

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, and the porous medium Schmidt number, Sc. For the Darcy’s limit of Sc >> Ra, the Sherwood number, Sh is a function of Ra only. However, for the region of high Ra, Sc can be related with Ra, Sc. 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.

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]:

\[ \mathbf{\nabla} \cdot \mathbf{u} = 0, \] (1)

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

\[ \left( \frac{\partial}{\partial t} + \mathbf{u} \cdot \mathbf{n} \right) C = D_C \nabla^2 C, \] (3)

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

where \( \mathbf{u} \) is the velocity vector, \( b \) the Forchheimer’s constant, \( K \) the permeability, \( \nu \) the kinematic viscosity, \( \mu \) the viscosity, \( P \) the pressure, \( g \) the gravitational acceleration, \( \rho \) the density, \( C \) the concentration, \( D_C \) the effective mass diffusivity, \( \beta \) 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

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the present system are the Darcy number $D_a$, 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

$$Da = \frac{K}{d^2}, \quad Ra = \frac{g \beta \Delta Ac^3}{D_y v}, \quad Ra_{D} = DaRa \quad KC = \frac{1}{bd} \quad Sc = \frac{v}{D_y}$$

and

$$Sh = \frac{md}{D_y \Delta Ac}$$

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 transport 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, $\lambda_\kappa$, and conduction in the core is characterized by the Taylor scale, $\lambda_\tau$. 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

$$m \sim D_y \eta \Delta uc,$$  \hspace{1cm} (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:

$$m_c \sim u_c c_c,$$  \hspace{1cm} (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:

$$m \sim m_c.$$  \hspace{1cm} (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:

$$c - c_t = \Delta C,$$  \hspace{1cm} (8)

where $\Delta C$ is the concentration difference of the whole layer. By rearranging the above relation, we can derive the following relation

$$Sh = \frac{m}{D_y \Delta C} \sim \frac{(d/\eta_1)}{1-(d/\eta_1)Pe_i},$$  \hspace{1cm} (9)

where $Pe_i = u_i/d/D_y$ 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:

$$P_\beta = P_\lambda + (-\epsilon),$$  \hspace{1cm} (10)

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

$$P_\lambda = (-\epsilon_i),$$  \hspace{1cm} (11)

where $P_\lambda$ and $\epsilon_i$ denote the buoyancy energy production and the buoyancy energy dissipation, respectively.

Arpaci [5] described volume-average dissipation rate as the product of local dissipation rate in vortex tubes $\nu (u_i^3/\lambda^2)$ and volume fraction of vortex tubes of diameter $\eta_1 (\eta/\lambda)^2$. Then, the volume-averaged dissipation rate for this model becomes

$$\epsilon \sim \nu (\frac{u_i^3}{\lambda})^2 \left(\frac{\eta_1}{\lambda}\right)^2,$$  \hspace{1cm} (12)

where $\lambda$ and $\eta_1$ denote Taylor and Kolmogorov scales, respectively. Now, we assume the local dissipation rate as $\nu (u_i^3/K)$ by considering dimensional reasoning. It implies that Kolmogorov scale is $O(\sqrt{K})$ in Darcy’s limit, i.e.

$$Da_k = \frac{K}{\eta_1^2} \sim O(1).$$  \hspace{1cm} (13)

Then the dissipation rate becomes

$$\epsilon \sim \frac{u_i^3}{K \lambda^2},$$  \hspace{1cm} (14)

The local production rate in eddies of size $\lambda$ is $(u_i^3/\lambda)$, and then the and volume-averaged inertial production rate becomes

$$P_\lambda \sim \frac{(u_i^3)}{K \lambda^2} \left(\frac{\eta_1}{\lambda}\right)^2.$$  \hspace{1cm} (15)

Now, we assume the local production rate as $b u_i^3$ 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.

$$KC_T = \frac{1}{bk} \sim O(1).$$  \hspace{1cm} (16)

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

$$P_\beta \sim \nu (\frac{u_i^3}{K \lambda^2}) + bu_i^3 \left(\frac{\eta_1}{\lambda}\right)^2.$$  \hspace{1cm} (17)
From the buoyancy energy balance, the following relations can be obtained:

$$u \frac{c^2}{l} - D \frac{c^2}{\lambda_c} \text{ or } u_i \frac{c^2}{\lambda_c},$$  

(18)

$$Pr_c \approx \frac{u_i}{D} \left( \frac{1}{\eta_c} \right).$$  

(19)

In the above equations, $u_i$ and $c_i$ 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 $\lambda_c$ with $\lambda_c$, $\eta$ with $\eta_c$ and obtain the following:

$$\lambda_c \sim l^{1/3} \left\{ \eta_c^2 + \frac{D_b k}{v} \right\}^{1/6} \left\{ \frac{D_c v^2}{K_p k} \right\}^{1/6},$$  

(20)

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

$$\eta_c^{2/3} \sim \left\{ \eta_c^2 + \frac{D_b k}{v} \right\}^{1/6} \left\{ \frac{D_c v^2}{K_p k} \right\}^{1/6}.$$  

(21)

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

$$\frac{\lambda_c^3}{\eta_c^3} \sim \left\{ \frac{\eta_c^2 + D_b k}{v} \right\}^{1/6}.$$  

(22)

According to Arpaci’s results [4], the buoyancy production term $P_p$ can be represented by

$$P_p = \frac{g D_b k c}{v}.$$  

(23)

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

$$\eta_c^{1/3} \sim l^{1/6} \left\{ \eta_c^2 + \frac{D_b k}{v} \right\}^{1/6} \left\{ \frac{D_c v^2}{K_p k} \right\}^{1/6},$$  

(24)

where the rms of concentration fluctuations is assumed to be proportional to the imposed concentration difference ($c-\Delta C$). Then the above Eq. (24) becomes

$$\frac{\eta_c}{l} = A \left( \frac{\eta_c + B}{1/1} \right)^{1/2} \text{Ra}_D^{1/2},$$  

(25)

where $\text{Sc}_p = \text{Sc} \frac{K}{D_a}$ is the porous medium Schmidt number. From Eqs. (22) and (25), the following relation can be obtained,

$$\frac{\lambda_c^3}{\eta_c^3} = C \left[ \frac{\eta_c}{l} \right]^{3/4} \left\{ \left( \frac{\eta_c}{l} \right) + D^c \right\}^{-1} \left( \frac{\eta_c}{l} \right) \left( \frac{\eta_c}{l} \right) \left( \frac{\eta_c}{l} \right) \left( \frac{\eta_c}{l} \right),$$  

(26)

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

$$Sh \sim \frac{1/\eta_a}{1 - (1/\eta_a)(1/\lambda_c)^{2}},$$  

(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 $\text{Sc}_p$, Eqs. (25) and (26) are reduced as

$$\frac{\eta_c}{l} \sim (\text{Ra}_D \text{Sc}_p)^{1/2} \left( \frac{\lambda_c^3}{\eta_c^3} \right) \sim (\text{Ra}_D \text{Sc}_p)^{-1/2}.$$  

(28)

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

$$Sh = \frac{d_1 (\text{Ra}_D \text{Sc}_p)^{1/2}}{1 - d_2 (\text{Ra}_D \text{Sc}_p)^{-1/2}},$$  

(29)

The above relation is hold for the region of $\text{Sc}_p^{1/2} >> \eta_c/(\text{Ra}_D \text{Sc}_p)^{1/2}$, i.e. $\text{Sc}_p < \text{Sc}_p$. 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 $Sh \sim (\text{Ra}_D \text{Sc}_p)^{1/2}$ 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 anode. At the cathode following reduction reaction occurs:

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

while the following oxidation reaction proceeds at the anode,

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

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$_2$SO$_4$ 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:

$$Sh = \frac{9.16 \times 10^3 (\text{Ra}_D \text{Sc}_p)^{1/2}}{1 - 9.97 (\text{Ra}_D \text{Sc}_p)^{3/4}},$$  

(30)

for $\text{Ra}_D \text{Sc}_p \geq 10^{11}$. The coefficients in the above equations have
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 $Sh \sim Ra^{0.5} Sc_p 10^{11}$.

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 $Ra, Sc_p$, the mass transfer can be related with $Sh \sim Ra^{0.5}$. In comparison with experimental results, the present correlation looks very promising for $Ra, Sc_p 10^{11}$.

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References