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Free convective mass transfer at down-pointing pyramidal electrodes

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Abstract—A limiting current technique was used for the measurement of the free convective mass transfer rate at entire down-pointing pyramids and also at the individual faces of the pyramids. The cathodic deposition of Cu^{2+} ions at electrodes of varying geometries was used as the mass transfer process, the supporting electrolyte being sulphuric acid. The mass transfer rate at a single inclined pyramidal surface was correlated by the equation

$$Sh_L = 0.78(Ra_{L,\theta})^{0.25}$$

for the $Ra_{L,\theta}$ range 9.3×10^6 to 2×10^{11}. The mass transfer data for the entire pyramid were correlated using a method which includes an interference factor taking account of the fact that the upward-facing horizontal surface is exposed to fluid which has already been depleted in copper ions. The dependence of the interference factor on the aspect ratio of the pyramid (L/b) was established.

1. INTRODUCTION

This paper describes an experimental investigation of mass transfer in free convection at down-pointing pyramidal electrodes using the well-known limiting diffusion current technique (LDCT) of mass transfer measurement. The down-pointing pyramidal electrode is a case of a three-dimensional object with one upward facing horizontal triangular face and three inclined triangular faces.

Several previous accounts of work on free convective mass transfer at inclined surfaces [1–3], upward horizontal surfaces [4–7] and three-dimensional objects [8–11] are known to the authors, all of which made use of the LDCT. Patrick *et al.* [1], as part of a broader investigation, studied free convection mass transfer to inclined down-facing rectangular surfaces and the results were well correlated by the equation

$$Sh_L = 0.68(Ra_L \cos\theta)^{0.25} \quad (1)$$

for $6 \times 10^4 \leqslant Ra_{L,\theta} \leqslant 3 \times 10^9$, θ being the inclination angle from vertical. The results of Fouad and Ahmed [3] for down-facing planes also follow equation (1), even up to a $Ra_{L,\theta}$ value of 10^{12}, suggesting, rather surprisingly, that a predominantly laminar flow persists up to this high value of Rayleigh number.

Free convective mass transfer at horizontal electrodes has also received considerable attention using the electrochemical method [4–6], diameter (for circular planes) [5, 6] or length (for rectangles) [4] being used as characteristic dimensions in correlating equations. Lloyd and Moran [7] investigated natural convection adjacent to unshrouded upward facing horizontal surfaces formed by circular, square, rectangular and right triangular planforms. The data for all planforms were reduced to a single correlation using the characteristic length recommended by Goldstein *et al.* [12]

$$L_G = \frac{\text{surface area}}{\text{surface perimeter}}. \quad (2)$$

The data for the turbulent regime were correlated by the expression

$$Sh = 0.15(Ra)^{0.33} \quad (3)$$

in the range $8 \times 10^6 \leqslant Ra \leqslant 1.6 \times 10^9$. This characteristic length of equation (2) appears to bring all the data into the common correlation, including those for surfaces such as the right triangles.

Weber *et al.* [8] measured and correlated natural convection mass transfer from a variety of spherical and non-spherical three-dimensional objects, including pyramids in several orientations. The charac-

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NOMENCLATURE

A_{pt}	total surface area of pyramid
A_i	area of a single inclined pyramid surface
A_{it}	area of all inclined pyramid surfaces
A_h	area of horizontal base of pyramid
b	base of pyramid (Fig. 1)
c_b	bulk concentration of copper ions
c_{CuSO_4}	bulk concentration of copper sulphate
$c_{H_2SO_4}$	bulk concentration of sulphuric acid
D	diffusion coefficient of copper ions
F	Faraday constant
g	gravitational acceleration
H_p	height of pyramid
H_h	height of horizontal triangular base of pyramid (Fig. 1)
I_L	limiting diffusion current
k	mass transfer coefficient
L	length of inclined surface of pyramid
L_G	characteristic length of Goldstein [equation (2)]
L_W	characteristic length of Weber [equation (4)]
n	charge number of copper ion
Ra	Rayleigh number
$Ra_{L,\theta}$	Rayleigh number based on inclined surface length and on $g\cos\theta$
S_S	surface area of a sphere with the same volume as a pyramid
S_p	surface area of a pyramid
Sh	Sherwood number
Sh_L	Sherwood number based on inclined surface length
T	electrolyte temperature.

Greek symbols

$\Delta\rho$	density difference between bulk solution and interface
ρ	density
μ	dynamic viscosity
θ	inclination angle from the vertical (see Fig. 1)
Ψ	sphericity ($= S_s/S_p$).

teristic dimension for such objects, which is sensitive to orientation, was defined as

$$L_W = \frac{\text{surface area}}{\text{perimeter projected onto horizontal plane}}. \quad (4)$$

For objects with sphericity $\Psi > 0.6$ Weber *et al.* [8] obtained the universal correlation

$$Sh = Sh_0 + 0.53[f(Sc)\cdot Ra]^{0.256} \quad (5)$$

where

$$f(Sc) = \left[1 + \frac{0.5}{Sc^{9/16}}\right]^{-16/9} \quad (6)$$

and Sh_0 is the stagnant medium Sherwood number. The Weber characteristic dimension (L_W) was used by Sedahmed and Nirdosh [9], who investigated free convection mass transfer at horizontal cylinders with active ends.

Worthington *et al.* [10] studied free convective mass transfer at horizontally oriented cuboids and found that the overall measured rate of mass transfer is lower than the value predicted by summing the rates of mass transfer at the different individual faces. This led the authors to use a correction factor which they termed the 'interference factor'.

In a previous paper [11] we investigated free convective mass transfer at vertical cylindrical electrodes with active upper and lower ends. Again it was found that the mass transfer rates at the single surfaces were not additive because of significant interactions caused by leading edge effects.

Due to the fact that the study of Weber *et al.* [8] on free convective mass transfer at pyramidal electrodes was very limited (two pyramids, both with constant height to base ratio) it was decided to carry out a much fuller investigation of this particular geometry. The objectives of the present work were:

(a) to measure the mass transfer rates at the triangular inclined surfaces and the horizontal base of a downpointing pyramid;
(b) to measure the mass transfer rate at entire downpointing pyramids with varying aspect ratio;
(c) to correlate data for such surfaces taking account of interaction between the individual surfaces.

Such mass transfer measurements are known to provide extremely good simulation of heat transfer by free convection [13]. Mass transfer data for electrochemical systems in natural convection are also pertinent to the kinetics and mechanisms of processes such as electrodeposition, electroforming and electropolishing.

2. EXPERIMENTAL

The experiments were performed in a cylindrical 3 dm^3 glass container of internal diameter 15 cm and height 25 cm. Copper sulphate concentration varied from 0.015 to 0.238 M. Each solution contained 1.5 M sulphuric acid as a supporting electrolyte. The electrolyte temperature was carefully measured and always lay within the range 18–21°C, being constant to ± 0.1°C during each individual experiment. The pyramidal electrodes were machined from solid

copper. Each electrode was supported using a 1 mm diameter steel wire glued into a hole in the centre of the horizontal base. This wire also served as a current carrier. The wire was lacquered to insulate it from the electrolyte. The pyramidal cathodes were placed in the centre of the container. The counter electrode (anode) was a cylindrical copper mesh of diameter 14 cm and height 24 cm. The arrangement of the apparatus is similar to that shown previously [11]. The actual Cu^{2+} concentration was periodically determined by spectrophotometric analysis, to an accuracy of approximately 2%.

The usual electrical circuit for limiting current measurement was employed, consisting of a d.c. power supply with a voltage regulator, a high impedance voltmeter and a multi-range ammeter. Limiting currents were obtained by the well known procedure which has been reported in detail previously [14]. The anode acted as a reference electrode in view of its high area compared to that of the cathode. Under such conditions polarization is negligible at the anode and the cell current–voltage relationship depends only on the conditions prevailing at the cathode. The onset of the limiting current was sharp and reproducible, and its value was determined to an accuracy of $\pm 2\%$.

Table 1 lists all the geometric characterics of the pyramids used. This work considers sets of pyramids with constant inclination angle θ, constant length of inclined surface L and varying aspect ratios (length to side of base). In this investigation L ranged from 0.57 up to 7.86 cm and inclination angle from -4.5 up to $-50.8°$. Values of L are estimated to be accurate within 1–2%. Inclination angles are counted negative to indicate the down-facing orientation of the triangular pyramid faces and for consistency with the work described in [1].

The mass transfer controlled limiting currents at the inclined surface and at the upward facing horizontal surface were measured separately and in combination e.g. at the pyramid with three active inclined surfaces and at the entire pyramid with the upfacing top surface also simultaneously active. Surfaces not required to be active were stopped off with lacquer.

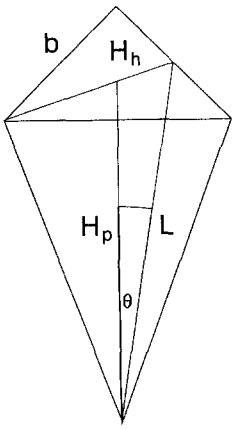

Fig. 1. Geometric parameters of down-pointing pyramids.

The geometric parameters of the down pointing pyramids are illustrated in Fig. 1.

3. RESULTS AND DISCUSSION

3.1. *Mass transfer data calculations*

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

$$k = \frac{I_L}{AnFc_b}. \tag{7}$$

The area in this equation was the total available for mass transfer for the particular experiment. The correction for the attachment of the supporting wire was small, never being more than 1.5% of the exposed area and usually being much less.

For the inclined triangular surfaces, the data were expressed in the form of a slant height Sherwood number and a slant height Rayleigh number

Table 1. Electrode geometries

Pyramid	b (cm)	L (cm)	θ (°)	H_p (cm)	H_h (cm)	A_i (cm^2)	A_{it} (cm^2)	A_{pt} (cm^2)	A_{it}/A_h	L/b	L_w (cm)	ψ
1	1.05	0.57	−31.5	0.49	0.83	0.30	0.90	1.33	2.06	0.54	0.42	0.62
2	2.15	1.19	−31.5	1.02	1.86	1.28	3.87	5.87	1.93	0.55	0.91	0.64
3	3.60	1.97	−31.5	1.68	3.12	3.55	10.64	16.26	1.89	0.55	1.50	0.64
4	5.34	2.96	−31.5	2.52	4.62	7.90	23.71	36.04	1.92	0.55	2.25	0.64
5	7.14	3.95	−31.5	3.37	6.18	14.10	42.31	64.37	1.92	0.55	3.00	0.64
6	1.16	1.96	−10	1.93	1.00	1.14	3.41	4.02	5.81	1.69	1.15	0.62
7	2.31	1.97	−20	1.85	2.00	2.28	6.83	9.14	2.95	0.85	1.32	0.67
8	3.39	1.96	−30	1.70	2.94	3.22	10.00	14.98	2.00	0.59	1.47	0.64
9	4.34	1.98	−40	1.52	3.76	4.30	12.90	21.05	1.58	0.46	1.62	0.59
10	5.22	1.99	−50	1.28	4.52	5.20	15.58	27.38	1.32	0.38	1.75	0.51
11	2.17	0.805	−50.8	0.51	1.88	0.87	2.62	4.66	1.28	0.37	0.71	0.51
12	2.22	1.20	−32.2	1.06	1.92	1.33	3.99	6.12	1.87	0.54	0.92	0.64
13	2.20	2.06	−17.9	2.00	1.91	2.27	6.81	8.91	3.24	0.94	1.35	0.68
14	2.17	3.97	−9.0	3.93	1.88	4.31	12.93	15.03	6.16	1.83	2.31	0.62
15	2.13	7.86	−4.5	7.83	1.84	8.37	25.11	27.07	12.8	3.70	4.24	0.53

$$Sh_L = \frac{kL}{D} \tag{8}$$

$$Ra_{L,\theta} = \frac{g\Delta\rho L^3}{\mu D}\cos\theta. \tag{9}$$

This approach to data treatment was previously used for the correlation of free convective heat and mass transfer at inclined plates [1, 2, 20] and at cones with an insulated base [15].

The diffusivity of the Cu^{2+} ions was calculated using the equation

$$\frac{D\mu}{T} = (2.495 + 0.0173c_{CuSO_4} + 0.0692c_{H_2SO_4}) \times 10^{-15}\frac{N}{K} \tag{10}$$

due to Fenech and Tobias [4], where C is in mol dm^{-3}. Density and viscosity were calculated using data of Eisenberg *et al.* [16]. The $\Delta\rho$ terms were taken from Wilke *et al* [17]. The effect of migration on the copper deposition rate was negligible; the migration contribution for the highest concentration of copper sulphate (0.23 M) was 1.5% [18]. Values of Sh_0 were calculated by the method outlined by Clift *et al.* [19].

3.2. *Single active surfaces*

Mass transfer coefficients for a single inclined triangular surface for different pyramid lengths for pyramids numbered 11–15 are shown in Fig. 2. These are dependent both on the length and inclination angle [1]. Due to this fact the effect of pyramid length and inclination angle were investigated separately. The mass transfer coefficients to a single inclined surface were measured at pyramids 1–5 (constant inclination angle, varying length (Fig. 3a)) and at pyramids 6–10 (constant length, varying inclination angle (Fig. 3b)). From Fig. 3a,b it follows that the mass transfer coefficient depends chiefly on the surface length and the inclination angle begins to show a greater influence for inclination angles greater than $-40°$. The effect of both length and inclination angle for a single concentration of copper sulphate is shown in Fig. 3c. Values of K were plotted against L for pyramids 11–15 (curve c). K values on curve b were obtained as follows. To the lengths of pyramids 11–15 values of inclination angle were attributed according to Table 1. For each inclination angle (with the exception of $-4.5°$) values of K were taken from Fig. 3b.

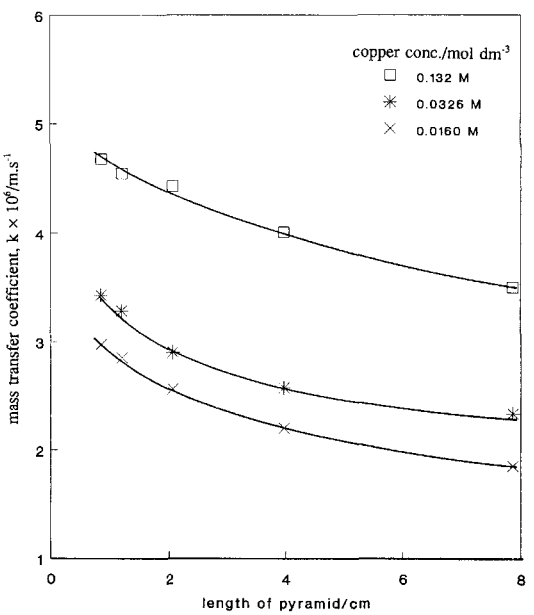

Fig. 2. The effect of length (and inclination angle) on mass transfer coefficient for a single face of down-pointing constant base pyramids for varying $CuSO_4$ concentrations (pyramids 11–15).

A plot of Sh_L against $Ra_{L,\theta}$ for the single inclined triangular surfaces is shown as Fig. 4. A least squares fit of the data yields the relation

$$Sh_L = 0.68(Ra_{L,\theta})^{0.259}. \tag{11}$$

Forcing a slope of 1/4, as has been reported in the literature for laminar flow on inclined planes [1, 2, 15, 20], gives

$$Sh_L = 0.78(Ra_{L,\theta})^{0.25} \tag{12}$$

for data in the $Ra_{L,\theta}$ range 9.3×10^6 to 2×10^{11}. This equation is plotted as the line in Fig. 4 and can be seen to represent the data well. The higher value of the coefficient in equation (12) for a single inclined triangular face of a down-pointing pyramid in comparison with equation (1) of Patrick *et al.* [1] for an inclined rectangular surface, may be explained by the fact that the triangular surface is fed by a fresh electrolyte, not only at the lower edge of the surface, as for a rectangular face, but all along the inclined edges of the triangle. This must inevitably lead to a higher mean mass transfer coefficient.

Results for the mass transfer to the horizontal triangular upward facing surface are shown in Fig. 5 as a plot of Sherwood number against Rayleigh number, with the height of the triangular horizontal base (H_h) as characteristic dimension. The least square analysis gives the correlation

$$Sh_{H_h} = 0.203(Ra_{H_h})^{0.323}. \tag{13}$$

Forcing a slope of 1/3 as reported in the literature for turbulent flow on upward facing horizontal planes [4–7, 20] gives the relation:

$$Sh_{H_h} = 0.176(Ra_{H_h})^{0.33} \tag{14}$$

for Ra_{H_h} in the range from 5×10^7 to 2.2×10^{10}. This equation is plotted as the broken line in Fig. 5. This gives very good agreement with the correlation for upward facing surfaces given by Patrick *et al.* [21].

3.3. *Mass transfer at combinations of surfaces*

Mass transfer coefficients for all the inclined triangular surfaces for different pyramid lengths of pyramids 11–15 are shown in Fig. 6 for four different $CuSO_4$ concentrations. The mass transfer correlation

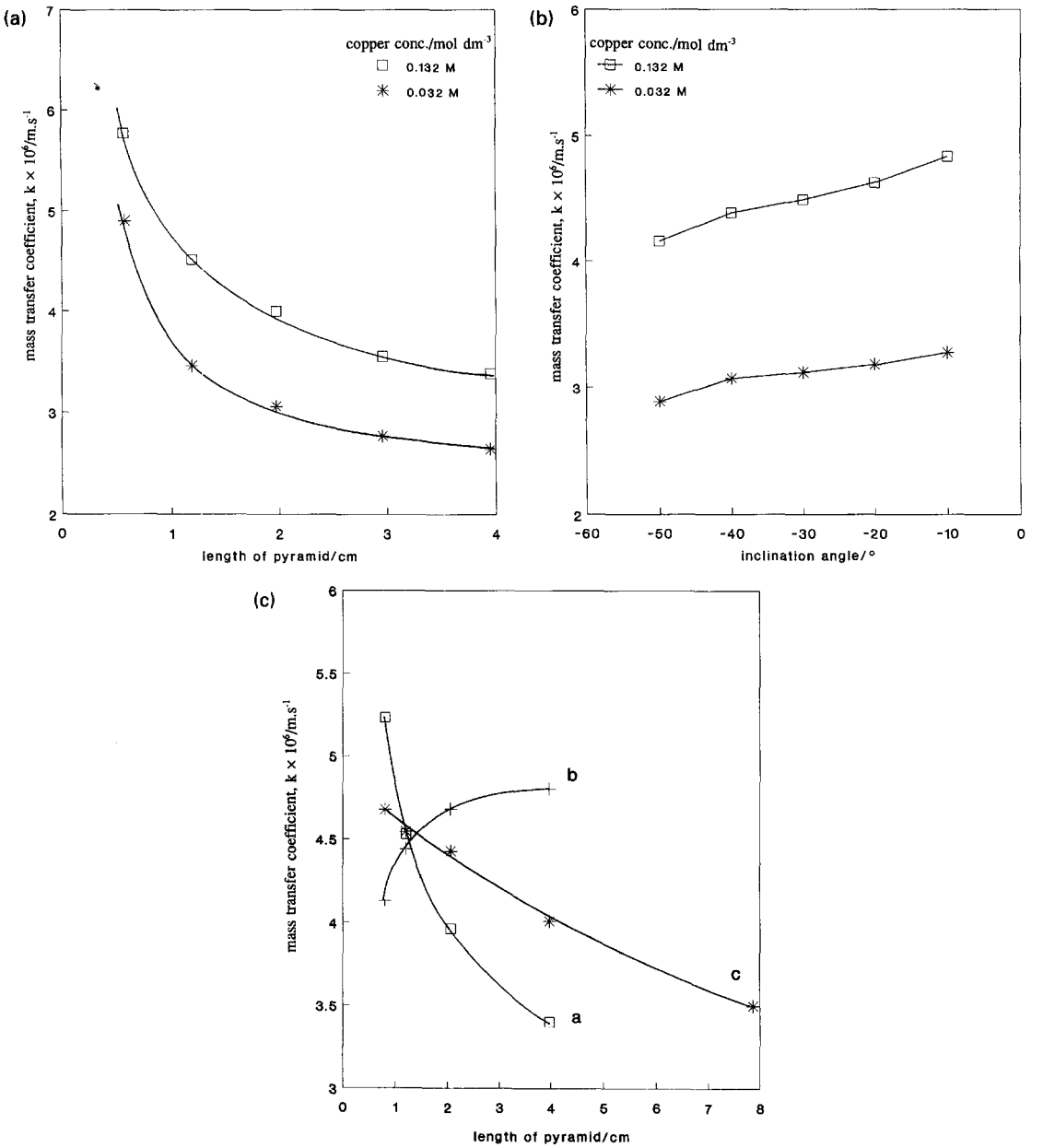

Fig. 3. (a) The effect of length on mass transfer coefficient of a single inclined surface of a down-pointing pyramid of constant inclination angle (pyramids 1–5). (b) The effect of inclination angle on mass transfer coefficient of a single inclined surface of a down-pointing pyramid of constant length (pyramids 6–10). (c) Simultaneous effect of length and inclination angle on mass transfer coefficient at a single inclined surface of a down-pointing pyramid, $c = 0.132$ M, □ pyramids 1–5 (constant angle), + pyramids 6–10 (constant length), * pyramids 11–15.

for all the inclined surfaces simultaneously active is shown in Fig. 7. Forcing a slope of 1/4 gives the relationship

$$Sh_L = 0.714(Ra_{L,\theta})^{0.25} \quad (15)$$

for the same $Ra_{L,\theta}$ range as equation (12). The coefficient in equation (15) is lower than that in equation (12), since the mass transfer rates at the single inclined suraces are not additive because of interactions at the pyramid edges. However, mass transfer is still higher than for inclined rectangular faces [1, 2, 15, 20].

Mass transfer for the separate surfaces of pyramids 11–15 and for the surfaces in combination are plotted in Fig. 8 for a single concentration of copper sulphate (0.132 M). This clearly shows the superior mass transfer performance of the up-facing horizontal surface and the fact that a single triangular inclined surface gives higher mass transfer than the combined inclined surfaces.

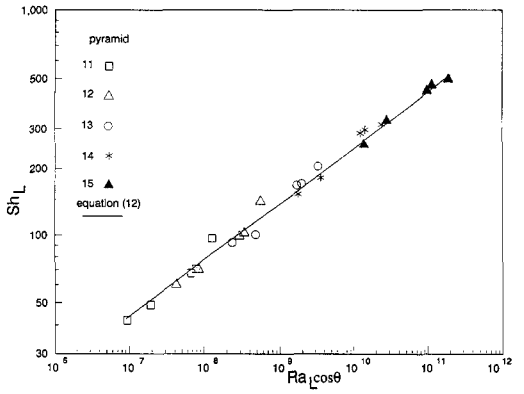

Fig. 4. Mass transfer correlation for single inclined triangular surfaces.

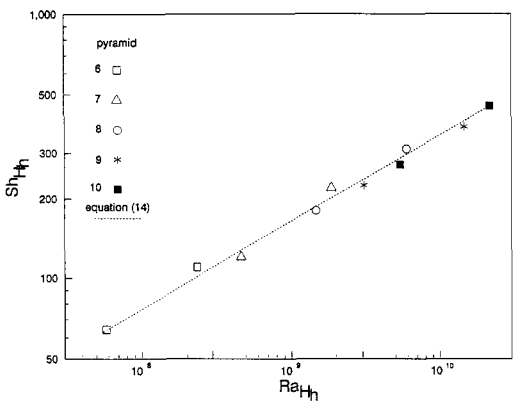

Fig. 5. Mass transfer correlation for upward-facing horizontal triangular surfaces.

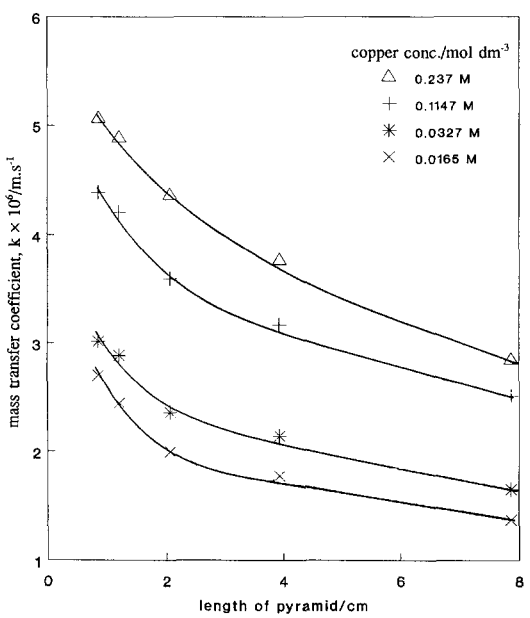

Fig. 6. The effect of length (and inclination angle) on mass transfer coefficient for all inclined surfaces simultaneously active (constant pyramid base).

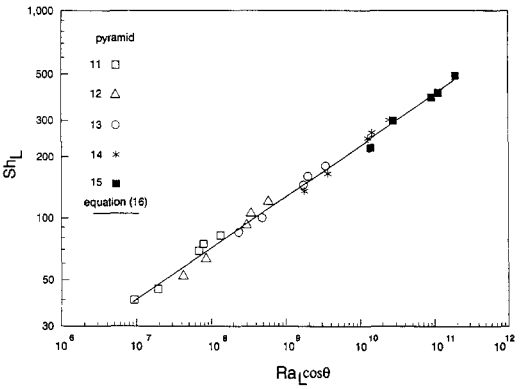

Fig. 7. Mass transfer correlation for all inclined faces simultaneously active.

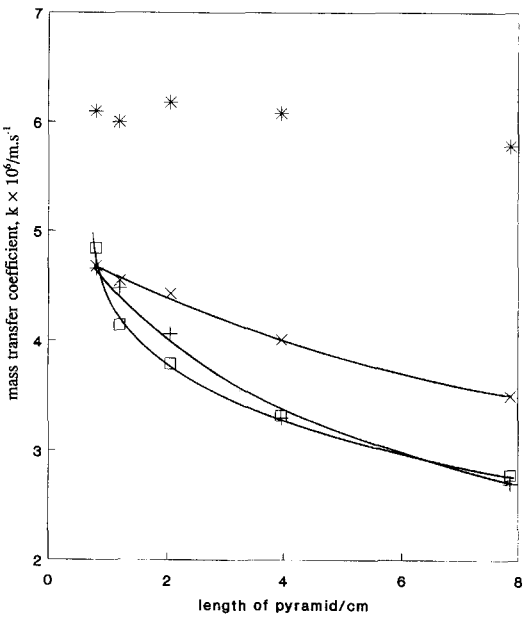

Fig. 8. The effect of length on mass transfer coefficient for different surfaces for a single concentration of copper sulphate (constant pyramid base). Pyramid surfaces considered, × single inclined triangular surface, + combination of all inclined triangular surfaces, * upward-facing horizontal surface, □ total surface.

The effect of pyramid length, L (and inclination angle), on the mass transfer coefficient for the entire pyramids 11–15 is shown in Fig. 9 for four different $CuSO_4$ concentrations.

3.4. *Overall data correlation*

3.4.1. *Approach using Weber characteristic dimension.* The total mass transfer results from pyramids 11–15 are plotted using the characteristic length defined by Weber *et al.* [8] in Fig. 10. The Weber correlation (equation (5)) is also shown. It is seen that the data from all the present pyramids lie above equation (5). This may be explained by several facts:

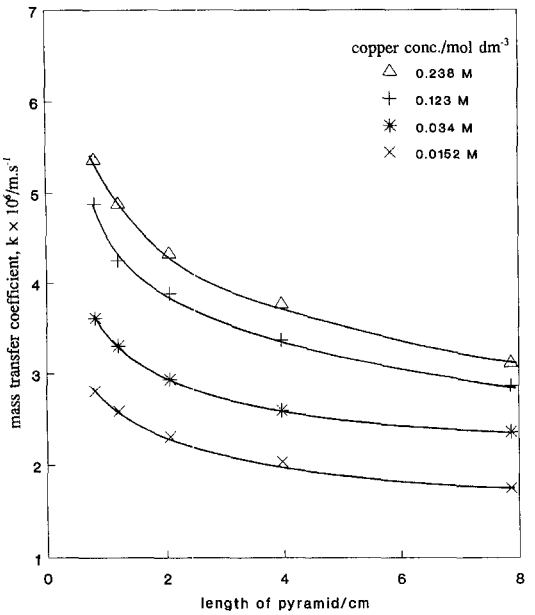

Fig. 9. The effect of length on total mass transfer coefficient for downpointing pyramid (constant pyramid base).

(i) the term expressing the influence of inclination angle is not present in the Weber correlation;

(ii) Weber recommended equation (5) for objects with sphericity $\Psi > 0.6$ and two of the present pyramids (11 and 15) have sphericity values outside this limit;

(iii) the down-pointing pyramids have no down-facing horizontal surface as do other three dimensional objects (cuboids, vertical cylinders).

Worthington *et al.* [10] and the present authors [11] also observed discrepancy with the Weber approach when correlating natural convective mass transfer data to cuboids [10] and vertical cylinders with active ends [11]. Nevertheless this probably presents the best possible correlation based on a single characteristic length and a least squares fit through data yields the relation:

$$Sh_{L_w} - Sh_0 = 0.673(Ra_{L_w})^{0.247} \quad (16)$$

for Ra_{L_w} in the range 1×10^7 to 3×10^{10}.

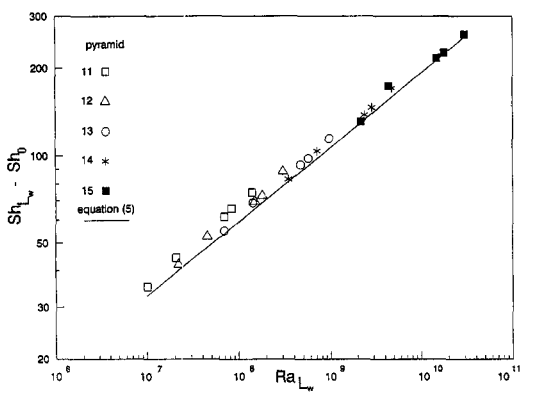

Fig. 10. Correlation of total pyramidal mass transfer data using the Weber *et al.* [8] characteristic dimension.

3.4.2. *Summation approach to correlation for entire down-pointing pyramids.* By summing the mass transfer rates from correlations for the separate sides the total mass transfer performance can be predicted. The advantage of this method is discussed in refs. [10, 11]. In the present approach the correlation for all the inclined surfaces was taken as equation (15). For the upward facing horizontal surfaces the correlation was taken as equation (14), which is in excellent agreement with the correlation of Patrick and Wragg [21]. The mass transfer rates for separate surfaces were correlated using length of pyramid (L) and height of horizontal base of pyramid (H_h) as characteristic lengths. The resultant predicted natural convection mass transfer rate for down-pointing pyramids becomes

$$Sh_L - Sh_0 = \frac{[4.284L(\cos\theta)^{0.25} + 0.3048bRa_L^{1/12}]}{6L + b\sqrt{3}} Ra_L^{0.25} \quad (17)$$

in the region $9 \times 10^6 \leqslant Ra_L \leqslant 2 \times 10^{11}$.

Introducing the relationship

$$\cos\theta = \frac{\sqrt{L^2 - \frac{1}{12}b^2}}{L} \quad (18)$$

to equation (17) yields

$$Sh_L - Sh_0 = \frac{[4.284L^{3/4}(L^2 - \frac{1}{12}b^2)^{1/8} + 0.3048bRa_L^{1/12}]}{6L + b\sqrt{3}} Ra_L^{0.25} \quad (19)$$

where L and b are the inclined surface pyramid length and the base of the horizontal surface of the pyramid, respectively, and Ra_L is a Rayleigh number based on the length of the inclined surface of the pyramid.

3.4.3. *Summation approach with interference.* The behaviour predicted by equation (19) was compared with the mass transfer data for pyramids 11–15. It was found in every case that the predicted rate was higher than the actual data, but that the shape and gradient of the prediction were well matched. The flow of the fluid up the inclined surfaces of the pyramid means that the upward facing horizontal surface is exposed to a solution which has already been depleted of copper ions. Thus, the overall mass transfer for a pyramid is lower than that for the equivalent summed separate surfaces (see Fig 8). A multiplying factor, f (an interference factor), may be introduced to equation (19) to represent the lower rate of mass transfer at the upward facing horizontal surface. This equation now

Table 2. Dependence of interference factor, f, on pyramid geometry

Pyramid	11	12	13	14	15
f	0.91	0.76	0.67	0.63	0.58

becomes

$$Sh_L - Sh_0 = \frac{[4.284L^{3/4}(L^2 - \frac{1}{12}b^2)^{1/8} + f(0.3048bRa_L^{1/12})]}{6L + b\sqrt{3}} \times Ra_L^{0.25} \quad (20)$$

for turbulent flow.

Values of f were obtained from equation (20) and calculated for each pyramid. These are tabulated in Table 2. f varies between 0.58 for the tallest pyramid and 0.91 for the smallest pyramid. Sh_L–Sh_0 has been plotted to show the data from pyramids 11–15 against $\phi(L, b, Ra_L)$. Ra_L in Fig. 11. $\phi(L, b, Ra_L)$ is given by

$$\phi(L, b, Ra_L) = \left[\frac{4.284^{3/4}(L^2 - \frac{1}{12}b^2)^{1/8} + f(0.3048bRa_L^{1/12})}{6L + b\sqrt{3}}\right]^4 \quad (21)$$

for turbulent flow.

It can be seen that all the data fit the line representing equation (20) very well. All the points lie within a deviation of 3–4% from the line and the fit is much better than that for the Weber correlation. Figure 12 shows the dependence of f on the pyramidal aspect ratio (L/b). The plot shows that for low values of L/b (from 0.35 to 0.8) the interference factor decreases strongly and for higher values of L/b (1.5 and more) the decrease is much more gradual.

As with work reported in refs. [10] and [11], the separate sides summation approach incorporating an interference factor has proved highly successful in correlating mass (heat) transfer data for natural convection at a three-dimensional solid, and may be recommended for design calculation purposes.

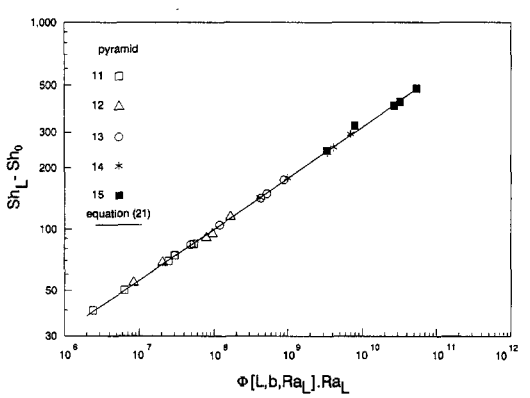

Fig. 11. Overall correlation of entire pyramid data in terms of equation (20).

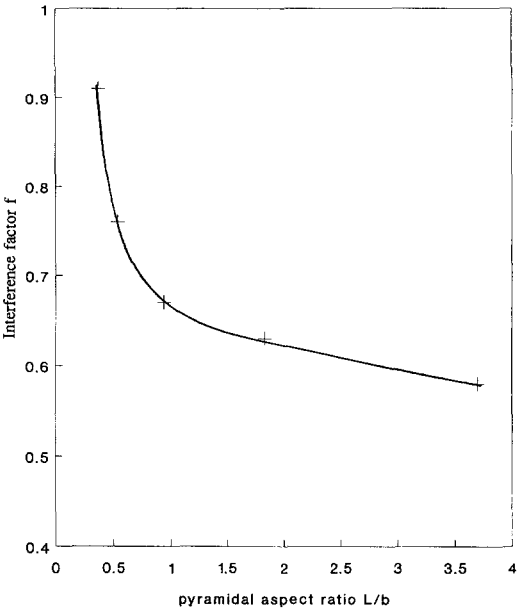

Fig. 12. Plot showing variation of interference factor, f, with pyramidal aspect ratio L/b.

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