# An electrochemical study of mass transfer in free convection at vertical arrays of horizontal cylinders 

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Rates of mass transfer between an electrolyte and vertical arrays of horizontal cylinders have been measured using the limiting current electrolytic technique. The system used was the deposition of copper at the test cathode cylinders from an acidified cupric sulphate solution. Various combinations of solution concentration, cylinder diameter, number of cylinders and cylinder spacing have been used, including experiments on single cylinders. Results for single cylinders have been correlated by the equation.

$$
\mathrm{Sh}_{0}=0.56\left(\mathrm{Sc} \mathrm{Gr}_{\mathrm{m}, \mathrm{~d}}\right)^{0.25}
$$

which agrees well with previous work on both heat and mass transfer. In arrays of cylinders the mass transfer rate, normalized with respect to a single cylinder, either decreased or increased with array position, depending on the particular combination of experimental variables. This behaviour has been explained in terms of the opposing effects of the interacting concentration and velocity fields between cylinders. The findings lend support to the suggestion of Marsters [1] that a position-based Grashof number in the range $10^{6}$ to $10^{7}$ determines the transition between a decrease and an increase in mass transfer up an array.

The results are relevant to the modelling of tubular heat exchangers in free convection dominating conditions, and also illustrate the important effect of boundary layer carry-over in determining current distribution in multi-electrode electrochemical cells.

## Notation

A Surface area
$C$ Concentration of transferring species
$c_{\mathbf{p}} \quad$ Heat capacity
d Cylinder diameter
D Diffusion coefficient
$F \quad$ Faraday constant
$g \quad$ Gravitational acceleration
$\mathrm{Gr}_{\mathrm{h}, \mathrm{d}}$ Cylinder Grashof number for heat transfer $\left(g \Delta \rho_{\mathrm{h}} d^{3} / \nu^{2} \rho_{i}\right)$
$\mathrm{Gr}_{\mathrm{h}, \mathrm{x}}$ Positional Grashof number for heat transfer
$\mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ Cylinder Grashof number for mass transfer ( $g \Delta \rho_{\mathrm{m}} d^{3} / v^{2} \rho_{i}$ )
$\mathrm{Gr}_{\mathrm{m}, \mathrm{x}}$ Positional Grashof number for mass transfer
$h \quad$ Heat transfer coefficient
$i \quad$ Cylinder number
$I_{\mathrm{L}} \quad$ Limiting electrolysis current
$k \quad$ Thermal conductivity
$K_{\mathrm{L}} \quad$ Mass transfer coefficient
$N \quad$ Mass transfer rate
$\mathrm{Nu} \quad$ Nusselt number ( $h d / k$ )
Pr Prandtl number $\left(c_{\mathrm{p}} \mu / k\right)$
$\sigma \quad$ Cylinder spacing
Sc Schmidt number ( $\mu / \rho D$ )
Sh $\quad$ Sherwood number ( $K_{\mathrm{L}} d / D$ )
$X \quad$ Distance up array from bottom
$z \quad$ Number of electrons exchanged
$\mu \quad$ Electrolyte dynamic viscosity
$v \quad$ Electrolyte kinematic viscosity
$\rho \quad$ Density
$\Delta \rho \quad$ Density difference between solution bulk and interface

## Subscripts

m refers to mass transfer
h refers to heat transfer
$\infty \quad$ refers to bulk solution
s refers to liquid-solid interface
0 refers to a single cylinder

## 1. Introduction

When mass or heat transfer occurs at closely spaced objects the transfer rate may be affected by the interaction of the boundary layers produced at each surface. Thus in the case of diffusion-controlled electrolysis the rate of an electrodeposition process in a multi-cathode system may be considerably influenced by the hydrodynamic and mass transfer boundary layers emanating from a neighbouring surface especially in free convection dominated situations.

Heat transfer cases appear to have received most attention in the literature. Marsters [1] has presented results of experimental work on heat transfer by free convection at vertical arrays of horizontal metal cylinders in air. The temperature excess at each cylinder was measured for varying thermal dissipation rates and cylinder spacings and for arrays consisting of 3,5 and 9 cylinders. The temperature excess, normalized with respect to that of a single cylinder, was plotted against elevation in the array and was found generally to increase with elevation in closely spaced arrays. In arrays with large spacing the temperature excess decreased monotonically with elevation. These effects were explained by considering the interaction of the temperature and velocity fields from cylinder to cylinder. Marsters also observed that in closely spaced arrays the excess temperature sometimes fell for the uppermost cylinder and postulated a transition in behaviour at positionbased Grashof numbers, $\mathrm{Gr}_{\mathrm{h}, \mathrm{x}}$, in the region $10^{6}$ to $10^{7}$.

Related work on this problem has also been contributed by Lieberman and Gebhart [2] who observed the behaviour of thin wires in arrays of various inclinations. The resulting interacting temperature fields were observed interferometrically. The general trends of this work are similar to those observed by Marsters. Earlier experiments had been performed by Eckert and Soehngen [3] in 1948. In vertical arrays of three cylinders, the Nusselt number decreased with position up an array. This study also included experiments on interaction in staggered groupings of cylinders. Interferograms from the work of Soehngen of the temperature fields at a single heated cylinder and in a staggered array are presented in [4].

In the present paper results of experiments in an analogous mass transfer system are reported where measurements have been made using the limiting electrolysis current technique. This method has recently been widely used in the measurement of mass transfer in both free and forced convection (e.g. see $[5,6,7]$ ). The mass transfer process chosen was the cathodic electrodeposition of copper from cupric sulphate solutions containing $1 \cdot 5 \mathrm{M}_{2} \mathrm{SO}_{4}$ as swamping electrolyte. This eliminates migration transport of the $\mathrm{Cu}^{++}$ions and the mass transfer close to the electrode surface is thus diffusion-controlled. The density gradients in the fluid near the elec-trode-electrolyte interface produced by the deposition process lead to an upward free convection flow analogous to that in the case of the heated cylinders previously discussed. Determination, from current-potential curves, of the limiting current, facilitates the calculation of the mass transfer coefficient, $K_{\mathrm{L}}$, since at limiting conditions the interface concentration of reacting ions approaches zero. Thus

$$
\begin{equation*}
K_{\mathrm{L}}=\frac{N_{\mathrm{Cu}}{ }^{++}, \mathrm{L}}{A C_{\infty}}=\frac{i_{\mathrm{L}}}{\mathrm{zFAC}} \tag{1}
\end{equation*}
$$

In the experiments, cylinder diameter, cylinder spacing and copper ion concentration have all been varied and arrays of 2,4 and 6 cylinders have been investigated.

Mackley [8] has recently presented an extensive study of the shell side transfer behaviour of baffled shell and tube heat exchangers using a similar electrochemical modelling technique. In
this work the range of observations did not extend down to low and zero flow rates, and the present studies might be used to augment Mackley's observations by indicating the behaviour of such systems in conditions where free convection dominates.

Electrochemical free convection mass tranfer experiments on single horizontal cylinders were earlier reported by Schutz [9] who was able to correlate his findings using the dimensionless equation.

$$
\begin{equation*}
\mathrm{Sh}=\frac{K_{\mathrm{L}} d}{D}=0.53\left(\mathrm{Sc} . \mathrm{Gr}_{\mathrm{m}, \mathrm{~d}}\right)^{0.25} \tag{2}
\end{equation*}
$$

This equation agrees exactly with established correlations in the heat transfer literature for single horizontal cylinders which may be expressed as [10].

$$
\begin{equation*}
\mathrm{Nu}=0.53\left(\operatorname{Pr} . \mathrm{Gr}_{\mathbf{h}, \mathrm{d}}\right)^{0.25} \tag{3}
\end{equation*}
$$

This equation is valid in the range $10^{3}<$ Pr. $\mathrm{Gr}_{\mathrm{h}, \mathrm{d}}<10^{9}$

## 2. Apparatus and experimental method

The apparatus consisted of an array of horizontal cylindrical copper cathodes mounted in a single vertical plane between two rigid vertical supports. The arrangement for a four-cylinder array is shown in Fig. 1. The electrode support frame was


Fig. 1. Method of support of a 4-cylinder array.
mounted on the base of a cylindrical perspex tank which held 251 of electrolyte. The tank was supported on a rigid steel frame equipped with adjustable screw-feet to allow precise levelling of the cathodes. Two anodes were provided, one on each side of the cathode array in the form of vertical curved copper plates whose combined surface area was much greater than the total cathode area. Up to six cylinders could be mounted in an array, diameters of $28 \cdot 3,19 \cdot 1$ and 9.4 mm being used. Additional single-cylinder experiments were performed with electrodes of 6.2 and 3.1 mm diameter. All the cylinders were 50 mm in length and were mounted on co-axial nylon rods which carried the current leads. The ends of the cylinders were plugged with perspex discs.
The electrical circuit was designed to facilitate the measurement of the current and potential of each individual cylinder with all the cylinders simultaneously active. The circuit is shown in Fig. 2. The current flowing at each individual cylinder was measured by determining the voltage drop produced across a series of standard 10 ohm resistors.

The power source was a KSM stabilized power supply ( $0-10 \mathrm{~V}, 0-3 \mathrm{~A}$ ), and the current and potential measuring meters were a Pye Scalamp Megohm/Volt Voltmeter, and a Farnel type TM39 Microvoltmeter respectively. Prior to each run the electrodes were polished manually with increasingly fine emery cloth, degreased in


Fig. 2. Electrical circuit.
sodium hydroxide solution and washed in distilled water before being immersed in the electrolyte. A small potential was applied to each electrode to allow an even starting deposit of copper to form on the surface.

The potential was then increased in steps of about 50 mV and readings for each cylinder were taken successively for each potential increment. This was continued until hydrogen evolution occurred. An interval of 5 min was allowed between each potential step to allow equilibrium to be obtained. Arrays of 1, 2, 4 and 6 cylinders with spacings of $4 d, 3 d, 2 d, 3 / 2 d, 5 / 4 d$ and $9 / 8 d$ were used. Two nominal $\mathrm{CuSO}_{4}$ concentrations of 0.05 and $0.10 \mathrm{~mol} \mathrm{l}^{-1}$ were employed. In fact some deviation from these concentrations took place from day to day due to solvent evaporation and chemical copper dissolution and a continual check was kept on the actual concentration for each run. Thus all calculations have been performed using actual concentrations, though for simplicity graphs of results show the nominal concentration.

## 3. Results

### 3.1 Single cylinders

It is important that results for single cylinders should be both consistent among themselves and in agreement with established quantitive relationships for such systems in order to provide a norm against which the behaviour of arrays may be compared and discussed. In Fig. 3 current-potential points have been plotted for a single active cylinder at different positions in a six-cylinder array and it is clear that the limiting currents are in good agreement. Further experiments were performed with single cylinders by themselves. From such current-potential curves limiting currents were estimated and mass transfer coefficients calculated using Equation 1. The relevant dimensionless groups were calculated and sample results are given in Table 1. In the calculations the diffusion coefficients were taken from the data of Arvia et al. [11], the viscosities and densities from Eisenberg et al. [12] and the $\Delta \rho$ terms were calculated using the procedure of Wilke, Eisenberg and Tobias [5].

Fig. 4 shows a logarithmic plot of $\mathrm{Sh}_{0}$ against


Fig. 3. Current-potential points for single cylinders only active at different positions in a 6 -cylinder array.
$\mathrm{Sc} \mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ for all the single cylinder results. The solid line represents the correlating equation:

$$
\begin{equation*}
\mathrm{Sh}_{0}=0.56\left(\mathrm{Sc} \cdot \mathrm{Gr}_{\mathrm{m}, \mathrm{~d}}\right)^{0.25} \tag{4}
\end{equation*}
$$

which agrees well with the results of Schutz as given by Equation 2. There is also good agreement with the analogous heat transfer Equation 3 , and it is also seen that scatter of results is small. These single cylinder results thus form a reliable standard against which the array cylinder behaviour may be normalized. There is a distinct change in the gradient of the plot in the region of $\mathrm{Sc} . \mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ of about $2 \times 10^{9}$ which indicates the transition to turbulence.

The magnitudes of the Sc group given in Table 1 emphasize an important difference between the solid to air heat transfer work of Marsters and that of the present system. Whereas the Prandtl number for air is of the order of 0.7 , the Schmidt numbers for the electrolyte solution are approximately 2600 . Because of this great difference in magnitude the boundary layer thickness for mass transfer is far less than that for heat transfer. Thus in a situation where the concentration or temperature fields from one cylinder directly affect the performance of the cylinder above, a considerable difference in behaviour as between the two systems would be anticipated. The reduction in transfer rate with height in an array which Marsters observed

Table 1. Results for natural convection at single horizontal cylinders

| Run Number | Temp ( ${ }^{\circ} \mathrm{C}$ ) | $\begin{gathered} \mathrm{CuSO}_{4} . \\ \mathrm{Conc} . \\ \left(\mathrm{mol} 1^{-1}\right) \end{gathered}$ | Cylinder diameter (mm) | $\begin{gathered} I_{\mathrm{L}} \\ (\mathrm{~mA}) \end{gathered}$ | $\underset{\left(\mathrm{m} \mathrm{~s}^{-1}\right)}{K_{\mathrm{L}}}$ | Sh | Sc | $\mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ | Sc. $\mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 22.5 | 0.050 | $28 \cdot 3$ | 105 | $2.45 \times 10^{-6}$ | $145 \cdot 5$ | 2470 | $9.85 \times 10^{5}$ | $2.43 \times 10^{9}$ |
| 201 | $22 \cdot 5$ | 0.050 | $28 \cdot 3$ | 104 | $2.42 \times 10^{-6}$ | 144 | 2470 | $9.85 \times 10^{5}$ | $2.43 \times 10^{9}$ |
| 202 | $22 \cdot 5$ | 0.050 | $28 \cdot 3$ | 105 | $2.45 \times 10^{-6}$ | $145 \cdot 5$ | 2470 | $9.85 \times 10^{5}$ | $2.43 \times 10^{9}$ |
| 203 | $22 \cdot 2$ | 0.051 | $19 \cdot 1$ | 74 | $2.56 \times 10^{-6}$ | $103 \cdot 5$ | 2510 | $2.84 \times 10^{5}$ | $7.15 \times 10^{8}$ |
| 204 | $20 \cdot 3$ | 0.051 | $19 \cdot 1$ | $70 \cdot 3$ | $2.44 \times 10^{-6}$ | $103 \cdot 5$ | 2760 | $2.77 \times 10^{5}$ | $7.65 \times 10^{8}$ |
| 205 | $20 \cdot 3$ | 0.051 | $19 \cdot 1$ | $69 \cdot 3$ | $2.40 \times 10^{-6}$ | 102 | 2760 | $2.77 \times 10^{5}$ | $7.65 \times 10^{8}$ |
| 208 | $20 \cdot 3$ | 0.051 | $9 \cdot 4$ | 41 | $2.88 \times 10^{-6}$ | 60.2 | 2760 | $3.31 \times 10^{4}$ | $9.12 \times 10^{7}$ |
| 209 | $20 \cdot 3$ | 0.051 | $9 \cdot 4$ | 39 | $2.74 \times 10^{-6}$ | 57.2 | 2760 | $3.31 \times 10^{4}$ | $9.12 \times 10^{7}$ |
| 210 | $20 \cdot 3$ | 0.051 | $9 \cdot 4$ | 39.9 | $2.80 \times 10^{-6}$ | 58.5 | 2760 | $3.31 \times 10^{4}$ | $9.12 \times 10^{7}$ |
| 211 | $20 \cdot 3$ | 0.052 | $6 \cdot 2$ | $28 \cdot 4$ | $3.02 \times 10^{-6}$ | 41.6 | 2760 | $9.5 \times 10^{3}$ | $2.62 \times 10^{7}$ |
| 212 | $20 \cdot 3$ | 0.052 | $6 \cdot 2$ | 28 | $2.98 \times 10^{-6}$ | 41.0 | 2760 | $9.5 \times 10^{3}$ | $2.62 \times 10^{7}$ |
| 213 | $20 \cdot 3$ | 0.052 | $6 \cdot 2$ | 29.0 | $3.09 \times 10^{-6}$ | $42 \cdot 6$ | 2760 | $9.5 \times 10^{3}$ | $2.62 \times 10^{7}$ |
| 216 | $20 \cdot 3$ | 0.052 | $3 \cdot 1$ | 18.0 | $3.83 \times 10^{-6}$ | $26 \cdot 4$ | 2760 | $1.215 \times 10^{3}$ | $3.35 \times 10^{6}$ |
| 217 | $20 \cdot 3$ | 0.052 | $3 \cdot 1$ | 17.4 | $3.70 \times 10^{-6}$ | $25 \cdot 5$ | 2760 | $1.215 \times 10^{3}$ | $3.35 \times 10^{6}$ |
| 73 | 21.7 | 0.064 | $9 \cdot 4$ | $50 \cdot 5$ | $2.77 \times 10^{-6}$ | 55.9 | 2580 | $4.47 \times 10^{4}$ | $1.16 \times 10^{8}$ |
| 86 | $22 \cdot 0$ | 0.099 | $9 \cdot 4$ | 94 | $3.31 \times 10^{-6}$ | 67.1 | 2600 | $6.81 \times 10^{4}$ | $1.77 \times 10^{8}$ |
| 87 | 22.0 | 0.099 | $9 \cdot 4$ | 93 | $3.28 \times 10^{-6}$ | $66 \cdot 5$ | 2600 | $6.81 \times 10^{4}$ | $1.77 \times 10^{8}$ |
| 89 | $20 \cdot 1$ | 0.099 | $19 \cdot 1$ | 161.5 | $2.78 \times 10^{-6}$ | 120 | 2860 | $5.27 \times 10^{5}$ | $1.51 \times 10^{9}$ |
| 90 | $20 \cdot 1$ | 0.099 | $19 \cdot 1$ | 169 | $2.93 \times 10^{-6}$ | 127 | 2860 | $5.27 \times 10^{5}$ | $1.51 \times 10^{9}$ |
| 91 | $20 \cdot 3$ | $0 \cdot 100$ | 28.3 | 242 | $2.82 \times 10^{-6}$ | 181 | 2860 | $1.73 \times 10^{6}$ | $4.94 \times 10^{9}$ |
| 94 | 20.5 | $0 \cdot 100$ | $6 \cdot 2$ | 67 | $3.58 \times 10^{-6}$ | 49.6 | 2820 | $1.86 \times 10^{4}$ | $5.24 \times 10^{7}$ |
| 95 | 20.5 | $0 \cdot 100$ | $6 \cdot 2$ | $64 \cdot 5$ | $3.45 \times 10^{-6}$ | 47.8 | 2820 | $1.86 \times 10^{4}$ | $5.24 \times 10^{7}$ |
| 98 | 20.8 | $0 \cdot 100$ | $3 \cdot 1$ | 40 | $4.19 \times 10^{-6}$ | 29.0 | 2810 | $2.34 \times 10^{3}$ | $6.58 \times 10^{6}$ |
| 99 | $20 \cdot 8$ | $0 \cdot 100$ | $3 \cdot 1$ | 41 | $4.29 \times 10^{-6}$ | 29.7 | 2810 | $2.34 \times 10^{3}$ | $6.58 \times 10^{6}$ |



Fig. 4. Logarithmic plot of $\mathbf{S h}_{\mathrm{o}}$ against $\mathbf{S c} . \mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ for single cylinders.


Fig. 5. Current-potential curves for an array of six simultaneously active cylinders (Run number 233).


Fig. 6. Plots of normalized Sherwood number against dimensionless array position for 2-cylinder arrays.


Fig. 7. Plots of normalized Sherwood number against dimensionless array position for 4 -cylinder arrays.
for small spacings would be expected only to occur at very much smaller spacings in the present mass transfer system.

### 3.2 Arrays of cylinders

Typical current-potential curves for an array with all cylinders simultaneously active are shown in Fig. 5 where a distinct and different limiting current plateau is discernible for each individual cylinder. The amount of experimental data collected during the work was large and some sample results for 2, 4 and 6 cylinder arrays are shown in Figs. 6, 7 and 8, respectively, as plots of normalized Sherwood number, $\mathrm{Sh}_{i} / \mathrm{Sh}_{0}$ against dimensionless position in the array, $X / X_{\max }$. These plots are analogous to those representing Marsters [1] heat transfer results given as Figs. 8 and 9 of that paper. The dominant feature of the present results is the general tendency for cylinder Sherwood numbers to increase with height in an array. There are
some exceptions to this general trend, notably between the first and second cylinders at close spacings, and at the uppermost cylinder in large arrays, e.g. Figs. 8a, c. It is also consistently clear that mass transfer rates are lower the closer the array spacing.


Fig. 8. Plots of normalized Sherwood number against dimensionless array position for 6 -cylinder arrays.


Fig. 9. Typical reproducibility of results for arrays of cylinders.

Reproducibility of readings was less good for the arrays than for the single cylinders, and most runs were repeated two or three times. Figs. 9a and b show typical scatter of results for experiments repeated four times and twice respectively. Mean values were used in the presentation of Figs. 6, 7 and 8. The scatter is attributable to slight misalignments of the arrays, variations in electrode condition and external disturbances to which high Schmidt number systems such as this, with their associated thin boundary layers, are very susceptible.

## 4. Discussion

The explanation for the trends in the magnitude of the normalized Sherwood number with array position, as depicted in Figs. 6, 7 and 8, may be approached in an analogous manner to that of Marsters for his heat transfer work. Each successive cylinder up an array is embedded in a concentration and velocity field due to the active cylinders beneath it. Depending on the geometry of the particular array and the magnitude of the density gradients, either the reduced concentration will dominate causing a decrease in mass transfer, or the enhanced velocity will dominate causing an increase in mass transfer. Thus with closely spaced cylinder pairs as in Fig. 6a at $9 / 8$ spacing and Fig. 6b at 5/4 and $9 / 8$ spacing the carry-over of the mass transfer boundary layer to the second cylinder causes a substantial reduction in mass transfer rate at that cylinder. With small spacing a relatively large part of the electrode is in contact with slow moving fluid areas where the boundary layer is thick and the mass transfer rate consequently low. At larger spacings there is less restricted space between the cylinders and the velocity field becomes the dominant influence causing an increase in mass transfer at the upper cylinder as shown, for instance, in Fig. 6a for the $4 d, 3 d$ and $2 d$ spacings. It is of interest in further illustrating this point to compare the lines of Figs. 6a, b and c for the identical spacing of $5 / 4 \mathrm{~d}$. For the 28.3 mm electrodes where both the actual separation between the cylinders and the cylinder diameter is larger, there is an increase in mass transfer rate between cylinders 1 and 2, whereas for the $19 \cdot 1$ and 9.4 mm electrodes there is a marked
decrease in mass transfer. A further point is illustrated in Fig. 6d which shows lines for the same diameter electrodes at identical spacing but in different $\mathrm{CuSO}_{4}$ concentrations. The $0 \cdot 10 \mathrm{moll}^{-1}$ concentration solution produces the larger $\Delta \rho$ and hence a stronger convective flow than the $0.05 \mathrm{~mol}^{-1}$ solution.

Similar consistent trends are apparent in Figs. 7 and 8. For these taller arrays the induced velocity fields generally dominate causing increases in mass transfer with elevation, but it is again apparent that the mass transfer rates become consistently lower with decreasing spacing. Some plots display a decrease in mass transfer between the first two cylinders followed by an upswing in the trend as the array is ascended. This behaviour is observed in Fig. 7a at $9 / 8 d$. spacing, in Fig. 7b at $5 / 4 d$ and $9 / 8 d$, in Fig. 7c at $9 / 8 d$ and in Figs. 8a, b and c at $9 / 8 d$. A similar phenomenon was observed by Marsters in the heat transfer studies, and by using a positional Grashof number, $\mathrm{Gr}_{\mathrm{h}, \mathbf{x}}$, Marsters postulated that the transition between decreasing and increasing mass transfer occurred in the range $10^{6}<\mathrm{Gr}_{\mathrm{h}, \mathrm{x}}<10^{7}$. Calculation of a similar position-based Grashof number for mass transfer, $\mathrm{Gr}_{\mathrm{m}, \mathrm{x}}$, which is related to the cylinder Grashof number through the relation.

$$
\begin{equation*}
\operatorname{Gr}_{\mathrm{m}, \mathrm{x}}=\operatorname{Gr}_{\mathrm{m}, \mathrm{~d}}[\sigma(i-1)]^{3} \tag{5}
\end{equation*}
$$

leads to the values of $\mathrm{Gr}_{\mathrm{m}, \mathrm{x}}$ tabulated in Table 2. This represents cylinders at which a change
has taken place from decreasing to increasing mass transfer rate.

The critical values of the positional Grashof numbers fall within the transition range $1.2 \times 10^{6}$ $\longleftrightarrow 1 \cdot 1 \times 10^{7}$, thus falling very nearly within that postulated by Marsters.

It is also of interest to examine the results for the two cylinder arrays. In Table 3 are given the positional Grashof numbers for the upper cylinder where there is a decrease in mass transfer at that cylinder, and in Table 4 the values for cases where there is an increase. It is evident that for the decreasing mass transfer rates all the $\mathrm{Gr}_{\mathrm{m}, \mathrm{x}}$ values lie below $1.4 \times 10^{6}$, whereas for increasing mass transfer rates, with one exception, they lie above $1.8 \times 10^{6}$.

Another feature of the present work is that in some instances there is a fall-off in mass transfer rate at high array positions. This is seen, for example, in Figs. 8a, b, c and d. In some cases there is a tendency for a levelling-off of the transfer rate at the highest cylinder, for example in Fig. 8 b at $5 \cdot 4 d$ and $9 / 8 d$ spacing. This suggests that there may be a further upper transition at which the concentration field carry-over outweighs the effect of the increased velocity. Marsters experiments did not reach such high values of ScGr and this effect was not observed.

In order to further clarify aspects of the behaviour of arrays of cylinders in free convection we propose to do further work covering more extreme cases e.g. tall arrays, thin cylinders,

Table 2. Transition points between decreasing and increasing mass transfer rate

| Run number | No. in array | $\begin{gathered} d \\ (\mathrm{~mm}) \end{gathered}$ | Spacing <br> (s) | $i_{\text {crit }}$ | $\begin{gathered} \text { Nominal } \\ \text { conc. } \\ \left(\operatorname{mol} I^{-1}\right) \end{gathered}$ | $G r_{\text {m, }}$ | $\mathrm{Gr}_{\text {m,x }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 235 | 4 | $19 \cdot 1$ | 3/2 | 3 | 0.05 | $2.8 \times 10^{5}$ | $7.6 \times 10^{6}$ |
| 236 | 4 | $19 \cdot 1$ | 5/4 | 3 | 0.05 | $2.8 \times 10^{5}$ | $4.4 \times 10^{6}$ |
| 238 | 4 | $19 \cdot 1$ | 9/8 | 3 | 0.05 | $2.8 \times 10^{5}$ | $3.2 \times 10^{6}$ |
| 82 | 4 | $19 \cdot 1$ | $9 / 8$ | 3 | $0 \cdot 10$ | $5.6 \times 10^{5}$ | $6.4 \times 10^{6}$ |
| 26 | 4 | $28 \cdot 3$ | $9 / 8$ | 3 | 0.05 | $1.0 \times 10^{6}$ | $1 \cdot 1 \times 10^{7}$ |
| 75 | 6 | $9 \cdot 4$ | 3/2 | 4 | 0.05 | $4.6 \times 10^{4}$ | $4.2 \times 10^{6}$ |
| 106 | 6 | $9 \cdot 4$ | 3/2 | 3 | $0 \cdot 10$ | $6.6 \times 10^{4}$ | $1.2 \times 10^{6}$ |
| 109 | 6 | $19 \cdot 1$ | 9/8 | 3 | $0 \cdot 10$ | $5.5 \times 10^{5}$ | $6.3 \times 10^{6}$ |
| 108 | 6 | $19 \cdot 1$ | 5/4 | 3 | $0 \cdot 10$ | $5.5 \times 10^{5}$ | $8.6 \times 10^{6}$ |
| 72 | 6 | $19 \cdot 1$ | $9 / 8$ | 3 | 0.05 | $3.5 \times 10^{5}$ | $4.0 \times 10^{6}$ |
| 234 | 6 | $19 \cdot 1$ | 5/4 | 3 | 0.05 | $2.8 \times 10^{5}$ | $4.3 \times 10^{6}$ |
| 24 | 6 | $28 \cdot 3$ | $9 / 8$ | 3 | 0.05 | $1.0 \times 10^{6}$ | $1.1 \times 10^{7}$ |

Table 3. Positional Grashof numbers for 2-cylinder arrays where the upper cylinder mass transfer rate is less than the lower

| $\begin{gathered} \text { Run } \\ \text { number } \end{gathered}$ | Cylinder diameter (mm) | Cylinder spacing <br> (d) | $\begin{gathered} \text { Nominal } \\ \text { conc. } \\ \left(\mathrm{mol} \mathrm{1}^{-1}\right) \end{gathered}$ | $\mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ | $\mathrm{Gr}_{\mathrm{m}, \mathrm{x}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 115 | $9 \cdot 4$ | 5/4 | $0 \cdot 10$ | $6.6 \times 10^{4}$ | $1.3 \times 10^{5}$ |
| 77 | 99.4 | 3/2 | 0.05 | $4.6 \times 10^{4}$ | $1.6 \times 10^{5}$ |
| 103 | 9.4 | 3/2 | $0 \cdot 10$ | $6.7 \times 10^{4}$ | $2.3 \times 10^{5}$ |
| 76 | $9 \cdot 4$ | 2 | 0.05 | $4.5 \times 10^{4}$ | $3.4 \times 10^{5}$ |
| 232 | $19 \cdot 1$ | 9/8 | 0.05 | $2.72 \times 10^{5}$ | $3.8 \times 10^{5}$ |
| 231 | $19 \cdot 1$ | 5/4 | 0.05 | $2.72 \times 10^{5}$ | $5.3 \times 10^{5}$ |
| 230 | $19 \cdot 1$ | 3/2 | 0.05 | $2.72 \times 10^{5}$ | $9.2 \times 10^{5}$ |
| 35,36 | 28.3 | $9 / 8$ | 0.05 | $1.0 \times 10^{6}$ | $1.4 \times 10^{6}$ |

Table 4. Positional Grashof numbers for 2-cylinder arrays where the upper cylinder mass transfer rate is higher than the lower

| Run number | Cylinder diameter (mm) | Cylinder spacing <br> (d) | Nominal conc. ( $\mathrm{mol} \mathrm{l}^{-1}$ ) | $\mathrm{Gr}_{\mathrm{m}, \mathrm{d}}$ | $\mathrm{Gr}_{\mathrm{m}, \mathrm{x}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 112 | 9.4 | 2 | 0.10 | $6.6 \times 10^{4}$ | $5.3 \times 10^{5}$ |
| 113 | $9 \cdot 4$ | 3 | $0 \cdot 10$ | $6.6 \times 10^{4}$ | $1.78 \times 10^{6}$ |
| 42, 43 | $28 \cdot 3$ | 5/4 | 0.05 | $1.1 \times 10^{6}$ | $1.81 \times 10^{6}$ |
| 229 | $19 \cdot 1$ | 2 | 0.05 | $2.75 \times 10^{5}$ | $2.25 \times 10^{6}$ |
| 10, 11, 12 | 28.3 | 3/2 | 0.05 | $9.6 \times 10^{5}$ | $3.40 \times 10^{6}$ |
| 114 | $9 \cdot 4$ | 4 | $0 \cdot 10$ | $6.6 \times 10^{4}$ | $4.20 \times 10^{6}$ |
| 207 | $19 \cdot 1$ | 3 | 0.05 | $2.73 \times 10^{5}$ | $7.41 \times 10^{6}$ |
| 46, 48 | 28.3 | 2 | 0.05 | $1.1 \times 10^{6}$ | $8.80 \times 10^{6}$ |
| 220 | $28 \cdot 3$ | 3 | 0.05 | $8.81 \times 10^{5}$ | $2.38 \times 10^{7}$ |
| 219 | $28 \cdot 3$ | 4 | 0.05 | $8.82 \times 10^{5}$ | $5.64 \times 10^{7}$ |

large and very small spacings, and to supplement this with optical investigations to elucidate the flow patterns occurring. Further work with staggered, rather than in-line, arrays and with small forced flows would also be of interest in modelling further real heat and mass transfer situations.

## 5. Conclusions

(a) Mass transfer rates between single horizontal cylinder cathodes and an electrolyte have been correlated by the equation

$$
\mathrm{Sh}_{0}=0.56\left(\mathrm{Sc} . \mathrm{Gr}_{\mathrm{m}, \mathrm{~d}}\right)^{0.25}
$$

(b) When cylinders were incorporated into
vertical arrays with all cylinders simultaneously active, considerable deviations from single cylinder behaviour were observed due to interactions between the velocity and concentration fields.
(c) A critical positional Grashof number in the range $1.2 \times 10^{6}$ to $1.1 \times 10^{7}$ tends to characterize the transition between decreasing and increasing mass transfer up an array.

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