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Mass transfer to planar and expanded metal electrodes in bubble columns

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Mass transfer rates at planar electrodes and electrodes of expanded metal placed in the centre of a bubble column were measured. The gas velocity and the physical properties of the electrolytic solutions were varied and different types of expanded metal were investigated. In some cases increases in the mass transfer coefficient over the planar electrode value of more than 100% were obtained. Dimensionless correlations are presented for the different systems.

Nomenclature

A	mean mesh aperture
D	diffusivity
D_c	column diameter
g	acceleration due to gravity
Ga	Galileo number $= gL^3/\nu^2$
Gr	Grashof number $= g\Delta\varrho L^3/\varrho\nu^2$
k	mass transfer coefficient
L	electrode height
r	radial position
R	column radius
Re	Reynolds number $= R_h V_s/\nu$
R_h	hydraulic radius $= \varepsilon/\varphi$
Sc	Schmidt number $= \nu/D$
Sh	Sherwood number $= kL/D$
V_s	superficial velocity
ε	gas void fraction
ε_M	porosity of expanded metal
ν	kinematic viscosity
ϱ	density
φ	electrode area per unit volume
ψ	electrode area per unit net area

1. Introduction

For many years bubble columns have been employed in chemical industries as absorbers, extractors, reactors, electrochemical cells, etc. Although they present economic and operating advantages over mechanically stirred devices, the design and performance characteristics are not yet well defined.

The present paper deals with gas stirred electrolytic cells. Three kinds of stirring may be distinguished:

(i) cells with gas evolving at the working electrode [1, 2].

(ii) cells with gas evolving at the counter-electrode [3, 4].

(iii) cells with gas sparging from the outside [5, 6, 18].

Little investigation appears to have been done on the last type of electrochemical reactor despite the industrial use in electrowinning, electrorefining of metals and in organic synthesis.

Recent studies on mass transfer to wall electrodes in a gas sparged cell [7] accounted for the favourable enhancement of mass transfer by this kind of agitation and established a relation between the mass transfer coefficient and the gas hold-up. The results were correlated for short mass transfer lengths by the relationship

$$Sh = 0.231(Sc\,Ga)^{1/3}(L/D_c)^{-0.194}\varepsilon^{0.246} \qquad (1)$$

and for fully developed mass transfer by

$$Sh_\infty = 0.256(Sc\,Ga)^{1/3}\varepsilon^{0.254} \qquad (2)$$

In this work mass transfer coefficients were determined experimentally for electrodes placed in the centre of a circular electrolytic cell, gas being introduced through a perforated plate at the bottom. Both planar electrodes and electrodes of expanded metal were tested.

Expanded metal electrodes were shown to be very effective in diverting gas bubbles evolved in a chlor-alkali membrane cell [8] or in alkaline water electrolysis [9] resulting in a significant decrease of the ohmic drop and a desirable reduction of the cell potential.

These electrodes are also preferred in many other cases owing to the high space-time-yield that may be achieved. They present a higher specific area than conventional flat electrode configurations and, due to their three-dimensional structure, these electrodes act as turbulence promoters.

Free convective mass transfer rates at vertical expanded metal electrodes have been measured in earlier work [10]. It was found that a dimensionless parameter characterizing the geometry of the expanded metal had to be defined in order to correlate the experimental data and the following correlation was

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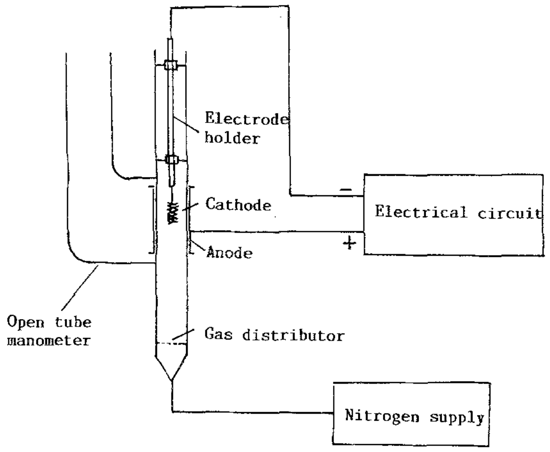

Fig. 1. Experimental set-up.

obtained

$$Sh = 1.29(Sc\ Gr)^{0.27}(R_h/A)^{0.46} \quad (3)$$

The same geometric parameter was used [11] to correlate mass transfer data obtained for flow cells working with expanded metal electrodes [12, 13]. In this case

$$Sh = 0.377Re^{0.515}Sc^{0.33}(R_h/A)^{0.38} \quad (4)$$

In the present investigation the turbulence-promoting nature of the expanded metal is combined with the mass transfer enhancing action of gas bubbles thus combining augmentative techniques. The principal purpose is to determine the effect of fluid dynamic parameters and the geometric characteristics of the electrodes on the mass transfer coefficient. The influence of the physical properties of the solution is also analysed.

2. Experimental details

Mass transfer coefficients were determined by the electrochemical method. They were derived from the values of limiting current obtained for the reduction of ferricyanide ions in alkaline solutions.

Fig. 1 shows a diagram of the experimental set-up. The cell was a column 5 cm in inner diameter and 100 cm high constructed from a lucite tube. The gas was introduced into the column through a sparger spaced at the bottom.

Two perforated plates of lucite, 0.5 cm thick, were used as gas distributors; one with six holes 0.05 cm in diameter (*D* 1/2–6), the other with eight holes 0.1 cm in diameter (*D* 1–8), all drilled on a circle at 1.25 cm from the column axis.

For the measurement of the gas void fraction by the manometric method, there were several pressure taps along the column. These were connected to open tube manometers filled with the electrolytic solution. Nitrogen, humidified before entering the cell, was used as sparging gas at velocities ranging from 0.078 to 8.2 cm sec^{-1}. Gas void fractions varying between 0.0033 and 0.27 were obtained. The test electrodes were sheets of electroless expanded stainless steel (nickel-plated) and were placed at the column axis. A planar vertical nickel electrode (2 cm × 3 cm) was also used for comparison purposes.

Fig. 2, where a schematic representation of the expanded metal electrodes is presented, shows the different dimensions which characterize the expanded metal and the different mesh orientations which were tested. Table 1 summarizes the characteristics of the expanded metal electrodes employed. The materials A to E presented a rhomboidal design and the materials F and G had a hexagonal design. Furthermore electrodes of expanded metal of fine structure ($\psi \leqslant 1.5$; materials A–D) and of large structure ($\psi > 1.5$; materials E–G) can be distinguished.

The anode, a nickel-plated copper tube 14 cm high and 5 cm in inner diameter, replaced part of the

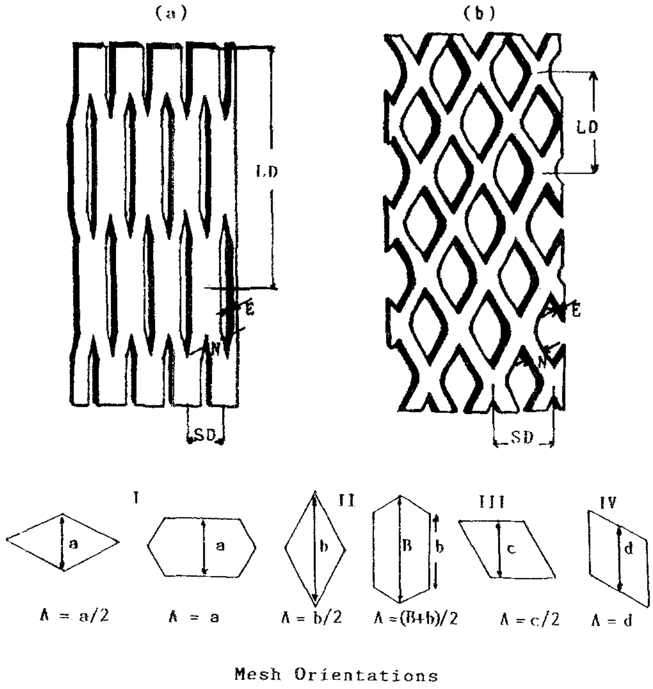

Fig. 2. Characterization and mesh orientations of expanded metal (a) hexagonal design, large structure; (b) rhomboidal design, fine structure.

Table 1. Summary of the characteristics of the expanded metal electrodes employed

Material	*LD-N-E*	*Width* cm	*Height* cm	ψ	*SD* mm	*A* mm	ε_M	φ cm^{-1}	R_h mm	R_h/A	*Orientation*
A	6–0.70–0.6	2.10	3.10	1.26	3.8	1.30	0.833	10.50	0.79	0.61	I
		2.05	2.93	1.26	3.8	1.23	0.833	10.50	0.79	0.64	III
B	10–0.95–0.4	2.16	2.90	1.30	4.55	1.60	0.872	10.88	0.80	0.5	I
		2.09	3.12	1.30	4.55	3.94	0.872	10.88	0.80	0.203	II
		2.15	3.11	1.30	4.55	1.47	0.872	10.88	0.80	0.54	III
		2.06	2.94	1.30	4.55	4.3	0.872	10.88	0.80	0.19	IV
C	10–1.30–0.6	2.10	3.08	1.50	5.1	3.55	0.863	8.33	1.04	0.29	II
		2.18	3.11	1.50	5.1	2.40	0.863	8.33	1.04	0.43	III
		1.90	2.95	1.50	5.1	3.90	0.863	8.33	1.04	0.27	IV
D	12–0.95–0.4	2.05	3.15	1.15	5.55	2.10	0.909	9.63	0.94	0.45	I
		2.08	3.33	1.15	5.55	5.10	0.909	9.63	0.94	0.18	II
		2.145	3.0	1.15	5.55	1.95	0.909	9.63	0.94	0.48	III
		2.30	3.18	1.15	5.55	5.45	0.909	9.63	0.94	0.17	IV
E	16–2.0–1.0	3.175	4.0	1.56	7.3	2.1	0.827	5.11	1.62	0.77	I
		2.22	3.18	1.56	7.3	6.11	0.827	5.11	1.62	0.265	II
		2.04	3.20	1.56	7.3	2.0	0.827	5.11	1.62	0.81	III
F	16.3–2.5–1.0	2.27	3.19	2.02	6.0	1.2	0.664	8.08	0.82	0.68	I
		2.23	3.25	2.02	6.0	5.7	0.664	8.08	0.82	0.14	II
G	28.5–2.0–1.0	2.25	2.90	1.85	6.5	2.35	0.803	5.6	1.43	0.61	I
		2.38	3.35	1.85	6.5	12.8	0.803	5.6	1.43	0.11	II

column wall surrounding the cathode. The location of the electrodes was based on previous studies [14] on the axial gas hold-up distribution; they were placed in the zone of constant gas voidage, this is at 30 cm from the sparger.

The electrolytic solutions used were all 0.01 M equimolar in potassium ferri- and ferrocyanide. 0.5 M NaOH (solution S_1) or a buffer 0.4 M equimolar $Na_2CO_3/NaHCO_3$ (solutions S_2 to S_4) were used as indifferent electrolyte. In order to change the liquid properties sodium carboxymethyl cellulose was added to solutions S_2, S_3 and S_4. All the solutions presented Newtonian behaviour. Their physical properties and the working temperature are listed in Table 2. Viscosities and densities were measured by conventional methods; the diffusion coefficients were obtained with a pipe wall electrode as described elsewhere [15]. The experimental conditions covered the following ranges

$$0.0033 \leqslant \varepsilon \leqslant 0.27$$

$$0.078 \leqslant V_s \leqslant 8.2\,\mathrm{cm\,sec^{-1}}$$

$$8.61 \times 10^{10} \leqslant Sc\,Ga \leqslant 5.66 \times 10^{11}$$

3. Results

3.1. *Planar electrodes*

Fig. 3 shows the experimental results for the planar electrode placed on the column axis. As can be seen, the gas hold-up affects the mass transfer rate in the same way for both gas distributors and for all the solutions employed, $k \propto \varepsilon^c$. Taking account of this and in order to obtain a dimensionless relationship, the experimental data were correlated according to Cavatorta and Böhm [7] in the form $Sh = a(ScGa)^b \varepsilon^c$. The following relation was obtained

$$Sh = 0.362(Sc\ Ga)^{1/3}\varepsilon^{0.235} \qquad (5)$$

with a standard deviation of 4.7%. The experimental data obtained for $\varepsilon < 0.01$ were excluded from the regression analysis, since the reproducibility found at the lowest gas void fractions was generally poor. At these low porosities the liquid is hardly agitated and the mass transfer rate depends on whether there is a central stream of bubbles or bubble-rise near the wall.

Table 2. The physical properties and working temperature of the solutions

Solution	*Conc. of CMC* $g\,100\,ml^{-1}$	*T* °C	$\mu \times 10^2$ $g\,cm\,sec^{-1}$	$D \times 10^6$ $cm^2\,sec^{-1}$	ϱ $g\,cm^{-3}$	*Sc*
S_1	–	21.8	1.07	6.12	1.024	1767
S_2	0.15	22.1	2.32	5.04	1.069	4306
S_3	0.30	25.4	3.44	5.52	1.068	5835
S_4	0.45	23.0	6.38	5.15	1.070	11 578

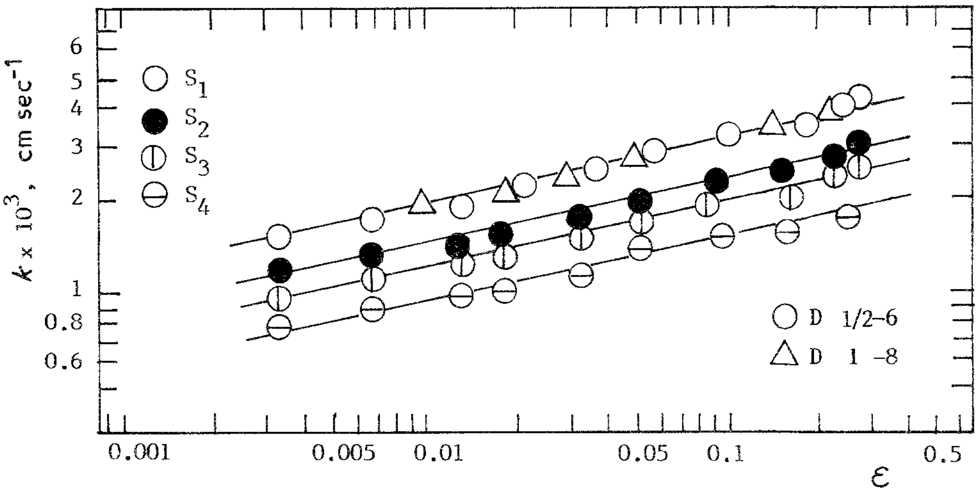

Fig. 3. Experimental mass transfer results for a planar electrode placed in a bubble column.

3.2. *Expanded metal electrodes*

As can be seen from Fig. 4, showing the mass transfer results obtained for one expanded metal electrode, the influence of the physical properties of the electrolyte is the same as that encountered with the flat electrode.

Fig. 5 shows some typical data obtained with the materials B, D, E and F for solution S_1. It appears that the mesh orientation and hence the geometric parameter (R_h/A) scarcely affect the mass transfer rate. It also can be observed that higher mass transfer coefficients are obtained with the materials of fine structure. The same behaviour is found with the other materials.

Electrodes made from materials A to D, resembling wire gauzes because of the relatively large free area, yield higher mass transfer rates than electrodes made from materials E to F. These are characterized by a large relation of working area to projected area, their aspect tending to planar electrodes. It should be mentioned that the mesh design of this group of electrodes, rhomboidal or hexagonal, seems to produce the same effect on mass transfer.

In view of the evident difference between electrodes of fine and of large structure, the experimental results were correlated separately for both groups; 156 data points for the former and 93 for the latter.

Thus, for $\varepsilon \geqslant 0.01$ and $\psi \leqslant 1.5$, and taking into account the geometric factor (R_h/A) used to describe other mass transfer problems, the following relationship is obtained

$$Sh = 0.906(Sc\ Ga)^{1/3}\varepsilon^{0.311}(R_h/A)^{0.077} \quad (6)$$

with a standard deviation of 6.8%.

The small exponent on (R_h/A) indicates the weak dependence of mass transfer on the mesh orientation of the expanded metal, as was already observed in Fig. 5.

Excluding the geometric factor in the regression analysis, in order to simplify the formula, the correlation is as follows:

$$Sh = 0.841(Sc\ Ga)^{1/3}\varepsilon^{0.311} \quad (7)$$

the standard deviation now being 7.8%.

Since the exponent on (R_h/A) for the electrodes of large structure was found to be almost the same as for

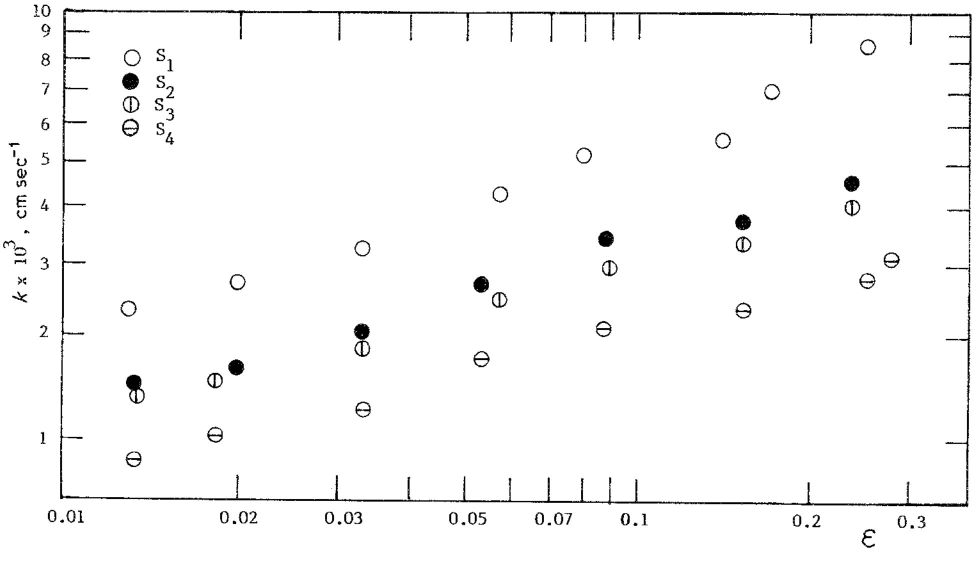

Fig. 4. Experimental mass transfer results for an expanded metal electrode placed in a bubble column. (Material C; orientation III.)

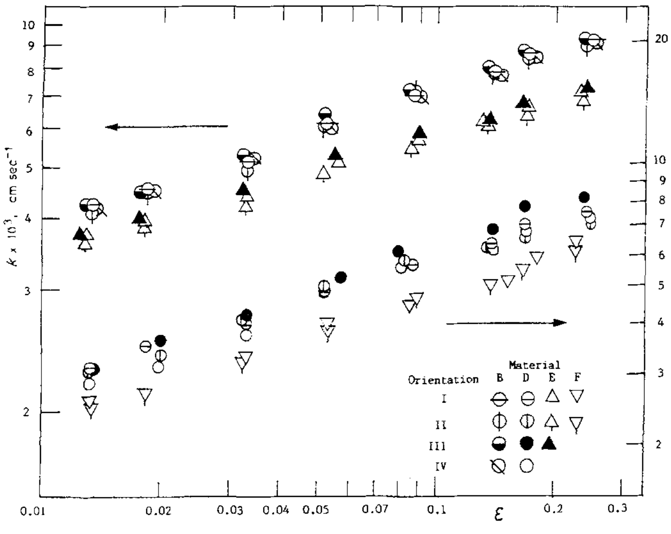

Fig. 5. Experimental mass transfer coefficients for expanded metal electrodes in bubble columns.

the fine structured electrodes, the geometric parameter was also left out in the treatment of data corresponding to the second group of electrodes to yield the much simpler correlation

$$Sh = 0.607(Sc\ Ga)^{1/3}\varepsilon^{0.278} \qquad (8)$$

valid for $\varepsilon \geqslant 0.01$ and $\psi > 1.5$. The standard deviation is 6.9%.

4. Discussion

4.1. *Planar electrodes*

As mentioned before the empirical equations (1) and (2) hold for wall-side mass transfer in bubble agitated cells. Thus for the same column diameter and a wall-electrode of the same length as that of the flat-electrode used in this investigation, equation (1) would be:

$$Sh = 0.255(Sc\ Ga)^{1/3}\varepsilon^{0.246} \qquad (9)$$

Comparing this relationship with equation (5) it follows that, under otherwise similar operating conditions, mass transfer coefficients are 45–50% higher for the electrode placed in the centre of the column that for the wall-electrode. This is in agreement with the radial variation of a gas hold-up. It is known that the gas void fraction is maximum at the centre and decreases as the column wall is approached [16], according to

$$\varepsilon_r = 2\varepsilon[1 - (r/R)^2] \qquad (10)$$

Patil and Sharma [17] found similar results when studying the variation of local mass transfer coefficients in a 38 cm i.d. bubble column and explained the decrease in the radial direction by the reduction in the radial component of the liquid circulation velocity as the wall is approached.

4.2. *Expanded metal electrodes*

As expected, bubbling is highly effective in promoting mass transport to the electrodes. Depending on the gas void fraction, limiting currents are 15 to 20 times those obtained under natural convection conditions.

When compared with the planar electrode, the increments achieved with the fine structured expanded metal exceed 100%, as follows from equations (5) and (7). Even for the electrodes of large structure (equation (8)), mass transfer coefficients are 40 to 60% higher than for a smooth surface. However, all the investigated materials are of interest since they augment the mass transfer coefficient over the smooth plate value. The smaller increase obtained with the large structured electrodes will be compensated by the greater active area per unit net area.

It is also worth noticing that the exponent of the gas hold-up tends to the exponent obtained with a smooth surface as the structure of the expanded metal tends to the planar geometry.

Furthermore it is interesting to note, that the geometric parameter (R_h/A), indispensable for describing free and forced convective mass transfer at expanded metal electrodes, has practically no effect in gas stirred cells. In this case the improvements are due to a combination of the turbulence-promoting configuration of the expanded metal and the eddies generated by the bubbles. Although the main liquid flow is upwards in the core zone of the column and downwards near the wall, turbulent fluctuations are produced close to the surface in all directions, explaining the relative unimportance of the mesh orientation. Nevertheless mass transfer depends on the distribution and density of the promoters over the surface.

A single correlation was derived using all the experimental data. This expression is, for $\varepsilon \geqslant 0.01$:

$$Sh = 0.92(Sc\ Ga)^{1/3}\psi^{-0.6}\varepsilon^{0.3} \qquad (11)$$

The accuracy, expressed through the standard deviation of 10%, is still acceptable in view of the practical utility and simplicity of equation (11).

5. Concluding remarks

A significant increase in performance of electrolytic cells may be achieved by using expanded metal as electrode material and sparging gas from the outside. The combined action of the turbulence-promoting geometry of the electrode and the bubble agitation, producing turbulent fluctuations very close to the transferring interface, is of considerable benefit in improving mass transfer.

Correlations for the evaluation of mass transfer coefficients, taking account of geometric aspects of the expanded metal were derived and discussed.

For practical purposes a simple general correlation is presented which describes mass transfer for a great variety of materials, operating in gas stirred cells.

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