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Investigation of Transport Phenomena in a Highly Heterogeneous Porous Medium

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This work focuses on solute mass transport in a highly heterogeneous two-region porous medium consisting of spherical low-hydraulic conductivity inclusions, embedded in a high-hydraulic conductivity matrix. The transport processes occurring in the system are described by three distinct time scales. The first time scale reflects the characteristic time for convective transport in the high-conductivity matrix. The second time scale reflects the characteristic time for diffusive transport in the low-conductivity inclusions. The third time scale reflects the characteristic time for convection within the inclusions. Two Péclet numbers can be defined that compare the time scales and provide qualitative insight into the net transport behavior in two-region media. To model this system, four different representations were developed: (1) a Darcy-scale model that involved direct microscale computation over the entire domain of the
experimental system, (2) a direct microscale simulation computed on a simplified domain that had similar geometric parameters (e.g. volume fraction of inclusions) as the complete domain for the experimental system, (3) a volume averaged model (after Chastanet and Wood [2008]) which uses a constant mass transfer coefficient and (4) a volume averaged model which employs a time-dependent mass transfer coefficient. Two different experimental conditions were investigated: a high flow rate, and a low flow rate. Detailed understanding of the experimental system was developed, which led to accurate prediction of the system’s behavior for the higher flow rate. Accurate early time fit of the data was achieved for the experiment with the lower flow rate, while late time behavior between the models and experimental data diverged. Further investigations of the experimental system were conducted to examine possible sources of errors that could lead to an inaccurate description of the system’s properties. Additional mixing within the system, inhomogeneous distribution of the effective diffusion coefficient and imprecise initial estimates of the hydraulic parameters are all possible explanations for the inaccurate model representation of the system’s behavior for the lower flow rate case.
Investigation of Transport Phenomena in a Highly Heterogeneous Porous Medium

by

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APPROVED:

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Major Professor, representing Chemical Engineering

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Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Daniel Vogler, Author
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Chapter 1 – Introduction and Overview

This work focuses on modeling solute mass transport in a highly heterogeneous two-region porous medium consisting of spherical low-hydraulic conductivity inclusions, embedded in a high-hydraulic conductivity matrix. This system is investigated for two different flow rates.

Transport processes in heterogeneous porous media present complex geometries and time-dependent mass transfer behavior that can be difficult to model. Accurate representation of the system’s behavior faces various obstacles, such as boundary conditions, sufficient knowledge about the systems geometry and precise estimates of the parameters describing the domain.

The system under consideration was investigated experimentally by Harrington [2010] and consists of a coarse matrix with 203 spherical inclusions that have significantly different transport parameters than the matrix material. The low-conductivity region is also denoted as the $\omega$-region while the high-conductivity region is referred to as the $\eta$-region. The precise geometry of the system is known and the basic material properties of $\omega$- and $\eta$-region have been measured [Harrington, 2010].

The transport processes occurring in the system are described by three distinct time scales. The first time scale reflects the characteristic time for convective transport in the high-conductivity matrix. The second time scale reflects the characteris-
tic time for diffusive transport in the low-conductivity inclusions. The third time scale reflects the characteristic time for convection within the inclusions. Two Péclet numbers can be defined that compare the time scales and provide qualitative insight into the net transport behavior in two-region media.

To model this system, four different representations were developed: (1) a Darcy-scale model that involved direct microscale computation over the entire domain of the experimental system, (2) a direct microscale simulation computed on a simplified domain that had similar geometric parameters (e.g. volume fraction of inclusions) as the complete domain for the experimental system, (3) a volume averaged model (after Chastanet and Wood [2008]) which uses a constant mass transfer coefficient and (4) a volume averaged model which employs a time-dependent mass transfer coefficient.

Detailed understanding of the experimental system was developed, which led to accurate prediction of the system’s behavior for the higher flow rate. Accurate early time fit of the data was achieved for the experiment with the lower flow rate, while late time behavior between the models and experimental data diverged. Further investigations of the experimental system were completed to examine possible sources of error that could lead to an inaccurate model of the system’s properties. Additional mixing within the system, inhomogeneous distribution of the effective diffusion coefficient and imprecise initial estimates of the hydraulic parameters are possible reasons for an inaccurate representation of the system’s behavior for the lower flow rate case.

The previous research on this topic is reviewed in Chapter 2 (Literature Re-
view). Focus is especially put on two region models and the mass transfer mechanisms and terms employed. The concept of "mobile" and "immobile" transport regions and the Péclet number $Pe$ as a means to characterize transport behavior are presented.

In Chapter 3 (Materials and Methods), a detailed description of the experimental system is given and the models for mass transport are introduced. Transport models with a fully resolved and a simplified geometry are developed to represent the system. These models are then extended to obtain upscaled solutions for the system by using volume averaged models.

In Chapter 4 (Results), the breakthrough curves of the simulations are presented. The system properties are examined further in Chapter 5 to achieve more accurate fitting of the experimental data.

In Chapter 5 (Discussion), the results are discussed and interpreted. Transport mechanisms characterizing the system are classified by the introduction of the Péclet numbers $Pe_{\omega}$ and $Pe_{\eta\omega}$ for the two regions.

In Chapter 6 (Conclusion), final remarks and results that can be taken from this study are offered. The behavior of the experimental system can be modelled by the direct numerical simulation model with the simplified domain (Section 3.2.4) or the volume averaged models (Section 3.3). The fully resolved system, which requires significantly more computational power, does not enhance the accuracy of the results.
Chapter 2 – Literature Review

Heterogeneous, anisotropic porous media have been the focus of interest for a long time. Understanding the global behavior of such systems is crucial in order to be able to apply the methods of chemical and environmental engineering to real problems.

This work focuses on solute transport in highly heterogeneous porous media that can be represented as a two-region system. A two region model features two distinct sets of hydraulic parameters for each region. In the past, two-region models have been employed to model processes like adsorption onto solids, mass transfer via diffusion between the matrix and stagnant regions or mass exchange between regions with different flow fields. This Chapter gives an introduction into previous work to predict the behavior of mass-transfer between the two regions and the total system.

Solute transport in porous media is usually described with a convection dispersion equation - CDE. The classical form of the CDE for a non-reacting solute is formulated as follows

$$\varepsilon \frac{\partial c}{\partial t} = \nabla \cdot (\varepsilon \mathbf{D} \cdot \nabla c) - \varepsilon \mathbf{v} \cdot c$$  \hspace{1cm} (2.1)

where the velocity $\mathbf{v}$ is given by Darcy’s law:

$$\mathbf{v} = -K \cdot \nabla h$$  \hspace{1cm} (2.2)
Here, \( c \) represents the concentration of the solute in the liquid phase, \( \varepsilon \) is the porosity of the media, \( \mathbf{D} \) is the dispersion tensor, \( \mathbf{K} \) stands for the hydraulic conductivity and \( h \) denotes the hydraulic head. Complex heterogeneous systems can pose various difficulties when modeling, such as unknown or time-dependent boundary conditions, insufficient knowledge of system parameters (e.g. porosity, geometry, or hydraulic conductivity) or uncertainty as to how the different regions will influence each other and affect solute transport.

Figure 2.1 illustrates how a heterogeneous system might be organized. Here, three different length scales are defined that define regions of distinct properties;
For this work, the three scales are defined as follows. The *microscale* is defined by the size of a representative volume of one of the two media, and it is also referred to as the Darcy scale. The *macroscale* characterizes a larger scale that consists of different regions with varying hydraulic parameters. The macroscale is therefore heterogeneous even though it may consist of regions that are homogeneous on the microscale. The *field scale* embodies the whole system and is mainly relevant for systems that are larger than the laboratory scale.

If the system consists of two regions that are characterized by distinct sets of parameters, various classifications can be made. A mobile zone refers to a region of the matrix where convection is the dominant transport parameter. Conversely, in an immobile zone, diffusion is the dominant transport mechanism.

### 2.1 Mobile-Immobile behavior due to Adsorption

When adsorption is occurring in the system, it is crucial to represent the mass transfer between the solute adsorbed onto the solid and the matrix. Wilson [1948] was among the first to investigate the effect of adsorption on the diffusion equation. In this formulation, there is a solid-phase solute exchange between two zones.

\[
\frac{\partial c}{\partial t} = D\nabla^2 c - \frac{\partial A}{\partial t}, \quad \frac{\partial A}{\partial t} = \lambda c - \mu A
\] (2.3)
Here, $A$ is the amount of solute sorbed onto the matrix, $D$ the diffusion coefficient and $\lambda$ and $\mu$ are constants quantifying the adsorption process. These two partial differential equations are coupled via a mass transfer term and the condition that the overall amount of solute in the system is conserved or that the change over time is linked to sink/source-terms. The condition developed by Wilson [1948] for the total mass conservation in a system consisting of two sorbing sheets that are separated by the distance $l$ is

$$(R + 1)y + l\left(\frac{\partial y}{\partial x}\right) = \text{constant} \quad (2.4)$$

where $R$ relates the solute concentration in the liquid $c$ to the adsorbed concentration on the solid $A$ with $A = Rc$. $y(x, t)$ is the total amount of solute in one region and $x$ denotes the distance from the surface of the sheets. Numerical simulation of the system developed by Wilson [1948] was provided by Crank [1948]. Crank introduced a non-linear relation between the solute concentration in the matrix and on the surface. An equation of the form

$$A = k_1c^{k_2} \quad (2.5)$$

was suggested, where $k_1$ and $k_2$ are constants that correspond to the properties of the system investigated.

The distinction between equilibrium and non-equilibrium conditions is essential for understanding the dominant transport processes. Equilibrium and non-equilibrium
conditions are typically presented by

\[
\text{equilibrium : } \quad A = k_1 c + k_2 \quad \quad (2.6)
\]

\[
\text{non-equilibrium : } \quad \frac{\partial A}{\partial t} = k_1 c - k_2 A \quad \quad (2.7)
\]

Lapidus and Amundson [1952] examined the two cases (Eqs. 2.6 and 2.7) with basic correspondances. Again, \(k_1\) and \(k_2\) are parameters related to the adsorption process. Non-equilibrium conditions (Eq. 2.7) are represented by transient conditions for the adsorption process [Bajracharya and Barry, 1997]. If the system is at equilibrium (Eq. 2.6), a change in solute concentration in one phase will have an immediate effect on the solute concentration of the other phase at the boundary. An immediate effect can be assumed if the time lag of the system’s response to the charge in concentration is small in comparison to the time scales of other transport processes. These two models contain two important assumptions. First, the equilibrium model (Eq. 2.6) correlates the amount of adsorbed solute on the surface to the concentration of solute in solution. Each point in the system is always at equilibrium and the mass transfer from solution to the surface is assumed to be instantaneous. Second, if transport rates are fast relative to the adsorption process, the adsorption process will be time dependent. That means that the system will not be at equilibrium at all times. The maximum amount of adsorbed matter is given by the equation (Eq. 2.7) of the non-equilibrium case.
2.2 Mobile-Immobile behavior due to permeability contrasts

Systems consisting of low-permeability regions embedded in a high-permeability matrix are another important two-region system that can have distinct characteristic which is investigated in the following section. Deans [1963] examined the effect of non-flowing (immobile) regions on transport phenomena. Deans [1963] divides the medium into a finite number of mixed cells (the concentration is assumed to be uniform in each cell) to model the effects of diffusion.

\[
\frac{dc_i}{d\tau} = c_{i-1} - c_i
\]  

(2.8)

\(\tau\) denotes a dimensionless time. The solution for the simple cell model by Deans and Lapidus [1960] has only the length of the mixing cell as a parameter. If the number of mixing cells is small, an asymmetric breakthrough curve (BTC) behaviour results, which becomes symmetric when a large number of cells are used, as found by Aris and Amundson [1957].

The model of Deans and Lapidus [1960] was extended by adding a stagnant volume fraction and a mass-transfer factor as two additional parameters. This capacitance model [Deans, 1963] was used to estimate the longitudinal dispersion coefficient for a mobile-immobile system.

In 1964, Coats and Smith investigated the asymmetric behavior of BTC with the capacitance model developed by Deans [1963]. Coats and Smith [1964] modeled the contribution of dead-end pore volume to the mobile phase. While the mobile phase is described by the convection diffusion equation, it is linked to the dead-
end pores through a simple diffusion process. Coats and Smith [1964] propose the equation for the 1-D case

\[ D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} = f \frac{\partial c}{\partial t} + (1 - f) \frac{\partial S}{\partial t} \] (2.9)

in which \( S \) denotes the solute concentration in the stagnant region and \( f \) gives us the volume fraction of the pore space that is occupied by the mobile zone. Transfer between two regions with distinct hydraulic properties is assumed to be driven by the concentration gradient. It occurs via simple diffusion with a first order transfer rate \( \alpha \)

\[ (1 - f) \frac{\partial c^*}{\partial t} = \alpha(c - S) \] (2.10)

The larger the mass transfer coefficient gets, the faster is the exchange process between the two regions. The extreme would be instant exchange or the equilibrium condition. This model was examined further by van Genuchten and Wierenga [1976], who found a good agreement and description of asymmetric BTC and tailing. In their study, van Genuchten and Wierenga [1976] also concluded that minor changes of the dispersion coefficient would have a relatively small impact on the concentration profile at the effluent. The authors extended the model to account for adsorption in addition to zones of stagnant water. The authors found that small mobile zone fractions (in comparison to the total system volume) could cause early breakthrough. They also found that large dead-end pore spaces lead to tailing in the BTC as trapped solute is released slowly over time.

The analytical solutions that were obtained by Coats and Smith [1964] and van
Genuchten and Wierenga [1976] are both valid for a semi-infinite-column and a step input at the influent. Smedt and Wierenga [1979] extended this work to a more general time convolution solution

\[ c_m = \int_0^\tau \frac{\partial c'}{\partial \tau} Jd\tau \]  

\[ c_{im} = \int_0^\tau \frac{\partial c'}{\partial \tau} (1 - J)d\tau \]  

Here, \( c' \) stands for the solution of the same problem without considering the immobile region, \( \tau \) is the time variable over which is integrated and \( J \) is a function that describes the mass transfer. It can be formulated in the form of a power-series

\[ J(a, b) = exp(-a - b) \sum_{n=0}^{\infty} \frac{b^n}{n!} \sum_{m=0}^{n} \frac{a^m}{m!} \]  

\( a \) and \( b \) are coefficients that describe the respective mass transfer. In a similar fashion, Rao et al. [1980] developed a model to calculate the mass transfer coefficient for the leaching of solute out of spheres. Experimental data was compared with a purely Fickian diffusion model and the model developed by Rao et al. [1980]. The model employed solute transfer from the spheres into solution which depended on the difference in concentration of the solute between the sphere and the solution. A time-dependent mass transfer coefficient was calculated to match the experimental data best. In this model, the mass transfer coefficient depends on the molecular diffusion coefficient, the volumetric water content within the spheres, the radius of the spheres, and a coefficient relating the volumetric water content within spheres.
and solution to each other. The mass transfer coefficient is also found to be a decreasing function of time. Dependencies of mass transfer coefficients for non-spherical geometries were also discussed in this work.

Most of the work mentioned here has focused on mass transfer between the mobile and the immobile zone if the diffusion length between the two zones is relatively short or mass transfer and adsorption occur instantaneously. Bibby [1981] provided an approach that is valid when the solute transport between the immobile and the mobile region is time dependent. The approach showed a good agreement with experimental data.

Skopp et al. [1981] extended the previous models of mobile-immobile zones to the case where two mobile regions exist, each having significant convective transport. In this work, the two mobile regions were linked with a linear mass transfer term. It was shown that the model approaches the convection dispersion equation when the interaction coefficient is large enough. Given that each region has distinct hydraulic parameters and transport properties, a single equation can be written for each region ($\eta$ and $\omega$)

$$\frac{\partial c_\eta}{\partial t} = D_\eta \frac{\partial^2 c_\eta}{\partial x^2} - v_\eta \frac{\partial c_\eta}{\partial x} - \frac{\alpha (c_\eta - c_\omega)}{\theta_\eta}$$  (2.14)

$$\frac{\partial c_\omega}{\partial t} = D_\omega \frac{\partial^2 c_\omega}{\partial x^2} - v_\omega \frac{\partial c_\omega}{\partial x} + \frac{\alpha (c_\eta - c_\omega)}{\theta_\omega}$$  (2.15)

Note that the subscripts $\eta$ and $\omega$ denote the high-conductivity matrix and the low-conductivity region respectively. This model reduces to the dead-end pore model of Coats and Smith [1964] if $v$ and $D$ are zero in one region.
Gerke and van Genuchten [1993] extended the mass transfer coefficient by developing a first-order term for transient conditions and regions of varying saturation. The authors [Gerke and van Genuchten, 1993] derive the mass transfer coefficient $\alpha$ to be of the form

$$\alpha = \frac{\beta}{a^2} K_i \gamma$$  \hspace{1cm} (2.16)

Here, $\beta$ is a dimensionless factor related to the geometry, $a$ is a characteristic length of the geometry employed in the model, $K_i$ is the hydraulic conductivity near the interface of the two zones and $\gamma$ is a dimensionless scaling factor. Various approaches to link the hydraulic conductivity to the pressure heads in the two zones were tested. The best fitting result for the hydraulic conductivity was obtained with the integration method

$$K_i = \frac{1}{h_\omega - h_\eta} \int_{h_\eta}^{h_\omega} K_i(h) dh$$  \hspace{1cm} (2.17)

The scaling factor $\gamma$ enabled an improvement of fitting and, after scaling, the upstream weighted and arithmetic-averaged methods provided the best fit. The scaling factor is introduced to obtain matching results at the value of half of the maximum amount of horizontal infiltration.

Upstream weighted: \hspace{1cm} $K_i = K_i(h_\eta)$ \hspace{1cm} (2.18)

Arithmetic Average: \hspace{1cm} $K_i = 0.5[K_i(h_\eta) + K_i(h_\omega)]$ \hspace{1cm} (2.19)
To be able to classify the different characteristic times for the process, a dimensionless time is adopted

\[ t^* = \frac{t}{t_{0.5}} \]  

(2.20)

Here, \( t_{0.5} \) marks the time when half of the maximum amount of cumulative solute transfer is reached. Investigations by Gerke and van Genuchten [1993] yielded the following general conclusions for their model of cumulative water transfer between regions. The model lead to an underestimation of solute transfer for early times and an overprediction of solute transfer after half of the maximum transfer has been reached (for \( t^* > 1 \)). Gerke and van Genuchten [1993] also investigated the use of a non-linear mass transfer term of the form

\[ \Gamma = \alpha [h_\eta - h_\omega]^p \]  

(2.21)

where \( p \) is a dimensionless exponent. The authors found that the value of \( p \) had a small effect on the resulting simulations; however, there was a general tendency for improved predictions at early times (\( t^* < 1 \)) and worse predictions for later times (\( t^* > 2 \)). Ultimately Gerke and van Genuchten [1993] concluded that an exponent of \( p = 1 \) gives sufficiently accurate results.

The dependency of the mass transfer coefficient \( \alpha \) on various factors can be found in a study of Young and Ball [1995].

Another approach to model mass transfer between regions was studied by van Genuchten and Wierenga [1976]. They used a sorption model to account for mass transfer between regions. They found \( \alpha \) to depend on the retardation factor \( R \) of
the immobile zone, the velocity $v$ in the mobile zone, the column length $l$ and the form and duration of input (pulse or step input). The authors [van Genuchten and Wierenga, 1976] found a relation for $\alpha$ that takes the form

$$\alpha = \frac{K_\alpha \varepsilon_{im} D_p}{a^2}$$

(2.22)

where $K_\alpha$ is a dimensionless time-dependent coefficient, $D_p$ is the diffusion coefficient on the pore scale, $\varepsilon_{im}$ is the porosity of the immobile zone and $a$ is the radius of the spheres used in the model. The two parameters $R$ and $v$ cause an increase of $\alpha$ as they are increased. The time, the input form and $l$ lead to a decrease of the mass transfer coefficient $\alpha$ if they are increased. This can be explained as following; a high retardation factor leads to longer times until equilibrium between zones is reached, which requires a higher $K_\alpha$ to model the process. Rao et al. [1980] had previously noted that an increase of the ratio $v/l$ leads to an increase of the first order coefficient. The duration and form of the input affects how long it takes for the two regions to reach equilibrium and thereby determines whether the mass transfer coefficient decreases or increases.

A more sophisticated mass transfer model was developed by Haggerty and Gorelick [1995]. This model enables the combination of various mass transfer terms (e.g. for adsorption or diffusion) to account for changes in the domain on the microscale or processes that occur simultaneously and is, hence, termed a “multirate model”. It is also very useful if various different geometries need to be implemented at once. Furthermore, it has been shown that the multirate model is consistent with
a simple diffusion model. If the geometry and its parameters are known, the new model can provide more accurate results for the system because it is possible to give a more accurate representation of the system properties in the model.

Guswa and Freyberg [2000] investigated the effect of a lense shaped inclusion in a porous medium with a system similar to the “mobile-mobile” region system by Skopp et al. [1981]. The movement of solute by convection and diffusion in the inclusions and the effect of the inclusions on tailing were a main part of the study. This is different from the initial stagnant region models by [Wilson, 1948] and [Coats and Smith, 1964] in which convection and dispersion were only prominent in the mobile phase.

The dominant process can be expressed with the inclusion Péclet number $Pe$ which relates the diffusive flux $Dc/L^2$ to the characteristic time for convective flux $vc/L$.

$$Pe = \frac{vL}{D}$$ (2.23)

High $Pe$ ($Pe > 1$) indicate that convection is the dominant mass transport process whereas low $Pe$ indicate that diffusion dominates mass transport. To describe all transport parameters accurately, it is important to recognize the phenomena occurring in the immobile zone. In media with only a few inclusions, the breakthrough curve can show behavior similar to step functions and will likely not be as smooth as if diffusion is the dominant process. This is caused by a lack of mixing of solute within the system.
2.3 Non-local in time models

The work of Haggerty et al. [2000] further examines the description of mobile-immobile zone systems. The authors [Haggerty et al., 2000] examined the tailing displayed at long times after the initial effects of convective transport no longer dominate the BTC. A simple expression for the concentration at late times was found to be

\[ c = t_{ad} \left( C_0 g - m_0 \frac{\partial g}{\partial t} \right) \]

(2.24)

for \( t \ll t_{ad} \) and \( t_\alpha \ll t_{ad} \). Here, \( t_\alpha \) is the mean residence time in the immobile domain, \( t_{ad} \) is the convection injection pulse, \( g \) is a memory function and \( m_0 \) is the zeroth moment. The study was motivated by the fact that the BTC of rate-limited mass transfer models exhibit power law behavior at late times. Earlier work had already shown the possibility and importance of estimating capacity coefficients or rate coefficients from late time data instead of the main peak. In a power law, a property of the system (e.g. concentration \( c \)) changes as a power of another factor of relevance in the process (e.g. time \( t \): \( c \propto t^{-k} \)). The exponent \( k \) can be evaluated by plotting existing data on a double-logarithmic graph. The value of the exponent found [Hadermann and Heer, 1996] for the single-rate diffusion model was \(-3/2\) as long as \( t \) is not larger than \( t_\alpha \). Haggerty and Gorelick [1995] give a detailed explanation of BTC and power law behavior for various cases. As they explain, the particular process and geometry associated with mass leaving the immobile zone will determine the form of decline of the breakthrough curve at large times. Schumer et al. [2003] further examined the description of the transient behavior
of mass exchange between mobile and immobile zone by applying power laws as investigated earlier by Haggerty et al. [2000]. The mobile-immobile model (MIM) by Coats and Smith [1964], for example, predicts exponential decline to an asymptotic limit. Schumer et al. [2003] develop equations to describe the behaviour of a two-region system with power law tails and examine the issue of mass conservancy for such a model.

Another study regarding the comparison of the CDE with Fickian dispersion and the MIM model was done by Sanchez-Vila and Carrera [2004]. The main goal of the study was to see if a mass transfer model would lead to exactly the same moments of the BTC as the CDE with Fickian dispersion. The authors reproduce the first three moments obtained with the CDE, while the fourth moment remains a close fit. This shows the possibility to use both models interchangeably. While the mass transfer model is more likely to capture the asymmetry of the process and its tailing, it is difficult to generalize this model for different velocities. Even though both models have their limitations, it is very important to see that they both give the same results for the first three moments and can accurately represent each other.
Chapter 3 – Materials and Methods

3.1 The Experimental System

The system under consideration has been described in detail by Harrington [2010]. Three different volumetric flow rates were considered in the original work. Because the two lower flow rates were very similar, this work focuses on comparing the results from the smallest flow rate (Experiment 1) and the largest flow rate (Experiment 3). The experimental system consisted of a box with the following dimensions: $L = 100 \text{ cm}$; $W = 50 \text{ cm}$; $H = 20 \text{ cm}$. The box was filled with two different media: a coarse matrix with fine-textured spherical inclusions that is denoted the $\eta$-region and 203 randomly placed low-conductivity spheres with a diameter of $d_\omega = 5 \text{ cm}$ that are denoted the $\omega$-region. The porosity $\varepsilon$, density $\rho$, hydraulic conductivity $K$ and volumetric fraction $f$ of the $\eta$- and the $\omega$-regions are summarized in Table 3.1. No spheres were placed within 5 cm of the in-

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon$</th>
<th>$\rho$</th>
<th>$K$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$-region</td>
<td>0.40 ± 0.0041</td>
<td>2.50 ± 0.014</td>
<td>$7.77 \times 10^{-4} \pm 0.22 \times 10^{-4}$</td>
<td>0.867</td>
</tr>
<tr>
<td>$\omega$-region</td>
<td>0.31 ± 0.0055</td>
<td>2.43 ± 0.014</td>
<td>$1.83 \times 10^{-6} \pm 0.16 \times 10^{-6}$</td>
<td>0.133</td>
</tr>
</tbody>
</table>
let or outlet. The porous medium was initially saturated ($c_{sat}$) with 25 mg/L lithium bromide and 1.5 mg/L fluorescein, which functioned as tracers. With this configuration, tracer-free water was pumped into the system at different flow rates ($Q_1 = 5.6 \text{ mL/min} = 9.3 \times 10^{-8} \text{ m}^3/\text{s}$ and $Q_3 = 45.2 \text{ mL/min} = 7.5 \times 10^{-7} \text{ m}^3/\text{s}$)
to obtain the mass recovery curves by measuring the outlet concentration versus time [Harrington, 2010]. The standard error of the experimental data was determined to be 0.026. This was calculated by comparing the experimental data to the benchmark concentration used for normalizing the concentration [Harrington, 2010]. The experimental data from Experiment 1 was used for this calculations as Experiment 1 has the largest quantity of experimental data points. The calculations were performed for times in which the measured effluent concentration should be $c_{sat}$.

### 3.1.1 Parameters

Most of the parameters needed to model the system can be taken directly from Section 3.1. The properties of fluorescein were used to model solute mass transport, which gives the molecular diffusion coefficient $D_{Fl} = 4.9 \times 10^{-10} \, m^2/s$ [Rani et al., 2005]. The effective diffusion coefficients in the matrix and inclusions were computed with Maxwell’s equation

$$D_{\eta} = D_{Fl} \frac{2}{3 - \varepsilon_{\eta}} = 3.77 \times 10^{-10} \, m^2/s$$

(3.1)

$$D_{\omega} = D_{Fl} \frac{2}{3 - \varepsilon_{\omega}} = 3.64 \times 10^{-10} \, m^2/s$$

(3.2)

To obtain a value for the dispersivity of the coarse matrix, breakthrough experiments [Harrington, 2010, Section 3.4.2] were made with a system that solely consisted of the coarse matrix of the $\eta$-region. These experiments provided mass re-
covery curves that were inverse fitted by using the convection-dispersion equation (CDE) [Harrington, 2010]

\[
\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = \nabla \cdot (D_{\text{eff}} \nabla c)
\]

(3.3)

where \(D_{\text{eff}}\) denotes the effective dispersion coefficient. These inverse fits were used to obtain estimates for the longitudinal dispersivity in the \(\eta\)-region \(\alpha_{L,\eta}\) and the dispersion in the \(\omega\)-region \(D_\omega^*\) which are listed in Table 3.2. In principle, all of the experimental results should be predictable with a single dispersivity for the \(\eta\)-region \((\alpha_{L,\eta})\), as dispersivity only depends on the geometry of the system. The results reported by Harrington [2010] are listed in Table 3.2. To obtain a single

<table>
<thead>
<tr>
<th>parameter</th>
<th>(D_\omega^*) (10^{-10} \text{ [m}^2/\text{s]})</th>
<th>(\alpha_{L,\eta}) [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>given</td>
<td>3.77</td>
<td>0.0052</td>
</tr>
<tr>
<td>Experiment 1 fit</td>
<td>0.90</td>
<td>0.3169</td>
</tr>
<tr>
<td>Experiment 3 fit</td>
<td>3.29</td>
<td>0.0272</td>
</tr>
</tbody>
</table>

value for the dispersivity \(\alpha_{L,\eta}\) that is applicable to all experiments, the arithmetic mean was used for these values, leading to \(\alpha_{L,\eta} = 0.129 \text{ m}\). The total initial mass of fluorescein in the system was calculated by assuming complete saturation at \(t = 0\), taking into account the respective volumetric fractions of the \(\eta\)- and \(\omega\)-region and their porosities. A pore volume of 0.0388 m\(^3\) (out of the total volume of 0.1 m\(^3\)) was computed for the system. This value was used to conduct the numerical
simulations for accuracy of the transport parameters and mass conservation. The finite element software COMSOL Multiphysics® was used to carry out the simulations for the systems described below (Sections 3.2 and 3.3).

3.2 Direct Numerical Simulation Models

3.2.1 Equations

The governing equation for the direct numerical simulation (DNS) model is the CDE. The complete system of equations representing mass and momentum transport is specified by the following equations

- **Darcy’s law**: \( \mathbf{v} = -\frac{K}{\mu} \nabla p \) (3.4)

- **CDE**: \( \frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = \nabla \cdot (D_{\text{eff}} \cdot \nabla c) \) (3.5)

- **Initial Conditions**: \( c_\eta|_{t=0} = c_\omega|_{t=0} = c_{\text{sat}} \) (3.6)

- **Interfacial B.C.**: \( c_\omega = c_\eta \) at \( A_{\eta \omega} \) (3.7)

- **Upstream B.C.**: \( c_\eta|_{x=0} = 0 \) (3.8)

- **Downstream B.C.**: \( \frac{\partial c_\eta}{\partial x}|_{x=L} = 0 \) (3.9)

For convenience, all concentrations were normalized, which gives the following initial condition \( c_{\eta,\text{norm}}|_{t=0} = c_{\omega,\text{norm}}|_{t=0} = 1 \).
3.2.2 Convergence Analysis

A convergence analysis was carried out to ensure sufficient refinement of the mesh and accurate results of the iterative solver. The second moment of the mass recovery curve versus time was used to display the sensitivity of the model in regard to mesh refinement

\[ m(c) = \sum_{i=1}^{n} c_i \cdot t_i^2 \]  \hspace{1cm} (3.10)

The minimum and maximum element size were gradually decreased to find the mesh parameters that provide sufficient accuracy (i.e. the second moment remained stagnant after gradually refining the mesh). Similarly, the absolute and relative tolerances of the solver were refined until changes between solutions obtained with varying tolerance parameters were found to be negligible. The concentration at the effluent was calculated with a surface integration over the surface area of the effluent. The average concentration at the outlet was calculated and compared to other simulations and the experimental data.

3.2.3 Fully-Resolved System

A DNS simulation of the system mentioned above (Section 3.1), with the boundary and initial conditions from Section 3.2.1, was performed. This model included the exact geometry described above (Section 3.1). As mentioned previously, the results from the convergence analysis for the simplified system (Subsection 3.2.4) were used to compute the fully-resolved model. The results show that this is a reasonable
assumption, as measured by the correspondence between the fully-resolved and simplified models.

3.2.4 Simplified System

One approach for modeling the system described above is with a simplified representation of the system. For this model, the x-dimension of the system was kept constant, but the y- and z-dimension of the system were reduced (10 cm each). The ratio of the volume of the \( \omega \)-region to the total volume was kept the same as in the original experiment (\( V_\omega / V_{\text{total}} = 0.133 \)). No inclusions were placed within 5 cm of the inlet or outlet of the system. The spheres were placed randomly in the system with a code generated with MATLAB® (Appendix C).

3.3 Volume Averaging

3.3.1 Motivation for Volume Averaging

The method of volume averaging [Whitaker, 1999] provides the tools to reduce the number of degrees of freedom of a system with various distinct scales (i.e. microscale and macroscale). This is especially convenient for a highly heterogeneous system with a complex geometry where a DNS model can be difficult. Upscaling is particularly helpful for modelling natural formations with strong scale dependency of the flow characteristics. Two volume averaged models were developed that implement the two-region effects in form of a mass transfer coefficient - (MTC) that
Figure 3.3: The simplified system with the included spheres

Figure 3.4: The simplified system with influent (left) and effluent (right)

was non-transient in the \textit{quasi-steady model} and transient in the \textit{uncoupled model}.

The following section gives an overview of the development of the upscaled mass balance equations via volume averaging.
3.3.2 Upscaled mass balance equations

There are numerous detailed approaches and applications to volume averaged models [Whitaker, 1999; Quintard, 1993; Wood et al., 2003; Cherblanc et al., 2003 or Chastanet and Wood, 2008]. This work focuses on the investigations by Chastanet and Wood [2008]. The authors investigated mass transfer between two regions by developing three mass transfer coefficients \( \alpha \) with different dependencies upon time to solve the closure problem. Three upscaled models were developed. The first was a fully coupled model that made no simplifications regarding time-dependence for the closure problem. The second was an uncoupled model where the time-dependency of the effective mass transfer coefficient was decoupled from the macroscale transport. The third was a quasi-steady model that assumed the mass transfer coefficient to be constant. The uncoupled model and the quasi-steady model are both investigated in this work.

Formulation of the mass balance equations and boundary conditions for the microscale was carried out according to Chastanet and Wood [2008]

\[
\varepsilon_\eta \frac{\partial c_\eta}{\partial t} = \nabla \cdot (\varepsilon_\eta D^*_\eta \cdot \nabla c_\eta) - \varepsilon_\eta v_\eta \cdot \nabla c_\eta, \quad \text{in the } \eta\text{-phase} \tag{3.11}
\]

\[
\varepsilon_\omega \frac{\partial c_\omega}{\partial t} = \nabla \cdot (\varepsilon_\omega D^*_\omega \cdot \nabla c_\omega), \quad \text{in the } \omega\text{-phase} \tag{3.12}
\]

B.C. 1 \( c_\omega = c_\eta \), on \( A_{\eta\omega} \) \tag{3.13}

B.C. 2 \( -(\varepsilon_\eta D^*_\eta \cdot \nabla c_\eta) \cdot n_{\eta\omega} = -(\varepsilon_\omega D^*_\omega \cdot \nabla c_\eta) \cdot n_{\eta\omega}, \) on \( A_{\eta\omega} \) \tag{3.14}
The unit normal vector \( \mathbf{n}_{\eta \omega} \) points from the \( \eta \)-phase towards the \( \omega \)-phase. The parameters \( \mathbf{D}^*_\eta \) and \( \mathbf{D}^*_\omega \) are the total dispersion tensors for the \( \eta \)- and \( \omega \)-regions respectively. B.C. 3 represents the no-slip boundary condition at the wall (denoted by \( \beta \)).

To model species transport, the flow field had to be specified. As the system received a continuous volumetric flow rate, it was assumed that the flow field was quasi-steady, and the momentum balance equations took the following form

\[
\nabla \cdot \mathbf{v}_\eta = 0, \quad \text{in the } \eta \text{-phase} \tag{3.16}
\]

\[
\text{B.C. 1 } \quad \mathbf{v}_\eta \cdot \mathbf{n}_{\eta \omega} = 0, \quad \text{on } A_{\eta \omega} \tag{3.17}
\]

\[
\text{B.C. 2 } \quad \mathbf{v}_\eta \cdot \mathbf{n}_{\eta e} = 0, \quad \text{on } A_{\eta e} \tag{3.18}
\]

\[
\mathbf{v}_\eta = \left( -\frac{K_\eta}{\varepsilon_\eta} \nabla h_\eta \right), \quad \text{in the } \eta \text{-phase} \tag{3.19}
\]

The initial conditions of both regions were known (Eq. 3.6) to be

\[
c_\eta|_{t=0} = c_\omega|_{t=0} = c_{\text{sat}} \tag{3.20}
\]

To proceed to volume averaged equations, certain length scale restrictions have to be met. The characteristic length of the inclusions, \( \ell_\omega \), is the diameter \( d_\omega \) (see Section 3.1) while the characteristic length of the \( \eta \)-region, \( \ell_\eta \), is roughly the distance between the inclusions (see Figure 2.1). The two characteristic length
scales, $\ell_\eta$ and $\ell_\omega$, have to be significantly smaller than the characteristic length scale of the averaging volume, the radius $r_0$. The radius of the averaging volume on the other hand has to be substantially smaller than the smallest characteristic length of the field scale, which is denoted by $L$. A detailed description of the derivation of these constraints can be found elsewhere (Whitaker [1999], Section 1.3).

$$\ell_\eta, \ell_\omega \ll r_0 \ll L.$$ (3.21)

The superficial and the intrinsic averages were defined in order to continue the averaging process of the equations:

Superficial Average:

$$\langle \psi_\gamma \rangle = \frac{1}{V} \int_{V_\gamma} \psi_\gamma dV$$ (3.22)

Intrinsic Average:

$$\langle \psi_\gamma \rangle^\gamma = \frac{1}{V_\gamma} \int_{V_\gamma} \psi_\gamma dV$$ (3.23)

The parameter $\psi_\gamma$ refers to the value of property $\psi$ in the $\gamma$-phase. For the $\eta$- and $\omega$-regions, $\gamma$ can be replaced by the respective subscripts $\eta$ or $\omega$. Depending on the process, the gradient of the average might not be the same as the average of the gradient of a parameter. Therefore, the spatial averaging theorem [Howes and Whitaker, 1985] is introduced.

$$\langle \nabla \psi_\gamma \rangle = \nabla \langle \psi_\gamma \rangle + \frac{1}{V} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \psi_\gamma dA$$ (3.24)
Without knowledge about the microscale property, \( \psi_\gamma \), Eq. 3.24 is difficult to solve. This makes the decomposition of the parameter \( \psi_\gamma \) crucial. The decomposition relates the value of the property \( \psi_\gamma \) at any given point \( \mathbf{x} \) within the averaging volume \( \mathcal{V} \) to the intrinsic average \( \langle \psi_\gamma \rangle^\gamma \) and the spatial deviation \( \tilde{\psi}_\gamma \):

\[
\psi_\gamma = \langle \psi_\gamma \rangle^\gamma + \tilde{\psi}_\gamma
\] (3.25)

The spatial deviation \( \tilde{\psi}_\gamma \) enables the assignment of a value of \( \psi_\gamma(\mathbf{x}, t) \) in relation to the intrinsic average \( \langle \psi_\gamma \rangle^\gamma \) to each point. With these definitions in place, one can average Eqs. 3.11 and 3.12 to a new set of macroscale mass balance equations:

\[
\varepsilon_\eta \varphi_\eta \frac{\partial (c_\eta)^\eta}{\partial t} = \nabla \cdot \left[ \varepsilon_\eta \varphi_\eta D_\eta^* \cdot \left( \nabla \langle c_\eta \rangle^\eta + \frac{1}{V_\eta} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \tilde{c}_\eta dA \right) \right] - \nabla \cdot (\varepsilon_\eta \varphi_\eta \langle \tilde{v}_\eta \tilde{c}_\eta \rangle^\eta) - \varepsilon_\eta \varphi_\eta \langle \mathbf{v}_\eta \rangle^\eta \cdot \nabla \langle c_\eta \rangle^\eta - W(t)
\] (3.26)

\[
\varepsilon_\omega \varphi_\omega \frac{\partial (c_\omega)^\omega}{\partial t} = \nabla \cdot (\varepsilon_\omega \varphi_\omega D_\omega^* \cdot \nabla \langle c_\omega \rangle^\omega) + W(t)
\] (3.27)

where

\[
W(t) = \varepsilon_\omega \varphi_\omega \frac{d}{dt} \left( \int_0^t B(t - \tau) C_{\eta\omega}(\tau) d\tau \right)
\] (3.28)

\[
C_{\eta\omega} = (\langle c_\eta \rangle^\eta - \langle c_\omega \rangle^\omega)
\] (3.29)
Details of this derivation are given by Chastanet and Wood [2008]. Here, $B(t)$ is the kernel function

\[
B(t) = 15 \frac{D_\omega}{a^2} + 6 \frac{D_\omega \varepsilon_\omega \varphi_\omega}{a^2} \sum_{n=1}^{\infty} \exp \left( -\frac{q_n^2 D_\omega}{a^2} t \right)
\]

(3.30)

with $q_n$ standing for the positive roots of

\[
\tan q_n = \frac{3q_n}{3 - q_n^2}
\]

(3.31)

that are not zero. The derivation of $B(t)$ will be demonstrated in the closure problem. The momentum balance for the microscale (Eq. 3.19) can also be transformed, which gives

\[
\langle v_\eta \rangle_\eta = -\frac{K'_\eta}{\varepsilon_\eta} \cdot \nabla \langle h_\eta \rangle_\eta
\]

(3.32)

and

\[
K'_\eta = \frac{2K_\eta}{3 - \varphi_\eta} I
\]

(3.33)

and the associated boundary conditions. $K'_\eta$ is the effective hydraulic conductivity, while $\langle h_\eta \rangle_\eta$ denotes the hydraulic head of the macroscale. Eq. 3.33 is the Maxwell relation [1873]. The interior boundary conditions are now included in these equations, but the macroscale boundary and initial conditions still need to be specified. The spatial deviations $\tilde{c}_\eta$ and $\tilde{v}_\eta$ are not known and prevent the solving of equations (3.26 and 3.27). $\tilde{c}_\eta$ and $\tilde{c}_\omega$ need to be expressed in terms of $\langle c_\eta \rangle_\eta$ and $\langle c_\omega \rangle_\omega$. This is called the closure of the equations and developing an expression
for the standard deviations is called the *closure problem*. The problem is simplified by assuming that the diffusion coefficient and the dispersion tensor are constant [Wood et al., 2003]. The following assumptions simplify the closure problem. First, assume perfect mixing in the \( \eta \)-phase only for the solution of the closure problem. The concentration of \( \langle c_\eta \rangle_\eta \) is therefore equal to the concentration at the surface of the inclusions \( A_{\eta\omega} \). The average of the spatial deviations is taken to be zero within the averaging volume. For the sake of the closure problem, the correlation term \( \nabla \cdot (\varepsilon_\eta \varphi_\eta \langle \tilde{v}_\eta \tilde{c}_\eta \rangle) \) is neglected. This is safe to do when the convection term \( \varepsilon_\eta \varphi_\eta \langle \mathbf{v}_\eta \rangle_\eta \cdot \nabla c_\eta \) is considerably bigger than the correlation term (Chastanet and Wood [2008]).

\[
\nabla \cdot (\varepsilon_\eta \varphi_\eta \langle \tilde{v}_\eta \tilde{c}_\eta \rangle) \ll \varepsilon_\eta \varphi_\eta \langle \mathbf{v}_\eta \rangle_\eta \cdot \nabla \tilde{c}_\eta \tag{3.34}
\]

The nonlocal diffusion term is significantly smaller than the diffusion term

\[
\frac{\varepsilon_\eta \varphi_\eta \mathbf{D}_\eta^*}{V_\eta} \int_{A_{\eta\omega}} n_{\eta\omega} \tilde{c}_\eta dA \ll \nabla \cdot \varepsilon_\eta \varphi_\eta \mathbf{D}_\eta^* \cdot \nabla \tilde{c}_\eta \tag{3.35}
\]

which allows one to neglect the nonlocal diffusion term. To solve the closure problem, the representative volume is assumed to be periodic. This assumption modifies the boundary conditions. The closure problem can then be solved, and the closed form of the macroscale mass balance equations formulated for
the $\eta$-phase

$$\varepsilon_\eta \varphi_\eta \frac{\partial \langle c_\eta \rangle^n}{\partial t} = \nabla \cdot (\varepsilon_\eta \varphi_\eta D^{**}_{\eta} \cdot \nabla \langle c_\eta \rangle^n) - \varepsilon_\eta \varphi_\eta \langle v_\eta \rangle^n \cdot \nabla \langle c_\eta \rangle^n$$

$$- \alpha(t) \left( \langle c_\eta \rangle^n - \langle c_\omega \rangle^\omega \right)$$

(3.36)

and the $\omega$-phase

$$\varepsilon_\omega \varphi_\omega \frac{\partial \langle c_\omega \rangle^\omega}{\partial t} = \nabla \cdot (\varepsilon_\omega \varphi_\omega D^*_{\omega} \cdot \nabla \langle c_\omega \rangle^\omega) + \alpha(t) \left( \langle c_\eta \rangle^n \langle c_\omega \rangle^\omega \right)$$

(3.37)

with the effective macroscale dispersion being defined with

$$D^{**}_{\eta} \cdot \nabla \langle c_\eta \rangle^n = \left( D^*_{\eta} \cdot \nabla \langle c_\eta \rangle^n + \frac{D^*_{\eta}}{V_\eta} \cdot \int_{A_{\omega}} \mathbf{n}_{\eta\omega} \tilde{c}_\eta \, dA - \langle \tilde{v}_\eta \tilde{c}_\eta \rangle^n \right)$$

(3.38)

The resulting mass transfer term for the fully coupled model is

$$W(t) = \varepsilon_\omega \varphi_\omega \int_0^t \frac{\partial C_{\eta\omega}^\omega}{\partial \tau} (\tau - t) B(\tau) d\tau + \varepsilon_\omega \varphi_\omega C_{\eta\omega}^\omega(0) B(t)$$

(3.39)

Here, the relation

$$\alpha(t) = \frac{W(t)}{C_{\eta\omega}^\omega t}$$

(3.40)

holds, which enables calculation of the mass transfer coefficient $\alpha(t)$, to apply it in Eqs. 3.36 and 3.37. If the time scale of macroscopic concentration difference $C_{\eta\omega}$ is assumed to be large compared to that of the kernel function $B(t)$ while solving the closure problem, then the mass transfer for the uncoupled model can be rewritten
as:

\[
\alpha(t) = 15 \frac{D_\omega \varepsilon_\omega \varphi_\omega}{a^2} + 6 \frac{D_\omega \varepsilon_\omega \varphi_\omega}{a^2} \sum_{n=1}^{\infty} \exp \left( -\frac{q_n^2 D_\omega}{a^2} t \right) \tag{3.41}
\]

where \( q_n s \) are defined in Eq. 3.31. If it is assumed that all parameters are behaving quasi-steady for the closure problem, the assumption of a non-transient \( \alpha \) is made. Eq. 3.41 then reduces to its quasi-steady form:

\[
\alpha(t) = 15 \frac{D_\omega \varepsilon_\omega \varphi_\omega}{a^2} \tag{3.42}
\]

The values used to calculate the mass transfer coefficient are listed in Table 3.3. In Figure 4.1, the behavior of the quasi-steady MTC and the uncoupled MTC over time is shown.

At this point all the equations needed to apply volume averaging to the system and compare the results with the DNS models have been derived. Additional assumptions made to apply our system are: no reaction occurring within the system (non-reactive tracer) and no adsorption of the tracer onto the matrix material.
Chapter 4 – Results

This chapter focuses on comparing the breakthrough curves (BTC) obtained by the models developed in the Sections 3.2.3, 3.2.4 and 3.3 with the experimental data [Harrington, 2010]. For the remainder of this study, Experiments 1 and 3 are denoted Experiments A and B respectively, for simplicity. The system was initially saturated with solute; thus, normalizing the concentration at the outlet gives the value $1$ for $c/c_0$ at $t = 0$. The concentration in the effluent was observed to decline over time until solute had completely left the system. The period of time during which the bulk of solute in the matrix is flushed out of the system (which results in a rapid decline of the BTC) is referred to as “early time.” Once the bulk of the solute has left the matrix, the BTC asymptotically declines. This period is referred to as “late time.”

Using the theory described in Chapter 3 (Eqs. 3.41 and 3.42), values for the decoupled mass transfer coefficient, and the quasi-steady mass transfer coefficient were computed. Plots of the quasi-steady mass transfer coefficient (MTC), the uncoupled MTC, and the polynomial fit that was obtained for the uncoupled MTC are shown in Figure 4.1. It is apparent in the plots that the mass transfer coefficient for the uncoupled model reaches asymptotic behavior early in comparison to the total time required for the experimental procedures. This is particularly noticeable in experiments with slow flow rates, as the observed tailing occurs rather late in
comparison to the transient behavior of $\alpha$ in the uncoupled model. The value of $\alpha$ for the uncoupled model approaches the value of the MTC in the quasi-steady model asymptotically. For late times, the uncoupled and the quasi-steady models predict the same mass transfer coefficient that accounts for solute transfer between the $\eta$- and the $\omega$-regions.

Figure 4.1: Plot of the mass transfer coefficient (MTC) for the uncoupled model and the quasi-steady model. The uncoupled MTC of the volume averaged model is approximated by a polynomial to simplify implementation of the MTC in simulations.
4.1 Experiment A \((Q = 9.3 \times 10^{-8} \text{ m}^3/\text{s})\)

In Figure 4.2, the normalized concentration as a function of time is plotted for each of the four models considered (simplified system, fully-resolved system, uncoupled mass transfer model and quasi-steady mass transfer model). For Experiment A, the results of the quasi-steady and decoupled mass transfer models resemble each other closely, diverging slightly only at late times. Note that the simplified system has the same volumetric ratio of inclusions to overall volume as the fully-resolved system. Even though the simplified system has a cross-sectional area that is exactly ten times smaller than that of the fully-resolved system, the BTC of the two models match each other closely for both experiments. The BTC of Experiment A is reproduced reasonably well by all of the DNS models at late times. After a crease in the experimental data, the results of the simulations start to diverge from the experimental data. Possible causes for this behavior will be investigated in Chapter 5. The BTC of the uncoupled (transient) MTC model and the BTC of the quasi-steady (non-transient) model match one another closely. This is to be expected, as it is possible to see in Figure 4.1 that the uncoupled MTC approaches the quasi-steady MTC at early times in comparison to the overall duration of the experiment. At early times, convection in the \(\eta\)-region makes up the bulk of the mass recovery, and transfer of solute from the inclusions does not influence mass recovery at the outlet significantly. The DNS models and the volume averaged models predict almost identical BTC until late times, when the DNS models and the volume averaged models diverge. The volume averaged models predict less
tailing than the DNS models and the experimental data in this regime.

Figure 4.2: The results for Experiment A of the two DNS models and the two volume averaged models in comparison to the experimental data. (a) Linear concentration scale. (b) Logarithmic concentration scale.
4.2 Experiment B ($Q = 7.5 \times 10^{-7} \, \text{m}^3/\text{s}$)

In Experiment B, at early time, all models show similar behavior and the modeled BTC closely match the experimental data. At the transition between early and late time, all models overpredict the experimental data, which changes for later times and leads to underprediction of the tailing displayed by the experiment data. The DNS models predict significantly more spreading of the BTC than is observed in the data. This phenomenon is especially visible in the double-logarithmic plot (Figure 4.3, b) of the results for Experiment B. An overestimation of the dispersivity in the $\eta$-region could be the cause for extensive smearing of the BTC. This hypothesis will be examined further in Chapter 5.

The shape of the four BTC predicted by the models closely resemble one another. At late time, the DNS models predict less tailing than the volume averaged models. This is the opposite outcome of the results from Experiment A, where the DNS models show more tailing for late times. The BTC of the DNS models resemble each other closely while the volume averaged models do not show exactly the same BTC. The quasi-steady model displays more tailing for late-times. Overall, the respective differences between the DNS models and the volume averaged models are almost negligible in comparison to the fluctuations apparent in the experimental data.
Figure 4.3: The results for Experiment B of the two DNS models and the two volume averaged models in comparison to the experimental data. (a) Linear concentration scale. (b) Logarithmic concentration scale.
4.3 Mass Conservation

Assuming that $c/c_0 = 1$ at $t = 0$, the amount of total mass of fluorescein initially in the system for both experiment setups can be calculated. Using the volumetric fractions $f_\eta$ and $f_\omega$ and the respective porosities $\varepsilon_\eta$ and $\varepsilon_\omega$, the total pore space was computed to be $0.0388 m^3$. Assuming $c_\eta = c_\omega = c_{sat}$ at $t = 0$, the total mass initially in the system was computed to be $58.2 mg$. As a check on the fully-resolved DNS model, the total mass in the system was also computed by integrating the concentration directly at $t = 0$ with COMSOL Multiphysics®. These results match the theoretical result closely. The experimental value yields a maximum true percent relative error of $3.4\%$. Analysis found the discrepancy in mass recovery to fully occur at early times, possibly due to large concentration gradients or the numerical methods employed to calculate mass conservation. Therefore, the discrepancy in total recovered mass does not significantly influence the tailing behavior of the models.
Chapter 5 – Discussion

5.1 Characterization of transport mechanisms

Characterizing the dominant transport mechanisms can help to identify the hydraulic properties which have the strongest effect on the models’ behavior. As the mean velocity of the system changes, so does the characteristic time for convection through both regions. The characteristic time for diffusion (Eq. 5.2), however, always remains the same regardless of flow rate. The ratio of hydraulic conductivity between the $\eta$-region and the $\omega$-region is about 425, which is similar to experiments performed by other investigators [Zinn et al., 2004; Golfier et al., 2007].

A useful dimensionless number that can be used to compare the mass transport processes within the regions is the Péclet number. The Péclet number compares the magnitude of convective transport to diffusive transport

$$Pe = \frac{v}{L_C} \frac{L_D^2}{D}$$

(5.1)

Here, $L_C$ and $L_D$ are the characteristic length scales associated with the convective and the diffusive process respectively, and $D$ denotes the effective diffusion coefficient. In the case investigated, the characteristic lengths are the radius, $r$, of the inclusions and the total length of the system $L$. The accompanying relation to compare convective and diffusive processes in the $\omega$-region is the Péclet number
\[ Pe_{\omega\omega} = \frac{||\langle v_\omega \rangle\omega||}{r} \frac{r^2}{D_\omega} = \frac{||\langle v_\omega \rangle\omega||}{D_\omega} \]  

\[ (5.2) \]

\[ ||\langle v_\omega \rangle\omega|| \] is the magnitude of the intrinsic velocity in the \( \omega \)-region (Eq. 3.23) and \( D_\omega \) denotes the effective diffusion coefficient of fluorescein (Section 3.1.1). With \( Pe_{\omega\omega} \), the relation of convective and diffusive flux in the \( \omega \)-region can be examined.

It is also possible to define a Péclet number \( Pe_{\eta\omega} \) that relates the magnitude of the convective flux in the \( \eta \)-region to the diffusive flux in the \( \omega \)-region

\[ Pe_{\eta\omega} = \frac{||\langle v_\eta \rangle\eta||}{L} \frac{L^2}{D_\omega} \]

\[ (5.3) \]

The Péclet number for the \( \eta \)-region \( Pe_{\eta\eta} \) is expressed as

\[ Pe_{\eta\eta} = \frac{||\langle v_\eta \rangle\eta||}{L} \frac{L^2}{D_\eta} = \frac{||\langle v_\eta \rangle\eta||}{D_\eta} \]

\[ (5.4) \]

The magnitude of the intrinsic velocities \( ||\langle v_\omega \rangle\omega|| \) and \( ||\langle v_\eta \rangle\eta|| \) were computed numerically from the DNS models (Table 5.1). The values for the Péclet numbers

| parameter | \( Q_{in} \) [ml/min] | \( v_x \) [m/s] | \( ||\langle v_\eta \rangle\eta|| \) [m/s] | \( ||\langle v_\omega \rangle\omega|| \) [m/s] |
|-----------|----------------|--------------|----------------|----------------|
| EXP A     | 5.6            | 9.37 \times 10^{-7} | 1.08 \times 10^{-6} | 4.02 \times 10^{-9} |
| EXP B     | 45.2           | 7.50 \times 10^{-6} | 8.62 \times 10^{-6} | 3.21 \times 10^{-8} |
resulting from the intrinsic velocities are summarized in Table 5.2. Investigating

<table>
<thead>
<tr>
<th>parameter</th>
<th>$Pe_{\omega\omega}$</th>
<th>$Pe_{\eta\omega}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP A</td>
<td>0.264</td>
<td>1.776</td>
</tr>
<tr>
<td>EXP B</td>
<td>2.114</td>
<td>14.173</td>
</tr>
</tbody>
</table>

the velocities in the $\eta$- and $\omega$-regions reveals that both $||\langle v_{\omega}\rangle||$ and $||\langle v_{\eta}\rangle||$ increase with proportion to the volumetric flow rate that serves as a boundary condition at the influent. This also applies to the respective Péclet numbers $Pe_{\omega\omega}$ and $Pe_{\eta\omega}$. Figure 5.1 shows the information from Table 5.1 about the mass transfer mechanisms in the $\eta$- and $\omega$-region. Experiments from other researchers [Zinn et al., 2004; Golfier et al., 2007] are included in Figure 5.1 for comparison.

5.2 Analysis of the BTC with respect to the prevalent mass transport mechanisms

The Péclet numbers $Pe_{\omega\omega}$ and $Pe_{\eta\omega}$ allow a characterization of the main transport processes occurring in the two experiments; In Experiment A, $Pe_{\omega\omega}$ is well below 1, indicating that diffusive transport is more dominant than convective transport within the inclusions. For this experiment, $Pe_{\eta\omega}$ is slightly larger than 1, which shows that convective transport in the matrix is larger than diffusive transport in the inclusions. Diffusive transport is still significant in comparison to the convective
Figure 5.1: Plot of the two Péclet Numbers $Pe_{\omega\omega}$ and $Pe_{\eta\omega}$ for Experiment A (abbreviated here by “Exp A”) and Experiment B (“Exp B”). The plot is divided into regions with respective dominant mass transport processes. Experiments from other authors [Zinn et al., 2004; Golfier et al., 2007] are included. 

processes in the high-conductivity material. Figure 5.1 shows that Experiment A is close to the solute transport regime where local mass equilibrium is prevalent. The low-conductivity inclusions are labeled as an “immobile” region for Experiment A because diffusion is the dominant transport process in these regions. Therefore, Experiment A falls into the “mobile-immobile” region.

The Péclet numbers $Pe_{\omega\omega}$ and $Pe_{\eta\omega}$ in Experiment B are larger than 1, with the
value of $Pe_{\eta \omega}$ being significantly larger than 1. As expected from the high flowrate in Experiment B, this signifies that diffusion is very small in the matrix compared to convection. A value of $Pe_{\omega \omega}$ greater than 1 indicates that convection is the dominant mass transport process in the inclusions, making the $\omega$-region a “mobile” region. This holds even though the intrinsic velocity $||\langle v_\omega \rangle||_\omega$ is more than two orders of magnitude below the intrinsic velocity $||\langle v_\eta \rangle||_\eta$ in the matrix. Experiment B is therefore in the “mobile-mobile” region (see Figure 5.1).

The change of the low-conductivity region from an immobile regime in Experiment A to a mobile regime in Experiment B marks a very important difference between the two experiments. In Experiment A, the diffusion coefficient is essential for describing the tailing that occurs while the diffusion coefficient has only a marginal influence on the prediction of Experiment B. The opposite is true for the hydraulic conductivity $K_\omega$; $K_\omega$ is crucial to accurately predict tailing in Experiment B whereas it is not significantly important for Experiment A (see Appendix B). The conclusions and possible improvements to the models that can be drawn from the sensitivity analysis will be discussed in the following paragraph.

In Figures B.3 and B.4, it is evident how the hydraulic conductivity in the $\omega$-region $K_\omega$ affects the mass recovery of Experiments A and B. In accordance with the respective regimes that transport processes in Experiment A and Experiment B belong to (see Figure 5.1), the effect of the variation of $K_\omega$ is small for Experiment A and quite significant for Experiment B because convection is the dominant mass transfer process in the inclusions for Experiment B. The results produced with the sensitivity analysis (Appendix B) hint at the possibility that the effective diffusion
and the hydraulic conductivity in the $\omega$-region are not equal in all spheres, but might instead vary enough between the spheres to affect the experiments. Such effects are very difficult to model in retrospect if no detailed knowledge about the distribution of the effective diffusion coefficient is known. Haggerty and Gorelick [1995] explain how small-scale variations of parameters can be taken into account with a “multirate” model. Assuming a non-constant distribution of effective diffusion and the hydraulic conductivity, estimating the exact distribution is impossible. Another possible factor of error is the value assumed for the longitudinal dispersivity $\alpha_{L,\eta}$. In Experiment B, the convective pulse is not represented accurately by the simulations. The BTC predicted by the DNS models do not show a distinct difference. There is also no significant difference between the BTC of the two volume averaged models. The slight difference between the BTC of the volume averaged models can be explained as follows. The time dependence of the MTC (Figure 4.1) predicts a larger MTC which leads to higher mass transfer at early times in the uncoupled model than in the quasi-steady model. This leads to a faster concentration decline within the inclusions at early times in the uncoupled model. Therefore, the quasi-steady model has less solute leaving the system at early times which leads to larger tailing at late times. This behavior can be observed in the Figures 4.2 and 4.3.

The BTC of the DNS models match the BTC of the volume averaged curves perfectly during early times until they start to diverge as the asymptotic portion of the BTC is reached. Tailing is predicted with improved accuracy in respect to the initial parameters by all models, but is not matched perfectly by any model.
Analysis of the predictions made by the models for Experiment B indicated that the averaged dispersivity $\alpha_{L,\eta}$ does not adequately represent the system’s behavior. The dispersivity in the matrix $\alpha_{L,\eta}$ was therefore recalculated with an approach presented by Whitaker [1999, Section 3.3.]. Here, the effective dispersion tensor $D_{\text{eff}}$ is related to the dispersion coefficient $D_\eta$, which needs to be obtained by a one-region model with the properties of the $\eta$-region

$$D_{\text{eff}} = D_\eta \left( I + \frac{1}{V_\eta} \int_{A_{\eta\omega}} n_{\eta\omega} b_\eta dA \right) - \langle \tilde{v}_\eta b_\eta \rangle \eta$$

This equation (Eq. 5.5) derives a macroscale representation of $D_{\text{eff}}$ from the homogeneous dispersion coefficient $D_\eta$ and a model that represents a unit cell of the $\omega$-region on the microscale. The closure variable $b_\eta$ was calculated with COMSOL Multiphysics® and a thorough derivation of $b_\eta$ can be found in Whitaker [1999, Section 3.3.3.]. This led to a dispersivity of $\alpha_{L,\eta} = 0.029$ m. This dispersivity $\alpha_{L,\eta}$ provides a very accurate representation of the convective pulse seen in the BTC (Figure 5.2). The tailing predicted by the models matches the BTC of the experiments more closely, but does not yet provide a perfect fit. Harrington [2010, Section 3.3.2.] gave reason to assume that the hydraulic conductivity for the $\omega$-region could be 3 times lower than the value reported. This gives a conductivity of $K_\omega = 0.667 \times 10^{-6} \text{ m/s}$, which matches the value reported for the material that was used to sinter the inclusions. The new value for $K_\omega$ lies within one standard deviation of the average of the hydraulic conductivities as reported by Harrington [2010]. This value provides a very accurate fit to the convective pulse that can be
Figure 5.2: Results of the four models in comparison to the experimental data for a dispersivity value in the $\eta$-region of $\alpha_{L,\eta} = 0.029 \, m$. (a) Linear concentration scale. (b) Logarithmic concentration scale.
seen in the BTC as well as the tailing of the BTC (see Figure 5.3). The new value for $K$ provides an excellent fit for the late time behavior of Experiment B. The volume averaged models do not predict the tailing of the BTC as accurately as the DNS models, due to the indirect implementation of the hydraulic conductivity $K_\omega$ in the calculation of the effective dispersion coefficient.

While the models of Experiment B provide a good representation of the BTC of the experimental data, the DNS models and volume averaged models do not represent the diffusion dominated tailing of Experiment A accurately. The DNS models describe the tailing occurring in the system better than the volume averaged models. A sensitivity analysis was performed for the diffusivity, which shows high dependency of the model on the effective diffusion coefficient (see Figures B.1 and B.2). The effective diffusion coefficient may diverge from the estimated values (Eq. 3.1 and Eq. 3.2) because of clogging of the pores that can be caused by the sintering process employed to create the inclusions. As expected from Figure 5.1, the effective diffusion coefficient has a smaller effect on Experiment B than on Experiment A. Figures B.1 and B.2 show that the effective diffusion coefficient affects the numerical models' at times later than the BTC of the experimental data. This is evidenced by the change in shape of the BTC. Therefore, the diffusion coefficient alone cannot account for the difference between the modeled BTC and the experimental data. The simulations show the typical shape of convection dominated transport at early times and diffusion dominated transport at late times [Haggerty and Gorelick, 1995]. Investigation of the experimental procedure was therefore performed to evaluate possible reasons for the discrepancy between the
Figure 5.3: Results of the four models in comparison to the experimental data for a dispersivity value in the $\eta$-region of $\alpha_{L,\eta} = 0.029 \ m$ and a hydraulic conductivity in the $\omega$-region of $K_\omega = 0.667 \times 10^{-6} \ m/s$. (a) Linear concentration scale. (b) Logarithmic concentration scale.
models and the experimental data

1. Clogging of the pores in the inclusions due to the sintering process can greatly lower the effective diffusion coefficient, which can lead to an overprediction by the value calculated in Eqs. 3.1 and 3.2. As shown before, the effective diffusion coefficient is crucial to accurately predict Experiment A.

2. The hydraulic conductivities $K_\omega$ measured for the spheres [Harrington, 2010] span a range from $K_\omega = 0.3 \times 10^{-6} \text{ m/s}$ to $K_\omega = 7.4 \times 10^{-6} \text{ m/s}$. This suggested that the initial value for $K_\omega$ needed to be reinvestigated to achieve a better fit of the experimental data. The new hydraulic conductivity $K_\omega = 0.667 \times 10^{-6} \text{ [m/s]}$, which is consistent with the material used to sinter the spheres, provides an accurate fit of the late time behavior in Experiment B (see Figure 5.3).

3. Internal measurements of the concentration were taken at various points during Experiment A (see Harrington [2010], Appendix A.3). Extraction of fluid through internal ports can cause additional mixing in the matrix, which could explain the large dispersivity (Table 3.2) that was obtained with the inverse fit [Harrington, 2010] for Experiment A.

4. The tracers (fluorescein and bromide) can cause density differences, which can lead to longitudinal mixing of the solution. The system stood upright [Harrington, 2010] and fluid was being pumped in from the bottom. This created fluid flow in the opposite direction of gravitational forces. Sinking of the tracers in the opposite direction of main flow could have occurred if
the density difference in the tracer free solution that was pumped into the system was not accounted for by adding an additional substance to obtain equal densities for saturated and solute free aqueous liquid. This effect can be especially significant if convective forces are small, as in Experiment A.

5. Heterogeneities in the $\eta$-region could have been caused by the placement of the inclusions [Harrington, 2010] and the restrictions for tight packing of the $\eta$-region that this caused. This could have led to inaccurate estimates for the hydraulic parameters in the $\eta$-region.

6. Investigations of the experimental setup showed large fluctuations in temperature of the surrounding environment, which can lead to non-dispersive mixing in the system that has not been accounted for. The Nusselt number $Nu$, that relates convective heat transfer to conductive heat transfer, can be calculated according to Jiang et al. [2004]:

$$Nu = a \, Re^b = 22.7$$

with $a = 92.6$, $b = 0.61$ [Jiang et al., 2004] and the Reynolds number $Re$:

$$Re = \frac{vl_n}{\mu} = 0.1$$

This result indicates that convective heat flux has a stronger influence than conductive heat transfer. This causes temperature differences between the center and the boundary of the box if the exterior of the box heats up without
sufficient lateral flow. Large temperature differences can therefore cause mixing that spreads out the convective front and leads to greater dispersivity.

A combination of the effects mentioned above and especially the large value obtained for the inverse fit of the dispersivity give reason to assume that effects left unaccounted for led to a BTC of the experimental data that diverges from the models in late times.
Chapter 6 – Conclusions

A highly heterogeneous porous medium with low-conductivity spherical inclusions, embedded in a high-conductivity matrix was studied (Section 3.1). The system was intially saturated with two non-reactive tracers (fluorescein and bromide) and then flooded with solute free water. This was performed for two flow rates ($Q_1 = 9.3 \times 10^{-8} m^3/s$ and $Q_3 = 7.5 \times 10^{-7} m^3/s$). Four models were developed to represent the behavior of the system and compare the results to experimental data [Harrington, 2010]. Two of the models are DNS models that allow direct numerical simulation of (1) the fully-resolved system (Section 3.2.3) and (2) a simplified representation of the system (Section 3.2.4). The other two models employ the method of volume averaging (Section 3.3) and differ in the use of (3) a constant (quasi-steady solution) and (4) a transient (uncoupled solution) mass transfer coefficient to account for solute transport between the two regions. The following conclusions can be drawn from this study:

1. The two DNS models predict almost identical BTC for both experiments. Therefore, the DNS model with the simplified domain can be used to simulate the behavior of the fully-resolved system.

2. The results obtained by the two volume averaged models show only a small relative deviation.
3. The Péclet numbers $Pe_{\omega}$ and $Pe_{\eta\omega}$ are defined to relate transport processes to each other in the system. Convection is the dominant transfer mechanism in the matrix. In the inclusions, the dominant mass transport mechanism changes from diffusion in Experiment A to convection in Experiment B. This leads to the classification of the two regions as a "mobile-immobile" region for Experiment A and a "mobile-mobile" region for Experiment B.

4. The initially assumed longitudinal dispersivity $\alpha_{L,\eta} = 0.0129 \ [m]$ did not lead to an accurate prediction of dispersive processes in the $\eta$-region. The method of volume averaging was therefore employed to recalculate the value of $\alpha_{L,\eta} = 0.029 \ [m]$, which represents convective transport in the $\eta$-region and early time behavior accurately for Experiment B.

5. There is reason to assume that the hydraulic conductivity in the spheres $K_\omega$ [Harrington, 2010] does not represent the experimental system accurately, which led to a reinvestigation. The new hydraulic conductivity $K_\omega = 0.667 \times 10^{-6} \ [m/s]$, which is consistent with the material used to sinter the spheres, provides a very accurate fit of the late time behavior in Experiment B (see Figure 5.3).

6. The results illustrate that it is possible to represent the behavior of the fully-resolved system (Section 3.1) with a simplified model (Section 3.2.4) or a volume averaged model (Section 3.3). This especially holds true for early times, where only small differences between the models’ BTC are observable.

7. Numerous causes for the deviation of the models and the experimental data
of Experiment A were investigated in Chapter 5. It was concluded that too many uncertainties are connected with Experiment A to glean sufficient information for an accurate prediction of the system’s behavior with numerical models.
Bibliography


B. D. Wood, F. Cherblanc, M. Quintard, and S. Whitaker. Volume averaging for determining the effective dispersion tensor: Closure using periodic unit cells and


APPENDICES
Appendix A – Nomenclature

\( \mathcal{A}_{\gamma \kappa} \) area of the \( \gamma - \kappa \)-interface within the macroscopic region, \([m^2]\)

\( A_{\eta \omega} \) area of the \( \eta - \omega \)-interface, \([m^2]\)

\( A_{\eta e} \) area of the \( \eta \)-region and the wall, \([m^2]\)

\( a \) radius of the inclusions, \([m]\)

\( \mathbf{b}_\alpha \) vector field that maps the intrinsic average concentration onto \( \tilde{c}_{\alpha \alpha} \) for the \( \alpha \)-phase

\( B \) kernel function (Eq. 3.30)

\( c_\eta, c_\omega \) concentrations of the \( \eta \) and \( \omega \)-phase at the microscale \([kg/m^3]\).

\( \langle c_\eta \rangle, \langle c_\omega \rangle \) superficial average conc. of species A in \( \eta \) and \( \omega \)-phase, \([kg/m^3]\)

\( \langle c_{\alpha \eta} \rangle_\eta, \langle c_{\omega \omega} \rangle_\omega \) intrinsic average conc. of species A in \( \eta \) and \( \omega \)-phase, \([kg/m^3]\)

\( \tilde{c}_{\alpha \eta}, \tilde{c}_{\alpha \omega} \) spatial deviation concentration of species A in the \( \eta \) and \( \omega \)-phase, \([kg/m^3]\)

\( \mathbf{D}_\alpha \) hydrodynamic dispersion tensor, \([m^2/s]\).

\( D_{Fl} \) diffusion coefficient for fluorescein, \([m^2/s]\).

\( D_{\eta}, D_{\omega} \) effective diffusion coefficients in the two regions, \([m^2/s]\).

\( \mathbf{D}^*_\eta, \mathbf{D}^*_\omega \) estimated guess for the dispersion tensor \([m^2/s]\).

\( \mathbf{D}^{**}_{\eta \omega} \) effective dispersion tensor of the macroscale resulting from volume averaged equations \([m^2/s]\).
$h$ hydraulic head [m].

$K_{\eta}$ hydraulic conductivity in the $\eta$-phase [m/s].

$I$ unit tensor [-]

$l_{\eta}, l_{\omega}$ small length scale of the $\eta$ and $\omega$-phase [m]

$L$ smallest macroscale length-scale associated with the problem [m]

$n_{\beta\omega}$ unit normal vector directed from the $\beta$-phase toward the $\omega$-phase

$Pe_{\eta}, Pe_{\omega}$ Peclet number of the $\eta$ and $\omega$-phase [-].

$q_n$ positive roots of Eq. 3.31.

$r_0$ radius of the sphere in averaging volume [m]

$r_1$ outer radius of averaging volume [m]

$t$ time [s].

$\mathbf{v}$ velocity vector [m/s].

$\langle \mathbf{v}_{\eta} \rangle^{\eta}, \langle \mathbf{v}_{\omega} \rangle^{\omega}$ averaged intrinsic velocity in the $\eta$ and $\omega$-region [m/s].

$\mathcal{V}$ local averaging volume, [m$^3$]

$V_{\alpha}$ volume of the $\alpha$-phase within an averaging volume, [m$^3$]

$W$ effective mass transfer function [kg/(m$^3$s)]

$x_{\alpha}$ position vector locating the center of the averaging volumes, [m]

$y_{\alpha}$ position vector locating points within the averaging volume, [m]

$\alpha$ mass transfer coefficient [1/s]

$\eta$ denotes the high-conductivity matrix

$\omega$ denotes the low-conductivity inclusions

$\varepsilon_{\eta}, \varepsilon_{\omega}$ porosity in the $\eta$ and $\omega$-phase [-].
Appendix B – Sensitivity Analysis

In the sensitivity analysis, the effect of various hydraulic properties and system parameters on the system is investigated. The model used for all parts of the analysis is the DNS model with the simplified domain (3.2.4). As the two DNS models (Section 3.2.3 and 3.2.4) diverge only slightly, the sensitivity analysis was completed with the simplified system. As can be seen in Figures B.1, B.2, B.3 and B.4, the system parameters affect the behavior of the BTC significantly stronger than the choice which of the two DNS models is to be employed for the sensitivity analysis.

One of the parameters of special importance is the effective diffusion. From Chapter 5, it is known that the diffusion coefficient $D_\omega$ is especially important to display the late time mass recovery of Experiment A accurately. Figure B.1 shows that variation of the effective diffusion leads to significant changes of the BTC late time behavior of Experiment A. The effective diffusion also affected the BTC of Experiment B (see Figures B.1 and B.2) but the effects are visibly smaller.

The effect of the hydraulic conductivity in the $\omega$-region is of particular interest as it has a large impact on convection processes in the low-conductivity region. Figure B.3 shows that the behavior of the system does not strongly depend on the magnitude of the hydraulic conductivity $K_\omega$. This changes significantly for Experiment B where a large dependence on $K_\omega$ is observable (see Figure B.4).
Considering the analysis of the dominant transport parameters (Chapter 5), this is to be expected as convective transport in the $\omega$-regions is the dominating solute transport mechanism in Experiment B. This shows that comparatively small inhomogeneities between the inclusions can affect the result considerably.
Figure B.1: Affect of the effective diffusion coefficient $D_\omega$ on the mass recovery of Experiment A.

Figure B.2: Affect of the effective diffusion coefficient $D_\omega$ on the mass recovery of Experiment B.
Figure B.3: Affect of the hydraulic conductivity in the $\omega$-region $K_\omega$ on the mass recovery of Experiment A.

Figure B.4: Affect of the hydraulic conductivity in the $\omega$-region $K_\omega$ on the mass recovery of Experiment B.
Appendix C – Placement of Inclusions for the Simplified System

The inclusions for the simplified system were placed with a code created with MATLAB®. The code is shown below.

% This MATLAB code creates random packaging for a domain with
% L=1m; H=0.2m; W= 0.2m that is divided into 20x2x2 cells.
% No spheres are located within 5cm of the inlet or outlet.
%
% (c) Daniel Vogler

clear all, close all, clc

r=zeros(18,2,2);
coordinates=zeros(20,2,2);
s=0;

while s~=20
    r=randi([0,1],[18,2,2]);
    s=sum(sum(sum(r)));
end

for i=1:18
    for j=1:2
for k=1:2
    coordinates(i+1,j,k)=r(i,j,k);
end
end
end
coordinates
fprintf('The total number of spheres is %d', s)