MASS TRANSFER BETWEEN PARTICLES AND LIQUID IN SOLID-LIQUID TWO-PHASE UPFLOW IN VERTICAL TUBES

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Ion exchange resin particles and electrolyte solutions were transported upward through vertical tubes, and mass transfer coefficients between particles and liquid were obtained by measurement of the ion exchange rate under the condition of liquid-side mass transfer control. Tube sizes used were 1.96 and 3.00 cm inner diameter. Particle diameters ranged from 321 to 807 µm, and particle densities were in the range from 1190 to 1390 kg/m³. Other experimental variables were flow rate, species of counter-ion, fractional holdup of particles, and temperature.

Experimental results were correlated with the following empirical equation under the experimental conditions studied:

\[ Sh = 2 \times 0.44(\alpha^{1/3}D_p^{1/3}/\nu)^{0.47}\text{Sc}^{1/3} \]

where \( \alpha \), \( D_p \), \( \nu \), and \( \text{Sc} \) are energy dissipation rate per unit mass of liquid, particle diameter, kinematic viscosity of liquid, and delivered concentration of particles, respectively.

The above equation is nearly the same as published empirical ones for stirred tanks and bubble columns, which suggests that the effect of turbulent eddies on mass transfer could be identical although the macroscopic flow patterns are apparently different.

Introduction

Solid-liquid two-phase flow has been of practical importance in such a variety of engineering fields as hydraulic transport of solid particles and separation and/or recovery of heavy metal ions in waste water with ion exchange resin particles. For the design of a two-phase flow reactor, information of mass transfer rate between particles and liquid is essential.

Mass transfer between particles and liquid in turbulent flow is intrinsically affected by turbulence as well as by mean slip velocity of surrounding liquid. The effect of turbulence may predominate when particles are fully dispersed and freely move in the liquid. Several papers showed that mass transfer coefficients between liquid and solid or gas in stirred tanks were well correlated to energy dissipation rate, a measure of the intensity of turbulence. Harriott measured the dissolution rates for boric acid and benzoic acid particles flowing through a horizontal pipe of 2-in. inner diameter. For water velocities of 1 to 4 ft/s the coefficients were 1.2 to 2 times the values predicted for freely falling particles. He suggested that tests with other tube sizes would be needed to show if the power per unit volume of solution was really the proper correlating parameter. However, no further study has appeared on the correlation of mass transfer rate in solid-liquid two-phase flow.

In this study, styrene-type sulfonic acid cation exchange resins and electrolyte solutions were transported upward through vertical tubes, and mass transfer coefficients between particles and liquid were obtained by measurement of the ion exchange rate under the condition of liquid-side mass transfer control. The effects of such parameters as liquid flow rate, tube diameter, particle diameter, particle density, fractional holdup of particles, species of counter-ion in solution and temperature were examined to get more precise information of mass transfer rate in solid-liquid two-phase upflow.

1. Experimental Apparatus and Procedure

1.1 Apparatus

A schematic diagram of the vertical pipeline apparatus is shown in Fig. 1(a). The reactor tube was made of plexiglass. The particle injection system was provided 1.3 m downstream from the elbow. The manometer was used to measure liquid flow rate. The particle separator was attached for instantaneous separation of particles from liquid at the reactor outlet. Details of the particle injection line are presented in Fig. 1(b). Ion exchange resin...
particles were fluidized in a glass tube of 1.5 cm inner diameter with deionized water which was free from carbon dioxide before they were injected into the test section. It should be noted that for minimizing the concentration of counter-ion at the test section inlet it is necessary to wash away not only the counter-ion exuded from ion exchange resin particles, but also that produced by exchange with an extremely small amount of ions in water. The inner (outer) diameters and the lengths of vertical section of injection nozzle were 10(12) × 60 mm, and 6(8) × 40 mm, for the reactor tubes of diameter 3.00 cm and 1.96 cm, respectively. The photographed section is shown in Fig. 1 (c). A rectangular glass box filled with water was provided 7.5 m downstream from the injection point of particles to minimize distortion in the pictures taken through the side of the tube. The width of slit was fixed 0.1 to 0.3 cm wider than the depth of focus of a camera with a lens of 100 mm focal length.

1.2 Procedure

The reactant solution of a given cation was first circulated with a chemical pump, of which flow rate was controlled by a valve and a manometer; meanwhile, ion exchange resin particles were kept fluidized in the glass tube. When the temperature became constant through the system, the particles were then injected into the reactor tube by turning the cocks. Suspended stream was no longer circulated. Liquid and solid samples were separately collected by the particle separator during the period of constant injection rate of particles and consequently of the flat level of exit concentration. In a typical run, the fluctuation in concentration of the exit stream was within 5% for a duration of 30 sec. Cation concentration was determined by atomic absorption analysis. The instantaneous local velocities and hold-up of particles were determined with a stroboscope, a slit, and a camera, a method developed by Ohashi and Maeda. Time-mean velocity was calculated as the mean value of instantaneous velocities sampled over several hundred times.

2. Calculation of Mass Transfer Coefficient

The stoichiometric equation for cation exchange is shown by Eq. (1).

\[ Z_b R^+ A^{2-} + Z_a B^2+ = Z_a R^+ B^{2-} + Z_b A^{2-} \] (1)

The liquid-side mass transfer rate should determine the overall exchange rate under conditions which will be discussed in chapter 3.2. Under such conditions the material balance for the counter-ion B in the solution gives Eq. (2) at steady state:

\[ - \frac{d}{dx} \int_a^b (1-m_c)U_w cd s - \int_a^b k_{l} \alpha (c-c_i) ds = 0 \] (2)

where \( a = (6/D_p)m_c, \) \( m_c = (\pi D_p/6)N_s \), and \( ds \) is a differential increment of cross-sectional area in a tube. By assuming that the profile of concentration across the cross-section is flat and that the concentration at the interface between a particle and liquid is negligibly low, Eq. (3) is obtained for the mean mass transfer coefficient:

\[ k_L = \frac{U_p(1/L_p)(D_p/6)(V_L/V_p) \ln (c_o/c_e)}{N_{ds}} \] (3)

where

\[ k_L = \int_s N k_L ds / \int_s N ds \] (4)

\[ U_p = \int_s N U_p ds / \int_s N ds \] (5)

Material balance was precisely checked to evaluate the mean mass transfer coefficient.

3. Experimental Results and Discussion

3.1 Holdup and velocity distribution of particles

Examples of local holdup of particles across the cross-section are shown in Fig. 2. The distribution of particles can be considered nearly uniform except in the vicinity of the wall. Figure 3 represents examples of local velocities of particles in a tube. The solid line in the figure is the calculated liquid velocity by 1/7-power law. Figure 4 shows average liquid velocity vs. mean particle velocity defined by Eq. (5). More local holdup of particles in the central portion caused a slightly larger value of mean particle velocity.
than the average liquid velocity in a high-speed region. The same tendency was reported by Toda et al.\(^17\).

### 3.2 Mass transfer coefficient

It was ascertained beforehand that the effect of the elbow on the flow mechanics in the test section was negligible\(^13\). Experimental conditions are shown in Table 1. The experiments were conducted so as to satisfy the condition of liquid-side mass transfer control\(^5\). The induction period for a resin particle at the injection point was assumed to have no appreciable effect on overall mass transfer rate, since the time needed, for example, for a particle of 805 \(\mu\)m diameter to reach 1.1 times the terminal slip velocity was calculated to be 0.056 sec, and the extent of contribution to mass transfer due to large slip velocity during the induction period was calculated using Ranz-Marshall’s equation\(^15\) and was around 1\(\%\) of total mass transfer rate, at a bulk liquid velocity of 2.5 m/s where the particle residence time was 3.4 sec in the reactor tube.

Examples of experimental results are shown in Figs. 5 and 6, which represent the effects of particle diameter and tube diameter on mass transfer coefficient vs. mean liquid velocity, respectively. Such parameters as particle density, fractional holdup of particles and the species of counter-ion A in the resin phase had no appreciable effect on mass transfer coefficient under the experimental conditions studied.

The motion of particles suspended in turbulent flow is influenced by both gravity and the attack of various-sized eddies, which would create a relative velocity between particles and liquid. Much work has suggested the role of relative velocity in the mass transfer in turbulent flow. The slip velocity, the steady relative velocity due to gravity, was selected as a measure of relative velocity by a few researchers\(^3,11\). Although Fig. 3 shows that local slip velocities may be constant and of the order of the terminal velocity of a particle settling in a still liquid at any liquid velocity, Figs. 5 and 6 indicate that mass transfer coefficients increase remarkably with increase in mean liquid velocity. Therefore, it seems that the “slip velocity theory” based on the steady relative velocity is not applicable to the results under the experimental conditions studied.

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**Table 1 Experimental conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_T) [cm]</td>
<td>1.96, 3.00</td>
</tr>
<tr>
<td>(L_T) [cm]</td>
<td>850</td>
</tr>
<tr>
<td>(D_p [\mu m]/\rho_p [kg/m^3])(^+)</td>
<td>321/1290, 567/1280, 790/1190, 805/1280, 807/1390</td>
</tr>
<tr>
<td>(m_L [-])</td>
<td>lower than 0.014</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>10, 20, 30, 40</td>
</tr>
<tr>
<td>Ion exchange system</td>
<td>R-Na/K(^+), R-Na/Ba(^{2+}), R-K/Ba(^{2+})</td>
</tr>
<tr>
<td>(\varepsilon [m^3/s])(^++)</td>
<td>0.568 (\times 10^{-2}) - 2.68 (\times 10^{-2})</td>
</tr>
<tr>
<td>(U_{sl} [m/s])</td>
<td>0.47 - 2.52</td>
</tr>
<tr>
<td>(Re_T [-])</td>
<td>2.0 (\times 10^4) - 1.1 (\times 10^5)</td>
</tr>
<tr>
<td>(Sc [-])</td>
<td>250 - 2300</td>
</tr>
<tr>
<td>(c_0 [kmol/m^3])</td>
<td>lower than 1 (\times 10^{-3})</td>
</tr>
<tr>
<td>Fractional attainment of ion exchange equilibrium [%]</td>
<td>lower than 4</td>
</tr>
</tbody>
</table>

* Styrene-type sulfonic acid cation exchange resin (DIAION, SK104-116)
** Diffusion coefficients were estimated values for counter-ion B with the Nernst equation\(^14\)
Meanwile, instantaneous relative velocity would be influenced not only by large-scale eddies but also by small ones of micro or Kolmogorov's scale. Since "the universal equilibrium range" would exist under the experimental conditions studied, it is allowable to apply energy dissipation rate based on Kolmogorov's theory of isotropic turbulence to the correlation as postulated by Kuboi et al. Although the local value of energy dissipation rate in the vicinity of the wall could be tenfold or more than that in the core region, the volumetric average value would not be so diversified through the cross-section. Consequently, the energy dissipation rate per unit mass of liquid, $\varepsilon$, defined by Eq. (6) was introduced to correlate the experimental results.

$$\varepsilon = 2f \left( \frac{U_0}{\nu} \right)^{1/3} D_T$$

Figure 7 shows an example of mass transfer coefficient vs. $\varepsilon$. From this figure, the mass transfer coefficient may be taken to be independent of tube diameter. The fact that the same energy dissipation rate gave the same mass transfer coefficient independent of tube diameter, combined with lack of appreciable effect of particle density, may indicate that the effect of eddies predominates in the overall mass transfer process under the experimental conditions studied.

The exponent of Schmidt number was fixed at 1/3 from Fig. 8, where $(\varepsilon^{1/3}D_p^{1/3}/\nu)$, specific power group, was introduced as a correlating dimensionless parameter. Figure 9 shows Sherwood number vs. specific power group and Schmidt number. The figure indicates that the empirical equation, Eq. (7), satisfactorily correlates all the experimental results with a standard deviation of 10.7% in the range where $12 < (\varepsilon^{1/3}D_p^{1/3}/\nu) < 190$, $250 < Sc < 2300$, and $md < 0.014$.

$$Sh = 2 + 0.44(\varepsilon^{1/3}D_p^{1/3}/\nu)^{1/3}Sc^{1/3}$$

In Fig. 10, this empirical equation is compared with the published ones for stirred tanks and bubble columns, and also with experimental data for horizontal flow by Harriott. It is apparent that Eq. (7) is nearly the same as empirical ones for stirred tanks and bubble columns. This might be evidence that the effect of turbulent eddies on mass transfer in two-phase flow can be considered identical with those in stirred tanks and bubble columns in the developed turbulent region, although the macroscopic flow patterns are apparently different.

**Concluding Remarks**

Ion exchange resin particles and electrolyte solutions were transported upward through vertical tubes, and
mass transfer coefficients between particles and liquid were obtained by measurement of the ion exchange rate under the condition of liquid-side mass transfer control.

Energy dissipation rate per unit mass of liquid was found to be adequate to explain the characteristic dependency of flow rate and tube diameter on mass transfer coefficient in two-phase flow.

Sherwood number was satisfactorily correlated to the specific power group and Schmidt number in vertical upflow with a standard deviation of 10.7% under the experimental conditions studied:

\[ Sh = 2 + 0.44 \left( \frac{\varepsilon^{1/2} D_p^{4/3} \nu}{\nu} \right)^{6.63} Sc^{1/3} \]

12 < \left( \frac{\varepsilon^{1/2} D_p^{4/3} \nu}{\nu} \right) < 190, 250 < Sc < 2300, m_e < 0.014

The above equation is nearly the same as published empirical ones for stirred tanks and bubble columns, which suggests that the effect of turbulent eddies on mass transfer could be identical.

Acknowledgment

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Nomenclature

- A = ion species A
- a = interfacial area per unit volume of liquid [m²/m³]
- B = ion species B
- c = concentration of counter-ion B [kmol/m³]
- D = diameter [m]
- ε = diffusion coefficient [m²/s]
- f = friction factor f=0.082Re_v^{-1/4} [-]
- k_L = local liquid-side mass transfer coefficient [m/s]
- k_{L*} = mean liquid-side mass transfer coefficient defined by Eq. (4) [m/s]
- L_r = reactor length [m]
- m_e = fractional holdup of particles in tube [-]
- m_d = delivered concentration of particles [-]
- N = number of particles per unit reactor volume [m⁻¹]
- Re = Reynolds number based on tube diameter \[ 4\left( \frac{U_{m/2}}{D_t} \right) \] [-]
- Sc = Schmidt number \( \nu/\varepsilon \) [-]
- Sh = Sherwood number \( k_L D_p/\varepsilon \) [-]
- s = cross-sectional area [m²]
- U_p = time-mean velocity of particles [m/s]
- U_m = mean particle velocity defined by Eq. (5) [m/s]
- U_w = time-mean velocity of liquid [m/s]
\( V \) = sampling volume for arbitrary time interval \\
\( x \) = axial distance from reactor inlet \\
\( y \) = radial distance from wall \\
\( Z_A, Z_B \) = ionic valence \\
\( \epsilon \) = energy dissipation rate per unit mass of liquid \\
\( \rho \) = density \\
\( \nu \) = kinematic viscosity \\
\(<\text{Subscripts}>\) \\
\( \text{av} \) = average value across cross-section \\
\( i \) = at interface between particles and liquid \\
\( e \) = at reactor exit \\
\( j \) = \( j \)-th part of cross section, \( j=1, 2, \ldots, 20 \) \\
\( L \) = liquid \\
\( \text{max} \) = maximum value \\
\( o \) = at reactor inlet \\
\( p \) = particle \\
\( T \) = tube \\

Literature Cited 