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Application of the Limiting-Current Method to Mass
Transfer in Packed Beds at Very Low Reynolds Numbers

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Abstract

The limiting-current technique is used to obtain mass-transfer
coefficients at very low Reynolds numbers $(Re < 0.1)$ in a packed
bed consisting of stainless steel spheres. The data show that for
$Re < 0.015$ the Nusselt numbers are below those predicted by existing
empirical correlations. The results are discussed in the light of
some mathematical models for packed beds reported in the literature.

Introduction

A large number of processes have been (or are still being)
developed which require a liquid flowing at low velocities through
a porous electrode or a packed bed.

Processes using flow-through porous electrodes are, for example,
electro-organic synthesis,[6] removal of metal ions from waste streams,[2,20]
and desalination of seawater.[9] A variation of the porous electrode
is the fluidized electrode,[5,13] where the electrode consists of
spheres. This type of electrode may find applications in the removal
of metal ions from waste streams containing particles which might
otherwise plug up the porous electrode.[31]

Low velocities in packed beds are required for ion-exchange
processes, catalytic processes, adsorption, and chromatography.

Empirical studies

Under certain conditions the reaction rate in a porous electrode
may become limited by the mass-transfer rate of the reactant in the
solution to the electrode surface. In that case we have the same
situation as in a packed bed. An exception is the ion-exchange
process, where migration may be important even if there is no current
flowing,[30] or where resistance to mass transfer inside the particles
may contribute to the mass-transfer coefficient.[15] In any case,
availability of reliable mass-transfer coefficients at very low
Reynolds numbers is essential in the design of porous electrodes and
packed beds. A large number of experimentally obtained mass-transfer
correlations can be found in the literature. They have been summarized

by Karabelas et al.[10]

Unfortunately, only a few researchers have extended their experiments to the region of Re' less than 0.1. Of these, Wilson and Geankoplis[33] used the dissolution of benzoic acid spheres in water and a mixture of water and propylene glycol. They propose the following correlation to represent their data:

$$\epsilon Nu' = 1.09(Pe')^{1/3} , \qquad (1)$$

but their experimental points scatter considerably for values of the Reynolds number less than 0.1. The same can be said about the results of Kunii and Smith.[11]

It is well known that in the limit of very low Reynolds numbers and in the absence of natural convection, the Nusselt number is only dependent on the Péclet number and the geometry of the flow system. Hence eq. 1 suggests that natural convection has not been important in the experiments of Wilson and Geankoplis.[33] The region where natural convection becomes dominant depends of course on the Grashof number and the Reynolds number of the system.

Karabelas et al.[10] used the limiting-current technique (reduction of ferricyanide in the presence of excess sodium hydroxide) to investigate mass transfer in packed beds over a large range of Reynolds numbers (0.1 < Re' < 1000) , including the effect of natural convection. Their electrodes, however, consisted of a single active sphere placed at different locations in the bed. There are two objections to this technique, especially if used in the low range

of Reynolds numbers investigated here. The first is that the diffusion

layer around a sphere is increasingly influenced by those of

neighboring spheres as the Reynolds number is decreased. Secondly,

if natural convection occurs, the distortion of the velocity profile

near a sphere would also be influenced by natural convection effects

on neighboring spheres. Also, channeling may occur.

Since the technique used by these authors is very similar to

the one used here, we are interested to see under what conditions

natural convection becomes important. They obtained the dependence

of the Nusselt number on the Reynolds number in the lowest range by

extrapolating to the value obtained for no flow at all. The solution

of the diffusion equation in the absence of convection for steady

mass transfer to a particle gives a constant value for the Nusselt

number; the value depends on the particle geometry. For a sphere

diameter of 1/2 in., they find that $Nu' \simeq 1.5$ in the bed with no

flow. Since $Nu' = 2$ for a sphere in an infinite, stagnant medium

(without adjacent surfaces), this indicates that natural convection

in this system is not important if spheres with a diameter smaller

than 1/2 in. are used.

For $Re' < 10$ and in the absence of natural convection they

propose:

$$Nu' = 4.58(Pe')^{1/3} , \qquad\qquad (2)$$

which has the same dependence on the Péclet number as equation 1, but

gives values of the Nusselt number which are about 10 percent higher

for $\varepsilon = 0.26$.

Almost identical experiments have been performed by Mandelbaum and Böhm,[14] who used the same electrochemical technique but employed Raschig rings instead of spheres. Mass-transfer coefficients were obtained by averaging the measured currents of six randomly placed active rings.

Gracon[7] used stacked disks of woven metal screen in studying slow flow through porous electrodes at the limiting current. Unfortunately, he did not calculate mass-transfer coefficients for this system, probably because the concentration of the reacting species at the bed outlet was practically equal to zero. Under those circumstances, small uncertainties in the measured current will give rise to large uncertainties in the Nusselt number, as will be shown later.

Even though the limiting-current method may be more complicated to implement than the dissolution technique, especially if the whole bed is to be active, with proper choice of reacting species it is particularly suited for measurements at low Reynolds numbers for the following reasons: First, the ferrocyanide/ferricyanide redox system in excess supporting electrolyte and with low reactant concentration level gives less natural convection effects than common dissolution techniques since the excess of product near the electrode surface counteracts the depletion of the reactant near the surface.[21] Of course this is also true for the density differences between the inlet stream and the outlet stream of the bed. Second, no change in surface area occurs. This becomes particularly advantageous if long times are

needed to reach steady state in the flow system. Lastly, we can calculate the mass-transfer coefficients in three independent ways: (1) from the change in reactant concentration, (2) from the change in product concentration, and (3) from the limiting current.

Selman[22] gives an extensive review of limiting current methods, their reliability, and the systems for which they have been used.

Mathematical models

In order to be able to predict mass-transfer coefficients in packed beds from an assumed pore geometry, one first has to solve the Navier-Stokes equations with the corresponding boundary conditions. The early models of packed beds involve straight tubes and include a random orientation in the bed as well as a distribution of the tube radii.[23] Prediction of mass-transfer coefficients with this model were not attempted until recently by Sörensen and Stewart.[26] These authors solved the extended Graetz problem including axial diffusion in the range of Péclet numbers of interest here. An additional dimensionless variable for this model is the ratio of tube length to tube diameter, the wall beyond and before the active region being insulated. They contend that the form of the solution is applicable to mass transfer in packed beds at low Reynolds numbers where axial diffusion becomes important. For $Pe > 100$, they find that the Nusselt number has the same dependence on the Reynolds number as correlations 1 and 2, whereas for $Pe < 10$ the Nusselt number drops below the values predicted by these correlations.

The obvious disadvantage of the straight-tube models is that they do not take into account the converging-diverging nature of actual channels in packed beds. To overcome this shortcoming Happel[8] developed the free-surface model, which accurately predicts pressure drops in packed beds at low Reynolds numbers. Kusik and Happel[12] used a combination of the free-surface model and boundary-layer theory, valid for high Schmidt numbers and for Reynolds numbers beyond the region investigated here. In order to extend the free-surface model to predictions of mass-transfer rates at low Reynolds numbers, Pfeffer and Happel[19] solved the convective diffusion equation for this geometry; they assumed constant concentrations both on the surface of the sphere and at the free surface. This may be a first order correction to the boundary-layer model, but it is not applicable to very low Reynolds numbers since, as several authors have pointed out,[16,30] the boundary condition at the free surface represents a sink of material. This model also predicts a 1/3 exponent of the Péclet number for $Pe' > 100$, while for $Pe' < 100$ the Nusselt number gradually reaches a constant value. Nelson and Galloway[16] combined the geometry of the free-surface model and Danckwerts' surface-renewal theory to explain the low heat-transfer coefficients observed at low Reynolds numbers.[11] Though it does remove the objection mentioned above, the concept of a surface renewal frequency is not realistic in creeping flow. El-Kaissy and Homsy[4] modified the free-cell model by assuming distorted instead of spherical cells. Since they used a boundary-layer solution, their results are valid for high Reynolds numbers.

Payatakes et al.[18] solved the Navier-Stokes equations for a periodically constricted tube, but the pertinent solution of the convective diffusion equation has not been obtained yet.

Sörensen and Stewart[27] calculated the velocity field around a cubic array of spheres for creeping flow. Subsequently, they obtained the solution to the boundary-layer equation[29] and the convective-diffusion equation.[28] The latter results are also pertinent to our experimental observations.

Calculation procedure

The theory of porous electrodes has been reviewed recently by Newman and Tiedemann.[17] We confine ourselves to the situation where the cell is operated at the limiting current. Averaging procedures for the pertinent quantities are given in Dunning's thesis.[3]

At the limiting current, the concentration of the reactant at the electrode surface approaches zero. Also, in the presence of supporting electrolyte the influence of migration on the reactant may be neglected. For low Péclet numbers the axial mixing coefficient E is primarily determined by molecular diffusion:

$$E = \frac{D_R}{\tau} , \tag{3}$$

where τ is a tortuosity factor about equal to 1.4. Molecular diffusion in the axial direction does not become dominant until very low values of the Péclet number are reached.[24] With these assumptions, we define the local mass-transfer coefficient k_m :

$$v \frac{dc_R}{dx} = -k_m a c_R , \tag{4}$$

so that k_m can be calculated by integrating equation 4 over the length of the bed:

$$\frac{c_{R,0}}{c_{R,L}} = \exp \left(\frac{a k_m L}{v} \right) . \tag{5}$$

The relation between the average current density in the solution i_2 and the reactant concentration c_R is given by Faraday's law. For the reduction of ferricyanide to ferrocyanide it takes the form:

$$v \frac{dc_R}{dx} = \frac{1}{F} \frac{di_2}{dx} , \tag{6}$$

with the boundary condition:

$$i_2 = 0 \quad \text{at} \quad x = L . \tag{7}$$

This boundary condition implies that the counterelectrode (anode) is located at $x < 0$. The limiting cell current I_{lim} (which, of course, is measured experimentally) follows from integration of equation 6:

$$I_{lim} = vF(c_{R,0} - c_{R,L}) . \tag{8}$$

In evaluating the potential distribution in the solution, we can neglect the diffusion potential and use Ohm's law:

$$i_2 = -\kappa \frac{d\Phi_2}{dx} \, , \tag{9}$$

with the boundary condition:

$$\Phi_2 = 0 \quad \text{at} \quad x = 0 \, . \tag{10}$$

The potential drop in the solution across the bed $\Delta\Phi_2$ is then given by:

$$\Delta\Phi_2 = vF \frac{c_{R,0}}{\alpha\kappa} [-1 + (1 + \alpha L)e^{-\alpha L}] \, , \tag{11}$$

where

$$\alpha = ak_m/v \, . \tag{12}$$

The equations presented here (and derived by Bennion and Newman[2]) serve as a basis for the design of a porous electrode which can be used for mass-transfer studies.

Design Considerations

In choosing a porous electrode suitable for studying mass-transfer rates in packed beds, several criteria have to be met:

1. The solid matrix should be representative of common packing material in packed beds, yet should have a low resistivity between all parts of the solid matrix.

2. The electrochemical reaction rate should be fast with respect to the transfer rate of reacting species from the bulk solution to the electrode surface.

3. A long limiting current plateau should be obtained. This enables accurate evaluation of the limiting current.

4. The electrode surface should not change with time due to deposition or dissolution reactions.

5. No side reactions may occur.

For our experiments we have chosen the reduction of ferricyanide. This reaction has been used in numerous mass-transfer experiments because the reaction is fast (if the electrode surface is properly treated), it does not change the electrode surface, and it gives a long limiting current plateau before hydrogen starts to evolve. Actually, the length of the plateau will appear to decrease as the flowrate through the bed is increased, since a higher ohmic potential drop is included before the limiting current is reached. This can be seen from equation 11. The same equation also shows that the ohmic potential drop can be reduced by decreasing the ratio of the reactant concentration to the concentration of the supporting electrolyte. On the other hand, a decrease in reactant concentration will decrease the limiting current (see equation 8) and hence the accuracy of the current measurement. Similarly, the accuracy with which the reactant concentration can be determined by analytical methods will diminish. Hence there is a maximum permissible flowrate for any design, dependent upon the current density and ohmic potential drop in the solution, the height of the bed, and the distance between cathode and anode.

If hydrogen starts to evolve, it will occur first at the front of the electrode since the potential difference between electrode and

solution is largest at the front. (See equation 11.) It is also possible that oxygen will be produced at the anode. Whether hydrogen or oxygen is produced first depends upon the pH of the solution. Consequently, our desire to obtain a limiting current, and hence a large potential difference between cathode and solution everywhere in the bed must be balanced against our wish to avoid hydrogen evolution or any other side reaction.

The reliability of the data is strongly dependent upon the ratio of the inlet to the outlet concentrations. This ratio may be neither too small nor too large. In either case, small inaccuracies in determining the concentrations or the limiting current will have a large effect on the mass-transfer coefficient calculated from equation 5. Moreover, if this ratio is close to unity, equation 8 shows that the limiting current becomes too small to be measured accurately at all. These considerations set a lower as well as a higher limit on the allowable flowrates through the bed.

Mass-transfer coefficients calculated from equation 5 do not reflect the influence of axial dispersion upon the overall bed behavior. It is possible, however, to include this influence in the calculations of the mass-transfer coefficients.[32] We have not done so in view of equation 3 and the findings of Wilson and Geankoplis[33] that in the range of Péclet numbers investigated here no axial mixing effects could be detected. An alternative, and perhaps more valid, interpretation is that equation 5 defines an average overall mass-transfer coefficient describing the actual behavior of a packed bed at limiting current.

Experimental

Details of the experimental apparatus and procedure can be found in Appel's thesis[1] and will not be given here.

The electrochemical cell used for the determination of mass-transfer coefficients in packed beds was a modified version of the cells used by Bennion and Newman[2] and by Yip.[34] These modifications were made to reduce entrance and exit effects. The bed diameter was 8.8 cm, and the packing consisted of 5/32 in. stainless steel spheres. To avoid channeling, the spheres were packed such that a rhombohedral or hexagonal close packing was obtained. The anode was placed above the cathode, with the feed inlet placed in between. Part of the feed stream flowed through the cathode, part through the anode; the flowrate through the anode was always about 20 percent higher than the flowrate through the cathode. In addition, the anode consisted of four layers of spheres, and the cathode consisted of three layers, so that a limiting current was insured at the cathode. The cathode contained 1259 ± 1 spheres and had a porosity of 0.372, a specific interfacial area of 9.50 cm^{-1}, and a thickness of 1.06 cm.

The electrolyte was an equimolar solution (0.01 $\underline{M}$) of ferrocyanide and ferricyanide with potassium nitrate (0.950 ± 0.005 $\underline{M}$) as supporting electrolyte. This solution was supplied from a constant-head tank; feed and outlet streams were interrupted to avoid stray currents. The temperature of the system was kept at $25\pm0.05°C$.

The limiting-current curves were obtained by increasing the potential of the working electrode stepwise with respect to the

reference electrode, starting at the equilibrium potential. At each increment, the current was measured after steady state had been reached.

For each run, samples of the inlet and outlet streams were taken; subsequently the composition, the density, the viscosity, and the conductivity were determined. The measurements of the last three quantities can be summarized by three numbers: 1.058 ± 0.001 g/cm^3 for the density, 0.868 ± 0.007 cp for the viscosity, and 0.0884 ± 0.0003 mho/cm for the conductivity. The effective conductivity κ within the pores can then be estimated to be 0.02 mho/cm.

The accuracy of the current measurements was 0.5 mA; the concentrations of the ferrocyanide and the ferricyanide (determined by titration) are estimated to be accurate within 5×10^{-8} mole/cc. Measured values are given in Table I.

Diffusivities were not measured, but were calculated from Smyrl's data:[25]

$$\frac{\mu D_{ferri}}{T} = 0.168 \times 10^{-9} \; \frac{cm^2}{sec} \frac{poise}{°K} \; . \qquad (13)$$

Results

In Figure 1 the current is plotted as a function of $U - U_{equil}$ for different Reynolds numbers. At low flowrates a long limiting-current plateau is obtained, which becomes shorter as the flowrate is increased. As discussed before, this effect can be attributed to the increasing contribution of the ohmic potential drop at increasing

Table I. Measure variables in the packed bed experiments.
The pH of the solution was 5.9, and the particle
diameter was 0.397 cm.

Concentrations, 10^{-6} mole/cm^3

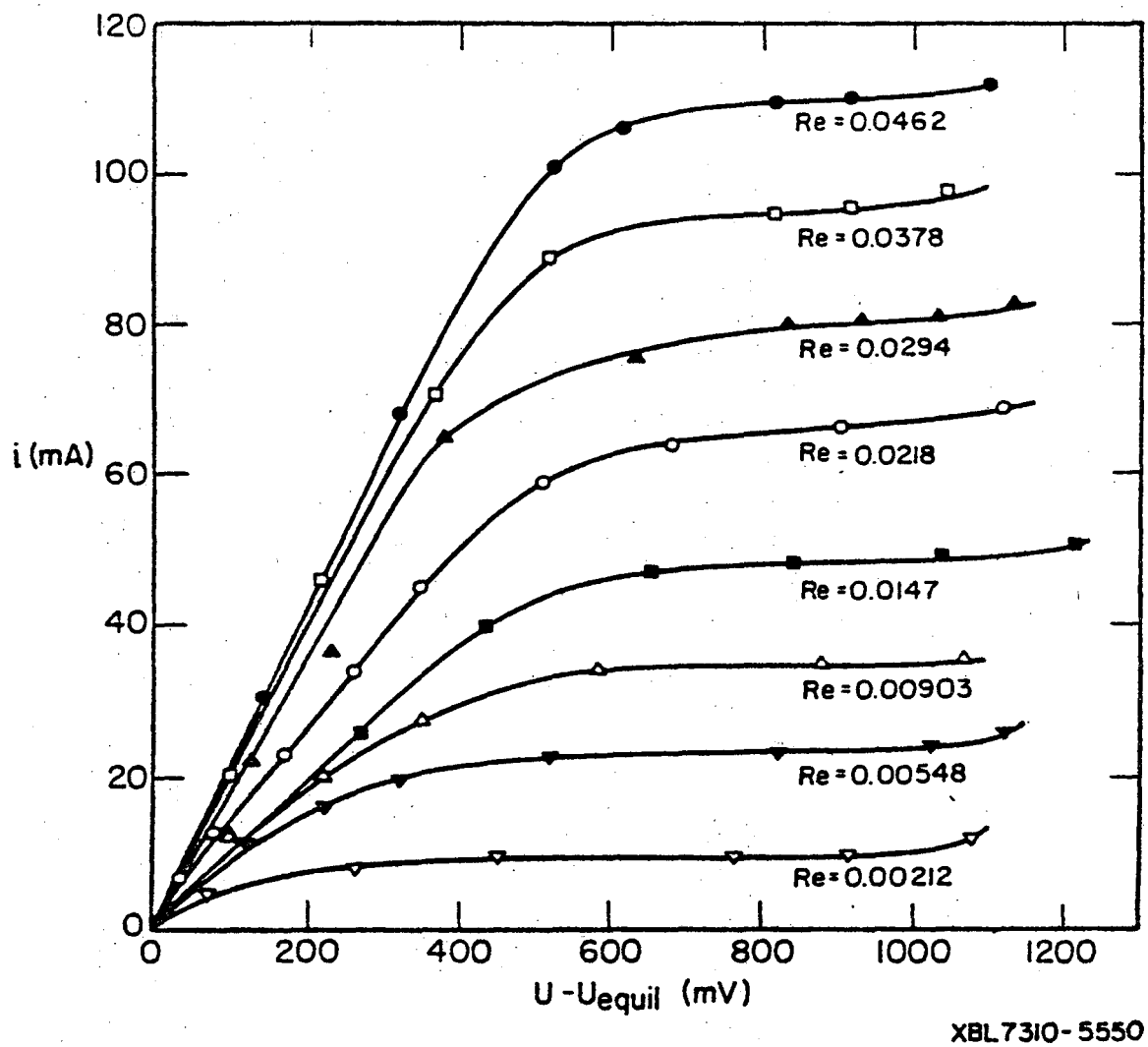| Run #	Ferricyanide		Ferrocyanide		i_{lim} mA	Flow-rate cc/sec
	Inlet	Outlet	Inlet	Outlet		
8	9.92	3.34	9.50	16.18	66.9	0.104
10	9.78	1.60	9.54	17.82	34.4	0.0432
11	9.48	2.43	9.42	16.69	47.9	0.0700
12	9.59	3.71	9.48	15.31	80.3	0.143
13	9.98	1.04	9.17	18.22	23.5	0.0265
15	10.06	4.19	10.11	15.81	80.0	0.142
16	10.06	4.69	10.11	15.44	94.6	0.183
17	10.06	4.98	10.11	15.25	110.1	0.224
19	9.97	0.53	9.98	19.47	9.54	0.0103

Figure 1. Limiting-current curves.

flowrates and indicates an upper limit for the allowable flowrates. At very high voltages, the slope of the curve increases. This indicates that a side reaction has occurred, probably the evolution of hydrogen. No bubbles have been detected in the cathode, however. The values of $\Delta\Phi_2$ calculated from equation 11 range from 2 to 42 mV.

The mass-transfer coefficients were calculated from equation 5. The inlet concentration of the ferricyanide ion was obtained analytically; the exit concentration of the ferricyanide ion was obtained in three different ways:

1. Analytically.

2. By subtracting the difference between inlet and outlet concentrations of the ferrocyanide ion (also determined analytically) from the inlet concentration of the ferricyanide ion.

3. Same as 2, but the difference between the ferricyanide concentrations was obtained from the limiting-current value, according to equation 8. If, for any run, the mass-transfer coefficient calculated by any of these methods deviated more than 10 percent from the mean, that run was discarded. Calculated quantities are shown in Table II, where k_m is the mean of the three determinations.

Application of the Graetz analysis through the concept of straight cylindrical pores in the bed suggests that the appropriate Nusselt number to use is:

$$Nu = \frac{\varepsilon k_m}{a D_R} \, . \qquad\qquad (14)$$

Table II. Calculated variables in the packed bed experiments.

Run #	$D_{ferri} \times 10^5$ cm/sec	$k_m \times 10^5$ cm/sec	Nu	Re	Pe
8	0.584	18.4	1.24	0.0218	30.4
10	0.583	12.8	0.860	0.0090	12.6
11	0.583	15.7	1.05	0.0147	20.5
12	0.572	21.5	1.47	0.0294	42.6
13	0.574	10.0	0.69	0.0055	7.88
15	0.576	19.6	1.34	0.0294	42.0
16	0.575	22.3	1.52	0.0378	54.2
17	0.574	25.5	1.74	0.0462	66.5
19	0.575	5.1	0.35	0.00212	3.05

Similarly, the Péclet number is defined as:

$$Pe = \frac{v}{aD_R} \, .$$
(15)

The Nusselt number has been plotted as a function of the Péclet number in Figure 2. It shows that our experimental values start to deviate from correlation 1 below Pe = 100 . For comparison, we have plotted the Graetz solution of Sörensen et al.[26] for a ratio of tube length to tube radius of one. This is an appropriate value for packed beds, and, although our values are also below their predicted values, they also show a deviation from the 1/3 exponent of the Péclet number as the Péclet number is decreased. A similar trend is predicted by the regularly packed sphere model of the same authors.[28]

In the light of these findings and because of the mentioned need for accurate mass-transfer correlations in packed beds at very low flowrates, further investigations in this area (including natural convection effects and the effect of varying the bed thickness) would be very valuable.

Conclusions

It has been shown that the limiting-current method is suitable for obtaining mass-transfer coefficients in packed beds, in particular at very low Reynolds numbers, provided proper design and experimental procedures are followed.
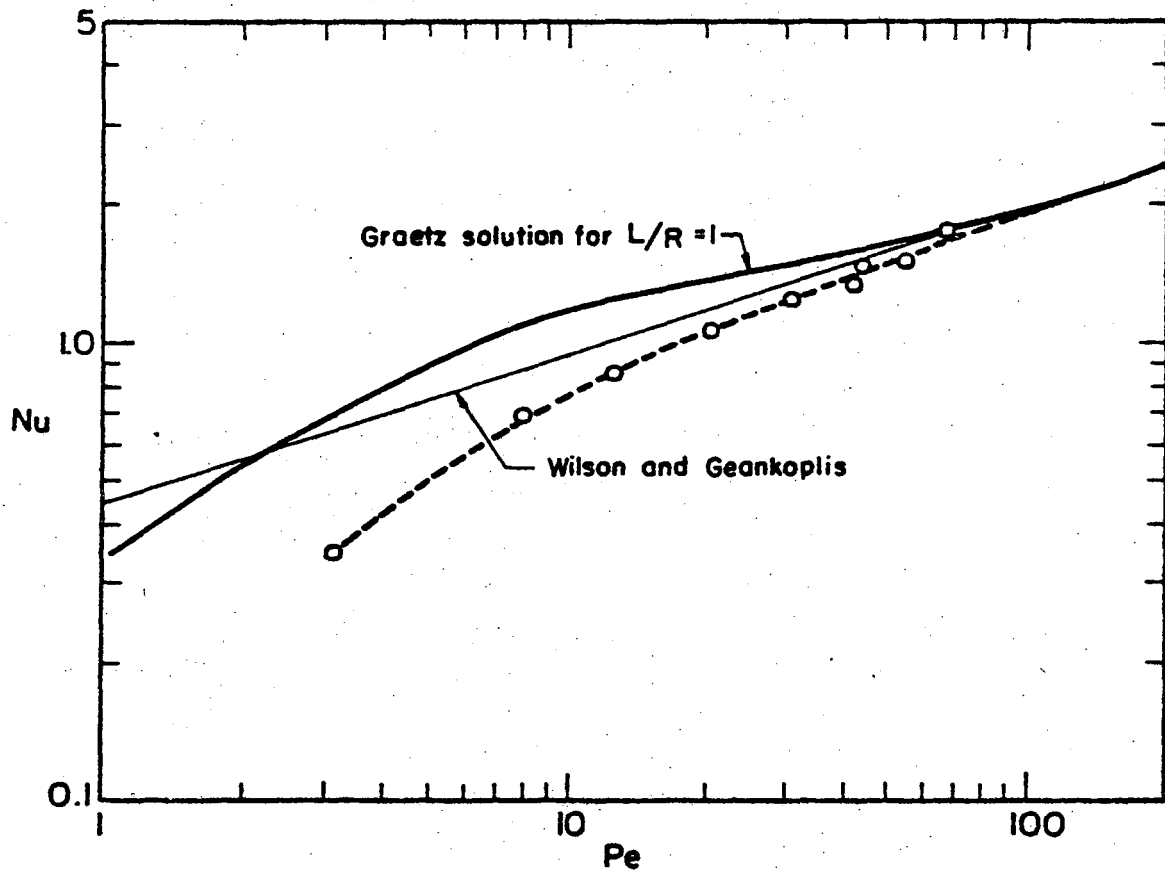
Figure 2. Nusselt number as a function of Péclet number
for packed beds.

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Also, previous empirical correlations are found to break down at low values of the Péclet number. Our experimental results are in line with recent theoretical predictions.

Acknowledgement

Notation

a specific interfacial area, cm^{-1}

$c_{R,0}$ feed concentration, $mole/cm^3$

$c_{R,L}$ exit concentration, $mole/cm^3$

c_R reactant concentration per unit volume of solution, $mole/cm^3$

d_p sphere diameter, cm

D_R diffusion coefficient of reactant in feed solution, cm^2/sec

E axial mixing coefficient, cm^2/sec

F Faraday's constant, 96487 C/equiv.

i_2 superficial current density in pore phase, A/cm^2

I_{lim} limiting cell current density, A/cm^2

k_m coefficient of mass transfer between flowing solution and electrode surface, cm/sec

L thickness of bed, cm

$Nu = \epsilon k_m/aD_R$, modified Nusselt number

$Nu' = k_m d_p/D_R$, Nusselt number

$Pe = ReSc$, modified Péclet number

$Pe' = Re'Sc$, Péclet number

R equivalent tube radius, cm

$Re = v/a\nu$, modified Reynolds number

$Re' = vd_p/\nu$, Reynolds number

$Sc = \nu/D_R$, Schmidt number

T   absolute temperature, deg K

U   cathode potential, V

v   superficial fluid velocity, cm/sec

x   distance from bed entrance, cm

$\alpha = ak_m/v$, cm^{-1}

ε porosity

κ conductivity of solution within the electrode, mho/cm

μ dynamic viscosity of solution, g/cm-sec

ν kinematic viscosity of solution, cm^2/sec

τ tortuosity factor

Φ_2 electric potential in the solution, V

$\Delta\Phi_2$ electric potential difference in the solution between bed

        inlet and bed outlet

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