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FREE CONVECTION MASS TRANSFER AT MESH ELECTRODES

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Abstract—Free convection mass transfer at vertical mesh electrodes has been investigated experimentally by measuring limiting currents for the cathodic reduction of ferricyanide ions. Electrode height and electrolyte concentration have been varied to provide a range of $Sc \times Gr$ from 2×10^5 to 5×10^{10}. The data have been compared with previous theoretical and experimental expressions obtained for free convection at vertical plates and a basically similar behaviour pattern has been observed. Suggestions have been put forward to explain a sensitivity to concentration additional to that described by the Grashof group.

NOMENCLATURE

A,	total area of electrode surface [cm^2];
C_b,	bulk concentration of transferred species [mol/cm^3];
D,	diffusion coefficient [cm^2/s];
F,	Faraday's constant (96 500 C/g equiv.);
g,	acceleration due to gravity [cm/s^2];
Gr,	Grashof number, $gh^3\Delta\rho/\rho_i\nu^2$;
h,	electrode height [cm];
i_L,	limiting electrolysis current [A];
k,	average mass-transfer coefficient [cm/s];
Sc,	Schmidt number, ν/D;
Sh,	Sherwood number, kh/D;
z,	electrons transferred in electrode reaction.

Greek symbols

ν,	kinematic viscosity [cm^2/s];
μ,	dynamic viscosity [g/s cm];
ρ,	density [g/cm^3];
$\Delta\rho$,	density difference between bulk electrolyte and electrode interface [g/cm^3];
ρ_i,	interfacial density [g/cm^3].

1. INTRODUCTION

THE FUTURE development of electrochemical reactors is inevitably linked with the problem of evolving suitable electrode forms. The mass-transfer characteristics of an electrode and their relation to geometric and hydrodynamic factors are clearly of fundamental importance to any electrochemical reaction system. The work described in this paper is concerned with an assessment of the performance of mesh electrodes in natural convection conditions with electrode height and the concentration of the reacting species as the main variables.

There appears to be no previous investigation of mass transfer with natural convection at mesh structures. Vögtländer and Bakker [1] have described mass-transfer experiments involving electrolyte solutions flowing transversely past single wires and gauzes, and there have also been a number of studies of the analogous forced convection heat-transfer problem. In natural convection conditions the case of the plane vertical plate has received attention from various workers using both electrochemical [2–5] and dissolution techniques [6]. Theoretical solutions have also been established [7] with which experimental data compare favourably in both streamline and turbulent free convection conditions. The related cases of plane horizontal electrodes [8] and spheres and horizontal cylinders [9] have also received experimental treatment. However, the system under present discussion has so far escaped both experimental and theoretical attention.

2. PRELIMINARY DISCUSSION

A mesh electrode surface is one of some geometric complexity as compared to the usual plane forms previously treated mathematically. From the diagram of Fig. 1, it can be seen that mass transfer will take place at continuous tall, narrow, vertical areas W, a series of short, vertical areas X, inward facing vertical areas Z, and horizontal areas Y, some upward and some downward facing. However these different areas will not behave as independent sections but there will be a complex pattern of boundary-layer interaction among the various regions. The mass-transfer performance will be largely controlled by the formation of overall mass transfer and hydrodynamic boundary layers along the vertical electrode faces. It is at once clear that previous theoretical treatments of vertical electrode performance will be inadequate in describing fully the present system, though comparison will be of considerable interest.

For the experiments described a medium mesh with a count of forty square apertures per inch has been selected, and the height of the electrode and the concentration of the reacting species in the electrolyte have been varied. The well established technique of measuring limiting currents for the cathodic reduction of ferricyanide ions from equimolar solutions of potassium ferro and ferricyanide in an excess of sodium hydroxide has been employed. In this system the effects of ionic migration are negligible, and since at the limiting current the concentration of the reacting species is reduced to zero at the electrode–solution interface the mass-transfer coefficient is given by

$$k = \frac{i_L}{zFAC_b}. \tag{1}$$

Several examples of the use of this technique in the investigation of problems in chemical engineering science may be found in the recent literature [1, 3, 5, 10–14].

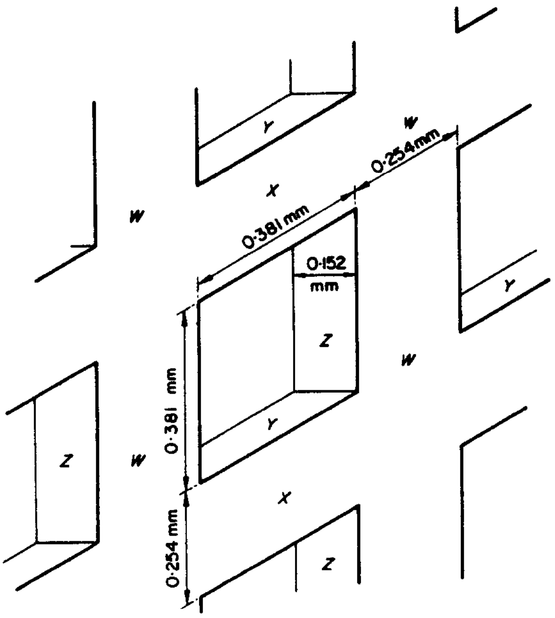

FIG. 1. Structure and dimensions of electrode mesh.

3. EXPERIMENTAL

The studied electrodes were constructed from sheets of an electroformed nickel clad copper mesh* with a thickness of 0·0152 cm and an aperture width of 0·0381 cm, dimensional tolerances being ±0·00127 cm. Eight mesh cathodes were employed each 4 cm in width and varying in height between 0·15 and 5·83 cm. The electrode geometries are summarized in Table 1, tolerances on the total surface area figures being ±2 per cent. Figure 1 gives an

Table 1. Summary of electrode geometries

Electrode number	Height (cm)	Width (cm)	Nominal face area (cm^2)	Total surface area (cm^2)
1	5·83	4·0	46·60	43·4
2	3·88	4·0	31·02	28·9
3	2·89	4·0	23·12	21·55
4	1·89	4·0	15·12	14·05
5	1·02	4·06	8·28	7·70
6	0·59	4·0	4·72	4·38
7	0·30	4·0	2·40	2·23
8	0·15	4·06	1·218	1·13

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* Trade name "Perflec"; manufactured by N. Greening and Sons Ltd, Warrington, Lancashire.

idealized picture of the mesh geometry since it is difficult to achieve a perfectly rectangular structure, and irregularities may marginally affect the calculated total surface areas.

The electrodes were supported by means of projections extending from their sides which fitted into small vertical slots in a perspex supporting frame. Electrical leads were soldered to the projecting portions which were then well lacquered so that the region did not act as a mass-transfer surface. Two vertical nickel plate anodes connected in parallel were similarly supported from the perspex frame on either side of the test cathode. The active area of the anodes measured 4·5 × 7·2 cm, and the anode to cathode distances were 1·5 cm. The electrodes and supporting framework were enclosed in a simple cylindrical vessel holding approximately 500 ml of electrolyte.

Solutions of the electrolyte were made up using distilled water and analar reagents, and were all 2 M in sodium hydroxide and of equimolar concentrations in potassium ferricyanide and ferrocyanide of 0·01, 0·02, 0·05, 0·10 and 0·20 M. Current–voltage curves were obtained for the cathodic reduction of ferricyanide ions which exhibited a very marked plateau region which permitted the convenient reading of limiting current values. The operating temperature was maintained at all times between 22 and 23°C.

4. RESULTS

From the limiting currents determined by examination of the current–voltage curves, the values of the mass-transfer coefficients were calculated using equation (1). In this equation the total exposed area of each electrode was used (i.e. including that of the four sides of the apertures). The variation of the mass-transfer coefficient with electrode height is shown in Fig. 2, for two electrolyte concentrations. This graph shows clearly the effect of boundary-layer development over the mesh surfaces; with the very short electrodes and thin boundary layers, the mass-transfer coefficient is seen to approach infinity, whereas as the electrode length increases the values decline and level out.

An overall correlation of the data in terms similar to those established for the case of natural convection at a plane vertical plate [2–4, 6, 7] was envisaged. Accordingly the relevant dimensionless groups *Sh*, *Sc* and *Gr* were calculated, values for the physical properties being taken from various sources [15, 16, 3]. The accuracy in determining the Grashof number is estimated at ±10 per cent at low concentrations. The results have been plotted in the form of a log–log plot of the Sherwood number against the product of the Schmidt and Grashof numbers in Fig. 3. Also included on this plot are the theoretical prediction for streamline flow

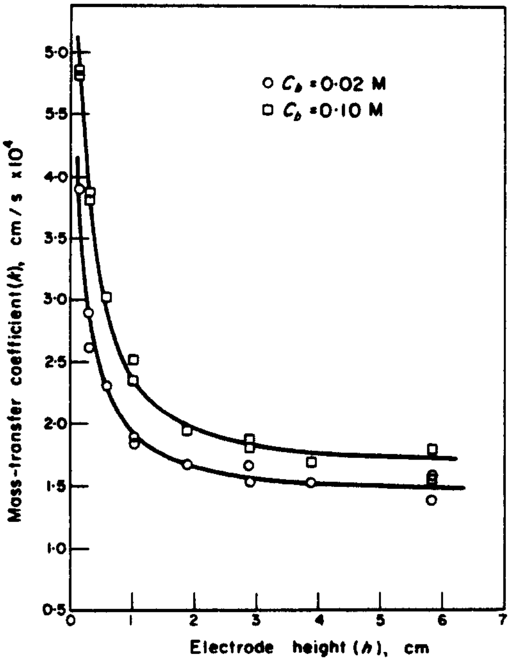

FIG. 2. Variation of the mass-transfer coefficient with electrode height (constant concentration).

$$Sh = 0{\cdot}665\,(Sc\ Gr)^{0{\cdot}25} \tag{2}$$

obtained by integrating the appropriate expression from [7] and the empirical correlating lines of Wilke *et al.* [4]

$$Sh = 0{\cdot}673\,(Sc\ Gr)^{0{\cdot}25} \qquad (3)$$

and Fouad and Gouda [3]

$$Sh = 0{\cdot}45\,(Sc\ Gr)^{0{\cdot}25}. \qquad (4)$$

The experimental data may thus be conveniently compared with these equations. Equations (2) and (3), which are inseparable on the graph, are shown as line A–A, and equation (4) as line B–B. The present mesh electrode data are seen to be roughly correlated by the Fouad and Gouda expression for plane electrodes, with maximum deviations of about 27 per cent.

However, closer examination of the present data as presented in Fig. 3 reveals the inadequacy of the type of equation discussed above as a strict correlation. Experimental points for different concentrations are observed to lie on quite distinct straight lines throughout the whole range of electrodes employed. The data lie higher with increasing electrolyte concentration, indicating the necessity of a further term, some function of concentration, in addition to those present in equation (4). It should be pointed out however that there is no apparent tendency for the data to deviate from the slope of 0·25 characteristic of dominant streamline convective behaviour.

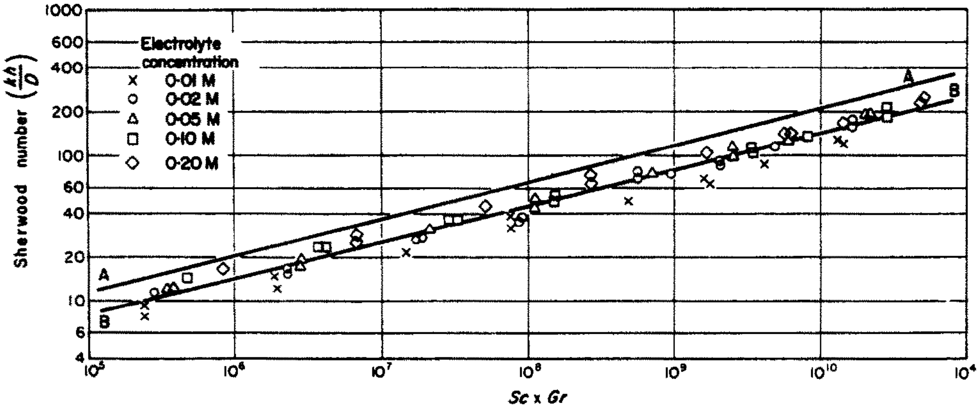

FIG. 3. Plot of *Sh* against *Sc Gr*.

The region of $Sc \times Gr$ employed, 2×10^5 up to 5×10^{10}, is that in which streamline flow behaviour would be expected, and in this region the similarity in performance between the present mesh electrodes and the plane plate electrodes of other workers is very marked. The results of Fouad and Gouda lie lower than predicted by [2] and the authors attribute this to the difficulty and uncertainty in predicting the interfacial compositions. Since the present work, employing the same electrolyte system, is subject to the same difficulty, comparison with the Fouad and Gouda data is more meaningful and the coincidence with this data more striking.

The concentration dependence of the mass-transfer data may be explained as follows. At low electrolyte concentrations the concentration of reactive species in the confined mesh spaces, becomes very low due to the polarization and little mass transfer occurs at the bounding surfaces of the apertures. The overall performance thus falls below that of the plane vertical plate since a considerable portion of the surface area is non-active. As the bulk concentration increases convection becomes stronger and boundary layers thinner so that access of fluid to the mesh spaces becomes progressively improved and mass transfer takes place at the

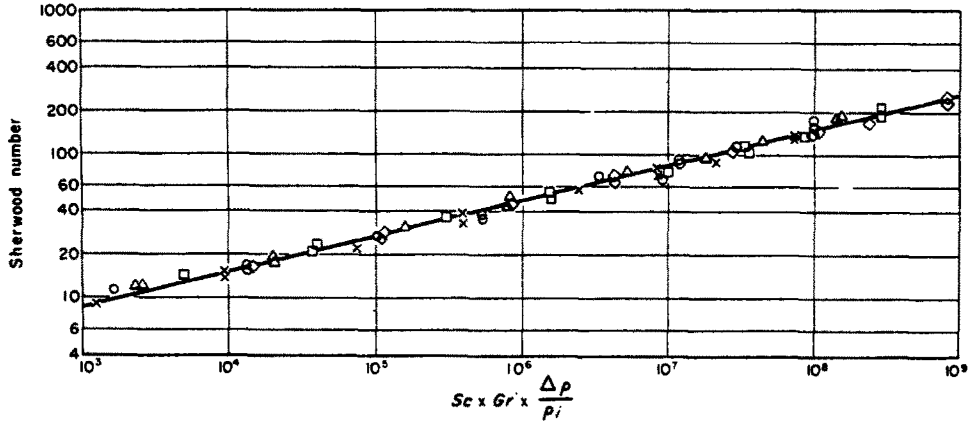

FIG. 4. Plot of Sh against Sc Gr $(\Delta\rho/\rho_i)$.

bounding surfaces of the spaces so that the overall performance approaches that of the flat plate. Two effects may further increase the mass-transfer rates. Firstly, since the bounding surfaces of the mesh spaces are now active convection must take place to and from these surfaces and the convective streams will merge with the main streamlines causing slight disturbances which will be quickly dissipated in the main streamlines but which will enhance mass transfer slightly. Secondly, since the surface of the electrolyte is discontinuous there will be a tendency toward boundary-layer decay and re-establishment, each bar of the mesh acting as a leading edge within a partially developed mass-transfer boundary layer. This latter effect, like the others, is concentration dependent and it is significant that inclusion of a further dimensionless density difference parameter with the $Sc \times Gr$ term yields a very good correlation as shown by Fig. 4.

The equation of the correlating line is:

$$Sh = 1{\cdot}5\left(Sc\,Gr\,\frac{\Delta\rho}{\rho_i}\right)^{0\cdot25} \tag{5}$$

However this equation is not being proposed as a true correlation since other factors may be involved and a satisfactory correlating equation may be of some complexity and difficult to establish precisely. It is hoped that further studies may contribute to a fuller understanding of the problem.

The conclusion of the present work is the fact that a vertical mesh electrode exhibits very similar free convection mass-transfer behaviour to that of a plane vertical plate of the same total exposed area. However a further effect of concentration difference has been shown to affect the performance.

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Résumé—Le transport de masse par convection naturelle à des électrodes poreuses verticales a été étudiée expérimentalement en mesurant les courants limites pour la réduction cathodique des ions ferrocyanure. On a fait varier la hauteur de l'électrode et la concentration de l'électrode pour avoir une gamme de $Sc \times Gr$ allant de $2 \cdot 10^5$ à $5 \cdot 10^{10}$. Les résultats ont été avec des expressions théoriques et expérimentales antérieures obtenues pour la convection naturelle sur des plaques verticales et l'on a observé une configuration fondamentalement semblamble. On a suggéré des explications pour l'existence d'une sensibilité à la concentration supplémentaire à celle décrite par le groupe de Grashof.

Zusammenfassung—Der Stoffübergang an senkrechten Maschenelektroden bei freier Konvektion wurde durch Messung der Grenzströmungen für die kathodische Reduktion von Ferricyanidionen experimentell untersucht. Elektrodenhöhe und Elektrolytenkonzentration wurden variiert, so dass der Bereich $Sc \times Gr$ von 2×10^5 bis 5×10^{10} erfasst wurde. Die Ergebnisse wurden mit früheren theoretischen und experimentellen Ausdrücken, die für freie Konvektion an senkrechten Platten erhalten worden waren, verglichen. Ein im wesentlichen ähnliches Verhaltensschema wurde dabei beobachtet. Vorschläge wurden gemacht, eine Konzentrationsabhängigkeit, zusätzlich zu der durch die Grashof-Gruppe beschriebenen, zu erklären.

Аннотация—Экспериментально исследовался массообмен при свободной конвекции на вертикальных сетчатых электродах путем измерения предельных токов при катодном восстановлении ионов, содержащих соль железосинеродистой кислоты. Для получения диапазона $Sc \times Gr$ от 2×10^5 до 5×10^{10} изменяли высоту электрода и концентрацию электролита. Данные сравнивались с предыдущими теоретическими и экспериментальными выражениями, полученными для свободной конвекции на вертикальных пластинах. В основном, наблюдается аналогичная картина поведения.