MASS TRANSFER BETWEEN FINE PARTICLES AND LIQUIDS IN AGITATED VESSELS

SATORU ASAI, YASUHIRO KONISHI AND YUKIYASU SASAKI

Department of Chemical Engineering, University of Osaka Prefecture, Sakai 591

The mass transfer coefficients between solid particles and turbulent liquids were measured in agitated vessels. For large particles characterized by large values of the specific power group ($\gamma^{1/3}d^{4/3}/v$), the measured mass transfer coefficients were in good agreement with Levins and Glastonbury's correlation. For fine particles less than 100 μm, however, the mass transfer coefficient deviated below their correlation, reaching more rapidly the theoretical limiting value $Sh = 2$ for molecular diffusion in an infinite stagnant fluid. This lends the first quantitative support to the postulate that fine particles may stay in and move together with microeddies. A new correlation for the mass transfer coefficient is presented. The effect of particle density and vessel diameter on the mass transfer coefficients was found to be negligible. Furthermore, the effect of solid particle concentration was found to be of little importance in the range of specific surface area up to at least 3000 m^2/m^3 of liquid.

Introduction

Mass transfer between suspended solid particles and liquids is important in many industrial processes. Agitated vessels are often used because they are effective in suspending solid particles and lead to good mass transfer rates. There have been numerous studies of the rates of mass transfer from or to solid particles suspended in agitated liquids. **Table 1** shows a summary of the previous representative experimental work with dilute suspensions of particles. Various approaches have been used to correlate the mass transfer coefficients. These empirical correlations depend mainly on three theoretical bases: the slip velocity model, the penetration model, and Kolmogoroff's theory of local isotropic turbulence. However, these studies have mainly dealt with mass transfer for large particles of more than a few hundred micrometers.

Today, fine particles of up to about 100 μm are commonly encountered in many industrial processes: as catalyst particles in slurry reactors, crushed ores in leaching tanks, cell cultures in biochemical reactors, and others. Although such processes are of industrial importance, very limited information has been available on the prediction of the mass transfer coefficient.

Harriott[5] studied the effect of particle size on the mass transfer coefficient. For large particles of more than 200 μm, the coefficient was almost independent of particle size. But for fine particles less than 100 μm, the coefficient increased greatly with decreasing particle size as expected from the theory for mass transfer

to or from a sphere to an infinite stagnant fluid, which yields the Sherwood number $Sh = 2$. Unlike the behavior of Harriott's data, Nagata and Nishikawa[10] showed that the mass transfer coefficient decreased with particle size over the range of 10 to 60 μm. Thereafter, the coefficient was found to remain nearly constant for 0.9–10 μm particle size. This constant value was much smaller than the value equivalent to $Sh = 2$. They also reported that the data obtained with particles smaller than 40 μm were not in good correlation with their correlation expression for large particles shown in Table 1. Levins and Glastonbury[8] and Sano *et al.*[12] obtained some data for fine particles of 30–60 μm, along with numerous data for large particles. Both found that the data points for fine particles fell slightly below their respective correlation lines for large particles.

For a dense suspension of fine particles, only one recent study is available. Yagi *et al.*[13] investigated the effect of particle concentration on the mass transfer

Table 1. Previous correlations of mass transfer coefficient

Investigators	Correlation	
Barker and Treybal (1960)[1]	$Sh' = 0.0518(T^2n/v)^{0.833}Sc^{1/2}$	(1)
Harriott (1962)[5]	$Sh = f[Sh^*, d_i, n, T, H]$	(2)
	$Sh^* = 2 + 0.6(dv_t/v)^{1/2}Sc^{1/3}$	
Brian *et al.* (1969)[3]	$Sh = f[(\varepsilon^{1/3}d^{4/3}/v)^{1/3}, Sc^{1/3}]$	(3)
Miller (1971)[9]	$Sh = 2 + 0.222(\varepsilon^{1/3}d^{4/3}/v)^{4/3}Sc^{1/3}$	(4)
Nagata and Nishikawa (1972)[10]	$Sh = 0.101(d_idn/v)^{0.83}Sc^{1/3}$	(5)
Levins and Glastonbury (1972)[8]	$Sh = 2 + 0.5(\varepsilon^{1/3}d^{4/3}/v)^{0.62}Sc^{1/3}$	(6)
Sano *et al.* (1974)[12]	$Sh = [2 + 0.4(\varepsilon^{1/3}d^{4/3}/v)^{3/4}Sc^{1/3}]\phi$	(7)

Table 2. Experimental systems and their physical properties (25°C)

Run No.	Systems	Particle diameter d [μm]	Particle density ρ [kg/m³]	Kinematic viscosity $\nu \times 10^7$ [m²/s]	Diffusivity $D \times 10^9$ [m²/s]
	Dilute suspension				
1	Cation exchanger–10^{-3} kmol/m³ NaOH sol.	23–842	1190, 1290	8.96	2.13
2	Anion exchanger–10^{-3} kmol/m³ HCl sol.	27, 202	1110	8.96	3.33
3	Anion exchanger–10^{-3} kmol/m³ H$_2$SO$_4$ sol.	27, 202	1110	8.96	2.60
4	Anion exchange–10^{-3} kmol/m³ Oxalic acid sol.	27, 202	1110	8.96	1.92
5	Anion exchanger–10^{-3} kmol/m³ Picric acid sol.	27, 202	1110	8.96	1.49
6	Anion exchanger–(10^{-3} kmol/m³ HCl + 32 wt% Sucrose) sol.	27, 202	1140	27.0	1.15
7	Copper–5×10^{-3} kmol/m³ Iodine sol.*	31–966	8190	6.49	1.68
8	Copper–(5×10^{-3} kmol/m³ Iodine + 32 wt% Sucrose) sol.*	5–102	8190	32.2	0.340
9	Lead sulfate–Water	23	6200	8.96	0.994
10	Lead sulfate–44 wt% Glycerine sol.	20	6200	30.1	0.267
	Dense suspension				
11	Anion exchanger–10^{-3} kmol/m³ HCl sol.	43, 57	1110	8.96	3.33
12	Anion exchanger–(10^{-3} kmol/m³ HCl + 32 wt% Sucrose) sol.	43, 57	1140	27.0	1.15

* Containing 3.0 kmol/m³ KI and 5×10^{-3} kmol/m³ H$_2$SO$_4$

coefficients and found that the mass transfer coefficients for 25.5 μm particles decreased rapidly as the specific surface area of the particles increased from 100 to 3000 m²/m³ of liquid.

The purpose of this study is to present experimental data on the rates of solid-liquid mass transfer for fine particles, to develop a correlation for the mass transfer coefficient, and to clarify the effect of particle concentration.

1. Experimental

The agitated vessel used in the experiments is shown in **Fig. 1**. The vessel, constructed of glass, was cylindrical with a flat bottom. The vessel diameter was usually 13.2 cm, but in some runs a vessel of 9.0 cm diameter was also used to determine the effect of vessel diameter. Standard baffles were attached to the internal wall. The stirring speed ranged from 2.2 to 25 s^{-1}. At its agitation intensity all the solid particles were suspended. The power consumption for agitation was measured by using a torsion dynamometer. The liquid temperature was kept at 25°C.

Most of the mass transfer experiments were carried out in dilute suspension by operating the vessel batchwise. Some experiments were also performed in dense suspension in order to find out the effect of solid particle concentration. It was hard to measure the effect of dense suspension in a batch operation, because the solution concentration changed very rapidly owing to the tremendous surface area of the particles. Thus the agitated vessel was operated continuously with respect to the liquid and batchwise with respect to the solid particles. The solution flowed out of the vessel through a glass filter.

The mass transfer rates were measured by using the
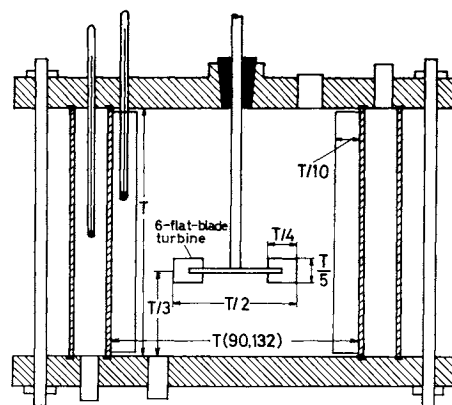
Fig. 1. Schematic diagram of agitated vessel

systems listed in **Table 2**, which provide a wide range of physical properties. The rate process for all these systems was controlled by the mass transfer rate of the transferring solute to or from the particles under the present experimental conditions. The solid particles used were sized by screening or wet classification so that more than 90% of particles fell within the range of 0.9–1.1 times the average size. The particle size distribution was measured by the microscopic method and/or the sedimentation method. The particle concentration was less than 1.2 kg/m³ (0.05 volume%) and the specific surface area based on liquid volume was less than 50 m²/m³ in the dilute suspension. For the dense suspension, they were up to 7.2 kg/m³ (3 volume%) and 3000 m²/m³, respectively. The aggregation of particles was found to be negligible by observation of the particles in liquid samples under a microscope. The change in particle size during the experimental run was also negligible, since ion exchange resins or sparingly soluble materials
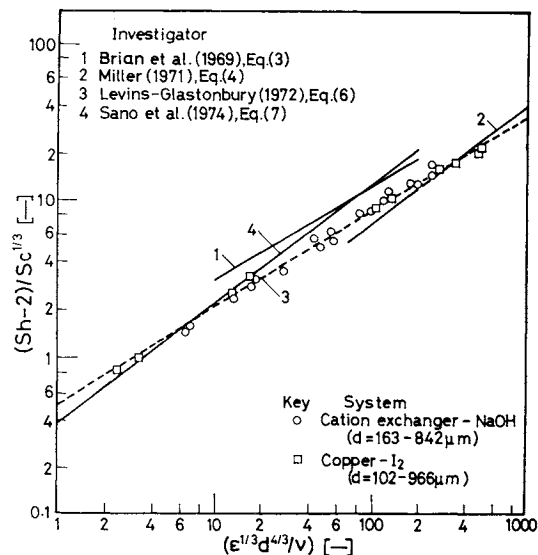
were used as solid particles.

In batch operation, the mass transfer coefficients were evaluated from the time variation of the transferring solute concentration in the solution. The concentrations of $PbSO_4$, NaOH and the four acids (HCl, H_2SO_4, oxalic acid, picric acid) were determined by monitoring the change in electrical conductivity of the solution. The concentration variation of I_2 was determined by iodometric titration. In continuous operation, on the other hand, the mass transfer coefficient was calculated from the liquid flow rate and the difference in transferring solute (HCl) concentrations in the inlet and outlet streams. The mass transfer coefficient was independent of liquid flow rate $((4.3 - 12.3) \times 10^{-6}$ m³/s). This fact indicates that the liquid in the agitated vessel was completely mixed and the contribution of liquid flow to the energy dissipation rate ε was negligibly small.

The diffusivities of transferring solute were measured by the diaphragm cell technique, while those of the electrolytes in water were predicted by the Nernst-Haskell equation.[11] The particle density was determined by the water displacement method. The kinematic viscosity of the solution* was measured by the conventional technique.

2. Results and Discussion

We will first discuss the mass transfer in dilute suspension. Prior to mass transfer experiments with fine particles, the mass transfer data for large particles of 102–966 μm were obtained for particles of ion exchange resins with a neutral density and of heavy copper. The experimental results are compared with previous correlations of mass transfer coefficient for large particles with the specific power group $(\varepsilon^{1/3}d^{4/3}/v)$ in **Fig. 2**. The present experimental data agree well with Levins and Glastonbury's correlation, Eq. (6) in Table 1, with an average deviation of 12%. The observed Sherwood number was independent of particle density, indicating that the effect of gravity is negligible in comparison with that of the eddy motion at the particle surface.

Figure 3 shows the results for fine particles of copper, anion exchangers and cation exchangers. Mass transfer coefficients k for a given kinematic viscosity v are plotted against particle diameter d on logarithmic coordinates, with the energy dissipation rate ε as a parameter. The solid lines represent Levins and Glastonbury's correlation, Eq. (6), which could explain the mass transfer data for large particles above 100 μm. The broken lines show the theoretical

---

* The values of the kinematic viscosity shown in Table 2 refer to the values for the solution, not including particles. For analysis of the experimental data shown later, the apparent kinematic viscosity of the solutions including particles was estimated by the expressions of Ishii and Zuber.[7] The corrections were less than 7%.

Fig. 2. Comparison of observed mass transfer coefficients for large particles with previous correlations
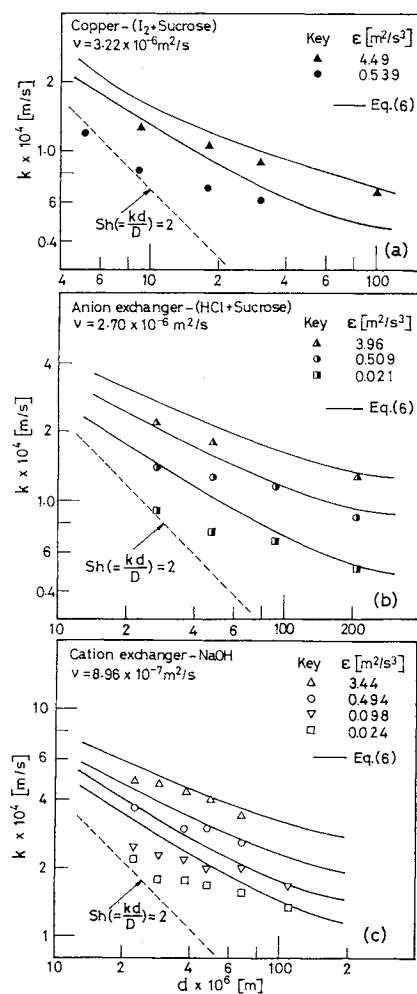
Fig. 3. Effect of relevant parameters on mass transfer coefficients for fine particles

limiting value equivalent to $Sh = 2$ for mass transfer between a solid sphere and an infinite stagnant fluid. It can be seen that for particles smaller than 50 μm,

most of the observed mass transfer coefficients cannot be well correlated by the expression of Levins and Glastonbury. As the particle diameter and energy dissipation rate decrease, and as the kinematic viscosity increases, the data points deviate further below the solid lines and finally reach the theoretical limiting correlation $Sh = 2$. Nagata and Nishikawa[10] postulated that fine particles less than 40 μm may be smaller than the dimensions of the microeddies, and that they may be embodied in the eddies. As described above, however, their experimental data showed unanticipated behavior in that the rate of mass transfer became much smaller than that of the molecular diffusion when the particle diameter decreased greatly, and their postulate has not been proven experimentally.

To clarify further the difference in mass transfer mechanism at small and large values of particle size, the diffusivity dependency of the mass transfer coefficients was investigated at the two particle sizes of 27 and 202 μm by making use of the neutralization of solutions of four acids (HCl, H_2SO_4, oxalic acid and picric acid) with anion exchangers. The results are shown in **Fig. 4**. For a large particle of 202 μm, the mass transfer coefficient k varies as the 2/3 power of the diffusivity D. This exponent agrees well with the theoretical prediction for mass transfer in a laminar boundary layer. On the other hand, for a fine particle of 27 μm, the mass transfer coefficient is proportional to the diffusivity and satisfies substantially the limiting theoretical value $Sh = 2$. Thus, the difference in mass transfer mechanism between large and fine particles was experimentally verified. This is the first quantitative verification of the postulation of Nagata and Nishikawa[10] that mass transfer to or from very fine particles suspended in a turbulent liquid occurs by molecular diffusion, not by turbulent diffusion.

According to Kolmogoroff's theory, the dimension of the microeddy is proportional to the 3/4 power of the kinematic viscosity v and is inversely proportional to the 1/4 power of the energy dissipation rate ε. Thus, as the kinematic viscosity increases or the energy dissipation rate decreases the dimension of the microeddy becomes large and tends to embody the particle. The specific power group refers to the ratio of particle size to length scale of the smallest eddy. Thus, the above-mentioned behavior of downward deviation of the data from the solid lines with decreasing particle diameter and energy dissipation rate and with increasing kinematic viscosity may be attributed to the behavior with the decrease of the specific power group.

Therefore, the specific power group was used to correlate the mass transfer coefficient for fine particles. The conventional linear combination of Ranz-Marshall type, such as Eq. (6), does not describe
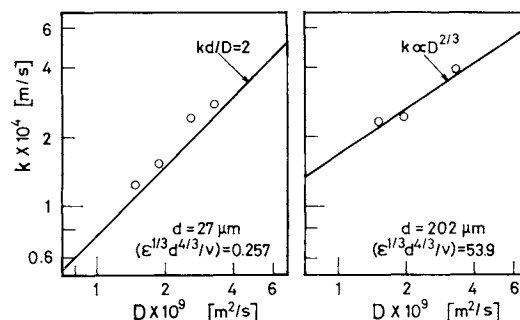

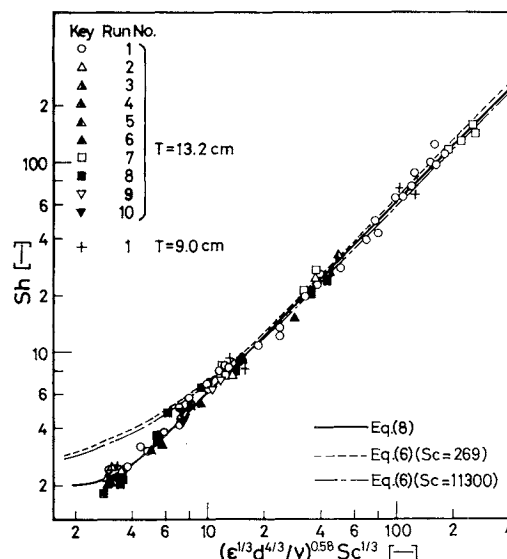**Fig. 4.** Effect of diffusivity on mass transfer coefficients

Fig. 5. Correlation of present experimental data

correctly the behavior of the Sherwood number near 2. Therefore, we adopted the empirical correlation proposed by Churchill and Usagi,[4] which combines two limiting asymptotes Y_1 and Y_2 of Y in the nonlinear form of $Y^n = Y_1^n + Y_2^n$ to give a general approximate solution for Y. Consequently, the following empirical correlation was obtained:

$$Sh = [2^{5.8} + \{0.61(\varepsilon^{1/3}d^{4/3}/v)^{0.58}Sc^{1/3}\}^{5.8}]^{1/5.8} \quad (8)$$

where

$$0.0229 < \varepsilon^{1/3}d^{4/3}/v < 495$$

$$269 < Sc < 11,300$$

The coefficients and exponents in Eq. (8) were determined by the Simplex method. This correlation is compared with all the experimental data for the large and fine particles in **Fig. 5**. The solid line represents the present correlation, Eq. (8). The even and uneven broken lines show Levins and Glastonbury's correlation, Eq. (6) for $Sc = 269$ and 11,300, which correspond respectively to the smallest and largest value under the present experimental conditions. Good agreement between the experimental data and the present correlation can be seen from this figure.

The average deviation is 7.1%. Levins and Glastonbury's correlation, however, leads to noticeable error with decreasing specific power group, the deviation reaching 66% at the abscissa value of 3.

It may be noted that the effect of particle density does not appear, although this correlation also includes data for heavy copper particles and ion exchange particles with neutral density. This suggests that the gravity effect is insignificant for mass transfer between particles and agitated liquids. Also, no effect of vessel diameter is observed. This justifies the use of the average value of the energy dissipation rate ε.

In **Fig. 6**, the present correlation is compared with the previous experimental data, which were obtained for fine particles less than 100 μm under conditions of dilute suspension. The value of the energy dissipation rate ε was evaluated by the method of Bates et al.[2] where the values are not stated. At the higher abscissa values, the reported values of the Sherwood number agree substantially with the correlation expression. But at the lower abscissa values, the data points scatter widely. The present correlation is roughly in agreement with the data of Sano et al.[12] and Yagi et al.[13]

As for the effect of fine particle concentration on the mass transfer coefficient, recently Yagi et al.[13] studied the dissolution of fine particles of $Ca(OH)_2$ into water in a dense suspension, using the continuous flow method. Their data are shown in **Fig. 7**. The particle diameter was 25.5 μm, and the particle concentrations were in the range up to 2 volume %. They found that when surface area of the particles per unit liquid volume, which was used to represent the particle concentration, varied up to 3000 m^2/m^3, the mass transfer coefficient decreased rapidly, and that the effect of agitation was slight. These tendencies were qualitatively explained in their paper by a model assuming the situation where two or more particles are embodied in the microeddy and move together, and then the diffusion from the surface of one particle is impeded by that from other adjacent particles.

In the present work, the mass transfer coefficients were measured under the condition of the same specific surface area as that of Yagi et al. Figure 7 shows the measured Sherwood number for runs 11 and 12, together with the data of Yagi et al. Unlike the findings of Yagi et al., no effect of particle concentration was observed in the same range of the specific surface area up to 3000 m^2/m^3 of liquid. A clear explanation for the difference in the two experimental results cannot be given here. In the experiments of Yagi et al., however, the dissolved concentration of $Ca(OH)_2$ in the inflow was reduced by chemical reaction with CO_2. This results in the production of $CaCO_3$. The aggregation of particles and/or the deposition of $CaCO_3$ on the surface of
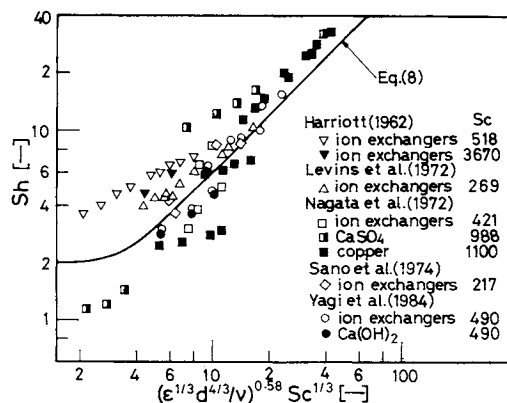

Fig. 6. Comparison of present correlation, Eq. (8), with previous data

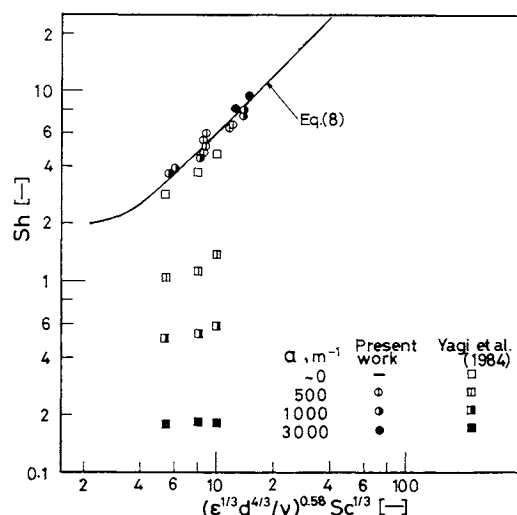**Fig. 7.** Effect of specific surface area of particle on mass transfer coefficient

$Ca(OH)_2$ particles may be partly responsible for the difference in behavior between their data and ours. The present result indicates that the distance between adjacent particles is still large enough to be regarded as infinite and Eq. (8) may still be applied. It is widely accepted that for catalytic reactions the typical solid concentrations are in the range of 10 to 20 kg/m^3 of liquid,[6] namely in the order of magnitude of 1000 to 2000 m^2/m^3. Thus, the effect of particle concentration is of little importance in such a solid concentration range.

Conclusion

The mass transfer coefficients between fine particles and liquids were measured in agitated vessels. As the particles diameter decreased, the values of the mass transfer coefficient deviated below the previous correlation for large particles and finally satisfied the theoretical correlation $Sh = 2$. The experimental data were well correlated by Eq. (8). No effects of particle density and particle concentration were observed in

the experimental range of specific surface area up to $3000\,\mathrm{m^2/m^3}$ of liquid.

Nomenclature

D	= liquid-phase diffusivity	$[\mathrm{m^2/s}]$
d	= particle diameter	$[\mathrm{m}]$
d_i	= impeller diameter	$[\mathrm{m}]$
H	= height of vessel	$[\mathrm{m}]$
k	= mass transfer coefficient	$[\mathrm{m/s}]$
k^*	= mass transfer coefficient for a particle falling at its terminal velocity	$[\mathrm{m/s}]$
n	= agitation speed	$[\mathrm{1/s}]$
Sc	= Schmidt number, v/D	$[-]$
Sh	= Sherwood number (referred to the particle), kd/D	$[-]$
Sh'	= Sherwood number (referred to the vessel), kT/D	$[-]$
Sh^*	= Sherwood number (used in Harriott's correlation), k^*d/D	$[-]$
T	= vessel diameter	$[\mathrm{m}]$
v_t	= terminal velocity	$[\mathrm{m/s}]$
ε	= energy dissipation rate per unit mass of liquid	$[\mathrm{m^2/s^3}]$
v	= kinematic viscosity of liquid	$[\mathrm{m^2/s}]$
ρ	= particle density	$[\mathrm{kg/m^3}]$
ϕ	= shape factor of particles	$[-]$

Literature Cited

1) Barker, J. J. and R. E. Treybal: *AIChE J.*, **6**, 289 (1960).
2) Bates, R. L., P. L. Fondy and R. R. Corpstein: *Ind. Eng. Chem.*, Process Des. Dev., **2**, 310 (1963).
3) Brain, P. L. T., H. B. Hales and T. K. Sherwood: *AIChE J.*, **15**, 727 (1969).
4) Churchill, S. W. and R. Usagi: *AIChE J.*, **18**, 1121 (1972).
5) Harriott, P.: *AIChE J.*, **8**, 93 (1962).
6) Hofmann, H.: "Reaction Engineering Problems in Slurry Reactors,"; In E. Alper (ed.), "Mass Transfer with Chemical Reaction in Multiphase Systems," Vol. II, p. 174, Martinus Nijhoff, The Hague (1983).
7) Ishii, M. and N. Zuber: *AIChE J.*, **25**, 843 (1979).
8) Levins, D. M. and J. R. Glastonbury: *Trans. Inst. Chem. Engrs.*, **50**, 132 (1972).
9) Miller, D. N.: *Ind. Eng. Chem.*, Process Des. Dev., **10**, 365 (1971).
10) Nagata, S. and M. Nishikawa: Proceedings of First Pacific Chemical Engineering Congress, Pt 3, 301, Kyoto (1972).
11) Reid, R. C., J. M. Prausnitz and T. K. Sherwood: "The Properties of Gases and Liquids," 3rd ed., p. 591, McGraw Hill, New York (1977).
12) Sano, Y., N. Yamaguchi and T. Adachi: *J. Chem. Eng. Japan*, **7**, 255 (1974).
13) Yagi, H., T. Motouchi and H. Hikita: *Ind. Eng. Chem.*, Process Des. Dev., **23**, 145 (1984).