Mass Transfer in a Packed, Pulsed Column

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Equations in terms of a pulse Reynolds number and dimensionless pulse velocity are presented for mass transfer coefficients in pulsed flow in a packed bed. Mass transfer from the wall and from the particles is considered. The development, applicable up to a particle Reynolds number of 40, is based upon a previous study of pulsed laminar flow in an empty tube.

The experimental measurements consisted of rates of dissolution of β-naphthol from the wall and from the particles within the bed. From these data time-average mass transfer coefficients $\overline{k_p}$ were computed. The improvement in $\overline{k_p}$ increased with frequency and decreased with average flow rate, although the increase was always less than in an empty tube at equivalent conditions.

Steady flow measurements indicated that the coefficient for mass transfer from the tube wall was influenced by the degree of settling of the bed. This effect could be related to the change in porosity accompanying the settling process. A new empirical correlation is proposed to account for the effect of porosity changes.

It has been demonstrated (*3, 8, 9*) that pulsation of the liquid stream improves mass transfer rates between fluid and solid phases. In order to interpret the effects of pulsation quantitatively the simple arrangement of laminar flow in a circular tube has been used recently (*4*) for an experimental and theoretical study of mass transfer coefficients at the tube wall. The results of that work indicate that the effect of pulsation is a function of pulse Reynolds number α and a dimensionless pulse velocity Φ. The objective of the present study is to describe the effects of pulsation on mass transfer from the tube wall of a packed bed and from particles to fluid within the bed. For this purpose the concept of a pulse Reynolds number and pulse velocity will also be used.

In a packed column the additional variable of porosity is introduced. This parameter depends in a complicated and unpredictable way upon the ratio of the diameter of the particles and the tube, the radial position, and the arrangement of the particles. This latter factor can be varied by tapping the packed unit, and it was found that the mass transfer coefficient, from the tube wall, was particularly sensitive to this kind of porosity change.

Previous work (*11*) on mass transfer from the wall, in steady flow, was not concerned with this problem. Hence a secondary objective, necessary before the pulse effect on mass transfer from the wall of a packed bed could be examined, was to develop for steady flow mass transfer an empirical correlation including the influence of porosity.

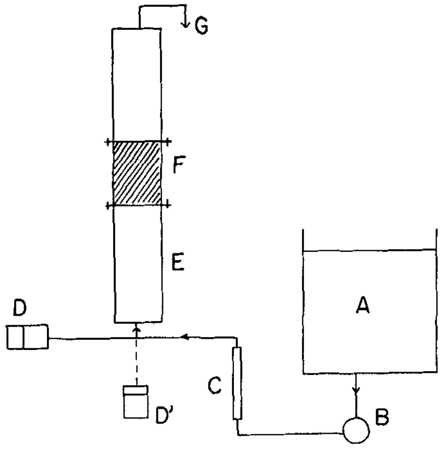

Fig. 1. Apparatus for pulsed flow in packed bed.

EXPERIMENTAL WORK

A schematic diagram of the apparatus, Figure 1, shows the flow system. Water from the storage tank *A* flowed through centrifugal pump *B* to the bottom of the straight stainless steel tube *E*. Different columns were employed in the two phases of the work. In mass transfer from the wall the column was ¾-in. I.D. and the length of the test section 12.5 cm.; for mass transfer within the bed the column inside diameter was 4.76 cm. and three lengths were employed 4.67, 7.46, and 12.5 cm. Two pulsators, of different amplitude range, were used for the studies within the bed. Only one, a piston pump, was employed for mass transfer from the wall. This pump (*D*) had a horizontal plunger, while the other (*D*) was vertical. Both pumps were attached to the bottom of the stainless steel tube with smooth, equal diameter connections. The amplitude of the pulse in the packed bed was calculated from the stroke of the pump and the ratio of the diameters of the pump plunger and the packed tube. The vertical pulsator was based on an eccentric design, while the horizontal one operated on a ratchet type of mechanism.

The test section for the wall measurements consisted of a hollow tube of β-naphthol packed with inert lead spheres and clamped to the stainless steel tube with flanges. The flanges and gaskets were designed to eliminate, as far as possible, an uneven interface between the naphthol cylinder and stainless steel tubing. Not more than five runs were made with each cylinder, which limited the change in dissolving area to less than 1%.

For mass transfer within the bed β-naphthol particles (Table 1) were used in a stainless steel tube. The particles were used

TABLE 1. PARTICLE SIZES AND SHAPES

Shape	Equivalent diameter (diameter of sphere of equal volume), cm.
Cylindrical diameter = 0.717 cm. height = 0.743 cm.	0.572
Dished head cylindrical diameter = 0.960 cm. total height = 0.378 cm.	0.720
Dished head, cylindrical diameter = 1.036 cm. total height = 0.392 cm.	0.761
Dished head, cylindrical diameter = 0.800 cm. total height = 0.359 cm.	0.642
Spherical diameter = 0.635 cm.	0.635

for six runs and then discarded. The variation in area for each set of runs was less than 2%. To hold the particles in the test section 40-mesh stainless steel screens were inserted at both ends. The bed was prepared by slowly adding particles with simultaneous tapping of the test section. To investigate the effect of settling of the bed (porosity) the time for filling the section, and hence the amount of tapping, was varied. The porosity was determined from the known volume of the test section and its weight before and after addition of particles.

Leva and Grummer (5) noted that particles in a bed settle for some initial period because of vibration in the equipment. This same phenomenon was observed in this study for mass transfer from the wall; that is for approximately 30 min. the mass transfer coefficient increased with time after initiating the flow through the bed. Presumably the increase in transfer coefficient is due to a rearrangement of particles and accompanying decrease in void fraction. Constant results were achieved after about ½ hr. Hence in obtaining the final data samples were taken for analysis after at least ½ hr. of operating time. This effect was not noted for mass transfer from the particles.

Under these operating conditions the reproducibility of the data was better than 10%.

The β-naphthol particles employed for particle-fluid mass transfer, except for the 0.635-cm. spheres, were pelletted in a press employing different average pressures (2 to 6 atm.) for each pellet. This produced variations in the densities of particles. The volume and area of the particles were calculated from the dimensions given in Table 1 and checked by water displacement of groups of approximately fifty pellets. No variation in density was found for different particles of the same size. The 0.635-cm. spheres were made by pouring molten β-naphthol in a special die (*10*) accurately drilled to produce hemispherical cavities in two brass plates.

The liquid samples were analyzed, soon after withdrawal from the apparatus, in a spectrophotometer. The absorbance was measured in the ultraviolet range (285 μ) and compared with a calibration curve prepared from samples of known concentration.

The flow rate was controlled with a rotameter (C) and measured with a graduated cylinder over relatively long time intervals.

SCOPE OF DATA

Data were obtained for the most part at flow conditions commonly called laminar, that is at particle Reynolds number less than 40. The range of variables studied is shown in Table 2.

MASS TRANSFER RESULTS BETWEEN FLUID AND TUBE WALL

The runs were always initiated with naphthol-free water in the tank A. Hence an average mass transfer coefficient k could be computed from the measured volumetric flow rate V, exit concentration C_1, and area S, from

$$V(C_1 - 0) = k\, S(\Delta C)_{lm}$$

TABLE 2. SCOPE OF DATA

	Mass transfer conditions	
	Wall-to-fluid	Particle to fluid
Particle Reynolds number		
steady flow	1 to 65	4.5 to 20
pulsed flow	1 to 18	4.5 to 20
Particle diameter, cm.	0.13 to 0.45 spheres	Pellets, cylinder and sphere (Table 1)
Pulse amplitude (based upon empty tube), cm.	3.04 to 5.77	0.488 to 3.73
Pulse frequency, min.$^{-1}$	0 to 48	0 to 48
Pressure, atm.	1.0	1.0
Temperature, °C.	25 deg.	27 to 35 deg.
Porosity	0.40 to 0.45	0.35 to 0.47

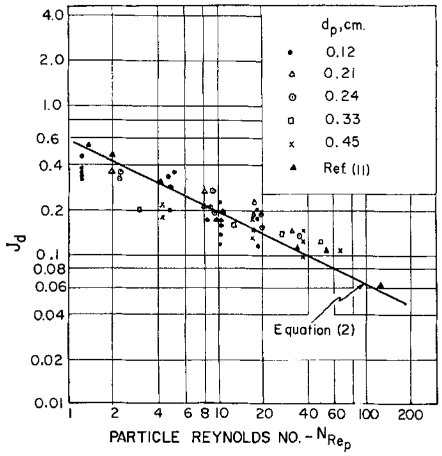

Fig. 2. Yagi and Wakao correlation (*11*) for steady flow.

or

$$k = \frac{V}{S} \ln \frac{C_s}{C_s - C_1} \tag{1}$$

The concentration at the wall was assumed to be the saturated value C_s. This result, which is 5.34×10^{-3} g. moles/liter at 25°C. (7) was corrected in accordance with the temperature of the run. In steady flow measurements in a packed bed Yagi and Wakao (*11*) found that the entrance region had little effect on the average k when the length to diameter ratio in the tube was greater than 4. Hence the results calculated from the present experiments, where the ratio was 6.6, should be close to the asymptotic value of the transfer coefficient. Applied to steady flow data Equation (1) gave values of k_o; for pulsed flow average values $\overline{k_p}$, with respect to time over the period of the pulse, were obtained from the same expression.

Illustrations of the pulsed flow data* are given in Figures 5 and 6, where the effects of frequency n, amplitude A, particle size, and flow rate are shown. It is seen that pulsation causes an increase of mass transfer coefficient of up to tenfold at high frequencies and small flow rates. The published value (6) for the diffusivity of β-naphthol in water at 25°C. gives a Schmidt number of 771. This value was used in the equations and correlations that are presented later.

Analysis of Steady Flow Results

Yagi and Wakao presented the following equation for mass transfer coefficients at the wall in a packed bed at steady flow at $N_{Re_p} < 40$:

$$J_D = \frac{k_o}{\overline{\overline{u}}} (N_{Sc})^{2/3} = 0.60\ (N_{Re_p})^{-1/2} \tag{2}$$

Deviations of 50% were found between the equation and the authors' data at the same N_{Re_p} (as shown in Figure 2), presumably due in part to variations in porosities from run to run.

To investigate this effect further approximately sixty runs were made, at several flow rates, in which the porosity was intentionally varied by tapping the test section various amounts during the filling process. Figure 3 illustrates the results obtained for different particle sizes at the same flow rate. It is apparent that large variations can occur in k_o for the same particle size, depending upon the value of the porosity.

To introduce the effect of porosity in the correlation of steady flow data the characteristic length was chosen as

* Complete data are on file in the College of Engineering, University of California, Davis, California.

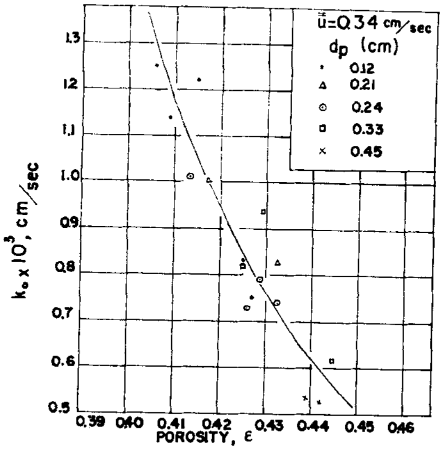

Fig. 3. Effect of porosity on mass transfer coefficients in steady flow.

$d_p \dfrac{\epsilon_w^3}{(1-\epsilon_w)^2}$ rather than d_p. This parameter was obtained by comparing the expressions for the friction factor in packed beds (*2*) and in an empty tube:

$$f_p = \frac{75}{\dfrac{\bar{\bar{u}}\rho d_p}{\mu}\dfrac{\epsilon^3}{(1-\epsilon)^2}} \quad \text{(packed bed)} \tag{3}$$

$$f = \frac{16}{(u\rho\, D_c)/\mu} \quad \text{(empty tube)} \tag{4}$$

As mass transfer at the wall is involved, the wall porosity ϵ_w was used rather than the average porosity ϵ. Since only average void fractions were measured, it was necessary to obtain a relationship between ϵ_w and ϵ. For this purpose ϵ_w was considered to be the mean porosity in the region of $d_p/2$ from the tube wall. The measurements of Benanati and Brosilow (*1*) on ϵ vs. radial distance were used to relate ϵ and ϵ_w.

The experimental data were correlated by the least-mean-square technique, fixing the coefficient of the Schmidt number at 1/3. The resulting equation is

$$\frac{k_o\, d_p}{D}\frac{\epsilon_w^3}{(1-\epsilon_w)^2} = 0.40\left[N_{Rep}\frac{\epsilon_w^3}{(1-\epsilon_w)^2}\right]^{0.65}(N_{Sc})^{1/3}$$

or

$$Sh_p = \frac{k_o\, d_p}{D} - 0.40\,(N_{Rep})^{0.65}\left[\frac{(1-\epsilon_w)^2}{\epsilon_w^3}\right]^{0.35}(N_{Sc})^{1/3} \tag{5}$$

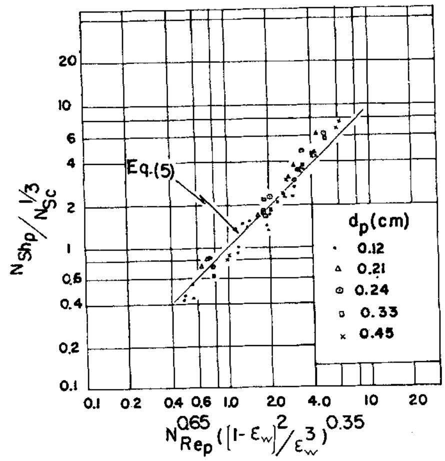

Fig. 4. Correlation of steady flow mass transfer coefficients.

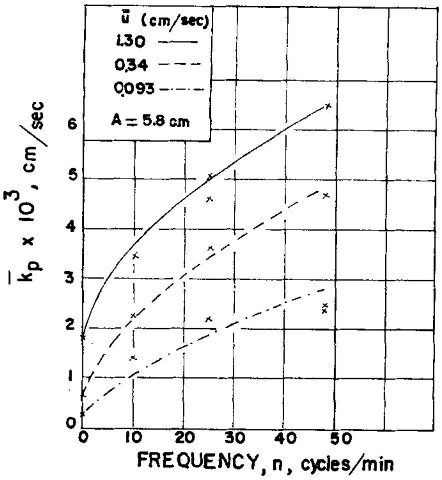

Fig. 5. Effect of frequency on mass transfer coefficients (d_p = 0.45 cm.).

The characteristic length occurs in the mass transfer correlation in both Sherwood and Reynolds numbers. Hence the porosity effect must be included in both, leading to the net result given by Equation (5). This tentative correlation for spherical particles satisfactorily interprets the effect of porosity, as shown in Figure 4. Also comparison of Figures 2 and 4 reinforces the conclusion that some of the deviations in Figure 2 are due to variations in porosity. Equation (5) is used in the next section as a basis for determining the effect of pulsation.

Analysis of Pulsed Flow Results

The data shown in Figures 5 and 6, when compared with Figures 3 and 4 of reference *4*, indicate that the fractional increase in mass transfer coefficient due to pulsation is less in a packed bed than in an empty tube at a given amplitude, frequency, and steady velocity $\bar{\bar{u}}$. Furthermore the results demonstrate that $(\bar{k}_p - k_o)/k_o$ decrease as $\bar{\bar{u}}$ increases (Figure 5) and increases as d_p increases (Figure 5 and 6). This becomes evident when it is noted that $k_o = \bar{k}_p$ at zero frequency.

The complexity of the steady flow in a packed bed and the uncertainty about the reflection of pressure waves in a porous media make difficult an analytical and fundamental analysis of the effect of pulsation. Because of this it is helpful to use as much as possible the analytical results of the empty pipe study (*4*). There the effect of pulsation was found to depend upon a dimensionless pulse velocity Φ and pulse Reynolds number α. For packed bed condi-

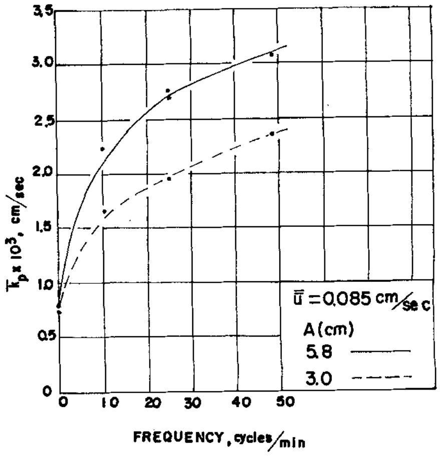

Fig. 6. Effect of amplitude and frequency on mass transfer coefficients (d_p = 0.13 cm.).

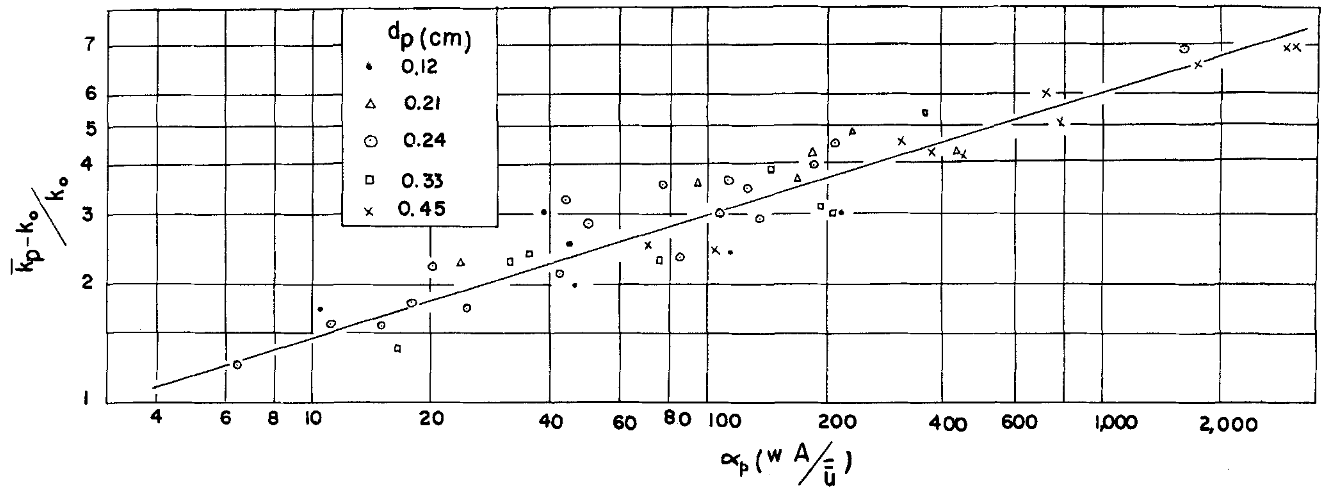

Fig. 7. Increase in mass transfer coefficients due to pulsation.

tions (noted by subscript p) these parameters will be defined:

$$\Phi_p = \frac{wA}{\bar{\bar{u}}} \tag{6}$$

$$\alpha_p = d_p \frac{\epsilon_w^3}{(1-\epsilon_w)^2} \left(\frac{w\rho}{\mu} \right)^{1/2} \tag{7}$$

For an empty tube the definition of Φ is also given by Equation (6). The ratio of amplitude to the time-average velocity is the same in a packed bed as in an empty tube, if there is no absorption of the wave. This condition is closely approached for a nearly incompressible fluid such as water. Hence Φ_p for the bed is equal to Φ for the empty pipe, defined in Equation (6).

Equation (7) differs from the expression for α for an empty tube (4) by replacing the tube radius with d_p $(\epsilon_w^3)/(1-\epsilon_w)^2$. This substitution is based upon the same reasoning as used in developing the expression for the characteristic length in the preceding section on steady flow mass transfer.

The mass transfer coefficient data were correlated in terms of these two groups. The results indicate that the fractional increase in coefficient due to pulsation can be represented by the expression

$$\frac{\bar{k}_p - k_o}{k_o} = 0.75 \, (\Phi_p \, \alpha_p)^{0.30} \tag{8}$$

This least-mean-square fit to all of the pulsed data [Equation (8)] is shown as a solid line in Figure 7. The average deviation is 13%, which is about within the accuracy of the experimental data.

MASS TRANSFER RESULTS BETWEEN PARTICLE AND FLUID

The mass transfer coefficients for this case were also calculated from Equation (1), with S as the total surface of the particles in the bed.

To test the experimental procedure runs were first made for steady flow and the results compared with published data (*7, 10*). The experimental data were about 6.7% (average deviation) lower than the correlation reported by Williamson et al. (*14*). Since this latter correlation is based largely on data for spheres, the agreement was considered satisfactory.

Attempts were made to vary the porosity by tapping, but this was possible only for the cylindrical pellet. This could be due to the small values of D_c/d_p and to particle shape; a similar effect was observed for the wall to fluid experiments. The larger lead spheres showed a narrower range of porosities than the smaller ones.

Each set of pulsed runs was accompanied by steady flow runs performed at the same N_{Re_p} (based on the average steady velocity $\bar{\bar{u}}$). This procedure gave an accurate value of $\frac{\bar{k}_p - k_o}{k_o}$, without reference to any steady state correlation of data for different particle shapes.

The variation of the mass transfer coefficient with pulse characteristics was similar to that for the wall-to-fluid case; for example the shape of the curves $\bar{k}_p$ vs. n was similar to those of Figure 5 and 6. However the fractional increase in mass transfer was less. The variation of $\bar{k}_p$ with amplitude, at constant frequency, is illustrated in Figure 8, where data for both pulsators are shown.

Analysis of Pulsed Flow Results

As the general characteristics of particle-to-fluid results were similar to those for mass transfer from the wall, the effects of frequency and amplitude were correlated in terms of the same parameters, a pulse velocity and Reynolds number. However the average porosity ϵ was employed instead of the wall value, so that the pulse Reynolds number is

$$\alpha_p{}^1 = d_p \frac{\epsilon^3}{(1-\epsilon)^2} \left(\frac{w\rho}{\mu} \right)^{1/2} \tag{9}$$

For the cylindrical and dished shaped pellets d_p was taken as the diameter of the sphere with the same volume as the particle. The data are plotted in Figure 9 as the fractional increase in mass transfer coefficient vs. $\Phi_p \, \alpha_p{}^1$.

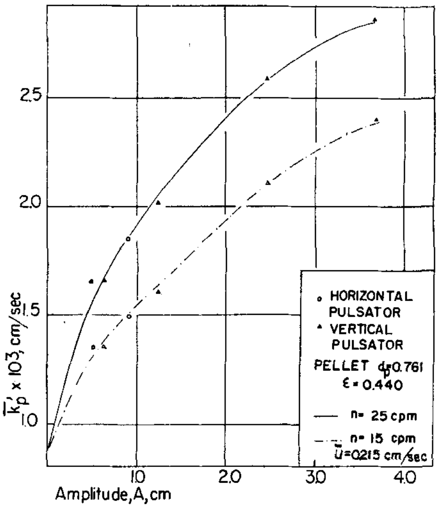

Fig. 8. Effect of amplitude on particle mass transfer coefficients.

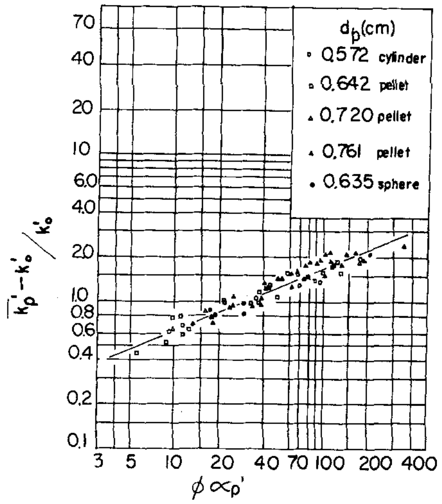

Fig. 9. Increase in particle mass transfer coefficients due to pulsation.

The solid line, from which the data deviate by an average of 10%, can be represented by the equation

$$\frac{\overline{k}_p{}^1 - k_o{}^1}{k_o{}^1} = 0.24\ (\alpha_p{}^1\ \Phi_p)^{0.42} \qquad (10)$$

If the porosity function was not included in the definition of $\alpha_p{}^1$, the data plotted as in Figure 9 scattered significantly.

Steady flow mass transfer coefficients within the bed are significantly larger than those from the wall at the same conditions. This may be due to the more intense turbulence expected within the bed than near the wall. From studies in empty tubes at higher Reynolds numbers (*4*) it has been found that turbulence reduces the effect of pulsation. Hence increased turbulence may also explain the smaller effect of pulsation of $\overline{k}_p{}^1$ for particle-to-fluid mass transfer than for wall mass transfer.

CONCLUSIONS

The results indicate that the parameters which determine the effects of pulsation on mass transfer in a packed bed are of the same form as those for an empty tube. The increase in transfer coefficient due to pulsation is less for mass transfer from the particle than from the wall. Also the increase is less for both of these processes than for mass transfer from the wall of an empty tube.

The distinguishing features between mass transfer with pulsed flow in a packed bed and in an empty tube are: the smaller pore spaces, which reduces the pulse Reynolds number α_p or $\alpha_p{}^1$ in comparison with α in an empty tube, and the presence of turbulence in the wake of the particles, even at low flow rates. These two characteristics tend to reduce the effect of pulsation in a packed bed.

It has been shown also that porosity changes affect steady flow mass transfer from the wall of a packed bed.

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NOTATION

A = pulse wave amplitude, based upon empty tube, and defined as one half of the pump stroke multiplied by the square of the ratio of the diameter of the pump cylinder to the tube diameter, cm.

C = concentration of β-naphthol, g. mole/cc.; C_s = concentration of saturated solution; C_1 = concentration at the exit of the test section

D = diffusivity of β-naphthol in water, sq. cm./sec.

D_c = tube diameter, cm.

d_p = equivalent particle diameter (diameter of sphere of equal volume), cm.

f = friction factor in an empty tube: f_p refers to a packed bed

$J_d = \dfrac{k_o}{\overline{\overline{u}}} (N_{Sc})^{2/3}$

k = average mass transfer coefficient, cm./sec.; $\overline{k}_p$ = time-average value for pulsed flow; k_o = value for steady flow

V = flow rate, cc./sec.

n = pulse frequency, cycles/min.

$N_{Re_p} = \dfrac{\overline{\overline{u}}\rho\, d_p}{\mu}$

$N_{Sc} = \mu/\rho D$

$N_{Sh_p} = \dfrac{k_o\, d_p}{D}$

S = area of dissolving surface, sq. cm.

$\overline{\overline{u}}$ = average steady flow velocity (superficial), cm./sec.

w = angular velocity, $\dfrac{2\pi n}{60}$, sec.$^{-1}$

Greek Letters

α = pulse Reynolds number, empty tube, $R\left(\dfrac{w\rho}{\mu}\right)^{1/2}$

α_p = pulse Reynolds number, packed bed, $\dfrac{d_p \epsilon_w{}^3}{(1-\epsilon_w)^2}\left(\dfrac{w\rho}{\mu}\right)^{1/2}$

$\alpha_p{}^1 = \dfrac{d_p\, \epsilon^3}{(1-\epsilon)^2}\left(\dfrac{w\rho}{\mu}\right)^{1/2}$

ϵ = average volume porosity

ϵ_w = integrated porosity, from the tube wall to a distance $d_p/2$ from the wall

Φ, Φ_p = pulse velocity, $\dfrac{wA}{\overline{\overline{u}}}$

μ = fluid viscosity, g./(cm.) (sec.)

ρ = density of fluid, g./cc.

LITERATURE CITED

1. Benenati, R. F., and C .B. Brosilow, *A.I.Ch.E. Journal*, **8**, 359 (1962).
2. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1962).
3. Bretznajder, S., L. Lesniewicz, and W. Pasiuk, *Chem. Stos.*, **3**, 275 (1958).
4. Krasuk, J. H., and J. M. Smith, *Chem. Eng. Sci.*, **18**, 591 (1963).
5. Leva, M. and M. Grummer, *Chem. Eng. Progr.*, **43**, 713 (1947).
6. Moyle, M. P., and M. Tyner, *Ind. Eng. Chem.*, **45**, 1794 (1953).
7. McCune, L. K., and R. H. Wilhelm, *Ind. and Eng. Chem.*, **41**, 1124 (1949).
8. Saint James, R., and G. P. Graham, *Genie Chimique*, **86**, 1 (1961).
9. Shirotsuka, T., and N. Honda, *Kagaku Kikai*, **21**, 287 (1958).
10. Williamson, J. E., K. E. Bazaire and C. J. Geaukoplis, *Ind. Eng. Chem. Fundamentals*, **2**, 127 (1963).
11. Yagi, S., and N. Wakao, *A.I.Ch.E. Journal*, **5**, 79 (1959).

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