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The effects of local hydrodynamics on mass transfer in disordered porous media

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THE EFFECTS OF LOCAL HYDRODYNAMICS ON MASS TRANSFER
IN DISORDERED POROUS MEDIA

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

Gordon A. and Mary Cain Department of Chemical Engineering

by

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Interfacial area</td>
</tr>
<tr>
<td>( A_i )</td>
<td>Interfacial area from ( i )th interface</td>
</tr>
<tr>
<td>( A_t )</td>
<td>Total interfacial area</td>
</tr>
<tr>
<td>( \tilde{A} )</td>
<td>Dimensionless surface area</td>
</tr>
<tr>
<td>( a_0 )</td>
<td>Specific surface area</td>
</tr>
<tr>
<td>( C )</td>
<td>Solute concentration</td>
</tr>
<tr>
<td>( C^* )</td>
<td>Equilibrium concentration</td>
</tr>
<tr>
<td>( \bar{C} )</td>
<td>Dimensionless concentration</td>
</tr>
<tr>
<td>( D )</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>( D_{b,a.} )</td>
<td>The diameter of benzoic acid sphere</td>
</tr>
<tr>
<td>( D_h )</td>
<td>Dispersion coefficient</td>
</tr>
<tr>
<td>( D_{mean} )</td>
<td>The average diameter of porous media</td>
</tr>
<tr>
<td>( F_{i}^{0} )</td>
<td>Mass transfer rate from interface to the fluid</td>
</tr>
<tr>
<td>( g )</td>
<td>gravity</td>
</tr>
<tr>
<td>( J )</td>
<td>Mass flux</td>
</tr>
<tr>
<td>( k )</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>( k_i )</td>
<td>Mass transfer coefficient at individual interfaces</td>
</tr>
<tr>
<td>( k' )</td>
<td>Mass transfer rate coefficient</td>
</tr>
<tr>
<td>( L )</td>
<td>The thickness of surface layer</td>
</tr>
<tr>
<td>( l )</td>
<td>Characteristic length</td>
</tr>
<tr>
<td>( l_i )</td>
<td>The distance from single point to ( i )th grid point in grid method</td>
</tr>
<tr>
<td>( m )</td>
<td>Exponent term in mass transfer correlation</td>
</tr>
</tbody>
</table>
\( \bar{m} \)  The average of \( m \)

\( N_{esc} \)  The number of particle that permanently escaped from the source sphere

\( N_{sl} \)  The number of displacement inside the surface layer

\( n \)  Normal vector

\( Pe \)  Peclet Number

\( q \)  Darcy velocity

\( Re \)  Reynolds number

\( Sc \)  Schmidt number

\( Sh \)  Sherwood number

\( Sh' \)  Modified Sherwood number

\( s_W \)  Water saturation

\( u \)  Velocity

\( \bar{\bar{u}} \)  Dimensionless velocity

\( v_i \)  The velocity at \( i \)th grid point in grid method

\( W \)  Random number in random walk

\( x \)  Site-specific parameter to correct global \( Pe \) to local \( Pe \)

\( z \)  The individual \( m \) over averaged \( m \)

\( \delta_M \)  The length of each move in random walk

\( \epsilon \)  Porosity

\( \phi \)  The solid void fraction

\( \mu \)  Viscosity

\( \Delta t \)  Time step for each move in random walk
ABSTRACT

Interfacial mass transfer in disordered media was studied experimentally and numerically. The dissolution of solid benzoic acid spheres in packed columns showed the existence of spatial variations in mass transfer coefficients in monodisperse and polydisperse packings at the same overall Peclet number. The concept of a local Peclet number (single-particle average) was introduced to quantify the effect of local hydrodynamics on local mass transfer. Correlations between Sherwood number and Peclet number having the form \( \text{Sh}_i = A \cdot (x_i Pe)^m \) were used to quantify data from various sites in each packing. These experiments also showed that the exponent \( m \) varies significantly from site to site.

Stochastic simulations of interfacial dissolution in two-dimensional porous media were conducted, and mass-transfer-coefficient distributions similar to experimental results were obtained. The local velocity profiles available in the numerical simulations allowed a more detailed analysis to be made of local hydrodynamics and their effects on mass transfer. These result showed that mass transfer is affected by both large- and small-scale structure in the material. The large-scale structure affects the magnitude of local velocities and the small-scale structure (e.g., gap spacing between neighboring spheres) affects the shape of local streamlines. Particles exposed to large velocity gradients at their surface and/or particles for which streamline closely hugged their surfaces were observed to have higher rates of mass transfer.

The correlation accuracy can be improved when two parameters (local Peclet number \( x \cdot Pe \) and exponent \( z \cdot m \) ) were used in correlation such as \( \text{Sh} = A \cdot (x_i Pe)^{m z_i} \). Further analysis showed that there is a strong correlation between \( x_i \) and \( z_i \) and only one variable is needed to correct both
the local Peclet number and the exponent term. A correlation was presented as

\[ Sh = A(x, Pe)^{0.8965 m x, 0.158} \]

for the specific data generated in this work.

In the future, the use of distributed mass-transfer correlations similar to those presented in this study may improve modeling of NAPL remediation.
CHAPTER 1

INTRODUCTION

1.1 NAPL CONTAMINATION AND REMEDIATION

The release of non-aqueous phase liquids (NAPLs) from underground storage tanks, pipeline ruptures and illegal disposal of waste materials is a primary source of groundwater contamination by organic chemicals (Powers et al., 1992). Common NAPLs include chemicals such as hydrocarbon fuels and chlorinated solvents. As NAPLs migrate through the subsurface, interfacial forces act to form “globules” or “blobs” of the organic liquid in the saturated and unsaturated zones. One study (Conrad et al., 1992) showed that the trapped NAPL blobs were of the magnitude of 200 $\mu m$, slightly smaller than the mean grain size. These immobile and discrete blobs that become trapped in subsurface systems, partition slowly into the aqueous and vapor phases that flow through the contaminated zone, and exist as a long-term pollution source. Table 1.1 shows the properties of some common NAPLs (Miller et al., 1990).

Although the solubility of NAPLs in water is very small, the effluent concentration from the contaminated soil is still high enough to be above the criteria regulated by the relevant laws (Powers et al., 1994). NAPLs can oftentimes exist as a contamination source for tens or hundreds of years before they disappear naturally. Therefore remediation is necessary to speed up the clean-up process. Pump-and-treat techniques (Mackay et al., 1989) are common remediation methods. Wells are dug upstream and downstream of the groundwater contamination source. Polluted water is removed downstream of the source and treated to remove contaminants. Then, clean water is pumped into the subsurface upstream of the source. In this way the contaminated zone is forcibly flushed, and the NAPL dissolution rate is increased. Many additional methods are used to reduce the time required for remediation. One example is to add surfactants into the
injected water to increase the solubility of NAPLs in water, thus increasing dissolution rates (Imhoff et al., 1995). Another example is to inject biomaterials that are capable of degrading NAPLs in substances into harmless byproducts. These processes are called biodegradation or bioremediation (Coates et al., 2000). Generally, groundwater remediation is costly and time-consuming, but is crucial for reasons of public health. Hence, tremendous efforts have been expended for research on NAPL dissolution in subsurface systems.

Table 1.1 Properties of NAPLs

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Trichloroethylene</th>
<th>1,1-Dichloroethylene</th>
<th>Ethylene Dibromide</th>
<th>Benzoic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum contam. level</td>
<td>mg/L</td>
<td>0.005</td>
<td>2.0</td>
<td>0.005</td>
<td>0.007</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Aqueous solubility</td>
<td>mg/L</td>
<td>180</td>
<td>515</td>
<td>1100</td>
<td>400</td>
<td>4.3</td>
<td>2900</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>kg/L</td>
<td>0.879</td>
<td>0.867</td>
<td>1.46</td>
<td>1.22</td>
<td>2.7</td>
<td>1.08</td>
</tr>
<tr>
<td>Boiling point</td>
<td>°C</td>
<td>80.1</td>
<td>110.8</td>
<td>86.7</td>
<td>31.9</td>
<td>131.6</td>
<td>122.4 melting</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>cP</td>
<td>0.65</td>
<td>0.59</td>
<td>0.58</td>
<td>0.33</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>NAPL-aqueous interfacial tension</td>
<td>dyne/cm</td>
<td>35</td>
<td>35</td>
<td>36</td>
<td>37</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient in water</td>
<td>cm²/s × 10³</td>
<td>0.90</td>
<td>0.80</td>
<td>0.84</td>
<td>0.96</td>
<td>0.93</td>
<td>0.9908</td>
</tr>
</tbody>
</table>
1.2 MASS TRANSFER IN POROUS MEDIA

It is crucial to understand the mechanisms governing interfacial mass transfer in order to make remediation treatments economically and environmentally efficient. Many factors such as NAPL properties, injected fluid properties, groundwater flow rate, and subsurface structure influence the effectiveness of the treatment. Usually, the in-situ dissolution of NAPLs is characterized by the interfacial mass transfer rate in heterogeneous porous media. Typically, the rate of mass transfer in packed beds and porous media is quantified using empirical relationships between the Sherwood number and the Peclet number.

A significant amount of theoretical and laboratory research has been conducted to study NAPL dissolution in subsurface systems. Initially the majority of the research focused on homogeneous porous media, overlooking the effect of geological heterogeneity, which is ubiquitous in real systems. In recent years, a large amount of work has addressed contaminant transport in heterogeneous systems. But most of these studies used continuum models, which contain lumped parameters to describe the average interfacial mass transfer rate throughout the domain. Traditional continuum models cannot reflect mass transfer in heterogeneous systems very well, particularly during later stages of remediation. For example, the phenomena of tailing and rebound are commonly observed at pump-and-treat sites. Tailing (Cunningham et al., 1998) refers to the progressively slower rate of decline in dissolved contaminant concentration with continued operation of a pump-and-treat system. Rebound is the fairly rapid increase in contaminant concentration that can occur after pumping has been discontinued for a period of time (EPA/625/R-95/005, 1996). Tailing and rebound contribute to long treatment periods and large volumes of injected fluid. Previous research (EPA/625/R-95/005, 1996) showed that traditional continuum models can’t predict the tailing effect very well. Some models can predict
the increase in effluent concentration with decreasing groundwater flow rate. But the precision of these models needs to be improved to predict the specific behavior. A great deal of the poor precision in modeling is due to an incomplete understanding of mass transfer in porous media, along with poor empirical methods for quantifying the effects.

Mass transfer coefficients, which are used for continuum-level modeling of transport, represent spatially averaged quantities. However, at the pore scale, spatial variations in the mass-transfer rate will occur because of the disorder and heterogeneity found in most porous media, which in turn affects local hydrodynamics. In many applications, knowledge of these local values and their variation is of little use or interest. However, in cases where mass transfer occurs from discrete sites distributed within the porous medium, the local variations are important because the average rate of mass transfer may be significantly different than what is predicted from empirical correlations. This discrepancy would be particularly evident if a spatial correlation existed between the location of the discrete sites for mass transfer and other morphologic parameters that influence flow. For real processes, this type of correlation is probably more the norm than the exception because of the high degree of coupling found in most porous-media transport processes. Many experimental and numerical studies have demonstrated the existence of distributions in the mass transfer coefficient (or mass transfer rate coefficient) through porous media. Certain studies have showed that distributed mass transfer coefficients can provide better predictions than the average value (Haggerty et al., 1998). It has also been shown that the mass transfer coefficient distribution is associated with heterogeneities in the local geometry and flow, although few studies directly linked the detailed local hydrodynamics to the mass transfer characteristics.
1.3 SCOPE AND RESULTS OF THIS RESEARCH

Our study found that non-uniform mass transfer rates exist in porous media because of pore-scale heterogeneity. It is demonstrated that local pore-level structures contribute significantly to the local and overall mass transfer by limiting the rate at which contaminant is transported from the interface to an area of rapidly flowing bulk fluid. In this research, both experimental work and numerical modeling were conducted to study the influence of local heterogeneity on mass transfer at the pore-scale level. Benzoic acid spheres, which have a solubility in water that is close to that of most NAPLs and exist as a solid at room temperature, were put into packed beds for dissolution experiments. Mass transfer coefficients were calculated based on the dissolution results. We selected benzoic acid spheres based on two considerations: 1) The mass-transfer coefficient can be obtained using the known interface area. 2) By measuring dissolution from single spheres, local mass transfer information was obtained to show the influence of pore scale heterogeneity. The experimental results show that differences in local structure and hydrodynamics cause the local Peclet number to vary by an order of magnitude. Additionally, the exponent in the Sherwood versus Peclet number relationship varies between approximately 0.3 and 0.7.

In order to understand the mechanism of mass transfer heterogeneity, a sub-pore-scale model was used to study the roles of heterogeneity and local hydrodynamics on mass transfer. First, a one-thousand-sphere 2-D porous medium was created to represent the heterogeneous porous medium. 2-D modeling was used because of the need for streamline resolution of flow, which is a computationally intensive calculation. The solution from a high-resolution network model (HRNM) (Liu et al, 2002), which computes the velocity field in a 2-D packed bed using the boundary element method, was used. Then, the dissolution of individual spheres in the medium
was simulated using a stochastic (random walk) approach. The advantages of the random walk method are that the concentration field is not needed in order to obtain the dissolution rate, and high accuracy can be achieved for a wide range of Peclet numbers. Ten source spheres from different locations in the porous medium were selected. Dissolution rates and mass transfer coefficients were calculated for different flowrates (Peclet numbers) for each sphere selected. The numerical results give the common power-law relationship between Sherwood number and Peclet number that is often observed experimentally:

\[ Sh = A \cdot Pe^m. \]  

(1-1)

However, distributions of the coefficient \( A \) and the exponent \( m \) were observed. In contrast to the packed bed experiments, detailed local information was available for each single sphere in the medium. Therefore, the influence of local geometry and hydrodynamics on mass transfer could be studied. It was found that both large-scale and small-scale structures affect the local mass transfer characteristics. Large-scale structure affects the magnitude of local flow, and small-scale structure affects the shape of local streamlines and the magnitude of the velocity gradient. It was concluded that high mass transfer rates are related to large velocity gradients and pore geometry that cause streamlines to closely follow a particle’s surface.

Further study also indicated that there is a strong correlation between \( x_i \) and \( z_i \) when \n
\[ Sh = A \cdot (x_i Pe)^{m i z}; \]

was used. This suggests both local Peclet number and the exponent \( m \) are site-specific and affected by similar phenomenological behavior. A correlation was introduced with

\[ Sh = A(x_i Pe)^{0.8965 m i z^{0.158}} \]

where one variable (i.e., \( x_i \)) is used to describe the effect of local structure on both local Peclet number and exponent.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 NAPL FORMATION IN SUBSURFACE SYSTEMS

The migration of NAPL contaminants in subsurface systems is a complex process. Following a spill or leak, NAPLs generally migrate downward through the vadose zone due to gravitational force. If the spill is sufficiently large it will eventually reach the water table. LNAPLs (lighter than water) will spread laterally in the capillary fringe zone while DNAPLs (denser than water) will continue to migrate vertically through the saturated zones until a low permeability boundary is encountered, potentially resulting in the formation of a DNAPL pool at the bottom of an aquifer (Oolman et al., 1995).

Three forces control the behavior of NAPLs in the subsurface: capillary forces, viscous forces and gravitational forces. For multiple fluid phases in an aquifer, capillary forces are usually dominant over viscous forces and gravitational forces, which causes the trapping of organic liquids in water-wet porous media. The trapped organic liquid remains behind as small immobilized, disconnected pockets of liquid, called blobs or ganglia, no longer connected to the main body of organic liquid. This state is referred to as the residual organic liquid saturation (Conrad et al., 1992).

The sizes and shapes of NAPLs in porous media have been studied in both visual micro-models and packed columns. Observations from micro-models provide better opportunity for visualization but depend strongly on the model pore structure. Results from packed columns are closer to the real situation than those from visual micro-models. Conrad’s experimental results (1992) in etched glass micro-models and sand columns showed that in the saturated zone, large amounts of residual organic liquids are trapped as isolated blobs of microscopic
size. The experiments in sand column showed that blobs are slightly smaller than the mean grain size, about 200 \( \mu m \). The size, shape and space distribution of these blobs affects their dissolution into the water phase. Powers et al. (1992) also examined the shape and size of entrapped NAPLs by a polymerization technique in sand columns with various particle-size distributions. Columns containing styrene were subjected to high temperature and pressure to initiate the polymerization reaction. Results showed that the NAPL distribution depends on porous media grading and mean grain size. NAPLs entrapped in coarse-grained uniform media were primarily single blobs, the absolute size of which was greater than that of singlets entrapped in finer media. A much larger fraction of NAPLs entrapped in graded sands was found to exist as large, multiple-pore space blobs, which despite their sizes had relatively little contribution to the total surface area. The experimental results also revealed a dependence of dissolution rate on the distribution pattern of entrapped NAPLs, as well as upon aqueous phase velocity. Similarly, Mayer et al. (1996) observed the DNAPLs migration process in 2-D cell and analyzed the NAPL size distribution as a function of aqueous phase velocity, NAPL densities, and interfacial tension between aqueous phase and NAPLs.

Previous studies showed conclusively that NAPLs exist as discrete blobs in the subsurface system. The shapes and sizes of blobs depend on the fluid and media properties.

2.2 NAPL DISSOLUTION IN POROUS MEDIA

The development of a theory for NAPL dissolution in porous media can be traced along three sequential steps. These steps are mass transfer from a single object to surrounding fluid, mass transfer in uniform packed beds, and mass transfer in porous media. There have been extensive studies on all of these mass transfer phenomena.
2.2.1 Mass transfer from single object to the fluid

The analysis of heat and mass transfer from single object to surrounding fluid has provided the foundation for understanding mass transfer in packed beds and porous media. The flow and transport behavior around an object are determined by the following flow equation (2-1) and mass balance equation (2-2).

\[ \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u} + \rho \mathbf{g} \quad (2-1) \]

\[ \mathbf{u} \cdot \nabla C = D \cdot \nabla^2 C \quad (2-2) \]

The velocity and concentration profiles around an object can be obtained by solving these coupled equations with appropriate simplifications and boundary conditions. Based on the resulting concentration profile, the dissolution rate \( J \) can be calculated according to the concentration gradient at the surface of the object.

\[ J = \oint_A -D(\nabla C \cdot \mathbf{n})dA \quad (2-3) \]

\( D \) is the solute diffusion coefficient in fluid, \( \nabla C \cdot \mathbf{n} \) is the normal concentration gradient at the surface of the object, and \( A \) is the surface area.

A mass transfer coefficient \( k \) is defined according to equation (2-4) to describe the interfacial mass transfer between the object and fluid phase:

\[ J = k \cdot a_0 \cdot (C^* - C) \quad (2-4) \]

\( k \) is usually determined empirically for various situations. \( C^* \) is the equilibrium concentration of solute in fluid and \( C \) is the average concentration of solute in fluid. The term \( a_0 \) (cm\(^2\)/cm\(^3\)) is the specific interfacial area between object and fluid. A Sherwood number is defined and calculated based on equation (2-5)

\[ Sh = \frac{k \cdot l}{D} = \frac{-l}{a_0 (C^* - C)} \oint_A (\nabla C \cdot \mathbf{n})dA \quad (2-5) \]
where \( l \) is the characteristic length of dissolution process. Nondimensionalization of equations (2-2) and (2-5) gives equations (2-6) and (2-7).

\[
P e(\mathbf{u} \cdot \nabla \mathbf{C}) = \nabla^2 \mathbf{C} \tag{2-6}
\]

\[
Sh = -\frac{2l^2}{(area)} \int (\nabla \mathbf{C} \cdot \mathbf{n})d \mathcal{A} \tag{2-7}
\]

The Peclet number is defined as \( Pe = \frac{\mathbf{u} \cdot l}{D} \). \( \mathbf{C} \), \( \mathbf{u} \) and \( \mathcal{A} \) are dimensionless concentration, velocity and interfacial area.

Equations (2-6) and (2-7) show that both the Sherwood number and the dimensionless concentration are functions of Peclet number and Reynolds number, which is \( \Re = \frac{\rho \cdot \mathbf{u} \cdot l \cdot \mu}{\mu} \).

\[
\mathbf{C} = f(Pe, \Re) \tag{2-8}
\]

\[
Sh = f(Pe, \Re) \tag{2-9}
\]

Leal (1992) used an asymptotic analysis to derive the Sherwood number and Peclet number relationship for a single object in uniform flow and creeping flow. The results show that a power relationship (2-10) exists under low and high Peclet number conditions.

\[
Sh = c + A \cdot Pe^n \tag{2-10}
\]

However the form of equation (2-10) varies under different conditions, as shown in Table 2.1.

Leal concluded that at low Peclet number, the concentration field near the body is dominated by diffusion and is thus relatively insensitive to details of the fluid motion. Convection effects in the low Peclet number regime arise from the velocity field at large distances from the body, which determines the concentration field and the dependence of Sherwood number on Peclet
number. On the other hand, at high Peclet number, the mass transfer is confined to a very thin region near the body’s surface and it is only the local velocity distribution in this region that matters. As a consequence, at high Peclet number the transport process should be independent of far-field changes in the flow (in contrast with low Peclet number situation).

**Table 2.1 Summary of $Sh$ vs. $Pe$ correlation from Leal’s work**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure conduction</td>
<td>$Sh = 2$</td>
</tr>
<tr>
<td>Low $Re$, low $Pe$</td>
<td>$Sh = 2 + A \cdot Pe$</td>
</tr>
<tr>
<td>Low $Re$, high $Pe$</td>
<td>$Sh = A \cdot Pe^{1/3}$</td>
</tr>
<tr>
<td>Low $Re$, high $Pe$, slip boundary conditions</td>
<td>$Sh = A \cdot Pe^{1/2}$</td>
</tr>
<tr>
<td>Closed streamline</td>
<td>$Sh = 8.9$</td>
</tr>
</tbody>
</table>

The specific form of the relationship has also been examined experimentally by Steinberger et al. (1960), for example, who studied the dissolution of single benzoic acid spheres in water. Bowman et al. (1961) and Friedlander (1975) addressed the same problem by solving the Stokes equation and convection-diffusion equation to obtain concentration profiles around a sphere. All of these authors obtained similar power correlations between Sherwood number and Peclet number (or Reynolds number), as summarized in Table 2.2.

**Table 2.2 Mass transfer coefficient correlations for dissolution from single object**

<table>
<thead>
<tr>
<th>Mass transfer coefficient correlation</th>
<th>Conditions</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sh = 0.978Pe^{1/3}$</td>
<td>Thin boundary layer, large $Pe$</td>
<td>Single sphere in the fluid</td>
</tr>
<tr>
<td>$Sh = 2 + \frac{9}{16} Pe + \frac{9}{64} Pe^2 + \cdots$</td>
<td>Thick boundary layer, small $Pe$</td>
<td></td>
</tr>
<tr>
<td>$Sh = 0.89Pe^{0.33}$</td>
<td>Boundary layer flow</td>
<td>Single sphere</td>
</tr>
<tr>
<td>$Sh = Sh_0 + 0.347(Re Sc^{1/2})^{0.62}$</td>
<td>Dissolutions of single benzoic acid sphere in columns</td>
<td>Steinberger, et al. 1960</td>
</tr>
</tbody>
</table>
2.2.2 Mass transfer in packed beds

The prediction of particle-to-fluid mass transfer in packed beds and porous media is important for a number of chemical and environmental processes. Examples include catalytic or ion exchange reactors (Mak et al., 1993), chromatography, drug release devices (Varelas et al., 1995), and the dissolution of contaminants in groundwater (Geller et al., 1993). Prediction of mass transfer rates in these and other situations can be difficult because of the strong dependence of mass transfer on hydrodynamics near the particle-fluid interfaces. These effects are usually lumped into empirical equations that vary considerably depending on properties of the media and the fluids. Hence, improving fundamental knowledge of mass transfer in disordered systems is an important step toward developing more general design equations as well as modeling mass transfer in cases where empirical equations are not effective.

Early experiments to quantify the mass transfer in packed beds were made by measuring the dissolution of benzoic acid spheres in a packed bed (Williamson et al., 1963). These results showed that the $J$ factor for mass transfer decreases as Reynolds number to the $-0.66$ power for Reynolds numbers above approximately 0.1. Many other dissolution experiments in packed beds were conducted and selected results are summarized in Table 2.3.

Besides experimental work, there have been numerous modeling works for dissolution in packed beds. Pfeffer et al. (1964) obtained the same functionality discussed above using a sphere-in-cell model. The system is treated as a set of concentric spheres. Each sphere consists of a particle and the surrounding fluid envelope, which has a free outside surface. The entire disturbance due to each particle is confined to the cell of fluid with which it is associated. The final result was $Sh$ is proportional to $Pe^{1/3}$ for low Reynolds and high Peclet numbers. Their work also showed that mass transfer rates increase as bed porosity decreases, but quantitative results
were limited to high Peclet numbers since the model incorporated a thin diffusion boundary layer at the sphere surface.

Table 2.3 Mass transfer coefficient correlations in packed beds

<table>
<thead>
<tr>
<th>Mass transfer coefficient correlations</th>
<th>Conditions</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \textit{Sh} = 2.4 \cdot \varepsilon^{0.67} \cdot \textit{Re}^{0.33} \cdot \textit{Sc}^{0.42} )</td>
<td>( 0.08 &lt; \textit{Re} &lt; 125 )</td>
<td>Williamson et al., 1963</td>
</tr>
<tr>
<td>( \textit{Sh} = 1.09 \cdot \varepsilon^{-1} \cdot \textit{Pe}^{0.33} )</td>
<td>( 0.0026 &lt; \textit{Re} &lt; 55 ) ( 0.35 &lt; \varepsilon &lt; 0.75 ) ( 950 &lt; \textit{Sc} &lt; 70600 )</td>
<td>Geankoplis et al., 1966</td>
</tr>
<tr>
<td>( \textit{Sh} = 0.25 \cdot \varepsilon^{-1} \cdot \textit{Pe}^{0.69} )</td>
<td>( 55 &lt; \textit{Re} &lt; 1500 )</td>
<td></td>
</tr>
<tr>
<td>( \textit{Sh} = 1.26 \left( \frac{\varepsilon}{\textit{We}} \right)^{1/3} \textit{Pe}^{1/3} )</td>
<td>( \textit{Sc} &gt; 100 ) Low ( \textit{Re} ), High ( \textit{Pe} )</td>
<td>Pfeffer et al., 1964</td>
</tr>
<tr>
<td>( \textit{Sh} = \frac{\phi_s}{6(1-\varepsilon)^2} \textit{Pe} )</td>
<td>( \textit{Pe} &lt; 10 )</td>
<td>Kunii et al., 1966</td>
</tr>
<tr>
<td>( \textit{Sh} = \frac{1 - (1/L) \int_0^L \text{erf} \left( \frac{x}{2d_p} \right) (\textit{Pe} \gamma)^{1/2} dx}{1 + 1/L \int_0^L \text{erf} \left( \frac{x}{2d_p} \right) (\textit{Pe} \gamma)^{1/2} dx} )</td>
<td>High ( \textit{Re} ) and high ( \textit{Pe} )</td>
<td>Doytcheva et al., 1993</td>
</tr>
<tr>
<td>( \textit{Sh} = 0.55 + 0.25 \cdot \textit{Pe}^{1.5} )</td>
<td>( 0.5 &lt; \textit{Pe} &lt; 100 )</td>
<td>Pfannkuch et al., 1984</td>
</tr>
</tbody>
</table>

Nelson et al. (1975) used a similar concept with different boundary conditions. The Sherwood number was derived based on the concentration gradient at the sphere surface. Results at two limiting cases are presented below.

\[
\lim_{\varepsilon \to 1} \textit{Sh} = 2 + \alpha \textit{Re}^{1/2} \textit{Sc}^{1/3} \tag{2-11}
\]

\[
\lim_{\textit{Re} \to 0} \textit{Sh} = \frac{1}{(1-\varepsilon)^{1/3}} \left[ \frac{1}{(1-\varepsilon)^{1/3} - 1} \right] \frac{\alpha^2}{2} \textit{Re} \textit{Sc}^{2/3} \tag{2-12}
\]

This sphere-in-cell model was also used by Coutelieris et al. (1995) to find the velocity profile in an array of spheroidal particles. An analytic solution to the high-Peclet-number concentration field for adsorption at the particle surface showed that when the long axis of the
spheroids are normal to the flow direction, the thinnest part of the concentration boundary layer is along the equator rather than at the front stagnation point. Mass transfer was found to be proportional to $Pe^{1/3}$ for all orientations. The same authors later refined the boundary conditions used with the convection-diffusion equation and performed a numerical solution that was valid to Peclet numbers as low as 5.

The relationship between Sherwood and Peclet numbers is known to be linear in the $Pe \to 0$ limit, but this behavior has also been observed at finite Peclet numbers in heterogeneous packings. Kunii et al. (1967) gathered a large set of experimental data showing a nearly linear relationship between Peclet number and Nusselt number for Peclet numbers less than 10. To reproduce this $Nu \propto Pe$ behavior mathematically, they used a channeling model, where the system is modeled as particle aggregates with channels between them. Equilibrium is assumed in the stagnant block. 2-D mass transfer is restricted to molecular diffusion in the direction of flow, which is assumed to be plug flow. The result is that Sherwood number is proportional to Peclet number for Peclet numbers less than 10.

Martin (1978) used a somewhat similar technique, modeling a higher porosity region within a uniform packing (with the high porosity regions representing wall effects or packing nonuniformity). The Ergun equation was used to predict the fraction of flow through the two regions. This approach showed that the Peclet number exponent may exceed unity in cases where the Peclet number is low and inertial effects cause the fraction of flow in the low-porosity zone to increase with increasing total flowrate. Doytcheva (1993) studied the dissolution of a microsphere in fixed bed and obtained a relationship using an active plug flow cell model. The final result was that Sherwood number is proportional to Peclet number at high Reynolds numbers and high Peclet numbers. Rexwinkel et al. (1997) used both published and new experimental data to
further interpret low Peclet number results. It was demonstrated that when dilute beds (containing mostly inert particles) are used for low Peclet number experiments, the measured mass transfer rate depends on the relative position of active particles, which in some cases may lead to the misinterpretation of measured mass transfer coefficients.

Some correlations in packed beds are listed in Table 2.3. All of them show similar power-law behavior but important differences in the functionality arise. However, few works have addressed the reasons for these variations in functionality.

2.2.3 Mass transfer in porous media

Numerous engineering examples can be found where mass transfer does not occur uniformly within a material. However, the case that best illustrates this phenomenon is probably the NAPL dissolution problem discussed above. At the continuum level, this dissolution is modeled using lumped mass-transfer coefficients, which in turn is quantified using empirical equations. The empirical equations used in groundwater modeling are based loosely on the chemical engineering equations discussed in the previous section, but because of heterogeneity and other factors in the subsurface, additional terms are often introduced. The result is a large number of equations with various forms and functionalities (as in Table 2.4), which is indicative of the complexity of the mass transfer processes. One of the significant problems to this strongly empirical approach is that the design equations do not provide effective tools for studying underlying fundamentals related to the mass transfer process.

NAPL dissolution in porous media is relatively complicated because the residual saturation, shape and size of NAPLs in the porous media and flow pattern are all influenced by the structure of system. Traditionally, equilibrium was assumed when modeling contaminant dissolution, which means the concentration of a contaminant in any phase is defined in terms of its
concentration in other phases at the same location by an equilibrium partitioning relationship (Abriola et al., 1985). However, field data frequently indicate that the concentration of solutes in groundwater at NAPL contamination sites are lower than the corresponding equilibrium value (Mercer et al., 1990). Such data suggest that certain processes limit the extent of mass transfer from NAPLs to the aqueous phase. The non-equilibrium condition can be attributed to the following phenomena: 1) rate-limited interface mass transfer; 2) physical bypassing of the mobile phase around the contaminated region due to the relative permeability effects and heterogeneity; 3) the presence of low NAPL concentrations; 4) diffusion of one component in multiphase NAPLs; 5) the presence of porous media heterogeneity at various scales (Mayer et al., 1996; Powers et al., 1992).

The following rate-limited model is frequently used to describe the fate of NAPLs in the porous media (Powers et al., 1992).

$$\varepsilon \cdot s_w \frac{\partial C_i}{\partial t} = \nabla \cdot \left( \varepsilon \cdot s_w \cdot D_h \cdot \nabla C_i \right) - q \cdot \nabla C_i + \left(1 - \frac{C_i}{\rho_w}\right) F_i^0 a_0 \quad (2-13)$$

The change of NAPL concentration in the aqueous phase is attributed to the dispersion, convection and interface mass transfer. If porosity ($\varepsilon$), water saturation ($s_w$), Darcy velocity ($q$), dispersion coefficient ($D_h$) and mass flux ($F_i^0$) from the NAPLs to water phase are known, the transient effluent concentration ($C_i$) at some downstream point can be determined. Mass flux from NAPL phase to aqueous phase is expressed as:

$$F_i^0 = k_i \cdot (C_i^* - C_i) \quad (2-14)$$

where $C_i^*$ is NAPL concentration at interface and $C_i$ is NAPL concentration in aqueous phase. $C_i^*$ can be considered as the NAPL equilibrium concentration in aqueous phase. A large amount of research has concentrated on determining the mass transfer coefficient $k$ for
groundwater systems. Experiments conducted in 1-D porous columns indicated that

Sherwood number is a function of the Reynolds number, Schmidt number \((Sc = \frac{D \cdot \mu}{\rho})\), particle size distribution and NAPL saturation. Some relationships are listed in Table 2.4.

Because NAPLs trapped in the soil have random shape and size, it is impossible to determine accurately the interfacial area between NAPLs and aqueous phase. So \(k\) and \(a_0\) are often lumped together to form the mass transfer rate coefficient \(k'\).

\[
k' = k \cdot a_0
\]

Accordingly a modified Sherwood number is defined as:

\[
Sh' = \frac{k' \cdot l_c^2}{D}
\]

**Table 2.4 Empirical mass transfer coefficient correlations in porous media**

<table>
<thead>
<tr>
<th>Mass transfer (rate) coefficient correlation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sh = 1.1068 \cdot (\varepsilon \cdot s_w)^{-1} \cdot Re^{0.28} \cdot Sc^{0.33})</td>
<td>Dwivedi et al., 1977</td>
</tr>
<tr>
<td>(Sh = Sc^{0.33} \cdot (\varepsilon \cdot s_w)^{-1} \cdot (0.765Re^{0.18} + 0.365 \cdot Re^{0.614}))</td>
<td></td>
</tr>
<tr>
<td>(Sh = 0.55 + 0.25 \cdot Pe^{1.5})</td>
<td>Pfannkuch et al., 1984</td>
</tr>
<tr>
<td>(Sh' = 12.0 \cdot \theta_n^{0.73} \cdot Re^{0.75} \cdot Sc^{0.5})</td>
<td>Miller et al., 1990</td>
</tr>
<tr>
<td>(Sh' = 57.7 \cdot d_{so}^{0.64} \cdot Re^{0.61} \cdot U_i^{0.41})</td>
<td>Powers et al., 1992</td>
</tr>
<tr>
<td>(Sh' = 70.5 \cdot \theta_n^{4/9} \cdot Re^{1/3} \cdot \theta_{m_i}^{5/9} \cdot \phi_{ai}^{-11/9} \cdot \left(\frac{dp}{d_{ni}}\right)^{5/3})</td>
<td>Geller et al., 1993</td>
</tr>
<tr>
<td>(Sh' = 340 \cdot Re^{0.71} \cdot \phi_{ai}^{-1} \cdot \phi_{ai}^{0.87} \cdot (\frac{X}{dp})^{-0.31})</td>
<td>Imhoff et al., 1994</td>
</tr>
<tr>
<td>(Sh' = 4.13 \cdot Re^{0.598} \cdot \delta^{0.673} \cdot U_i^{0.369} \cdot \left(\frac{\theta_n}{\theta_{n,a}}\right)^{(0.518 + 0.114 \delta + 0.10 U_i)})</td>
<td>Powers et al., 1994</td>
</tr>
</tbody>
</table>
Numerous experiments have been conducted in 1-D and 2-D columns to study the mass transfer rate coefficient for NAPL dissolution in porous media. Miller et al.’s result (1990) indicated that in homogeneous media the mass transfer coefficient is related to the aqueous phase velocity and NAPL saturation level but not significantly to the mean particle size. Geller et al.’s model (1993) represented the NAPLs as isolated spheres that shrink with dissolution. The model accounted for the reduced permeability of a region of residual NAPLs relative to the permeability of the surrounding clean media that causes the flowing water to partially pass through the residual NAPLs. Imhoff et al. (1993) used a different experimental technique and obtained similar results in a homogeneous system.

Real subsurface media are almost exclusively heterogeneous, which has led to studies of NAPL dissolution in heterogeneous systems. Powers et al. (1992) explored the influences of porous media characteristics, NAPL type and aqueous phase velocity on NAPL dissolution rate through evaluation of series of laboratory column studies. Results showed that entrapped NAPL distribution depends on the porous media grading and grain size and revealed a dependence of dissolution rate on NAPL distribution properties as well as aqueous phase velocity. A phenomenological model for mass transfer was developed that incorporated the grain size parameters as a surrogate measure of NAPL distribution in the mass transfer rate coefficient correlation. Powers et al. (1994) also performed similar experiments to study the transient nature of the dissolution process. These experiments indicated a more complex phenomenon than the uniform propagation of a mass transfer zone. As demonstrated by experiment, effluent concentrations well below the equilibrium saturation were observed for long times. Furthermore, these effluent tails were more pronounced in graded media where the initial ganglia size distribution was broader.
Illangasekare et al.’s experiments (1995) indicated that migration path and velocity of a NAPL plumes were considerably altered by the presence of heterogeneity within the soil. These heterogeneities produced macro-scale entrapment in which saturations were much higher than the residual saturation produced in homogeneous formations. This result suggests that models for homogeneous systems need modification before they can simulate the complex entrapment and transport behavior that occurs under heterogeneous conditions.

Manivannan et al.’s experiment (1996) in a 2-D heterogeneous flow cell showed some unexpected results, in which the effluent concentration rose over time. It was suggested that sufficient water flow through the NAPL contaminated coarse sand zone to cause an increase in the relative permeability and effluent concentration over time. Therefore not only the porous media structure, but also NAPL distribution can influence the aqueous phase flow pattern.

Some mathematical models that were developed to study NAPL dissolution in porous media considered the influence of heterogeneity. Sørensen et al. (1995) demonstrated the effect of heterogeneity on NAPL dissolution. Through the use of a simple two-domain and parallel column model, they suggested that the non-equilibrium dissolution of NAPLs might contribute to non-uniform flow patterns and NAPL distribution. Their studies also demonstrated that quantification of the heterogeneous NAPL distribution is necessary to adequately model the NAPL dissolution process. Mayer’s 2-D model (1996) simulated the case of NAPL emplacement and dissolution in both homogeneous and heterogeneous porous media systems. The heterogeneity was expressed by a stochastic realization of the scaling function $\delta(x)$ which was approximated by a log-normal distribution. The simulations demonstrated that spatial statistics related to the porous media properties, and the corresponding spatial distribution of residual NAPLs are important determinants of NAPL dissolution. The observed decreases in NAPL
dissolution rate were attributed to the existence of relatively immobile regions of NAPLs with saturations greater than the residual saturation, or so-called NAPL pools.

### 2.2.4 The effect of heterogeneity on mass transfer at pore-scale

The impact of heterogeneity of porous media on mass transfer has been addressed by previous studies. Brusseau (1991) modeled the transport of organic chemicals in heterogeneous porous media. The model accounted for media heterogeneity, and a good match was achieved between the model and experimental data. Haggerty et al. (1998) examined the variability in mass transfer rates from experimental work of Farrel (1994a, b) and quantified the effects of multiple, simultaneous mass transfer processes on unsaturated column experiments using a diffusion model with statistical distribution of diffusion coefficients. They concluded that even in relatively homogeneous porous media, extreme variability in diffusion coefficients must be invoked to represent mass transfer in the experiments that examined. Also, models using lognormal distributions of diffusion coefficients generally represent mass transfer much better than models using either single coefficient or two diffusion rate coefficients. Further, Kennedy et al. (1997) placed sphere and pendular rings of TCE in an artificial porous media consisting of a single layer of glass beads. Because of the simple geometry of the trapped phase, pore-scale mass transfer coefficients could be calculated. A considerable scatter in Sherwood number was observed at a given mean flux. It was hypothesized that this variation in local mass transfer rates is caused by variations in local pore velocity. But no connection between local structure and local Sherwood number was established.

The average mass transfer coefficients used to predict dissolution rates represent spatially averaged quantities, while at the pore scale, spatial variations in the mass-transfer rate will occur because of the disorder and heterogeneity found in most porous medium. Previous experimental
and modeling works revealed the spatial variances of mass transfer rate and the importance of using mass transfer rate distribution to the prediction of mass transfer in porous media. However, those studies didn’t give fundamental explanations for the mass-transfer heterogeneity. A very detailed understanding of the micro-scale process affecting the trapping and removal of residual contamination can be achieved by the application of a pore-scale numerical model.

A Network model is one type of pore-scale model. Lowry et al. (1995) modeled the porous media as a 3-D network of pore bodies and throats. A random network approach was developed that provided stochastic geometry and variable connectivity. Immiscible displacement occurred via piston-displacement and a simulated film-flow mechanism. Residual ganglia were trapped during imbibition. Wetting phase continuity was maintained during drainage, disallowing the entrapment of wetting phase ganglia. Results showed that pore-scale geometry significantly affects the residual saturation, the ganglia volume distribution, and the interfacial area between nonwetting phase and wetting phase. Thus, a constitutive theory for NAPL dissolution in porous media should incorporate certain relevant pore-scale parameters in order to be valid over a wide range of conditions and porous media types. Dillard et al. (2000) also simulated NAPL dissolution in porous media using network model. They simplified the network geometry to a lattice of cubic chambers and rectangular tubes that represent pore bodies and pore throats. The pore-size distribution of the network was calibrated by matching simulated and experimental drainage and imbibition capillary pressure–saturation curves. The network model reproduced the observed hydraulic conductivity and produced relative permeability curves that were representative of a consolidated porous media. The model successfully predicted the solute concentration versus Peclet number and modified Sherwood number versus Peclet number, which compared favorably with experimental results of Powers et al. (1992). The model also
accounted for the impact of changes in NAPL volume by recomputing the spatially variable map of modified Sherwood number, $Sh'$.

What the network models capture are the averaged effects, but without real pore-scale geometry and flow information. They are not able to provide a fundamental representation of local mass transfer rate (coefficient) heterogeneity. Wang et al. (1997) examined the heat and mass transfer from ordered and random arrays of cylindrical particles to the surrounding fluid for conditions of low Reynolds numbers and high Peclet numbers. Detailed flow in the immediate vicinity of the particles was solved with multipole expansions and the heat transfer problem was solved by integrating the boundary layer equation between stagnation points on the particle surface. This approach allowed differentiation between regions of the surface that are exposed to ‘fresh’ fluid versus regions of the surface next to recirculating fluid where the thermal boundary layer is thicker. For disordered arrays, the overall Nusselt number was found by averaging over all particles. Tables II and III from their paper show that the average rate of mass transfer is generally lower in random packings (except when flow is aligned with a regular array, in which case the recirculation patterns have a larger impact).

Stochastic modeling has frequently been used to obtain concentration profiles or mass transfer rates. This method avoids solving the differential equations. The random walk, a simple and efficient stochastic method for particle tracking, has been applied to many studies, such as dispersion in porous media (Sternberg et al., 1996), injection peaks in columns (Wentzell et al., 1993), and sorption in heterogeneous porous media (Berglund et al., 1996). The random walk method has the following advantages: 1) it is simple to implement; 2) the total concentration profile is not needed; 3) numerical errors can be reduced as compared to finite difference and finite element methods; 4) It allows a large range of Peclet numbers to be modeled. Bekri (1995)
described the details of random walk simulations and applied this method to the study of
dissolution in porous media. The result indicated that when the process is not reaction-limited,
the dissolution pattern and rate depend on the dominant transport process. If $Pe < 1$, dissolution
occurs around the wider parts of pore space. If convection is dominant, dissolution is mostly
localized along the main flow path and dissolution rate increase with flow rate. Verberg et al.
(2000) simulated the acid erosion process in a fractured material. The stochastic particles from
the erosion source were traced and the local dissolution rate was obtained from the flux of tracer
particles across the surfaces. Quite different patterns of dissolution were found at large and small
length scales, which suggests a strong coupling between transport and morphology.

The quality of a pore-scale model used for studying the mass transfer in porous media
strongly depends on the accuracy of velocity solution. Usually the velocity profile must be
solved using an appropriate numerical method. It is computationally intensive and difficult to
obtain these solutions for heterogeneous materials, particularly if streamline resolution is
required and if the domain is large. Liu et al. (2002) solved the Stokes equation in 2-D packed
bed. Domain decomposition is used to avoid generating a full matrix (which for this size of
problem would be essentially unsolvable). The discretized, boundary-integral form of the Stokes
equation is applied to each subdomain. This procedure gives a large, block-diagonal matrix with
sparse off-diagonal terms and the matrix equation is solved using a preconditional biconjugate
gradient method, giving boundary stresses and velocities through the flow domain. Point
velocities can be obtained quite rapidly by performing a local boundary integral calculation over
a single subdomain once the above equation is solved. This method provides very accurate
solution for flow through 2-D packed beds. In this study, the high resolution network model (
HRNM developed by Liu et al. (2002) is used to obtain the velocity solution. Subsequently, a random walk is used to study the impact of local hydrodynamics on local mass transfer.
CHAPTER 3

EXPERIMENTAL STUDY OF MASS TRANSFER IN PACKED BEDS

To experimentally examine the variation in local mass transfer rates, experiments were conducted to determine the mass transfer coefficient at the interface of single-benzoic acid spheres embedded in disordered (but macroscopically uniform) packed beds. The rationale for this approach is twofold. First, the interface area is known precisely (in contrast to dissolution studies using nonaqueous fluids, where the interface area is incorporated into a lumped mass transfer rate coefficient). Second, the use of a single sphere allows for the quantification of mass transfer at a single point in the packing. Hence, the benzoic acid sphere acts as a probe for effects caused by local structure and hydrodynamics. Unfortunately, the approach does not allow for direct analysis of local structure or hydrodynamics near the dissolving interface. Instead, it makes use of statistical variations in mass transfer from one location in the bed to another to infer certain phenomenological behavior. The effects of local hydrodynamics on mass transfer behavior are examined in later chapters.

3.1 MATERIALS AND EXPERIMENTAL PROCEDURE

3.1.1 Benzoic acid spheres

Solid benzoic acid spheres were produced using a precisely machined aluminum mold with hemispheric holes in each half of the mold. To create the spheres, benzoic acid powder was melted and injected into the mold, at which point it was cooled and separated into two parts to remove the spheres. Spheres of diameter 6.4, 4.8, 3.2, and 2.4 mm were created using the mold. The final sizes were adjusted by placing the spheres in warm water with agitation.
Sphere diameters were determined by measuring the mass and by imaging the sphere through a stereo-zoom microscope. The imaging procedure was also used to ensure that a spherical shape was obtained and that no significant defects existed on the sphere surface.

### 3.1.2 Column dissolution tests

Three glass columns were used for the experiments with inner diameters of 25, 50 and 150 mm, respectively. The columns were manufactured specifically for these tests and were designed to ensure uniform inlet and outlet flow and to minimize dead volume outside the packing. Figure 3.1 shows a schematic of the experimental setup. Table 3.1 shows properties of the homogeneous packing and Table 3.2 shows the distributions of sphere sizes used to create the heterogeneous packings in the columns. The size distribution for the two heterogeneous packings is identical, but the mean diameter for the larger packing is three times greater. In all columns, benzoic acid spheres of 3.0 mm diameter were used, which allowed us to analyze the dissolution of both large and small spheres relative to the average sphere diameter in a packing. This approach was required for two reasons. First, small-diameter benzoic acid spheres were difficult to create. Second, when small benzoic acid spheres (i.e., ~1.0 mm diameter) were used in the 50 mm column, effluent concentrations were near the limit of detection, making the mass-transfer analysis less accurate. Column flow rates were adjusted so that the ranges of Reynolds and Peclet numbers were identical in the two heterogeneous packings.

<table>
<thead>
<tr>
<th>Table 3.1 Experimental conditions for homogeneous packed bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter</td>
</tr>
<tr>
<td>Bed height</td>
</tr>
<tr>
<td>Particle size of porous media</td>
</tr>
<tr>
<td>Porosity</td>
</tr>
<tr>
<td>Benzoic acid sphere size</td>
</tr>
<tr>
<td>Flow rate</td>
</tr>
</tbody>
</table>
Table 3.2 Experimental conditions used with polydisperse packings

<table>
<thead>
<tr>
<th></th>
<th>Bed1</th>
<th>Bed2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column ID (mm)</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>Column length (cm)</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>Sphere diameter in bed (mm)</td>
<td>0.6 (10%)</td>
<td>1.8 (10%)</td>
</tr>
<tr>
<td></td>
<td>1.0 (30%)</td>
<td>3.0 (30%)</td>
</tr>
<tr>
<td></td>
<td>2.0 (30%)</td>
<td>6.0 (30%)</td>
</tr>
<tr>
<td></td>
<td>3.0 (20%)</td>
<td>9.0 (20%)</td>
</tr>
<tr>
<td></td>
<td>6.0 (10%)</td>
<td>18.0 (10%)</td>
</tr>
<tr>
<td>Average sphere diameter (mm)</td>
<td>2.2</td>
<td>6.6</td>
</tr>
<tr>
<td>Benzoic acid sphere diameter (mm)</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>$D_{benzoic acid} / D_{mean}$</td>
<td>1.36</td>
<td>0.45</td>
</tr>
<tr>
<td>Flow rates tested (cm$^3$/min.)</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Schmidt number</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Reynolds number tested</td>
<td>1077</td>
<td>1077</td>
</tr>
<tr>
<td></td>
<td>0.718</td>
<td>0.718</td>
</tr>
<tr>
<td></td>
<td>0.539</td>
<td>0.539</td>
</tr>
<tr>
<td></td>
<td>0.359</td>
<td>0.359</td>
</tr>
<tr>
<td></td>
<td>0.180</td>
<td>0.180</td>
</tr>
</tbody>
</table>
To perform a dissolution test, a benzoic acid sphere was placed randomly into the packing, ensuring only that the sphere was not near the inlet or outlet and was at least a couple of sphere diameters away from the wall. The dissolution test itself consisted of injecting deionized water upward through the column using a continuous flow syringe pump. The effluent from the column was directed through a flow cell, where the UV absorbance was recorded at 60-second intervals. Flow at a single injection rate continued until steady state was reached, thus giving dissolution data that could be translated into a steady-state mass transfer coefficient. Flowrates were changed from low to high (see Table 3.1 and Table 3.2 for specific values) because the higher flowrate conditions reached steady state more quickly. This approach minimized the amount that a sphere dissolved during the initial data points from the five flowrates tested. During a test, a sphere would lose at most 6% of its surface area.

3.1.3 RTD measurement

Residence time distributions (RTDs) were measured for every packing by performing tracer tests at the conclusion of a dissolution test. The RTDs were obtained by injecting a pulse of potassium dichromate immediately after the final mass transfer data point was measured. The peak wavelengths for benzoic acid and potassium dichromate are 225 and 360 nm respectively. Therefore, the presence of benzoic acid during the tracer test did not affect the absorbance measurement for potassium dichromate. This fact was confirmed by performing RTD tests with and without benzoic acid present in solution. The RTDs were calculated based on the effluent concentration and analyzed to ensure that macroscopic flow distributions were similar for each packing. For example, Figure 3.2 shows some RTD curves for different disorder packed beds. Tests in beds with abnormal RTD performance, such as the dotted color curves, were discarded.
3.2 EXPERIMENTAL RESULTS

3.2.1 Mass transfer in monodisperse packings

An initial set of experiments was performed in packings composed of uniform glass spheres 3 mm in diameter. Each packing contained a single, dissolving sphere of similar size as the glass sphere's (2.76-3.01 mm). For each packing, a single, steady-state mass transfer coefficient was calculated at $Re=1.68$ and $Pe=1690$. By measuring the mass transfer at only a single rate, dissolution of the spheres was minimized, thus enabling the packing to be disassembled and repacked with the same sphere in a different random location (if its size and shape were still suitable). This approach allowed observation of the same sphere’s behavior at four to five different locations within the packings, which was important to ensure that variations in the mass transfer rate were caused by local structure and hydrodynamics rather than undetectable differences between individual benzoic acid spheres.

Table 3.3 lists local mass transfer coefficients for 16 different sites within the packings (obtained using four different spheres).
Table 3.3 Mass transfer coefficient for single spheres in uniform packed bed

<table>
<thead>
<tr>
<th>Sphere No.</th>
<th>Diameter (mm)</th>
<th>$k \times 10^3 \text{cm/s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.84</td>
<td>0.81</td>
</tr>
<tr>
<td>1</td>
<td>2.89</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>2.76</td>
<td>0.96</td>
</tr>
<tr>
<td>1</td>
<td>2.92</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>2.77</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>2.82</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>2.87</td>
<td>1.02</td>
</tr>
<tr>
<td>1</td>
<td>2.93</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>2.98</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>3.01</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>2.81</td>
<td>1.12</td>
</tr>
<tr>
<td>1</td>
<td>2.79</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>2.86</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>2.78</td>
<td>1.23</td>
</tr>
<tr>
<td>3</td>
<td>2.92</td>
<td>1.48</td>
</tr>
<tr>
<td>1</td>
<td>2.86</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Three important observations can be made. First, the local rate of mass transfer (meaning averaged over a single-sphere surface) varies by a factor of two, even in this highly uniform packing. Second, this effect is clearly caused by the random positioning of the dissolving sphere rather than an anomalous characteristic of any one sphere or by erroneous surface-area measurement. The wide variation in the five mass transfer measurements obtained using sphere #1 emphasizes this second point. Third, the mass transfer rates obtained for any one sphere did not increase or decrease monotonically during its series of runs (e.g., the minimum and maximum rates for sphere 1 were measured at locations 3 and 4 out of five total). This last observation demonstrates that the slight dissolution of a sphere over time is not responsible for the observed variation in mass transfer rates.

3.2.2 Mass transfer in polydisperse packings

The results from the monodisperse packing provide a quantitative baseline for the phenomenon being examined. However, a greater focus was placed on polydisperse packings for
a couple of reasons. First, they provide more disorder at the pore-scale, and thus were more appropriate for the study being conducted. Second, with a distribution of sphere diameters, more than one size of benzoic acid sphere (relative to the mean diameter) could be introduced as a surrogate sphere in the packing. This procedure in essence allows the characteristic length for averaging the local mass transfer coefficient to be varied. As described previously, the relative diameter was changed by holding the benzoic acid sphere diameters constant and using two column sizes. The larger column was a scaled replica of the small column in all respects except for length. Dimensionless numbers were held constant for the two column sizes.

Each dissolution experiment in the polydisperse beds included mass transfer measurements at different flowrates (see Table 3.2). This approach elucidated not only differences in the mass transfer coefficients with location but also differences in Sherwood number versus Peclet number functionality.

Figure 3.3 is a plot of Sherwood number versus Peclet number for $D_{b,a}/D_{mean} = 1.36$. The lines on the plot are least-squares fits for each individual sphere (i.e., each for a different random location within a packed bed). These results show clearly that the mass transfer coefficient for single spheres in the packings does not conform to a single $Sh$ versus $Pe$ relationship, which would be the case if the bed were uniform at the pore scale. Instead, there exists a spatial distribution of mass transfer coefficients at any one Peclet number, as well as a distribution of Peclet number exponents.

Clearly, some data sets in Figure 3.3 do not conform exactly to the power law relationship, as evidenced by lines that do not pass directly through data points. When these cases are examined individually (see Figure 3.4 for three examples, including the worst fit from all the data sets) two observations can be made. First the curvature is smooth and concave down. Second, the overall
deviation from a linear fit sometimes exceeds what would be expected from experimental error alone. (Estimates of maximum experimental error are shown in Figure 3.4. Its source is mostly from calculation of the surface area of dissolving spheres).

The above observations suggest phenomenological behavior rather than experimental error or an artifact. Two plausible explanations exist. First, the data points were obtained moving from high to low Peclet numbers, meaning that the interfacial area of the benzoic acid spheres was slightly lower at lower Peclet numbers. (This decrease in area was not accounted for when calculating mass transfer rates because slight changes to a non-spherical shape would tend to offset it.) However, the error bars do account for this possible decrease in area, so it is clearly not the sole reason for the nonlinear form of the data. A more likely explanation is the increase in the power-law exponent as the Peclet number decreases. This trend is consistent with the behavior

Figure 3.3 $Sh$ vs. $Pe$ for 28 independent dissolving spheres: $D_{b,a}/D_{mean}=1.36$
shown in Figure 3.4. Notwithstanding the curvature observed in many of the data sets, a linear least-squares analysis was used for reasons of simplicity and so that the equations for the local behavior remained in analogous form to accepted empirical relationships (i.e. power law form).

Figure 3.4 Data for three dissolving spheres from the Figure 3.3 data set showing the quality with which the \( Sh \) vs. \( Pe \) relationship is satisfied

Figure 3.5 shows the complete data set for the larger column, in which \( \frac{D_{b,a}}{D_{mean}} = 0.455 \) (meaning that the diameter of the dissolving sphere was small compared to the mean for the column).

It was expected that these data would exhibit a larger distribution of mass transfer coefficients than for \( \frac{D_{b,a}}{D_{mean}} = 1.36 \) since velocity fluctuations are less likely to be averaged toward the mean in a smaller region of flow. Although the data are somewhat indicative of this
trend, it is not as significant as we expected. The two cases can be compared using Figure 3.3, Figure 3.5 and the statistics in Table 3.4.

![Figure 3.5 Sh vs. Pe for 20 independent dissolving spheres: $D_{\text{b.a.}}/D_{\text{mean}} = 0.455$](image)

**Table 3.4** Average values of $Sh$ and standard deviation as a function of $Pe$ for the heterogeneous packed beds

<table>
<thead>
<tr>
<th>$Pe$</th>
<th>$D_{\text{b.a.}}/D_{\text{mean}} = 1.36$</th>
<th>$D_{\text{b.a.}}/D_{\text{mean}} = 0.455$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean $Sh$</td>
<td>S.D.</td>
</tr>
<tr>
<td>181</td>
<td>29.7</td>
<td>5.4</td>
</tr>
<tr>
<td>361</td>
<td>40.1</td>
<td>6.5</td>
</tr>
<tr>
<td>542</td>
<td>46.2</td>
<td>7.2</td>
</tr>
<tr>
<td>722</td>
<td>50.1</td>
<td>7.4</td>
</tr>
<tr>
<td>1080</td>
<td>57.1</td>
<td>8.4</td>
</tr>
</tbody>
</table>
3.3 DATA ANALYSIS

3.3.1 Local Peclet number

Figure 3.3 and Figure 3.5 show that a spatial distribution of local mass transfer coefficients exists at any one average Peclet number. Additionally, the differences in slope indicate that the power-law exponents also vary locally. We address the most obvious aspect of the data first. The marked difference in the intercepts of the lines suggests that if one were to write the equation

\[ Sh = A \cdot Pe^m \]  

(3-1)

for each sphere in the packing, the coefficient \( A \) would take on a distribution of values so as to give the appropriate distribution of local mass transfer coefficients (assuming for the moment that \( m \) can be considered constant). Since the coefficient \( A \) contains information about the shape of the streamlines (see e.g., Friedlander et al. 1957, Leal 1992), one would have physical justification for allowing it to vary from one particle to the next. However, the Peclet number seems to be a better candidate for assigning distributed values because of its role as a lumped parameter describing the relative importance of convective versus diffusive transport, which presumably varies at the pore scale.

To implement this approach mathematically the equation for the local Sherwood number is written as

\[ Sh_i = A \cdot (x_i \cdot Pe)^m \]  

(3-2)

where \( Sh_i \) indicates a discrete set of local Sherwood numbers (e.g., one for each particle in the bed) and \( x_i \) are dimensionless corrections to the global Peclet number. The term \( x_i Pe \) is thus a local Peclet number averaged over the neighborhood of a single sphere \( i \).

To determine the distribution \( x_i \) for the data from Figure 3.3 or Figure 3.5, we assume for the moment that \( A \) and \( m \) in equation (3-2) are spatially invariant. A least-squares regression is
performed to find \( A, \ m, \) and \( x_i \) (using an entire data set from one of the columns). The regression gives \( n \) values of the correction factors \( x_i \), where \( n \) is the number of repeated data points for any one type of bed. One additional constraint is imposed, forcing the average of \( x_i \) equal to unity. This constraint forces the average of all local Peclet numbers to equal the macroscopic Peclet number for the bed.

Using values of \( x_i \) from the regression, the Peclet numbers were corrected so as to represent local values rather than an average value for the packed bed. Figure 3.6 shows the local Sherwood number as a function of the local Peclet number for the \( D_{b,a}/D_{mean} = 1.36 \) data.

The line in this plot represents an empirical relationship between the Sherwood number and the local Peclet number:

\[
Sh = 4.65(xPe)^{0.365}
\]

(3-3)

The equivalent plot for \( D_{b,a}/D_{mean} = 0.455 \) is showed as in Figure 3.7 with equation of

\[
Sh = 2.34(xPe)^{0.492}
\]

(3-4)

### 3.3.2 Peclet number exponent

The lines in Figure 3.3 and Figure 3.5 have a range of slopes as well as intercepts, which suggests extending the above approach to produce a distribution of exponents. While the additional step may not be justified based on practical considerations, it does help elucidate fundamental information about the relationship between hydrodynamics and local mass transfer.

In keeping with the rationale used above, we calculate an average value of \( m \) along with a distributed parameter to correct this exponent based on local effects (which also allows us to write a single empirical equation as a function of the local Peclet number). So that \( x_i \) remains a linear correction to \( Pe \). Equation (3-1) is rewritten as

\[
Sh_i = A(x_i Pe)^x m
\]

(3-5)
Figure 3.6 $Sh$ vs. local $Pe$ for all $D_{b.a.}/D_{mean} = 1.36$ data
Figure 3.7 $Sh$ vs. local $Pe$ for all $D_{b,a}/D_{mean} = 0.455$ data
where $z_i$, like $x_i$, is a distributed parameter that takes on a set of discrete values for the case of the benzoic acid spheres. The role of $z_i$ is clearly to make the local Sherwood number either less or more sensitive to changes in the Peclet number, although its ties to physical behavior are more difficult to infer than for $x_i$. For the $D_{b,a}/D_{mean} = 1.36$ data (which were obtained using 28 different benzoic acid spheres), the least-squares calculation requires the determination of 58 unknowns ($A, m, 28$ values of $x$, and $28$ values of $z$) using 140 data points ($5$ flowrates $\times 28$ spheres). Figure 3.8 shows $Sh_i$ versus $(x_i Pe)^{z_i}$ for $D_{b,a}/D_{mean} = 1.36$. The regression line is

$$Sh_i = 5.89(x_i Pe)^{0.36 z_i} \quad (3-6)$$

![Figure 3.8 Sh vs. (xPe)^z for all D_{b,a}/D_{mean}=1.36 data](image-url)
The improvement in the coefficient of determination from Figure 3.6 to Figure 3.8 is 0.974 to 0.989. The equivalent $Sh_i$ versus $(x_i Pe)^{z_i}$ data and regression line $D_{b,a}/D_{mean} = 0.455$ are shown in Figure 3.9, where the regression line is

$$Sh_i = 4.11(x_i Pe)^{0.49 z_i} \quad (3-7)$$

and the improvement in the coefficient of determination is 0.959 to 0.994.

![Figure 3.9 Sh vs. (xPe)$^z$ for all $D_{b,a}/D_{mean}$=0.455 data](image)

### 3.4 DISCUSSIONS

#### 3.4.1 Phenomenological arguments

To infer phenomenological details from the data presented here, first consider the fundamental nature of the $Sh$ versus $Pe$ relationship. For flows, where the velocity varies linearly with respect to the Reynolds number, one can show from dimensional analysis that mass transfer
is a function of the Peclet number only (Leal, 1992). One would expect this functionality to roughly hold in these experiments since the range of Reynolds numbers was 0.18 – 10.8, meaning that inertial effects were finite but small.

Figure 3.10 shows the distributions of $x_i$, which indicate that well over an order-of-magnitude variation in the local Peclet number exists because of pore-scale effects. Specifically, when the outlying points are included, the ratio of maximum to minimum local Peclet numbers within a single bed is approximately 70. We presume that local hydrodynamics play a dominant role in causing the local Peclet number to vary (i.e., the natural disorder in a packing, both at the pore scale and larger scales, allows certain particles to be subjected to higher velocities than others).

![Figure 3.10 Histogram of the distributed parameter $x$, showing the relative distribution of local Peclet numbers in the packed beds](image)

$D_{b,a.}/D_{ave} = 1.36$

$D_{b,a.}/D_{ave} = 0.455$
However, one can make an equally valid argument that the characteristic length for diffusion appearing in the local Peclet number should vary depending on local geometry.

The distribution \( z \) can be interpreted in two ways (Figure 3.11). If one assumes that the exponent \( m \) is constant regardless of local effects (i.e., taking on the value of the slope in Figure 3.3 and Figure 3.5), then \( z_i \) quantifies the nonlinear relationship between injected flowrate and local Peclet number. However, physical reasoning would argue against a constant value of \( m \) for local mass transfer. Specifically, theoretical analyses that give for smooth bodies in creeping flow (Pfeffer & Happel, 1964) assume a thin concentration boundary layer in which the tangential velocity varies linearly with distance away from the dissolving surface.

![Histogram of the distributed parameter \( z \), showing the relative distribution of local Peclet number exponents in the packed beds](image)

**Figure 3.11** Histogram of the distributed parameter \( z \), showing the relative distribution of local Peclet number exponents in the packed beds
The concentration boundary layers in our experiments have thickness $O\left(\frac{d}{Pe^{1/3}}\right) \approx 0.1d$ for the largest Peclet numbers tested. This thickness is roughly equal to the pore size in an unconsolidated sphere pack. Hence, one would expect hydrodynamics within the concentration boundary layer to be influenced quite strongly by the geometry of neighboring spheres, and therefore that the exponent might indeed vary from one site to another in the bed. That the average exponent for the $D_{b,a}/D_{mean} = 0.455$ experiments ($m = 0.49$) is quite different from the boundary-layer limit of $m = \frac{1}{3}$ is consistent with these arguments since the smaller spheres in a packing can reside within tighter spaces in the packing (where characteristic lengths for transport are smaller).

Using this line of reasoning, we interpret $z_i$ as a pre-exponential factor for $m$, which thereby allows the Peclet-number exponent to assume a distribution of values. To make phenomenological arguments about the effects of local flow and structure on the product $z_i \tilde{m}$, we consider extreme values of this exponent. Values near unity arise for equilibrium processes and/or very low Peclet numbers; at this limit, doubling the injected flowrate simply sweeps solute twice as quickly from its source. On the other hand, $z_i \tilde{m} < \frac{1}{3}$ indicates that local mass transfer is particularly insensitive to changes in the overall flowrate. One phenomenological reason for this behavior is if solute must diffuse through a stagnation zone before being swept away by convection (assuming stagnation zone is largely unaffected by flow).

Finally, we note that a significant correlation exists between values of $z_i$ versus $x_i$ as shown in Figure 3.12. The trend supports at least the first half of the above argument: that high values of the Peclet number exponent occur where the local Peclet number is smallest.
3.4.2 Practical considerations

The equations given in the previous section allow one to predict the range of local mass transfer coefficients within a packed bed. This information is valuable for two reasons. The first is to quantify the variation in mass transfer rates in applications where uniform behavior is important (e.g., in chromatography or certain catalytic reactions). These calculations may be important for design purposes. The second situation is where mass transfer occurs from dispersed interfaces within a porous material. In these cases, a mass transfer coefficient predicted from a general equation may not be representative of the rate of mass transfer from the specific interfaces in the system. This is particularly true if a correlation exists between interface properties and local Peclet number, which is the case in a number of real phenomena.
For situations where dispersed interfaces exist, one may require a spatially averaged mass transfer coefficient for the bed. To calculate this quantity, one can write the total mass transfer rate as the sum over all interfaces:

\[
\sum_i k_i a_i (C^* - C) = \bar{k} a_i (C^* - C)
\]  

(3-8)

The subscript \(i\) indicates the individual interfaces, \(k_i\) and \(\bar{k}\) are the individual and average mass transfer coefficients, \(a_i\) and \(a_i\) are the individual and total interfacial areas, and \(C^*\) and \(C\) are the equilibrium and free-stream concentrations of the solute. We have assumed that \(C\) remains dilute with respect to \(C^*\), which essentially states that the concentration difference in equation (3-8) is independent of position in the packed bed. Rearranging and canceling terms one obtains

\[
\bar{k} = \sum_i \left( \frac{a_i}{a_i} k_i \right)
\]  

(3-9)

\[
Sh = \sum_i \left( \frac{a_i}{a_i} Sh_i \right) = A \sum \left[ \frac{a_i}{a_i} (x_i Pe)^{z_i/m} \right]
\]  

(3-10)

The unsubscripted Sherwood number is the global Sherwood number for the bed. It quantifies the total mass transfer from the bed, even for cases where mass transfer occurs from a set of distributed interfaces that may exhibit mass transfer rates different from the average value for the bed.

To use equation (3-10) is clearly not trivial. One must know the distribution of local Peclet numbers \((x_i Pe)\), the distribution \(z_i\), and the distribution of local interface areas. Furthermore, Figure 3.12 shows that there exists a correlation between \(x_i\) and \(z_i\), and for certain applications these parameters may also be correlated with the interface area.
As a first approximation, one might infer $x_i$ from existing theories for velocity distributions (e.g., Shaqfeh et al., 1992). Additionally, it is hoped that pore-scale modeling will help elucidate how local structure affects the distribution of local Peclet numbers. Rigorous studies may be justified for applications where controlling the rate of mass transfer is critical from a design perspective. In less critical applications, we would hope to obtain simple corrective terms for current equations, which would quantitative modeling efforts.
CHAPTER 4

SIMULATION OF MASS TRANSFER IN A 2-D PACKED BED

The experimental work in Chapter 3 and other studies (Illangasekare 1995, Søresens 1995, Manivannan 1996 and Mayer 1996) indicate the existence of mass transfer rate (coefficient) distributions in homogeneous and heterogeneous porous media. This observation is understandable because the mass transfer behavior is strongly dependent on flow properties, and in disordered and heterogeneous porous media the pore scale spatial variation in local structure and hydrodynamics would cause distributions of mass transfer rates. Some early studies addressed the effect of media heterogeneity on overall mass transfer rates and the benefits of using the mass transfer coefficient distribution rather than single mass transfer coefficient in modeling efforts. However, few of them investigated the influence of pore-scale hydrodynamics on local mass transfer, which we believe is an important factor in some applications, such as dissolution of discrete NAPL globs in subsurface systems.

In this part of the research, the phenomenological relationship between local mass transfer rates and local hydrodynamics in heterogeneous media is investigated. Numerical simulations of flow and mass transfer are performed in two-dimensional heterogeneous media, and the dissolution of individual particles is simulated. As with the experimental work, statistical analyses are used to quantify expected values of local Peclet numbers. Additionally, the statistical results are compared to the detailed local hydrodynamics, which is not possible in the experimental part. These comparisons allow phenomenological interpretations of the statistical results to be made, which is a first step in explaining the widely varying mass-transfer results that are observed in natural porous media.
A couple of significant differences exist between this work and previous numerical results. First, heterogeneous structures are examined, which of course is significant because of the effect on hydrodynamics. Second, we focus on the spatial variation of single-particle mass transfer within a packing rather than on average behavior. Finally, we use stochastic modeling, which allows finite-Peclet-number regimes to be examined. At the values of Peclet number examined here (17 - 1700), neighboring particles influence the concentration boundary layers. A limitation of the study is that it is performed in two dimensions, which prevents direct comparison with the experimental packed-bed results. However, our main interest at this point is in examining the phenomenological behavior, and good insight can be gained even in two dimensions.

The model porous medium is shown in Figure 4.1. It is created by randomly distributing 1000 circular particles within a specified domain. Radii are randomly selected from a log normal distribution. A collective rearrangement algorithm is used to remove overlaps and to ensure that some minimum gap distance exists between particles. Table 4.1 is a list of parameters describing the bed.

**Table 4.1 The list of parameters for 2-D heterogeneous porous medium**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of spheres</td>
<td>1000</td>
</tr>
<tr>
<td>Average sphere diameter</td>
<td>1.67</td>
</tr>
<tr>
<td>Standard deviation in sphere size</td>
<td>0.256</td>
</tr>
<tr>
<td>Minimum sphere diameter</td>
<td>0.72</td>
</tr>
<tr>
<td>Maximum sphere diameter</td>
<td>20.71</td>
</tr>
<tr>
<td>Bed length</td>
<td>103</td>
</tr>
<tr>
<td>Bed height</td>
<td>51</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Figure 4.1 The disordered packed bed for mass transfer simulation (numbers indicate the particles selected for mass transfer calculation)
Although the modeling could be performed in a much smaller simulation domain, the larger
domain with 1000 spheres is used for two reasons: to capture effects present at both small and
moderate scales and variations in mass transfer between all particles can be tied to a single
average Peclet number.

To better understand this rationale, consider the velocity field near a particle in a disordered
packed bed. Its shape and magnitude depend on small-scale effects (gap spacing and orientation
immediately adjacent to the particle surface) as well as local pressure gradients, which are
primarily a function of larger-scale heterogeneity. Smaller flow domains could be examined by
arbitrarily changing the direction and magnitude of the pressure gradient. But, this latter
approach would not allow variations in mass transfer to be quantified relative to a global Peclet
number for the bed (which is inevitably what has to be done experimentally).

In the model, we assume that the solute concentration is dilute everywhere and thus has no
effect on fluid properties. Similarly, we assume that concentration profiles from upstream
particles have no effect on downstream mass transfer. These assumptions allow the flow problem
to be decoupled from the mass transfer problem, and the numerical modeling is performed in two
steps: calculation of the velocity profile followed by calculation of the rate of interfacial mass
transfer.

4.1 VELOCITY CALCULATIONS

Since we assume low-Reynolds number flow, the velocity is governed by the Stokes equation
in two dimensions, which requires a computationally intensive solution for large, disordered
domains. A detailed description of the numerical procedure was given by Liu et al. (2002), but
described briefly below for completeness.
The Stokes equations are solved using a boundary-element method. Domain decomposition is used to avoid generating a full matrix (which for this size problem would be essentially unsolvable). The initial decomposition into subdomains is performed using a Delaunay tessellation. The subdomains are then refined and enlarged by removing interior particle-to-particle boundaries to improve the conditioning of the final matrix equation.

The discretized, boundary-integral form of the Stokes equation is applied to each subdomain. This procedure gives a large, block-diagonal matrix with sparse off-diagonal terms arising from unknown velocities and stresses on interior boundaries. The matrix equation is solved using a preconditioned biconjugate gradient method, giving boundary stresses and velocities throughout the flow domain.

Once the above solution is obtained, point velocities can be obtained quite rapidly by performing a local boundary integral calculation over a single subdomain. The efficiency with which these velocities can be recovered is crucial when using a stochastic algorithm. For instance, the mass-transfer data presented below required on the order of $10^9$ independent velocity computations to be made.

In this study, over 90% of computation time is spent on calculating the velocities at various locations. Therefore, further improvements in the speed of velocity computations can greatly benefit the total computation time. The BEM (boundary element method) uses following three steps to get velocities for a given point. 1) Locate the subdomain in which the point resides. 2) Retrieve the boundary information for that subdomain from the data files. 3) Perform a boundary integration to obtain the point velocity.

This routine has two drawbacks when being used in this study: 1) sometime the entire bed is searched prior to finding the subdomain in which the point is located. 2) Boundary values are
retrieved from a large data file (that holds information of all bed), although only local information is needed during each simulation. In order to reduce the simulation time, an additional step was developed for recovering velocities based on the BEM solution. A dense grid (500×1000) around the source sphere is created (as shown in Figure 4.2) and velocities at each grid point are calculated using the BEM solution. A data file is created to hold the grid point numbers, grid point coordinates and grid point velocities.

![Figure 4.2 The illustration of grids around one source sphere](image)

When calculating the velocity at point $P$ (see Figure 4.2), we first locate the grid block to which the point belongs. This step can be performed very quickly because the grid-point information is sorted (counterclockwise, from inner to outer) in the data file. A simple equation can directly relate the values $i$ and $j$ (as in Figure 4.2) based on the point coordinates and source particle radius and coordinates. Then, velocities at four corners of grid block (such as $i$, $i+1$, $j$, and $j+1$ in Figure 4.2) are quickly accessed, and the velocity at point $P$ is obtained based on the following equation.
where $v_i$ is the velocity at $i$th grid point and $l_i$ is the distance from the point $P$ to the $i$th grid point. The accuracy of this method was checked, and the difference between the direct BEM calculation and this rapid calculation is less than 1%. However, the computation time is reduced significantly.

4.2 MASS TRANSFER CALCULATIONS

In the steady-state, velocity appears only as a parameter in the convection-diffusion equation,

$$u \cdot \nabla C = D \nabla^2 C,$$

which allows the concentration problem to be decoupled from the flow problem. The finite element method and a stochastic method are discussed below as methods for the solution of equation (4-2) for the case of dissolution from a single particle interface.

4.2.1 Finite element method

A finite element algorithm was developed to solve equation (4-2) with boundary conditions $C = C^*$ at the particle surface and $u \cdot \nabla C = 0$ far from the particle. These boundary conditions impose solute equilibrium at the particle surface, and that transport in the direction of flow occurs only by convection far away from the particle. The rate of mass transfer is then found by computing

$$J = \oint (C \cdot u) \, dA$$

at the outer boundary surface. The solute concentration distribution is obtained and the effect of velocity on dissolution is revealed, as in Figure 4.3.
The advantage of this method is that the steady-state solute concentration profile is available. However, this approach is only effective at moderate Peclet numbers even with an upwinding scheme and local grid refinement. We were not able to obtain consistently good results at high Peclet numbers. Additionally, the results strongly depend on the boundary conditions, such as the location for imposing \( \mathbf{u} \cdot \nabla C = 0 \). The mass transfer coefficient varies with the size of FEM domain and that makes the comparison between different particles unreliable. Therefore, no quantitative conclusions are made based on FEM method.

### 4.2.2 Stochastic method

Because of the above problems with the finite element method, a stochastic algorithm is used to model the mass transfer process. The random-walk algorithm is run by tracking a large number of tracer particles as they are displaced through the pore space by convective-diffusive motion. Each numerical displacement is made according to

\[
\Delta \mathbf{r} = \mathbf{u} \cdot \Delta t + \sqrt{4 \cdot D \cdot \Delta t} \cdot \mathbf{W}
\]

where \( D \) is diffusion coefficient and \( \mathbf{W} \) is a random Gaussian variable with variance equal to zero (Öttinger, 1996). To maintain computational efficiency as well as accuracy, a uniform characteristic displacement length \( \delta_{m} \) is imposed regardless of whether a tracer particle is in a

Figure 4.3 Concentration profile in packed bed under high and low flow velocities

The advantage of this method is that the steady-state solute concentration profile is available. However, this approach is only effective at moderate Peclet numbers even with an upwinding scheme and local grid refinement. We were not able to obtain consistently good results at high Peclet numbers. Additionally, the results strongly depend on the boundary conditions, such as the location for imposing \( \mathbf{u} \cdot \nabla C = 0 \). The mass transfer coefficient varies with the size of FEM domain and that makes the comparison between different particles unreliable. Therefore, no quantitative conclusions are made based on FEM method.

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where \( D \) is diffusion coefficient and \( \mathbf{W} \) is a random Gaussian variable with variance equal to zero (Öttinger, 1996). To maintain computational efficiency as well as accuracy, a uniform characteristic displacement length \( \delta_{m} \) is imposed regardless of whether a tracer particle is in a
region of low or high velocity (Wen et al. 1995). Hence, the time step $\Delta t$ associated with a
displacement varies with position, and is calculated from the equation (4-4) for the two-
dimensional case.

$$\delta_M = |v(r)|\Delta t + \sqrt{4D\Delta t} \quad (4-4)$$

In this problem, our concern is determining the rate of mass transfer from a single circular
interface in the bed, which can be thought of as a dissolving particle. The approach does not
require the concentration profile itself to be determined, which simplifies the stochastic problem
to some extent.

Consider a thin layer of fluid adjacent to the dissolving interface. The thickness of this
surface layer $L$ is large compared to $\delta_M$ but small compared to the concentration boundary layer,
and convective transport is negligible in the surface layer. The stochastic algorithm is run by
sequentially releasing a large number of tracer particles from the interface and following their
motion as governed by equation (4-3). For each tracer particle released, the number of
displacements that are detected within the surface layer is recorded as $N_{sl}$, and the tracer particle
is followed until it either returns to the interface or it travels far enough away that it will not
return within any reasonable probability. In this study, the tracer particle is considered to have
permanently escaped the dissolution surface if it is downstream of the source sphere and a
distance away that is at least 2.5 times the largest sphere diameter. It has been verified that when
the maximum escape distance is larger than 2.5 times the largest sphere diameter, the simulation
results remain unchanged. When the particle moves into the source sphere, it sinks into the
source and ceases moving. For non-source spheres in the bed, a reflection boundary condition is
used, in which the tracer particle ‘bounces back’ into the fluid and keep moving.
In the surface layer, motion is primarily by diffusion. Hence, each displacement step represents a constant time interval

$$\Delta t = \frac{\delta^2}{4D}. \quad (4-5)$$

Furthermore, since a steady-state process is being modeled, the appearance of a tracer particle in the surface layer means that a tracer particle could be found at that same position during any snapshot of length $\Delta t$. This observation allows the number of tracer-particle observations in the surface layer ($N_{sl}$) to be related to the equilibrium solute concentration $C^*$. The number of tracer particles that ultimately escape the surface ($N_{esc}$) is equivalent to the number that escape during any time interval $\Delta t$. Viewing each tracer particle as a packet of solute, $N_{sl}$ and $N_{esc}$ can be related to the molar flux from the surface:

$$\mathbf{q} \cdot \mathbf{n} = k(C^* - C_0) = \frac{N_{esc}}{\Delta t} C^* \frac{L}{N_{sl}} \quad (4-6)$$

where $C_0 \equiv 0$. Equation (4-6) allows the mass transfer coefficient to be calculated by counting $N_{sl}$ and $N_{esc}$ in an ensemble of tracer-particle trajectories.

The critical parameters in the simulation are $\delta_M$, $L$, and $N_{rel}$. The use of a small characteristic displacement distance $\delta_M$ improves resolution, but penalizes computation time. So, it’s value is determined on a case-by-case basis by ensuring that the results are nearly invariant when it is decreased. Typically, choosing $\delta_M$ to be on the order of 1/100 of the expected boundary layer thickness has given satisfactory results. $L$ must be sufficiently large to allow a true random walk within the surface layer, while at the same time being sufficiently small so that significant concentration gradients are not present in the surface layer. We have used $L = 10\delta_M$ for most results, again, ensuring that results are essentially invariant with respect to this parameter. $N_{rel}$ is determined on a case-by-case basis by ensuring that convergence has occurred and computation
time is reasonable. Results presented below were obtained using 0.00025, 0.0025 and 4000 for values of $\delta_M$, $L$ and $N_{rel}$ respectively. Figure 4.4 shows the flow chart for simulating the dissolution of single particle in the packed bed with the random walk method.

To check the stochastic algorithm, the rate of mass transfer in a square array of spheres with solid volume fraction $\phi = 0.12$ was calculated to compare the simulation results conducted by others. The domain is a $13 \times 13$ sphere array as Figure 4.5. The velocity solution was first obtained using the boundary element method. Then, the dissolution rate from the center sphere in the domain (marked in Figure 4.5) was simulated. Using five data points in the range $7.9 \times 10^4 \leq Pe \leq 1.58 \times 10^6$, results from the stochastic algorithm give $m = 0.321$ and $A = 0.732$ in the mass transfer correlation $Sh = APe^m$. These values compare favorably with boundary layer results valid for high $Pe$ number, which give $m = 1/3$ and $A = 0.71$ (Wang et al., 1997), where this latter value is the $O(Pe^{1/3})$ coefficient in the expansion. The reasons for the small discrepancies probably include statistical uncertainty in the stochastic results, numerical error in the computational algorithms used here and/or in Wang et al.’s work (1997), and the fact that the boundary layer results reflect only the leading order contribution to convective transport whereas results from the current research are not restricted as such.

![Figure 4.5 The domain used to verify stochastic method](image)

Figure 4.5 The domain used to verify stochastic method
Specify $L$ (surface layer length)
$\delta_M$ (constant displacement)
$S_{max}$ (maximum moving steps)
$L_{max}$ (escape distance)

For one tracer particle at $P_1 (x_1, y_1)$
1. Generate two random numbers $R_1$ and $R_2$
2. Obtain $u_{x1}$ and $u_{y1}$ at $P_1$ with grid method
3. Calculate $\Delta t$ based on $u_{x1}$, $u_{y1}$, $R_1$, $R_2$ and $\delta_M$
4. Calculate displacement at $x$ and $y$ directions
   \[
   \Delta x = u_{x1} \cdot \Delta t + \sqrt{2DR_1} \\
   \Delta y = u_{y1} \cdot \Delta t + \sqrt{2DR_2}
   \]
5. Obtain new point $P_2 (x_2, y_2)$ based on
   \[
   x_2 = x_1 + \Delta x \\
   y_2 = y_1 + \Delta y
   \]
6. Calculate the distance between $P_2$ and $P_1$

If $P_2$ is inside source sphere
   Yes
If $P_2$ is far from source
   Yes
If max moves is reached
   Yes
   Particle back to $P_1$
   No
   If $P_2$ is in inside another sphere
       Yes
Let $P_1 = P_2$
   No
   Add 1 to $N_{es}$
       Yes
   If $P_2$ is inside the surface layer
       Yes
       End one sphere
          Record result
   No
   Release another tracer particle

If $P_2$ is the last particle
   Yes
   This particle ends.
      Record results.
No

Figure 4.4 Flow chart for random walk simulation
4.3 MASS TRANSFER IN HETEROGENEOUS MEDIA

Ten particles from the bed were selected for making mass-transfer calculations. These choices are indicated and numbered in Figure 4.1. Since our specific goal is to elucidate differences caused by local hydrodynamics, this set contains a large variety of conditions (e.g., relatively high versus low flow rates, relatively close versus open geometries). Because of its small size and the choices made, this set is not intended to collectively represent the average mass-transfer behavior for the porous medium.

Mass-transfer coefficients were found for each of the ten particles for a range of global Peclet numbers ($\frac{u\alpha}{D}$) between 17 and 1700. The images in Figure 4.6 are created from the stochastic algorithm by plotting a point at each location that a tracer particle is detected (for a limited number of trajectories for clarity). The data are from particle #404 in the bed, at Peclet numbers 17, 170 and 1700. These images do not give a quantitative indication of solute concentration, but they clearly show the influence of the Peclet number on transport.

![Figure 4.6 Tracer particle locations during stochastic simulation of mass transfer.](image)

The center bed particle is #404: (a)$Pe=17$; (b)$Pe=170$; (c)$Pe=1700$
If one plots $Sh$ versus $Pe$ as shown in Figure 4.7, significant differences are observed in the mass transfer behavior of each particle. These differences are caused by variations in particle size as well as differences in local flow fields. To remove the effect of particle size (since the focus of this work is on the hydrodynamics) the data are recast as $Sh_i$ versus $Pe_i$. Here, the characteristics length used in $Pe_i$ and $Sh_i$ is the radius of particle $i$ rather than the average radius of particles for the bed. Figure 4.8 shows the same mass transfer data, but revised accordingly. Even after accounting for size effects, the mass transfer correlations remain widely varied because of difference in local velocity fields.

Figure 4.7 $Sh$ versus $Pe$ number relationship for the individual particles
To quantify the effect of the local hydrodynamics statistically, a spatially distributed coefficient $x$ was introduced, as was done in Chapter 3. This parameter further adjusts the Peclet number (i.e., in addition to the use of a local characteristic length) to account for an increased or decreased rate of mass transfer because of shape and magnitude of the local hydrodynamics.

When combined with $Pe$, the result is the best statistical estimate of the local Peclet number to which a given particle is exposed: $x_i Pe$.

In both the experimental work and the current analysis, $x$ takes on only a discrete set of values, one value for each particle for which the mass-transfer rate is measured. The distributed values $x_i$ are found using a least-squares regression of all the data to the equation $Sh = A_i (x_i Pe)^{m_i}$. Table 4.1 contains values of $A_i$, $m_i$, and $x_i$ for the active particles, where $A_i$ and $m_i$ come from the
equation $Sh = A(Pe)^m$. Figure 4.9 is a plot of $Sh_i$ versus the local Peclet number $x_i Pe_i$ for all data. The line is the equation $Sh = 0.876(x_i Pe)^0.462$.

Table 4.2 Mass transfer statistics for active particles in the packing.

<table>
<thead>
<tr>
<th>Particle #</th>
<th>$a/\bar{a}$</th>
<th>$A_i$</th>
<th>$m_i$</th>
<th>$x_i$</th>
<th>$\langle \Delta v_\theta/\Delta r \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>0.645</td>
<td>0.547</td>
<td>0.555</td>
<td>1.184</td>
<td>1.24</td>
</tr>
<tr>
<td>186</td>
<td>0.733</td>
<td>0.725</td>
<td>0.499</td>
<td>1.135</td>
<td>1.21</td>
</tr>
<tr>
<td>404</td>
<td>0.491</td>
<td>1.542</td>
<td>0.296</td>
<td>0.297</td>
<td>0.75</td>
</tr>
<tr>
<td>436</td>
<td>0.734</td>
<td>0.982</td>
<td>0.438</td>
<td>0.666</td>
<td>0.74</td>
</tr>
<tr>
<td>452</td>
<td>1.118</td>
<td>0.430</td>
<td>0.572</td>
<td>2.816</td>
<td>1.41</td>
</tr>
<tr>
<td>467</td>
<td>0.733</td>
<td>0.746</td>
<td>0.494</td>
<td>1.088</td>
<td>1.19</td>
</tr>
<tr>
<td>573</td>
<td>0.839</td>
<td>0.634</td>
<td>0.524</td>
<td>1.084</td>
<td>1.28</td>
</tr>
<tr>
<td>754</td>
<td>0.927</td>
<td>1.037</td>
<td>0.428</td>
<td>0.717</td>
<td>0.75</td>
</tr>
<tr>
<td>861</td>
<td>0.748</td>
<td>0.890</td>
<td>0.459</td>
<td>0.749</td>
<td>0.87</td>
</tr>
<tr>
<td>921</td>
<td>0.598</td>
<td>1.266</td>
<td>0.357</td>
<td>0.269</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Figure 4.9 $Sh$ versus $xPe$ for ten spheres
4.4. DISCUSSIONS

4.4.1 Qualitative interpretation of the statistical analysis

In the experimental work described in Chapter 3, the analysis was limited to a statistical interpretation of the mass-transfer data. However, with a numerical approach, detailed hydrodynamics are available as a tool for interpreting the data in Table 4.2. Figure 4.10 contains images of the velocity profiles for the ten particles arranged according to decreasing values of $x_i$. Arranging the images in this way is helpful because, since the size effect is captured by $Pe_i$ and since the distribution $x_i$ is normalized, the correction factor $x_i$ isolates the effect of local hydrodynamics, which is the factor being addressed in this chapter. Color indicates the magnitude of velocity. For clarity, quivers for the velocity are not plotted. However, the velocity field can be visualized by considering that the net flow direction in the packing is left to right.

Using Figure 4.10 and Table 4.2, a number of observations can be made. First, it is apparent that the magnitude of the velocity is important, but not the dominant factor that affects local mass transfer rates. Particles 452, 467, 573, and 404 are all exposed to very high local velocities, but the hydrodynamic scaling factors for these four particles span the whole range of measured values. Instead, the velocity gradient is the more crucial parameter (which is also evident from the boundary layer equations for mass transfer). In heterogeneous porous media, the largest velocity gradients occur where relatively high flowrates are forced through constricted passages. These situations typically arise because of a coupling between large-scale and small-scale effects. This coupling is exemplified by particle 452, which has small gaps adjacent to it but is exposed to a relatively high flowrate because of its position within the large-scale structure. As seen in Figure 4.1, it sits within a chain of locally high-porosity regions that carry a proportionally larger amount of flow. This specific pore morphology causes large velocity
Gradients to form in the particle-particle gaps, and consequently gives the highest value of the local Peclet number out of the ten particles examined.

Figure 4.10 Local velocity fields for ten particles analyzed. Color corresponds the magnitude of the velocity. Overall flow direction in the bed is left to right.

A second important factor is how closely streamlines follow a particle’s surface. In unbounded low-Reynolds number flow (and in many ordered porous materials), the highest velocity gradients are necessarily localized to the equator of a particle (assuming flow is toward a pole). In random porous media however, local geometry can force streamlines to hug a particle’s surface more closely, thus forming high velocity gradients over a large fraction of the surface. This phenomenon is illustrated by particle 94, which despite being in a region of low
flow has a high value of $x_i$ (and therefore a high rate of mass transfer in relative terms) because of this hydrodynamic effect.

These same effects are apparent with particles 404 and 921. Despite being located near regions of high velocity, both particles are adjacent to much larger voids than other particles are. Consequently, the velocity gradients are smaller, and because the streamlines do not hug the particles tightly, there are regions of slow flow at the upstream and downstream stagnation points.

### 4.4.2 Predictions of local Peclet numbers from hydrodynamics

For practical applications, it is desirable to formulate simpler methods of estimating variations in local mass transfer, for instance from pore network modeling. From the above discussion and from boundary-layer theory, the velocity gradient seems to be the most viable parameter that correlates well with the local mass transfer rate, and at the same time could be estimated from a simpler model. For instance, using a network model, the velocity gradient could be approximated using local flowrates and local pore dimensions. To implement this approach, the specific functionality of the velocity gradient would be obtained from solutions of the boundary-layer equations for heat or mass transfer at high Peclet numbers. For instance, when the boundary layer equations are cast in the form of a power-law relationship, the velocity gradient appears in the coefficient $A$, inside a surface integral (see equations 10 and 11 from Sørensen et al., 1974).

To assess how well a characteristic velocity gradient could be used to characterize the local hydrodynamic effects on mass transfer, the average velocity gradients for each particle are estimated. These estimates are obtained by calculating the average magnitude of the tangential velocity component at fixed distance from the particle surface (at $r = 1.1\bar{r}$). This position is
chosen because it represents (very approximately) the outer edge of the concentration boundary layer for \( Pe = 1000 \). The resulting values of \( \frac{\Delta \phi}{\Delta r} \) are normalized and reported in Table 4.2.

If the velocity gradient were constant over the surface, it would appear as a \( (\partial u_\theta / \partial r)^{1/3} \) term in the boundary-layer solution for \( A \). Similarly, the statistical parameter \( x_i \) is raised to the power \( m \) in the Sherwood number correlation. Hence, a direct comparison of these two independent parameters should be indicative of how effective a simple correlation might be for characterizing local hydrodynamics. This comparison is made in Figure 4.11 using a parity plot of the two distributed values. Although there is certainly some correlation between the two parameters, it is not sufficiently correlated to use as a basis for quantitative calculations. (Other simple measures of local hydrodynamics that were investigated showed similarly weak correlations with \( x_i \).)

The failure to generate a stronger correlation using averaged descriptions of the local hydrodynamics is indicative of the complexity of the mass transfer process (i.e., its strong dependence on detailed streamline shape). These results are somewhat discouraging with regard to the development of simpler techniques for estimating local mass transfer from discrete interfaces. However, network modeling, which is a powerful intermediate-level technique, is still evolving rapidly. Hence an important area of future research is the development of new tools that can be integrated with network modeling to provide estimates of streamline-scale behavior. Methods have already been pursued to a certain extent. One approach is imposing assumed velocity profiles onto pore-scale fl owrates, which can then be used for particle tracking or estimates of velocity gradients (Thompson et al., 1997). A second option is to simplify network geometry to a point where more rigorous hydrodynamic or mass-transfer calculations can be made (Dillard et al., 2000).
Figure 4.11 Comparison of the statistical estimate of the local Peclet number versus the average velocity gradient over each particle's surface.
CHAPTER 5

A STUDY OF THE EXPONENT \( m \) IN MASS TRANSFER CORRELATIONS

5.1 THE DISTRIBUTION OF THE EXPONENT TERM \( m \)

The Experimental and numerical studies in Chapter 3 and Chapter 4 show the power-law relationship between the Sherwood and Peclet numbers. When data were correlated based on the constant exponent \( m \), the traditional correlation \( Sh = A Pe^m \) was rewritten as \( Sh = A(x Pe)^m \) which includes a new parameter \( x \) to correct the global Peclet number to a site-specific local Peclet number. The magnitude of \( x \) describes the impact of local structure on local mass transfer and is affected by the local velocity scale, local velocity gradient and local velocity profile, as discussed in Chapter 4. However, the meaning and function of the exponent \( m \) in the correlations was not discussed.

Intuitively, \( m \) reflects the sensitivity of Sherwood number to changes in the value of Peclet number, and it plays an important role in the correlation. In many applications, it is crucial to quantify how the specific functionality between Sherwood and Peclet changes. For example, in the design of NAPL remediation treatments, an accurate value for \( m \) would allow one to provide accurate predictions for the amounts of fluid and lengths of time required for clean-up under different operating conditions (Jia et al., 1999). However, reasons for variations in this parameter have not been addressed significantly in prior research.

Leal (1992) mentioned that for mass transfer from single objects to the surrounding fluid, the exponent \( m \) tends to be unity for low Peclet and low Reynolds number, and drops to 1/3 for high Peclet and low Reynolds number. This can be interpreted by arguing that at low Peclet number, the mass transfer rate is limited by convection. In this limit, equilibrium is approached, and doubling the injected flowrate simply sweeps solute twice as quickly from its source. On the
other hand, a high Peclet number implies a diffusion-controlled mass transfer process, and mass transfer is less sensitive to changes in the overall flowrate.

The mechanism of mass transfer in porous media is much more complicated than mass transfer from a single object. Numerous experimental and modeling studies conducted in packed beds and porous media have given various $m$ values under different conditions (see Tables 4.1, 4.2 and 4.3). It should be noted that all $m$ values from previous studies were based on the overall mass transfer through the domain. No study was conducted to investigate the site-specific value for $m$ and the connection between its value and the local hydrodynamics, although distributions of mass transfer rates were indeed used in certain modeling studies.

We feel it is necessary to study the role of the exponent $m$ in the mass transfer correlation for the following reasons:

1) The results presented in Chapter 3 and Chapter 4 show that the value of $m$ exhibits significant variance, even within a macroscopically homogeneous porous medium. These observations suggest a dependence of $m$ on local structure.

2) The use of distributed values for $m$ in environmental and chemical-engineering modeling may improve the accuracy of predictions.

3) Studying the behavior of $m$ can enhance our fundamental understanding of mass transfer.

4) Previous studies (Jia et al., 1992) showed that NAPL dissolution rate in porous media is sensitive to the value of exponent $m$.

Additionally, techniques for high-resolution pore-scale modeling provide the possibility of linking this parameter to fundamental mass transfer phenomena.
5.2 THE CORRELATION BETWEEN LOCAL PECLET NUMBER AND THE EXPONENT $m$

In Chapters 3 and Chapter 4, when data from individual spheres were correlated based on $Sh = A Pe^m$, distributions of $m$ values were obtained, such as in Figure 3.11 and Table 4.2. When data were correlated based on $Sh = A(x_i Pe)^m$, only $x_i$ was assigned a site-specific value, while $m$ remained constant for a given bed. A second type of correlation was presented in Chapter 3, which used $Sh = A(x_i Pe)^m$ to contain two site-specific variables $x_i$ and $m$. Both $x_i$ and $m$ were shown to have distributed values within a single bed, which are significant with respect to the experimental and/or numerical errors.

Using the experimental and numerical data from Chapters 3 and 4, three sets of data ($m_i$ versus $x_i$) were obtained. Figure 5.1 shows the plot of result.

![Graph](image)

**Figure 5.1 $m_i$ versus $x_i$ for three packed beds**

Although data from the three beds have similar trends ($m_i$ decreases with the increase of $x_i$), there is not a single correlation that applies to all data. However, when the data were normalized
with $z_i = m_i / \bar{m}$, where $\bar{m}$ is the average of all $m_i$ in one bed, the results become unified, as shown in Figure 5.2 for the three different packings.

![Figure 5.2](image.png)

**Figure 5.2** $z_i$ versus $x_i$ for data from experimental and numerical results

Obviously there is a very strong correlation between $x$ and $z$, which can be described fairly well with the empirical equation $z_i = 0.8965x_i^{-0.158}$. Then data in each bed can be correlated with

$$Sh = A(x_i Pe)^{0.8965 \bar{m} x_i^{-0.158}}$$

(5-1)

This relationship implies that although both the local Peclet number and the exponent $m$ exhibit spatial variations, only a single parameter (i.e. $x_i$ in equation 5-1) is needed to reflect the effect of local hydrodynamics on mass transfer. From a phenomenological perspective, the implication is that local Peclet number and exponent term in the correlation are determined by the same hydrodynamic effect. For example, a large local velocity gradient would decrease $x_i$ and increase $m_i$ ($m_i = 0.8965 \bar{m} x_i^{-0.158}$) simultaneously.
In this analysis, $m$ is a parameter specific to each bed. Its values are 0.460, 0.360 and 0.490 for 2-D porous medium, disordered packing with $D_{b.a.}/D_{mean}=1.36$ and disordered packing with $D_{b.a.}/D_{mean}=0.455$ respectively. To determine whether the parameter $m$ is universal, the data from all three beds were lumped together: Figure 5.3 shows the plot of $Sh$ vs. $x_i Pe^{z_i}$. Figure 5.4 shows the corresponding relationship between $x_i$ and $z_i$.

The correlation accuracy between $Sh_i$ and $x_i Pe^{z_i}$ is not as good as before when data from individual beds were correlated. Also the correlation between $z_i$ and $x_i$ is not as strong as before. This comparison suggests that Equation (5-1) applies to a single packing, to which a specific value of the parameter $m$ is needed to describe its behavior.

![Figure 5.3 $Sh_i$ versus $x_i Pe^{z_i}$ for all data](image)
5.3 THE MASS TRANSFER PARAMETERS IN THE MODIFIED POROUS MEDIUM

In order to elucidate how changes in structure and hydrodynamics affect mass transfer behavior, the two-dimensional disordered bed used for stochastic modeling in Chapter 4 was adjusted by changing the local structures of three spheres (94, 404 and 467). The neighborhood around sphere 94 was changed to open up the pore space slightly, while the neighborhood surrounding sphere 404 was packed significantly tighter. Finally, the channels between sphere 467 and its neighboring spheres were reduced significantly in size. No additional spheres were added to the bed, and the sizes of all spheres remain unchanged. In this way the global flow field was affected only slightly, despite the dramatic changes in local hydrodynamics around source spheres 404, 467 and 94. Comparison of the mass transfer from these spheres (before and after the changes) can help in interpreting specific effects related to local hydrodynamics.
The velocity field in the revised packing was obtained using the high resolution network model (Liu et al., 2002). Figure 5.5 provides a comparison of the local flow profiles around the three source spheres that were changed. Velocity profiles around the three selected spheres are plotted using a larger scale than before and the plots show that the flow patterns in the immediate vicinity of 94, 404 and 467 change dramatically, while the far-field flows change only slightly. In addition, changes in the velocity fields around the other seven source spheres are not detectable visually. This small change in the velocity field near a non-changed sphere is shown in Figure 5.6, which is a plot of grid point velocities around sphere 452 (1000 points). The velocities were calculated on the same grid points before and after the change.

Stochastic simulations for the dissolution of the ten selected spheres were conducted as in Chapter 4 using the same parameters (i.e., particle number, step size, total number of displacement steps, and surface layer thickness). The $Sh$ vs. $Pe$ results for the seven unchanged spheres remained similar to the previous bed. However, the results for spheres 404, 94 and 467 were changed significantly. Table 5.1 summarizes the results after the change compared to Table 4.2

Figure 5.7 shows the $Sh$ versus $Pe$ correlation for sphere 404 before and after the local structure change. Figure 5.5 shows that after the change, sphere 404 is very tightly enclosed by 4 neighboring spheres, but quite open outside this small aggregate. This local structure reduces the strength of convective transport near the surface of sphere 404. Therefore, at low global Peclet numbers, the dissolution of 404 reflects diffusion-dominated dissolution (i.e., the Sherwood number is very small and almost independent of Peclet number). However, as Peclet number increases, convection begins to play a role and the exponent increases very quickly (at low Peclet
number and low Reynolds number, \( m \to 1 \), Leal 1992). Figure 5.7 also indicates that the power-law relationship is not necessarily valid over a wide range of Peclet number.

Figure 5.5 Velocity profile comparisons for three selected spheres (before and after the change)
Table 5.1 Mass transfer statistics for active particles in the packing (modified bed)

<table>
<thead>
<tr>
<th>Particle #</th>
<th>$\frac{a}{\bar{a}}$</th>
<th>$A_i$</th>
<th>$m_1$</th>
<th>$x_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>921</td>
<td>0.598</td>
<td>1.269</td>
<td>0.357</td>
<td>0.267</td>
</tr>
<tr>
<td>754</td>
<td>0.927</td>
<td>1.038</td>
<td>0.428</td>
<td>0.714</td>
</tr>
<tr>
<td>436</td>
<td>0.734</td>
<td>0.984</td>
<td>0.438</td>
<td>0.663</td>
</tr>
<tr>
<td>94</td>
<td>0.645</td>
<td>0.937</td>
<td>0.441</td>
<td>0.850</td>
</tr>
<tr>
<td>186</td>
<td>0.733</td>
<td>0.728</td>
<td>0.499</td>
<td>1.131</td>
</tr>
<tr>
<td>861</td>
<td>0.748</td>
<td>0.891</td>
<td>0.459</td>
<td>0.746</td>
</tr>
<tr>
<td>573</td>
<td>0.839</td>
<td>0.635</td>
<td>0.524</td>
<td>1.081</td>
</tr>
<tr>
<td>452</td>
<td>1.118</td>
<td>0.430</td>
<td>0.572</td>
<td>2.816</td>
</tr>
<tr>
<td>467</td>
<td>0.733</td>
<td>0.328</td>
<td>0.756</td>
<td>3.435</td>
</tr>
</tbody>
</table>

Figure 5.6 Velocity value comparison for 1000 grid points around sphere 573 before and after change
Figure 5.5 shows that the narrow channels between sphere 467 and its neighboring spheres create a high velocity gradient. The local Peclet number of sphere 467 based on $Sh = A(xPe)^m$ after the change is higher than before. This result verifies that velocity gradient is the dominant factor that affects the local Peclet number.

Figure 5.5 shows a qualitatively similar flowrate passing by sphere 94 after the change in local structure. But, the spacing between sphere 94 and its neighbors is significantly larger than before. The result, shown in Figure 5.9, is a lower mass transfer coefficient after the change. This can be explained by a smaller velocity gradient (due to the more open geometry), and also that the streamlines do not hug the sphere as tightly as in the previous case.
Figure 5.8 Comparison of $Sh$ vs. $Pe$ relationship for sphere 467
(before and after the change)

Figure 5.9 Comparison of $Sh$ vs. $Pe$ relationship for sphere 94
(before and after the change)
CHAPTER 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 CONCLUSIONS

The effect of local hydrodynamics on interfacial mass transfer in porous media was studied in this research. Although the heterogeneity of mass transfer rates in porous media has been indicated by others, previous studies have focused on the overall mass transfer coefficient and few studies have addressed the effects of local geometry and flow on site-specific mass transfer coefficients and rates. In this dissertation, mass transfer in porous media was studied experimentally and numerically. The dissolution rates of solid benzoic acid spheres in homogeneous and heterogeneous packed columns were measured to study the distribution of mass transfer coefficients. The mass transfer process was also modeled in a two-dimensional heterogeneous porous medium using a stochastic algorithm, which allowed an analysis to be made of the local hydrodynamics and their effect on mass transfer.

Experiments showed that local mass transfer coefficients in macroscopically uniform packed beds can vary over an order of magnitude, which in turn causes a spatial distribution of mass transfer rates within the bed. To quantify these effects, a new parameter $x$ was first introduced to adjust the global Peclet number so that it represents a local value in the Sherwood number correlation:

$$Sh = A \cdot (x, Pe)^m$$  \hspace{1cm} (6-1)

Both experimental and numerical results showed that a distribution of local Peclet numbers exists for different sites in the beds. The results show clearly that mass transfer is affected by large- and small-scale structures of materials. Large-scale structure affects pressure gradients in a region, and therefore the magnitude of local flowrates. The small-scale structure affects the
shape of local streamlines and the magnitude of velocity gradients. The analysis of data from pore-scale modeling shows that high local rates of mass transfer, which corresponds the high local Peclet number $xPe$, are related to large velocity gradients at the surface and pore geometry that cause streamlines to closely follow a particle’s surface. However, the effort to quantitatively connect local hydrodynamics with local mass transfer using a simplistic approach was unsuccessful.

The role of the exponent term in mass transfer correlations was discussed. When data from individual sites were correlated with

$$Sh = A \cdot Pe^m,$$  \hspace{1cm} (6-2)

the result shows that a distribution of local values of the exponent $m$ exists. When the standard empirical correlation (6-1) is rewritten as

$$Sh = A \cdot (x_i Pe)^{m z_i},$$  \hspace{1cm} (6-3)

to include two variables (local Peclet number and exponent $m$), the correlation accuracy is improved. Both experimental and numerical data show that there is a strong correlation between $x_i$ and $z_i$, which means that both local Peclet number and the exponent $m$ are governed by the same flow phenomenon, and only one variable is needed to quantify variations in mass transfer due to local structural effects.

This research has both fundamental and practical contributions to the study of mass transfer in porous media. The new correlations, such as equations (6-1) and (6-3), present new ways to describe the mass transfer distribution in porous media. The effects of large- and small-scale media structure on mass transfer behavior could be quantified statistically using these new correlations. The analysis of mass transfer properties and corresponding flow profiles provides insight into the connection between mass transfer and hydrodynamics. A further study with more
detailed flow and mass transfer information will give deeper understanding in this area. Also, improved understanding of mass transfer coefficient distributions can improve how certain phenomena are described, such as long effluent tails during NAPL remediation.

6.2 FUTURE DIRECTIONS

The scope of this research included quantitative descriptions of the specific porous medium structures examined, but was limited to phenomenological explanations of more general effects. Efforts to produce generalized but quantitative correlations using averaged descriptions of the local hydrodynamics was unsuccessful. Hence an important area of future research is the development of new tools to provide estimates of streamline-scale behavior. Network modeling, a powerful intermediate-level technique, is a good candidate for this task. Methods have already been pursued to a certain extent, such as imposing assumed velocity profiles onto pore-scale flowrates for particle tracking or estimates of velocity gradients (Thompson et al., 1997), and simplifying network geometry to a point to make more rigorous hydrodynamic or mass-transfer calculations (Dillard et al., 2000).

The study of the mass transfer rate and coefficient distribution has practical significance in NAPL transport in porous media. Various studies (Geller et al., 1993, Sørensen et al. 1995, Mayer, 1996) show that modeling can provide much better predictions when using mass transfer rate distributions or multi-mass transfer rates, rather than single mass transfer rate. Based on this research, the variations in overall mass transfer rate are believed to originate from the distributions of mass transfer coefficient and the distributions of interfacial area. So the overall mass transfer coefficient, which is used in traditional continuum models, would change over time because the contributions of individual dissolution sources would vary with the time. Hence, another important area for future research is to apply the results from experimental and
numerical studies to field-scale model to improve modeling accuracy. In these models, the mass transfer rate distribution could be determined using a mass transfer coefficient distribution and interface area distribution. The total mass transfer rate will be dynamic and very low during late stages of the dissolution process because NAPLs that have not disappeared yet are those with very slow mass transfer coefficients.
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