

MASS TRANSFER IN PACKED BEDS IN ANNULAR ELECTROLYTIC REDOX REACTIONS

By

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Fluid-solid technique has been applied to widespread commercial operations involving diffusion-controlled reactions. In recent years ionic mass transfer studies [1, 2] in the presence of fluidized solids have been reported from these laboratories. Except for the qualitative studies [3] of the behaviour of the coefficients there is no work on ionic mass transfer in packed beds in annular cells. However some work [4] has been done in these laboratories in square channels.

In an earlier paper [5] ion transfer rates in diffusion-controlled reactions for the case of reduction of oxygen at silver cathode in presence of excess indifferent electrolyte flowing through packed cells of glass spheres and rockwool shot were shown to be considerably improved due to the presence of the particles. The data were found to be in good agreement with the reported works on other types of mass transfer processes.

The present paper deals with the study of ionic mass transfer in packed annular cells for the case of reduction of ferricyanide ion and oxidation of ferrocyanide ion at copper and nickel electrodes in presence of excess sodium hydroxide as indifferent electrolyte.

The apparatus [5] and the experimental techniques [1, 5, 6, 7] have been described in detail elsewhere. The apparatus essentially consisted of an electrolyte storage tank, a pump for circulating the electrolyte, a test section consisting of calming sections and an electrolytic cell, rotameters for measuring the rate of flow of electrolyte and a capillary arrangement for measuring the electrode potentials with reference to standard calomel electrode.

The electrolyte consisted of equimolar potassium ferrocyanide and ferricyanide (0.01 M) in 0.5 N sodium hydroxide. It was kept in circulation through the packed bed of non-conducting solids and after steady flow is established the limiting currents were evaluated at each flow rate in a manner described earlier [1, 6, 7] from current-electrode potential curves at a point where dE/dI

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is maximum. Typical current-electrode potential curves for the reduction of ferricyanide ion are shown in Fig. 1.

In the case of cathodic reduction of ferricyanide ion nitrogen is bubbled through the electrolyte in the storage tank to eliminate any oxygen contamination since its presence can introduce appreciable errors especially when the depolarizing agent concentrations are low. The electrolytes were analysed by permanganate titration [8] for ferrocyanide ion and by the iodimetric proce-

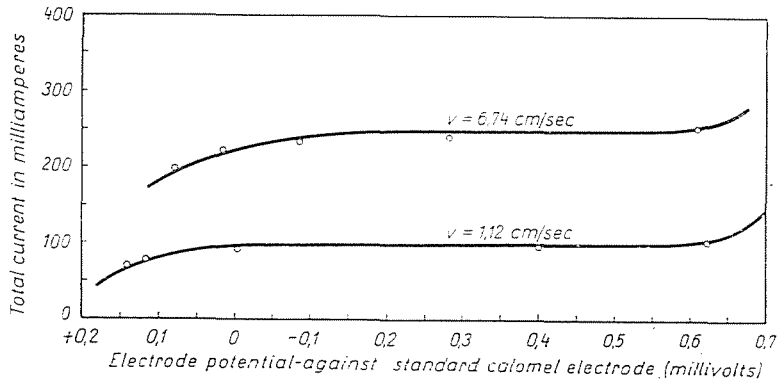


Fig. 1. Polarization curves. Ferricyanide reduction

dure [9] for the ferricyanide ion. Copper and nickel plated copper tubes were used as the test electrodes. The electrodes were cleaned and then polished with 0000 emery paper.

Results

The systems and the range of variable studied are given in Tables A and B. The mass transfer coefficients are calculated in a manner described in the earlier studies [1-7, 10] from the measured limiting currents and the concentrations of the electrolytes.

The effect of the particle size which has a characteristic influence on transfer processes in fluid-solid systems is illustrated by plotting the mass transfer coefficient for various sizes of bed materials as a function of superficial velocity in Fig. 2. As reported earlier [5] the coefficient increased with decrease in particle size.

In the present studies the equivalent diameter of the packed bed is varied from 1.25 to 1.625 cm. by varying the diameter of the central electrode. The data obtained in two annuli of different equivalent diameters are shown in a plot (Fig. 3) of K_L vs. V . The close agreement between these two sets of data indicates that the equivalent diameter of the annulus has virtually no influence

Table A
Systems investigated

Experiment number	System	Material	Electrode diameter inches	Length inches	Solids	Packed Bed Dp cm.	Z inches	% voids	Temperature °C			
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)			
M- 1	Ferri-Ferro Cyanide couple	Copper	0.375	6.0	Glass spheres	0.593	12.0	37.8	32.5			
M- 2					Glass spheres	0.489		41.0	33.5			
M- 3					Rock wool shot	0.1867		40.0	33.0			
M- 4					1/4 inch berl saddles	0.852		57.3	32.0			
M- 5					Sand	0.3969		44.0	33.0			
M- 6					Glass beads	0.6		42.9	34.3			
M- 7					1.0	Glass spheres		0.489	12.0	41.0	31.0	
M- 8					0.500	6.0		Glass spheres	0.593	12.0	38.1	30.5
M- 9					Glass spheres	0.489		38.5	29.5			
M-10					Rock wool shot	0.1867		40.0	31.5			
M-11					0.625	6.0		Glass spheres	0.489	12.0	38.8	32.0
M-12					1.0	Rock wool shot		0.1867	12.0	39.0	32.0	
M-13					0.750	2.0		Rock wool shot	0.1867	12.0	39.0	34.0
M-14					Rock wool shot	0.0776		38.8	34.0			
M-15					Glass spheres	0.489		6.0	41.0	35.0		
M-16					0.750	2.0		Glass beads	0.300	6.0	45.1	34.0
M-17					Rock wool shot	0.1867		38.0	34.5			
M-18					Rock wool shot	0.131		38.5	34.5			
M- 19					Rock wool shot	0.0776		38.8	34.3			
M-20					0.375	9.0		Glass spheres	0.489	18.0	41.0	35.4
M-21					Sand	0.3969		44.0	34.5			
M-22		Nickel	0.375	6.0	Glass spheres	0.489	12.0	41.0	33.0			

Table B
Range of variables investigated

Factor	Max. value	Min. value	Max./min. value
Particle diameter cm.	0.852	0.0776	10.97
Superficial velocity cm./sec.	33.4	0.151	221.1
Particle Reynolds number	2815	1.449	1943
Voidage	0.573	0.378	1.52
Packing height inches	18	6	3
L/D ratio of electrode	24.0	1.6	15.0

on the mass transfer coefficient. Such a result is expected since in well-designed packed beds where wall effects are negligible, the particle diameter rather than the bed diameter is important.

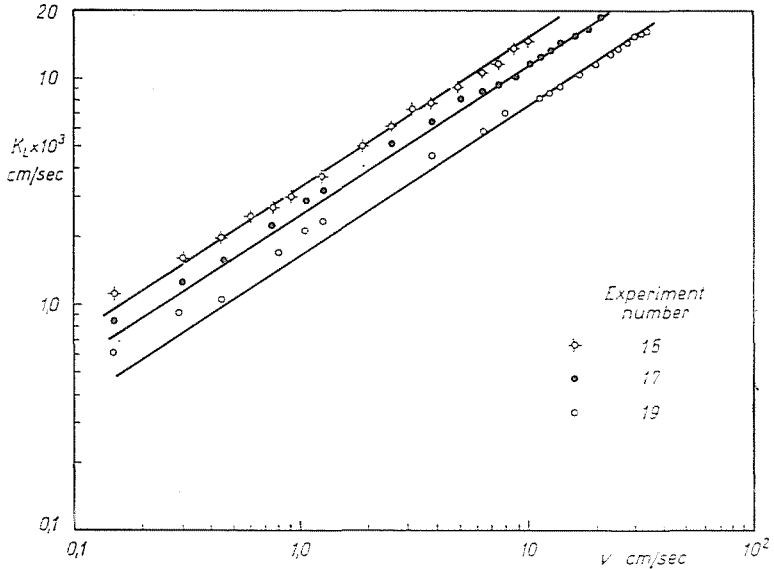


Fig. 2. Effect of particle size

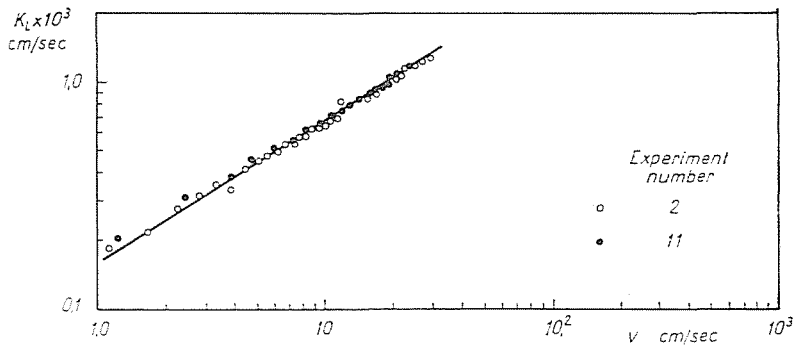


Fig. 3. Effect of equivalent diameter

The data with two different bed heights of 6 — in. and 12 — in. with 2 — in. long electrodes were plotted in Fig. 4—a as K_L vs. V and no effect on mass transfer coefficient is noted. The increase in the bed height for the same electrode length merely serves to add to the equalizing section.

Central electrodes of three different lengths (2.6 and 9 — in.) with length diameter ratios 2.6, 16 and 24 are investigated. The mass transfer coefficients are plotted against velocity in Fig. 4—b. Since the coefficients with the three

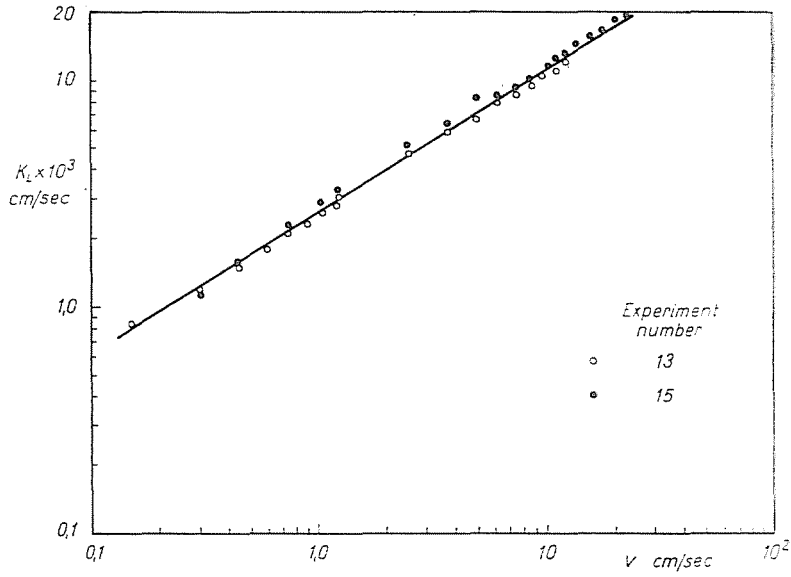


Fig. 4a. Effect of height of packing

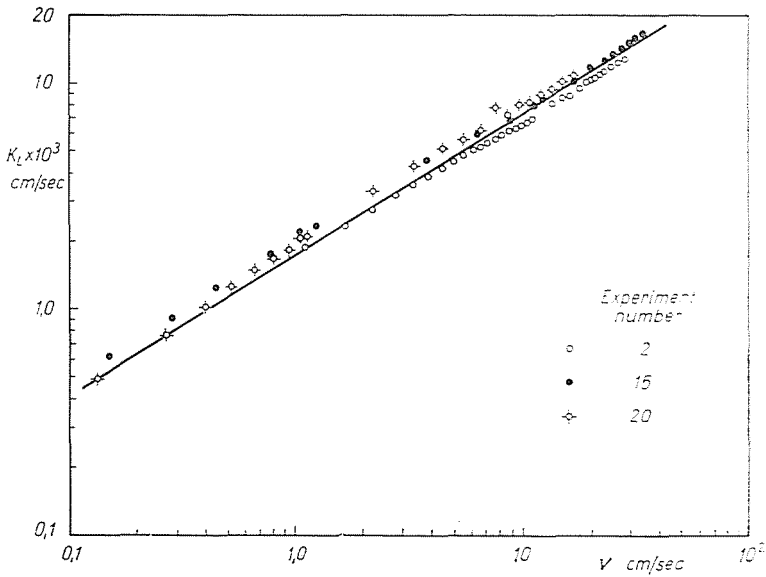


Fig. 4b. Effect of electrode length

L/D ratios of electrodes show a close agreement in the figure, it is obvious that there is no effect of length to the electrode.

In view of the close agreement of the data for the reduction of oxygen with the existing mass transfer correlations reported in an earlier paper [5] an attempt was made to correlate the data with the three systems by expressing the results in terms of J_D -factors and modified Reynolds numbers. The entire experimental data for the reduction of ferricyanide ion, oxidation of ferrocy-

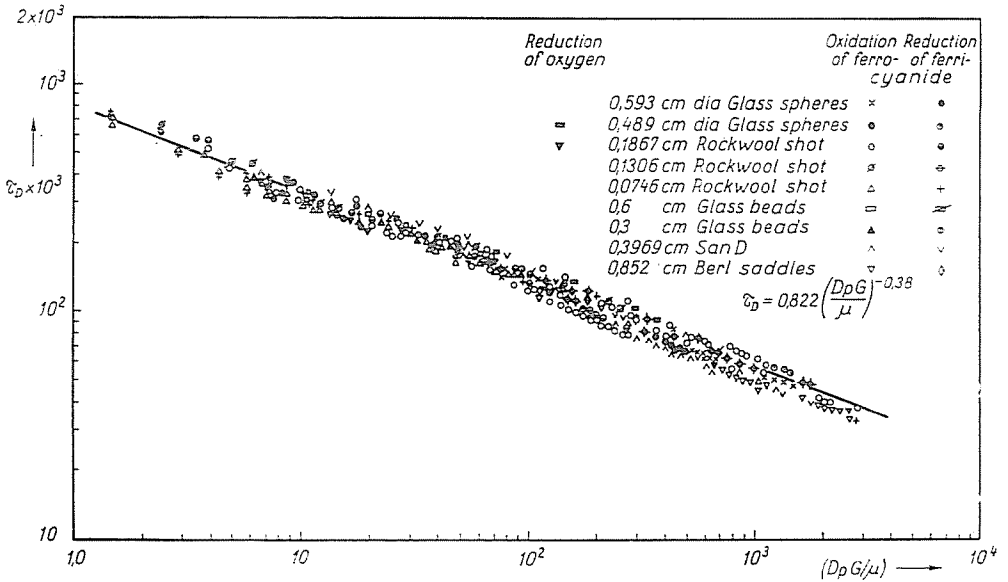


Fig. 5. Mass transfer correlation

nide ion and the reported data for the reduction of oxygen are plotted in Fig. 5 and it resulted in a single straight line with an exponent value of -0.38 on modified Reynolds numbers. Figure 5 reveals that the conventional $2/3$ power on the Schmidt group accounts for a Schmidt number variation from 256 to 1150. In the present investigation both spherical and non-spherical particles are employed the void fraction having been varied only from 0.378 to 0.573 and the figure reveals that there is no perceptible effect of the void fraction in this range. The close agreement of the data obtained with copper and nickel electrodes in the figure reveals that there is no catalytic action of these materials on these reactions. The equation of the line in Fig. 5 representing the entire experimental data within $\pm 10\%$ is given by

$$J_D = 0.822 (\text{Re})^{-0.38}. \quad (1)$$

Although the data cover a range of modified Reynolds numbers from 2800 to 1.5, no transition from turbulent to viscous region is observed in the figure. Thus this study which covers a wide range of variables substantiates the earlier report [5] on the lack of trend of transition in these systems.

Conclusions

Based on about 500 runs on three diffusion-controlled processes it is concluded that

1. As reported earlier the flow of electrolyte through packed solids can increase the rate of ionic mass transfer by about tenfold compared to that in absence of solids. The increase in the ionic mass transfer coefficients is due to the increased turbulence consequent to the presence of the particles. An increase in the particle size decreases the rate of ionic mass transfer.

2. Either the equivalent diameter of the annuli, the length of the electrode or the packing height has virtually no influence on the ionic mass transfer coefficient.

3. Copper and nickel for the oxidation of ferrocyanide ion and for the reduction of ferricyanide ion do not show any catalytic action in these reactions.

4. In the range of voidages covered the void fraction has no significant effect on mass transfer coefficient.

5. The entire experimental data for the oxidation of ferrocyanide ion, reduction of ferricyanide ion and the reported data on the reduction of oxygen have been correlated by the following equation:

$$J_D = 0.822 \left(\frac{D_P G}{\mu} \right)^{-0.38} \quad 1 < \frac{D_P G}{\mu} < 2800 \quad (1)$$

which represents the data with an average deviation of $\pm 10\%$.

6. The correlation represented by equation (1) is useful for predicting the limiting current densities and the surface concentrations, C_S , in diffusion-controlled electrode reactions in packed beds.

Nomenclature

D	diameter of the electrode, cm.
D_L	diffusion coefficient, cm. ² /sec.
D_P	particle diameter, cm.
G	superficial mass velocity, gm./cm. ² .
J_D	$(K_L/V) (\mu/\rho D_L)^{2/3}$, mass transfer factor, dimensionless.
K_L	average mass transfer coefficient, cm./sec.
L	length of the electrode, cm.
Re	$(D_P G/\mu)$, modified Reynolds numbers, dimensionless.
V	superficial velocity, cm./sec.
Z	height of the packing, cm.
μ	viscosity of the electrolyte, gms./cm. sec.
ρ	density of the electrolyte, gms./cm. ³ .

Summary

Experiments were conducted to study ion transfer rates in diffusion-controlled electrode reactions from flowing electrolytes to the surfaces of different sizes of electrodes in presence of packed non-conducting particles. Various sizes and configurations of bed materials were used.

The ionic mass transfer coefficients evaluated from limiting current densities at different flow rates for the case of reduction of ferricyanide ion, oxidation of ferrocyanide ion together with the reported data on reduction of oxygen are correlated in terms of J_D factors and modified Reynolds numbers. The data covering the range of modified Reynolds numbers from 1.5 to 2800 has not shown any transition from laminar to turbulent flow in these systems.

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