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Electrochemical Ionic Mass Transfer Correlation in Fluid-Saturated Porous Layer

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Abstract – A new ionic mass transfer correlation is derived for the fluid-saturated, horizontal porous layer. Darcy-Forchheimer model is used to explain characteristics of fluid motion. Based on the microscales of turbulence a backbone mass transfer relation is derived as a function of the Darcy-Rayleigh number, Ra_D and the porous medium Schmidt number, Sc_p. For the Darcy's limit of Sc_p>>Ra_D, the Sherwood number, Sh is a function of Ra_D only. However, for the region of high Ra_D, Sh can be related with $Ra_D Sc_p$. Based on the present backbone equation and the electrochemical mass transfer experiments which are electro plating or electroless plating, the new ionic mass transfer correlation is suggested in the porous media.

Key words: Ionic Mass Transfer Correlation, Porous Media, Texture, Microscale Turbulence Model, Electroless Plating, Conductivity

1. Introduction

The convective motion driven by buoyancy-forces is a well-known phenomenon, and has attracted many researchers' interests. The analysis of the buoyancy-driven phenomena in porous media has been used in a wide variety of engineering applications, such as geothermal reservoirs, agricultural product storage system, packed-bed catalytic reactors, the pollutant transport in underground and the heat removal of nuclear power plants, ion-transport in fiber-texture. The buoyancy-driven phenomena in porous media are actively under investigation for the development of engineering application [1].

One of the important problems in buoyancy-driven phenomena is the heat transfer characteristics in thermally fully-developed state. To analyze this problem Howard [2] proposed the boundary layer instability model in which the heat transfer for very high Rayleigh numbers has a close relationship with stability criteria. Based on Howard's concept, Long [3] and Cheung [4] introduced the backbone equations to predict the heat transport in horizontal fluid layers. By considering microscales of thermal turbulence, Arpaci [5] derived a heat transfer correlation for buoyancy-driven convection.

The experimental determination on the buoyancy-driven convection for a high Rayleigh number is very difficult due to the side effects and the difficulties in the control of boundary conditions. Furthermore, the observation of the convective motion in the porous media is hardly detected due to the structural complexity. To overcome the above mentioned problems, electrochemical systems [7-11] under the limiting current condition [12] have been used in the natural convection fields especially for the very large Rayleigh number situations. Lee *et al*. [13] and Chung *et al*. [14] showed that this method can be extended to the system of the fluid-saturated porous media.

In the present study a new mass transfer correlation for fluid-saturated, horizontal porous layer is studied by considering the analogy between heat transfer and mass transfer. By employing Arpaci's [5] microscale turbulence model, we propose the new backbone equations for the buoyancy-driven mass transfer. And also, we conducted mass transfer experiments for the ionic mass transfer system.

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2. Theoretical Modeling

2-1. Governing Equations

The system considered here is a fluid-saturated porous layer where electrochemical mass transfer is occurred. For this system the governing equations of flow and concentration fields are expressed employing the Boussinesq approximation and Forchheimer's extension [1]:

$$\nabla \cdot \mathbf{u} = 0\,, \tag{1}$$

$$\mathbf{u} + \frac{bK}{\nu}|\mathbf{u}|\mathbf{u} = \frac{K}{\mu}(-\nabla P + \rho\mathbf{g})\,, \tag{2}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{u}\cdot\nabla\right)C = D_e\nabla^2 C\,, \tag{3}$$

$$\rho = \rho_r[1 + \beta(C - C_r)]\,, \tag{4}$$

where **u** is the velocity vector, b the Forchheimder's constant, K the permeability, ν the kinematic viscosity, μ the viscosity, P the pressure, **g** the gravitational acceleration, ρ the density, C the concentration, D_e the effective mass diffusivity, β the thermal expansion coefficient. The subscript "r" represents the reference state. The detailed discussion on physical properties can be found in the work of Katto and Masuoka [6]. The important parameters to describe the present system are the Darcy number Da, the Rayleigh number Ra, the Darcy-Rayleigh number Ra_D, the Cozeny-Karman number KC, the Schmidt number Sc and the Sherwood number Sh defined by

$$Da = \frac{K}{d^2},\ Ra = \frac{g\beta\Delta C d^3}{D_e \nu},\ Ra_D = DaRa\ KC = \frac{1}{bd}\ \ Sc = \frac{\nu}{D_e}$$

$$\text{and } Sh = \frac{md}{D_e \Delta C},$$

where d and m denote the layer thickness and the mass flux, respectively.

2-2. Turbulent Mass Transport Modeling

For the fully developed turbulent buoyant convection regime, the buoyancy-driven convection can be described by the two-layer model. The mass transfer resistance is mainly confined within the sublayer next to the boundaries. The turbulent properties of flow belong to the core region. The sublayer thickness is assumed to be the Kolmogorov scale, η_c, and conduction in the core is characterized by the Taylor scale, λ_c. The schematic of the concentration distribution in the layer is depicted in Fig. 1. The mean mass flux in the sublayer may be written as

$$m \sim D_e \frac{c}{\eta_c} \sim uc, \tag{5}$$

where c is the concentration at the interface, and u is the sublayer velocity. The above relation means that the order of magnitude of mass fluxes due to the diffusion and the convection is nearly same. In core region, we may neglect the diffusive mass flux with respect to convective flux and write mass flux as follows:

$$m_t \sim u_t c_t, \tag{6}$$

where the subscript "t" means the turbulent core region. At the interface of two layers, the mass flux must be continuous, then the following relation can be obtained:

$$m \sim m_t. \tag{7}$$

From the turbulent model of Arpaci [5], where the concentration reversal exist between the core and sublayer region as shown in Fig. 1, the following relation can be assumed:

$$c - c_t = \Delta C, \tag{8}$$

where ΔC is the concentration transport difference of the whole layer. By rearranging the above relation, we can derive the following relation

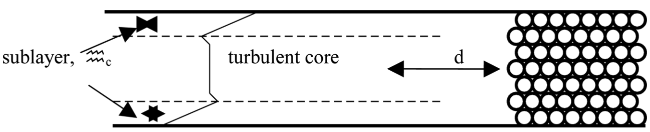

Fig. 1. Sketch of two-layer model.

$$Sh = \frac{m}{D_e \Delta C} = \frac{(d/\eta_c)}{1-(d/\eta_c)Pe_t}, \tag{9}$$

where $Pe = u_t d/D_e$ is the turbulent Peclet number.

Long [3] and Cheung [4] proposed the backbone equations to predict the heat transport for the horizontal fluid layer heated internally or from below. By taking microscales of thermal turbulence into account, Arpaci [5] proposed a new heat transfer correlation for the homogeneous fluid layers. Here, we will extend Arpaci's model into the porous-saturated horizontal fluid layers. From the balance of the mean kinetic energy of velocity fluctuation, the following relation can be obtained:

$$P_\beta = P_i + (-\varepsilon), \tag{10}$$

where P_β, P_i and $(-\varepsilon)$ denote the buoyant production, inertial production and viscous dissipation, respectively. And, the following relation can be obtained from the buoyancy energy balance:

$$P_c = (-\varepsilon_c), \tag{11}$$

where P_c and ε_c denote the buoyancy energy production and the buoyancy energy dissipation, repectibvely.

Arpaci [5] described volume-average dissipation rate as the product of local dissipation rate in vortex tubes $\nu(u_t^2/\eta^2)$ and volume fraction of vortex tubes of diameter η, $(\eta/\lambda)^2$. Then, the volume-averaged dissipation rate for this model becomes

$$\varepsilon \sim \nu\left(\frac{u_t}{\eta}\right)^2\left(\frac{\eta}{\lambda}\right)^2 \tag{12}$$

where λ and η denote Taylor and Kolmogorov scales, respectively. Now, we assume the local dissipation rate as $\nu(u_t^2/K)$ by considering dimensional reasoning. It implies that Kolmogorov scale is $O(\sqrt{K})$ in Darcy's limit, *i.e.*

$$Da_K = \frac{K}{\eta^2} \sim O(1). \tag{13}$$

Then the dissipation rate becomes

$$\varepsilon \sim \nu \frac{u_t^2}{K}\left(\frac{\eta}{\lambda}\right)^2. \tag{14}$$

The local production rate in eddies of size λ is (u_t^3/λ), and then the and volume-averaged inertial production rate becomes

$$P_i \sim \left(\frac{u_t^3}{\lambda}\right)\left(\frac{\lambda}{l}\right). \tag{15}$$

Now, we assume the local production rate as bu_t^3 from the momentum equation. This implies that the Taylor scale is O(1/b), and the Carman-Kozeny number based on the Taylor scale is O(1), *i.e.*

$$KC_T = \frac{1}{b\lambda} \sim O(1). \tag{16}$$

Then, Eqs. (10), (14) and (15) lead to

$$P_\beta \sim \nu\left(\frac{u_t^2}{K}\right)\left(\frac{\eta}{\lambda}\right)^2 + bu_t^3\left(\frac{\lambda}{l}\right). \tag{17}$$

From the buoyancy energy balance, the following relations can be obtained:

$$u_t\frac{c_t^2}{l}\sim D_e\frac{c_t}{\lambda_c^2} \text{ or } u_t\sim D_e\frac{1}{\lambda_c^2}, \tag{18}$$

$$Pe_t\sim\frac{u_t l}{D_e}\sim\left(\frac{l}{\lambda_c}\right)^2. \tag{19}$$

In the above equations, u_t and c_t denote the root-mean-square (rms) value of velocity and concentration fluctuations, respectively, l is the integral scale having the same order of magnitude with d. Also, the mechanical and buoyant dissipation are assumed to be isotropic. It seems reasonable to assume that the momentum and the concentration boundary layer thicknesses have the same scale in buoyancy driven convection. Then, in Eqs. (17) and (18), we replace λ with λ_c and η with η_c and obtain the following:

$$\lambda_c\sim l^{1/3}\left\{\eta_c^2+\frac{D_e bK}{\nu}\lambda_c\right\}^{1/6}\left(\frac{D_e^2\nu}{KP_\beta}\right)^{1/6}, \tag{20}$$

Although, l and λ_c are two different scales, in the isotropic limit they are replaced with the same isotropic scale η_c. Then the following relationship can be obtained:

$$\eta_c^{2/3}\sim\left\{\eta_c^2+\frac{D_e bK}{\nu}\eta_c\right\}^{1/6}\left(\frac{D_e^2\nu}{P_\beta K}\right)^{1/6} \tag{21}$$

The above Eqs. (20) and (21) yields

$$\frac{\lambda_c^3}{\eta_c^2}\sim l\left\{\frac{\eta_c^2+\lambda_c D_e bK/\nu}{\eta_c^2+\eta_c D_e bK/\nu}\right\}^{1/2}. \tag{22}$$

According to Arpaci's results [4], the buoyancy production term P_β can be represented by

$$P_\beta=\frac{gD_e\beta c}{\eta_c}. \tag{23}$$

Substituting the above Eq. (23) into Eq. (21) yields the following:

$$\eta_c^{1/3}\sim l^{1/6}\left\{\eta_c+\frac{D_e bK}{\nu}\right\}^{1/6}\left(\frac{D_e^2\nu}{KgD\beta\Delta Cl}\right)^{1/6}, \tag{24}$$

where the rms of concentration fluctuations is assumed to be proportional to the imposed concentration difference (c~ΔC). Then the above Eq. (24) becomes

$$\frac{\eta_c}{l}=A\left\{\frac{\eta_c}{l}+\frac{B}{Sc_p}\right\}^{1/2}Ra_D^{-1/2}. \tag{25}$$

where Sc_p=Sc KC/Da is the porous medium Schmidt number. From Eqs. (22) and (25), the following relation can be obtained,

$$\left(\frac{\lambda_c}{l}\right)^2=C\left(\frac{\eta_c}{l}\right)^{3/4}\left\{\frac{(\eta_c/l)+DSC_p^{-1}(\eta_c/l)(l/\lambda_c)}{(\eta_c/l)+BSc_p^{-1}}\right\}. \tag{26}$$

A, B, C and D are undetermined constants. Arpaci [4] proposed the Sherwood number as the following form

$$Sh\sim\frac{l/\eta_c}{1-(1/\eta_c)(1/\lambda_c)^{-2}}, \tag{27}$$

which is backbone of Eq. (9). Substituting the Eqs. (25) and (26) into the above relation, we can obtain the heat transfer correlation for fluid-saturated horizontal porous media.

For the limiting case of very small Sc_p, Eqs. (25) and (26) are reduced as

$$\frac{\eta_c}{l}\sim(Ra_D Sc_p)^{-1/2} \text{ and } \left(\frac{\lambda_c}{l}\right)^2\sim\left(\frac{\eta_c}{l}\right)^{6/5}\sim(Ra_D Sc_p)^{-5/7}. \tag{28}$$

And the Sherwood number of Eq. (27) is expressed as

$$Sh=\frac{d_1(Ra_D Sc_p)^{1/2}}{1-d_2(Ra_D Sc_p)^{-3/14}}. \tag{29}$$

The above relation is hold for the region of $Sc_p^{-1}\gg\eta_c/l\sim(Ra_D Sc_p)^{-1/2}$, *i.e.* $Sc_p \ll Ra_D$. This region has been called Forchheimer's flow regime. For this regime, Wang and Bejan [15] and Yoon and Choi [17] suggested the relation of $Sh\sim(Ra_D Sc_p)^{1/2}$ through the scale analysis. The two coefficients d_1 and d_2 might be determined from existing experimental data by Jung [19].

3. Results and Discussion

The convective system employed in the present investigation is that of the electrochemical redox reaction of copper ion in aqueous copper sulfate. This electrochemical system has been widely used in studying buoyancy-driven phenomena as copper sulfate has a reasonable solubility in water and does not form soluble product on the electrode surface [7-14]. As shown in Fig. 2, the copper plates saturated with spherical beads in a horizontal are used as both the cathode and the anode. At the cathode following reduction reaction occurs:

$$Cu^{2+}+2e^-\rightarrow Cu,$$

while the following oxidation reaction proceeds at the anode,

$$Cu\rightarrow Cu^{2+}+2e^-.$$

In Jung's experiment [19] same as in Fig. 2, the electrolyte consists of 0.05~0.2 M $CuSO_4$ solution with 1.5 M H_2SO_4 as a supporting electrolyte, where sulfuric acid was added as a supporting electrolyte to lessen the electromigration effect. Copper ion was deposited on the cathode electrode under the limiting current condition, and was dissolved from the anode one.

Comparing the experimental results with theoretical one, a new correlation of the Sherwood number is proposed at the fully-developed buoyancy-driven convection:

$$Sh=\frac{9.16\times10^{-5}(Ra_D Sc_p)^{1/2}}{1-9.97(Ra_D Sc_p)^{-3/14}} \tag{30}$$

for $Ra_D Sc_p\geq10^{11}$. The coefficients in the above equations have

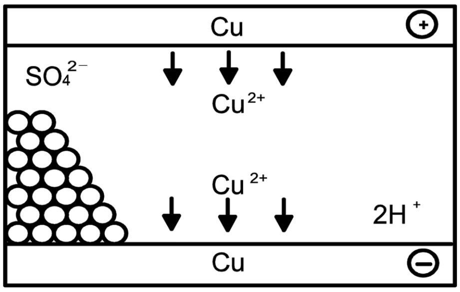

Fig. 2. Schematic of ionic mass transport in a horizontal porous layer.

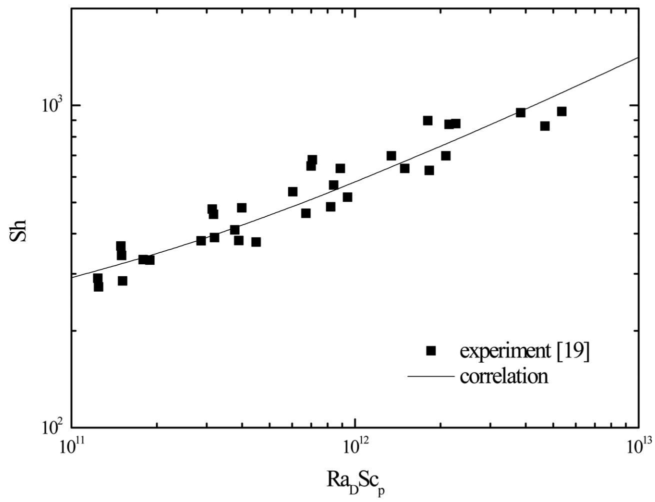

Fig. 3. Comparison of correlations with experimental data.

been obtained through the regression analysis of experimental results in the present porous layer. Fig. 3 shows the comparison of experimental results described by symbols and theoretical ones by curves in good agreement for $Ra_D Sc_p \geq 10^{11}$.

4. Conclusions

The mass transfer characteristics of the porous layer are predicted as a function of the Darcy-Rayleigh number by considering the microscales of turbulence. Based on the proposed backbone equation, a new correlation of the Sherwood number for the fluid-saturated, horizontal porous layer was proposed. For the limiting case of very high $Ra_D Sc_p$, the mass transfer can be related with $Sh \sim Ra_D^{1/2}$. In comparison with experimental results, the present correlation looks very promising for $Ra_D Sc_p \geq 10^{11}$.

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