Portugaliae Electrochimica Acta 21 (2003) 295-313

PORTUGALIAE ELECTROCHIMICA ACTA

Effect of Gas Sparging on the Rate of Mass Transfer at Horizontal Cylinders

A.A.Taha*, A.M. Ahmed, A.A. Bayoumy

Department of Chemistry, Faculty of science, University of Alexandria, Alexandria, Egypt

Received 2 September 2002; accepted in revised form 19 August 2003

Abstract

The rate of mass transfer was studied at (i) a single horizontal cylinder cathode and (ii) a vertical array of closely spaced horizontal cylinders and an array of separated cylinders. The mass transfer coefficients were obtained by measuring the limiting current of the cathodic reduction of alkaline potassium ferricyanide. Variables studied were: cylinder diameter, physical properties of the solution, and nitrogen flow rate. The mass transfer coefficient was found to increase with increasing nitrogen superficial velocity. Decreasing the diameter was found to increase the mass transfer coefficient. The mass transfer data were correlated by the following equations:

For single horizontal cylinder cathode: $J = 2.138\ (Re.\ Fr)^{-0.24}$

For an array of closely spaced cylinders: $J = 50.118\ (Re.Fr)^{-0.32}$

For an array of separated cylinders: $J = 100\ (Re.Fr)^{-0.28}$

Possible practical application of gas sparged array of horizontal cylinders in building electrochemical reactors are discussed.

***Keywords*:** Mass transfer, horizontal cylinders, gas sparged, electrochemical reactor.

Introduction

The electrochemical technique has recently been recognized as one of the powerful tools for pollution control and electro-organic and electro-inorganic synthesis. Since most of the reactions involved in electrochemical pollution control, organic and inorganic electrosynthesis are diffusion controlled, a suitable means should be used to enhance the rate of mass transfer in the electrochemical reactor. The traditional method for enhancing the rate of mass transfer in

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* Corresponding author. E-mail address: ghada_113@hotmail.com

electrochemical reactor has been mechanical pumping of the fluid through the reactor or rotating the electrode itself (cylinder or disc). In a recent development Ibl et al. [1,2] and Ettel et al. [3] have tested the effect of gas sparging on the rate of mass transfer using a parallel plate electrochemical reactor. They came to the conclusion that gas sparging is an effective way of stirring and is cheaper than mechanical stirring. Since then, gas sparging has been used to enhance the rate of liquid-solid mass transfer at vertical cylinder electrodes [4], fixed bed electrode [5], vertical bubble column [6], horizontal and vertical screens [7-9]. Zarraa et al. [10,11] studied the effect of N_2 sparging on the rate of mass transfer at a single sphere and a fixed bed of spheres using the diffusion controlled dissolution of copper in acidified $K_2Cr_2O_7$. Noseir et al. [12] studied the effect of nitrogen sparging on the rate of mass transfer at a fixed bed of Raschig rings under different conditions of bed height, physical properties of the solution, ring diameter. The authors used the diffusion controlled dissolution of copper in acidified $K_2Cr_2O_7$ to correlate their data.

The object of the present work is to study the mass transfer behaviour of gas sparged electrochemical reactor which uses an array of horizontal cylinders as a working electrode. The use of vertical arrays of horizontal cylinders as electrode was suggested by Sedahmed and Nirdosh [13] who studied the natural convection mass transfer behaviour of the electrode. The advantage of this geometry is that the electrode can serve also as a heat exchanger by passing cold water in the cylinders to remove excess of heat generated during electrolysis and which may adversely affect the performance of the reactor; e.g in electroorganic synthesis the product may be heat sensitive, in this case it is imperative to cool the reactor in order to avoid product decomposition. Also in case of inorganic synthesis such as chlorate production, excess of heat should be removed to increase the yield. The use of an array of gas sparged horizontal cylinders would eliminate the need for an external heat exchanger (cooler) and accordingly would reduce the capital cost of electrochemical plants.

The rate of mass transfer was measured by the well known electrochemical technique which involves measuring the limiting current of the cathodic reduction of $K_3[Fe(CN)_6]$ in the presence of a large excess of NaOH as supporting electrolyte.

Results and Discussion

Figs. (1-3) show typical current-potential curves (polarization curves) with a well defined limiting current plateau at single cylinders and at arrays of horizontal cylinders under different conditions of N_2 superficial velocity, cylinder diameter, cylinder spacing in case of the cylinder array and NaOH concentrations. The limiting current of the cathodic reduction of $K_3[Fe(CN)_6]$ (I_L) was determined from these curves and was used in calculating the mass transfer coefficient (K) from the equation:

$$I_L/ZF = KAC \tag{1}$$

where Z is the number of electrons involved in the reaction; F= Faraday's constant (96 500 coulomb); A is the cathode area; C is the ferricyanide concentration.

Comparison of the results of Fig. (2) and Fig. (3) which were obtained for 7 cylinders of different diameters and the same solution concentration for zero gas velocity (natural convection) shows that the increase in the limiting current for the larger cylinder array (Fig. 3) is not proportional to the increase in array area.

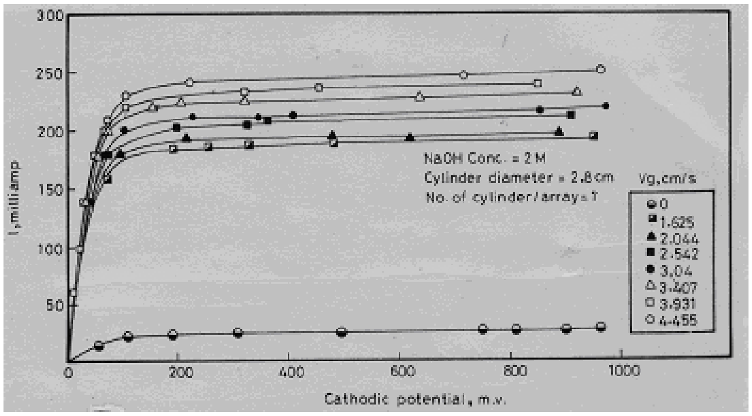

Figure 1. Polarization data at a single horizontal cylinder (Single cylinder).

This can be explained by the increase in the thickness of the hydrodynamic boundary layer and diffusion layer with increasing cylinder diameter, this leads to decreasing the average mass transfer coefficient and the limiting current at the array with the larger cylinder diameter.

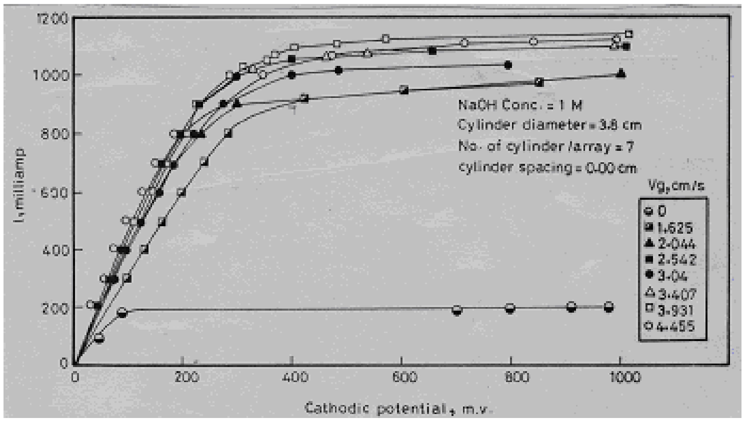

Figure 2. Polarization data at an array of horizontal cylinders (Closely spaced cylinder array).

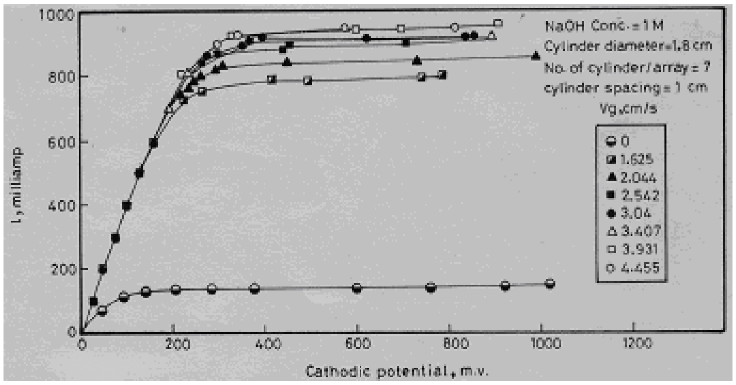

Figure 3. Polarization data at an array of horizontal cylinders (Separated cylinder array).

Figs. (4 and 5) show that the superficial gas velocity increases the limiting current and the mass transfer coefficient at single cylinders according to the equations:

$$i_L = a\, V_g^{0.241} \qquad (2)$$

$$K = a_1\, V_g^{0.209} \qquad (3)$$

The superficial gas velocity V_g was obtained by dividing the volumetric gas flow rate (measured by a rotameter) by the cross sectional area of the cell.

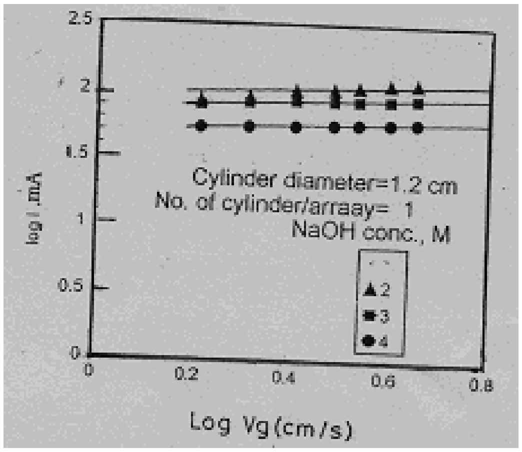

Figure 4. Effect of superficial gas velocity on the limiting current of the cathodic reduction of $K_3[Fe(CN)_6]$.

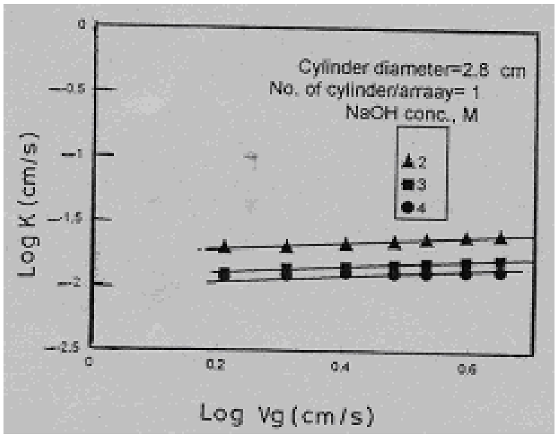

Figure 5. Log K versus Log V_g for the cathodic reduction of $K_3[Fe(CN)_6]$ at a single horizontal cylinder.

For arrays of closely spaced horizontal cylinders, Figs. (6 and 7) show that the limiting current and the mass transfer coefficient increase with increasing N_2 superficial velocity according to the equations:

$$i_L = a_2 V_g^{0.191} \qquad (4)$$

$$K = a_3 V_g^{0.192} \qquad (5)$$

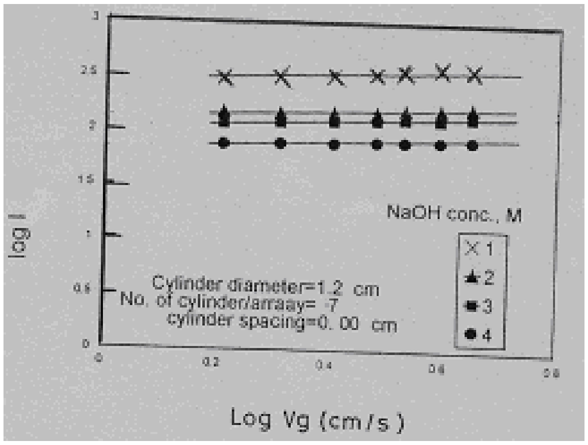

Figure 6. Effect of superficial gas velocity on the limiting current of the cathodic reduction of $K_3[Fe(CN)_6]$ at an array of closely spaced horizontal cylinders.

Figs. (8 and 9) show the effect of N_2 superficial velocity on the limiting current and the mass transfer coefficient at an array of separated cylinders, the data fit the equations:

$$i_L = a_4 V_g^{0.198} \tag{6}$$

$$K = a_5 V_g^{0.198} \tag{7}$$

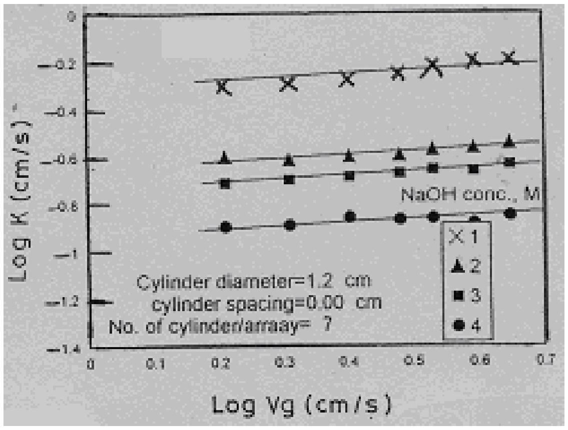

Figure 7. Log K versus Log V_g for the cathodic reduction of $K_3[Fe(CN)_6]$ at an array of closely spaced horizontal cylinders.

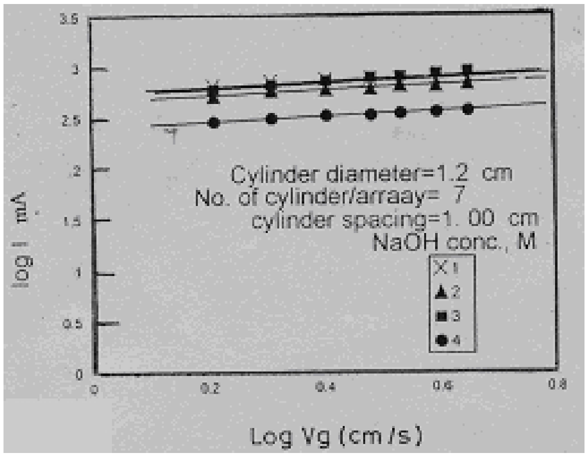

Figure 8. Effect of superficial gas velocity on the limiting current of the cathodic reduction of $K_3[Fe(CN)_6]$ at an array of separated horizontal cylinders.

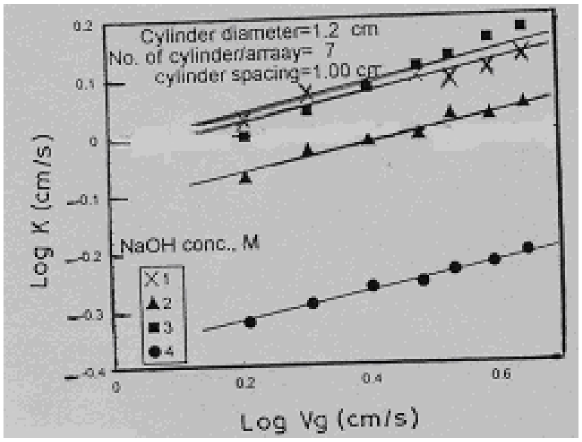

Figure 9. Log K versus Log V_g for the cathodic reduction of $K_3[Fe(CN)_6]$ at an array of separated horizontal cylinders.

Comparing eqs. (2-7) shows that the mass transfer coefficient at single cylinders is more sensitive to the superficial gas velocity than closely spaced or separated arrays as indicated by the V_g exponents shown in eqs. (2-7). Eqs. (4-7) show that separated arrays are more sensitive to gas sparging than closely spaced arrays as indicated by the V_g exponents in these equations. It seems that the boundary layer separation and eddy formation in the wake of each cylinder of the separated cylinder array play an important role in increasing the sensitivity of separated array to gas sparging more than closely spaced array where there is no available free space between successive cylinders. The lower sensitivity of arrays of separated cylinders to gas sparging compared to single cylinders may be attributed to eddy damping in the limited space between cylinders in case of the separated cylinder array, this effect being absent in case of single cylinders.

Table 1 summarizes the velocity exponent obtained by different authors who studied the effect of gas sparging on the rate of mass and heat transfer, and shows that the present exponents are in agreement with the values obtained in heat and mass transfer.

Table 1. Effect of the superficial gas velocity on the mass and heat transfer ($K \alpha V^n$ or $h \alpha V^n$).

Author	Experimental method	n
Noseir et al. [14]	Mass transfer	0.242
Bohm et al. [6]	Mass transfer	0.250
Sharma et al. [15]	Mass transfer	0.290
Ibl et al. [1]	Heat transfer	0.360
Lewis et al. [16]	Heat transfer	0.172
Fair et al. [17]	Mass transfer	0.220
Steiff and Weinspach [18]	Heat transfer	0.220
Hart [19]	Heat transfer	0.250
Present work	Mass transfer (single)	0.209
Present work	Mass transfer (closely spaced)	0.192
Present work	Mass transfer (separated)	0.198

The substantial increase in the limiting current and mass transfer coefficient by gas sparging may be attributed to the following effects:

i- The rising bubbles induce an upward axial flow of the solution past the horizontal tubes, reducing the diffusion layer thickness δ with a consequent increase in K ($K= D/\delta$). Besides N_2 bubbles impinge on the tube surface and disturb the diffusion layer with a consequent increase in the rate of mass transfer.

ii- According to Kast [20] a fluid element in front of the rising bubble receives a radial momentum (in addition to the axial momentum); this radial momentum contributes a great deal to the enhancement of the rate of mass transfer of the electroactive ion to the tube surface as the bubble swarm moves past it.

iii- A turbulent wake is formed behind each gas bubble forming the swarm [2] as it moves upward through the tube array; this turbulence contributes to enhancing the rate of mass transfer at the tube array and single tube surface.

Figs. (10-12) show the effect of the cylinder diameter on the mass transfer coefficient, the data fit the equations:

For single cylinders: $K\alpha\ d^{-0.189}$

For closely spaced cylinder: $K\alpha\ d^{-0.128}$

For separated cylinder: $K\alpha\ d^{-0.416}$

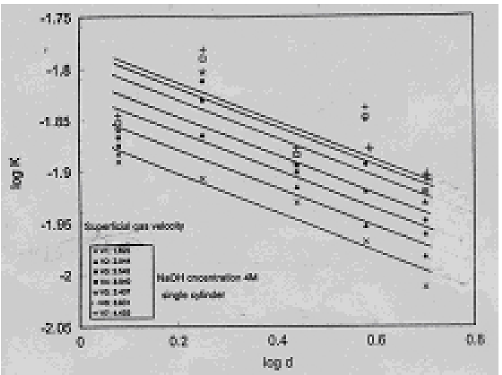

Figure 10. Effect of single cylinder diameters on the mass transfer coefficient at different superficial nitrogen velocity.

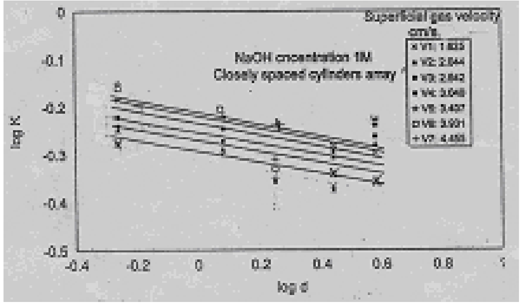

Figure 11. Effect of cylindrical tube diameters on the mass transfer coefficient at different superficial nitrogen velocity.

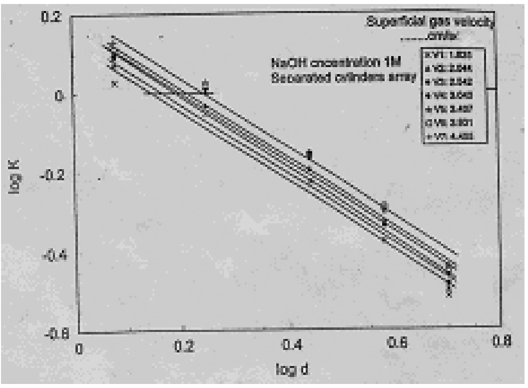

Figure 12. Effect of cylindrical tube diameters on the mass transfer coefficient at different superficial nitrogen velocity.

The decrease in the mass transfer coefficient with increasing electrode diameter may be attributed to the growth of a hydrodynamic boundary layer and a diffusion layer, whose thickness increases with increasing tube diameter. The diameter exponents in this work (-0.189 and -0.128) are in fair agreement with the values (-0.251) obtained by Nosier et al. [14] for horizontal cylinders. The diameter exponent (-0.416) in case of a vertical array of separated horizontal cylinders is in agreement with the values (-0.50) obtained by Lewis et al. [16] for vertical cylindrical heaters.

An overall mass transfer correlation of the data was envisaged using the method of dimensional analysis. For single gas sparged horizontal cylinder, the mass transfer coefficient can be related to other variables by the following functional equation:

$$K = f(\mu, g, \rho, D, d, V_g) \tag{8}$$

Dimensional analysis leads to:

$$\left(\frac{K}{V}\right)\left(\frac{\mu}{\rho D}\right)^{\alpha} = \beta\left(\frac{V_g^3\rho}{\mu g}\right)^{\gamma} \tag{9}$$

i.e

$$St\,(Sc)^{\alpha} = \beta\,(Re.Fr)^{\gamma} \tag{10}$$

According to previous theoretical and experimental studies in heat and mass transfer [21] the value of α is 0.66; accordingly the above equation can be written in the form:

$$St.Sc^{0.66} = \beta\ (Re.\ Fr)^{\gamma} \tag{11}$$

i.e.

$$J = \beta\ (Re.\ Fr)^{\gamma} \tag{12}$$

where J is the mass transfer factor.

Fig. 13 shows that the single cylinder mass transfer data for the conditions $1364 < Sc < 9565$; $0.2085 < Re.Fr < 8.9372$; fit the equation:

$$J = 2.138\ (Re.Fr)^{-0.24} \tag{13}$$

with an average deviation of ± 17%.

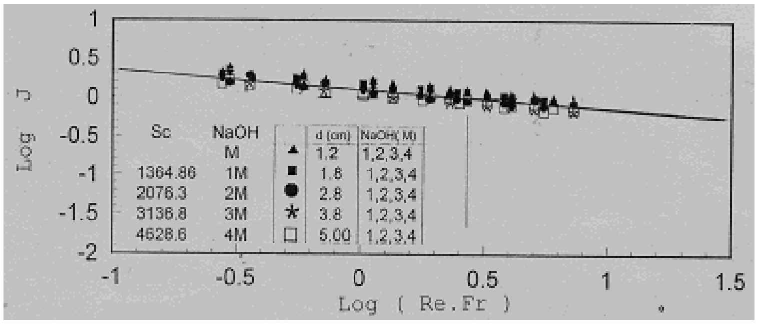

Figure 13. Overall mass transfer correlation for gas sparged horizontal Single cylinder of different diameters.

Fig. 14 shows that for arrays of closely spaced cylinders the mass transfer data for the same range of conditions fit the equation:

$$J= 50.118\ (Re.Fr)^{-0.32} \tag{14}$$

with an average deviation of ± 20 %.

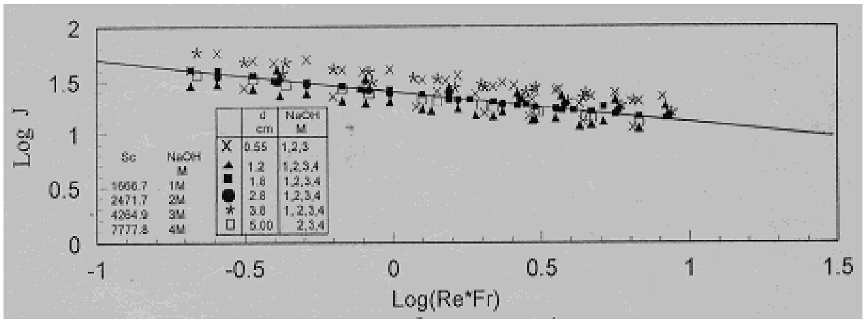

Figure 14. Overall mass transfer correlation for gas sparged vertical array of closely spaced cylinders.

Fig. 15 shows that for arrays of separated cylinders the mass transfer data for the same range of conditions fit the equation:

$$J= 100\ (Re.Fr)^{-0.28} \qquad (15)$$

with an average deviation of ± 17 %.

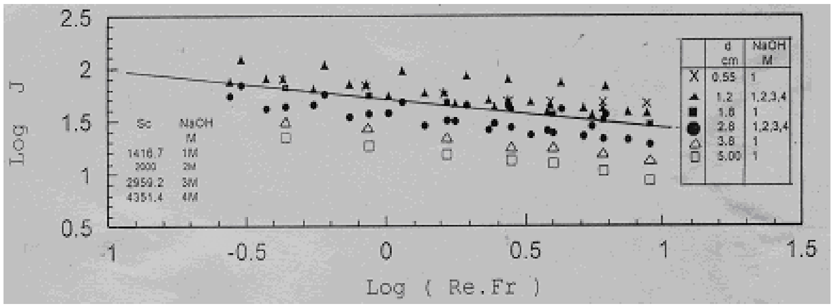

Figure 15. Overall mass transfer correlation for gas sparged vertical array of separated cylinders.

In related previous studies, Ib1 [22] who studied mass transfer rates at gas sparged vertical plate, and Cavatorta and Bohm [6] who studied the effect of gas sparging on the rate of mass transfer at the inner surface of a vertical tube, correlated their data in a manner similar to that used in natural convection, namely:

$Sh= aSc^{0.33}.Ar^{0.33}$

where Ar is Archimedes number = $\dfrac{g.L^3 1-\in}{\gamma 2\in}$

where L is the electrode height, γ is the kinematic viscosity and $\in$ is the gas holdup which is the ratio between the volume occupied by the gas and the total volume of the gas-liquid dispersion. Although the above equation correlates the data of Ibl, and Cavatorta and Bohm quite well, it is not practical because it needs measuring the gas holdup in the reactor beside the fact that the gas holdup may not be uniform inside the reactor. The advantage of the present method of correlation using the dimensionless groups J, Re and Fr is that it obviates the need to measure the gas holdup which is not easy to measure.

Since a sintered glass distributor of a fixed pore size was used in the present study, the question arises as to whether the mass transfer correlations obtained in this study can be extended to other cases where the gas distributor has a different pore size. Ibl [1] in his study of the effect of N_2 sparging on the rate of mass transfer at vertical plates found that the size of the gas distributor has a negligible effect on the rate of mass transfer. Also, in the area of heat transfer in bubble columns it was found that the rate of heat transfer is independent on the bubble size or the pore size of the distributor [23]. In view of this it follows that the mass transfer correlation obtained in this study is of an universal nature, being its applicability only limited by the range of Fr.Re and Sc used in the present study.

Experimental technique

The experimental set up is shown in Fig. 16. Nitrogen gas was passed from a pressurized nitrogen cylinder through a regulator unit to the cell. The electrolytic cell was a cylindrical glass container of 7.5 cm diameter and 41 cm height. It was fitted at its bottom with a 9 cm diameter sintered glass distributor (G4). Nitrogen flow rate was measured by means of a calibrated rotameter and was controlled by means of a plastic valve. The anode was a cylindrical stainless sheet, while the cathode was made of nickel plated copper single cylinder or of an array of nickel plated horizontal copper cylinders. Each array was made of 7 horizontal parallel cylinders supported at their ends by two vertical strips of isolated copper. Two types of array were used namely an array of closely spaced cylinders and an array of separated cylinders.

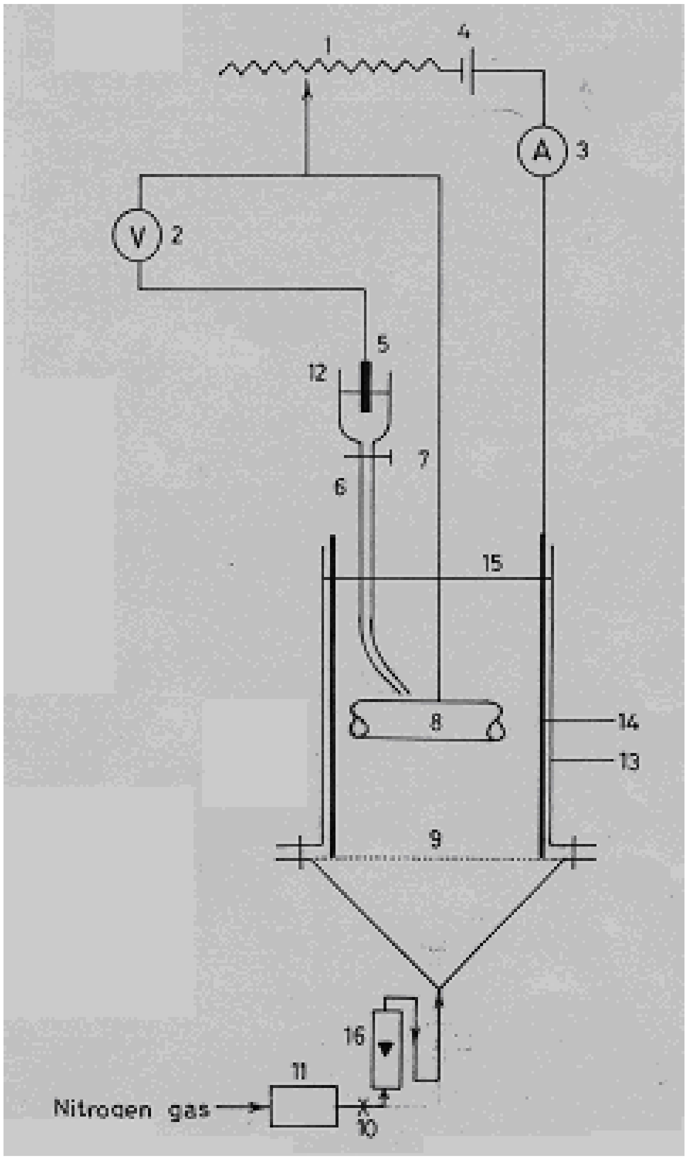

Figure 16. Schematic view of apparatus. 1- Variable resistance (rheostat); 2- D.C. high impedance voltmeter; 3- D.C. ammeter; 4- D.C. power supply; 5- reference electrode; 6- Luggin tube; 7- Insulated current feeder; 8- Nickel plated copper cylinder cathode; 9- air distributor (sintered glass G4); 10- control valve; 11- pressure regulator; 12- glass cup; 13- glass column; 14- stainless-steel cylindrical anode; 15- electrolyte level; 16- calibrated gas rotameter.

The electrical circuit consisted of 6 volts d.c. power supply fitted with a voltage regulator (rheostat), connected in series with a multirange ammeter and the cell. The cell anode was connected to the positive terminal of the d.c. power supply, while the cathode was connected to its negative pole. A high impedance multirange voltmeter was used to measure the cathode potential against a reference electrode made of a nickel wire dipped in the cup of a luggin tube filled with a solution identical in composition with that of the cell. The tip of the Luggin tube was placed 0.5-1 mm far from the cathode. The superficial nitrogen velocity ranged from 1.625 to 4.5 cm/s.

Rates of mass transfer were measured at single cylinder cathode and arrays of horizontal cylinders by determining the limiting current of the cathodic reduction of ferricyanide ion dissolved in a large excess of NaOH as supporting electrolyte. In the presence of an excess of supporting electrolyte the transport of ferricyanide ions to the electrode takes place solely by diffusion and convection while transfer by electrical migration is eliminated [24]. Current-potential curves (polarization curves) from which the limiting current was determined, were constructed by increasing the cell voltage and measuring the steady state cell current, 2 minutes were allowed to reach the steady state.

Polarization curves with a well defined limiting current plateau were obtained under different conditions. The solution used was made of equimolar amount of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ dissolved in 1,2,3,4M NaOH; all chemicals were of A.R. grade, distilled water was used in preparing all solutions.

Table 2. Physical properties of the solutions used at 25 °C.

Solution composition NaOH (Molar)	10^3 μ kg/m.s	ρ kg/m^3	D x 10^{10} m^2/s	Sc
1	1.1042	1046.08	6.693	1577
2	1.3832	1084.99	5.508	2314
3	1.7449	1121.23	4.335	3590
4	2.0204	1160.4	3.1054	5676

Mass transfer was measured for gas sparged:

i. Single horizontal tube cathode with diameters: 0.55, 1.2, 1.8, 2.8, 3.81, 5.00 cm, all cylinders had 4 cm length.

ii. Vertical array of horizontal tube cathode, with 7 horizontal tubes per array. Two types of array were used namely:

a- Closely spaced cylinder array i.e cylinder separation=0.

b- Separated cylinder array where cylinder separation was fixed at 1cm.

Electricity was supplied to the cathode through a 1mm nickel plated copper wire welded to the single cylinder cathode, the wire was insulated except at the contact with the cathode. Array cathode was fed by electricity through the supporting strip. Single cylinder cathodes and array cathodes were placed in the middle of the container. The anode was a cylindrical sheet of stainless steel lining the wall of the container. Before each experiment, the cathode was degreased, then washed. Electrolyte was kept in a dark bottle to avoid the decomposition of ferricyanide by sunlight. A fresh solution was used for six days without any change. Temperature was kept constant at 25±1 °C during each run.

The effect of the following variables on the mass transfer rate of ferricyanide species were studied:

1. Supporting electrolyte concentration and the physical properties of the solution (Sc).
2. Nitrogen flow rate.
3. Cathode geometry (single cylinder; an array of closely spaced horizontal cylinders and an array of separated cylinders).

Conclusions

The technical importance of the overall mass transfer eqs. (13-15) obtained in the present study for gas sparged cylinders and gas sparged array of horizontal cylinders is outlined in the following:

1. The overall mass transfer equation for gas sparged single cylinder can be used to predict the rate of diffusion controlled processes taking place at single cylinder such as electroplating and electropolishing where gas sparging is used frequently to enhance the rate of mass transfer. The mass transfer coefficient (K) needed for

limiting current calculation from eq. (1) can be calculated from the overall mass transfer equation of gas sparged single cylinder equation.

2. The overall mass transfer correlation obtained for gas sparged array of horizontal cylinders can be used in the design and operation of electrochemical reactors used to conduct diffusion controlled processes such as removal of heavy metal ions e.g. Hg^{++}, Hg^{+}, Cu^{++}, Ag^{+}, Cd^{++}, Pb^{++} from industrial waste solutions, and electroorganic and inorganic synthesis. It is noteworthy that gas sparging will not only enhance the rate of mass transfer in electrochemical reactors using gas sparged arrays of horizontal cylinders but also will enhance the rate of heat transfer generated during electrolysis. The removal of such heat is crucial in case of the electrosynthesis of heat sensitive organic compounds which may be decomposed by excess heat; in this case the internal side of the array tubes can be used for cooling the cell by passing cold water through them, i.e., in this case the array would have a dual function, namely the outer surface of the tubes of the array will act as an electrode, while the inner side will act as a heat exchanger.

Nomenclature

K = mass transfer coefficient, cm/s.

Z = number of electrons involved in the reaction.

F = Faraday's constant.

A = the cathode area.

h = heat transfer coefficient, J/cm^2 sK.

V_g = superficial N_2 velocity, cm/s.

D = diffusivity of the reactant, cm^2/s.

d = cylinder diameter, cm

g = accleration due to gravity, cm/s^2

Dimensionless groups

Fr = Froude number (V_g^2/gd)

J = Mass transfer factor (St $Sc^{0.66}$)

Re = Reynolds number ($\rho Vd/\mu$)

Sh = Sherwood number (kd/D)

Sc = Schmidt number ($\mu/\rho D$)

St = Stanton number (K/V_g)

Greek letters

μ = viscosity of the solution, g/cm s.

ρ = solution density, g/cm^3

$\in$ = gas holdup $\left[\in = \frac{\text{gasvolume}}{(\text{gasvolume} + \text{solutionvolume})} \right]$

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