EFFECTS OF PHYSICAL AND CHEMICAL HETEROGENEITIES ON TRANSPORT AND REACTION PROCESSES IN POROUS MEDIA

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by

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ABSTRACT

In the natural subsurface various minerals and properties are often distributed heterogeneously. Numerous chemical and physical phenomena are influenced by heterogeneities such as contaminant transport, mineral dissolution, weathering, soil formation, nuclear waste disposal, hydrocarbon recovery, and migration of heavy metal. For example, precise modeling of transport is crucial for remediation scenario design in the event of a contaminant spill. Additionally, understanding mineral dissolution is of great importance since weathering is a common source of some elements crucial for the oceans and other ecosystems. Mineral distributions vary from random, homogenous patterns at one end of the spectrum to clustered zones and layers at the other end, which creates chemical heterogeneity. Even in a media purely made of a single mineral, physical properties such as permeability may differ spatially, resulting in physical heterogeneity. These heterogeneous distributions affect fluid flow, transport and reaction processes. Here we experimentally and numerically investigated the effect of chemical and physical heterogeneity on fluid flow, transport and reaction in porous media. We also proposed a new reactive transport model to simulate the soil formation process from Marcellus shale parent rock, which helped us in determining the key controlling parameters of the mineral dissolution and precipitation processes in natural settings.

Spatial variations in subsurface physical properties have profound impacts on flow and solute transport. It is important to understand and quantify the role of heterogeneity structure in determining effective parameters at large scales in order to precisely model processes that are affected by fluid flow and transport such as mineral dissolution. There is a consensus that spatial patterns and heterogeneity structure play a critical role in determining solute transport. Various numerical studies have identified connectivity and correlation length as key parameters that determine solute breakthrough. Although connectivity and correlation length have been found to be critical in these modeling studies, they have not been systematically examined and confirmed experimentally. Existing experimental work on solute transport has mostly focused on single spatial patterns with one correlation length. The objective of the physical heterogeneity part of this work is to systematically understand and quantify the role
of correlation length in determining effective permeability and solute transport using flow cell experiments and modeling approaches.

In order to determine how physical heterogeneity structure, in particular correlation length, controls flow and solute transport, we used non-reactive solute transport in two-dimensional (2D) sand boxes (21.9 cm by 20.6 cm) and four modeling approaches, including 2D Advection-Dispersion Equation (ADE) with explicit heterogeneity structure, 1D ADE with average properties, and non-local Continuous Time Random Walk (CTRW) and fractional ADE (fADE). The goal of the physical heterogeneity part of the work was to answer two questions: 1) How and to what extent does correlation length control effective permeability and breakthrough curves (BTC)? 2) Which model can best reproduce data under what conditions? Sand boxes were packed with the same 20% (v/v) fine and 80% (v/v) coarse sands in three patterns that differ in correlation length. The Mixed cases contained uniformly distributed fine and coarse grains. The Four-zone and One-zone cases had four and one square fine zones, respectively. A total of 7 experiments were carried out with permeability variance of 0.10 (LC), 0.22 (MC), and 0.43 (HC). Experimental data show that the BTC curves depend strongly on correlation length, especially in the HC cases. The HC One-zone (HCO) case shows distinct breakthrough steps arising from fast advection in the coarse zone, slow advection in the fine zone, and slow diffusion, while the LCO and MCO BTCs do not exhibit such behavior. With explicit representation of heterogeneity structure, 2D ADE reproduces BTCs well in all cases. CTRW reproduces temporal moments with smaller deviation from data than fADE in all cases except HCO, where fADE has the lowest deviation.

Well-mixed batch reactor reaction rate studies result in high dissolution rates, which are usually up to five orders of magnitude greater than field-scale rates. In the natural subsurface, solid materials of different properties are distributed unevenly with various spatial patterns. Numerous factors have been examined to explain the discrepancies between well-mixed laboratory rates and those measured in fields. Parameters such as chemical and physical heterogeneities, velocity, and flow distribution are commonly ignored in the well-mixed batch reactor rate measurements. Some modeling studies have shown that spatial distribution of minerals in porous media affects large-scale mineral dissolution. Experimental studies on the effect of spatial pattern of distribution of chemical heterogeneity on mineral
dissolution reaction rate are scarce except for a few studies on magnesite dissolution rates. Large-scale dissolution rates can be affected by both physical and chemical heterogeneities.

In the chemical heterogeneity part of the study we examined the effect of calcite spatial distribution on its dissolution rate under various flow velocities and permeability contrast conditions. Dissolution data of reactive fluid flow (pH=4) through two-dimensional (2D) flow cells (20.0 cm by 20.0 cm) was collected. The flow cells were packed with the same amount of calcite and sand with Mixed and One-zone patterns. The Mixed case contained uniformly distributed calcite and sand grains while the One-zone case had one square calcite zone in the middle of the flow cell. The experiments were carried out at three flow rates (1.435, 7.175, 14.35 m/d) and the dissolution process was simulated using reactive transport modeling. In addition to velocity, effect of parameters such as permeability ratio (calcite permeability/sand permeability), and transverse dispersivity on calcite dissolution were examined numerically. The goal of this part of the study was to answer the following questions: 1) What is the extent of the effect of physical and chemical heterogeneities on mineral dissolution? 2) What are the parameters that control significance of mineral spatial pattern on overall dissolution?

In general, dissolution rates were higher in cases with higher mass transfer in the reactive zone. Increase of advective mass transfer with higher velocity or higher permeability ratio increased the rates. Increase of dispersive mass transfer with increase of transverse dispersivity also increased the rate. Four orders of magnitude of change in large-scale dissolution rate (Flow cell scale) were observed in the studied cases. The effect of spatial pattern was studied through use of a parameter $\beta_{Z/M}$, defined as the One-zone large-scale rate divided by rate of its corresponding Mixed case. The $\beta_{Z/M}$ values normally range between 0 and 1. Larger values of $\beta_{Z/M}$ mean lesser effect of the spatial pattern and smaller, closer to 0 values indicate significant role of heterogeneity. Changes of transverse dispersivity ($1.4\times10^{-3}$ cm– $1.4\times10^{-1}$ cm) resulted in a $\beta_{Z/M}$ range of 0.10 – 0.37. A minimum $\beta_{Z/M}$ of 0.06 was observed numerically at high velocity with low permeability ratio. While changes of permeability ratio ($9.4\times10^{-4}$ – $3.7\times10^{1}$) induced a $\beta_{Z/M}$ change of 0.06 to 0.88, changes of velocity ($1.435\times10^{-1}$ m/d– $1.435\times10^{2}$ m/d) did not affect $\beta_{Z/M}$ as significantly (0.15 - 0.22). The insignificant role of velocity on rate ratio was attributed to high reactivity of calcite because
the solution reaches equilibrium upon contact with the reactive material at all flow velocities. Percentage of grains that participated in the dissolution reaction effectively (saturation=IAP/K_{eq}< 0.1) increased with increase of permeability ratio and transverse dispersivity. In most cases all the effective surface area was at the calcite-sand interface except at high velocity and high permeability ratio. Under these conditions higher percentage of the total surface area was reacting effectively because advection time scale was shorter than reaction time scale and acidic inlet penetrated deeper into the reactive zone. In addition, large-scale reaction rates were related to dimensionless Peclet (Pe) and Damkohler (Da) numbers. Higher Pe and lower Da values were correlated with higher dissolution rate. Our results quantify the significance of mineral spatial distribution on reaction rates and weathering. Our results point to potential control of underlying chemical and physical heterogeneities on mineral dissolution, which can regulate ecosystem functioning and water cycling.

To understand controls of geochemical reaction rates in natural systems, we modeled soil formation from Marcellus shale parent rock using reactive transport modeling with laboratory measured rate laws. Marcellus Shale is a black shale formation that is rich in organic matter and pyrite. The dissolution of Marcellus shale can lead to release of heavy metals and cause significant environment problems, especially with the extensive use of hydraulic fracturing during the production of natural gas. Here, we use soil formation and aqueous geochemistry data as constraints to understand the processes and develop a reactive transport model during Marcellus shale weathering. The simulation was carried out from approximately 10,000 years ago when the formation was first exposed after the last glacier to the present time. Our results indicated two distinct stages during the weathering. At the first 500 ~ 1,000 years, pyrite dissolved fast and Fe(OH)$_3$ was the main precipitate. After pyrite depletion, chlorite dissolved primarily with vermiculite being the major precipitate. Field data can only be reproduced when the specific surface areas of the reactive minerals were decreased by orders of magnitude from laboratory-measured values, indicating the significantly lesser available surface area under natural conditions. Our sensitivity analysis indicated the important role of specific surface area, flow rate, and reactive gases (CO$_2$ and O$_2$). It was found that CO$_2$ accelerates the weathering process and impacts pH profile and
elemental concentrations in both solid and aqueous phases. In the cases with limited source of oxygen, unreacted pyrite remained in the system even after 10,000 years and ultimately dropped pH. However, the effect of O\textsubscript{2} on the solid phase (porosity) was less than the effect of CO\textsubscript{2}. In addition, increase of flow rate increased the extent of weathering, and vice versa. However, the effects of flow rate on both solid and aqueous phases were less significant than the effect induced by changes of surface area and reactive gases.

Chemical and physical heterogeneities lead to significant spatial variations in mineralogical, geochemical, and physical properties and have profound impacts on the flow, transport, and reaction processes. Understanding these processes are crucial in many applications, including contaminant fate and transport, chemical weathering, geological carbon sequestration, environmental remediation, and energy extraction. Most studies on the effect of physical heterogeneity on solute transport have focused on porous media with short correlation length. We observed significant non-Fickian transport with long correlation length even with relatively low permeability variance. Stratified low permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface. In addition, we found that mineral spatial distribution can affect reaction rates up to a factor of 20. This is increasingly important in several geochemical processes that occur over geologic time. For example, weathering and soil formation directly depend on mineral dissolution. Understanding weathering can help us predict a wide variety of processes from atmospheric CO\textsubscript{2} levels to species concentrations in oceans and ecosystems.
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<td>Correlation length (cm)</td>
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<tr>
<td>$\sigma^2_{\ln K}$</td>
<td>Permeability variance ($m^2$)</td>
</tr>
<tr>
<td>C</td>
<td>Solute concentration ($mol/m^3$)</td>
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<tr>
<td>t</td>
<td>Time (s)</td>
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<tr>
<td>D</td>
<td>Combined dispersion–diffusion tensor ($m^2/s$)</td>
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<td>Flow velocity in the main flow direction (m/s)</td>
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<td>$v_y$</td>
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<td>Dispersion in the main flow direction ($m^2/s$)</td>
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<td>Flux-averaged concentration ($mol/m^3$)</td>
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<tr>
<td>$Q_i$</td>
<td>Flow rate from each outlet, i (ml/min)</td>
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<td>$\psi(s,t)$</td>
<td>Probability density function for just s and transition t</td>
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<td>$c(s,t)$</td>
<td>Concentration at point s and time t ($mol/m^3$)</td>
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<td>$p(s)$</td>
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<tr>
<td>$c_a$</td>
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<tr>
<td>$c_m$</td>
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<tr>
<td>$C_{Ca(II)}$</td>
<td>Total Ca$^{2+}$ concentration ($mol/m^3$)</td>
</tr>
<tr>
<td>$R_{CaCO_3}$</td>
<td>Calcite dissolution rate ($mol/s$)</td>
</tr>
<tr>
<td>$k_1, k_2, k_3$</td>
<td>The rate constants ($mol \cdot m^{-2} \cdot s^{-1}$)</td>
</tr>
<tr>
<td>$a_{H^+}$</td>
<td>Activity coefficient of H$^+$</td>
</tr>
<tr>
<td>$a_{H_2CO_3}$</td>
<td>Activity coefficient of H$_2$CO$_3$</td>
</tr>
<tr>
<td>A</td>
<td>Surface area ($m^2$)</td>
</tr>
<tr>
<td>IAP</td>
<td>Ion activity product</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>$R$</td>
<td>Large-scale reaction rate ($mol/s$)</td>
</tr>
<tr>
<td>$Q_T$</td>
<td>Total flow rate (ml/min)</td>
</tr>
<tr>
<td>$\beta_{Z/M}$</td>
<td>Rate ratio of zoned reaction rate over mixed rates</td>
</tr>
<tr>
<td>$R_{OZ}$</td>
<td>Reaction rate of One-zone case</td>
</tr>
<tr>
<td>$R_M$</td>
<td>Reaction rate of Mixed case</td>
</tr>
<tr>
<td>$A_e$</td>
<td>Effective surface area of calcite ($m^2$)</td>
</tr>
<tr>
<td>$A_T$</td>
<td>Total surface area of calcite ($m^2$)</td>
</tr>
<tr>
<td>$A_I$</td>
<td>Interface surface area of calcite ($m^2$)</td>
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<tr>
<td>RP</td>
<td>Reaction potential</td>
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<tr>
<td>$l$</td>
<td>Characteristic length of the reactive zone ($cm$)</td>
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<td>Pore volume ($cm^3$)</td>
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<td>Velocity in the reactive zone ($cm/s$)</td>
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<tr>
<td>$v_{sz}$</td>
<td>Velocity in the sand zone ($cm/s$)</td>
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<td>Activity of species I</td>
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<td>$n$</td>
<td>Degree of dependence of reaction rate on the activity of species i</td>
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<td>Permeability ratio of the reactive zone over non-reactive zone</td>
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To those who defined unconditional love for me, my mom and dad
Chapter 1

Introduction

1.1 Importance

Different properties of natural porous media are typically distributed unevenly with random spatial patterns (Allen-King et al., 1998; Barber et al., 1992; Liermann et al., 2011; Sudicky et al., 2010; Zinn and Harvey, 2003). These spatial patterns range from uniformly distribution of minerals at one end to clustered minerals distributed with significant heterogeneity at the other end (de Marsily et al., 2005; Koltermann and Gorelick, 1996; Peng et al., 2012). Both physical and chemical types of heterogeneity are common in almost all natural porous media such as soil, ground water aquifers, and hydrocarbon reservoirs.

The spatial distribution of the physical properties of a porous media such as porosity, permeability, and dispersivity is called physical heterogeneity. Spatial variations in subsurface physical properties such as permeability values result in formation of preferential flow paths, channels when fluids flow in the natural subsurface. Therefore, physical heterogeneity have profound impact on the flow and transport processes in many applications such as contaminant transport (Anderson, 1979), enhanced oil recovery from hydrocarbon reservoirs (Al Shahri et al., 2014; Smith et al., 2000), and microbial biodegradation (Harvey et al., 1993) in porous media. Recent advances in technology have significantly enhanced our computational capability. However, understanding these processes is only possible through precise modeling of fluid flow in heterogeneous media, which requires modeling at the scale of smallest heterogeneity. However, resolving spatial heterogeneities at every fine scale is computationally prohibitive, if not impossible (Dagan et al., 2013; Jankovic et al., 2013). Therefore, we usually use effective parameters. It is important to understand how small-scale heterogeneity affect large-scale processes and “effective” parameters, normally used for large-scale quantification.
Chemical heterogeneity is a condition when minerals of different kind and compositions are unevenly distributed in the porous media (Li et al., 2011; Noiriel et al., 2007; Wilkin et al., 1996). Coupling of transport processes and chemical heterogeneity can significantly influence mineral dissolution in natural systems. Variations in physical properties of porous media may lead to significant changes in the flow field (Chen et al., 2001; Fetter, 1999; Hubbard and Rubin, 2000; Newell et al., 1990; Rubin and Gomez-Hernandez, 1990). Reactive species are moved along the flow lines in the porous media and disperse into reactive mineral zones advancing mineral dissolution. Large-scale dissolution rates can be affected by either physical or chemical heterogeneity or a combination of them.

Understanding mineral dissolution and precipitation are of great importance for several applications in environmental and geological systems. Mineral dissolution impacts processes both on the large time scale relevant to geological process over hundreds to millions of years and on the small scale processes that occur over annual to decadal scale. In the large time scale, mineral dissolution is the most significant process that regulates atmospheric CO$_2$ levels (Berner, 1995). Mineral dissolution also releases elements important for plant growth including Ca, K, and P that sustain ecosystems (Huntington, 2000). In addition, flux of some of these dissolved elements is crucially important for the oceans (Kump et al., 2000). Mineral dissolution and weathering play an important role in ecosystem development as well (Carey et al., 2005). For example, soil mineral dissolution can reduce the impacts of acid deposition on ecosystems (Ohte and Tokuchi, 1999). Additionally, mineralization of carbon dioxide gas reduces the risk of CO$_2$ leakage into the atmosphere after CO$_2$ sequestration in geological formations (Friedmann, 2007; Zhang et al., 2013).

In the small time scale, several processes that impact human society on the annual to decadal period depend on mineral dissolution. Mineral dissolution may be responsible for adding harmful elements to ecosystems and also be implemented to prevent spread of harmful elements in chemical remediation sites (Yokoyama et al., 2005). Mineral dissolution can impact the release of contaminants into the environment by changing soil and groundwater chemistry (Birkefeld et al., 2006; Morrison et al., 2012; Sobanska et al., 2000). For example, it has been found that calcite dissolution reaction with acidic water may result in release of uranium cations into the ground water (Keating et al., 2011). Also, during enhanced oil
recovery, acidizing, or acid fracturing scenarios in petroleum reservoirs, several rock properties such as, porosity and permeability may change due to mineral dissolution or precipitation reactions which can significantly impact production (Bacci et al., 2011; Crawshaw and Boek, 2013; Le Gallo et al., 1998).

Marcellus shale is the largest gas reservoir in the United States. The recoverable natural gas from the reservoir is estimated to range between 141 trillion cubic feet (TCF) and 489 TCF (Blohm et al., 2012). Understanding the geochemical system and water rock interaction can assist researchers in risk analysis studies and also minimize negative products of hydraulic fracturing process. In addition, physical and chemical properties of the matrix fracture network may change due to these interactions, which ultimately changes hydrocarbon recovery from the reservoir. Understanding the water-rock interactions in Marcellus shale is also important for quantifying the environmental impacts of natural gas development. Since the same set of reactions are involved during soil generation, understanding soil generation can be a useful tool in order to understand the geochemical and reactive-transport mechanisms involved in interaction between Marcellus shale rock and water. However, dominant factors controlling soil generation process differ between cases with different mineralogy and hydrology. Due to numerous factors affecting soil generation over a relatively long period of time, only few models have adequately captured mechanisms involved in the process (Brantley and White, 2009b; Minasny et al., 2008).

1.2 Literature Review

*Physical heterogeneity.* The effects of small-scale spatial variation of permeability on effective permeability have been examined extensively for more than four decades (Dagan et al., 2013; Freeze, 1975). Numerical, statistical, or stochastic methods have been used to quantify effective permeability from spatial distribution profiles obtained synthetically or through imaging (Desbarats, 1987; Di Federico et al., 2010; Sun et al., 2011; Vernerey, 2012). In addition to the magnitude of permeability variation between zones, effective permeability depends on the spatial distribution of permeability (Desbarats, 1987). It has been found that the effective permeability of high permeability porous media containing low permeability
lenses is controlled by the volume fraction of the high permeability zones, the relative
direction of different zones to the main flow direction, and connectivity of the pore structure
(Bernabe et al., 2003; Bernabe et al., 2004; Bernabe et al., 2011). If the main flow direction is
parallel to the zonation, the effective permeability can be calculated by arithmetic averaging
of permeability of different zones. The effective permeability is equal to the harmonic
averages if the flow is perpendicular to the mineral (Song and Renner, 2006).

Solute transport in heterogeneous porous media has been studied extensively using
experimental, numerical, and field studies (Barth et al., 2001; Chao et al., 2000; Loveland et
al., 2003; Schincariol and Schwartz, 1990; Silliman, 2001; Ursino et al., 2001; Welty and
Gelhar, 1994). Solute transport is usually analyzed by Advection Dispersion Equation (ADE)
based models. However, many researchers have observed early breakthrough and long
tailing, which cannot be captured by conventional advection dispersion equations (Berkowitz
et al., 2006; Klise et al., 2008; Levy and Berkowitz, 2003; Rovey and Niemann, 2005; Zinn et
al., 2004). This under prediction of the late-time concentrations of a solute increases the risk,
clean up time, and cost upon contamination of a site. The tailing effects have long been
attributed to heterogeneity of permeability values in porous media, which result in formation
of channeling and preferential flow paths (Levy and Berkowitz, 2003). However, the use of
Fickian based transport equations to model solute transport in porous media have been
questioned recently. For example, it has been shown that use of high resolution permeability
data may not improve the capability of ADE to predict tailing (Klise et al., 2008). Various
numerical studies have identified connectivity and correlation length, λ, of porous media as
key parameters that determines solute transport and long tailing (Renard and Allard, 2013;
Willmann et al., 2008; Zinn and Harvey, 2003). In general, there is a consensus that the
spatial patterns and heterogeneity characteristics play a critical role in determining solute
transport (Beaudoin et al., 2010; de Dreuzy et al., 2007; Fiori et al., 2010; Gotovac et al.,
2009; Pedretti et al., 2013). However, there is no study to our knowledge that systematically
assesses the effect of spatial pattern, permeability variance, and correlation length on solute
transport in heterogeneous porous media.

Extensive work has been done to capture early breakthrough and tailing during solute
transport in heterogeneous porous media using several modeling approaches such as, multi-
rate mass transfer model (Haggerty and Gorelick, 1995; Haggerty et al., 2000), the dual porosity model (Gerke and Vangenuchten, 1993), as well as non-local in space and time methods (Bolster et al., 2010; Dentz et al., 2011; Huang et al., 2006; Major et al., 2011; Willmann et al., 2010). These methods replace detailed permeability field information with statistical parameters of the time it takes for a particle to travel a random distance. Here we used a non-local in time model and a non-local in space model to capture anomalous transport. The non-local in time framework of Continuous Time Random Walk (CTRW) developed by Berkowitz’s group has been extensively used in order to capture anomalous transport (Berkowitz, 2002; Berkowitz and Scher, 1998, 2001, 2009). Non-Fickian transport has also been analyzed using the non-local in space method of Fractional Advection Dispersion Equation (fADE) (Benson et al., 2001; Benson et al., 2000; Huang et al., 2006).

CTRW models solute transport process as a series of particle transitions over a distance and direction $s$, in time $t$ (Berkowitz et al., 2006). The most important part of implementing the CTRW model is the identification of proper probability density function (pdf) $\psi(s,t)$ that physically describes transport in the desired system. BTC are calculated using the evolution of the ensemble particles positions. Under the assumption of infinite non-Fickian transport through an infinite porous medium, the pdf can be approximated as a pure power law form $\psi(s,t) \rightarrow t^{1-\beta}$. However, solute transport may return to Fickian after traveling over a certain length. Truncated Power Law (TPL) form of $\psi(t)$ such that allows the quantification of the start and end time of non-Fickian behavior has been successfully used to model transport under these circumstances (Berkowitz et al., 2006; Berkowitz and Scher, 2009; Bijeljic and Blunt, 2006). Both these pdfs use a parameter called dispersion parameter, $\beta$. The value of $\beta$ is between 0 and 2 for non-Fickian transport. Where the value of $\beta$ is larger than 2 CTRW becomes as same as ADE. Since the deviation of $\beta$ values from 2 is a measure of the non-Fickian behavior, values of $\beta$ between 1 and 2 indicate less extent of non-Fickian behavior compared to those between 0 and 1.

Fractional Advection Dispersion Equation (fADE) is a non-local in space method that has been used to describe non-Fickian transport in heterogeneous media (Benson et al., 2000). The most common fADE for conservative solute transport uses $\alpha_f$ as the order of the fractional differentiation typically between 1 and 2 (Meerschaert et al., 1999). More deviation
from 2 is indicative of more heterogeneity and non-Fickian flow. All these models have their pros and cons and can predict non-Fickian transport under some conditions.

Most studies of non-Fickian flow in porous media have focused on a “benchmark” medium with high permeability variance and short correlation length. The effects of spatial pattern of physical properties in cases with relatively lower permeability variances and longer correlation lengths on transport have not been investigated systematically. In addition, capabilities and limitations of the non-local models in predicting non-Fickian flow are not clearly known.

**Chemical heterogeneity.** Mineral dissolution rates have been extensively investigated both in laboratory experiments and field studies over the recent decades (Chou et al., 1989; Gautelier et al., 1999; Pokrovsky et al., 2009). Most experimental mineral dissolution rate measurements have been carried out in well-mixed batch reactors or flow-through reactors. In addition to experimental studies, mineral dissolution rates have often been quantified based on observed mineral depletion fronts in the natural formations (Anderson et al., 2002; Brantley et al., 2008; Brantley and White, 2009a; Brimhall and Dietrich, 1987; Casey et al., 1993; Lebedeva et al., 2007; Maher, 2010, 2011; Maher et al., 2004; Maher et al., 2006; Navarre-Sitchler and Brantley, 2007; Phenrat et al., 2010; Velbel, 1993; White, 2008; Zhu, 2005, 2009). However, it has been consistently reported by many researchers that mineral dissolution rates calculated from field data are two to five orders of magnitude slower than the well-mixed laboratory measured rates (Luttge et al., 2013; Maher, 2010; Maher et al., 2004; Navarre-Sitchler and Brantley, 2007; Reeves and Rothman, 2013; Swobodacolberg and Drever, 1993; White, 1995; White and Brantley, 2003). Under similar conditions, dissolution rate of the same material was found to be 2-3 orders of magnitude higher in flow-through column experiments than those in the field (Swobodacolberg and Drever, 1993). In another study, experimental dissolution rate of more than four orders of magnitude faster that the field dissolution rates were measured from soil mineralogy analysis (Bandstra and Brantley, 2008; White et al., 1996). Since, mineral dissolution plays central role in many applications and also in processes that occur over a wide range of geological time scale, understanding the cause of this discrepancy is essential for our capability to understand and predict many processes.
Many studies have focused on determining the reason of the difference between laboratory and field rate measurements. Various reasons have been proposed to explain this discrepancy including the precipitation of the secondary mineral, the effect of reaction affinity, fluid residence time, the age of the reacting material, and the effective surface area that takes part in dissolution reactions (Alekseyev et al., 1997; Anbeek, 1993; Maher, 2010; Maher et al., 2009; Nugent et al., 1998; Steefel and Van Cappellen, 1990; Swobodacolberg and Drever, 1993; Zhu et al., 2004). In a few recent experimental studies, it has been shown that spatial variation of distribution of physical properties such as porosity and permeability and also heterogeneous distribution of different minerals in the porous media may affect the dissolution rate of mineral and cause the rate discrepancy (Li et al., 2007a, b; Molins et al., 2012).

In the natural subsurface different minerals are distributed with different patterns, which creates chemical heterogeneity. This heterogeneity has been ignored in most experimental rate measurements studies. These studies have been usually carried out in well-mixed batch reactors or in homogenous flow-through columns. The extent of studies on the role of mineral distribution on overall reaction rates is very limited. Recently, a few modeling studies have shown that even with the same amount of reactive mineral distribute in a non-reactive matrix, the spatial pattern of distribution results in changes in spatial changes in reaction product concentrations resulting in spatial changes in small-scale reaction rates, which ultimately changes overall reaction rates (Li et al., 2006, 2007a, b; Molins et al., 2012). Both physical and chemical heterogeneities affect mineral dissolution rates. However, there are very few experimental studies on the effect of chemical and physical heterogeneity on mineral dissolution rates (Li et al., 2014; Salehikhoo et al., 2013). In spite of numerous studies on the effect of physical heterogeneity on flow and transport using quasi-2D flow-cells, the coupled effect of physical and chemical heterogeneities on mineral dissolution has not been studied in quasi-2D experiments.

**Marcellus shale weathering.** The ability to precisely simulate the soil formation process by mineral dissolution and precipitation can facilitate prediction of changes in soil chemistry and mineral dissolution rate induced by changes in temperature and air, and rain compositions due to global climate change (Moore et al., 2012; Williams et al., 2003). Many factors hinder our
understanding of the weathering process, which has been happening over thousands of years. However, this topic has been the focus of several studies recently (Bluth and Kump, 1994; Fletcher et al., 2006; Millot et al., 2002; Moore et al., 2012; Navarre-Sitchler and Brantley, 2007; Navarre-Sitchler et al., 2011). Two to five orders of magnitude difference between experimentally measured mineral dissolution rates with field rates suggest fundamental differences of this process over these two scales. We need to reduce reactive surface area of minerals to successfully model the weathering process. It is known that surface area may be reduced due to coating of the surface of grains by oxides or clays or precipitation of secondary mineral (Fletcher et al., 2006). In addition, fluid in some parts of the porous media such as dead-end pores may be in close to equilibrium condition resulting in decrease of the overall extent of reactions (Moore et al., 2012).

The soil formation process is affected by numerous physical, chemical, and biological factors. Successful modeling of soil generation depends on finding dominant factors in each case among numerous possible factors such as precipitation of secondary minerals (Maher et al., 2006; Maher et al., 2009), flow velocity through the soil (Brantley and White, 2009b), erosion (Riebe et al., 2003; West et al., 2005), composition of the reacting fluid (Oelkers et al., 1994), and biological activity (Drever and Stillings, 1997) among others.

Some factors of weathering are related to mineral properties and are likely to be transferable between field sites. Other factors depend on the environment and differ from site to site. The factors are both chemical and physical, that may change over time (White and Brantley, 2003). The reactive surface area may decrease with time (White and Brantley, 2003). Organic acid may be produced due to biological activity and can impact the soil formation process. The organic reduced pH values and also changes saturation of the solution with respect to the mineral, which changes the weathering process significantly (Drever and Stillings, 1997). Secondary mineral precipitation such as clays and oxyhydroxides precipitation reduced the amount of the surface of grains exposed to fresh fluid and physically decrease the effective surface area (Maher et al., 2009; Nugent et al., 1998).

Physical factors such as rainfall, erosion, and temperature can also affect the weathering process significantly (West et al., 2005). Climatic parameters such as temperature and precipitation significantly affect the weathering process (Kump et al., 2000). It has been
shown that the weathering advance rate extensively depends on advection and diffusion processes (Brantley and White, 2009b). Hydrological heterogeneity also affects weathering through creation of regions with different rates of advection and even formation of immobile zones where advection is negligible and the sole transport process is diffusion (Green et al., 2005; White et al., 2005). Physical erosion changes the flow field over time and also exposes new mineral surfaces that may have not been in direct contact with the outside solutions to weathering (Kump et al., 2000; Riebe et al., 2003). The geochemical systems of Marcellus shale water-rock interaction is not fully understood. Involvement of numerous hydrogeochemical parameters in the weathering process has not been modeled yet. In addition, the key controlling parameters of Marcellus shale weathering are unknown.

1.3 Objective

Investigating the effect of chemical and physical heterogeneities on solute transport and mineral dissolution is the main purpose of this study. We propose to systematically quantify the extent of non-Fickian solute transport in low heterogeneity sand box through modeling and reproducing experimental data from 2D sand boxes. In addition, the combined effects of physical and chemical heterogeneities on calcite dissolution were assessed through dissolution experiments in 2D flow cells followed by reactive transport modeling. We also used reactive transport modeling to simulate the soil formation process during Marcellus shale weathering. The code was used to identify the key controlling parameters of the weathering process.

The central questions we want to answer in the physical heterogeneity part of the study are: 1) How and to what extent does correlation length control effective permeability and breakthrough curves (BTC)? 2) Which model can best reproduce data under what conditions? In order to answer these questions we used a 2D Advection-Dispersion-Equation (ADE) that explicitly incorporates the exact heterogeneity structure, a 1D ADE approach that assumes homogeneous systems using average porosity and permeability, a well-known non-local in space fADE, and the extensively used non-local in time method CTRW framework were also used.
The purpose of the chemical heterogeneity part of this study is to quantify the significance of calcite spatial pattern on the dissolution rate under a wide range of physical parameters. Specifically, the goal is to answer the following questions: 1) What is the extent of the effect of physical and chemical heterogeneities on mineral dissolution? 2) What are the parameters that control significance of mineral spatial pattern on overall dissolution? We used intermediate-scale 2D flow cell experiments and numerical modeling. Injection of non-reactive tracer and pH indicator were performed to calculate physical and transport parameters and visualize the experiments, respectively. The effects of parameters such as velocity, permeability ratio, and transverse dispersivity on the dissolution process were examined as well.

In the Marcellus shale weathering part, we developed a reactive transport model based on the soil formation process. Reactive transport models can be used to understand the weathering process and the key controlling factors. However, such a model has not yet been developed for Marcellus shale. The objective of this work is to develop a model for chemical weathering of Marcellus shale using soil formation and aqueous geochemistry data. The central questions we intend to answer in this part are: 1) What are the major components of the Marcellus shale weathering reaction network? 2) What are the key controlling parameters of the weathering process? Sensitivity of the weathering process to parameters such as specific surface area, flow rate, and availability of reactive gases (O\textsubscript{2} and CO\textsubscript{2}) inside the soil column to react with the soil water was analyzed.

Chapter 1 provided an introduction to the entire work. Chapters 2 include our first published paper on the effect of physical heterogeneity on fluid flow and transport processes in the journal of Water Resources Research. Chapter 3 is the last version of our second paper on the effect of chemical and physical heterogeneities on mineral dissolution, which will be submitted to Geochimica et Cosmochimica Acta. Chapter 4 includes our third paper on Soil formation and weathering in Marcellus shale that will also be submitted to the journal of Geochimica et Cosmochimica Acta. Chapter 5 provides the conclusion of the work and gives suggestions for future research. All published and the written chapters have gone through substantial editing by the co-authors.
1. Introduction


5. Conclusion and Future Research
Chapter 2

Solute Transport in Low Heterogeneity Sand Boxes: the Role of Correlation Length and Permeability Variance

2.1 Introduction

In the natural subsurface, solid materials of different properties are distributed unevenly with various spatial patterns (Allen-King et al., 1998; Barber et al., 1992; de Marsily et al., 2005; Scheibe et al., 2006; Sudicky et al., 2010; Zinn and Harvey, 2003). Mineral spatial distributions vary from random and even configurations at one extreme to large and clustered zones or layers at the other end of the spectrum (Jin et al., 2013; Koltermann and Gorelick, 1996; Li et al., 2011). This leads to significant spatial variations in subsurface properties and has profound impacts on flow and solute transport (Desbarats and Bachu, 1994). It is important to understand and quantify the role of heterogeneity structure in determining processes and effective parameters at large scales.

The effects of small-scale spatial variation on effective permeability $\kappa_{\text{eff}}$ have been examined extensively for more than four decades (Dagan et al., 2013; Freeze, 1975). Most studies quantify effective permeability with synthetic or imaged small-scale distribution using mathematical, numerical, geostatistical, or stochastic methods (Desbarats, 1987; Di Federico et al., 2010; Sun et al., 2011; Vernerey, 2012). The effective permeability has been found to depend on the volume fraction of high permeability zones, pore connectivity, and the relative direction of mineral distribution to the main flow (Bernabe et al., 2003; Bernabe et al., 2004; Bernabe et al., 2011). Effective permeability depends not only on the magnitude of permeability variation, but also on the spatial distribution characteristics (Desbarats, 1987). Effective permeability can be calculated as the arithmetic average of different zones if the flow is parallel to the zonation and as harmonic average if the flow is perpendicular to the zonation (Song and Renner, 2006). These studies have provided the foundation for the quantification of effective permeability. Compared to the large number of theoretical and numerical work, experimental studies are rather scarce. In particular, most experimental
studies have used one specific spatial distribution without systematically vary heterogeneity structure to understand its role in controlling effective permeability.

Similarly, solute transport in heterogeneous media has been investigated extensively in numerical (Barth et al., 2001; Fernandez-Garcia et al., 2005; Willmann et al., 2008), experimental (Chao et al., 2000; Cortis et al., 2004; Levy and Berkowitz, 2003; Oostrom et al., 1992; Silliman, 2001), and field studies (Leblanc et al., 1991; Welty and Gelhar, 1994). Extensive work has been done to capture the anomalous, non-Fickian behavior commonly observed in heterogeneous media using, for example, the dual porosity model (Gerke and Vangenuchten, 1993), multi-rate mass transfer model (Haggerty and Gorelick, 1995; Haggerty et al., 2000), as well as non-local methods (Bolster et al., 2010; Dentz and Bolster, 2010; Major et al., 2011; Willmann et al., 2010). Berkowitz and co-workers developed the framework of Continuous Time Random Walk (CTRW) that is non-local in time (Berkowitz and Scher, 1998, 2001, 2009; Di Donato et al., 2003). Fractional Advection Dispersion Equation (fADE) is non-local in space and has also been extensively used (Benson et al., 2001; Benson et al., 2000; Huang et al., 2006; Pachepsky et al., 2000).

In general, there is a consensus that spatial patterns and heterogeneity structure play a critical role in determining solute transport (Beaudoin et al., 2010; de Dreuzy et al., 2007; Fiori et al., 2011; Gotovac et al., 2009; Jankovic et al., 2003, 2009; Pedretti et al., 2013; Ramasomanana et al., 2013; Srzic et al., 2013). Various numerical studies have identified connectivity and correlation length as key parameters that determine solute breakthrough (Renard and Allard, 2013; Willmann et al., 2008; Zinn and Harvey, 2003). Zinn and Harvey (2003) showed that connectivity in low conductivity zones significantly increases dispersivity value. Pedretti et al. (2013) demonstrated that stratification induced by vertical layers of different permeability controls the shape of breakthrough curves. The BTC tailing becomes increasingly significant with increasing connectivity in low permeability zones (Willmann et al., 2008). With the same global correlation length, long correlation lengths in low permeability zones leads to more significant increase in longitudinal dispersivity compared to those in high permeability zones (Fiori et al., 2010). Non-normal transport has been observed when the travel distance is comparable to the correlation length regardless of permeability
variance while normal transport occurs when the travel distance is more than 20 times longer than the correlation length (Gotovac et al., 2009).

Although connectivity and correlation length have been found to be critical in these modeling studies, they have not been systematically examined and confirmed experimentally. Existing experimental work on solute transport has mostly focused on single spatial patterns with one correlation length (Cortis et al., 2004; Levy and Berkowitz, 2003; Silliman and Simpson, 1987; Zinn et al., 2004). The objective of this work is to systematically understand and quantify the role of correlation length in determining effective permeability and solute transport using flow cell experiments and modeling approaches. The central questions we ask are: 1) How and to what extent does correlation length determine effective permeability and breakthrough curves under different permeability variation conditions? 2) Which model can reproduce the data under what conditions?

Heterogeneous porous media were represented by a series of 2D flow cells (21.9 cm by 20.6 cm by 1.0 cm) packed with the same 20% (v/v) fine sands and 80% (v/v) of coarse sands however in different patterns. The Mixed pattern contained uniformly distributed fine and coarse sand grains. Four-zone cases had four square fine zones (4.5 by 4.5 cm) embedded in coarse sand matrix. The One-zone cases had all fine grains in one square zone (9 cm by 9 cm) in the middle of the flow cell within the coarse sand matrix. Large correlation length corresponds to natural systems that are commonly characterized by layered structures or zones with distinct properties at length scales comparable to the scale of the whole domain (Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salehikhoo et al., 2013). Three series of flow cells were studied with permeability variance \( \sigma^2_{lnK} \) varying from 0.10 to 0.43 (here \( K \) refers to permeability). Compared to studies with orders of magnitude permeability difference between fine and coarse zones, the \( \sigma^2_{lnK} \) here was relatively small. The extent of permeability variation differs significantly in different natural subsurface systems. For example, the Bordon site (Borden, Ontario) is well known as relatively homogenous with low \( \sigma^2_{lnK} \) values around 0.20 (Mackay et al., 1986), while the Macrodispersion Experiment (MADE) site in Mississippi is known to be highly heterogeneous with \( \sigma^2_{lnK} \) around 4.5 (Boggs et al., 1992).
Several modeling approaches were used here to capture the breakthrough curves. The 2D Advection-Dispersion-Equation (ADE) explicitly incorporates the heterogeneity structure. The 1D ADE approach assumes homogeneous media using average porosity and permeability. The well-known and extensively used non-local in space fADE and non-local in time method CTRW framework were also used. These four methods were compared to understand which model works better under what conditions.

2.2 Methodology

FLOW CELL EXPERIMENTS

Spatial distribution patterns of sandboxes. Quartz sands from Portage Lumber were packed into 7 transparent Plexiglas sandboxes of the dimension 21.6 cm by 20.9 cm by 1.0 cm. The sand grains were packed into three spatial patterns (Mixed, Four-zone, and One-zone) that contained fine (black) and coarse zones (gray) as illustrated in Figure 2-1. The Mixed pattern contains homogeneously mixed fine and coarse sands. The Four-zone pattern has 4 fine zones of 4.5 cm×4.5 cm distributed in the center of each quarter of the sandbox. The One-zone pattern has one fine zone of 9 cm×9 cm in the middle of the flow cell. All fine zones align in parallel to the sides of the flow cell. In all three cases, the coarse sand occupies 80% (v/v) of the total volume, with the rest being the fine sand. The three patterns differ in their “dimensionless correlation length”, \( \lambda/L \), defined as the ratio of the spatial correlation length (Kitanidis, 1997; Webster and Oliver, 2007) of the permeability field \( \lambda \), over the length of the sand box in the main flow direction, L. The values of \( \lambda/L \) were 0.001, 0.244, and 0.447 for the Mixed, Four-zone, and One-zone cases, respectively.

The size of the sand grains varies between 0.05 to 0.84 mm to represent the range in the natural subsurface, as shown in Table 2-1. The finest sand (FSI) and the coarsest sand (CSII) in Table 2-1 were used to generate the largest size and permeability contrast between fine and coarse zones in High Contrast series (High Contrast Mixed (HCM), Four-zone (HCF), and One-zone (HCO)). Another three sand boxes were packed using the fine sand FSII and the coarse sand CSI of lower size and permeability contrast for Low Contrast Mixed
(LCM), Four-zone (LCF), and One-zone (LCO) cases. An additional medium contrast flow cell was packed using the medium sand size contrast (FSI and CSI) with the One-zone (MCO) pattern. As will be discussed later, the fine and coarse zones of each size range have their own permeability values. In each series, the global permeability variance $\sigma^2_{\ln K}$, a measure of the extent of variation (Gelhar, 1993), is the same. The $\sigma^2_{\ln K}$ values are 0.430, 0.260, and 0.100 for the HC, MC, and LC series, respectively. These variances are similar to those of low heterogeneity natural geological formations such as Borden ($\sigma^2_{\ln K}=0.29$) and Cape Cod ($\sigma^2_{\ln K}=0.26$) (Leblanc et al., 1991; Mackay et al., 1986).

As shown in Figure 2-1d, the flow cell setup consists of 10 inlet injection ports, the sand box, and 3 outlet sampling ports. A digital camera was used to qualitatively document the visualization tests where dyed water was injected from the inlet plane, as will be discussed later.

![Flow cell setup diagram](image)

**Figure 2-1** Schematic diagrams of spatial distribution of coarse and fine sand grains for (a) Mixed case, (b) Four-zone case, (c) One-zone case; (d) Schematics of the experimental setup. All three patterns have the same 80% volume of coarse sand and 20% volume of fine sand. The sandboxes are of the size 21.6 cm by 20.9 cm by 1 cm.

**Wet packing procedure.** A wet packing procedure (Minyard and Burgos, 2007) was used to prevent the trapping of air bubbles in the porous media that can lead to pore-clogging and change of permeability. The packing was done layer by layer to remove air and to establish different zones. One side of the flow cell was removed and water was poured to a height of 2 cm. The sand was then added, shaken, and stirred to remove all trapped air bubbles. Plastic
strips were planted in the cell before packing the fine sand zones to keep sands of different zones from mixing. After each fine sand zone was packed, the plastic strips were carefully removed. When all parts of the sandbox and connections were filled with sand and water, the removed side of the flow cell was screwed back on and the desired patterns in Figure 2-1 were verified visually. A small amount of sand was added to the sandbox from valves to make the packing as tight as possible. Silicone caulking was used to seal off the system and to avoid leakage. All connections to the cell and sampling points were covered with a fine mesh in order to prevent sand from flowing out of the system. The effect of the mesh on the flow was verified to be negligible by measuring changes in pressure drop before and after implementing the mesh in 1D columns.

**Determination of porosity and permeability.** The solid volumes of the fine and coarse zones were calculated from the weight and density of the sand. The porosity of each zone was determined based on the difference between the solid volume and the bulk volume estimated from the dimension of the zones. Values of porosity for each zone are shown in Table 2-1. The average porosity was calculated based on the volume of water used during the wet-packing and the total volume of the sand box.

Effective permeability was determined in two steps. First, one-dimensional columns were packed using each type of sand grains to determine permeability of the individual zones packed with each type of sand. Pressure gradients along the sand columns were measured at five steady state flow rates, 0.10, 0.15, 0.20, 0.25, and 0.30 ml/min. A Crystal Engineering pressure gauge (XP2i-DP) that can measure a 15 psi differential pressure with the precision of 0.001 psi was used. To ensure steady state condition, each flow rate was kept constant until a differential pressure was stabilized for 15 minutes with a maximum variation of 0.005 psi. Using the measured flow rate and pressure gradient, Darcy’s law was used to calculate the absolute permeability of the columns packed with each sand type.
Table 2-1 Grain size and porosity of sand boxes

<table>
<thead>
<tr>
<th>Schematic</th>
<th>Cases</th>
<th>Coarse grain size (mm)</th>
<th>Fine grain size (mm)</th>
<th>Coarse zone porosity</th>
<th>Fine zone porosity</th>
<th>Average porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>Low contrast, Mixed (LCM)</td>
<td>0.42 – 0.50 (CSI)</td>
<td>0.10 – 0.21 (FSII)</td>
<td>32.96 %</td>
<td>32.96 %</td>
<td>32.39 %</td>
</tr>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>Low contrast, Four-zone (LCF)</td>
<td>0.42 – 0.50 (CSI)</td>
<td>0.10 – 0.21 (FSII)</td>
<td>38.22 %</td>
<td>29.20 %</td>
<td>36.88 %</td>
</tr>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>Low contrast, One –zone (LCO)</td>
<td>0.42 – 0.50 (CSI)</td>
<td>0.10 – 0.21 (FSII)</td>
<td>37.95 %</td>
<td>22.70 %</td>
<td>34.65 %</td>
</tr>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>Medium contrast, One-zone (MCO)</td>
<td>0.42 – 0.50 (CSI)</td>
<td>0.05 – 0.09 (FSII)</td>
<td>36.41 %</td>
<td>21.18 %</td>
<td>32.91 %</td>
</tr>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>High contrast, Mixed (HCM)</td>
<td>0.59 – 0.84 (CSII)</td>
<td>0.05 – 0.09 (FSI)</td>
<td>31.42 %</td>
<td>31.42 %</td>
<td>30.89 %</td>
</tr>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>High contrast, Four-zone (HCF)</td>
<td>0.59 – 0.84 (CSII)</td>
<td>0.05 – 0.09 (FSI)</td>
<td>35.16 %</td>
<td>22.3 %</td>
<td>33.34 %</td>
</tr>
<tr>
<td><img src="image" alt="Schematic" /></td>
<td>High contrast, One-zone (HCO)</td>
<td>0.59 – 0.84 (CSII)</td>
<td>0.05 – 0.09 (FSI)</td>
<td>34.48 %</td>
<td>21.19 %</td>
<td>29.12 %</td>
</tr>
</tbody>
</table>

The effective permeability of the Mixed cases was determined by measuring permeability of the 1D columns packed with sands of mixed gran size range using the above method. Attempts to measure pressure drop directly in the 2D flow cell failed due to the relatively short length of the flow cell compared to its width, which resulted in pressure fluctuation along the inlet plane. As an alternative, the effective permeability of Four-zone or One-zone cases was calculated using 2D numerical simulation in CrunchFlow. CrunchFlow can simulate the advective, dispersive, and diffusive transport processes coupled with chemical reactions (Molins et al., 2012; Singha et al., 2011). The code essentially solves Darcy’s equation for the distribution of steady state flow velocity. The measured permeability values for the coarse and fine zones were used to set up the permeability distribution in the 2D model domain. The outlet side was set exactly the same as the experimental setup. That is, it was a no flow boundary except at the three outlets. Hydraulic heads were assigned at the inlet...
and outlet boundaries, with the left and right boundaries set as no flow boundary. The hydraulic head in the main flow direction was adjusted to be consistent with the flow rate data from the three outlets by minimizing the sum of squared residuals. The effective permeability was calculated using Darcy’s law with the measured overall flow rate data and the hydraulic gradient that matched the flow rate data. The effective permeability therefore represents the equivalent, averaged value assuming a homogeneous porous medium at the flow cell scale.

**Flow-through tracer experiments.** Tracer experiments were carried out by injecting a solution of $1.25 \times 10^{-4}$ mol/L sodium bromide through ten inlets at a constant overall flow rate of 0.7 ml/min using a Harvard Apparatus syringe pump. The dye phenol red was used to visualize the process. This flow rate corresponds to an average velocity around 1.3 m/day, which is in the high end of natural groundwater flow velocity (Newell et al., 1990). The residence times vary from 187 minutes to 237 minutes, depending on the average porosity of the sandboxes. The effluents were collected through the three outlets every 15 minutes. Bromide concentrations were measured using the Dionex ICS2500 Ion Chromatography. Each experiment was carried out for 8.5 hours, equivalent to approximately three pore-volumes.

**MODELING APPROACHES**

**2D and 1D Advection Dispersion Equations (ADE): Determination of local and global dispersivity.** Transport modeling was used in two different approaches to understand solute transport and to determine the local (grid block) and effective dispersivity. In one approach, 2D ADE modeling was set up with the computational domain exactly like that of the flow cell experiment, with explicit distribution of measured permeability and porosity in fine and coarse zones. The model also explicitly set up the three outlets at the top boundary. The constraints were the three flow rates and the breakthrough curves from the three individual outlets. The explicit incorporation of spatial distribution enabled the simulation of heterogeneous flow fields and was used to obtain the dispersivity at the local grid block scale. In another approach, the 1D ADE was solved to simulate the whole flow cell as a homogeneous system as if we do not know the detailed heterogeneous distribution. The three outlets are combined into one overall outlet in the calculation with the total flow rate and the
flow-rate averaged tracer breakthrough curves as constraints. In this case, the effective or global dispersivity at the flow cell scale was obtained by matching the averaged breakthrough data.

2D ADE modeling with explicit heterogeneity structure: local dispersivity. The classical 2D ADE equation was solved using CrunchFlow (Steefel and Lasaga, 1994):

$$\frac{\partial c}{\partial t} + \nabla (-D \nabla c + v c) = 0$$

where $C$ is the solute concentration (mol/m$^3$), $t$ is the time (s), $D$ is the combined dispersion–diffusion tensor (m$^2$/s), $v$ (m/s) is the flow velocity vector and can be decomposed into $v_x$ and $v_z$ in the directions parallel and transverse to the main flow. The dispersion-diffusion tensor $D$ is defined as the sum of the mechanical dispersion coefficient and the effective diffusion coefficient in porous media $D^*$ (m$^2$/s). At any particular location (grid block) with flow velocities in longitudinal and transverse directions being $v_x$ and $v_z$, their corresponding $D_L$ and $D_T$ are the dispersion coefficients (m$^2$/s) given by

$$D_L = D^* + \alpha_L v_x$$

$$D_T = D^* + \alpha_T v_y$$

Here $D^*$ is the effective diffusion coefficient in porous media (m$^2$/s), $\alpha_L$ and $\alpha_T$ are the longitudinal and transverse dispersivity (m). The ratio of $\alpha_L/\alpha_T$ has been reported to be between 6 and 20 (Boggs et al., 1992). In this work, $\alpha_T$ was set to be 0.1×$\alpha_L$ in all models. A common tortuosity value of 2.0 for unconsolidated porous media (Armatas, 2006; Salem and Chilingarian, 2000) was used to relate $D^*$ to the aqueous diffusion coefficient $D_0$ of $2.0 \times 10^{-9}$ m$^2$/s for bromide (Fetter, 1999).

In all cases, the size of grid block was 0.1 cm × 0.1 cm. The grid-size effect was eliminated by increasing the resolution to the extent that the produced BTCs do not change with increasing resolution. The total number of grid blocks is 209×216. Three outlets were established explicitly at the effluent boundary to have exactly the same setup as shown in Figure 2-1d. The local dispersivity values were obtained by matching the breakthrough data from individual outlets. Although the dispersivity $\alpha_L$ is the same for all grid blocks, $D_L$ is different for each grid block due to the spatial variation in the flow field, as will be discussed later.
**1D ADE with averaged properties assuming homogeneous systems: global effective dispersivity.** To obtain the effective dispersivity at the flow cell scale, the averaged breakthrough curves were obtained by flux-averaging the concentrations from their respective outlets as follows:

\[
\overline{C} = \frac{\sum_{i=1}^{3} C_i Q_i}{\sum_{i=1}^{3} Q_i}
\]  

(4)

where \(\overline{C}\) represents the flux-averaged concentration, \(C_i\) and \(Q_i\) are the experimentally measured concentration and flow rate from each outlet \(i\). Accumulated effluent water volume from each outlet was summed and divided by the experiment duration to determine the averaged flow rate. The averaged flow rate and breakthrough curve were used as constraints to obtain the global effective dispersivity for each sandbox using the 1D form of the ADE Equation (1). Averaged porosity and effective permeability values were used assuming homogeneous sand boxes without spatial variations in properties. The obtained dispersivity \(\alpha'\) therefore represents the effective dispersivity at the scale of the sand box.

**Continuous Time Random Walk (CTRW) analysis.** Here we use the CTRW framework to analyze the non-Fickian or "anomalous" behavior in the heterogeneous porous media (Berkowitz and Scher, 1998; Kosakowski et al., 2001). The CTRW framework portrays the transport process as a series of transition steps with displacements \(s\) and times \(t\) (Berkowitz et al., 2006). It can capture non-Fickian behavior where the traditional ADE often fails. Detailed mathematical background can be found in literature (Berkowitz et al., 2000; Levy and Berkowitz, 2003).

Implementation of CTRW requires the identification of proper probability density function (pdf) \(\psi(s,t)\) that physically describes transport in a system. For transport in porous media, it is sometimes approximated as a pure power law form \(\psi(s,t) \rightarrow t^{1-\beta}\), where the use of a pure power law means that the non-Fickian transport will endure forever during transport through an infinite porous media with repeated spatial patterns such as the ones in Figure 2-1. Here we use the Truncated Power Law (TPL) form of \(\psi(t)\) that allows the quantification of the start and end time of non-Fickian behavior. It has been successfully used in understanding
observations at multiple scales (Berkowitz et al., 2006; Berkowitz and Scher, 2009; Berkowitz et al., 2000; Bijeljic and Blunt, 2006; Deng et al., 2008). The decoupled pdf is approximated as \( \psi(s, t) = p(s) \psi(t) \), where \( p(s) \) is the probability distribution of the length of the jumps and \( \psi(t) \) is the probability rate for a transition time \( t \) between sites (Berkowitz and Scher, 2010).

This results in the following equation

\[
\frac{\partial c(s, t)}{\partial t} = - \int_0^t \mathcal{M}(t-t')[v_\psi \cdot \nabla c(s, t') - D_\psi : \nabla \nabla c(s, t')] dt'
\]

where \( c(s, t) \) is the concentration normalized by the inlet concentration, \( v_\psi \) and \( D_\psi \) are the first and second moments of \( p(s) \) divided by the characteristic time \( \bar{t} \), and \( \mathcal{M}(t) \) is the memory function. The Laplace transform of the memory function is

\[
\tilde{\mathcal{M}}(u) = \tilde{\bar{t}}u \frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)}
\]

here \( \tilde{\bar{t}} \) is a medium characteristic time for a transition and \( \tilde{\psi}(u) \) is the Laplace transform of \( \psi(t) \)

\[
\psi(t) = N \frac{\exp(-t/t_2)}{(1 + t/t_1)^{1+\beta}}
\]

\[
N = [t_1 t_2^{-\beta} \exp(t_2^{-1}) \Gamma(-\beta, t_2^{-1})]^{-1}
\]

where \( t_1 \) and \( t_2 \) are the limits of the power law spectrum, \( \Gamma \) is the incomplete gamma function, and \( \tau_2 \equiv t_2/t_1 \).

The well-known conventional ADE is a specific form of CTRW where the value of \( \beta \) is larger than 2. The value of \( \beta \) is between 0 and 2 for non-Fickian transport. The deviation of \( \beta \) values from 2 is a measure of the non-Fickian behavior. Values of \( \beta \) between 1 and 2 indicate less extent of non-Fickian behavior than those between 0 and 1. The time scales \( t_1 \) and \( t_2 \) are the lower and higher time limits of the power law behavior that follow \( \psi(t) \propto (t/t_1)^{-1-\beta} \). The \( t_1 \) approximates the median transition time when the power law behavior starts, while the cutoff \( t_2 \) is the time where the power law behavior ends, which ensures that the transport evolves into a normal Fickian one when \( t > t_2 \). As such, the use of TPL form allows the quantification of the time needed to approach Fickian behavior.

It should be noted here that the statistical characteristics of uncorrelated velocity fields was used to project particle jumps in porous media. In some cases in our system, preferential
flow paths are visible and the velocity field is correlated, as shown later in Figure 2-3b-c. As such, transport can be modeled using correlated velocity fields (Dentz and Bolster, 2010; Le Borgne et al., 2011; Le Borgne et al., 2008a, b). The solution $c(s, t)$ determines the first arrival times based on BTC as a function of the parameters $v_r, D_r, \beta, t_1,$ and $t_2$. The parameters were adjusted simultaneously to reproduce the breakthrough curves using the CTRW tools (Cortis and Berkowitz, 2005).

**Fractional Advection Dispersion Equation (fADE).** Non local in space methods such as fADE have been used to describe non-Fickian transport (Benson et al., 2000). One of the most common fADEs for conservative solute transport is the following one-dimensional form (Meerschaert et al., 1999):

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^{\alpha_f} C}{\partial x^{\alpha_f}}$$  \hspace{1cm} (9)

Where $\alpha_f$ is the order of the fractional differentiation typically between 1 and 2 and is normally represented as $\alpha$ in fADE literature. Here we used $\alpha_f$ to avoid confusion with the dispersivity $\alpha$ in the ADE. With a continuous solute injection into a solute free medium at the inlet, the analytical solution to equation (9) is as follows (Benson et al., 2000; Huang et al., 2006):

$$C = C_0 \left[ 1 - F_{\alpha_f} \left( \frac{x - vt}{\cos(\pi \frac{\alpha_f}{2}) D t^{\frac{1}{\alpha_f}}} \right) \right]$$  \hspace{1cm} (10)

where $F_{\alpha_f}$ is the symmetric $\alpha$-stable probability function (Pachepsky et al., 2000) defined as

$$F_{\alpha_f}(y) = C(\alpha_f) + \frac{\text{sign}(1-\alpha_f)}{2} \int_0^1 \exp(-y^{\frac{\alpha_f}{\alpha_f-1}} U_{\alpha_f}(\phi)) d\phi$$  \hspace{1cm} (11)

Where $\phi$ is the integration variable, sign$(1-\alpha_f)$ is -1, 0, and 1 for $\alpha_f >1$, $=1$ and $<1$, respectively, $U_{\alpha_f}$ and $C(\alpha_f)$ are auxiliary functions of $\alpha_f$. Here $C(\alpha_f)$ is equal to 1 if $\alpha_f >1$ and is equal to 0.5 if $\alpha_f <1$ and
The analytical solution of the fADE formulation was applied and calibrated to the experimental data. The average velocity was first adjusted to match the mid arrival time of BTC. Other parameters, including D and $a_f$, were then adjusted to reproduce the BTC.

Optimization Methods. To capture the BTC tails and to keep consistency between different models for fair comparison, the best fit was obtained for all four models by minimizing $\sum_{i=1}^{N}(log c_i - log C_i)^2$, the sum of squared residuals between the logarithms of concentration data and the model predicted concentrations. Here N is the number of data points, $c_i$ is the model predicted concentration, and $C_i$ is the measured data. This is essentially a weighted minimization $\sum_{i=1}^{N} W_i (c_i - C_i)^2$, where the weight $W_i=1/C_i^2$ (Chakraborty et al., 2009). This is different from minimizing $\sum_{i=1}^{N}(c_i - C_i)^2$ that results in uniform fit to the model over the whole BTC. The logarithm minimization allows proper account of the fit to the BTC tails, which is important in solute transport in heterogeneous porous media. As will be pointed out later, the optimization method plays a large role in determining the performance of different models in capturing the BTCs.

Temporal Moment Analysis and Model Comparison. Characteristics of solute transport in porous media can be represented by key parameters such as first and second temporal moments (Dagan, 1990; Zhu et al., 2009; Zhu and Yeh, 2006). Here we use the moment analysis to measure the similarity between the experimental data and the predictions from the ADE, CTRW, and fADE frameworks. Some key parameters are defined as follows (Dagan, 1990; Riva et al., 2008). The first moment, $T_1$, is a measure of the mean advective time of fluid flow in porous media. It is defined as follows:

$$T_1 = \frac{\int_0^\infty t c(t) dt}{\int_0^\infty c(t) dt}$$

where $c(t)$ is the tracer concentration at time $t$.

The centered second order moment, $T_2$, represents the width of the tracer plume around its center of mass. It is calculated as follow:
The relative difference between the prediction and data for the overall BTC were calculated as follows:

\[
\delta_v (BTC) = \frac{\int_{t=0}^{\infty} |c_m - c_d| \, dt}{\int_{t=0}^{\infty} c_d \, dt}
\]  

(16)

where \(c_m\) and \(c_d\) are the predicted and measured concentration, respectively. This value compares the prediction of the overall breakthrough curves from different models, while \(\delta_v\) values for \(T_1\) and \(T_2\) calculated from equation (15) focus on the BTC characteristics.

### 2.3 Results and Discussion

**Average porosity and effective permeability.** As shown in Table 2-1, the two Mixed cases (LCM and HCM) have lower porosity than other sandboxes, similar to observations in other studies (Li et al., 2014; Salehikhoo et al., 2013). In other cases, the coarse zones have larger porosity compared to the fine zones. Surprisingly, the CSII sand zone has slightly lower porosity than the CSI sand zone, likely due to the larger size range of CSII grains (0.59 – 0.84 mm) compared to the relatively narrower size range (0.42 - 0.50 mm) of the CSI sand. In general, the LC series has higher average porosity than the HC cases.
Measured permeability values for sand grains of different sizes are shown in Table 2-2 together with their standard deviation. As expected, permeability values are relatively small for fine sands and larger for coarse sands. Measured permeability values of sand grains vary between $0.305 \times 10^{-12} \text{ m}^2$ for FSI (0.05 ~ 0.09 mm) and $1.576 \times 10^{-12} \text{ m}^2$ for the CSII (0.59 ~ 0.84 mm). Also shown in Table 2-2 and illustrated in Figure 2-2, the effective permeability of all sandboxes fall between that of their composing sand grains. The Mixed patterns (LCM and HCM) have relatively lower permeability than the other two cases for both LC and HC cases. This is a common observation even with the mixing of difference types of mineral grains (Li et al., 2014; Salehikhoo et al., 2013). This is because the fine grains can fill in the pore volumes between coarse grains in the Mixed cases. The LCF and LCO cases have the same effective permeability values that are close to the permeability of the coarse sand. This also occurs in the HCF and HCO cases. With the same One-zone distribution, the LCO case has an effective permeability similar to that of the MCO, primarily because they share the same coarse sand. The HCO case has much higher permeability than the LCO and MCO cases because it has much larger coarse sand grains. This indicates that when the correlation length is sufficiently large, the effective permeability is dominated by that of the coarse zone, which results in increasing effective permeability with increasing correlation length under the same permeability variance conditions.

The effective permeability of a heterogeneous porous medium can be calculated using various averaging techniques, including arithmetic ($K_{eff} = \sum_{i=1}^{n} x_i k_i$), harmonic ($1/K_{eff} = \sum_{i=1}^{n} x_i / k_i$), and geometric mean ($K_{eff} = \sqrt[n]{\prod_{i=1}^{n} k_i}$) of permeability in individual zones (Babadagli, 2006; Dagan, 1989; Song and Renner, 2006). Here $k_i$ is the permeability and $x_i$ is the volume fraction or layer thickness of the composing zone, $i$. The $K_{eff}$ values can be quantified using harmonic averaging if the main flow direction is perpendicular to the orientation of different permeability zones (cross layers) and by arithmetic averaging when the main flow is parallel to the orientation of the different zones (flow along stratification). The geometric mean can be used to estimate $K_{eff}$ when both parallel and perpendicular flows exist relative to the direction of zonation. That is, when there is not a dominant flow direction relevant to the zonation.
As shown in Table 2-2 and Figure 2-2, due to similar permeability values in the fine and coarse zones, the LC sandboxes have similar arithmetic and harmonic means and effective permeability. In contrast, the $K_{eff}$ values in the HC cases are much closer to the arithmetic mean. This is because the resistance to the flow is high with the low permeability fine sands. As a result, water preferentially flow through the coarse zone and the system acts if there are layers in parallel to the main flow direction. In contrast to observations in literature (Babadagli, 2006; Berg and Illman, 2011), the $K_{eff}$ values in all cases are higher than the geometric mean, indicating well-connected high permeability zones (Zinn and Harvey, 2003). In the LCM case, flow occurs in all directions due to the lower permeability contrast and the mixing pattern, leading to the similarity between different types of averaged permeability values.

### Table 2-2 Measured permeability of coarse and fine zones and effective permeability of 2D sand boxes

<table>
<thead>
<tr>
<th>Cases</th>
<th>grain size (mm)</th>
<th>Perm ratio</th>
<th>Permeability ($10^{-12}$ m$^2$)</th>
<th>Arithmetic mean ($10^{-12}$ m$^2$)</th>
<th>Harmonic mean ($10^{-12}$ m$^2$)</th>
<th>Geometric mean ($10^{-12}$ m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine sand I (FSI)</td>
<td>0.05 – 0.09</td>
<td>-</td>
<td>0.305±0.019</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fine sand II (FSII)</td>
<td>0.10 – 0.21</td>
<td>-</td>
<td>0.491±0.027</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coarse sand I (CSI)</td>
<td>0.42 – 0.50</td>
<td>-</td>
<td>1.090±0.006</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coarse sand II (CSII)</td>
<td>0.59 – 0.84</td>
<td>-</td>
<td>1.576±0.012</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Low contrast, Mixed (LCM)</td>
<td>FSII + CSI</td>
<td>2.21</td>
<td>0.756±0.016</td>
<td>0.970</td>
<td>0.876</td>
<td>0.732</td>
</tr>
<tr>
<td>Low contrast Four-zones (LCF)</td>
<td>FSII + CSI</td>
<td>2.21</td>
<td>0.877</td>
<td>0.970</td>
<td>0.876</td>
<td>0.732</td>
</tr>
<tr>
<td>Low contrast, One- zone (LCO)</td>
<td>FSII + CSI</td>
<td>2.21</td>
<td>0.882</td>
<td>0.970</td>
<td>0.876</td>
<td>0.732</td>
</tr>
<tr>
<td>Medium contrast, One-zone (MCO)</td>
<td>FSI + CSI</td>
<td>3.57</td>
<td>0.807</td>
<td>0.933</td>
<td>0.720</td>
<td>0.577</td>
</tr>
<tr>
<td>High contrast, Mixed (HCM)</td>
<td>FSI + CSII</td>
<td>5.17</td>
<td>0.823±0.019</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>High contrast, Four-zones (HCF)</td>
<td>FSI + CSII</td>
<td>5.17</td>
<td>1.140</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>High contrast, One-zone (HCO)</td>
<td>FSI + CSII</td>
<td>5.17</td>
<td>1.137</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
</tbody>
</table>
Figure 2-2 Measured permeability (filled black squares) for each sand type (first four cases) and for the Mixed cases (LCM and HCM), and the calculated effective permeability for the 2D sand boxes (filled black squares). Also shown are the arithmetic average (open circle), harmonic average (open triangle), and geometric mean (open diamond).

**Visualization test.** The tracer experiments were carried out in the three LC cases, with the main flow direction from the bottom to the top. The fluid flow was visualized using phenol red. Figure 2-3 compares the dye distribution during the water injection test (top) and the predicted bromide concentration profile (bottom) by the 2D ADE at 0.45 pore volumes. In these LC cases with the permeability ratio of 2.21, the difference between the two zones is visible, verifying successful packing of different zones. The predicted spatial profiles of Br concentration agree qualitatively with the images, with the formation of concentration gradients shaped by the spatial zonation. The images also show unevenness and irregularities at the fronts even in the “homogeneous” LCM case, while the model predicts smooth front in a perfectly homogeneous medium. This emphasizes the importance of small scale, unresolved heterogeneity that actually affect solute transport.
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-3.png}
\caption{Comparison between images from the dye-injection test (top) and the model prediction of Br concentration profiles (bottom) for the three LC cases at 0.45 pore volumes for (a) Mixed (LCM), (b) Four-zone (LCF), and (c) One-zone (LCO).}
\end{figure}

**Solute transport in high contrast (HC) cases.** Figure 2-4 shows the measured and simulated Br breakthrough curves (row i) and the calculated flow velocity field (row ii) from 2D ADE for the HC cases. The calculated flow velocities in the low and high permeability zones from the 2D ADE are within the same order of magnitude because the permeability ratio is only a factor of 5.1, much lower than the orders of magnitude permeability difference in studies for highly heterogeneous porous media (Levy and Berkowitz, 2003; Zinn et al., 2004). As expected, the HCM case has the homogeneous distribution of flow velocities except at the sampling outlets where relatively fast flow occurred because all flow converged to the outlets. As a result, the BTCs from the three outlets overlap. In the HCF and HCO cases, the fine zones have lower flow velocities compared to the coarse zone. The HCF case has a slightly higher flow channel in the middle and therefore slightly earlier breakthrough compared to the side outlets. In the HCO case, the flow rates are lower in the middle fine zone and higher at the sides. This results in earlier breakthrough from the sides starting at about 0.5 pore volumes and much later breakthrough from the middle outlet starting at around 1.0 pore volume. The
difference in the breakthrough time from the side and middle outlets is much larger in HCO than in HCF.

The predicted flow velocity distribution shows that the setup of the outlet boundary, or the presence of the three outlets, affects flow distribution in regions up to about 3-5 cm distant from the outlet plane in all three cases. The flow field further away from the outlet plane is not affected. Although not shown here, we also compared the output of 2D ADE with an open outlet boundary (without 3 outlets) to that with 3 outlets using the same set of parameters obtained from matching data. The comparison shows that the overall breakthrough curves in these two cases are almost identical with or without the 3 outlets, except that an open boundary led to about 5% earlier breakthrough in average than that with 3 outlets in the HC cases, which is considered negligible.

Figure 2-4 (i) Breakthrough curves from experiments (symbols) and from 2D ADE modeling (lines) and (ii) predicted profiles of local flow rates for the high contrast (a) HCM, $\alpha_L = 0.03$ cm, (b) HCF, $\alpha_L = 0.38$ cm, and (c) HCO, $\alpha_L = 0.45$ cm. The overall flow rate was 0.7 ml/min. The average residence times are between 187 minutes in the HCO case and 215 minutes for HCF due to different porosity.

The local longitudinal dispersivity values from the 2D ADE are 0.03, 0.38, and 0.45 cm for the HCM, HCF, and HCO cases, respectively. From a theoretically point of view, the local dispersivity values represent the intrinsic property of porous media because the
heterogeneous flow fields are explicitly simulated and therefore should be the same in all cases. However, this seems not the case here. The $\alpha_L$ values for the HCF and HCO cases are relatively similar and are much higher than that of the HCM case. This may indicate intrinsic difference between cases with very small and large correlation lengths. The longitudinal local dispersivity $D_L$ also vary spatially (not shown here), the distribution of which is exactly the same as that of the flow rates as indicated by Equation 2.

Figure 2-5 Comparison of overall breakthrough data (in $C/C_0$ and $\log_{10}(1-C/C_0)$) with predicted curve using 2D ADE, 1D ADE, CTRW, and fADE for (a) and (d) HCM; (b) and (e) HCF; and (c) and (f) HCO. The HCO case shows distinct breakthrough steps arising from fast advection in the coarse zone, slow advection in the fine zone, and slow diffusion.

Figure 2-5 shows the evolution of the overall breakthrough data and the prediction from the models. The data look significantly different between cases. In the HCM case, the bromide breaks through between 0.9 to 1.1 pore volumes and reached more than 99.9% of inlet concentration ($\log(1-C/C_0) = -3$) within approximately 1.2 pore volumes. In contrast, the breakthrough in the HCO starts much earlier, at approximately 0.5 pore volumes. The outlet concentration reached 99% of the inlet concentration at about 2.5 pore volumes ($\log_{10}(1-C/C_0) = -2$). The early breakthrough has a slope not as sharp as that in HCM, indicating slower
breakthrough than the HCM case. The BTC shows an apparent “step” at around 1.0 pore volume, the time when the breakthrough from the middle outlet starts, as shown in Figure 2-4c. This early breakthrough is primarily due to the “fast advection” from the higher flow channels at the sides with a characteristic median breakthrough time of 0.75 pore volumes, consistent with the medium arrival time from the side outlet shown in Figure 2-4c. Another step, or change in slope, occurs at around 2.0 pore volumes, when the breakthrough from the middle outlet ends. This second stage breakthrough is caused by the “slow advection” from the fine zone with a median arrival time of 1.5 pore volumes that is consistent with that from the side outlets shown in Figure 2-4c. After that, log(1-C/C_0) decreases much slower. This last stage is likely due to the “slow diffusion” because of the large size of the fine zone and small-scale heterogeneity. These different stages are similar to the observation in the fast flow high permeability contrast cases in (Zinn et al., 2004). The major difference is that the BTC from slow diffusion here is caused by the large fine zone, not by very low permeability zones.

The breakthrough of the HCF case is somewhat between those of HCM and HCO. It does not have three distinct stages. However, a slight change in slope does occur at approximately 1.2 pore volumes. In fact, it can be characterized by two stage breakthrough, with most breakthroughs between 0.7 to 1.5 pore volumes because the three outlets do not have very distinct breakthrough times. Later breakthrough due to diffusion occurs at much lower rates after about 1.6 pore volumes. In fact, the rates of the late breakthrough look similar between HCF and HCO, indicating this is not necessarily caused by the zonation. Instead it is probably more related to the small-scale, unresolved heterogeneity in the system.

With the exact set up of the heterogeneity structure, the 2D ADE (Equation 1) captures detailed stages in the BTC well. Although the 1D ADE does not capture the detailed breakthrough stages in HCO, it captures the “average” behavior of the BTC surprisingly well. It obtain a large $\alpha'$ value of 1.96 cm for HCO and a much smaller value of 0.15 cm in the HCM case. The 2D ADE also reproduces the shape of the HCF case almost perfectly, while the 1D ADE does not capture the later stage of the HCF breakthrough.

The CTRW reproduces the HCM and HCF curves almost perfectly however not the HCO curve. In the latter case, the CTRW curve describes the early breakthrough and the long tail well, however not the second stage characterized by the “slow advection” from the fine
zone. This is expected because the HCO has distinct zones at the scale comparable to the domain, which represents a non-stationary domain (Berkowitz et al., 2006). This is one of the CTRW limitations. Relatively large size of the low permeability zone in the HCO case separates exponential tails from each zone, which hinders the formation of a power law tail that a TPL model can often capture precisely (Willmann et al., 2008). Values of $\beta$ for the HCM, HCF, and HCO cases are 1.93, 1.72, and 1.56, respectively. Values of $t_1$ ($10^{0.4}$ min) are the same for HCF and HCO, both of which are higher than that of HCM. Larger $t_2$ values mean longer time to approach the Fickian behavior. This transition occurs much later in the HCO ($\sim6300$, $10^{3.8}$ min) and HCF ($\sim2500$, $10^{3.4}$ min) compared to the HCM ($\sim398$, $10^{2.6}$ min), indicating longer time needed to reach asymptotic Fickian behavior with increasing correlation length.

Compared to CTRW, the fADE does a much better job in reproducing the HCO data probably owing to the fact that the HCO case has large fine zone with lower permeability than that of the coarse zone, which facilitates the formation of the preferential flow path and channels. This is largely confirmed by the fact the fADE does not reproduce the data as well in the HCF case, where the preferential flow path is not as obvious in the HCO case.

Figure 2-6 Measured (symbols) and predicted (lines) local breakthrough curves for (a): LCM, $\alpha_L = 0.02$ cm; (b) LCF, $\alpha_L = 0.07$ cm; and (c) LCO, $\alpha_L = 0.34$ cm. Predicted overall breakthrough curves and data for (d) LCM; (e) LCF; (f) LCO.
**Solute transport in the low contrast (LC) cases.** The BTCs of the LC cases from the three outlets are similar to that of the HC cases, as shown in Figure 2-6. However, the difference between the break through times from different outlets is much smaller compared to the HC cases. The LCM case has longer tail than the HCM case, indicating a more heterogeneous system although they are both packed in mixed pattern. The BTC of LCF does not show staged breakthrough, while the LCO case does show an early fast breakthrough and long tail later. However, no “steps” are observed in the BTC due to the relatively small permeability contrast between zones. CTRW reproduces the data well in all cases, as shown in Figures 2-6d-f. 2D ADE also does a reasonable reproduction of the data. Both 1D ADE and fADE reproduce early part of the BTC however significantly underestimate the tails in LCM and LCF cases. In the LCO case, the fADE predicts a much earlier breakthrough than the data.

**Effects of permeability variance.** To quantify the effect of permeability variance, the three One-zone cases are compared in Figure 2-7. As shown in Figure 2-7a-c, the difference in breakthrough times between the middle and the side outlets increase with increasing permeability contrast. Correspondingly, the small-scale dispersivity values increase with increasing variance, with 0.34, 0.55, and 0.45 cm, respectively, for the LCO, MCO, and HCO cases.

The overall breakthrough curves become wider with earlier breakthrough and longer tails as the permeability variance increase. Correspondingly, the observed stages or steps in the BTCs become increasingly obvious from the LCO to HCO cases. As expected, the 1D ADE typically misses the tail. Surprisingly, it does better in the HCO case than in the LCO and MCO cases. Both 2D ADE and fADE reproduce the data increasingly better with increasing permeability variance while CTRW does better in the LCO and MCO cases than in the HCO case. The value of $t_1$ remains the same $10^{0.4}$ (0.4) minutes for all cases while the cut-off time $t_2$ increases with increasing permeability variance. This is expected because the travel time and distance for approaching Fickian typically increase linearly or nonlinearly with permeability variance (Fiori et al., 2010).
Figure 2-7 Measured (symbols) and predicted (lines) local breakthrough for (a): LCO, $\alpha_L = 0.34$ cm (b) MCO, $\alpha_L = 0.55$ cm, and (c) HCO, $\alpha_L = 0.45$ cm. Overall breakthrough and model output of 2D ADE, 1D ADE, fADE, and CTRW for (d) LCO; (e) MCO; (f) HCO.

**Moment analysis and model comparison.** The first moment $T_1$ measures the mean advection time of the plume center; the second moment $T_2$ measures the time scale relevant to the width of the plume. As shown in Figure 2-8, the $T_1$ values vary between approximately 240 to 300 minutes, comparable to the range of residence times between 188 and 237 minutes. The $T_1$ values increase with correlation length, with larger increase in the HC cases than in the LC cases. Values of $T_2$ increase significantly from approximately 1,000 to 8,000 min$^2$ in the HC cases and from 1,000 ~ 2,400 min$^2$ in the LC cases, indicating the significant impact of correlation length and permeability variance on solute plume.

To quantitatively compare different models, the relative difference between the data and model outputs were calculated for the overall breakthrough curves (equation (16)) and the two moments (equation (15)). As shown in Figure 2-8b, in most cases, CTRW and 2D ADE have the smallest deviation from data while 1D ADE and fADE have relatively larger deviation. Interestingly, the fADE predictions have smaller $\delta_v$ in all HC cases than in the LC cases. Within each permeability contrast series, the $\delta_v$ values increase with correlation length in all models, emphasizing the challenge in capturing the overall breakthrough with increasing correlation length.
Figure 2-8 (a) first moment $T_1$ and second moment $T_2$ as a function of dimensionless correlation length ($\lambda/L$); relative difference between data and modeling output ($\delta_v$) for (b) breakthrough curves, (c) $T_1$, and (d) $T_2$.

Figures 2-8c shows that most model captures the first moment well with $\delta_v$ values within 10%. Figure 2-8d shows that 2D ADE reproduces the closest $T_2$ in almost all cases. CTRW does better than fADE and 1D ADE in the LC cases. Consistent with observations in Figure 2-5, CTRW has larger deviation in the HC cases, especially in the HCO, where the $\delta_v$ is the largest among all models.

The fADE has larger $\delta_v$ values than CTRW in all cases except in the HCO case. Similar to observations in Figure 2-8b, the $\delta_v$ values of fADE for the moments decrease with increasing permeability contrast, as shown in the trend from LCO, MCO, to HCO. This can be attributed to the fact that fADE captures solute transport well when there is well connected low permeability zones with channel formation (Benson et al., 2000). In cases other than HCO, the permeability contrast and/or the correlation length are not sufficiently large to form channels, which may explain why fADE does not do as well as other models in these cases.

The 1D ADE reproduces $T_1$ reasonably well however generates the largest $\delta_v$ value for $T_2$ among all models in most cases. Interestingly, the 1D ADE has the largest $\delta_v$ values for $T_1$
in the LCM case and for T2 in the HCM case, where the sandboxes are expected to be homogeneous. This is consistent with the irregular shaped fronts and concentration gradients observed in Figure 2-3, which emphasizes the importance of the smaller-scale heterogeneity. Surprisingly, 1D ADE does well in the HCO case compared to other cases.

It is important to mention here that the optimization scheme plays a large role in determining the performance of all models. Note that here we compare models optimized by minimizing the residuals of logarithm of concentrations to capture the tail and to keep consistency for comparison. If the models are optimized by minimizing the residual of concentration, the ADEs do better for the overall shape of the breakthrough curves than CTRW and fADE, as shown in 2-A2a. However, they generate the largest deviation for both T1 and T2, as shown in Figures 2-A2c and d in the Appendix A. In addition, the C residual minimization also leads to much smaller dispersivity values, as shown in Table 2-A1. This indicates that if the ADEs are optimized by logarithm concentration residual minimization, they can better capture the solute transport characteristics than using the concentration residual minimization.

**Conditions for non-Fickian behavior.** To put our work in the context of others and to quantify conditions under which the non-Fickian behavior arises, we followed the method of Zinn et al. (2004) and defined two dimensionless numbers, the Peclet (Pe) and Damkohler (Da) numbers. The Peclet number is the ratio of the time scale of diffusion to the time scale of advection through the fine zones. The Damkohler number has various definitions in literature. For easy comparison Zinn et al. (2004), here we use their definition that $Da$ is the ratio of the time scale of advection across the whole flow cell to the time scale of diffusion through the fine zone. Quantitatively, they are defined as follows:

$$Pe = \frac{v_f R^2}{RD} = \frac{v_f R}{D} 
$$

$$Da = \frac{LD}{V_{cz} R^2} 
$$

Where D is the diffusion coefficient of bromide in porous media, L is the length of the flow cell, R is the characteristic length of the heterogeneity structure. For the Mixed case, the mean grain size was used for R. For the Four-zone and One-zone cases, the length of the fine zones was used. The $v_{fz}$ and $v_{cz}$ are the velocities in the fine and coarse zones, respectively.
Velocities were calculated using the permeability ratio of the fine ($K_{fz}$) and coarse zones ($K_{cz}$) and the average linear flow velocity of the flow cell. The average linear flow velocity was calculated as follows using the total flow rate ($Q$), average porosity ($\phi$), height ($h$), and width ($w$) of the flow cell:

$$v_{fz} = \frac{K_{fz}}{K_{cz}} \times \frac{Q}{hw\phi}$$

$$v_{cz} = (1 - \frac{K_{fz}}{K_{cz}}) \times \frac{Q}{hw\phi}$$

When the time scales of diffusion in the fine zone are smaller than that of advection in the flow cell, we expect limited tailing and the flow is close to Fickian. This essentially would be the top light gray region of the Figure 2-9 labeled with “Fickian region” ($Pe > Da^{-1}$ or $Pe > 1$). Tailing and non-Fickian flow are pronounced when advection or diffusion in the fine zone is much slower than advection in the flow cell, essentially the bottom left medium gray region labeled with “Advective mass transfer” for $Pe > 1$ and $Pe < Da^{-1}$ and the bottom dark gray region labeled with the “diffusive mass transfer” domain for $Pe < 1$.

Here the $Pe$ and $Da$ numbers for the 7 cases in this work were calculated and plotted with those from Zinn et al. (2004) and others in Figure 2-9, and were also listed in Table 2-3. Compared to other studies, our work provided a unique set of data that fill in the variable space with high $Pe$ and a wide range of $Da$ values. The $Pe$ values cover a relatively narrow high range due to the single high flow rate used. The Mixed cases have large $Da$ values due to their small fine zones and $R$ values. The One-zone cases have low $Da$ values because of their large fine zone and $R$ values. Both Mixed cases (HCM, LCM) are in the Fickian zone defined in Zinn et al. (2004), while the LCF and LCO are close to or at the Fickian-advective transition line. The HCO and MCO cases are in the advective mass transfer zone however very close to the transition line. Note that although HCM, LCM, LCF, and LCO cases are all within the “Fickian” region defined by Zinn et al. (2004), their breakthrough curves indicated non-Fickian transport, with $\beta$ values between 1.97 to 1.88 and $\alpha_f$ values lower than 2.0. This indicates that the division between Fickian and non-Fickian region may not be deterministic. Instead, one should consider a gray zone at the vicinity instead of a rigid line. In our case, it seems that the division line $Pe = Da^{-1}$ need to be moved up by 2 log$Pe$ units. This may also
indicate that although the division line works well for porous media with small correlation lengths, it may not work as well for media with large correlation length.

It is known that the extent of non-Fickian behavior increases when permeability contrast increases, which was what Zinn et al. (2004) focused on by having orders of magnitude contrast between the high and low permeability zones. Compared to their maximum contrast by a factor of 1,800, our maximum permeability contrast was a factor of 5.17. Our results indicate that even with relatively low permeability variance, non-Fickian behavior can be pronounced if the length of the fine zone is comparable to the domain length. This is particularly important because the non-Fickian behavior largely depends on the time scale of diffusion in and out of the fine zone. The time scale of diffusion depends on the characteristic length of the fine zone in quadratic form \( t_{\text{diff}} = \frac{R^2}{D} \) instead of linear form. Therefore, the time scale for diffusion increases with length much faster than that of advection.

Figure 2.9 Representation of dominant flow regime in the 7 cases in this work compared to other studies using Peclet and Damköhler numbers.
Dispersivity parameters. Table 2-3 summarizes the parameters that characterize the heterogeneity structure, permeability variance, and solute transport for all 7 cases. Figure 2-10 maps the global dispersivity $\alpha'$ and $\beta$ values from this work and literature data as a function of $\sigma_{\ln K}^2$ and $\lambda/L$. A large number of literature on measured dispersion coefficient exist. As have been shown in literature, residence time can have a large impact on dispersivity. The ones chosen here are those within the residence time range of 90 – 325 minutes, to be similar to the residence times of 188 - 237 minutes in our experiments. Figure 2-10a shows that much work has been done with dimensionless correlation length lower than 0.1. Our data fills in a variable space of low permeability variance and long correlation length where data are scarce. Our data show that in the LC cases with low $\sigma_{\ln K}^2$ values (0.1), both $\alpha'$ and $\beta$ values remain fairly constant and do not depend much on $\lambda/L$. Under the higher $\sigma_{\ln K}^2$ conditions (0.43), dispersivity and non-Fickian transport increased significantly with $\lambda/L$. In the HCO case, although the $\sigma_{\ln K}^2$ is only 0.43, the $\alpha'$ value of 1.96 cm is much larger than those from Zinn et al. (2004). Under similar flow rate conditions, their $\sigma_{\ln K}^2$ values were between 0.7 and 12.0 however their dispersivity varied between 0.46 and 0.70 cm. This indicates that even with a relatively low heterogeneous media, longer correlation length leads to dramatic increase in dispersivity. With small correlation length, even orders of magnitude increase in permeability ratio could not increase the dispersivity as much.

Figure 2-10a also shows that with similar small correlation length, increasing permeability variance leads to much more increase in dispersivity values when the permeability variance is below 1.0. Once the permeability variance is large than 1.0, the permeability variance has relatively low impact on dispersivity values. This indicates that as long as the permeability variance is sufficiently large that the fine zone acts as the immobile zone and is dominated by the diffusion process, further increase in permeability variance has relatively minor impact.
Figure 2-10 Dispersion parameters as a function of dimensionless correlation length and permeability variance (a) Global dispersivity $\alpha'$, (b) dispersion parameter $\beta$, (c) $t_1$, (d) $t_2$.

Similarly, the extent of non-Fickian behavior also increase significantly with the correlation length, as shown in Figure 2-10b with the increasing deviation of $\beta$ from 2. Comparison of our $\beta$ values to those from Levy and Berkowitz (2003) shows that they had a larger extent of non-Fickian behavior with relatively small correlation length due to the large $\sigma^2_{lnK}$ values up to 2.1. The use of TPL form in CTRW allows the quantification of the time scales for the onset and the end of the non-Fickian behavior. As shown in Figure 2-10c, values of $t_1$ are all within a minute and are lower under low permeability variance and low correlation length conditions. Values of $t_2$ increase with correlation length and permeability variance. Based on stochastic theory, the travel time to approach Fickian transport depends on permeability variance and on correlation length for low heterogeneity media (Dagan, 1989). In the HC cases, $t_2$ increased from $10^{2.6}$ to $10^{3.8}$ minutes for HCM to HCO, an increase of 1.2 orders of magnitude. In the LC cases, the value of $t_2$ increased from $10^{2.6}$ to $10^{3.5}$ minutes for LCM to LCO, an increase of 0.9 orders of magnitude. For the three One-zone cases with the same correlation length, the $t_2$ values increase from $10^{3.5}$ to $10^{3.8}$ minutes, almost a factor of 2, when $\sigma^2_{lnK}$ increases from 0.10 to 0.43. This indicates that the correlation length plays a more
significant role in determining the time needed to approach the asymptotic, Fickian transport regime.

Table 2-3 Characteristic parameters for solute transport in sandboxes

<table>
<thead>
<tr>
<th>Cases</th>
<th>$\lambda/L$</th>
<th>$\sigma^2_{\ln K}$</th>
<th>$^a$Local $\alpha$ (cm)</th>
<th>$^a$Global $\alpha'$ (cm)</th>
<th>$^b$Local $\alpha$</th>
<th>$^b$Global $\alpha'$</th>
<th>$t_1$ (min)</th>
<th>$t_2$ (min)</th>
<th>log(Pe)</th>
<th>log(Da)</th>
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<td>LCM</td>
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<td>0.02</td>
<td>0.13</td>
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<td>-0.92</td>
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<tr>
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<tr>
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<td>1.88</td>
<td>$10^{0.4}$</td>
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<td>-3.12</td>
</tr>
<tr>
<td>MCO</td>
<td>0.447</td>
<td>0.26</td>
<td>0.55</td>
<td>0.93</td>
<td>1.74</td>
<td>1.65</td>
<td>$10^{0.4}$</td>
<td>$10^{1.7}$</td>
<td>3.33</td>
<td>-3.27</td>
</tr>
<tr>
<td>HCM</td>
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<td>0.43</td>
<td>0.03</td>
<td>0.15</td>
<td>1.91</td>
<td>1.93</td>
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<td>-1.33</td>
</tr>
<tr>
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<td>HCO</td>
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<td>$10^{0.4}$</td>
<td>$10^{3.8}$</td>
<td>3.21</td>
<td>-3.37</td>
</tr>
</tbody>
</table>

$^a$ from 2D ADE optimized by minimizing residual of the logarithm of concentrations.

$^b$ from 1D ADE optimized by minimizing residual of the logarithm of concentrations.

2.4 Discussion and Conclusions

This work presents the first set of flow cell experiments that systematically measure the control of the correlation length on effective permeability and non-Fickian solute transport (Cortis et al., 2004; Levy and Berkowitz, 2003). Seven sand boxes (21.6 cm by 20.9 cm by 1.0 cm) were packed with sand grains of different size range in three spatial patterns of fine and coarse zones with dimensionless correlation length varying from 0.01 to 0.45. The sandboxes have three relatively low permeability variance ($\sigma_{\ln K}^2$), 0.10, 0.26, and 0.43, respectively, for the low (LC), medium (MC), and high contrast (HC) cases. This work provides a unique set of data under low permeability variance and increasing correlation length conditions where experiments have been rarely carried out. We chose to study low heterogeneity media due to their relevance in many geological settings and field sites (Leblanc et al., 1991; Mackay et al., 1986). The goal is to answer two questions: 1) How and to what extent does correlation length control effective permeability and breakthrough curves (BTC)? 2) Which model can best reproduce data under what conditions?

Effective permeability values in general increase with correlation length due to the formation of flow channels. Values of $K_{eff}$ typically fall between the arithmetic and harmonic mean of permeability of the fine and coarse zones. The $K_{eff}$ values of the HC flow cells are
closer to the arithmetic mean, indicating the formation of preferential flow path in the coarse zone. The $K_{eff}$ values of the LC flow cells, however, are closer to the harmonic mean, indicating the cross-layer type of flow distribution due to similar permeability between different zones. The geometric mean is far from the $K_{eff}$ values for most cases, indicating correlation in high permeability zones.

While the cases with short correlation length exhibits relatively low extent of non-Fickian transport, those with long correlation length shows significant tailing and non-Fickian transport. In particular, the HC One-zone (HCO) case shows distinct “steps” and stages of breakthrough arising from fast advection in the coarse zone, slow advection in the fine zone, and slow diffusion. With the same correlation length, the LCO and MCO cases do not exhibit the staged breakthrough, indicating that the permeability contrast between zones has to be sufficiently large in order for the correlation length to be important.

Four models have been used to simulate solute transport and reproduce the BTCs by minimizing the residual of logarithm concentrations. These include the 2D ADE that explicitly takes into account the heterogeneity structure, the 1D ADE that assumes homogeneous media with average porosity and permeability, and the non-local in time CTRW and non-local in space fADE. Comparing these models, 2D ADE typically has the lowest deviation from data. However, it is important to note that 2D ADE is more data “expensive” because it needs the exact heterogeneity structure as part of the input. In reality, we rarely have this kind of luxury. It is interesting to note that the relative deviation $\delta_v$ of 2D ADE for the first and second moments are the largest in the HCM case that is expected to be homogeneous, which indicates the importance of the small-scale, unresolved heterogeneity in controlling the solute transport in apparently “homogeneous” media.

CTRW reproduces the data and moments well in most cases except the HCO case. This is expected because the CTRW framework involves taking ensemble average over the entire domain assuming the heterogeneity length is much smaller than the domain (Berkowitz et al., 2006). The HCO case, however, is actually a non-stationary domain with comparable length scales of heterogeneity and the domain. It is possible that a correlated CTRW can reproduce the BTC in HCO case better, because the flow pattern in Figure 2-4 shows correlated flow channels. In addition, the Peclet numbers in the HCO case is $10^{3.21}$,
which is within the suggested flow conditions (Pe >100) where incorporating correlation can be critical (Bolster et al., 2014).

In contrast, the fADE does not reproduce the BTC as well as CTRW in most cases. However, it reproduces the data the best among all models for the HCO case. In fact, fADE reproduces the BTC increasingly well with increasing permeability contrast. This largely confirms that fADE is strong in reproducing BTCs well with high permeability contrast and well connected media. In other cases, the conditions do not allow the formation of channels and preferential flow path so that the fADE does not do well. Stratified low permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface (Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salehikhoo et al., 2013). It is expected that fADE will work better under these conditions.

With the optimization minimizing the residual of the logarithm concentration, even 1D ADE reproduces the average behavior of HCO BTC relatively well, although it does not capture the detailed stages of the breakthrough. The 1D ADE however also has the largest deviation from the 2nd moment of data for most cases, especially in the HCM case. It is important to note here that these conclusions are based on the optimization scheme that minimizing the residual of logarithm concentrations. With minimization of residual of concentration, the ADEs tend to have much larger deviation from the data for the prediction of moments, especially the second moment.

With the permeability variance of 0.43, the correlation length strongly controls the effective dispersivity and the extent of non-Fickian behavior, with the global dispersivity $\alpha'$ varying from 0.15 cm in the HCM case to 1.96 cm in the HCO case. Similarly, $\beta$ values from CTRW vary from 1.97 in the HCM case to 1.56 in the HCO case. Values of $t_2$, which represents the time scale needed to reach asymptotic dispersivity, increased with the correlation length from $10^{2.6}$ minutes in the HCM cases to $10^{3.8}$ minutes in the HCO case. In the LC cases, however, the effects of the correlation length are negligible. This indicates that the permeability variance needs to be sufficiently large for correlation length to be important in determining solute transport. This also implies that the solute needs to travel a longer time in a more heterogeneous media to experience sufficient heterogeneity to reach asymptotic,
Fickian behavior – a major finding in the subsurface stochastic hydrology in the past decades (Dagan, 1989).

Our comparison with literature data shows that the control of correlation length on the solute transport is potentially as strong as, if not larger than, that of permeability variance. This is because effective dispersivity and non-Fickian behavior depends largely on the time scale of diffusion in the fine zone, which increases fast with the characteristic length scale of the fine zone in the form of $R^2/D$. On the other hand, as long as the permeability variance is sufficiently large that the fine zone acts as the immobile zone, further increase in permeability variance has relatively minor impact. Interestingly, all our data fall in the Fickian region or the boundary of the Fickian and Advective mass transfer regime defined by Zinn et al. (2004). However, non-Fickian transport was observed in all cases.

Stratified low permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface (Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salehikhoo et al., 2013). Numerical studies have emphasized the importance of connectivity and correlation length in controlling solute transport. For example, Pedretti et al. (2013) concluded that the degree of stratification primarily control the late time distribution of the concentrations in convergent flow field tracer tests in realistic three-dimensional settings. In our work, we observe significant non-Fickian transport in the HCO case with relatively low permeability variance (0.43). Existing experimental work has mostly focused on porous media with short correlation length. Our work points to the need of studying systems with comparable correlation length to the domain of interest.

**Acknowledgements.** The raw data and some figures generated using models by minimizing residuals of concentration for 1D ADE and 2D ADE are shown in the appendix 2-A and 2-B. This work is supported by the Penn State Institutes of Energy and the Environment (PSIEE) and by the Department of Energy Office of Sciences Subsurface Biogeochemical Research (SBR) Program under the project number DE-FOA-0000311. We thank the associate editor Daniel Fernàndez-Garcia and four anonymous reviewers for their persistence in seeing a better paper out of this work and their diligent, meticulous, insightful, thought-provoking, and constructive comments that have significantly improved the paper. We thank Andrea Cortis for instructive and valuable discussion on CTRW and optimization schemes.
Chapter 3

The Effect of Spatial Pattern of Calcite Distribution on Reaction Rates in Heterogeneous Flow Cells

3.1 Introduction

Mineral dissolution influences numerous chemical and physical phenomena such as weathering (Maher, 2010; Moore et al., 2012), formation of soil (Brantley, 2010; White et al., 2005), nuclear waste disposal (Spycher et al., 2003), and migration of heavy metal particles (Liermann et al., 2011; Tuttle et al., 2009). Over geological time scale, mineral dissolution is the most significant process that regulates atmospheric CO$_2$ levels (Berner, 1995). Mineral dissolution and weathering is also a common source of some elements important for world oceans and other ecosystems (Liermann et al., 2011; Peng et al., 2004; Peucker-Ehrenbrink and Hannigan, 2000; Suchet et al., 2003; Tuttle et al., 2009). Mineral dissolution rates have been extensively investigated both in laboratory experiments and field studies during the recent decades (Chou et al., 1989; Gautelier et al., 1999; Pokrovsky et al., 2009). Although weathering rates have been quantified based on observed mineral depletion fronts in the field (Anderson et al., 2002; Brantley et al., 2008; Brantley and White, 2009; Brimhall and Dietrich, 1987; Casey et al., 1993; Lebedeva et al., 2007; Maher, 2010, 2011; Maher et al., 2004; Maher et al., 2006; Navarre-Sitchler and Brantley, 2007; Phenrat et al., 2010; Velbel, 1993; White, 2008; Zhu, 2005, 2009) most laboratory studies have been carried out in well-mixed batch or flow-through reactors. Well-mixed studies result in high dissolution rates, which are usually up to five orders of magnitude greater than field-scale rates (Maher et al., 2004; Navarre-Sitchler and Brantley, 2007; Swoboda-Colberg and Drever, 1993; White and Brantley, 2003).

Numerous factors have been examined to explain the discrepancies between well-mixed laboratory rates and those measured in fields. These include differences in the surface area of fresh and weathered minerals (Anbeek, 1993; White, 1995), the effect of reaction affinity (Maher et al., 2006), the precipitation of secondary minerals (Maher et al., 2009; Steefel and Van Cappellen, 1990), and the age of the reacting material (Maher et al., 2004) may
contribute to the discrepancy. Recently, this discrepancy has been examined from the perspective of spatial patterns of physical and chemical properties distribution in the porous media. Variations in hydrological properties of porous media such as permeability lead to significant change in the flow field (Chen et al., 2001; Fetter, 1999; Freeze and Cherry, 1979; Gelhar, 1993; Gelhar et al., 1992; Hubbard and Rubin, 2000; Newell et al., 1990; Rubin and Gomez-Hernandez, 1990). Reactive material move through the medium along the flow lines and therefore changes of the flow lines may result in change of mineral dissolution. Different mineral are distributed unevenly through the porous media which creates large-scale geochemical heterogeneity (Li et al., 2011; Li et al., 2010; Noiriel et al., 2007; Peters, 2009; Wilkin et al., 1996). Mineral spatial distributions vary from random, homogenous distribution at one end of the spectrum to large zones and layers at the other (Jin et al., 2013; Koltermann and Gorelick, 1996; Li et al., 2011).

Heterogeneous spatial distribution of physical and chemical properties has been found to reduce the overall magnesite reaction rates up to an order of magnitude (Li et al., 2014). The effect of physical heterogeneity on flow and transport processes has been studied for several decades (Berkowitz, 2002; Castro-Alcalá et al., 2012; Dagan, 1990; Gelhar, 1993; Gelhar and Axness, 1983; Gelhar et al., 1992; Zinn et al., 2004). However, chemical heterogeneity has attracted much less attention (Dentz et al., 2011a; Dentz et al., 2011b; Espinoza and Valocchi, 1998; Glassley et al., 2002; Li et al., 2006, 2007a, b; Tompson et al., 1996) and many of the studies have focused on adsorption (Espinoza and Valocchi, 1997). It was observed that the spatial distribution of sediments grains led to formation of flow channels, which resulted in much slower uranium desorption (an order of 3) compared to rates in homogenous media (Liu et al., 2014). In pore-scale modeling studies Li et al. (2006, 2007b) showed that spatial distribution of anorthite in porous media resulted in a factor of 3 lower overall rates, even with the same amount of mineral. At larger scale, compared to homogenous cases, uranium bioreduction reaction rates usually decreased due to physical and chemical heterogeneities. The amount of uranium that remained in the porous medium after bioremediation increased a factor of 1.7 due to heterogeneity (Li et al., 2011; Li et al., 2010). Majority of the studies on the effect of spatial distribution of mineral in porous media on mineral dissolution rates have been modeling ones (Li et al., 2011; Li et al., 2006, 2007b) except for a few studies. For
example, it was found that mineral spatial distribution causes unstable dissolution and wormhole formation in the porous media (Smith et al., 2013). In recent studies, it was observed that magnesite dissolution rates decreased from evenly distributed pattern to clustered parallel to main flow direction layer (Li et al., 2014; Salehikhoo et al., 2013). The capability of spatial pattern to induce changes of reaction rates depended on reactive zone orientation, flow velocity, and permeability contrast between zones.

The effect of physical and chemical heterogeneity on calcite reaction rates have not been experimentally studied in quasi-2D flow cells. Calcite is one of the most abundant minerals on the surface of earth (Smyth and Ahrens, 1997) with relatively high reactivity (Chou et al., 1989). Understanding calcite dissolution in natural setting is crucially important for processes such as development of oil and gas reservoirs (Yu et al., 2008) and geological CO₂ sequestration (Caldeira and Rau, 2000). The purpose of this study is to quantify the significance of calcite spatial pattern on the dissolution rate under a wide range of physical parameters. Specifically, the goal of this study is to answer the following questions: 1) What is the extent of the effect of physical and chemical heterogeneities on mineral dissolution? 2) What are the parameters that control significance of mineral spatial pattern on overall dissolution? We used intermediate-scale 2D flow cell experiments and numerical modeling. Injection of non-reactive tracer and pH indicator were performed to calculate physical and transport parameters and visualize the experiments, respectively. The effects of parameters such as velocity, permeability ratio, and transverse dispersivity on the dissolution process were examined as well.

3.2 Methodology

**Material preparation and sizes.** Calcite was purchased from Ward’s Natural Resources. Bulk analysis was performed using Inductively Coupled Plasma Emission Spectrometry (ICP-AES) and the chemical composition analysis indicated relatively pure calcite mineral. First, the calcite specimens were grounded and ultrasonically cleaned using acetone. Then, the powder was sieved and a wide range of grain smaller than 0.422 mm in diameter was included in the final batch. The grain surfaces were cleaned with 1% HCl for several seconds and then
washed a couple of times with deionized water and dried in the oven at 70°C overnight. The surface area was determined by N₂ gas sorption using the Brunauer-Emmett-Teller (BET) method (Micromeritics ASAP-2020 surface analyzer). The average BET surface area is 0.179 m²/g. Quartz sands from Portage Lumber were used as non-reactive mineral. The size of the sand grains varies between 0.422 to 0.599 mm.

**Flow cell packing.** To investigate the effects of spatial patterns of distribution of chemical and physical heterogeneities on fluid flow and reaction two flow cells were built as shown in Figure 3-1. The two cells are the Mixed case (MC) and One-zone case (OC). In both cases, there was 180.0 g of calcite. In the Mixed case, reactive mineral, calcite, was distributed randomly through the non-reactive mineral, quartz. In the One-zone case, all the calcite is accumulated in one square zone in the middle of cell which is almost 20% (v/v) of the whole porous medium. As shown in Figure 3-1c, the setup consists of inlet injection ports, the flow cell, and the outlet sampling ports. The outlet side contains seven sampling ports. A digital camera was used to document the visualization tests with pH indicator.

![Flow cell packing](image)

Figure 3-1 Schematics of different spatial distribution of sand and calcite for (a) Mixed case, (b) One-zone case. (c) Schematic of the experimental setup. Image of the (d) Mixed pattern, and (e) the One-zone pattern.
As shown in Figure 3-1c, transparent 2D plexiglass flow cells with dimensions of 20.0 cm by 20.0 cm by 1.25 cm were packed with minerals. In order to prevent the trapping of air bubbles in the porous media, which can change the hydraulic conductivity, wet packing procedure was performed (Minyard and Burgos, 2007). The packing was done layer by layer to remove air and to establish different zones. One side of the flow cell was removed and water was poured to a height of 2 cm. The minerals and water were then added layer by layer to remove air by shaking the material. Zone separation was established using temporary plastic strips, which kept minerals of different zones from mixing during the packing procedure. After the removed side of the flow cell was screwed back, silicon caulking was used to seal off the system. A small amount of sand was added to the sandbox from valves to make the packing as tight as possible. All connections to the cell and sampling ports were covered with a fine mesh in order to prevent minerals from flowing out of the system. The effect of the mesh on the flow was verified to be negligible by measuring changes in pressure drop before and after implementing the mesh in 1D columns.

Non-reactive tracer test and permeability determination. A one-dimensional column was packed using sand grains of 0.422 mm to 0.599 mm in diameter to determine the permeability of the sand zone in the One-zone case. Pressure gradients along the columns were measured at five steady state flow rates, 0.2, 0.4, 0.6, 0.8, and 1.0 ml/min. A Crystal Engineering pressure gauge (XP2i-DP) that can measure a 15 psi differential pressure with the precision of 0.001 psi was used. To ensure the steady state condition, each flow rate was kept constant until a differential pressure was stabilized for 15 minutes with a variation of 0.01 psi. Using the measured flow rate and pressure gradient, Darcy’s law was used to calculate the absolute permeability of the sand.

Non-reactive tracer tests were carried out to determine permeability of the calcite zone in the One-zone case and dispersivity in both mixed and one-zone cases. Tracer experiments were carried out by injecting a solution of 1.25×10⁻⁴ mol/L sodium bromide through ten inlets at a constant overall flow rate of 5.0 ml/min using a Harvard Apparatus syringe pump. The effluents were collected through the seven outlets every 5 minutes. Bromide concentrations were measured using the Dionex ICS2500 Ion Chromatography. After dissolution experiments, Azolitmin, a pH indicator (red 4.5-8.3 blue), was used to visualize the process.
**Dissolution test.** The dissolution experiments were carried out with pumping inlet solution into the porous media through ten inlets using a Harvard Apparatus syringe pump at the room temperature. The inlet solution used in all the experiments $10^{-3}$ M NaCl in deionized water with pH adjusted to 4.0. We used ten inlets to ensure homogenous flow across the injection plane. The flow rates used were 1.0, 5.0, and 10.0 ml/min. The flow cells were flushed with 20 pore volumes of brine, which contained $10^{-3}$ M NaCl in deionized water at flow rate of 20 ml/min to wash out the original solution in the column and ensure similar starting initial conditions. The effluent samples were collected at the outlets. The samples were stored in polypropylene plastic vials acidified with 2% HNO₃ beforehand and analyzed using a Perkin-Elmer Optima 5300 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

**Reactive transport modeling.** The reactive transport code CrunchFlow solves the well-known governing mass conservation equation for reactive transport modeling:

$$\frac{\partial (C_{Ca(II)})}{\partial t} = \nabla (-D \nabla C_{Ca(II)} + v C_{Ca(II)}) + R_{CaCO_3}$$

(1)

Here $C_{Ca(II)}$ is the total Ca$^{2+}$ concentration (mol/m$^3$), $t$ is the time (s), $D$ is the combined dispersion–diffusion tensor (m$^2$/s), $v$ (m/s) is the flow velocity vector, which is combination of $v_x$ and $v_y$, velocities in the directions parallel and transverse to the main flow direction, $R_{CaCO_3}$ is the calcite dissolution rate (mol/s).

The dispersion-diffusion tensor $D$ is defined as the sum of the mechanical dispersion coefficient and the effective diffusion coefficient in porous media $D^*(m^2/s)$. At any particular location (grid block) with flow velocities in longitudinal and transverse directions, their corresponding diffusion / dispersion coefficients $D_L$ (m$^2$/s) and $D_T$ (m$^2$/s) are calculated as follows:

$$D_L = D^* + \alpha_L v_x$$

(2)

$$D_T = D^* + \alpha_T v_y$$

(3)

Here $\alpha_L$ and $\alpha_T$ are the longitudinal and transverse dispersivity (m). The fixed diffusion coefficient of $1\times10^{-9}$ m$^2$/s was considered. Tortuosity was set to be 2 which is a common value for unconsolidated porous media (Armatas, 2006; Salem and Chilingarian, 2000). The dispersion coefficients vary spatially due to the non-uniform distribution of the permeability values resulting in spatial variation of velocity.
Three different parallel calcite dissolution reactions have been proposed in the literature (Chou et al., 1989):

\[
\begin{align*}
\text{CaCO}_3 + \text{H}^+ &\rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \\
\text{CaCO}_3 + \text{H}_2\text{CO}_3^0 &\rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \\
\text{CaCO}_3 &\rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}
\end{align*}
\]

Like other carbonate minerals, the reaction rate has been observed to follow a Transition State Theory (TST)-based rate law (Chou et al., 1989):

\[
R_{\text{CaCO}_3} = \left( k_1 a_{\text{H}^+}^n + k_2 a_{\text{H}_2\text{CO}_3^0}^n + k_3 \right) A \left( 1 - \frac{\text{IAP}}{K_{\text{eq}}} \right)
\]

where \( k_1 \), \( k_2 \), and \( k_3 \) are the rate constants (mol. m\(^{-2}\) s\(^{-1}\)), \( a_{\text{H}^+} \), and \( a_{\text{H}_2\text{CO}_3^0} \) are the activities of hydrogen ion and carbonic acid, \( A \) is surface area in m\(^2\), IAP is the ion activity product of Reaction (4), and \( K_{\text{eq}} \) is the equilibrium constant for Reaction (4). In the case of calcite dissolution, \( n=1.0 \) and \( k_1, k_2, \) and \( k_3 \) are \( 8.9 \times 10^{-1} \), 5.0 \times 10^{-4} \), and 6.5 \times 10^{-7}, respectively (Chou et al., 1989). In addition to calcite dissolution reaction, instantaneous aqueous speciation reactions were considered in the model. Typically, reactive transport codes divide the species into primary and secondary species. The code numerically calculates primary species concentrations, which determine chemistry of the system using the mass conservation equation. Then, the secondary species are calculated based on the primary species concentrations and equilibrium constants. Here, \( \text{Ca}^{2+}, \text{H}_2\text{CO}_3^0, \text{H}^+, \text{Na}^+, \text{Br}^-, \) and \( \text{Cl}^- \) were considered as the primary species. Secondary species were \( \text{OH}^-, \text{HCO}_3^-, \) and \( \text{CO}_3^{2-} \).

In all cases the size of each grid block was 0.1 cm \times 0.1 cm. The grid-size effect was eliminated by increasing the resolution to the extent that the produced effluent concentrations did not change with increasing resolution. In total there were 200 blocks in the x direction and 200 blocks in the y direction. No-flow boundaries were set for the two boundaries in the y direction (Side walls of the flow cells). Uniform flow condition was considered at the inlet and seven openings were designed in a no-flow boundary to simulate the seven outlets in Figure 3-1c. First, the experimental breakthrough curves of non-reactive tracers for all measured outlets were matched through assigning a single value of longitudinal dispersivity, \( \alpha_L \), to both the sand zone and the calcite zone and adjustment of permeability of the calcite.
zone in the One-zone case. Then, Ca$^{2+}$ concentration in the effluent from all sampling ports were matched by adjusting transverse dispersivity, $\alpha_T$.

**Concentration Averaging and dissolution rate calculation.** The overall species concentrations in the effluent were calculated by flux-averaging the concentrations based on flow rate from their respective outlets as follows:

$$C_{\text{Ca(II)},\text{out}} = \frac{\sum_{i=1}^{7} C_{\text{Ca(II)i}}Q_i}{\sum_{i=1}^{7} Q_i}$$  \hspace{1cm} (8)

where $C_{\text{Ca(II)},\text{out}}$ represents the effluent flux-averaged concentration, $C_{\text{Ca(II)i}}$ and $Q_i$ are the experimentally measured concentration and flow rate from each outlet $i$. Accumulated effluent water volume from each outlet was collected and divided by the experiment duration to determine the averaged flow rate. The effluent concentrations were used to calculate large-scale dissolution rates.

**Large-scale bulk dissolution rates $R$.** Dissolution in the flow cell typically reached steady state after 5-6 residence times. At the steady state, concentration of the effluent did not very with time. The steady state large-scale reaction rate $R$ (mol/s) was calculated as follows:

$$R = Q_T[C_{\text{Ca(II)},\text{out}} - C_{\text{Ca(II)},\text{in}}]$$  \hspace{1cm} (9)

Here $Q_T$ is the total flow rate (m$^3$/s), $C_{\text{Ca(II)},\text{out}}$ and $C_{\text{Ca(II)},\text{in}}$ are the effluent and influent Ca(II) concentrations, respectively (mol/m$^3$). This equation calculates rates based on mass conservation by summation of the overall loss of mass inside the flow cell.

The ratio of the large-scale rate difference between the One-zone cases $R_{OZ}$ over the corresponding Mixed case $R_M$ is defined as the rate ratio $\beta_{Z/M}$:

$$\beta_{Z/M} = \frac{R_{OZ}}{R_M}$$  \hspace{1cm} (10)

A rate ratio of one means the dissolution rates of the One-zone and the Mixed column are the same and spatial pattern does not matter. Increase of the effect of spatial pattern of heterogeneity distribution decreases the rate ratio value and larger deviation from 1.0 means more significant effects of spatial patterns.

**Surface area.** Here we used three surface area terms ($A_T$, $A_e$, $A_i$) to simplify analyze of our data (Li et al., 2014). $A_T$ is the total surface area of calcite, calculated by multiplying total calcite mass (g) and the measured BET surface area. $A_T$ is determined by the total amount of calcite packed in each cell, which was constant in our two cells at 180.0 g. The effective
surface area ($A_e$) was defined by the amount of calcite grains surrounded by far from equilibrium solution, which contribute to the overall dissolution reaction. Here we assumed calcite grains with IAP/$k_{eq}$ less than 0.1 as effectively reacting grains. The interface surface area ($A_I$) is the portion of $A_e$ that is on the calcite-sand interface, which we defined as the most outer layer of grid blocks of the calcite zone. For the Mixed case, since all calcite and sand grains are in contact, $A_I$ is equal to $A_T$. While $A_T$ is constant, $A_e$ depends on spatial distribution of calcite in porous media, flow velocity, reactivity, and permeability ratio. The portion of the reactive material that effectively dissolves was calculated by $A_e / A_T$. In addition, ratio of $A_I / A_e$ determines the extent of reaction occurrence only on the calcite-sand interface.

**Peclet and Damköhler number calculation.** We used Peclet (Pe) and Damköhler (Da) numbers to generalize our results. The Peclet number is the ratio of the time scale of diffusion to the time scale of advection through the reactive zones. The Damköhler number has various definitions in literature. Here, the Damköhler number, $Da$, is the ratio of the time scale of advection across the whole flow cell to the time scale of reaction in the flow cell. Quantitatively, they are defined as follows:

$$Pe = \frac{v_{rz} l^2}{l D_T}$$  \hspace{1cm} (11)

$$Da = \frac{L RP A_T}{v_{sz} v_p c_{eq,ca}}$$  \hspace{1cm} (12)

Where RP is reaction potential calculated from pH and the rate law as $RP = A\left(k_1 a^n_{H^+} + k_2 a^n_{H_2CO_3} + k_3\right)$. $D_T$ is the transverse dispersion in porous media, $L$ is the length of the flow cell, $l$ is the characteristic length of the reactive zone. For the Mixed case, the grid size of 0.1 cm was used for $l$. For the One-zone cases, the length of the reactive zones was used. The $v_{rz}$ and $v_{sz}$ are the velocities in the reactive and sand zones, respectively. Velocities were calculated using the permeability ratio of the reactive ($K_{rz}$) and sand zones ($K_{sz}$) and the average linear flow velocity of the flow cell. The average linear flow velocity was calculated as follows:

$$v_{rz} = \frac{K_{rz}}{K_{sz}} \times \frac{Q}{h w z \phi}$$  \hspace{1cm} (13)

$$v_{sz} = \left(1 - \frac{K_{rz}}{K_{sz}}\right) \times \frac{Q}{h w z \phi}$$  \hspace{1cm} (14)
using the total flow rate \( (Q) \), average porosity \( (\phi) \), height \( (h) \), width \( (w) \), and depth \( (z) \) of the flow cell.

### 3.3 Results and discussion

In this section we present the result of permeability and dispersivity determination test using nonreactive tracer transport. Ca(II) concentrations of the collected effluent fluids during the dissolution experiments are reported and numerically reproduced by incorporating the physical parameters. We then show the sensitivity of the dissolution reaction to changes in different physical and chemical parameters. We also show the large-scale dissolution rate as a function of Pe and Da dimensionless numbers.

**Permeability and dispersivity determination.** Pore volume of the Mixed case was measured to be 180.0 cm\(^3\), and it was 200.75 cm\(^3\) for the One-zone case. We used the same amount of calcite to pack both cells (180.0g), however, pore volume of the Mixed case was lower than the One-zone case due to the smaller calcite grains that filled out the space between larger grains of sand.

The breakthrough curves (BTC) of non-reactive tracer (Br\(^-\)) for the two cells are shown in Figure 3-2 a,c for the flow velocity of 7.18 m/d. BTCs from the middle outlet and three outlets on the left side of the cells were plotted, the other three outlets on the right were the same as the one on the left due to symmetry. BTCs from outlets of the Mixed case overlapped as expected. All concentrations reached \( C/C_0 = 0.5 \) at one residence time due to the relatively homogenous medium. Two-dimensional transport simulation was performed to fit the data and to determine the small-scale longitudinal dispersivity \( (\alpha_L) \). The BTCs from two-dimensional transport modeling of the Mixed case fitted the measured BTCs using \( \alpha_L = 0.05 \) cm. The Mixed case velocity field shown in Figure 3-2b shows a homogenous field with negligible flow deviation at the outlets, which explains the BTCs overlap. BTCs from the One-zone case show very different behavior than that of the Mixed case (Figure 3-2c). BTCs from the two outlets at the side of the cells reach \( C/C_0 = 1 \) earlier than one residence time. Solute completely reaches the next outlet closer to the middle outlet later with a longer tail. The solute does not completely reach the middle outlet even after five residence times.
Permeability of the sand zone in this case was measured to be $5.3 \times 10^{-12}$ m$^2$. In order to match the BTCs, we adjusted permeability of the calcite zone and local-scale longitudinal dispersivity ($\alpha_L$). Two-dimensional transport modeling best reproduced the BTCs using calcite zone permeability of $2.5 \times 10^{-13}$ m$^2$ and $\alpha_L=0.10$ cm. The flow field plotted using the modeling outputs shown in Figure 3-2d shows formation of two high flow velocity channels around the lower permeability calcite zone leading to solute breakthrough sooner than one residence time from the two outlets closer to the side of the cell. However, considerably lower flow velocities in the calcite zone postponed breakthrough from the middle outlet and resulted in a step like behavior in the BTC curve from this outlet. However, the data show longer tails than the model output, which may be due to non-Fickian transport as was observed in our previous study (Heidari and Li, 2014). Modeling study showed no effect of transverse dispersivity $\alpha_T$ on non-reactive solute breakthrough results in the studied range of 0.1 cm - 0.001 cm. However it has been shown that transverse dispersivity affects mineral dissolution and BTC especially in heterogeneous porous media (Li et al., 2014). Table 3-1 contains physical properties and experimental parameters of all experiments.

<table>
<thead>
<tr>
<th>Spatial pattern</th>
<th>Flow rate (ml/min)</th>
<th>Porosity</th>
<th>Sand volume fraction</th>
<th>$^1$Calcite volume fraction</th>
<th>$^2$Sand permeability (m$^2$)</th>
<th>Calcite permeability (m$^2$)</th>
<th>$\alpha_L$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed</td>
<td>1.0, 5.0, 10.0</td>
<td>0.360</td>
<td>0.500</td>
<td>0.140</td>
<td>$1.4\times10^{-12}$</td>
<td>$1.4\times10^{-12}$</td>
<td>0.05</td>
</tr>
<tr>
<td>One-zone</td>
<td>1.0, 5.0, 10.0</td>
<td>0.401</td>
<td>0.580</td>
<td>0.672</td>
<td>$5.3\times10^{-12}$</td>
<td>$2.5\times10^{-15}$</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$^1$Calcite is distributed evenly in the Mixed case and only in the middle in the One-zone case.
$^2$Calcite and sand permeabilities are the same in the Mixed case due to homogeneity.
Figure 3-2 Breakthrough curve comparison between experimental (symbols) and 2D transport modeling output for (a) the Mixed case and (c) the One zone case along with their corresponding spatial profile of velocity for (b) the Mixed case and (d) the One-zone case. Flow velocity was set to be 7.18 m/d. The best fit of the BTCs from four outlets of the Mixed case was achieved by setting $\alpha_L=0.05$ cm. The best fit of the BTCs from four outlets of the One-zone case was achieved by setting $\alpha_L=0.10$ cm and calcite zone permeability $K_{rz}=2.5\times10^{-13}$ m$^2$.

**Visualization test.** The dissolution experiments were carried out in both flow cells with the main flow direction from the bottom to the top. The pH profile was visualized using Azolitmin, a pH indicator. Figure 3-3 compares the pH distribution during the dissolution test (left) and the predicted pH profile (right) by the 2D numerical simulation at steady state. The predicted spatial profiles of pH agree qualitatively with the images, with the sudden increase of pH upon contact with calcite due to fast dissolution and H$^+$ consumption. Since there is calcite in the porous media at the outlet, pH increases very fast and the low pH zone is not visible.
Figure 3-3 Comparison of images of the pH profile between images (left) of (a) Mixed case, and (c) One-zone case and model-generated results (right) of (b) Mixed case, and (d) One-zone case.

The effect of velocity on calcite dissolution. Figure 3-4 illustrates the effect of spatial distribution of minerals in porous media on calcite dissolution reaction using Ca(II) breakthrough curves. Figure 3-4 show the fit of the modeling generated results to the effluent concentration data from individual outlets for flow velocities of 1.435 m/d, 7.175 m/d, and 14.35 m/d, respectively. Concentrations of Ca(II) in all experiments increased from the start of the experiment until they reached steady state condition. The Ca(II) breakthrough curves from all outlets reached steady state after around two residence times in the Mixed cases. In the One-zone case, concentration of Ca(II) in the effluent from outlets other than the middle one reached steady state around two residence times. However, Ca(II) BTC from the middle outlet did not reach the steady state till five residence times. Concentration curve from the middle outlet and the two on the side did not change with velocity. However, the curve from the third outlet, closer to the middle, changed with flow velocity and depended on the magnitude of transverse dispersivity. The fits in Figure 3-4 were obtained for flow velocities...
of 1.435 m/d, 7.175 m/d, and 14.35 m/d by setting transverse dispersivity $\alpha_T$ values to 0.018 cm, 0.014 cm, and 0.012 cm, respectively. The flux-averaged BTCs shown in Figure 3-4 show more than five times increase of effluent Ca(II) concentration from One-zone case to the Mixed case, however, the effect of velocity on the increase is small.

Figure 3-4 Experimental (symbols) and 2D modeling (lines) generated result BTCs from individual outlet and flux-averaged overall Ca(II) (a) at 1.435 m/d velocity, (b) 7.175 m/d, and (c) 14.35 m/d.

The effect of velocity on the flux-averaged effluent concentration from both Mixed and One-zone cases were not significant over the experimental conditions studied here. The effluent concentration of the Mixed case did not change with velocity, which is indicative of chemical equilibrium over the studied range. In the Mixed case, the solution reached equilibrium concentration upon exposure to the porous media due to very fast calcite dissolution reaction as shown in Figure 3-5a. Similarly, the solution reached equilibrium upon contacting the calcite zone in the One-zone case. Two narrow not-at-equilibrium zones formed on the sides of the calcite zone as shown in Figure 3-5b due to transverse dispersivity that dispersed Ca(II) outside of the calcite zone and $\text{H}^+$ ions into the zone to dissolve calcite. Figure 3-5c illustrates that the large-scale rate of calcite dissolution in the Mixed case increased linearly with increase of flow velocity. The trend of changes of large-scale rate with flow velocity in the One-zone case is similar, however, due to higher transverse dispersivity at 1.435 m/d flow velocity, the rate is slightly higher than the linear trend. In general, rate ratios $\beta$ were very close at 7.175 m/d and 14.35 m/d and slightly higher at 1.435 m/d. Rate ratio $\beta_{Z/M}$ did not change significantly with flow velocity, which may be due to high reactivity or high velocity (Salehikhoo et al., 2013).
The effect of Reactivity. The effect of velocity and reactivity on calcite dissolution reaction in both Mixed and One-cases is shown in Figure 3-6. In addition to calcite dissolution models, two more sets of models were designed with less reactivity. The experimental specific surface area of calcite (0.18 m$^2$/g) was decreased 2, 4, and 6 orders of magnitude in three cases. As seen in Figure 3-6a reaction rates increase linearly with velocity at the highest reactivity cases. This is indicative of reaching equilibrium concentrations even at very high flow rates. However, rates deviate from the linear increasing trend with velocity in the lower reactivity cases. Interestingly at the lowest reactivity case, rates of the Mixed case and One-zone case are the same at the highest velocity. This is because of far from equilibrium condition resulting in kinetic control regime.

Rate ratio indicates the extent of the effect of spatial pattern on the reaction for cases with different reactivity in Figure 3-6b. In the high reactive case, rate ratio $\beta_{ZM}$ changed with flow velocity only at lower flow velocities. Therefore, the rate ratio of our experiments did not significantly change with velocity due to high reactivity of calcite and relatively high flow velocities. Figure 3-6b demonstrates that the flow velocity region where the spatial pattern was more effective ($\beta_{ZM}$ close to 0) on reaction rates depended on reactivity. The important region moved from higher velocities for higher reactivity cases to lower velocities for lower reactivity cases.
The effect of transverse dispersivity. The model output were not sensitive to changes of transverse dispersivity for the Mixed cases since concentration gradient in the direction perpendicular to the main flow direction was negligible due to relative homogeneity of the porous media. However, transverse dispersivity $\alpha_T$ was found to be a key parameter controlling Ca(II) concentration in the effluent for the heterogeneous One-zone case. To examine the effect of transverse dispersivity $\alpha_T$ on the dissolution reaction we simulated additional cases by varying the value of transverse dispersivity $\alpha_T$ while keeping all other parameter constant. Effect of transverse dispersivity on calcite dissolution for the One-zone case is illustrated in Figure 3-7. Spatial profile of Ca(II) concentration at 7.175 m/d for cases with 0.0014 cm, 0.014 cm, and 0.14 cm are illustrated in Figure 3-7 a,b,c, respectively. Ca(II) in the solution spread wider in the higher $\alpha_T$ case and the transport of species at the interfaces on the sides of the reactive zone were more compared to the other cases. As a result, the flux-averaged Ca(II) concentration over the outlet plane shown in Figure 3-7d increased with increase of $\alpha_T$. The highest effluent Ca(II) concentration was for the case with $\alpha_T=0.14$ cm, which was $6\times10^{-5}$ mol/l, more than two times the concentration in other cases. The medium value of $\alpha_T=0.014$ cm, fitted the experimental Ca(II) effluent concentration at 7.175 m/d.
Figure 3-7 Sensitivity of the spatial profile of Ca(II) concentration in the porous media to changes of transverse dispersivity $\alpha_T$ values at (a) $\alpha_T=0.0014$ cm, (b) $\alpha_T=0.014$ cm, and (a) $\alpha_T=0.14$ cm. (d) Flux-averaged Ca(II) concentration in the effluent for cases with various transverse dispersivity values. (e) The coupled effect of changes of transverse dispersivity and velocity on rate ratio.

As shown in Figure 3-7, increase of transverse dispersivity increased mass transfer out of the calcite zone and decreased the area with zero Ca(II) concentration significantly. The large-scale reaction rates of the One-zone case increased and were closed to those of the Mixed case with increase of $\alpha_T$. Therefore, the values of rate ratio increased with increase of transverse dispersivity as shown in Figure 3-7e. We also examined the coupled effect of velocity and transverse dispersivity on reaction rates and rate ratio shown in Figure 3-7e. As illustrated, the slope of increase of rate ratio with transverse dispersivity increased with increase of velocity. The effect of transverse dispersivity on dissolution increased with increase of velocity since $\alpha_T$ values were multiplied by velocity values to calculate dispersion in the 2D ADER equation. The lowest rate ratio was 0.1 with low $\alpha_T$ at high flow velocity, which means an order of magnitude lower reaction rate for the One-zone case compared to its corresponding Mixed case rate. In general, transverse dispersivity, a measure of mass transfer between reactive and non-reactive zones, controlled the extent of Calcite dissolution.
**The effect of permeability ratio.** The Ca(II) spatial profiles of four different flow cells with different permeability ratios, ratio, calcite zone permeability to sand zone permeability $k_{\text{ratio}}$, at velocity of 7.175 m/d are shown in Figure 3-8. The permeability ratio of the reproduced experimental cases was around 0.05. To further examine the effect of permeability ratio on mineral dissolution, in addition to the 0.05 case, three other cases with permeability ratios of 0.005, 1.0, and 10.0 were designed and simulated numerically. As shown in Figure 3-8 a,b,c,d, the area with minimal Ca(II) concentration significantly depended on the permeability ratio. All the fluid that flowed through the calcite zone reached equilibrium concentration and the amount of the fluid directly depended on the permeability ratio. Higher permeability ratio resulted in higher fluid flow through the calcite zone and ultimately higher spread of Ca(II) in the porous media.

Figure 3-8e shows the increase of steady state Ca(II) concentration with increase of permeability ratio. At the lowest $k_{\text{ratio}}$ of 0.005, the effluent Ca(II) concentration reached steady state concentration of $0.15 \times 10^{-4}$ mol/l, less than 1/10 of the Mixed case concentration at $1.7 \times 10^{-4}$ mol/l. With the highest $k_{\text{ratio}}$ of 10.0, the steady state effluent Ca(II) concentration at $1.4 \times 10^{-4}$ mol/l was very close to the Mixed case concentration. Significance of the spatial distribution was very dependent on the values of $k_{\text{ratio}}$. As shown in Figure 3-8f, rate ratios decreased with flow velocity for all $k_{\text{ratio}}$ values. However, the decrease was much more rapid and significant for the cases with lower permeability ratio. The minimum rate ratio of 0.06 was observed with $k_{\text{ratio}}$ of 0.005 at high velocity. However, over the whole studied velocity range, the rate ratio of the case with $k_{\text{ratio}}$ of 10 stayed above 0.8, which is indicative of near Mixed case dissolution rates. In addition, the effect of velocity was small on the rate ratio values except for the very low range, where diffusion is the main transport mechanism. Rate ratio was more sensitive to changes of $k_{\text{ratio}}$ than any other studied parameter. In general, the importance of spatial distribution depended on the magnitude of the water that flows through the reactive zone and therefore majorly depended on the permeability ratio.

Rate ratio also increased rapidly with increase of permeability ratio. Cases with wider range of permeability ratios and flow velocities were numerically modeled. Large-scale rates from the One-zone cases reached values comparable with those of the Mixed case with
increase of permeability ratio that resulted in decrease of rate ratio. $k_{\text{ratio}}$ of 0.005 resulted in rate ratio of 0.1, while permeability ratio of 200 resulted in rate ratio of 0.88.

**Combined effects of parameters.** The combined effect of changes in parameters such as velocity, permeability ratio, and transverse dispersivity on reaction rate, effective surface area, and rate ratio are shown in Figure 3-9. As discussed before, the reactive solution reached equilibrium upon contact with calcite in our experiments with SSA=0.18 m$^2$/g. In most cases all the effective surface area was on the calcite-sand interface, which hindered our ability to analyze changes of effective surface are and interface surface area with changes of parameters such as velocity, permeability ratio, and transverse dispersivity. Therefore, in this section we used two orders of magnitude lower SSA to examine the combined effect of parameters on the mechanisms of mineral dissolution. Significance of spatial pattern on dissolution reaction was studied using the rate ratio parameter $\beta_{Z/M}$. Smaller values of rate ratio, closer to 0, is
indicative of higher effect of spatial distribution on mineral dissolution. Closer to 1 rate ratios indicate One-zone dissolution rate close to those of their corresponding Mixed cases. As illustrated in Figure 3-9a, increase of velocity and rate ratio resulted in increase of dissolution rates. At high permeability ratio and high velocity more than 4% of the total surface area was effectively dissolving and this amount decreased rapidly with decrease of velocity and permeability ratio (Figure 3-9b). As illustrated in Figure 3-9c, in most cases with measurable effective surface area 100% the $A_e$ is on the interface. However with increase of velocity and permeability ratio $A_I/A_e$ decreased and reached a minimum $A_I/A_e$ value of 0.4. Shown in Figure 3-9d, $\beta_{Z,M}$ decreases to 0.06 with decrease of permeability ratio, which shows almost an order of 20 effect on large-scale rates due to changes of permeability ratio and velocity. Figure 3-9e shows that dissolution rates increased with increase of transverse dispersivity especially at high flow velocities. The effective surface area increased from negligible amounts to a maximum of 3.36% shown in Figure 3-9f at high flow velocity with high transverse dispersivity. The $A_I/A_e$ did not change with changes of transverse dispersivity significantly and most of the reactive grains were at the calcite-sand interface. As shown in Figure 3-9h, high velocity and low dispersivity values produce a rate ratio of 0.10 which is significantly lower than that of low velocity and high dispersivity of 0.37 when dispersion and diffusion are relatively more effective on reaction.

With increase of velocity, advective mass transfer increased and therefore the dissolution rates increased. In the One-zone cases, increase of permeability ratio, increased the amount of flow that passed through the calcite zone and increased reaction rates. This increase in flow through the reactive zone resulted in the effective participation of a higher portion of the calcite surface area in the dissolution reaction. At high velocity and high permeability ratio, the grains deeper inside the reactive zone started reacting effectively resulting in decrease of $A_I/A_e$. As discussed before, the effect of velocity on rate ratio was small due to high reactivity of calcite. Increase of transverse dispersivity increased mass transfer at the calcite-sand interface. At higher dispersivity values, Ca(II) was transferred out of the calcite zone and H$^+$ ions moved inside and reacted with grains that are not at equilibrium with solution anymore. Since dispersion was calculated through multiplying velocity and dispersivity values, the effect of transverse dispersivity increased with increase of velocity. Higher velocity and
higher transverse dispersivity led to more reaction at the calcite-sand interface resulting in closer to Mixed case rates. However, the effect of transverse dispersivity on significance of spatial distribution were less than that of permeability ratio.

![Figure 3-9](image)

Figure 3-9 (a) Calculated large-scale dissolution rate, (b) \( \frac{A_e}{A_T} \), (c) \( \frac{A_I}{A_e} \), and (d) \( \beta_{ZM} \) of the One-zone flow cell under combinations of permeability contrast and flow velocities. The maximum effect of spatial distribution is at high velocity and low permeability ratio. (e) Calculated large-scale dissolution rate, (f) \( \frac{A_e}{A_T} \), (g) \( \frac{A_I}{A_e} \), and (h) \( \beta_{ZM} \) of the One-zone flow cell under combinations of transverse dispersivity and flow velocities. The maximum effect of spatial distribution is at high velocity and low transverse dispersivity. The influence of permeability ratio is more than transverse dispersivity.

**Large-scale rates as a function of dimensionless numbers.** Large-scale dissolution rates of 76 cases are plotted on a Pe, Da number field in Figure 3-10a. Large-scale rates ranged around four orders of magnitude (\( 10^{-3.2} - 10^{-7.0} \) (mol/s)) for cases with different spatial pattern, velocity, transverse dispersivity, and permeability ratio. Reaction rates were higher at higher Peclet numbers and lower Damkohler numbers. Increase of velocity increased both \( v_{rz} \) and \( v_{sz} \) resulting higher Pe and lower Da, respectively. At low Pe and high Da numbers reaction rates are less than \( 10^{-6} \) (mol/s). Points at this region represent those with low flow velocity (0.1435 m/d) or with low permeability ratio (0.00094). Low Pe numbers are due to low \( v_{rz} \) that led to mass transfer limitations and lower reaction rates. With increase of permeability ratio, Pe numbers increased and reaction rates increased as well. Increase of transverse dispersivity
decreased Pe numbers, however, the reaction rates did not change significantly. The highest rates were those from high velocity Mixed cases due to fluid flow in the Mixed cases, where advection controlled mass transfer. Pe and Da numbers account for all parameters including size of the flow cell, spatial pattern, velocity, permeability ratio, reactivity, and dispersion in their formulations and can be used to parameterize dissolution in various porous media. In general increase of Pe and decrease of Da numbers were correlated with increase of large-scale reaction rates. Figure 3-10b illustrates that reaction rates decreases with increase of Da numbers linearly on a log-log plane. Reaction rates drop four orders of magnitude with around four orders of magnitude increase of Da. Under fast flow regimes, Da numbers are smaller and large-scale rates are larger due to higher mass transfer from throughout the flow cell.

Figure 3-10 (a) Large-scale dissolution rates R as a function of dimensionless Damkohler (Da) and Peclet (Pe) numbers. Each circle represent a numerical model that resulted in calculation of a steady-state reaction rate. (b) Large-scale dissolution rates R as a function of Damkohler (Da) number.

3.4 Conclusion

In spite of decades of studies on the effect of physical heterogeneity on flow and transport in porous media, the effect of chemical heterogeneity in the form of spatial distribution of different minerals on geochemical processes such as mineral dissolution has not been studied comprehensively (Li et al., 2007a, b; Molins et al., 2012). Experimental studies on the role of chemical and physical heterogeneities on mineral dissolution is scarce, expect for a few
studies on dissolution of magnesite in 1D columns (Li et al., 2014; Salehikhoo et al., 2013). Here we present experimental data of the effect of spatial distribution of calcite resulting in coupled physical and chemical heterogeneities on mineral dissolution in 2D flow cells. The goal of this study is to answer the following questions: 1) What is the extent of the effect of physical and chemical heterogeneities on mineral dissolution? 2) What are the parameters that control significance of mineral spatial pattern on overall dissolution? A total of six experiments with Mixed and One-zone spatial patterns of calcite distribution in sand at flow velocities of 1.435 m/d, 7.175 m/d, and 14.35 m/d were carried out, which were numerically simulated. In addition to the experiments, numerical modeling was used to find dissolution rates of designed cases with wider range of parameters than those we were able to test experimentally.

Combination of parameters such as spatial pattern, velocity, dispersion, and permeability ratio can change mineral dissolution rates over four orders of magnitude. Rate of mass transfer is the most important parameter controlling mineral dissolution rate. Different parameters can contribute to the extent of mass transfer in porous media. Flow velocity is the most important parameter that controls rate of advective mass transfer. Under low flow velocities, transverse dispersion affects the overall mass transfer and leads to higher mineral dissolution. Spatial pattern of mineral distribution can affect large-scale mineral dissolution rates up to an order of magnitude. Due to high reactivity of calcite, dissolution rates of both Mixed and One-zone cases linearly increased with velocity. Therefore, changes of velocity did not affect the rate ratios as significantly as other parameters ($\beta_{Z/M} = 0.15 - 0.22$). At high flow velocities a minimum $\beta_{Z/M}$ value of 0.06 was observed with low permeability ratio. Mass transfer out of the calcite zone is limited under both these conditions. However, significance of spatial distribution changes more with changes of permeability ratio ($\beta_{Z/M} = 0.06 - 0.88$) than those of transverse dispersivity ($\beta_{Z/M} = 0.10 - 0.37$).

We compared our calcite dissolution results with previous similar studies on magnesite dissolution (Li et al., 2014; Salehikhoo et al., 2013). The effect of magnesite spatial distribution on dissolution depended more on flow velocity compare to our results for calcite. This is mainly due to considerably higher reactivity of calcite compared to magnesite. Mixed case affluent concentrations changed with velocity in the magnesite containing porous media,
while they were constant in the calcite ones. Compared to calcite a higher percentage of magnesite reacted effectively due to faster calcite reaction rates and reaching equilibrium concentrations upon exposure to calcite. The highest effective surface area for calcite was under 4.5% that is considerably lower than the maximum of 100% observed in the magnesite dissolution study. Therefore, most calcite reaction occurred on the calcite-sand interface resulting in high $A_f/A_e$ values close to 100% while the highest $A_f/A_e$ in the magnesite case is 60%. The extent of changes of rate ratio $\beta_{Z/M}$ with changes of permeability ratio were similar for calcite and magnesite, since the most important parameter affecting the significance of mineral spatial dissolution on reaction rate is the amount of fluid that flows through the reactive zone not the type of mineral.

Our result indicated the importance of heterogeneous distribution of chemical and physical parameters in porous media on mineral dissolution. We observed about four orders of magnitude difference in reaction rates under reactive flow in heterogeneous porous media. Parameters such as chemical and physical heterogeneities, velocity, and fluid flow are commonly ignored in well-mixed batch reactor rate measurements. However, It has been consistently reported by many researchers that mineral dissolution rates calculated from field data are two to five orders of magnitude slower those of the well-mixed laboratory rates (Luttge et al., 2013; Maher, 2010; Maher et al., 2004; Navarre-Sitchler and Brantley, 2007; Reeves and Rothman, 2013; Swobodacolberg and Drever, 1993; White, 1995; White and Brantley, 2003). We propose spatial pattern of distribution of physical and chemical parameters as a possible causes of this discrepancy. We found that mineral spatial distribution can affect reaction rates up to a factor of 20, which is important in several geochemical processes that occur over geologic time. For example, weathering and soil formation directly depend on mineral dissolution. Understanding weathering can help us predict a wide variety of processes from atmospheric CO2 levels to species concentrations in oceans and ecosystems.
Chapter 4
Understanding Geochemical System of Marcellus Shale Water-Rock Interaction using Reactive Transport Modeling

4.1 Introduction

Shale formations account for 25% of continental lithology (Suchet et al., 2003). Shale weathering is a common source of some elements important for world oceans (Peucker-Ehrenbrink and Hannigan, 2000; Suchet et al., 2003). Black shale is normally rich in organic material and numerous elements and during weathering these elements are dispersed in the environment and ecosystems (Liermann et al., 2011; Peng et al., 2004; Tuttle et al., 2009). Marcellus shale is the largest gas reservoir in the United States. The recoverable natural gas from the reservoir is estimated to range between 141 trillion cubic feet (TCF) and 489 TCF (Blohm et al., 2012). Due to this financial opportunity, in addition to natural weathering, the formation rock is exposed to considerable volume of external fluids during hydraulic fracturing process, which raises major concerns on environmental and safety issues (Olmstead et al., 2013; Schafft et al., 2013; Vidic et al., 2013; Walton and Woocay, 2013) including release of heavy metals (Liermann et al., 2011). Understanding fluid-Marcellus shale interaction can quantify environmental risks of the hydraulic fracturing process and facilitates better understanding of shale weathering. As such, it is important to develop models to understand and predict the water-rock interaction processes.

In the past decades, reactive transport modeling has advanced significantly and has been developed and used as a powerful tool in recent years to understand, quantify, and predict weathering for many geological formations (Brantley and White, 2009; Hausrath et al., 2008; Maher et al., 2006; Maher et al., 2009; Moore et al., 2012; Navarre-Sitchler et al., 2011; Steefel and Maher, 2009). Moore et al. (2012) used reactive transport modeling to understand the weathering of granitic parent rock and found that using dissolution of plagioclase feldspar coupled with precipitation of kaolinite are dominant during weathering. Using reactive transport modeling to analyze basalt weathering, Hausrath et al. (2008) showed that the dominant dissolving minerals were feldspars and augite while kaolinite and Fe(OH)₃
precipitation occurred. Navarre-Sitchler et al. (2011) analyzed weathering rinds of basalt and found that the reaction network is mainly a combination of plagioclase and augite dissolution followed by gibbsite, kaolinite, and goethite secondary precipitation. In another reactive transport study on marine sediments, Maher et al. (2006) found that secondary clay and calcite precipitation due to plagioclase dissolution dominate the reaction network. Maher et al. (2009) also studied weathering of soil chronosequence and determined that the weathering is mainly driven through dissolution of albite and K-feldspar and precipitation of kaolinite. Shale weathering has been studied before mainly for possible trace metal release (Liermann et al., 2011; Peng et al., 2004; Tuttle and Breit, 2009; Tuttle et al., 2009). Previous studies of Marcellus shale geochemistry suggest fast dissolution of pyrite, which increases permeability and exposes other minerals to weathering agents (Brantley et al., 2013). Other than pyrite, main participating minerals in the reaction network are believed to be illite, chlorite, vermiculite, and Fe(OH)₃ (Jin et al., 2010; Jin et al., 2013; Liermann et al., 2011). However, a reactive transport model can help us understand and quantify the reaction network more comprehensively.

The dominant factors controlling soil generation process differ between cases with different mineralogy and hydrology. Successful modeling of soil generation depends on finding dominant factors in each case among numerous possible factors such as field-scale reaction rates (White and Brantley, 2003), precipitation of secondary minerals (Maher et al., 2006; Maher et al., 2009), flow velocity through the soil (Brantley and White, 2009), erosion (Riebe et al., 2003; West et al., 2005), composition of the reacting fluid (Oelkers et al., 1994), and biological activity (Drever and Stillings, 1997; Lawrence et al., 2014; Wilson, 2004) among others. Brantley and White (2009) showed that the weathering advance rate extensively depends on transport parameters such as advection and diffusion. Navarre-Sitchler et al. (2011) suggested that as pore connectivity increases during weathering, the key controlling parameter changes from diffusion-controlled transport at early stages to mineral dissolution rates at later stages. Maher et al. (2006) suggested that precipitation of secondary minerals should be considered in analysis of mineral dissolution in natural systems. They also found that secondary clay precipitation is as important as transport in governing the amount of dissolution that occurs within a profile because clay minerals exert a strong control over the
reaction affinity of the dissolving primary minerals (Maher et al., 2009). In addition, biological activity may result in production of materials such as organic acid that influence the weathering process. Presence of organic acid can change dissolution rate due to lower pH values and also saturation of the solution with respect to the mineral, ultimately altering the weathering process (Drever and Stillings, 1997). Physical processes and parameters such as erosion, rainfall, and temperature can also affect the weathering process significantly (West et al., 2005). In general, dominant processes and factors controlling soil formation differ between different mineralogy and hydrology.

Marcellus shale is rich in organic matter and pyrite, with major composing minerals being chlorite, illite, vermiculite, Fe(OH)$_3$ and quartz. Major trace metals of Marcellus shale are Co, Cu, Mo, and Ni (Jin et al., 2010; Liermann et al., 2011). Understanding release of these elements into the environment during weathering is of great importance. Reactive transport models can be used to understand the weathering process and the key controlling factors. However, such a model has not yet been developed for Marcellus shale. The objective of this work is to understand the dominant processes and develop a model for chemical weathering of Marcellus shale using soil formation and aqueous geochemistry data. With similar types of reactions involved, the developed model can potentially be used to understand water-rock interaction during hydraulic fracturing and to predict environmental impacts of engineered Marcellus shale systems.

4.2 Methodology

**Soil and water chemistry data collection.** This study focuses on the black shale of the Middle Devonian Marcellus Formation within the Hamilton group. This formation underlies much of Pennsylvania, extending into Ohio, West Virginia, and New York (Faill, 1998; Obermajer et al., 1997). The soil and aqueous samples were collected from a forested northwest-facing planar hillslope located in Jackson Corner, Huntingdon County, Pennsylvania. The field site has been previously described (Jin et al., 2013; Mathur et al., 2012).

Soil and water sampling were carried out along the planar hillslope (defined by soil sites RT1, RT2 and VFS) at the ridgetop (MRT), middle slope (MMS), and valley floor
(MVF). Jin et al. (2013) measured elemental chemistry of soils following standard procedures (Suhr and Ingamells, 1900) using inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Perkin-Elmer Optima 5300. More details are presented by Jin et al. (2013). We used the soil chemistry data of the ridgetop samples in this study.

Pore water samples were collected following a method previously described by Mathur et al. (2012). First, lysimeters from SoilMoisture Equipment Corp (1900 series) were washed with 10% nitric acid and rinsed repeatedly with double deionized water. Then, lysimeters were emplaced at the ridgetop (MRT), mid-slope (MMS), and valley floor (MVF) locations. These “nests” allowed collection of soil pore waters at 10 cm depth intervals. After two weeks of lysimeters emplacement in May of 2010, weekly pore water samples were collected. Over the analysis period, element concentrations showed some variation with rainfall but no pattern was observed, other than the nitrate variations, which were attributed to perturbations related to emplacement of the lysimeters. A hand pump was used to suction lysimeters to -50 centibars pressure one week before each collection. Water sampling was carried out by lowering a PVC tubing into the cup and pumping out the water with a syringe. The pH values of the soil water were measured with a pH meter and an electrode calibrated with standard pH buffers (4 and 7). Aliquots (30 mL) were then acidified with 5 drops of ultrapure nitric acid and stored in pre-cleaned high density polyethylene (HDPE) bottles for cation analysis. Acidified pore water samples were analyzed for major cation concentrations using the ICP-AES equipment. A similar aliquot was stored without acid addition for anion analysis. Unacidified pore water samples were analyzed for anion concentrations using a Dionex ion chromatograph (ICS-2500).

**Initial mineralogy.** The initial chemical composition of the parent rock was determined based on elemental composition data from Jin et al. (2013) with certain adjustment (Jin et al., 2013)(Table 4-1). Jin et al. (2013) suggested close to 40 % quartz, 1-2 % pyrite, with the rest being illite and chlorite. In this work, small amount of albite (1.5%) was considered given observed trace concentration of sodium. Previous studies have indicated the transformation of chlorite to vermiculite during weathering (Jin et al., 2010; Jin et al., 2013). Fe(OH)$_3(s)$ was observed as a possible secondary mineral and therefore was included in the model.
Rain water chemistry. Annual rainfall approximates 1.0 meter in average in this area. Rainwater chemistry data was from two of the National Atmospheric Deposition Program sites in central Pennsylvania (PA-15 and PA-42). The concentrations in precipitation were determined from the monthly averages from 2006-2008 (Appendix 4-A). The data showed that the rainfall chemical concentrations are similar between the two sites. Dominant species are SO$_4^{2-}$, NO$_3^-$, and H$^+$, which is characteristic of acid rain in Pennsylvania. Dominant cations are Ca$^{2+}$, Na$^+$, and H$^+$, followed by Mg$^{2+}$ and K$^+$. Our study modeled weathering over 10,000 years. Industrialization and CO$_2$ production resulted in rainfall pH reduction in the last 100 years. Therefore, for the first 9,900 years the inlet pH was set to 5.5. The rainfall pH for the last 100 years was 4.4 based on the rainfall data.

Reactive transport modeling. The reactive transport code CrunchFlow was used to simulate the reaction and transport processes during soil formation from Marcellus shale parent rock. CrunchFlow solves mass, energy, and momentum conservation equations and has been previously used to simulate processes that involve only flow and transport or coupled transport and complex reaction networks (Heidari and Li, 2014; Li et al., 2014). In this work, we considered the rain flow through a column of Marcellus shale rock starting from 10,000 years ago at the end of the last glacier. Initial porosity of 9.0% was set throughout the column (Soeder, 1988).

CrunchFlow calculates concentration of species by solving the governing Advection-Dispersion-Reaction equation:

$$\frac{\partial C_i}{\partial t} = D_L \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} \pm \Sigma R$$  \hspace{1cm} (1)

where $C_i$ is the solute concentration of species i (mol/m$^3$), $v$ is flow velocity (m/s), $t$ is time (seconds), and $D_L$ is dispersion coefficients (m$^2$/s), which is a combination of diffusion and dispersion calculated by the following:

$$D_L = D^* + \alpha_L v$$ \hspace{1cm} (2)

where $D^*$ is the effective diffusion coefficient in porous media (m$^2$/s) and $\alpha_L$ is the longitudinal dispersivity (m). In this work, $\alpha_L$ was set to be 0.05 cm, which is a common value for homogenous columns (Salehikhoo et al., 2013). A common tortuosity value of 2.0 for transport in porous media (Armatas, 2006) was used to relate $D^*$ to the fixed aqueous diffusion coefficient $D_0$ of 1.0 ×10$^{-9}$ m$^2$/s. Length of the soil column was 120 cm. The
modeling was 1D and the size of each grid block was 0.1 cm. The total number of grid blocks is 1200. The grid-size effect was eliminated by increasing the resolution to the extent that the effluent concentrations did not change with increasing resolution.

The R term in equation 1 accounts for chemical reactions in the system. The reaction network solved by the code includes mineral dissolution and precipitation as well as aqueous complexation reactions. Classical Transition-State-Theory (TST) based rate laws were used to represent mineral reaction kinetics

\[
R = A k a_i^n \left(1 - \frac{IAP}{K_{eq}}\right)
\]

(3)

Where R is the rate (mol/s), A is the reactive surface area (m²), k is the rate constants (mol m² s⁻¹), a_i is the activity of species i, essentially the product of the activity coefficient and concentration of species i, n is the degree of dependence of reaction rate on the activity of species i, IAP is the ion activity product of the reactions, and K_{eq} is the equilibrium constant of the reactions. The saturation index (1-IAP/K_{eq}) is an indicator of the degree of saturation of the solution with respect to the minerals. When saturation index is less than one, the mineral dissolves and the R term is positive. When the saturation index is more than one, the solution is oversaturated and precipitation occurs.

Mineral dissolution and precipitation reactions, their corresponding equilibrium constants, and rate laws are listed in Table 4-1. The rate law in Table 4-1 does not include the saturation index. A list of the species used in the modeling is presented in Appendix 4-B.

**Base-case model matching steps.** The average annual rainfall is around 1 meter in this area. An estimated 10% to 50% infiltrates through the soil column and the rest goes to surface runoff or evaporation. Therefore, the flow rate was changed between 0.1m/year and 0.5 m/year during the modeling and the base-case fit was obtained at the flow rate of 0.35 m/year. Simulation processes suggested that the pH spatial profile is the master variable.

Soil water is usually in contact with air at shallow depths during dry seasons. It is found through modeling studies that considering the interaction between soil water and reactive gases(CO₂ and O₂ ) in air under the dry condition significantly affects weathering (Moore et al., 2012). Measurement showed that the amount of pyrite left in the soil at the present time is negligible compared to the amount of pyrite in the parent rock (Brantley et al., 2013). Pyrite dissolves through reaction with oxygen, which flows into the system in the form of O₂(aq) in
rain. However, our modeling analysis revealed that complete depletion of pyrite is only achievable through consideration of $O_2(g)$ interaction with soil water inside the column. CrunchFlow is not capable of simulating the dry condition. In order to account for the source of oxygen inside the column, we introduced a small fraction of oxygen as an imaginary mineral that releases $O_2(aq)$ into the system, $O_2(s) \leftrightarrow O_2(aq)$ With $\log(K_{eq})=1.0$ and rate constant $k=8 \times 10^{-10}$ mol/s, which makes the reaction kinetically controlled. In addition, in absence of pyrite, modeling data showed higher pH than those measured in the field. The source of this acidity may be due to $CO_2(g)$ being in contact with soil water at shallow depths due to dry condition or organic acid produced from biological activity (Drever and Stillings, 1997; Moore et al., 2012). Similar to oxygen, a source of $CO_2(aq)$ was considered to account for the acidity, $CO_2(s) \leftrightarrow CO_2(aq)$ With $\log(K_{eq})=1.3$ and rate constant $k=1 \times 10^{-4}$ mol/s, which makes the reaction thermodynamically controlled. We adjusted release of $CO_2(aq)$ into the system and changed specific surface areas of the dissolving minerals to fit the solid phase elemental compositions and the pH. Concentrations of other ions in the aqueous phase were calibrated by changing flow rate and the specific surface area of vermiculite which was the main secondary mineral that precipitated cations and released $H^+$ ion into the system. The matching criterion to obtain the best-fit model was minimization of the sum of the square of the differences between the model-predicted and the measured elemental compositions in both aqueous and solid phases under the condition that all modeling output are in the range of the measured data and the model is not underestimating or overestimating concentration of any element significantly.

**Sensitivity analysis cases.** Sensitivity of the model outputs to changes in several parameters were analyzed in order to determine the controlling parameters of the weathering processes. Effects of parameters such as diffusion and dispersion proved to be negligible on the weathering. However, specific surface area, flow rate, and availability of reactive gases significantly affected the modeling outputs. Table 4-2 list different properties and parameters used in our sensitivity analysis.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
<th>Initial Volume fraction</th>
<th>Reaction</th>
<th>Log(K_eq)</th>
<th>Rate Law</th>
<th>SSA in Model (m²/g)</th>
<th>SSA in lab (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>0.345</td>
<td>Quartz ↔ SiO₂ (aq)</td>
<td>-4.000</td>
<td>(10^{11.5} [H^+0.35+10^{-13.99} + 10^{-10.5} [OH]^{0.28})</td>
<td>1.0 x 10⁶</td>
<td>1.001-2.3</td>
</tr>
<tr>
<td>Illite</td>
<td>Mg₀.₁Fe₂⁺K₀.₇Al₃Si₃O₁₀·₄</td>
<td>0.180</td>
<td>Illite + 10.7 H⁺ ↔ 0.1 Mg²⁺ + 0.4 Fe²⁺ + 0.7 K⁺ + 3.0 Al³⁺ + 1.7 SiO₂ (aq) + 5 H₂O</td>
<td>9.026</td>
<td>(10^{0.80} [H^+0.51+10^{-12.48} [OH]^{0.28})</td>
<td>1.0 x 10⁶</td>
<td>42-137</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>0.020</td>
<td>Pyrite + H₂O + 3.5 O₂ ↔ 2 H⁺ + 2 SO₄⁻² + Fe²⁺</td>
<td>107.670</td>
<td>(10^{-8.30} [H^+]^{0.31} [O₂]^{0.5})</td>
<td>1.4 x 10⁴</td>
<td>0.05-2.80</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi₃O₈</td>
<td>0.015</td>
<td>Albite + 4 H⁺ ↔ Na⁺ + Al³⁺ + 3 SiO₂ (aq) + 2 H₂O</td>
<td>2.760</td>
<td>(10^{0.5} [H^+]^{0.5} + 10^{-12.9} + 10^{-0.5} [OH]^{0.5})</td>
<td>1.3 x 10⁵</td>
<td>0.042-0.49</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Mg₀.₃Fe₂⁺K₁.₂Al₄Si₃O₁₅</td>
<td>0.350</td>
<td>Chlorite + 16.8 H⁺ ↔ 0.8 Mg²⁺ + 0.4 Fe²⁺ + 1.2 K⁺ + 4.4 Al³⁺ + 3 SiO₂ (aq) + 12 H₂O</td>
<td>14.996</td>
<td>(10^{10.77} [H^+]^{0.36+10^{-10.09} [OH]^{0.36})</td>
<td>1.0 x 10⁹</td>
<td>1.1-7.7</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>Mg₀.₃₅Fe₀.₃₅K₀.₃₅Al₄Si₁₀O₃₂</td>
<td>0.000</td>
<td>Vermiculite + 14.4 H⁺ ↔ 0.35 Mg²⁺ + 0.35 Fe²⁺ + 1.0 K⁺ + 4.0 Al³⁺ + 1.6 SiO₂ (aq) + 12H₂O</td>
<td>-5.390</td>
<td>(10^{-4.13}[H^+]^{0.33})</td>
<td>6.0 x 10⁶</td>
<td>0.73-17.4</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>Fe(OH)₃</td>
<td>0.000</td>
<td>Fe(OH)₃ + 2H⁺ ↔ 0.25 O₂ (aq) + Fe²⁺ + 2.5 H₂O</td>
<td>-7.320</td>
<td>(10^{-8.4})</td>
<td>5.0 x 10¹⁵</td>
<td>7.47-259</td>
</tr>
</tbody>
</table>

\(\text{Notes:}\) (Bennett et al., 1988; Brady and Walther, 1990; House and Orr, 1992) \(\text{References:}\) (Bibi et al., 2011; Kohler et al., 2003; Suzuki-Muresan et al., 2011) (Kamei and Ohmoto, 2000; Kuechler and Noack, 2007; Liu et al., 2008; Truche et al., 2010) (Casey et al., 1991; Chou and Wollast, 1985b; Stillings and Brantley, 1995) (Black and Hesse, 2014; Brandt et al., 2003; Malmstrom et al., 1996) (Kalinowski and Schweda, 2007; Mareschal et al., 2009) (Whittmore and Langmuir, 1974; Yoshida et al., 2002) --- (Brantley et al., 2007) (Kohler et al., 2003) (Kalinowski and Schweda, 2007) (Peucker-Ehrenbrink and Hannigan, 2000) (Moore, 2008; Peucker-Ehrenbrink and Hannigan, 2000) (Kalinowski and Schweda, 2007)
Table 4-2 Properties of the studied cases for sensitivity analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Flow rate</th>
<th>SSA</th>
<th>Reactive gases in rain (inlet)</th>
<th>O₂ inside the column</th>
<th>CO₂ inside the column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base-case</td>
<td>0.35 m/year</td>
<td>Base-case (BC) Table 4-1</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Specific Surface Area (SSA)</td>
<td>0.35 m/year</td>
<td>Base-case×10</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>0.35 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>0.35 m/year</td>
<td>Base-case/10</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>3.5 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>0.35 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>0.035 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Availability of Reactive Gases</td>
<td>0.35 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>0.35 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>0.35 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>0.35 m/year</td>
<td>Base-case</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

4.3 Results and discussion

In this section we present the base case model that reproduces the pore water and soil profile data. The evolving spatial profiles of different minerals were then regenerated to understand the soil formation history over the past 10,000 years. We then show the sensitivity analysis to understand key controls of the weathering rates.

**Pore water chemistry.** The pH of soil pore water samples from 10 cm below the land surface, the closest values to the rain water pH, ranged from 3.7 to 4.2. The pH values of soil waters from the ridge top (MRT) location were about 0.4 units higher on average than those locations downslope (MMS, MVF). The pH increased with depth after 50 cm at all sampling locations. However, the trend of changes with depth were different shallower than 50 cm. In the ridge top and valley floor locations, the pH increased from surface to 30 cm and decreased between 30 cm and 50, while the decrease in the pH starts from the surface in the mid slope location (Figure 4-1a).
The dominant anions were \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \), varying in concentration more than 100 \( \mu \text{M} \) (\( \mu \text{mol/L} \)) (Figure 4-1b,c). Sulfate concentrations remained relatively constant with change of depth in the ridge top (MRT) location. However, as shown in Figure 4-1c, sulfate concentrations were increasing with depth in the valley floor (MVF) location while the mid slope (MMS) location showed a decreasing trend. Chloride concentrations were the lowest at the ridge top (MRT) location. Compared to other anions, \( \text{NO}_3^- \) concentrations were relatively small.

The dominant cations in the soil waters were \( \text{Ca}^{2+} \), \( \text{Na}^+ \), and \( \text{K}^+ \) followed by \( \text{Al} \) and \( \text{Mg}^{2+} \). Concentrations of \( \text{Na}^+ \) did not differ significantly with increase of depth. The lowest \( \text{Na}^+ \) concentrations were in the MRT site and its concentration increased in the downhill locations, MMS and MVF. While concentration of \( \text{K}^+ \) and \( \text{Al} \) were in the same range for all three locations, the \( \text{Al} \) concentrations (Figure 4-1f) consistently decreased with increase of depth, but concentrations of \( \text{Mg}^{2+} \) slightly increased with increase of depth. Similar to \( \text{Al} \), \( \text{Fe} \) concentrations consistently decreased with depth. The calcium ion in the solution was probably from organic matter since calcite should be depleted at these depths due to its relatively high reactivity.

The sums of the positive and negative charges in pore water chemistry were calculated using major elements (\( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and \( \text{Cl}^- \)). As is commonly reported for other soil waters, up to 50% charge difference was observed, consistent with the high concentrations of dissolved organic ions.
Figure 4-1 Ion concentrations data versus depth from all three sampling locations. (a) pH, (b) Cl⁻, (c) SO₄²⁻, (d) NO₃⁻, (e) F⁻, (f) Al, (g) K⁺, (h) Na⁺, (i) Ca²⁺, (j) Mg²⁺, (k) Fe, (l) Si.

**Base-case model.** Soil elemental composition data and pore water chemistry data from the Ridge top location were selected for simulation due to its primarily vertical infiltration of rain
water and therefore relatively simple hydrology. In Mid slope and Valley floor locations, lateral flow can become important, which can significantly complicate the flow representation. Ions in pore water can be concentrated due to evapotranspiration process that is currently not included in our model. To account for this, we normalized the measured ion concentrations using Cl− concentration ratio in atmospheric precipitation and in pore water (equation 4) based on the following formula:

$$M_{\text{Cl-normalized}}^* = [M]_{\text{porewater}} \times \frac{[\text{Cl}]_{\text{ppn}}}{[\text{Cl}]_{\text{porewater}}}$$  \hspace{1cm} (4)$$

Where $M_{\text{Cl-normalized}}^*$ indicates metal concentration “corrected” for evapotranspiration while $[M]_{\text{porewater}}$ is the measured metal concentration in pore water. We considered chloride as a conservative, non-reactive ion being introduced into the system solely from atmospheric precipitation, which makes Cl a perfect candidate to calculate the correction ratio. Correction ratio, $[\text{Cl}]_{\text{ppn}}/[\text{Cl}]_{\text{porewater}}$, is calculated through dividing Cl− concentration in precipitation, $[\text{Cl}]_{\text{ppn}}$, by concentrations in pore water, $[\text{Cl}]_{\text{porewater}}$ (Jin et al., 2011).

Figure 4-2 compares the Cl-corrected ion concentrations data and the modeling output. Concentrations of all elements and pH followed an increasing trend with increase of depth from the surface downward, except for the decreasing, 30-50 cm section. The pH values increased from 4.3 in the rainwater to 4.7 at the top 30 cm. Similarly, concentrations of all other elements, including K, Mg, Al, Fe, and Na increased with depth in this section. Between 30cm and 50 cm, the pH values decreased to reach a minimum of 4.3 at 50 cm. Spatial profiles of concentrations of all other elements followed the same trend as pH in the 30 – 50 cm section. In the deeper than 50 cm section, all concentrations, including K, Mg, Al, Fe, and Na, and the pH slightly increased with depth, however, with different slopes. Aluminum (Al) was the dominant element in the pore water, followed by potassium (K) and magnesium (Mg). Iron (Fe) concentrations were considerably lower than other cations.

At the present time, after 10,000 years of weathering, chlorite is the main dissolving mineral and vermiculite is the main precipitating mineral, as shown in Figure 4-2g. The dissolution reactions of chlorite, and illite consumes H+ and concentrates the solution because of the release of elements such as Al, K, Mg, and Fe. Around the depth of 30cm, the solution became over-saturated with respect to vermiculite and precipitation occurred. Vermiculite precipitation diluted the solutions with respect to Al, K, Mg, and Fe and releases H+. As
shown in Figure 4-2g, vermiculite precipitation rate reached a maximum at 30 cm. Consistently, the drop in aqueous concentration and pH started at the same depth. Aluminum (Al) was the main element in the composition of illite, chlorite, and vermiculite. The main source of Al, K, and Mg in the solution was from dissolution of chlorite followed by dissolution of illite. Iron existed in most of the primary minerals such as illite, and chlorite. Iron may precipitate as Fe(OH)$_3$ or vermiculite. However, if not depleted, the main source of iron in the solution was pyrite dissolution. Due to depletion of pyrite at the present time, Fe(OH)$_3$ precipitation rate was negligible compared to other minerals. Albite was the only mineral containing sodium (Na). Interestingly, Na concentration did not change significantly with depth.

Figure 4-3 compares elemental compositions of soil obtained from analyze of the field data and the model-generated output after 10,000 years of weathering. In general, two separate trends were observed in the elemental composition spatial profiles. An increasing trend that appeared in the profiles of Al, Mg, and K and a relatively constant trend in profiles of Fe, Na, and Si. Spatial profiles of aluminum, magnesium, and potassium indicated two distinct reaction zones, shallower than 50 cm and deeper than 50 cm. Elemental compositions of Al, Mg, and K rapidly increased with depth from the surface to 50 cm. However, elemental compositions did not vary significantly with depth in the deeper than 50 cm section. In contrast with this increasing trend, spatial profiles of iron, sodium, and silicon demonstrated relatively constant trends and their concentrations did not vary significantly with increase of depth. Aluminum was the most abundant metal in the soil and composed more than 6% of the weight of the soil at the surface and increased from the surface downward to more than 9% at the depth of 50 cm. After aluminum, iron and potassium were the most abundant metals in the solid phase. The spatial profile of sodium elemental composition was relatively constant around the small value of 0.2 %.
Figure 4-2 Comparison of pH (a) data from Ridge top location and the model-generated output. Comparison of elemental concentration in the pore water between the model output and the ridge top Cl-corrected data for (b) K, (c) Mg, (d) Al, (e) Fe, and (f) Na. (g) Spatial profiles of rates of the reactive minerals at the present time.
The elemental composition data of soil indicated that dissolution has occurred more extensively closer to the surface compared to the deeper parts. The spatial profile of Al, K, and Mg shown in Figure 4-3a,b,c indicated that these elements are being dissolved and washed away in minerals such as chlorite and illite. Interestingly, iron elemental weight percent in Figure 4-3d showed relatively constant values with increase of depth. Since Fe is relatively conservative, most of iron ions in the aqueous phase precipitated as Fe(OH)$_3$ or vermiculite and remained in the solid phase. As expected, Silicone was the most abundant species and composed more than 30% of the weight of the soil. Similar to Fe spatial profile,
the silicone profile showed constant elemental compositions with depth due to relatively low reactivity of quartz. Overall indicator of solid phase transformation is the porosity. The spatial profile of field porosity measurements in Figure 4-3g showed 40-60% porosity close to the surface. The porosity gradually decreased to 30-50% with depth. The model captured the spatial profile of porosity. The ultimate porosity in the model decreased from 45% at the surface to 35% at the bottom of the soil column.

Figure 4-4 demonstrates temporal evolution of spatial profiles of mineral volume fractions alongside their respective reaction rates evolution over 10,000 years of weathering. Expectedly, volume fraction of the dissolving minerals, chlorite, illite, albite, and pyrite decreased with time. The major dissolving mineral was chlorite, with its volume fraction decreasing from 35% to around only 2% over 10,000 years. In spite of the decrease in the pH values with time, the dissolution rates of chlorite decreased with time as shown in Figure 4-4b due to loss of reactive surface area. In contrast, illite did not dissolve as fast as chlorite, its volume fraction decreased for only about 2% over the same period. There was only 2% of pyrite available for dissolution at the beginning of the weathering process. However, pyrite was the fastest dissolving mineral and most of the pyrite and its grains completely dissolved in the first 2,000 years as shown in Figure 4-4c.

Vermiculite and Fe(OH)$_3$ were the major precipitating minerals. However, their dominance evolved over time. The geochemical reaction system extremely depended on availability of pyrite. Dominant reactions were considerably different during the first stage, while pyrite was still available and after depletion of pyrite. Within the first 500 ~ 1,000 years, Fe(OH)$_3$ was the main precipitating mineral, because pyrite was still present in the system, which dissolved and released Fe(II). Comparison between the spatial profiles of volume fraction of vermiculite and Fe(OH)$_3$ in Figure 4-4e,g demonstrated that only after 1,000 years close to 2% of Fe(OH)$_3$ precipitated out. After 1,000 ~ 2,000 years when pyrite was completely depleted, the main secondary mineral changed to vermiculite. At this stage, vermiculite started to significantly precipitate in the deeper parts of the column at 120 cm because of over-saturation of the solution with respect to vermiculite due to incremental increase of concentration of elements with depth. Over time, changes in the spatial profile of the pH resulted in movement of vermiculite precipitation front toward the surface. Peak of the
vermiculite precipitation depth decreased with time and reaches around 30 cm after 10,000 years. However, the rate of increase of vermiculite volume fraction decreased with time. Although dissolution occurred almost to the same extent throughout the column, vermiculite precipitated only at the deeper, over-saturated sections forming a slope in porosity profile. Porosity in the base-case model increased from the starting value of 9.0 % to around 50% at the top of the column and more than 30% at the bottom (Figure 4-4i), which is consistent with the field measurements.

Figure 4-5a shows a schematic of the main part of the reaction network and the role of reactive gases (O2 and CO2) during the weathering process. Chlorite dissolution driven by CO2 releases elements that later precipitate as vermiculite. Pyrite reacts with O2 and release Fe2+. The Fe2+ from both pyrite and chlorite dissolution reacts with O2 and precipitates as Fe(OH)3. Chlorite was dissolving two orders of magnitude faster than illite at the start of the weathering process, 10,000 years ago. As illustrated in Figure 4-5b, this difference decreased over time and reached about an order of magnitude at the present time. The reduction was due to loss of the reactive surface area of chlorite because of significant dissolution. Pyrite was dissolving relatively fast over the first 1,000 ~ 2,000 years, but the overall dissolution rate dramatically decreased after depletion, as expected. Low elemental composition of Na and also relatively constant concentration in pore water suggested limited albite dissolution rates, which were the lowest between the dissolving minerals. The competition between vermiculite and Fe(OH)3 to precipitate is depicted in Figure 4-5c. These minerals showed inverse trends, meaning increase of vermiculite reaction rate was coupled with decrease of Fe(OH)3 reaction rate, and vice versa. In general, Fe(OH)3 was precipitating faster than vermiculite at the beginning. However, the rate of Fe(OH)3 precipitation decreased over time while the rate of vermiculite precipitation increased until it reached a maximum around 5,000 years. After this point, the vermiculite precipitation rate slightly decreased because of lower saturation index.
Figure 4-4 Volume fraction evolution over time (Left) for (a) chlorite, (c) pyrite, (e) vermiculite, and (g) Fe(OH)₃ alongside temporal evolution of reaction rates (Right) for (b) chlorite, (d) pyrite, (f) vermiculite, and (h) Fe(OH)₃. (i) Porosity evolution over time. and (j) pH spatial profile over time. Lightest gray line is the starting point at 10,000 years ago and the darkest grey is the present condition.
Figure 4-5 (a) Schematic of the main part of the reaction network and the role of O$_2$ and CO$_2$ gases in the weathering process. Averaged reaction rates over the whole column for (b) dissolving and (c) precipitating minerals over time. (d) Different stages of the weathering process based on model-generated results described by three different stages of porosity increasing over 10,000 years separated by three slopes and related to mineralogy at different stages.

In conclusion, three different stages of porosity increase can be separated during the weathering process shown in Figure 4-5d. The slope of porosity increase decreased with time, which is indicative of lower extents of weathering as time passes. This is mainly due to slower dissolution of the reactive mineral at the later stages and is consistent with temporal evolution of volume fractions of the reactive minerals. The fastest stage started from the beginning of the modeling at 10,000 years ago and lasted almost 1,000 years. Dissolution in this stage was driven mainly by pyrite dissolution. In this stage pyrite dissolution produced significant amount of H$^+$ ions that reacted with mostly chlorite and dissolved considerable amount of this mineral (7-8%). Chlorite dissolution combined with relatively low vermiculite precipitation were the main reasons of the steep increase of porosity over this stage. The next stage started after pyrite depletion, when a considerable portion of chlorite still remained in the solid phase. In this stage chlorite dissolution was the main reason for porosity increase. However, compared to the first stage, more vermiculite was being precipitated, which decreased the rate of porosity increase. The second stage ended after 4,000 years from the start of the simulation.
Subsequently, the slowest stage of porosity started. The porosity increase during this stage was slower than both previous stages due to significant decrease of the available surface area for the chlorite dissolution reaction and relatively high vermiculite precipitation rates.

**Sensitivity analysis.** Controlling parameters of the Marcellus shale weathering process were determined through sensitivity analysis. Sensitivity of the model outputs to varying several parameters were analyzed. The modeling results responded strongly to varying the values of specific surface area, flow rate, and availability of CO$_2(g)$ and O$_2(g)$ inside the column during the weathering process. Among these, the most important parameter controlling the weathering of Marcellus shale is the surface area available for reactions.

The effects of changing the specific surface area (SSA) on characteristics of the weathering process in both solid and aqueous phases were analyzed. SSA of all minerals were changed for an order of magnitude from the base-case values. It has been shown that the reaction rates measured in batch experiments can be 2 to 5 orders of magnitude higher than reaction rates in the field (Lutgge et al., 2013; Maher, 2010; Maher et al., 2004; Navarre-Sitchler and Brantley, 2007; Reeves and Rothman, 2013; Swobodacolberg and Drever, 1993; White, 1995; White and Brantley, 2003). This discrepancy has hindered the use of TST type rate laws in predicting field scale processes. In the base-case analysis, we demonstrated that TST rate laws can be used in a reactive transport model to simulate and ultimately predict weathering processes at the field scale by adjusting SSA of the reactive minerals. During the fitting process, we reduced all specific surface areas up to five orders of magnitude compared to the measured values in the laboratory studies of batch reactor rates. These significantly lower SSA may be due to a combination of factor such as small reactive surface area, dead-end pores in contact with near equilibrium solutions, physical heterogeneity, and chemical heterogeneity.

Figure 4-6 compares results of the base-case model to cases with one order of magnitude higher and lower specific surface areas. After 10,000 years of weathering, only 2% of chlorite remained in the base-case model while more than 25% remained in the lower SSA case and it was completely depleted in the higher SSA case as shown in Figure 4-6a. More vermiculite precipitated in the higher SSA case compared to the base-case, however, Figure 4-6b shows that vermiculite barely precipitated in the lower SSA case. The pH (Figure
4-6c) in the lower SSA case continuously increased with depth. In contrast, spatial profiles of the pH in the base-case and the higher SSA case decreased at specific depths. The pH decreased at the surface in the higher SSA case and at 30 cm in the base-case. Spatial profile of porosity in Figure 4-6d demonstrates a considerable, close to 15% difference between the lower SSA and the base-case. The differences are more pronounced by analyzing the data over 10,000 years of weathering. Dissolution rate of Chlorite in the higher SSA case started one order of magnitude higher than the base-case, however, as shown in Figure 4-6e, it decreased rapidly. The chlorite dissolution rate in the base-case model also decreased with time, however, with a much lower slope. The rate did not change significantly with time in the lower SSA case. Compared to the base-case, vermiculite precipitation rate shown in Figure 4-6f was higher in the higher SSA case at the beginning but it dropped lower than the base-case rate after the first 2,000 years. Volume fraction of chlorite decreased from 35% to 0% after only 2,000 years in the higher SSA case, while it only decreased 7-8% in the lower SSA case over the whole weathering process. Similarly, the trend of changes of vermiculite volume fraction was very different. There was almost zero precipitation in the lower SSA case, but vermiculite volume fraction increased from 0% to 10% over the first 2,000 years in the higher SSA case. In conclusion, as shown in Figure 4-5i, porosity of the higher SSA case increased very quickly especially over the first 2,000 years to almost 35%. However, porosity of the lower SSA case increased only 10% over 10,000 years.

Varying specific surface area strongly changed both soil mineralogy and aqueous chemistry. In the higher SSA case, chlorite was depleted completely relatively fast. Due to higher saturation index as a result of chlorite dissolution, and also higher SSA, more vermiculite precipitated compared to other cases. Precipitation of vermiculite in the higher SSA case started at the surface and resulted in the decrease of pH at the surface. Most reactions in this case occurred in the first 2,000 years, while high dissolution rates of chlorite resulted in high precipitation rates of vermiculite. Both rates dropped rapidly with time after depletion of chlorite. As a result, porosity of the higher SSA case increased rapidly over the first 2,000 years to more than 90% of the ultimate porosity after 10,000 years. The reactions system was considerably different in the lower SSA case, slow dissolution of chlorite resulted in far from saturation condition with respect to vermiculite. The relatively dilute solution
combined with lower SSA of vermiculite led to almost zero precipitation of vermiculite. Since the drop in pH occurs due to vermiculite precipitation, spatial profile of pH in the lower SSA case continuously increased with depth. Limited chlorite dissolution and lack of vermiculite precipitation in this case resulted in only 7% increase in porosity over 10,000 years of weathering. In conclusion, two orders of magnitude difference in SSA strongly changed characteristics of the weathering process in both solid and aqueous phases. Since the extent of the variations of SSA are well within the 2-5 order of magnitude difference between laboratory measured rates and field scale rates, SSA proved to be the most important parameter controlling weathering of Marcellus shale.

The sensitivity of the model outputs to changes in flow rate was studied by changing the base-case flow rate for an order of magnitude. Calibrating the flow rate is very important for precise modeling of transport in reactive transport modeling. There is close to one meter of atmospheric precipitation annually in Pennsylvania. However, all of the rain water does not infiltrate through the soil and there is significant loss to evaporation and surface flows. We expected 10% to 50% of the 1 m/year rain water to infiltrate through the soil column. During the fitting process, the flow rate was changed in this range and finally the best fit shown in the base-case model was obtained using 0.35 m/year as the flow rate.
Figure 4-6 Analysis of the effect of specific surface area after 10,000 years of weathering on (a) chlorite volume fraction, (b) vermiculite volume fraction, (c) pH, and (d) porosity. Comparison of (e) average chlorite dissolution rate, (f) average vermiculite precipitation rate, (g) average chlorite volume fraction, and (g) average vermiculite volume fraction over 10,000 years. (i) Comparison of average porosity increase over 10,000 years between cases with 2 orders of magnitude difference in SSA.

Figure 4-7 compares the model-generated solid phase and aqueous phase elemental compositions between high flow rate, base-case, and low flow rate cases. The flow rates in the high and low flow rate cases were changed an order of magnitude from that of the base-case. The high flow case simulation was carried out with flow rate of 3.5 m/year, in contrast with 0.035 m/year flow rate in the low flow rate case. Spatial profiles of volume fraction of chlorite were very similar as shown in Figure 4-7a. There was about 1 % chlorite left on average in the high flow rate case, while there was 4 % left in the low flow rate case.
Differences were more pronounced in the spatial profiles of vermiculite volume fraction shown in Figure 4-7b. Vermiculite slightly precipitated only at the bottom of the soil column in the high flow rate case, but considerable precipitation occurred in the low flow rate case, where precipitation started close to the surface. The pH in the high flow rate case continuously increased with depth. The decrease in the pH occurred in the spatial profile of the base-case and the low flow rate case, however, at different depths (Figure 4-7c). Expectedly, both shape and value of the spatial profiles of porosity after 10,000 years depended on the flow rate. Chlorite dissolution rates over time did not differ significantly with varying the flow rate similar to its spatial profile of volume fraction. In contrast, precipitation rates of vermiculite over 10,000 years significantly depended on the flow rate. The reaction rates of the high flow rate case were more than one order of magnitude lower than the rates of other cases. The reaction rates trends were more similar in the base-case and the low flow rate case, however, vermiculite precipitated faster in the low flow rate case at the earlier stages of the weathering process. Expectedly, changes of volume fractions of chlorite over time were very close between different cases and the main difference was in the volume fraction of vermiculite. There was less than 1% of vermiculite precipitation in the high flow rate case compared to more than 8% in the low flow rate case. These differences resulted in 10% higher porosity in the high flow rate case compared to the low flow rate case as shown in Figure 4-7i.

Varying the flow rate significantly influenced the solid phase composition, however, the effects were not as much as the effects of changing the SSA. The aqueous chemistry also strongly depended on the flow rate. In general, chlorite dissolution was kinetically controlled and vermiculite precipitation was thermodynamically controlled. Since chlorite dissolution was kinetically controlled, the dissolution rates mainly depended on the duration of the reaction and the rate law and although higher flow rate meant more acid being supplied to the system, the chlorite dissolution occurred to the same extent among all cases. However, vermiculite precipitation rate was thermodynamically controlled and it only precipitated if the solution is over-saturated. In the higher flow rate case, due to higher volume of water being injected, the solution was more dilute and essentially further from over-saturation state that resulted in less precipitation compared to the low flow rate case. Vermiculite precipitation causes the decrease in pH and the flow rate controls the depth that that the decrease occurs at.
Since, at lower flow rates the solution reached over-saturation state sooner, precipitation occurred close to the surface and pH decreased at the surface. Higher dissolution and lower precipitation in the high flow rate case resulted in higher porosity compared to other cases. In conclusion, compared to the effect of changing the SSA, the aqueous chemistry strongly depended on the changes of flow rate while the effect of the flow rate on the solid phase was less significant.

Figure 4-7 Analysis of the effect of flow rate after 10,000 years of weathering on (a) chlorite volume fraction, (b) vermiculite volume fraction, (c) pH, and (d) porosity. Comparison of (e) average chlorite dissolution rate, (f) average vermiculite precipitation rate, (g) average chlorite volume fraction, and (g) average vermiculite volume fraction over 10,000 years. (i) Comparison of average porosity increase over 10,000 years between cases with 2 orders of magnitude difference in flow rate.
Figure 4-8 Comparison of the effect of the existence of CO$_2$(aq) and O$_2$(aq) inside the soil column to interact with the pore water after 10,000 years of weathering on (a) chlorite volume fraction, (b) vermiculite volume fraction, (c) pyrite volume fraction, (d) pH, and (e) porosity. Comparison of (f) average chlorite volume fraction, (g) average vermiculite volume fraction, and (h) average pyrite volume fraction over 10,000 years. (i) Comparison of average porosity increase over 10,000 years under different conditions.

Sensitivity of the model outputs to availability of air (O$_2$ and CO$_2$ gases) to interact with the aqueous phase inside the soil column was also examined. Oxygen is essential for pyrite dissolution and carbon dioxide controls acidity of the solution. Our soil analysis data indicated that pyrite has been completely depleted in the soil. The model showed that pyrite depletion and the base-case fit can be reached only through considering existence of both O$_2$ and CO$_2$ gases in the column. A total of four cases were studied in this section. In addition to the base-case model, three more cases, excluding source of each of the gases or both of them
from the column were designed and modeled to examine the effect of each gas individually and combined on the weathering process.

Figure 4-8 compares spatial profiles of elemental compositions in both aqueous and soil phases between all four cases. As shown in Figure 4-8a,b, spatial profile of chlorite and vermiculite volume fraction strongly depended on the availability of O2 and CO2 gases. The highest chlorite volume fraction remained in the case including O2, but without CO2 (O2NoCO2) and the lowest was in the case without O2 including CO2 (NoO2CO2). The highest precipitated vermiculite volume fraction was in the case without O2 and CO2 gases (NoO2NoCO2), while the lowest volume fraction was in the base-case, including both O2 and CO2 gases (O2CO2). Spatial profiles of pyrite volume fraction shown in Figure 4-8c shows that pyrite was completely depleted in the cases with oxygen supply inside the column, but there was still non-reacted pyrite left in the soil columns without oxygen supply. Similarly, values of the pH also strongly depended of availability of O2 and CO2 gases (Figure 4-8d). Comparison of the pH spatial profiles shown in Figure 4-8d demonstrates that the pH profiles of NoO2CO2 and NoO2NoCO2 cases were very close with the lowest pH values in the NoO2CO2 case. The highest pH values were obtained in the O2NoCO2 case. As shown in Figure 4-8e, the highest porosity values were reached in the O2CO2 case and the lowest values were in the O2NoCO2 case. The slope of decrease of volume fraction of vermiculite over time in the O2NoCO2 case was smaller than other cases resulting in close to 10 % difference in the remaining chlorite between them (Figure 4-8f). The NoO2NoCO2 case had the highest average vermiculite volume fraction and the O2CO2 case had the lowest. As shown in Figure 4-8i, rates of increase of porosity in the O2NoCO2 and NoO2NoCO2 pair were considerably smaller than the O2CO2 and NoO2CO2 pair. Ultimate porosities of the O2CO2 and NoO2CO2 pair were almost 10 % higher than the O2NoCO2 and NoO2NoCO2 pair.

Availability or lack of O2 and CO2 gases inside the soil column to interact with the pore water led to significant changes in mineralogy and aqueous chemistry. Availability of O2 results in fast depletion of pyrite throughout the whole column during the first couple of thousand years and since chlorite dissolution is kinetically controlled more chlorite remained behind in these cases. In contrast, lack of O2 inside the column caused partial dissolution of pyrite. Compared to the cases with oxygen, pyrite dissolved slower starting from the top
reacting with the oxygen in the inlet rain water. Since pyrite was left in the system, its
dissolution reaction was producing H\(^+\) ion, which led to significantly lower pH values in the
NoO\(_2\)CO\(_2\) and NoO\(_2\)NoCO\(_2\) cases. In addition, lack of supply of CO\(_2\) resulted in considerably
higher pH values. Although the average volume fractions were close between different cases
their respective spatial profiles strongly depended on the availability of the O\(_2\) and CO\(_2\) gases
in the column. Spatial profiles of porosity after 10,000 years and the trend of the porosity
increase over 10,000 years in the cases including CO\(_2\) were different from the cases without
CO\(_2\). However, mineralogies and spatial distributions varied significantly even among these
cases.

4.4 Conclusion

External fluids are being injected into the Marcellus formation during fracturing process
to enhance natural gas production. Geochemical reaction system of Marcellus shale upon
exposure to external fluid is relatively complex. A reliable geochemical model to simulate
water-rock interaction upon exposure of Marcellus shale to fracturing fluid has not been
developed yet. In this study we numerically modeled the soil formation process using
elemental concentration data of soil and pore water to capture the geochemical reaction
system.

Two distinct stages of weathering were distinguished over 10,000 years, before pyrite
depletion and after pyrite depletion. At the first stage, within the first 500 ~ 1,000 years,
pyrite dissolution released considerable amount of H\(^+\) ion into the system. Illite, chlorite, and
albite dissolved due to the acidic condition and Fe(OH)\(_3\) was the main precipitating mineral.
More than 2\% of Fe(OH)\(_3\) precipitated at some parts of the column over this relatively short
stage. After pyrite depletion, the geochemical reaction system significantly changed. The
main source of acidity was CO\(_2\), which was in contact with the pore water at shallow depths.
The extent of dissolution decreased and the dominant precipitating mineral changed to
vermiculite over this stage. Vermiculite precipitated throughout the column and prevented the
system to reach near-equilibrium conditions, which could potentially hinder further
dissolution. At the beginning of the second stage, vermiculite started to significantly
precipitate at the bottom of the column, however, the precipitation depth decreased with time toward the surface due to the changing geochemical condition. Over the second stage vermiculite precipitated in the column up its volume fraction reached almost 10% in some parts of the column while Fe(OH)$_3$ precipitation almost stopped.

Successful modeling of the weathering and consequently the soil formation processes depends on determining the controlling parameters among several hydrogeochemical processes. Our analysis revealed that the effects of changes in specific surface area, flow rate, and availability of CO$_2$ and O$_2$ gases to interact with soil water are considerable on the overall weathering process. Among these, changes of the specific surface area induced the largest impact on both aqueous and solid phase elemental composition of soil. Model outputs matched field measurements mainly by decreasing specific surface areas of the reactive minerals up to five orders of magnitude, which can be due to dead-end pores containing near equilibrium fluid and chemical and physical heterogeneity (Li et al., 2014; Moore et al., 2012; Salehikhoo et al., 2013). The extents of the decrease in specific surface of each mineral were different, for example chlorite surface area was only reduced to 1.0 m$^2$/g from the range of 1.1-7.7 m$^2$/g that has been reported in laboratory measurements (Black and Haese, 2014; Brandt et al., 2003; Malmstrom et al., 1996) while the specific surface area of vermiculite was decreased to 6.0×10$^{-6}$ m$^2$/g from laboratory value of 0.73-17.4 m$^2$/g (Kalinowski and Schweda, 2007; Mareschal et al., 2009). The sensitivity analysis showed that decrease of specific surface areas by an order of magnitude from the matched values reduced the porosity increase from 25% to just 10%. Our results indicated that pyrite can only be depleted completely if the fluid inside the soil column is in contact with atmospheric oxygen, which pointed toward unsaturated hydrologic flow condition. In addition, the extent of weathering after pyrite depletion suggested an additional source of acidity. This source may be due to contact with atmospheric CO$_2$ or organic acid production. We accounted for this source of acidity by considering interaction between CO$_2$$_{(g)}$ and soil water. The effect of CO$_2$ was more significant on the solid phase and porosity compared to O$_2$. The cases with source of CO$_2$ showed an additional average of 8% in porosity compared to the cases without CO$_2$. However, lack of O$_2$ resulted in partial dissolution of pyrite, which significantly changed aqueous chemistry. For example, since there was no pyrite left to drop the pH in cases with
O₂, the pH was 1-3 units higher compared to those without O₂. In addition to these factors, flow rate can be of relatively lower significance. Lower flow rate resulted in lower dissolution and higher precipitation, which ultimately reduced the extent of porosity increase over the 10,000 years of simulation. Higher flow rate increased dissolution and reduced precipitation due to lack of time to reach oversaturation with respect to vermiculite. Consequently, aqueous elemental compositions and pH significantly depended on the flow rate.

Globally, shale formations account for 25% of continental lithologies (Suchet et al., 2003). Mineral dissolution releases elements important for plant growth including Ca, K, and P that sustains ecosystems (Huntington, 2000). In addition, flux of some of these dissolved elements is crucially important for the oceans (Kump et al., 2000). Our model can be incorporated to simulate large time scale weathering of shale formations and flux of the components into oceans and ecosystems. In addition, the reaction network during natural weathering on the surface is similar to the network of water-rock interaction in subsurface. Validating a geochemical model with subsurface data is practically impossible due to rock and fluid sampling limitations. Therefore, our model can be implemented to water-rock interaction in the subsurface with replacing current parameters such as equilibrium constants and rate constants with high temperature parameters. Including heavy metal trace concentrations in the mineral composition, enables us to predict, assess, and hopefully alleviate the risks associated with further development of Marcellus shale gas production. As shown here, changes of flow rate and acidity significantly change the whole geochemical system which is crucially important especially since these scenarios are possible during the fracturing process.
Chapter 5

Conclusion and Future Research

Investigating the effect of chemical and physical heterogeneities on solute transport and mineral dissolution is the main purpose of this study. In the physical heterogeneity part of the thesis, we systematically quantified the extent of non-Fickian solute transport in low heterogeneity sand box through modeling and reproducing experimental data from 2D sand boxes. We used 2D Advection-Dispersion-Equation (ADE) that explicitly incorporates the exact heterogeneity structure, a 1D ADE approach that assumes homogeneous systems using average porosity and permeability, a well-known non-local in space fADE, and the extensively used non-local in time method CTRW framework were also used. In the chemical heterogeneity part, the combined effects of physical and chemical heterogeneities on calcite dissolution were assessed through dissolution experiments in 2D flow cells followed by reactive transport modeling. We used intermediate-scale 2D flow cell experiments and numerical modeling. Injection of non-reactive tracer and pH indicator were performed to calculate physical and transport parameters and visualize the experiments, respectively. The effects of parameters such as velocity, permeability ratio, and transverse dispersivity on the dissolution process were examined as well. In the Marcellus shale weathering chapter, we used reactive transport modeling to simulate the soil formation process during Marcellus shale weathering. The code was used to identify the key controlling parameters of the weathering process.

5.1 Physical Heterogeneity

Heterogeneous distribution of physical properties in porous media affects flow and transport. Chapter two presents the first set of flow cell experiments that systematically measure the control of the correlation length on effective permeability and non-Fickian solute transport (Cortis et al., 2004; Levy and Berkowitz, 2003). Seven sand boxes (21.6 cm by 20.9 cm by 1.0 cm) were packed with sand grains of different size range in three spatial
patterns of fine and coarse zones with dimensionless correlation length varying from 0.01 to 0.45. The sandboxes had three relatively low permeability variance ($\sigma_{\ln K}^2$), 0.10, 0.26, and 0.43, respectively, for the low (LC), medium (MC), and high contrast (HC) cases. Chapter two provides a unique set of data under low permeability variance and increasing correlation length conditions where experiments have been rarely carried out. We chose to study low heterogeneity media due to their relevance in many geological settings and field sites (Leblanc et al., 1991; Mackay et al., 1986). The goal is to answer two questions: 1) How and to what extent does correlation length control effective permeability and breakthrough curves (BTC)? 2) Which model can best reproduce data under what conditions?

While the cases with short correlation length exhibited relatively low extent of non-Fickian transport, those with long correlation length showed significant tailing and non-Fickian transport. In particular, the HC One-zone (HCO) case showed distinct “steps” and stages of breakthrough arising from fast advection in the coarse zone, slow advection in the fine zone, and slow diffusion. With the same correlation length, the LCO and MCO cases did not exhibit the staged breakthrough, indicating that the permeability contrast between zones has to be sufficiently large in order for the correlation length to be important.

Four models have been used to simulate solute transport and reproduce the BTCs by minimizing the residual of logarithm concentrations. These include the 2D ADE that explicitly takes into account the heterogeneity structure, the 1D ADE that assumes homogeneous media with average porosity and permeability, and the non-local in time CTRW and non-local in space $f$ADE. Comparing these models, 2D ADE typically had the lowest deviation from data. However, it is important to note that 2D ADE is more data “expensive” because it needs the exact heterogeneity structure as part of the input. In reality, we rarely have this kind of luxury. It is interesting to note that the relative deviation $\delta_v$ of 2D ADE for the first and second moments were the largest in the HCM case that was expected to be homogeneous, which indicates the importance of the small-scale, unresolved heterogeneity in controlling the solute transport in apparently “homogeneous” media.

CTRW reproduced the data and moments well in most cases except the HCO case. This was expected because the CTRW framework involves taking ensemble average over the entire domain assuming the heterogeneity length is much smaller than the domain
(Berkowitz et al., 2006). The HCO case, however, was actually a non-stationary domain with comparable length scales of heterogeneity and the domain. It is possible that a correlated CTRW can reproduce the BTC in HCO case better, because the flow pattern in Figure 4 shows correlated flow channels. In addition, the Peclet numbers in the HCO case is $10^{3.21}$, which is within the suggested flow conditions (Pe >100) where incorporating correlation can be critical (Bolster et al., 2014).

In contrast, the fADE did not reproduce the BTC as well as CTRW in most cases. However, it reproduced the data the best among all models for the HCO case. In fact, fADE reproduces the BTC increasingly well with increasing permeability contrast. This largely confirms that fADE is strong in reproducing BTCs well with high permeability contrast and well connected media. In other cases, the conditions did not allow the formation of channels and preferential flow path so that the fADE did not do well. Stratified low permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface (Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salehikhoo et al., 2013). It is expected that fADE will work better under these conditions.

Our comparison with literature data shows that the control of correlation length on the solute transport is potentially as strong as, if not larger than, that of permeability variance. With the permeability variance of 0.43, the correlation length strongly controlled the effective dispersivity and the extent of non-Fickian behavior, with the global dispersivity $\alpha'$ varying from 0.15 cm in the HCM case to 1.96 cm in the HCO case. Similarly, $\beta$ values from CTRW varied from 1.97 in the HCM case to 1.56 in the HCO case. In the LC cases, however, the effects of the correlation length were negligible. This indicates that the permeability variance needs to be sufficiently large for correlation length to be important in determining solute transport.

Stratified low permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface (Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salehikhoo et al., 2013). Numerical studies have emphasized the importance of connectivity and correlation length in controlling solute transport. For example, Pedretti et al. (2013) concluded that the degree of stratification primarily control the late time distribution of the concentrations in convergent flow field tracer tests in realistic
three-dimensional settings. In our work, we observe significant non-Fickian transport in the HCO case with relatively low permeability variance (0.43). Existing experimental work has mostly focused on porous media with short correlation length. Our work points to the need of studying systems with comparable correlation length to the domain of interest.

5.2 Chemical Heterogeneity

In chapter 3 we presented experimental data of the effect of spatial distribution of calcite resulting in coupled physical and chemical heterogeneities on mineral dissolution in quasi-2D flow cells. The goal of this part of the study is to answer the following questions: 1) What is the extent of the effect of physical and chemical heterogeneities on mineral dissolution? 2) What are the parameters that control significance of mineral spatial pattern on overall dissolution? A total of six experiments with Mixed and One-zone spatial patterns of calcite distribution in sand at flow velocities of 1.435 m/d, 7.175 m/d, and 14.35 m/d were carried out and were numerically simulated. In addition to the experiments, numerical modeling was used to find dissolution rates of designed cases with wider range of parameters than those we were able to test experimentally.

Combination of parameters such as spatial pattern, velocity, dispersion, and permeability ratio can change mineral dissolution rates over four orders of magnitude. Rate of mass transfer is the most important parameter controlling mineral dissolution rate. Different parameters can contribute to the extent of mass transfer in porous media. Flow velocity is the most important parameter that controls rate of advective mass transfer. Under low flow velocities, transverse dispersion affects the overall mass transfer and leads to higher mineral dissolution. Spatial pattern of mineral distribution can affect large-scale mineral dissolution rates up to an order of magnitude. Due to high reactivity of calcite, dissolution rates of both Mixed and One-zone cases linearly increased with velocity. Therefore, changes of velocity did not affect the rate ratios as significantly as other parameters ($\beta_{Z/M}$ = 0.15 - 0.22). At high flow velocities a minimum $\beta_{Z/M}$ value of 0.06 was observed with low permeability ratio. Mass transfer out of the calcite zone is limited under both these conditions. However, significance
of spatial distribution changes more with changes of permeability ratio ($\beta_{Z/M} = 0.06 - 0.88$) than those of transverse dispersivity ($\beta_{Z/M} = 0.10 - 0.37$).

We compared our calcite dissolution results with previous similar studies on magnesite dissolution (Li et al., 2014; Salehikhoo et al., 2013). The effect of magnesite spatial distribution on dissolution depended more on flow velocity compare to our results for calcite. This is mainly due to considerably higher reactivity of calcite compared to magnesite. Mixed case affluent concentrations changed with velocity in the magnesite containing porous media, while they were constant in the calcite ones. Compared to calcite a higher percentage of magnesite reacted effectively due to faster calcite reaction rates and reaching equilibrium concentrations upon exposure to calcite. The highest effective surface area for calcite was under 4.5% that is considerably lower than the maximum of 100% observed in the magnesite dissolution study. Therefore, most calcite reaction occurred on the calcite-sand interface resulting in high $A_I/A_e$ values close to 100% while the highest $A_I/A_e$ in the magnesite case is 60%. The extent of changes of rate ratio $\beta_{Z/M}$ with changes of permeability ratio were similar for calcite and magnesite, since the most important parameter affecting the significance of mineral spatial dissolution on reaction rate is the amount of fluid that flows through the reactive zone not the type of mineral.

Our result indicated the importance of heterogeneous distribution of chemical and physical parameters in porous media on mineral dissolution. We observed about four orders of magnitude difference in reaction rates under reactive flow in heterogeneous porous media. Parameters such as chemical and physical heterogeneities, velocity, and fluid flow are commonly ignored in well-mixed batch reactor rate measurements. However, It has been consistently reported by many researchers that mineral dissolution rates calculated from field data are two to five orders of magnitude slower those of the well-mixed laboratory rates (Luttge et al., 2013; Maher, 2010; Maher et al., 2004; Navarre-Sitchler and Brantley, 2007; Reeves and Rothman, 2013; Swobodacolberg and Drever, 1993; White, 1995; White and Brantley, 2003). We propose spatial pattern of distribution of physical and chemical parameters as possible causes of this discrepancy. We found that mineral spatial distribution can affect reaction rates up to a factor of 20, which is important in several geochemical processes that occur over geologic time. For example, weathering and soil formation directly
depend on mineral dissolution. Understanding weathering can help us predict a wide variety of processes from atmospheric CO2 levels to species concentrations in oceans and ecosystems.

5.3 Marcellus Weathering

External fluids are being injected into the Marcellus formation during fracturing process to enhance natural gas production. Geochemical reaction system of Marcellus shale upon exposure to external fluid is relatively complex. A reliable geochemical model to simulate water-rock interaction upon exposure of Marcellus shale to fracturing fluid has not been developed yet. In this study we numerically modeled the soil formation process using elemental concentration data of soil and pore water to capture the geochemical reaction system.

Two distinct stages of weathering were distinguished over 10,000 years, before pyrite depletion and after pyrite depletion. At the first stage, within the first 500 ~ 1,000 years, pyrite dissolution released considerable amount of H\(^+\) ion into the system. Illite, chlorite, and albite dissolved due to the acidic condition and Fe(OH)\(_3\) was the main precipitating mineral. More than 2% of Fe(OH)\(_3\) precipitated at some parts of the column over this relatively short stage. After pyrite depletion, the geochemical reaction system significantly changed. The main source of acidity was CO\(_2\), which was in contact with the pore water at shallow depths. The extent of dissolution decreased and the dominant precipitating mineral changed to vermiculite over this stage. Vermiculite precipitated throughout the column and prevented the system to reach near-equilibrium conditions, which could potentially hinder further dissolution. At the beginning of the second stage, vermiculite started to significantly precipitate at the bottom of the column, however, the precipitation depth decreased with time toward the surface due to the changing geochemical condition. Over the second stage vermiculite precipitated in the column up its volume fraction reached almost 10% in some parts of the column while Fe(OH)\(_3\) precipitation almost stopped.

Successful modeling of the weathering and consequently the soil formation processes depends on determining the controlling parameters among several hydrogeochemical
processes. Our analysis revealed that the effects of changes in specific surface area, flow rate, and availability of CO\textsubscript{2} and O\textsubscript{2} gases to interact with soil water are considerable on the overall weathering process. Among these, changes of the specific surface area induced the largest impact on both aqueous and solid phase elemental composition of soil. Model outputs matched field measurements mainly by decreasing specific surface areas of the reactive minerals up to five orders of magnitude, which can be due to dead-end pores containing near equilibrium fluid and chemical and physical heterogeneity (Li et al., 2014; Moore et al., 2012; Salehikhoo et al., 2013). The extents of the decrease in specific surface of each mineral were different, for example chlorite surface area was only reduced to 1.0 m\textsuperscript{2}/g from the range of 1.1-7.7 m\textsuperscript{2}/g that has been reported in laboratory measurements (Black and Haese, 2014; Brandt et al., 2003; Malmstrom et al., 1996) while the specific surface area of vermiculite was decreased to 6.0\times10^{-6} m\textsuperscript{2}/g from laboratory value of 0.73-17.4 m\textsuperscript{2}/g (Kalinowski and Schweda, 2007; Mareschal et al., 2009).

The sensitivity analysis showed that decrease of specific surface areas by an order of magnitude from the matched values reduced the porosity increase from 25\% to just 10\%. Our results indicated that pyrite can only be depleted completely if the fluid inside the soil column is in contact with atmospheric oxygen, which pointed toward importance of considering the interaction between air and soil water deep in the soil during dry seasons condition. In addition, the extent of weathering after pyrite depletion suggested an additional source of acidity. This source may be due to contact with atmospheric CO\textsubscript{2} or organic acid production. We accounted for this source of acidity by considering interaction between CO\textsubscript{2} (g) and soil water. The effect of CO\textsubscript{2} was more significant on the solid phase and porosity compared to O\textsubscript{2}. The cases with source of CO\textsubscript{2} showed an additional average of 8\% in porosity compared to the cases without CO\textsubscript{2}. However, lack of O\textsubscript{2} resulted in partial dissolution of pyrite, which significantly changed aqueous chemistry. For example, since there was no pyrite left to drop the pH in cases with O\textsubscript{2}, the pH was 1-3 units higher compared to those without O\textsubscript{2}. In addition to these factors, flow rate can be of relatively lower significance. Lower flow rate resulted in lower dissolution and higher precipitation, which ultimately reduced the extent of porosity increase over the 10,000 years of simulation. Higher flow rate increased dissolution and reduced precipitation due to lack of time to reach oversaturation with respect to
vermiculite. Consequently, aqueous elemental compositions and pH significantly depended on the flow rate.

Globally, shale formations account for 25% of continental lithologies (Suchet et al., 2003). Mineral dissolution releases elements important for plant growth including Ca, K, and P that sustains ecosystems (Huntington, 2000). In addition, flux of some of these dissolved elements is crucially important for the oceans (Kump et al., 2000). In addition, the reaction network during natural weathering on the surface is similar to the network of water-rock interaction in subsurface. Consequently, our model can be implemented to enhance design of fracturing fluid composition to maximize porosity and permeability increase with replacing current parameters with high temperature parameters. Including heavy metal trace concentrations in the mineral composition, enables us to predict, assess, and hopefully alleviate the risks associated with further development of Marcellus shale gas production. As shown here, changes of flow rate and acidity significantly change the whole geochemical system which is crucially important especially since these scenarios are possible during the fracturing process.

5.4 Future Research

Fully understanding mineral dissolution and precipitation is essential for various applications and therefore has received an increasing amount of attention in the research community recently. Based on our findings, we suggest five research directions for future research.

First, the extent of non-Fickian flow with other than squared spatial patterns with wider permeability variance and connectively can be studied. Parameters of the non-local models CTRW and fADE can be more reliably linked to underlying heterogeneity structures and characteristics with more research along these lines.

Second, the spatial patterns tested here did not provide us with a chance to examine the effect of flow orientation on calcite dissolution. Since layered structures are common in the natural subsurface, more dissolution experiments with fluid flowing perpendicular and
parallel to narrower layered shaped reactive zone may advance our understanding of mineral dissolution in natural settings.

Third, larger and smaller flow cells may be designed to examine the effect of scale of the study on mineral dissolution, which we expect to be significant and differ under different flow regimes.

Fourth, changing calcite grain size will result in changes of permeability and specific surface area, which can affect the overall mineral dissolution significantly.

Fifth, our Marcellus shale geochemical model can be implemented in fluid flow through a network of fractures at higher temperature by changing a few parameters to simulate the reaction network of water-rock interaction upon exposure of the parent rock to fracturing fluid. This study may help us predict and alleviate the negative environmental impacts of gas production from Marcellus shale through fracturing.


Appendix 2-A. Comparison between measured data and model prediction by minimizing the residual of concentrations for 1D ADE and 2D ADE.

Figure 2-A1. Comparison of overall breakthrough data with predicted curve using 2D ADE, 1D ADE, CTRW, and fADE for (a) HCM: $\alpha_f = 1.9$, $\beta = 1.93$, $t_1 = 10^{-1.1}$ min, $t_2 = 10^{2.6}$ min, $\alpha' = 0.08$ cm, (b) HCF: $\alpha_f = 1.78$, $\beta = 1.72$, $t_1 = 10^{-0.4}$ min, $t_2 = 10^{3.4}$ min, $\alpha' = 0.47$ cm, and (c) HCO: $\alpha_f = 1.58$, $\beta = 1.56$, $t_1 = 10^{-0.4}$ min, $t_2 = 10^{3.8}$ min, $\alpha' = 1.04$ cm. Here the 1D and 2D ADE curves are obtained by minimizing the residual of concentrations, while the CTRW and fADE are still the ones from minimizing the residual of logarithm concentrations.

With the minimization of concentration residual, the 2D ADE (Equation 1) captured the BTC curves well in the HCO case up to about 2.0 pore volumes when the first two stages end. Beyond that it quickly drops and cannot capture the later tails likely caused by the diffusion process associated with unresolved heterogeneity at scales smaller than the zonation. The 1D ADE captures the “average” behavior of the BTC in HCO, as shown in Figure 2-A1 c, however not the detailed stages in the tails shown in Figure 2-A1 f. The 1D ADE obtains a large $\alpha'$ value of 1.04 cm for HCO and a much smaller value of 0.08 cm in the HCM case. These values are much smaller than the 1.96 cm and 0.15 cm, respectively, for HCO and HCM, obtained by minimization of logarithm concentration. This indicates the importance of optimization method in reproducing the BTC curves.
Figure 2-A2. Relative difference between data and modeling output ($\delta_v$) for the overall breakthrough (a), first moment (b) and second moment (c) for all models. Here the 1D and 2D ADE curves are obtained by minimizing the residual of concentrations, while the CTRW and fADE are still the ones from minimizing the residual of logarithm concentrations.

As can be observed in Figure 2-A2 a, with the concentration residual minimization, the 2D ADE has the smallest deviation from the overall breakthrough. However, its deviation from the data is much larger than the CTRW and fADE with logC residual minimization. The comparison of this figure and Figure 2-8 in the main text indicates that the ADE curves, especially 2D ADE, capture the tails much better when they are optimized by minimizing residuals of logarithm concentration.

Table 2-A1. Characteristic parameters for solute transport in sandboxes

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<tr>
<th>Cases</th>
<th>$\lambda/L$</th>
<th>$\sigma_{lnK}^2$</th>
<th>Local $\alpha$</th>
<th>Global $\alpha$</th>
<th>Global $\alpha'$</th>
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$^a$ from 2D ADE with logC residual minimization  
$^b$ from 2D ADE with C residual minimization  
$^c$ from 1D ADE with logC residual minimization  
$^d$ from 1D ADE with C residual minimization
### Appendix 2-B: raw data from sandbox experiments

#### Table 2-B1. Breakthrough data in the form of $C/C_0$

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<th>LCO</th>
<th>MCO</th>
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<td>Right</td>
<td>Left</td>
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<td>0.0000</td>
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B: raw data from sandbox experiments
Table 2-B1. Breakthrough data in the form of $C/C_0$ (continued)

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Appendix 2-B2. Flow rates from 3 different outlets of sandboxes

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Appendix 4-A: Rain Water Chemistry

Table 4-A. Rain (inlet) Water Chemistry.

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<th>Concentration (mole/l)</th>
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<tr>
<td>Na⁺</td>
<td>10⁻₅.₆₅</td>
<td>Cl⁻</td>
<td>10⁻₅.₄¹</td>
</tr>
</tbody>
</table>

Appendix 4-B: Primary and Secondary Species

Reactive transport models typically divide the species into primary and secondary species. The primary species determine the chemistry of the system and the secondary species are written in term of primary species using the equilibrium constants of instantaneous reactions. Therefore, the number of reactions that the code solves reduces to the number of the primary species instead of the number of all involved species. The reduction saves computation time extremely, which is especially important in our study that involves numerous species and runs for thousands of years. A list of the primary and secondary species used here can be found in Table 4-B.
Table 4-B. Chemical species

<table>
<thead>
<tr>
<th>Primary species</th>
<th>Secondary species</th>
<th>Secondary species</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>HCO₃⁻</td>
<td>FeHCO₃⁺</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>CO₂⁻</td>
<td>FeOH⁺</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>CaCO₃(aq)</td>
<td>H₂SiO₄²⁻</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>CaCl⁺</td>
<td>MgCO₃(aq)</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>CaCl₂(aq)</td>
<td>MgCl⁺</td>
</tr>
<tr>
<td>Na⁺</td>
<td>CaHCO₃⁺</td>
<td>MgHCO₃⁺</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>CaOH⁺</td>
<td>OH⁻</td>
</tr>
<tr>
<td>SiO₂(aq)</td>
<td>Fe(OH)₃⁻</td>
<td>Fe(OH)₂⁺</td>
</tr>
<tr>
<td>O₂(aq)</td>
<td>Fe(OH)₂⁻</td>
<td>FeOH²⁺</td>
</tr>
<tr>
<td>CO₂(aq)</td>
<td>FeCO₃(aq)</td>
<td>FeCl²⁺</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>NaCO₃</td>
<td>FeCl₂⁺</td>
</tr>
<tr>
<td>HS⁻</td>
<td>NaOH(aq)</td>
<td>FeCl₂(aq)</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₄SiO₂(aq)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
VITA
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