. Eq. (10) is plotted as a solid line in Fig. 6. The exponent in Eq. (10) is the same as that in Eq. (7) which suggests that the flow at the cavity walls is dominant. The higher value of the coefficient in Eq. (7) indicates the positive contribution of the cavity base to the total cavity mass transfer coefficient.

3.4. Flow visualisation

3.4.1. Vertical cavities

Visualisation of the flow emerging from cavity mouths in the vertical orientation for the 0.16 mol dm^{-3} $CuSO_4$ electrolyte was carried out, Schlieren photographs being taken at specific times following sudden switch on of the limiting current potential. The current transients were also simultaneously recorded. In the present study Ra_d (based on cavity diameter) ranges from 2.5×10^8 to 9×10^8 and, according to previous heat transfer studies [1,2,4], the flow is considered to be ‘turbulent’.

The photographs and transients for vertical cavities of depths 0.65 and 3.81 are shown in Figs. 7 and 8, respectively. As with all the other cavities, these depths showed similar convection patterns. Flow begins as a ring of fluid emerging around the cavity diameter and is followed by a progressive necking of the resultant cylindrical plume. This then gives way to a single stream about 0.5 cm in diameter and, after about 50 s, some weak pulsation occurs. Pulsing was noticed on the transients, (when the recorder was in its most sensitive mode) with the current undulating around the steady value. This demonstrates that the mass transfer rate fluctuates in a regular fashion similar to the behaviour for upward facing horizontal discs [12]. The undershoot and overshoot in the current transients immediately following the early pure diffusional region, characteristic of shallower cavities, are also apparent and similar to those observed for upward facing horizontal discs [12]. The undershoot and overshoot become less pronounced with increasing cavity depth and are not visible for cavities of depth greater than 1.6 cm because of the dominant behaviour of the cavity wall flow. The decrease in current with time during the build up of the diffusion layer takes significantly longer for deeper cavities than for shallower cavities.

Further runs were conducted using cavities with inactive bases. There is little difference between the observed flow regimes for these cavities compared with the fully active ones except that the early stages of the plume appear less disturbed. Also, due to the base being inactive, the current-time transients do not exhibit the undershoot and overshoot typical of horizontal surfaces. Again the slow build up of diffusion layer for deep cavities is observed.

The interior surfaces of the cavities were investigated after each run and it was found that deposition of copper decreased down the cavity with little detectable deposit on the bases of the deepest ones. This phenomenon was also observed by Somerscales and Kassemi [3]. This suggests that there is a relatively stagnant, inactive region in the bottom of the deeper cavities.

Figs. 7 and 8 show that the flow from all the vertical cavities, with both active and inactive bases, begins in a similar manner. This is because the convection currents from the wall alone are the first to appear, with mass transfer from the base ‘catching up’ later. The inflow of the denser copper sulfate solution, in this flow stage, is probably down the

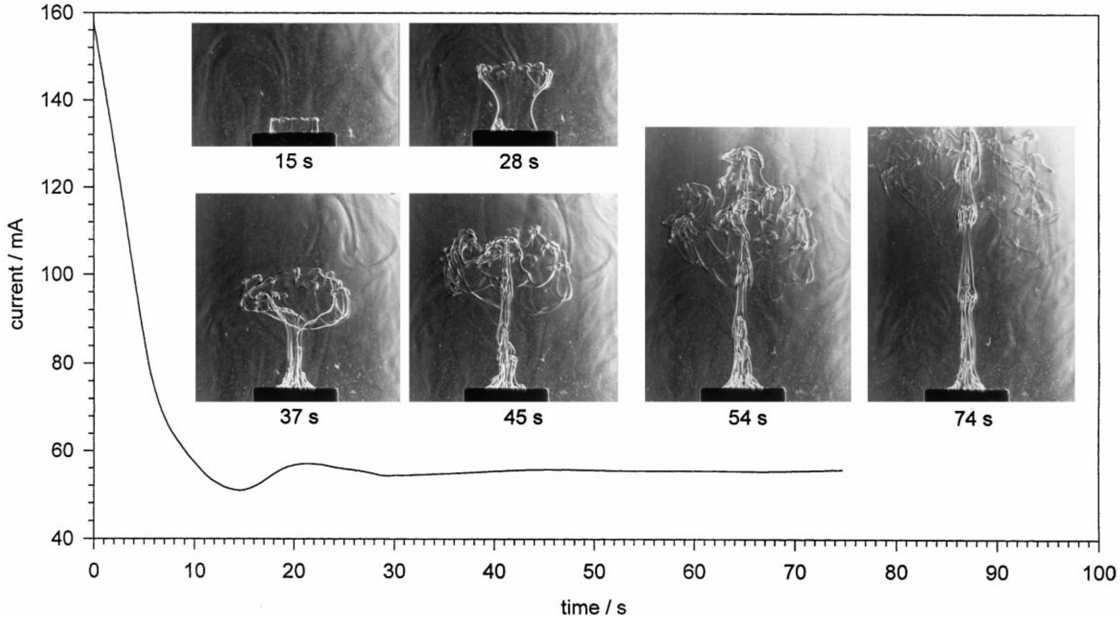

Fig. 7. Current transients and photographs of flow for total vertical cavity of depth 0.65 cm (in 0.16 mol dm^{-3} copper sulphate).

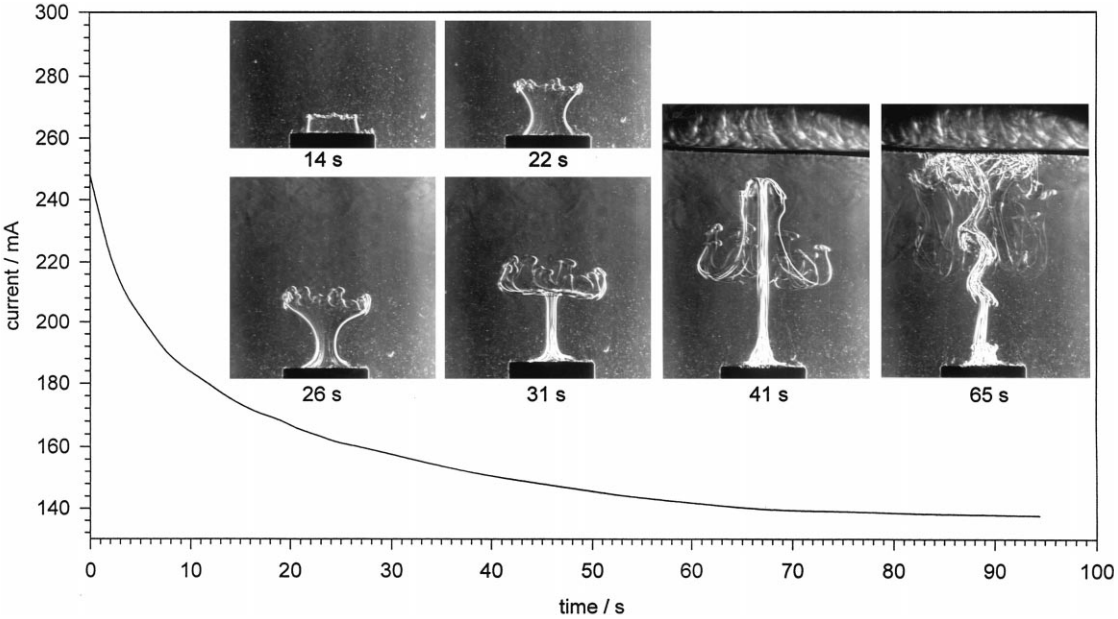

Fig. 8. Current transients and photographs of flow for total vertical cavity of depth 3.81 cm (in 0.16 mol dm^{-3} copper sulphate).

centre of the cavity. When the convective patterns from the cavity base reach the cavity top the ingress of electrolyte is probably replaced by radial inflow around the circumference. The precise mechanism of flow into, and within such convecting open cavities deserves further study.

3.5. Comparison of heat and transfer data for open vertical cavities

Comparison of mass and heat transfer data was previously carried out by Somerscales and Kassemi [3] with the aim of predicting heat transfer from mass transfer measurements. The cavity diameter was used as a characteristic length in *Gr* and *Sh* (*Nu*) and it was stated that the comparison was not entirely satisfactory.

To substantiate the analogy between heat and mass transfer for upward-facing vertical open cavities the present correlation (based on L_w) was compared with previous heat transfer data. [4,13–15] (based on *d*) and shown in Fig. 9. It can be seen that the best agreement was obtained with the correlation proposed by Martin [4] for $H/d = 3.7$ where water and ethylene glycol were used as fluids in the heat transfer tests. All other heat transfer correlations provide significantly lower heat transfer coefficients. It is noticable that the heat transfer data depend strongly on the *H*/*d* ratio. This ratio is very often introduced in the correlating equations as shown for example by Japikse and Winter [2] who compared analytical and experimental results for heat transfer in terms of Nu_a and $Gr_a\,Pr$ (a/H) numbers $(a = d/2)$. The discrepancy between heat and mass transfer data can be explained by the following reasons:

1. Schmidt numbers are several orders of magnitude higher than Prandtl numbers. The value of *Pr* depends on the fluid used for the particular heat transfer experiment (≈1 for air, ≈100 for water).
2. The transition from the laminar to the turbulent regime can be characterised by the transitional Grashof number [2] which depends on the fluid used for heat transfer measurement (for air it is 4×10^6–2×10^7, for water 10^5–10^6 and for ethylene glycol 3×10^3–1×10^4).
3. There is a considerable difference in the range of values of *H*/*d* used in the various experiments. The mass

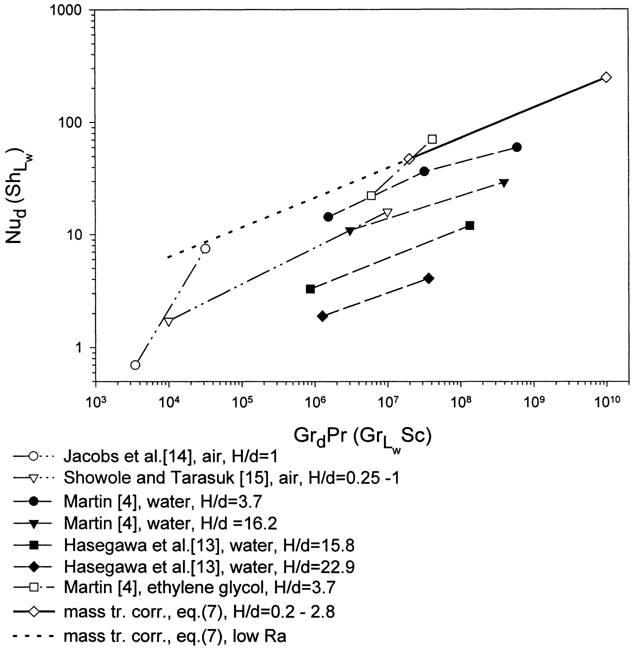

Fig. 9. Comparison of heat transfer data with the present mass transfer correlation.

transfer measurements were made with shallow cavities (H/d small) whereas many of the heat transfer tests (except those with air) were performed with much deeper cavities (H/d large).

4. Conclusions

1. Mass transfer rate for the total vertical cavity with all surfaces active is lower for shallow cavities ($H/d < 0.45$) and higher for deep cavities ($H/d > 0.5$) than for cavities with walls only active.
2. The present correlation for vertical cavities based on characteristic length L_w (surface area/perimeter projected onto a horizontal plane)

   $$Sh_{L_\mathrm{w}} = 0.559 Ra_{L_\mathrm{w}}^{0.265}$$

   for Ra_{L_w} in the range from 2×10^7 to 1.2×10^{10} and $\mathrm{Sc} \in \langle 2050, 2300 \rangle$ was found to be applicable for cavities with various depth/diameter ratios (0.2–2.8).
3. Data obtained by Sedahmed et al. [5] using an anode within the cavity have been shown to be unrepresentative of pure open cavity convection.
4. The current transients for deeper vertical cavities showed the slow build up of the steady state diffusion layer, whereas for shallow cavities an undershoot and overshoot, typical of up-facing horizontal surfaces, was observed.
5. The flow emerging from the mouth of vertical cavities with either active or inactive base was similar, showing a visible pulsing.

Acknowledgements

Financial support from the Royal Society for a visit to Exeter by J.K. is gratefully acknowledged.

Appendix A

The effect of migration in natural convection can be expressed by introducing a multiplicative correction factor, Ψ, for the pre-exponential coefficient C in the dimensionless (non-electrolytic) mass transport correlation

$$Sh = \Psi\ C\ (Ra)^{0.25} \tag{A1}$$

The value of Ψ depends on the composition of the $CuSO_4$–H_2SO_4 electrolyte and it is expressed in [10] as a function of the factor r

$$r = \frac{c_{\mathrm{H_2SO_4}}}{c_{\mathrm{H_2SO_4}} + 0.5 c_{\mathrm{CuSO_4}}} \tag{A2}$$

Values of Ψ were calculated for Cu^{2+} concentrations used in this study assuming total (a) and no (b) sulphate dissociation as shown in Table A.1. It is interesting to note that the limiting current correction factor does not approach unity for an excess of sulphuric acid as is the case in forced convection systems but is lower than 1. The total dissociation model is more appropriate. It can be seen that the migration correction factor is lower than 1 for all concentrations. The highest correction (3%) is for the lowest concentration of Cu^{2+} (0.04 mol dm^{-3}) while for Cu^{2+} concentration of 0.16 mol dm^{-3} it is only 1.5%.

Table A.1

$c_{\mathrm{CuSO_4}}$ (mol dm^{-3})	$c_{\mathrm{H_2SO_4}}$ (mol dm^{-3})	r	Ψ(a)	Ψ(b)
0.04	1.5	0.97	0.97	0.95
0.08	1.5	0.95	0.975	0.96
0.16	1.5	0.90	0.985	1.0
0.26	1.5	0.85	0.993	1.04

References

[1] D. Japikse, in: T.F. Irvine Jr., J.P. Hartnett (Eds.), On Advances in Heat Transfer, vol. 9, Academic Press, New York, 1973, pp. 1–111.

[2] D. Japikse, E.R.F. Winter, Single-phase transport processes in the open thermosyphon, Int. J. Heat Mass Transfer 14 (1971) 427.

[3] E.F.C. Somerscales, M. Kassemi, Electrochemical mass transfer studies in open cavities, J. Appl. Electrochem. 15 (1985) 405.

[4] B.W. Martin, Free convection in an open thermosyphon, with special reference to tubulent flow, Proc. Roy. Soc. London Ser. A 230 (1955) 502.

[5] G.H. Sedahmed, A.M. Ahmed, M.L. El-Rafey, A.Y. Hosney, E.A. Ayob, Natural convection mass transfer inside cylindrical cavities of different orientation, J. Appl. Electrochem. 25 (1995) 677.

[6] M.E. Weber, P. Austraukas, S. Petsalis, Natural convection mass transfer to nonspherical objects at high Rayleigh numbers, Can. J. Chem. Eng. 62 (1984) 68.

[7] D.W. Holder, R.J. North, Schlieren methods, Notes on Applied Science No. 31, National Physical Laboratory, London 1963.

[8] M. Eisenberg, C.W. Tobias, C.R. Wilke, Selected properties of ternary electrolytes employed in ionic mass transfer studies, J. Electrochem. Soc. 103 (1956) 413.

[9] C.R. Wilke, W. Tobias, M. Eisenberg, Correlation of limiting currents under free convective condition, J. Electrochem. Soc. 100 (1953) 513.

[10] N. Ibl, O. Dossenbach, in: E. Yeager, J.O'.M. Bockris, B.E. Conway, S. Sarangapani (Eds.), Proc. on Comprehensive Treatise of Electrochemistry, vol. 6, Plenum Press, New York, 1983, pp. 192–198.

[11] M.A. Patrick, A.A. Wragg, D.M. Pargeter, Mass transfer by free convection during electrolysis at inclined electrodes, Can. J. Chem. Eng. 55 (1977) 432.

[12] M.A. Patrick, A.A. Wragg, Optical and electrochemical studies of transient free convection mass transfer at horizontal surfaces, Int. J. Heat Mass Transfer 18 (1975) 1397.

[13] S. Hasegawa, K. Nishikawa, K. Yamagata, Heat transfer in an open thermosyphon, Bull. Jap. Soc. Mech. Eng. 6 (1963) 230.

[14] H.R. Jacobs, W.E. Mason Jr., E.T. Hikida, Proc. on natural convection in open rectangular cavities, 5th International Heat Transfer Conference, Tokyo, vol. 3, 1974, pp. 90–94.

[15] R.A. Showole, J.D. Tarasuk, Experimental and numerical studies of natural convection with flow separation in upward-facing inclined open cavities, J. Heat Transfer 115 (1993) 592.