MINERAL SPATIAL DISTRIBUTION AND FLOW VELOCITY IN DETERMINING CALCITE DISSOLUTION RATES IN POROUS MEDIA

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ABSTRACT

This work investigates the effects of mineral spatial distribution in porous media on dissolution rates. We measured the calcite dissolution rates by using column experiments, which are packed with the same amount of calcite mass but different mineral distributed patterns in quartz-sand column (the mixed, 2-cylinder, 1-cylinder column). The scale of each column is 2.65 cm in diameter and 10 cm in length. The mixed column has a homogeneously distributed calcite in the quartz column, and the 1-cylinder/2-cylinder column confines all the calcite particles within the middle cylindrical zone(s) that is parallel to the flow injection. We flushed the columns with acidic water at various flow velocities. Experimental data show the dissolution rate of calcite is approximately 1.6 to 2 times slower in the 1-cylinder column than in the mixed column, and the rates are about 1.6-2 orders of magnitude lower under the slowest flow velocity (0.31 m/day) compared to the fast flow velocity (m/day). Ratio (α) demonstrates the mineral spatial distributed effect playing an important role in column-scale rates. This is, the mineral spatial distributed effect is more significant under the conditions with fastest flow velocity and less homogeneously distributed reactive minerals (1-cylinder column). In the 1-cylinder column, the 2-D spatial profile modeling shows that the dissolution rates are larger by orders of magnitude at the calcite-quartz interface than the central region within the middle calcite-packed zone. Also, the range of dissolving calcite area at the calcite-quartz interface becomes wider with the increasing transverse dispersivity and under fast flow velocities. In contrast, transverse dispersivity does not affect local dissolution rates in the mixed column and all the calcite are dissolving. From those observations, we infer that transverse dispersivity caused by different mineral spatial distribution controls the mass transport in transverse direction. Two calculations in effective surface area are introduced to understand the above observations: (1) total surface area ($A_T$), representing the total calcite surface area by assuming that all the calcite particles are dissolving; (2) effective surface area ($A_e$), which is the surface area of effectively dissolving calcite at the calcite-quartz interface and inlet. Column-scale bulk rates (mol/s) increase with the increasing $A_e$ values while remain irrelevant to $A_T$ values. Also, the $A_e$ values increases with the increasing flow velocities. This suggests that the different measures in the surface area and flow velocities can be the possibilities causing the discrepancies between field and laboratorial measure rates. This work provides the way to
minimize the discrepancies in order to approach the calcite dissolution rate under natural subsurface conditions. The surface area of dissolving calcite at the interface of calcite and other non-reactive minerals needs be measured first, and then the rate constant (mol/m²/s) obtained in laboratory work can be used to infer the real rates. The results from this work also compare with the literature (L. Li, Salehikhoo et al., 2013), which applied the same experimental sets but used magnesite as their reactive mineral. The both cases have the similar conclusions about the effect of mineral spatial distribution. This work systematically quantifies the impact of mineral spatial heterogeneities on dissolutions using both experimental and modeling approach.
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CHAPTER 1. INTRODUCTION

Reactive solute transport coupled with mineral dissolution and precipitation plays an important role in many geochemical and geophysical issues, such as CO$_2$ sequestration, reservoir exploitations wasted water treatments, and anything related to underground flow and transport (Bain et al., 2001; Susan L. Brantley, 2010; Chang et al., 2011; Frye, Bao, Li, & Blumsack, 2012; Goddéris, Williams, Schott, Pollard, & Brantley, 2010; Godderis et al., 2013; Hamzaoui-Azaza, Ketata, Bouhlila, Gueddari, & Riberio, 2011; Iwakun, Ulrich, Biggar, & Sego, 2012; Landrot, Ajo-Franklin, Yang, Cabrini, & Steefel, 2012; C. Liu, Zachara, Qafoku, & Wang, 2008; C. Liu et al., 2004; Kate Maher, Steefel, DePaolo, & Viani, 2006; Pruess, 2008; Spycher, Sonnenthal, & Apps, 2003; Carl Steefel & Maher, 2009; Taron & Elsworth, 2009; Zhu, 2009; Zhu & Schwartz, 2011). Because mineral dissolution is one of the most important subsurface processes, studying the mechanism and rates of mineral dissolution is essential to understand the solute transport reactions.

Mineral dissolution reactions lead to the changing in reservoir properties while doing CO$_2$ injection and or energy production, which potentially bring up the technical difficulties. For an instance, the change in apertures of fractures can cause the shifts in fluid and thermal flow paths that alter the stress condition (Pruess, 2008; Taron & Elsworth, 2009). Moreover, carbonate minerals play an important role in the CO$_2$ budget, where growth fixes CO$_2$ into a solid mineral form and dissolution releases it (Ueta, Satoh, Nishimura, Ueda, & Tsukamoto, 2013). The mineral dissolution also has a major influence on the chemistry on fluid-rock-gas interaction (Hamzaoui-Azaza et al., 2011; Zhu & Schwartz, 2011). Moreover, climate change is affected by mineral dissolution reactions. For an example, the short-term climate change is influenced by the complex behavior of carbonate dissolution/precipitation (Goddéris et al., 2010; Godderis et al., 2013). Plus, a good understanding of geochemical characteristics, in this case, mineral dissolution reactions, can provide us with the information of dealing with the contamination problems (Frye et al., 2012; Iwakun et al., 2012; C. Liu et al., 2008; C. Liu et al., 2004).

Mineral dissolution reactions have been widely studied in laboratory work by using batch reactors, which create well-mixed condition (Berger, Cadore, Schott, & Dove, 1994; Eisenlohr, Meteva, Gabrovšek, & Dreybrodt, 1999; Fahrner, Schafer, Dethlefsen, & Dahmke, 2012; C. E. Knutson, Werth, & Valocchi, 2005; Noiriel, Steefel, Yang, & Ajo-Franklin, 2012; Pokrovsky, Golubev, & Schott, 2005; Tabelin, Igarashi, & Yoneda, 2012; A. S. Taylor, Blum, & Lasaga, 2000; van Grinsven & van Riemsdijk, 1992; White, Schulz, Lowenstern, Vivit, & Bullen, 2005). It also has been studied in homogeneous packed column experiments (A. S.
Taylor et al., 2000; van Grinsven & van Riemsdijk, 1992). The field studies of mineral dissolution reaction mainly focus on weathering reactions, which are usually quantified by mineral weathering fronts (S. P. Anderson, Dietrich, & George H Brimhall, 2002; S. L. Brantley, Bandstra, Moore, & White, 2008; Susan L. Brantley & White, 2009; Brimhall & Dietrich, 1987; Casey, Banfield, Westrich, & McLaughlin, 1993; Jin et al., 2010; Lebedeva, Fletcher, Balashov, & Brantley, 2007; K. Maher, 2010, 2011; Kate Maher et al., 2006; Navarre-Sitchler & Brantley, 2007; Rowe Jr & Brantley, 1993; White Art, 2008; Zhu, 2005, 2009).

However, rates observed in laboratory work are several orders of magnitude higher than those that have been done in field (Anbeek, 1993; S. P. Anderson et al., 2002; Susan L. Brantley & White, 2009; Casey, 1987; Casey et al., 1993; Navarre-Sitchler & Brantley, 2007; Swoboda-Colberg & Drever, 1993; White & Brantley, 2003). Previous studies suggest several factors that contribute to this rate discrepancy between laboratory and field work. For example, limitations of reactive surface area in natural porous media (Anbeek, 1993; Swoboda-Colberg & Drever, 1993; White, 1995; White Art & Peterson Maria, 1990), the effect of reaction affinity (Kate Maher et al., 2006; White, 1995; White & Brantley, 2003), slow precipitation of secondary minerals (Alekseyev, Medvedeva, Prisyagina, Meshalkin, & Balabin, 1997; Kate Maher et al., 2006; Kate Maher, Steefel, White, & Stonestrom, 2009; C. I. Steefel & Van Cappellen, 1990; Zhu, Blum, & Veblen, 2004), combination of the effect of affinity, clay precipitation, and residence time (K. Maher, 2010; Kate Maher et al., 2009; Zhu, 2009), and weathering happens (Li, Peters, & Celia, 2006; Malmström, Destouni, Banwart, & Strömberg, 2000; Malmström, Destouni, & Martinet, 2004; Meile & Tuncay, 2006; Miralles-Wilhelm & Gelhar, 2000; Song & Seagren, 2008; Wood & Whitaker, 2000), the above factors are continually discussed in details in the section of literature review sections.

However, those previous studies did not consider completely enough about the impact of spatial heterogeneity in natural system. The physical and chemical properties of natural system are usually highly heterogeneous in many complex forms, such as heterogeneous mineral distribution (Landrot et al., 2012; C. Liu et al., 2008; Peng, Hu, Ewing, Liu, & Zachara, 2012; Scheibe et al., 2006). There are many studies of the influence of physical heterogeneity, which indicate that physical heterogeneity plays a significant role on controlling the transport and subsurface processes (Berkowitz, 2002; Berkowitz & Scher, 2001; Castro-Alcalá, Fernández-Garcia, Carrera, & Bolster, 2012; Cirpka, Schwede, Luo, & Dentz, 2008; Cirpka & Valocchi, 2007; Dagan, 1990; R. Allan Freeze, 1975; Gelhar, 1993; Gelhar & Axness, 1983; Gelhar, Welty, & Rehfeldt, 1992; C. Knutson, Valocchi, & Werth, 2007; C. E. Knutson et al., 2005; Werth, Cirpka, & Grathwohl, 2006; Willingham, Werth, &
Valocchi, 2008; Zinn et al., 2004).

These studies develop an extensively investigation on physical heterogeneity, such as permeability and porosity. However, studies of chemical heterogeneity compared to physical heterogeneity are relatively inadequate. Therefore, we also need to develop the understanding required for chemical heterogeneity. Mineral reactions usually include numerous chemical species that are going through non-linear reactions. Some experimental and modeling works have demonstrated that the degree of heterogeneity in porous medium controls reaction rates. For example, the local dissolution rates are a function of local geochemical conditions controlled by local spatial mineral distribution in pore scale (Landrot et al., 2012; Li et al., 2006; Li, Peters, & Celia, 2007a, 2007b; Molins, Trebotich, Steefel, & Shen, 2012). As for the relatively large scale, the dissolutions rates are determined by the total local scale dissolution rates (Li et al., 2006; Li, Steefel, & Yang, 2008; Molins et al., 2012; Navarre-Sitchler & Brantley, 2007). However, a more systematic study for the influence of mineral spatial distribution still needs to be developed.

The previous study from Salehikhoo and Li et al, 2013, has been investigated the effect of magnesite spatial distribution on dissolution rates by doing column experiments. The magnesite zone embedded in the quartz-sand particles is perpendicular to the direction of inlet solution injection. Their study indicates that the biggest difference caused by mineral spatial distribution is approximately 14%.

In this work, calcite dissolution is going to be studied in a geochemical perspective. Among many different kinds of mineral dissolutions, calcite dissolution rate is one of the most important topics to study. Carbonate mineral, especially for calcite, is a very commonly seen mineral in reservoirs or aquifers. According to the previous study, sandstone reservoirs usually contain approximately 10% calcite. For highly cemented sandstone reservoirs, it can contain approximately 16%-30% calcite (T. R. Taylor, 1990). Calcite dissolution reaction has been widely studied in batch reactor that creates well-mixed conditions (Morse & Arvidson, 2002; Noiriel et al., 2012; Pokrovsky et al., 2005; Tabelin et al., 2012; White et al., 2005). Nevertheless, there is no study about the effect of variation in geochemical conditions on calcite dissolution rates but us.

This study used three different packed columns, the mixed, one-calcite-cylinder, and two-calcite-cylinder columns, in order to give different mineral distributed patterns. All the columns were injected with solution of pH 4 under flow rates of 0.31 m/d to 18.5 m/d. Calcium breakthrough curves, tracer data, and other minor elements were collected to build a reactive transport model. From these data collection, the understanding of geochemical heterogeneity can be further investigated.
2.1 Calcite Dissolution

The previous studies of carbonate dissolution have been limited to the effect of pH or the degree of undersaturation of solution to the mineral on the mineral dissolution rate (Dibble Jr & Tiller, 1981; Gautelier, Oelkers, & Schott, 1999; Honjo & Erez, 1978; Sjöberg, 1976). They suggest that the reaction rate is pH independent if pH is over 7.5. Furthermore, $[\text{CO}_3^{2-}]$ becomes insignificant if pH is lower than 8, because the dissolution rate gets very rapid and the influence of calcite surface area will become more important in this case. They also indicate that dissolution rates obtained from experimental results are several magnitudes greater than the dissolution rates obtained from field work. Batch reactor has been commonly used in experiments to test transport-controlled and interface-controlled of minerals by changing the stirring speed or adjusting pH (Rosso & Rimstidt, 2000).

The boundary of transport-controlled and interface-controlled region changes with pH (Plummer L, Parkhurst D, & Wigley T. M, 1979). The rate is strongly affected by transport mechanism between the surface of the mineral and the aqueous solution at low pH (Berner, 1975; Plummer L et al., 1979; Plummer L. N, Wigley T. M. L, & L, 1978; Rickard & Sjöberg, 1983; Sjöberg & Rickard, 1984b). In order to demonstrate the effect of both transport-controlled and interface-controlled, the calcite dissolution model (Chou, Garrels, & Wollast, 1989; Plummer L et al., 1979), which has been studied in the laboratory under both transport-controlled and interface-controlled condition.

The region of transport-controlled and interface-controlled is classified by pH and $P_{\text{CO}_2}$ (Chou et al., 1989; Pokrovsky et al., 2005; Pokrovsky, Golubev, Schott, & Castillo, 2009). In Figure 2, for $\text{pH} < 3.5$, which is also the low pH region, dissolution rate is dominated by transport. This region is controlled by reaction (1). In the meantime, calcite dissolution is characterized by a very low activation energy that is consistent with transport control. In this transport-controlled region, dissolution rate is fast enough that transport limits the rate, and the concentration of dissolved products in the aqueous solution layer around the dissolving calcite (the boundary layer) reaches the equilibrium concentration.

In contrast, for $\text{pH} > 3.5$, the rate is interface-controlled and the interfacial reaction is slower than transport (Figure 1), meaning that transport is not the dominant driving force in controlling the rate in this region anymore. Instead, diffusion is taking place at this stage. The speed of diffusion across the boundary layer is relatively faster than the rate of the interface reaction. The concentration of solutes in the layer is equal to the bulk concentration, but this
value is lower the equilibrium value. Finally, for pH > 5.5, precipitation reaction occurs in this region and also to be considered as important (Plummer L. N et al., 1978).

Furthermore, there are other studies that have been investigated the controlling factors of dissolution kinetics. For example, Figure 2 demonstrates the relationship of calcite dissolution kinetics, pH, and temperature dependence (Sjöberg & Rickard, 1984b). It shows that dissolution in the higher pH region is more dependent upon solution chemistry and $P_{CO_2}$. In their study, calcite dissolution kinetics are summarized in terms of solution pH and temperature. It basically follows the structure that has mentioned in the previous paragraph but with the additional temperature dependence involved. Three sections are classified as follows: (1) H$^+$-dependent, (2) transition, (3) and H$^+$-independent regime (Figure 2).

![Figure 1](image1.png)

**Figure.** Calcite dissolution rates versus pH at 298K and different CO$_2$ partial pressures. (Alkattan, Oelkers, Dandurand, & Schott, 2002; Busenberg & Plummer, 1982; Chou et al., 1989; Plummer L. N et al., 1978; Rickard & Sjöberg, 1983; Shiraki, Rock, & Casey, 2000; Sjöberg, 1978; Sjöberg & Rickard, 1984b). (Figure compiled by A. Zimmerman).

In Figure 2, it shows the role of temperature and pH on calcite dissolution kinetics, and it also demonstrates the boundaries for each section. Diffusion boundary layer (DBL) adjacent to the mineral surface controls mineral dissolution reaction in aqueous solutions (Z. Liu & Dreybrod, 1997). The boundaries of H$^+$-dependent, transition, and H$^+$-independent section locate around pH 4.0 and 5.5 at 25°C (Plummer L. N et al., 1978; Sjöberg & Rickard, 1984b). H$^+$ can pass through the diffusion boundary layer (DBL) under low temperatures, and then the boundaries move to higher pH levels.
When transport process becomes more dominant, the boundaries will move to lower pH under a condition of high temperatures. The variations in boundaries are greater at low temperatures due to the exponential nature of the temperature dependence. Also, H⁺-independent section and its boundaries are ionic strength dependent (Rickard & Sjöberg, 1983).

Transport-controlled factor gradually increases its importance when temperature goes up, while the interface-controlled factor becomes more dominant under lower temperatures. Besides, there are also many other factors that affect calcite dissolution in natural systems. Transport-controlled factor will be more precisely described by with restricted flow in the much smaller scale in environments, such as the pore spaces of rocks. Many studies (Erga and Terjesen, 1956; Terjesen et al., 1961; Nestaaas and Terjesen, 1969; Morse and Berner, 1972; Berner and Morse, 1974; Sjoberg, 1978) have extensively investigated the effects of inhibitions on the reaction kinetics. The inhibitory contaminant concentrations are commonly found in analytical grade reagents, since the dissolution rates are very sensitive to inhibitors. It is very likely to affect dissolution rates (Sjöberg, 1978).

**Figure. 2** Summation of calcite dissolution kinetics in terms of solution pH and temperature. DBL represents the Diffusion Boundary Layer (Sjöberg & Rickard, 1984b).

Other research also indicates different methods in the surface area measurement, such as BET surface area-normalized and geometric surface area-normalized can result in the variable results in dissolution rates (Cubillas, Köhler, Prieto, Chaïrat, & Oelkers, 2005). Moreover, the influence of dislocations and surface morphology in calcite dissolution has been investigated (MacInnis & Brantley, 1992).
2.2 Dissolution Rates in Laboratory Studies and Field Studies

Studies of dissolution reactions have been extensively investigated by field and laboratory work in different perspectives. Calcite is chosen in this work due to its importance regarding to natural reservoirs or aquifers. Sandstone reservoirs usually contain approximately 10% calcite. For highly cemented sandstone reservoirs, the level of calcite proportion can reach approximately 16%-30% (T. R. Taylor, 1990). However, the discrepancy between laboratory-measured and field-measured dissolution rates has been reported in many studies. The laboratory-measured dissolution rates are usually 2-5 orders of magnitude higher than the field-measured rates (Blum & Stillings, 1995; Hochella & Banfield, 1995; Kate Maher et al., 2006; Navarre-Sitchler & Brantley, 2007; Noiriel et al., 2012; Swoboda-Colberg & Drever, 1993; White & Brantley, 2003). The discussion in literatures regarding the field and laboratory studies are introduced in the following section.

Field Studies

In natural system, the quantification of mineral dissolution rates are usually done by the observation of weathering profile development. Observation and quantification in mineral depletion fronts are commonly used to conduct the dissolution rates in field (S. P. Anderson et al., 2002; S. L. Brantley et al., 2008; Susan L. Brantley & White, 2009; Brimhall & Dietrich, 1987; Casey et al., 1993; Jin et al., 2010; Lebedeva et al., 2007; K. Maher, 2010, 2011; Katharine Maher, DePaolo, & Lin, 2004; Kate Maher et al., 2006; Navarre-Sitchler & Brantley, 2007; White Art, 2008; Zhu, 2005, 2009). By observing the weathered profile and spatial variation, they can quantify the loss of mass and chemical element in sediment and further calculate dissolution rates (S. P. Anderson et al., 2002). In Maher et al., (2004) study, they calculated the dissolution rates by using U isotopes in pore fluid from sediment samples in field (Katharine Maher et al., 2004). The study of Zhu, (2005) and Rowe & Brantley, (1993) point out that it is hard to constrain the natural system, and the natural dissolution rate can be calculated by multiplying the samples of water fluxes in watershed and solute concentration in rivers.

Laboratory Studies

Calcite dissolution reaction has been widely studied in laboratory experiments by using batch reactor or parallel-flow through reactor, which create well-mixed conditions (Morse & Arvidson, 2002; Noiriel et al., 2012; Pokrovsky et al., 2005; Svensson & Dreybrodt, 1992; Tabelin et al., 2012; White et al., 2005). In the well-mixed environment, the dissolution rates
can be calculated by measuring changes in solution composition. Calcite dissolution rates also have been investigated in other different perspectives, including the effect of variable hydrodynamic conditions on dissolution kinetics, such as CO₂ partial pressure, pH, and temperature (Alkattan, Oelkers, Dandurand, & Schott, 1998; Alkattan et al., 2002; Arvidson, Ertan, Amonette, & Luttge, 2003; Plummer L. N et al., 1978; Pokrovsky et al., 2005; Pokrovsky et al., 2009; Shiraki et al., 2000; Sjöberg, 1978; Sjöberg & Rickard, 1984a, 1984b). In addition, the literatures studied the variation in measurement of surface speciation (Pokrovsky et al., 2005; Sjöberg & Rickard, 1983; Sjöberg & Rickard, 1984a) and the effect of observation of mineral dissolution rates in field work and laboratory work, and the variation in calcite dissolution rates under the different scales and heterogeneity in physical properties (Li et al., 2006; Li et al., 2008; Malmström et al., 2000; Noiriel et al., 2012; Yoon, Valocchi, Werth, & Dewers, 2012; Zhang et al., 2010; Zinn et al., 2004).

**Rate Discrepancy**

The discrepancy between laboratory an field-measured dissolution rates have been reported and investigated in many literatures. The laboratory-measured dissolution rates are usually 2-5 orders of magnitude higher than the field-measured rates (Blum & Stillings, 1995; Hochella & Banfield, 1995; Kate Maher et al., 2006; Navarre-Sitchler & Brantley, 2007; Noiriel et al., 2012; Swoboda-Colberg & Drever, 1993; White & Brantley, 2003). The literatures found out that the discrepancy can be caused by many factors: (1) differences in reactive surface area in natural porous media and prepared in laboratory, (2) the effect of reaction affinity (Kate Maher et al., 2006; White, 1995; White & Brantley, 2003), (3) precipitation of secondary minerals (Alekseyev et al., 1997; Casey et al., 1993; Kate Maher et al., 2006; Kate Maher et al., 2009; C. I. Steefel & Van Cappellen, 1990; Zhu et al., 2004), (4) the much lower fluid/mineral ratios in natural system compared to the higher fluid/mineral ratios in laboratory (Casey et al., 1993; White & Brantley, 2003; Zhu, 2005), (5) combination of the effect of affinity, clay precipitation, and residence time (K. Maher, 2010; Kate Maher et al., 2009; Zhu, 2009), (6) the age of weathering (Li et al., 2006; Katharine Maher et al., 2004; Malmström et al., 2000; Malmström et al., 2004; Meile & Tuncay, 2006; Miralles-Wilhelm & Gelhar, 2000; Song & Seagren, 2008; Wood & Whitaker, 2000), and (7) different scales and heterogeneity in physical properties (Li et al., 2006; Li et al., 2008; Malmström et al., 2000; Noiriel et al., 2012; Yoon et al., 2012; Zhang et al., 2010; Zinn et al., 2004).

In natural subsurface system, dissolution reactions usually get involved with solute transport and flow, and the above factors affect the dissolution reactions at different extent. In
addition, the natural subsurface system is very complex with highly heterogeneous properties, such as permeability and mineral spatial distribution. The change in the heterogeneous properties will significantly affect the dissolution reaction (Chen, Hubbard, & Rubin, 2001; Fetter, 1999; R. A. Freeze & Cherry, 1979; Gelhar, 1993; Gelhar et al., 1992; Hubbard & Rubin, 2000; Li, Gawande, Kowalsky, Steefel, & Hubbard, 2011; K. Maher, 2010; Rubin & Gómez-Hernández, 1990). However, the related discussions for heterogeneity are relatively inadequate compared to the influence of the above factors.

2.5 Physical and Geochemical Heterogeneities

The hydro-geological and geochemical conditions in subsurface systems, such as aquifers, oil and gas reservoirs, are greatly affected by flow and transport processes. The flow and transport are affected by the change in properties of spatial heterogeneity in natural subsurface system. The heterogeneity in subsurface can be classified into two parts: (1) physical heterogeneities, and (2) geochemical heterogeneities. Both physical and geochemical heterogeneities vary with the spatial distribution in the natural subsurface system. The change of physical properties, such as permeability or hydraulic conductivity, will change the flow velocity and further change the residence times (Chen et al., 2001; Fetter, 1999; R. A. Freeze & Cherry, 1979; Gelhar, 1993; Gelhar et al., 1992; Hubbard & Rubin, 2000; Newell, Hopkins, & Bedient, 1990; Rubin & Gómez-Hernández, 1990). On the other hand, the variation in geochemical properties, such as reactive mineral spatial distribution, will affect significantly on the local geochemical conditions (Dentz, Gouze, & Carrera, 2011; Dentz, Le Borgne, Englert, & Bijeljic, 2011; Li et al., 2011; Li et al., 2006, 2007a; Li, Steefel, Kowalsky, Englert, & Hubbard, 2010; Malmström et al., 2004; Molins et al., 2012; Noiriel, Madé, & Gouze, 2007; Noiriel et al., 2012; Plummer L et al., 1979; Salehikhoo, Li, & Brantley, 2013; Scheibe et al., 2006; Tompson, Schafer, & Smith, 1996).

Plus, the concentration of large numbers of aqueous and solid components, ranging over several orders of magnitude and multiplying fronts, can separate zones of distinct geochemical heterogeneity (Walter, Frind, Blowes, Ptaček, & Molson, 1994). The studies of physical heterogeneities affect flow and transport processes have been extensively discussed (Berkowitz, 2002; Berkowitz & Scher, 2001; Castro-Alcalá et al., 2012; Cirpka et al., 2008; Cirpka & Valocchi, 2007; Dagan, 1990; R. Allan Freeze, 1975; Gelhar, 1993; Gelhar & Axness, 1983; Gelhar et al., 1992; C. Knutson et al., 2007; C. E. Knutson et al., 2005; Werth et al., 2006; Willingham et al., 2008; Zinn et al., 2004). However, the researches about the role of geochemical heterogeneities plays in the reactive transport processes have not been done a lot compared to the studies of physical heterogeneities (Cirpka et al., 2008; Dentz,
Cortis, Scher, & Berkowitz, 2004; Dentz, Gouze, et al., 2011; Dentz, Le Borgne, et al., 2011; Glassley, Simmons, & Kercher, 2002; Li et al., 2011; Li et al., 2006, 2007a, 2007b; Li et al., 2010; C. Liu et al., 2008; Meile & Tuncay, 2006; Navarre-Sitchler & Brantley, 2007; Salehikhoo et al., 2013; Scheibe et al., 2006; Tompson et al., 1996; Werth et al., 2006; Willingham et al., 2008; Yabusaki et al., 2011; Yoon et al., 2012; Zhang et al., 2010).

However, the understanding of the impact of variation in geochemical properties in subsurface still remains insufficient. In other words, the influence of geochemical heterogeneity in subsurface on mineral dissolution rates needs to be investigated developed systematically.

Chapter 3. Methodology

The methodology can be roughly classified into two parts: (1) three types of column experiments, and (2) reactive transport modeling part. There are several tests, such as ICP-AES analysis and XRD analysis, all should have been done before we do the column experiments. Therefore, we can make sure that the samples we used are in high purity. Also, Brunauer-Emmett-Teller (BET) test needs to be done in order to get the information of surface area of the calcite samples. The column experiments were conducted by three types of columns, which are well-mixed quartz-calcite column, two-calcite-cylinder column, and one-calcite-cylinder column. The experiments acquired the information of effluent calcite concentrations. The overall mineral dissolution rates at column scale were determined by the data of effluent calcite concentrations. The reactive transport modeling was applied to confirm the results from the previous column experiments, which predicts local in-situ rates for each grid block of columns.

3.1 Column Experiments

Column experiments are used in this work to investigate the influence of these control factors, including mineral spatial distribution, flow velocity, and different minerals. The final results are determined by the effluent Ca(II) concentrations, which have been taken from column experiments to calculate overall dissolution rates at the column scale. The length of column is 10.5 cm and the diameter is 2.65 cm. We used three different types of columns, which were packed with the same total amount of calcite in the same total amount quartz matrix. These three types of columns are the well-mixed, two-cylinder, and one-cylinder columns, as shown in Figure 3. The volume of calcite within the total solid volume was 11.0% ± 0.5%. The mineral grain sizes were between 225 to 350 μm.
3.2 Mineral Preparation

ICP-AES and XRD Analysis
Inductively coupled plasma emission spectrometry (ICP-AES) is an analytical technique that employs the emission spectroscopy to detect trace metals. It consists of two parts: From the results of ICP-AES, there is 0.17% Mg, 0.05% each of Na and Sr, and 0.001% Si in the calcite sample, which means the calcite sample is high purity. X-ray diffraction analysis (XRD) also confirmed the composition of the calcite samples, which also showed that the calcite samples contained no other detectable crystalline phases.

Mineral Processing
After the calcite composition is tested by the ICP-AES and the XRD analysis, calcite sample needs to be grounded and sieved into grain size 225 to 350 um. After that, the grains are soaked it into 1% HCl solution to remove impurities. The surface of calcite particles is treated as the same procedure as stated in Chou et al. (1989). Using ultrasonic machine to clean the sample in acetone in order to get rid of fine particles. The samples are later soaked in distilled water for a few times, and then dry them in the oven for several hours.

3.3 Mineral Spatial Distribution
The study uses three columns with different spatial distribution of calcite. They are the (1) well-mixed, (2) two-calcite-cylinder, and (3) one-calcite-cylinders columns (Figure. 3). The well-mixed column consists of uniformly distributed calcite and quartz. The first column intends to create a scenario that has the highest interphase contact area with reactive mineral and non-reactive mineral. In this case, calcite grains represent reactive mineral and quartz represent non-reactive mineral. In the one calcite cylinder column, calcite grains are two calcite cylinders column, calcite grains are distributed in two individual cylinders, which are embedded in the non-reactive quartz column.
3.4 Column Packing

Wet packed method is used in the column packing process, which is using solution contained $10^{-3}$ M NaCl in deionized water to put into column when incremental masses of quartz are added into the column. The geometric distribution of the calcite and quartz for the three columns is showed in Figure 3. In the well-mixed column, calcite and quartz particles are uniformly distributed in the column. In the one calcite-cylinder column, there is one calcite-cylinder zone in the central of column, creating two regions in the column. One is a vertical reactive mineral cylinder and the rest part in the column is quartz sand matrix. (Figure. 4A). Calcite particles are focused in the central vertical zone and quartz sand particles are filled in the rest part of the column. As for the two calcite-cylinder column, the column contains two individual calcite-cylinders and creates two vertical reactive mineral zones. (Figure. 4B) Calcite particles are distributed in the vertical zones and the rest part of the column is filled with quartz sand particles. The three columns are sealed with caps and also use frit to keep the porous media in place.
3.5 Solution Injection Experiments

The columns are flushed with initial solution contained $10^{-3}$ M NaCl in deionized water with pH adjusted with NaOH to 9. After the flushing procedure is done, the columns are injected with inlet solution flowing vertically from bottom to top. The inlet solution consists of $10^{-3}$ M NaCl in deionized water with pH adjusted with HNO$_3$ to 4 and 10 ppm potassium bromide as a non-reactive tracer. The experiments are tested under room temperature (~22°C). The experiment tests five different flow velocities ranging from 0.31 to 18.5 m/d. 12 residence times are collected in effluent samples. Ca(II) concentration in effluent samples are tested by ICP-AES.

3.6 Physical Properties Tests

All the columns are packed with the same wet packing methods, so the physical properties of these columns are supposed to be very similar. In order to calculate the physical properties for each column, several tests are conducted to verify the assumption. There are BET analysis, permeability test, porosity test, and tracer analysis, and the details are discussed in the following sections.

BET Analysis

The BET analysis is a widely employed method to measure the specific surface area of solids, which is a process that measures the adsorption of gas molecules on a material solid phase. Nitrogen gas (N$_2$) is usually used to measure the specific surface in BET analysis. The BET
theory is the extension of the Langmuir theory that describes the monolayer molecular adsorption to the multilayer molecular adsorption under several conditions: (1) infinite layers of gas molecules can absorb onto a solid surface, (2) no interactions between adsorbed, and (3) the Langmuir theory can be used to describe each layer. The BET theory is defined as:

\[
(V(P_0 / P - 1))^{-1} = (C - 1)(V_m C)^{-1} x(P / P_0) + V_m C \quad \text{Eq. 1}
\]

Where \( V \) is the volume of absorbed gas, \( V_m \) is volume of gas absorbed in a monolayer, \( P \) is the equilibrium pressure of absorbing gas at a designated temperature, and \( P_0 \) is the saturation pressure of absorbing gas at a designated temperature, and \( C \) is the BET constant.

The specific surface area can be described as follows:

\[
S_{\text{BET, total}} = \frac{V_m N s}{V} \quad \text{and} \quad S_{\text{BET}} = \frac{S_{\text{total}}}{a} \quad \text{Eq. 2}
\]

Where \( S_{\text{total}} \) is the total surface area, \( V_m \) is monolayer molar volume of absorbed gas, \( N \) is Avogadro’s number, \( V \) is molar volume of absorbed as, \( s \) is adsorption cross section of absorbing species, and \( a \) is the mass of the absorbent.

**Permeability Test**

Darcy’s law is applied to calculate permeability of these three columns, and it is described by the following equation:

\[
Q = k A \left( \frac{P_{\text{bottom}} - P_{\text{head}}}{L} \right) \quad \text{Eq. 3}
\]

Where \( Q \) (ml/min) is flow rate, \( k \) (m\(^2\)) is permeability, \( A \) (m\(^2\)) is surface area of column, \( \mu \) (Pa* s) is viscosity of solute, \( P_{\text{bottom}}, P_{\text{head}} \) (Pa.) represents pressure for the bottom and head of column, and \( L \) is the length of column. A pressure gauge (Crystal Engineering, XP2i-DP) is used to measure the pressure for both ends of column under flow rates of 0.3, 0.5, and 1.0 (ml/min), which can measure a 15 psi differential pressure with a precision of 0.001 psi. In order to make sure the pressure has reached its steady-state condition, each flow rate have to stay at the same for 15 minutes for a differential pressure to stabilize. The DI water is used as inlet solution, so the viscosity of solute is \( 10^{-3} \) (Pa*s). The diameter of column is 2.56 cm and
the length of column is 10 cm. After these parameters are obtained, the permeability (k) can be calculated.

**Porosity Test**

The porosity is calculated by the porosity equation, which is the ratio between volume of void space and bulk volume. The porosity equation is expressed as follows:

$$\phi = \frac{V_{\text{void}}}{V_{\text{bulk}}} \quad \text{Eq. 4}$$

Where $\phi$ is porosity, $V_{\text{void}}$ is the total volume of void space, and $V_{\text{bulk}}$ is the total bulk volume.

In the column experiments, the porosity is the volume fraction of void. It can be determined by the total volume of calcite particles, quartz particles, and column. The way to calculate porosity can be written in the following expression:

$$\phi = 1 - \frac{V_{\text{calcite}} + V_{\text{quartz}}}{V_{\text{column}}} \quad \text{Eq. 5}$$

Where $V_{\text{calcite}}$ is the total volume of calcite particles, $V_{\text{quartz}}$ is the total volume of quartz particles, and $V_{\text{column}}$ is the volume of column.

**Tracer Analysis**

Tracer analysis is commonly used to determine physical characteristics and flow movement in reservoirs or aquifers. The criteria of selecting tracer are the low cost, ease of detection, low sorption and nonreactive with other species. The ionized tracer, which is added into the solution, will increase the electrical conductivity in the solution in order to be detected by electrodes. Also, the non-reactive tracer does not reactive with other species so it will not affect the reactions. Therefore, tracer analysis is extensively used to obtain physical properties of flow transportation, such as dispersivity, which is also used in our study. In this study, sodium bromide (10ppm) was employed as the tracer to obtain the dispersivity coefficients.

The dispersivity is a physical property of a media that quantifies the effective diffusion. There are two kinds of dispersivity, one is longitudinal dispersivity ($a_L$) and transverse dispersivity ($a_T$).

The sodium bromide was injected under flow rate of 3.6 m/d. The samples were collected every 0.33 residence times for 2.5 residence times. Using simulation approach by
CrunchFlow to match the effluent bromide breakthrough curve, which will be interpreted in details in the section of reactive transport modeling.

3.7 Reactive Transport Modeling

3.7.1 Reactions and Species and Reactive Transport Equations

Reactive transport modeling is used to match column experimental effluent data and to infer local “in situ” rates in each grid block. To understand the solute transport movements in the column experiments, the reactions and the aqueous species that participate in the reactions have to be known in the first place. Calcite dissolution kinetics reactions and aqueous speciation reactions occur simultaneously in the column experiments. Calcite dissolution kinetics reactions can be described in the following pathways:

\[
\text{CaCO}_3(s) + H^+ = \text{Ca}^{2+} + \text{HCO}_3^-
\]

\[
\text{CaCO}_3(s) + \text{H}_2\text{CO}_3^* = \text{Ca}^{2+} + 2\text{HCO}_3^-
\]

\[
\text{CaCO}_3(s) = \text{Ca}^{2+} + \text{CO}_3^{2-}
\]

The aqueous reactions, which are the fast reactions and also consider as at their equilibrium state, are also involved in the system. They are written as the following forms:

\[
\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-
\]

\[
\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-
\]

\[
\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}
\]

\[
\text{CaHCO}_3^+ = \text{Ca}^{2+} + \text{HCO}_3^-
\]

\[
\text{CaCO}_3^{(aq)} = \text{Ca}^{2+} + \text{CO}_3^{2-}
\]

Therefore, the species that participate in the reaction are Na\(^+\), Cl\(^-\), Br\(^-\), H\(^+\), OH\(^-\), SiO\(_2\)(aq), Ca\(^{2+}\), CaHCO\(_3\), CaCO\(_3\)(aq), H\(_2\)CO\(_3\), HCO\(_3\)\(^-\), and CO\(_3\)\(^{2-}\). These species can be categorized as primary species and secondary species according to their reaction rate. In this study, Na\(^+\), Cl\(^-\), Br\(^-\), H\(^+\), SiO\(_2\)(aq), Ca\(^{2+}\), and H\(_2\)CO\(_3\) are considered as primary species. The other species are considered as secondary species, because they can be written in terms of primary species using the mass action law of the fast reactions. The values of rate constant are listed in Table. 1. We used the values in Chou et al., 1989 as the reference and adjusted them to match the simulation. The details are discussed in Chapter 3.7.3. The equilibrium constants used in the model are from EQ3/6 database.
In the simulation, all the codes are written to satisfy the general mass transport equations, which can be written in terms of primary species concentration, and the following equation represents the reactive transport modeling:

$$V \frac{\partial (\phi C_{Ca(II)})}{\partial t} = V \nabla \cdot (\phi D_{Ca(II)} \nabla C_{Ca(II)}) - V \nabla \cdot (\phi u C_{Ca(II)}) + r_{CaCO_3} A \quad \text{Eq. 6}$$

Where $V$ represents the total volume of the porous media (m$^3$), $\phi$ is the porosity, $C_{Ca(II)}$ represents the summation of Ca(II) concentration (mol/m$^3$) in $Ca(II)$, $CaHCO_3^+$, and $CaCO_3(aq)$, $D_{Ca(II)}$ is the dispersion coefficient (m$^2$/s), $u$ is the flow rate (m/s), and $A$ is the surface area of calcite (m$^2$). The 2-D (two-dimensional) reactive transport modeling is the extension in terms of the Eq. 6. The simulation by using CrunchFlow is to solve the 2-D Advection-Dispersion Equation (Noiriel et al.), which can be expressed as follows:

$$\frac{\partial (C_{Ca(II)})}{\partial t} = D_L \frac{\partial^2 C_{Ca(II)}}{\partial x^2} + D_T \frac{\partial^2 C_{Ca(II)}}{\partial y^2} - v_x \frac{\partial C_{Ca(II)}}{\partial x} - v_y \frac{\partial C_{Ca(II)}}{\partial y} + r_{CaCO_3} A \quad \text{Eq. 7}$$

Where $C_{Ca(II)}$ is the total concentration of all species that contain Ca(II) (M), which is the summation of the concentrations of $Ca^{2+}$, $CaHCO_3^+$, and $CaCO_3(aq)$, $v$ is the advection flow velocity (m/s), $x$ and $y$ are the locations at the perpendicular direction (m), $t$ is reaction time (s), and $A$ is the calcite surface area per unit pore volume (m$^2$/m$^3$ pore volume). The $r_{CaCO_3}$ (mol/m$^2$/s) is the dissolution rate law of calcite given in the Eq. 7. $D_L$ and $D_T$ are longitudinal and transverse dispersion coefficients (m$^2$/s), which are listed as follows:

$$D_L = D^* + \alpha_L v_x \quad \text{Eq. 8}$$
$$D_T = D^* + \alpha_T v_y$$

Where $D^*$ is the effective diffusion coefficient (m$^2$/s), $\alpha_L$ and $\alpha_T$ are the longitudinal and transverse dispersivity (m). Moreover, the reaction follows the Transition State Theory (TST) based rate law:

$$r_{CaCO_3} = \left( k_1 a_{H^+,i} + k_2 a_{HCO_3^-,i} + k_3 \right) \left( 1 - \frac{IAP}{K_{eq}} \right) \quad \text{Eq. 9}$$
Where $k_1$, $k_2$, and $k_3$ values are rate constants, $a_{H^+}$ and $a_{H2CO_3^*}$ are the activities of hydrogen ion and carbonate acid, $IAP$ is the ion activity product, and $K_{eq}$ is the equilibrium constant for $CaCO_3(s)$. The reactive transport modeling is used to simulate column experiment.

**Table. 1 Chemical parameters used in the models**

<table>
<thead>
<tr>
<th>Aqueous speciation (at equilibrium)</th>
<th>Log $K_{eq}$</th>
<th>$k_1,k_2,k_3$(mol/m²/s, rate constant in this work)</th>
<th>$k_1,k_2,k_3$(mol/m²/s, rate constant in Chou et al., 1989)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O = H^+ + OH^-$</td>
<td>-14.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$H_2CO_3 = H^+ + HCO_3^-$</td>
<td>-6.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$HCO_3^- = H^+ + CO_3^{2-}$</td>
<td>-10.33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$CaHCO_3^+ = Ca^{2+} + HCO_3^-$</td>
<td>-1.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$CaCO_3(aq) = Ca^{2+} + CO_3^{2-}$</td>
<td>-3.33</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Kinetic reaction (log $K$ value is log $K_{sp}$ value)**

| $CaCO_3(s) + H^+ = Ca^{2+} + HCO_3^-$ $(k_1)$ | - | $3.16 \times 10^{-5}$ | $8.9 \times 10^{-1}$ |
| $CaCO_3(s) + H_2CO_3^* = Ca^{2+} + 2HCO_3^-$ $(k_2)$ | - | $3.2 \times 10^{-6}$ | $5.0 \times 10^{-4}$ |
| $CaCO_3(s) = Ca^{2+} + CO_3^{2-}$ $(k_3)$ | - | $2.0 \times 10^{-9}$ | $6.5 \times 10^{-7}$ |
3.7.2 Physical Parameters in Columns

The overall physical properties are showed in the following Table 2:

<table>
<thead>
<tr>
<th>Columns</th>
<th>Calcite (gram)</th>
<th>Quartz (gram)</th>
<th>$a_L$ (cm)</th>
<th>$a_T$ (cm)</th>
<th>$k \times 10^{-14}$</th>
<th>BET (m$^2$/g)</th>
<th>Ave. porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed</td>
<td>14.901</td>
<td>75.822</td>
<td>0.085</td>
<td>0.0085</td>
<td>6.13±0.18</td>
<td>0.115±0.0022</td>
<td>0.398</td>
</tr>
<tr>
<td>2-cylinder</td>
<td>13.991</td>
<td>75.220</td>
<td>-</td>
<td>-</td>
<td>6.08±0.16</td>
<td>0.115±0.0022</td>
<td>0.403</td>
</tr>
<tr>
<td>1-cylinder</td>
<td>14.966</td>
<td>76.801</td>
<td>0.1</td>
<td>0.036*</td>
<td>8.22±0.19</td>
<td>0.115±0.0022</td>
<td>0.426</td>
</tr>
</tbody>
</table>

* The value of $a_T$ is 0.002 under the flow velocity of 0.31 m/d.

**Dispersivity Determination**

The other purpose of tracer analysis is to acquire the value of dispersivities by matching the bromide breakthrough curves from tracer analysis and the modeling as well. CruchFlow software was used to complete the reactive flow transportation modeling part. The values of longitudinal dispersivity ($a_L$) and transverse dispersivity ($a_T$) can be obtained after the two bromide breakthrough curves are matched. The values of longitudinal dispersivity ($a_L$) for the mixed and 1-cylinder columns are 0.085 and 0.1, respectively. However, the change in transverse dispersivity ($a_T$) did not affect the matching results of bromide breakthrough curves in the mixed column. Laboratory values of the transverse-to-longitudinal dispersivity ratio ($a_T/a_L$) from literatures range from 0.04 to 0.2 (M. P. Anderson & Cherry, 1979; R. A. Freeze & Cherry, 1979; Kim, Jo, Kim, & Jury, 2004; Klotz, Seiler, Moser, & Neumaier, 1980). In this work, we used a typical transverse-to-longitudinal dispersivity ratio ($a_T/a_L$) 0.1 to obtain the value in transverse dispersivity (Kim et al., 2004). Therefore, transverse dispersivity value was suggested to be 0.0085 cm for the mixed column.

In contrast, in the 1-cylinder column, the variation in transverse dispersivity significantly change the outcome of tracer matching and effluent Ca(II) matching. The bromide and effluent Ca(II) breakthrough curves at flow velocity 3.6 m/d can get the best match when transverse dispersivity is 0.036. However, the matching results are really different when we apply the laboratory values of the transverse-to-longitudinal dispersivity ratio ($a_T/a_L$) from literatures mentioned before, which transverse dispersivities range from 0.0072 to 0.072. This change in the results of breakthrough matching demonstrates that
transverse dispersivity affect the reactive transport significantly. In addition, the value of $\alpha_T$ changes with the variation in flow velocity. The details will be discussed in the Chapter 3.7.3 and Chapter 4.

**Permeability and Porosity**

In order to obtain permeability, the pressure gauge (XP2i-DP, Crystal Engineering pressure gauge) was applied to measure pressure, which can measure a 15 psi differential pressure with a precision of 0.001 psi. The pressure gradients along the columns were measured with flow rates of 0.3, 0.5, and 1.0 ml min$^{-1}$). For the mixed, 2-cylinder, and 1-cylinder column, the permeability is $6.13 \times 10^{-14}$, $6.084 \times 10^{-14}$, and $8.22 \times 10^{-14}$ (m$^2$), respectively. The average porosity in this study is the empirical factor in this study, which is determined by the ratio between the mineral volume and column volume in each column. The values are confirmed by the water volume that filled in the pore space of each column.

**Different Surface Area Calculations ($A_T$, $A_e$, $A_l$)**

The definitions of these three different types of surface area need to be done first: (1) Total surface area ($A_T$); (2) Effective surface area; (3) Interface surface area. The total surface area ($A_T$) is analysis by the BET test that shows the calcite particles have a specific surface area of 0.115 m$^2$/g. The graph results can be found in the appendix. $A_T$ is the product of 0.115 m$^2$/g and calcite mass in different column, and it remains constant in the individual column.

The effective surface area ($A_e$) presents the surface area of calcite particles that actually dissolve in column. Therefore, these calcite particles do not reach the equilibrium state and have obviously higher local dissolution rates compared to others. $A_e$ is calculated by multiplying the effectively dissolving calcite mass (g) and BET surface area (m$^2$/g). The mass of dissolving calcite particles are determined by the data of 2-D spatial profile simulation. For the case of 1-cylinder column under the flow velocity of 3.6m/d, the way to calculate the amount of dissolving calcite mass by counting the particles with the local IAP/Keq < 0.5. The standard of IAP/Keq < 0.5 will change with the different flow velocity. As for the mixed column, $A_T$ is equal to $A_e$ because all the calcite particles are assumed to dissolve in the well-mixed environment.

The interface surface area is the idea of how much effective surface area is at the quartz-calcite interface. By introducing the idea of interface surface area, we can examine how much the calcite particles at the interface are contributing to the effective dissolving calcite particles. For the mixed column, the values of $A_T$, $A_e$, and $A_l$ are the same because all the calcite particles are assumed to be dissolving. For the 1-cylinder column, the first two grid
blocks at the interface are the main target we have to considerate. We calculate the calcite particles with the value IAP/Keq < 0.5 in the first two grid blocks of the interface.

3.7.3 Numerical Simulation

The calculations in the study are computed by the code CrunchFlow. CrunchFlow is a software for modeling flow and transport processes, which has been used to understand many complex geochemical systems (Carl Steefel, 2008; Carl Steefel & Maher, 2009). The initial and inlet conditions are set to simulate the calcite-quartz column experience, which are resente in Table 2. The volume fraction of calcite is approximately 11% in the mixed column and the calcite mineral is uniformly distributed in the quartz matrix. The portion of calcite in 2-cylinder and 1-cylinder columns is also 11%, but the calcite is packed as two cylinders and one cylinder that are surrounded by quartz matrix in each column. From the cross-section of the column in Figure. 5, each can be divided into 25×100 blocks, and the length of each block is 0.1 cm.

![Figure. 5 The cross-section in the column](image)

The simulations are consistent of four parts: the (1) total flow velocity, (2) tracer (Br⁻), (3) breakthrough curves of effluent Ca(II) concentration, and (4) 2D spatial profiles for local geochemical conditions. In the first part, the permeability test needs to be done first in order to narrow down the possibility of pressure range. Each grid block has its own block flow rate, and the summation of each block flow rate will be equal to the initial flow rates. The increase or decrease in permeability/pressure will change the model total flow rate. As such, the values
of pressure and permeability are modified within the measure range to get the match with the initial flow rate.

The purpose of the tracer analysis is to confirm that the models and experiments share similar physical properties. As such, the physical parameters are adjusted in the models to get the match of the tracer (Br⁻) experiment in the second part. The physical characteristics include porosity, surface area, permeability and dispersivity. Among all these characteristics, the porosity, surface area, and permeability are already obtained in the previous column experiments and total flow velocity simulation, and the calcite surface area has been tested by the BET test, which is 0.115 m²/g. The dispersivity is the only physical parameter needed to be adjusted. The longitude dispersivity ($\alpha_L$) for the mixed and 1-cylinder column is 0.085 and 0.2, respectively.

In the third part, the results of effluent Ca(II) concentration simulation should match the effluent Ca(II) concentration data from experiments by adjusting the rate constants of calcite dissolution reaction ($k_1$, $k_2$, $k_3$) in Eq. 9. The original rate constants used in this work are referred in Chou et. al., (1989), which are $k_1$, $k_2$, and $k_3$ values are $8.9 \times 10^{-1}$, $5.0 \times 10^{-4}$, and $6.5 \times 10^{-7}$ (mol/m²/s), respectively. In the mixed column, the original value of $k_1$, $k_2$, and $k_3$ are modified to new values of $3.16 \times 10^{-5}$, $3.2 \times 10^{-6}$, $2.0 \times 10^{-9}$ (mol/m²/s), because the original values would lead to the extreme high data in the Ca(II) breakthrough simulation, which do not match the effluent Ca(II) data in experiments. In contrast, the rate constants do not affect the Ca(II) breakthrough data in simulation for the 1-cylinder column. Instead, the transverse dispersivity ($\alpha_T$) turns out to be the factor affecting the Ca(II) breakthrough data matching for the 1-cylinder column. The value of transverse dispersivity ($\alpha_T$) is adjusted to 0.036 for the 1-cylinder column to match the Ca(II) breakthrough data from experiments. On the other hand, the value of transverse dispersivity ($\alpha_T$) does not change the outcome of Ca(II) breakthrough simulation in the mixed column. The details of the effect of transverse dispersivity ($\alpha_T$) are discussed in the Chapter 4.3.

After the physical and chemical parameters are all determined, the parameters (Table. 3) are used to conduct 2D spatial profiles simulation in order to infer the local geochemical conditions in columns. By observing the 2D spatial profiles, the variation in the local Ca(II), saturation state, pH, and rate can be successfully described. The discussion of 2D spatial profile is introduced in the following section of discussion.
Table 3 Initial and inlet conditions

<table>
<thead>
<tr>
<th></th>
<th>Initial Conditions</th>
<th>Inlet Conditions</th>
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</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
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<td>4.0</td>
</tr>
<tr>
<td><strong>OH</strong></td>
<td>1.0E-5 M</td>
<td>1.0E-10 M</td>
</tr>
<tr>
<td><strong>Ca^{2+}</strong></td>
<td>1.3E-4 M</td>
<td>0.0 M</td>
</tr>
<tr>
<td><strong>Na^{+}</strong></td>
<td>1.0E-3 M</td>
<td>1.0E-3 M</td>
</tr>
<tr>
<td><strong>Cl</strong></td>
<td>1.0E-3 M</td>
<td>1.0E-3 M</td>
</tr>
<tr>
<td><strong>Br</strong></td>
<td>0.0 ppm</td>
<td>10 ppm</td>
</tr>
<tr>
<td><strong>HCO_{3}^{-}</strong></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>CO_{3}^{2-}</strong></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>CaCO_{3(aq)}</strong></td>
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<td>0.0 M</td>
</tr>
<tr>
<td><strong>CaHCO_{3}^{+}</strong></td>
<td>Changeable</td>
<td>0.0 M</td>
</tr>
<tr>
<td><strong>SiO_{2(aq)}</strong></td>
<td>0.0 M</td>
<td></td>
</tr>
<tr>
<td><strong>CO_{2(aq)}</strong></td>
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<td>3.6E-4 M</td>
</tr>
<tr>
<td><strong>Calcite</strong></td>
<td>~11% (14.96 g)</td>
<td>0 g</td>
</tr>
<tr>
<td><strong>Quartz</strong></td>
<td>~ 89% (76.8 g)</td>
<td>0 g</td>
</tr>
</tbody>
</table>

3.8 Quantification of Dissolution Rates at Different Scales

According to the simulation mentioned previously, the column is divided into many grid blocks. The local dissolution rates are calculated within each grid block. After the local rates in every grid block are determined, the column-scale rates can be derived by the summation of local rates in each grid block. The influence of mineral distribution can be quantified by the calculation of rates.

3.8.1 Local In-situ Dissolution Rate

The local in-situ dissolution rates for the grid block \(i\) are mentioned in the above Eq. 9, which is listed follows:

\[
r_{CaCO_3} = \left(k_1a_{H^{+},j} + k_2a_{H_2CO_3^{+},j} + k_3\right)\left(1 - \frac{IAP_{j}}{K_{eq}}\right)
\]

Where \(r_{CaCO_3}\) represents the dissolution rate of \(CaCO_3\), \(a_{H^{+}}\) and \(a_{H_2CO_3^{+}}\) are the activities of
hydrogen ion and carbonate acid, \( IAP_i \) is the ion activity product, and \( K_{eq} \) is the equilibrium constant for \( \text{CaCO}_3(s) \). The local in-situ dissolution rate is varied based on spatially distributed and the aqueous movements.

### 3.8.2 Column-Scale Dissolution Rates

The steady-state column-scale reaction rates \( R_{\text{CaCO}_3} \) (mol/m\(^2\)/s) are computed as follows:

\[
R_{\text{CaCO}_3} = \frac{Q_T}{A_T} \left( C_{\text{Ca(II)},\text{out}} - C_{\text{Ca(II)},\text{in}} \right) \quad \text{Eq. 10}
\]

Where \( Q_T \) is the total flow rate (m\(^3\)/s), \( C_{\text{Ca(II)},\text{out}} \) and \( C_{\text{Ca(II)},\text{in}} \) are the concentrations of Ca(II) in the outlet and inlet of the column experiments (mol/L). In the experiment, the value of \( C_{\text{Ca(II)},\text{in}} \) is zero because the inlet solution does not contain any calcium ion. \( A_T \) is the total surface area of calcite in the whole column (m\(^2\)), \( r_{\text{CaCO}_3, j} \) is the rate at the grid block \( i \) and is determined according to the equation mentioned in 2.3.1, and \( A_i \) is the local calcite surface area at grid block \( i \).

The meaning of the steady-state column scale reaction rates come from the mass continuity of the whole system. From the above equation, the column scale dissolution rates equal to the summation of local in-situ rates in each grid block \( (r_{\text{CaCO}_3, j} \times A_i) \) divided by the total surface area \( A_T \). The equation describes the fact that the column scale rates are the area-averaged local scale rates.

### 3.8.3 Quantification of the Effects of Mineral Spatial Distribution

The way to quantify the effect of mineral spatial distribution is using ratio between column-scale reaction rates from the three columns, and the equation of ratio \( \alpha \) is as follows:

\[
\alpha = \frac{R_{\text{CaCO}_3,1\text{-cylinder}}}{R_{\text{CaCO}_3,\text{Mixed}}} = \frac{C_{\text{Ca}^{2+},\text{out},1\text{-cylinder}} - C_{\text{Ca}^{2+},\text{in},1\text{-cylinder}}}{C_{\text{Ca}^{2+},\text{out},\text{Mixed}} - C_{\text{Ca}^{2+},\text{in},\text{Mixed}}} \quad \text{Eq. 11}
\]

Where \( R_{\text{CaCO}_3,1\text{-cylinder}} \) and \( R_{\text{CaCO}_3,\text{Mixed}} \) are the column-scale reaction rates, which are calculated by using Eq. 10 for the 1-cylinder column and the Mixed column. In Eq. 10, \( Q_T \) and \( A_T \) are cancelled out because they are the same value. The Ca(II) inlet concentration in this
experiment is zero for the all columns. The ratio $\alpha$ value can be calculated by the difference of effluent Ca(II) concentration. The low $\alpha$ ratio indicates the greater effect in mineral spatial distribution. If the $\alpha$ ratio is close to 1, the effect of mineral spatial distribution is less important.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Effects of Mineral Spatial Distribution

Figure. 6 (A) Experimental and modeling breakthrough curves of tracer (bromide). The dots show the experimental results of the breakthrough curves for the mixed, 2-cylinder and 1-cylinder columns. The lines indicate the modeling results. The flow rate is 3.6 m/d with a residence time of 16 min.

Bromide was used as the non-reactive tracer in the column experiments. In Figure 6 A, the tracer breakthrough curves obtained from experimental data in the three columns (the mixed, 2-cylinder, and 1-cylinder column) share very similar trend that the three tracer breakthrough curves are almost overlapped, suggesting very similar physical properties of the columns. Moreover, the model outputs of the mixed and 1-cylinder column, also give the results of overlapping tracer breakthrough curves, which confirms that all the columns have similar outcome in terms of physical properties. The overlapping lines, which represent the tracer data conducted by model output, demonstrating the similar physical properties in the columns, such as average porosity.

The general performance of the three columns under flow rate 3.6 m/d is presented in...
Figure 7. Figure 7A shows the three columns share the similar trend in effluent Ca(II) concentrations but different degree of Ca(II) dissolutions, and they reach steady-state Ca(II) concentration after approximately two residence times. The mixed column has the higher steady-state effluent Ca(II) concentration (approximately $1.8 \times 10^{-4}$ M) than the 2-cylinder (approximately $1.1 \times 10^{-4}$ M) and 1-cylinder column (approximately $9.6 \times 10^{-5}$ M), which indicates the higher dissolution rates in the mixed column. The effluent Ca(II) concentration in Ca(II) in the 2-cylinder column is slightly higher than in the 1-cylinder column, which means the dissolution rates in 2-cylinder column is slightly greater than in 1-cylinder column. The difference in dissolution rates of the three columns demonstrates the effect of mineral spatial distribution: when reactive mineral grains are more homogeneously distributed (i.e., the mixed column), the higher dissolution rates they will be. The degree of homogeneously distributed of calcite mineral in mixed column is greater than in the 2-cylinder and 1-cylinder columns. As such, the mixed column has the higher dissolution rates and therefore the higher values in the effluent Ca(II) concentrations compared to the other two columns.

In the 2-cylinder column, there are two calcite zones are distributed in the sand matrix while the 1-cylinder column only has one calcite zone in the sand matrix. However, the difference in Ca(II) concentration between the 2-cylinder and 1-cylinder columns is relatively small, which may be due to the fact that the two calcite cylinders in the column is too close to each other. As such, the effect of two cylinders distribution does not make a significant difference in terms of the Ca(II) effluent concentrations. The trend of pH breakthrough curves in Figure 7B is consistent with the Ca(II) breakthrough curve in Figure 7A. The higher Ca(II) effluent concentrations mean the consumption in hydrogen ion is greater, and it leads to the decrease in pH. The Ca(II) dissolution in the mixed column is greater than the 2-cylinder and 1-cylinder column, and therefore the decrease in pH is also more significant.
Figure. 7 The breakthrough curves of Ca (II), pH, Mg(II), and Na. The dots show the experimental results of mixed, 2-cylinder and 1-cylinder columns under the flow rate 3.6 m/d with a residence time of 16 min. (A) Ca (II), (mol/L), (B) pH (C) Mg(II), (mol/L), (D) Na, (mol/L).

In order to infer the local dissolution rates and geochemistry, reactive transport modeling is applied to show the simulated 2-D spatial profile of Ca(II) concentration, pH, IAP/Keq, and local dissolution rates at steady-state condition for the mixed and 1-cylinder column under flow velocity 3.6 m/d. The model and experimental data of the 2-cylinder columns are very similar to the 1-cylinder column, so we chose to do the predicted 2-D spatial profile of the 1-cylinder column as representative. The parameters used in both columns are obtained from the previous model output in tracer and effluent Ca(II) breakthrough curves. The left and right figure of each pair in Figure 8 are for the mixed and 1-cylinder column, respectively.

In the mixed column (Figure 8, left), it shows the increasing values in Ca(II) and pH along the direction of injection flow, and therefore the value of IAP/Keq reaches 1 close to the outlet. The value of 1 in IAP/Keq means the equilibrium state is reached at the end of the column. According to Eq. 10, the local dissolution rates have correspondingly decreasing values by 1-2 orders of magnitude from inlet to outlet. Because calcite particles are distributed homogeneously, the dissolution occurs everywhere in the column without the transport limitation.
In the 1-cylinder column (Figure. 8, right), calcite particles are distributed in the middle calcite-cylinder zone. Therefore, there are increasing values in Ca(II) and pH in the middle zone along the direction of injection flow, indicating the reactions mainly happen in the middle zone. The increasing values in Ca(II) lead to the increasing values from 0~1 in IAP/Keq in the middle zone. The saturation index (IAP/Keq) close to 1 means that the equilibrium conditions is reached in the middle zone except for the inlet area. Correspondingly, the local dissolution rates decrease by 1~2 orders of magnitude due to the increasing values in Ca(II) in the middle zone. Also, the values of IAP/Keq in the region of inlet and calcite-quartz interface are close to 0, suggesting the calcite particles are dissolving in this region. Accordingly, the local dissolution rates in the region of inlet and calcite-quartz interface are 1-2 orders of magnitude higher than the lowest local dissolution rates close to the regions with local equilibrium state. In addition, the Ca(II) concentration in the quartz-sand zone is much more lower (from nearly 0 to 1 x 10⁻⁴ M) than in the calcite-distributed zone, suggesting the reactions barely take place within this zone.

In Figure C and D (right), the gradients along the horizontal direction are found at the calcite-quartz interface in the 1-cylinder column, while the same conditions do not exist in the mixed column. The gradients are likely resulted from the mass transport at the calcite-quartz interface. In other words, the gradients depend on how fast Ca(II) and carbonate can be transported between the calcite and quartz region. From this observation, we infer that there is a transport limitation in the calcite dissolution reactions within the 1-cylinder column. As such, the heterogeneous mineral distribution establishes a mass transport limitation, which is perpendicular to the direction of injection flow. In addition, the area of the concentration and rate gradients are found to be affected by transverse dispersivity and will be discussed in details in Chapter 4.3.

Figure. 8 Predicted 2-D spatial profile of local geochemistry and dissolution rates at steady-state for the mixed (left of each pair) and 1-cylinder (right of each pair) column: (A) Ca (II) concentration (mol/L), (B) pH, (C) IAP/Keq, and (D) Log rate (the local calcite rates
in each grid block in the units of mol/m²/s), under flow rate of 3.6 m/d. The vertical axis is the distance along with the column (0-100 mm), and the horizontal axis is the diameter of the column (0-25 mm).

In Figure 7 C, the trend Mg(II) breakthrough curve is reverse from what we observed in Ca(II) breakthrough (Figure 7 A). The 1-cylinder column has the highest effluent Mg(II) concentration at steady state and the mixed column has the smallest. However, the previous study of magnesite dissolution rate (Li, Salehikhoo, Brantley, & Heidari, 2013) states that the Mg (II) breakthrough curve shared the similar trend with the Ca(II) breakthrough curve that showed in Figure 7 A. The main difference between Li, Salehikhoo,* Brantley and Heidari, (2013) study and this study is the mineral that we used, and the previous one used the magnesite samples, which Mg(II) was their dominant composition. In our study, however, Ca(II) was the main composition of the calcite samples, and the portion of Mg(II) is approximately 0.17%. It means the fraction of Mg(II) is very small compare to Ca(II) in the calcite samples. The calcite dissolution reaction will be inhibited by the presence of magnesium cations (Mg(II)) under high pH (8.0–9.0), according to the previous study (Compton & Brown, 1994). From their study, it indicates that there are two possible reasons causing this situation. First, the inhibitor, which is Mg (II) in this case, could adsorb at a lattice site and prevent the transfer of CaCO₃ between the adsorbed state on the crystal lattice. Second, general adsorption of the inhibitor on the crystal surface may occur, so that the adsorbed inhibitor will compete with the adsorption of Ca (II). This action leads to the reducing in the amount of the latter on the surface. Also reducing the number of empty adsorption sites that can receive calcium or carbonate ions dissolving from lattice.

In the study, the same calcite samples are applied to the three column experiments, so the portion of magnesium should be the same. However, the outcome of the Mg(II) breakthrough curves are opposite from the Ca(II) breakthrough curves may due to the difference in mineral spatial distribution. In the mixed column, the calcite particles were distributed in a more evenly way, so there would be more Mg(II) getting involved in the inhibition action. On the other hand, for the 1-cylinder and 2-cylinder column, the calcite particles were much less homogeneously distributed compare to the mixed column, so Mg(II) participating in inhibition action in the 1-cylinder and 2-cylinder column is much less than in the mixed column. Therefore, the dissolving Mg(II) in the 1-cylinder and 2-cylinder column is larger than in the mixed column, which can be showed in Figure 18 C.
4.2 Effects of Flow Velocity and Column-scale Dissolution Rates

The overall performance of the mixed columns under four different flow rates is presented in Figure 9. In Figure 9 A, the four velocities reach the steady-state effluent Ca(II) concentrations after approximately two residence times. The highest Ca(II) effluent concentrations occur at the flow velocity of 0.31 m/d, indicating that the highest dissolution rates happen under slow flow rate. The effluent Ca(II) concentration of flow velocity 18.5, 0.31 m/d at steady state is 1.3 x 10^{-4} M and 2.0 x 10^{-4} M, respectively. The effluent Ca(II) concentration for high flow velocity of 18.5 m/d is lower than the slow flow velocity of 0.31 m/d, and this is because the slower flow velocity can lead to the longer residence time. Moreover, The Ca(II) dissolutions are greater under the slower flow velocities because of the effluent Ca(II) concentrations are higher. In Figure 9 B, the overall pH value of the slowest flow rate 0.31 m/d is slightly lower than the fastest flow rate 18.5 m/d. This phenomena is also consistent with the performance of effluent Ca(II) concentration in Figure 9 A. The consumption in hydrogen ion is larger when the Ca(II) effluent concentration is higher, which leads to the decrease in pH value. Reactive transport modeling is also used here to infer the influence of flow velocity on the local geochemistry and dissolution rates.

The simulation of 2-D spatial profile in Ca(II) concentration, pH, IAP/Keq, and local dissolution rates at steady-state for the 1-cylinder columns under flow velocity of 3.6 m/d,
0.31 m/d are shown in Figure 10. The top figures (Figure 10 A-D) represent 3.6 m/d and the bottom figures are for 0.31 m/d. In the mixed column, the values in Ca(II), pH, and IAP/Keq are increasing from the inlet to the outlet, and the degree of increase depends on the flow velocity. In the meantime, the local dissolution rates decrease by 5 orders of magnitude under the flow velocity of 0.31 m/d (bottom) along the direction of injection flow, while the rates only decrease by 1 order of magnitude under the flow velocity of 3.6 m/d. For the 1-cylinder column (Figure. 10, right), the values in Ca(II), pH, and IAP/Keq under both velocities are increasing in the middle part, and the values in local dissolution rates are correspondingly decreasing.

However, the degree of changing are different under different flow velocity. For example, the region with IAP/Keq close to 0 is wider at the inlet for the flow velocity of 3.6 m/d than velocity of 0.31 m/d. The values of IAP/Keq close to 0 indicate that the reactions are still happening and therefore the calcite particles are dissolving. The larger regions with IAP/Keq close to 0 under velocity of 3.6 m/d suggests the different mass of dissolving calcite particles. On the other hand, there are more local regions in middle zone reach the equilibrium state under the velocity of 0.31 m/d except for the interface and inlet. In other words, the less calcite particles are dissolving at the interface and inlet under the velocity of 0.31 m/d than 3.6 m/d. This shows the different degree of transport limitation at the calcite-quartz interface under different flow velocity, which also demonstrates the flow velocity can affect the degree of mass transport. This conclusion can also be confirmed by doing the breakthrough curves matching simulation to acquire the value of $\alpha_T$. The value of $\alpha_T$ is 0.036 for the 1-cylinder column under the velocity of 3.6 m/d while is 0.002 under the velocity of 0.31 m/d (Table. 2).
Figure 10 Predicted 2-D spatial profile of local geochemistry and dissolution rates at steady-state for the mixed and 1-cylinder column under flow velocities of 3.6 m/d (top row) and 0.31 m/d (bottom row). (A) Ca (II) concentration (mol/L), (B) pH, (C) IAP/Keq, and (D) Log rate (the local calcite rates in each grid block in the units of mol/m²/s). The vertical axis is the distance along with the column (0-100 mm), and the horizontal axis is the diameter of the column (0-25 mm).

In Figure 9C, the slowest flow rate has a generally higher effluent concentration in Mg(II), and the fastest flow rate has a lower effluent Mg(II) concentration, which also demonstrates the fact that the reaction time is longer for the slowest flow rate than the fastest flow rate. The trend of Mg (II) breakthrough curves are similar to the results in the work of Li, Salehikhoo, Brantley and Heidari (2013), and it will be elaborated in the following section.

The average effluent Ca(II) concentration under different log flow velocities (0.31, 3.6, 7.2, 18.5 m/d in terms of log flow rate is -1.105, 0.56, 0.86, 1.26 m/d, respectively) depicts the performance of calcite dissolution under different flow velocities in Figure 11. The average effluent Ca(II) concentration was calculated when effluent Ca(II) concentration reaches steady-state. The values of average effluent Ca(II) concentration decreases with the increasing flow velocities for the three columns. For the mixed, 2-cylinder, and 1-cylinder column, the average effluent Ca(II) concentration starts from 2.0 x 10^{-4} M to 1.45x 10^{-4} M, 1.8 x 10^{-5} M to 9.5 x 10^{-5} M, 1.4 x 10^{-5} M to 8.04 x 10^{-5} M, and 1.3 x 10^{-4} M to 7.9 x 10^{-5} M, respectively, with the decreasing flow velocities in logarithm scale range from -1.105 m/d to 1.26 m/d. Generally speaking, the average effluent Ca(II) concentrations are higher under
slow flow velocities, because the residence times for the slow flow velocities are long and allow reactions having more time to occur. This is also consistent with the Figure 9 A.

![Figure 11](image)

**Figure. 11** Average effluent Ca(II) concentrations for columns as a function of flow velocities in log values (-1.105, 0.56, 0.86, 1.26 m/d in log v are for 0.31, 3.6, 7.2, 18.5 m/d, respectively) under steady-state condition.

The column-scale rates are performed in Figure 12 A, they become greater with the increasing flow rates, which is opposite to the trend in Figure 11. Equation 10 explains the results of this scenario. The column rate is the product of effluent concentration and flow velocity, and the high flow velocity can still get the greater column rates even the effluent concentration is relatively lower. The local dissolution rates for flow velocity 0.31 m/d (Figure 10 D, bottom), they are 1-5 orders of magnitude higher at the region of inlet and calcite-quartz interface than the regions with local equilibrium state. On the other hand, for flow velocity of 3.6 m/d (Figure 10 D, top), the region with the higher local dissolution rates are concentrated at the interface and inlet. From this observation, we can see the area with the higher local dissolution rates at higher flow velocity (3.6 m/d) is bigger than the slower flow velocity (0.31 m/d), which indicates that the overall column-scale dissolution rate of high flow velocity is larger than low velocity. This observation is consistent with the local dissolution rates showed in Figure 12 A. Also, rates from 1-cylinder column are lower than those from the mixed column by approximately a factor of 0.2 – 2.
Figure 12 (A) Column-scale rates as a function of flow velocities in logarithm scale, -1.105, 0.56, 0.86, 1.26 m/d in logarithm scale are for 0.31, 3.6, 7.2, 18.5 m/d, and (B) the $\alpha$ ratio of the column-scale rates between the 2-cylinder, 1-cylinder columns and the mixed column as a function of flow velocities in logarithm scale.

The $\alpha$ value is the ratio between the column-scale rates of the three columns (Equation 11), which indicates the effect of mineral spatial distribution on column-scale rates. The $\alpha$ ratio is calculated based on the difference of effluent Ca(II) concentration and the flow velocity. A low $\alpha$ ratio suggests that column-scale rates of the 1-cylinder or 2-cylinder column is very different from the mixed column, indicating that mineral zonation distribution has an significant influence on column-scale rates. On the contrary, when the $\alpha$ ratio is close to 1, it means that the column-scale rates are not significantly affected by the mineral spatial distribution. In other words, mineral spatial distribution can be considered to be less important compared to those cases that have low values in $\alpha$ ratio. The general performance of the $\alpha$ ratio under different flow velocities is presented in Figure 12 B. For the $\alpha$ ratio between the 2-cylinder and mixed column, it starts from 0.79 at flow velocity of 0.31 m/d and decreases to 0.61 with the increasing flow velocity. This is likely because the diffusion process toward the homogenization of concentration is getting important when the long residence times occur due to the low flow velocities. Low flow velocities also bring to the local equilibrium condition and therefore the influence of mineral spatial distribution will be less relevant. As for the $\alpha$ ratio between the 1-cylinder and mixed column, it basically follows the same trajectory as the 2-cylinder column but the $\alpha$ ratio decreases from 0.72 to 0.5 with the increasing flow velocities, determining that there are more discrepancies among the columns with the increasing flow velocities.
4.3 Effects of Transverse Dispersivity

Figure 13 Sensitivity of the Ca(II) breakthrough curves to transverse dispersivity values ($\alpha_T$ values of 0.0072, 0.036, and 0.072 cm) for the mixed column (left) and the 1-cylinder column (right) under flow velocity of 3.6 m/d. The transverse dispersivity used in the model are referred in the literatures (M. P. Anderson & Cherry, 1979; R. A. Freeze & Cherry, 1979; Kim et al., 2004; Klotz et al., 1980)

In Figure 13 (left), the three model outputs are overlapped, suggesting the effluent Ca(II) breakthrough curves are not sensitive to the variation in transverse dispersivity values ($\alpha_T$) in the mixed column, because there is no concentration gradient in the horizontal direction that is vertical to the main flow. For the 1-cylinder column (Figure 13, right), $\alpha_T$ values control the effluent Ca(II) concentration data in the simulation. This is not surprising because the $\alpha_T$ is the parameter representing how much the mass transport is along the horizontal direction. The 1-cylinder column creates a transport limitation at the quartz-calcite interface, which makes the horizontal transport much more difficult than the well-mixed column. In the 1-cylinder column, only the calcite dissolution inside the middle zone reaches equilibrium, and the dissolution rates are restricted by how easy the mass transport is between two zones.

Figure 13 shows the effect of $\alpha_T$ on the effluent Ca(II) concentration for the 1-cylinder column. A value of $\alpha_T$ of 0.0072 cm results in much lower effluent Ca(II) concentrations, and a value of 0.036 cm has the best match with the experimental data, while the model output of a value of 0.072 cm are close to the experimental data in the mixed column. In the Figure 13, we found that transverse dispersivity ($\alpha_T$) is a very crucial factor for the 1-cylinder column when it comes to the Ca(II) breakthrough curves matching. The reason why transverse
dispersivity is important for fitting the Ca(II) breakthrough data, is because when calcite
dissolution reaches equilibrium condition in the middle calcite-cylinder zone, the rate of
dissolution is limited by how fast the mass transport is between the quartz-sand matrix and
calcite-cylinder zone.

Figure 14 shows spatial profiles of the effect of $\alpha_T$ on the effluent Ca(II) concentration
for the mixed and 1-cylinder column. The variation in $\alpha_T$ does not change the outcome of 2-D
spatial profile simulation in the mixed column. For the 1-cylinder column, however, it does.
When $\alpha_T$ is 0.0072 (cm), the mass transport is much more difficult at the calcite-quartz
interface compared to the larger $\alpha_T$ values. As such, the transport is more confined within the
middle part and further cause the more concentrated high values in Ca(II) and IAP/Keq in the
middle zone. In other words, there is a larger region with local equilibrium condition under $\alpha_T$
of 0.0072 (cm). Correspondingly, the region with minimum local rates are 2-3 orders of
magnitude lower than those with maximum local rates.

In contrast, a value of 0.072 (cm) in $\alpha_T$ leads to a relatively easier mass transport in
dissolution processes at the calcite-quartz interface, which further brings the larger region of
non-zero values in Ca(II) and smaller values in IAP/Keq compared to the $\alpha_T$ value of 0.072
(cm). This indicates the region of non-equilibrium state is larger in the $\alpha_T$ value of 0.0072
(cm). The values in local dissolution rate for $\alpha_T$ value of 0.072 (cm) are correspondingly
higher than the $\alpha_T$ value of 0.0072 (cm). This is because the higher rates only exist when the
reactions are still happening. In other words, the higher local dissolution rates can be found in
the region with non-equilibrium state. The region with non-equilibrium state for $\alpha_T$ value of
0.072 (cm) is larger than $\alpha_T$ value of 0.0072 (cm), which leads to the higher local dissolution
rates under the larger $\alpha_T$ value. For example, a value of 0.072 (cm) in $\alpha_T$ leads to a relatively
fast mass transport in dissolution within the calcite-cylinder zone, and the area with high
values ($> 1.4 \times 10^{-4}$ M) in Ca(II) concentration is larger compared to the other two $\alpha_T$ values.
The larger area with high Ca(II) concentration results in larger areas with higher IAP/Keq
values and higher local dissolution rates, which are also wider compared to the other two
smaller $\alpha_T$ values.

The middle calcite-distributed zones for the three $\alpha_T$ values reach local equilibrium
conditions except the region of interface and inlet. At the region of calcite-quartz interface
and inlet, there are the region with IAP/Keq close to 0 along the horizontal direction,
indicating the dissolving calcite particles grains exist at the interface and inlet. The larger
value in $\alpha_T$ leads to the bigger region with IAP/Keq close to 0, while the smaller value in $\alpha_T$
has a smaller region with IAP/Keq close to 0. It turns out that the transverse dispersivity will
affect the amount of actual dissolving calcite, and the amount of dissolving calcite will further
change the calculation in surface area. It brings out the other important discussion of effective surface area instead of total surface area.

Therefore, the transverse dispersivity can be considered as a way to measure how fast the transverse mass transport is at the interface. Moreover, it is also the key parameter to determine the effective surface area that quantifies the effectively-dissolving calcite surface area. By acknowledging the influence of the transverse dispersivity, it reinforces the importance of transverse mixing in terms of determining rates, which has been studied by other previous studies. For instance, calcite precipitation, has been shown to be controlled by the extent of transverse mixing in 2-D model subsurface sedimentary system (i.e., micro-model) and in 2-D flow through experiments (Tartakovsky, Redden, Lichtner, Scheibe, & Meakin, 2008; Zhang et al., 2010)

**Figure. 14** Spatial profiles of Ca(II) concentration (first row), IAP/Keq (second row), and local dissolution rates (third row) in the mixed column (the first left one in each row) and in the 1-cylinder column with three transverse dispersivity values ($a_T$) of 0.0072, 0.036 and 0.072 cm. These are for the flow velocity of 3.6 m/d. The vertical axis is the distance along
with the column (0-100 mm), and the horizontal axis is the diameter of the column (0-25 mm).

$A_e$ and $A_I$ respectively represent the surface area of effectively dissolving calcite particles and calcite particles located at the quartz-calcite interface. $A_T$ is the total surface area of all calcite particles. The values of $A_e$ and $A_T$ are equal in the mixed column because all the calcite particles are evenly distributed, so every calcite particle can react with the pore fluid and reach steady-state eventually. In contrast, not every calcite particle dissolves in the 1-cylinder or 2-cylinder column due to the horizontal transport limit at the quartz-calcite interface. For the all three columns, the value of $A_T$ are the same, which are calculated by the product of BET and total calcite mass ($0.115 \text{ m}^2/\text{g} \times \text{calcite mass in the different column}$).

The ratio $A_e/A_T$ represents that how many calcite particles are effectively dissolving. The ratio $A_I/A_e$ shows that how many the effectively dissolving calcite particles are at the interface. The data in Figure. 15 are obtained from the 1-cylinder column simulation under flow velocity of 3.6 m/d with the changing values in transverse dispersivity ($a_T$). In the 1-cylinder column, the $A_T$ value remains the same and equals to 1.72 ($\text{m}^2$) ($0.115 \text{ m}^2/\text{g} \times 14.97 \text{ g}$).

For Figure. 15 A, the values of $A_e$ and $A_I$ become higher with increasing ($a_T$). This fact indicates the larger $a_T$ would make the horizontal transport more effectively and therefore the amount of effectively dissolving calcite would increase. Both $A_e$ and $A_I$ increase faster when $a_T$ is higher than $10^{-2.5}$, demonstrating dispersion is the process controlling this faster transport under $a_T$ higher than $10^{-2.5}$. On the other hand, the diffusion is more dominant when $a_T$ is lower than $10^{-2.5}$ due to the slow increase in $A_e$ and $A_I$, which is illustrated in Eq. 8. As such, the portion of $A_I$ in $A_e$ increases faster when $a_T$ exceeds $10^{-2.5}$. This indicates that the horizontal transport limit is smaller with the increasing $a_T$, so the calcite particles at the interface dissolve more to contribute the $A_e$ value. Figure 15 B shows that the contribution of $A_I$ to the $A_e$ value. The $A_I$ contributed $\sim 39\%$ to $A_e$ when $a_T$ exceeds $10^{-2.5}$, while it only contributed $\sim 23\%$ when $a_T$ is lower than $10^{-2.5}$. This can be explained by the different mass transport at the interface, which is caused by the variation in $a_T$ value. When $a_T$ value is higher, the mass transport limitation becomes smaller and therefore more dissolving calcite particles are found at the interface. As such, $A_I$ value is higher when $a_T$ exceeds $10^{-2.5}$.

Since $A_T$ remains the same for all three columns, Figure. 15 C demonstrates that the column-scale bulk rates (mol/s) do not depend on the value of $A_T$. On the contrary, the column-scale bulk rates increase with the increasing $A_e$ and $A_I$, showing the $A_e$ and $A_I$ values affect the bulk rates significantly. This observation demonstrates the importance of
dispersivity is in the heterogeneous medium by affecting the bulk rates significantly. Moreover, the estimation in effective surface area ($A_e$) is the key parameter when we determine the bulk dissolution rate.

**Figure. 15** Under flow velocity of 3.6 m/day and the 1-cylinder column condition: (A) The values of the effective surface area ($A_e$) and interface surface area ($A_I$) as a function of transverse dispersivity ($a_T$) in logarithm scale; (B) The ratios ($A_e/A_t$ or $A_I/A_e$) as a function of transverse dispersivity ($a_T$) values; (C) Column-scale bulk rates (mol/s) as a function of $A_e$ or $A_I$, and the values of $A_e$ and $A_I$ are corresponding to the different $a_T$ values in (A).

### 4.4 The Effect of Reactive Minerals

The previous study of reactive mineral dissolution rate (Li et al., 2013; Salehikhoo et al., 2013) focused on the effect of spatial distribution on magnesite dissolution reaction, and the results can be utilized to compare with the results in our study. The results from their research are impressively similar to our study. In their study, the similar settings of column experiments were also used to investigate the role of mineral spatial distribution. The dimension of column and the central mineral-cylinder zone are the same as our column experiments. Magnesite-cylinder was packed in the quartz matrix and the same initial and inlet boundary concentration of solution are introduced as well. As such, the comparisons in the reactive mineral breakthrough curves, local dissolution rates, predicted 2-D spatial profiles for the magnesite and calcite case are discussed in the following paragraphs.

In order to compare the results of two reactive mineral dissolution reactions, the same injecting flow rate, 3.6 m/day, has been used to illustrate the outcome. Therefore, reactive mineral will be the only control factor between calcite and magnesite dissolution experiments.
In the mixed column, the steady-state mineral concentration of magnesite is approximately $1.61 \times 10^{-4}$ M (Figure 17 A) and the steady-state concentration of calcite is about $1.86 \times 10^{-4}$ M (Figure 17 B), which is slightly higher than magnesite. The similar situations also occur in the other columns. In the 2-cylinder, the steady-state concentration of the magnesite and calcite case is $9.47 \times 10^{-5}$ and $1.09 \times 10^{-4}$ M, respectively. In the 1-cylinder, the steady-state concentration of the magnesite and calcite case is $8.47 \times 10^{-5}$ and $9.8 \times 10^{-4}$ M, respectively. Magnesite dissolution reaction reaches the steady-state mineral concentration after nearly three residence times, but it only takes two residence times for the calcite case to reaches the steady-state condition. The longer residence time in the calcite case can also explain the higher effluent reactive mineral concentration in the calcite case. As such, the fact that calcite has faster dissolution rate can be made from the above observation. In other words, different mineral does have an impact on the performance of mineral dissolution rates.

![Figure 16](image)

**Figure. 16** A comparison of experimental breakthrough data (symbols) for magnesite and calcite dissolution reaction under flow velocity of 3.6 m/d. (A) Mg(II) concentration of magnesite (Li et al., 2013) and (B) Ca(II) concentration of calcite

Figure. 16A shows a comparison of the column-scale rates under different flow velocities based on two cases, which is calcite (this study) and magnesite dissolution (L. Li et al., 2003). The column-scale rates calculated by using Equation 10 according to the steady-state effluent reactive mineral concentration. The top row in Figure 18 is for this study and the bottom row is for Li et al., (2003). The number of reactive mineral zones represent the number of reactive mineral cylinders (i.e., the number of reactive mineral zones for the 2-cylinder column is 2). As for the mixed column, the reactive mineral particles for both studies can be treated as having an infinite number of small zones and therefore has the least
mass transport limitation.

The One-zone column, however, only has one reactive mineral zone so has the biggest mass transport limitation. The trend of column-scale rates for both cases share the similar trajectory. The mixed column has highest column-scale rates in both calcite and magnesite cases. The column-scale rates gradually decrease with the decreasing number of reactive mineral zones. In the calcite case (Figure 17 A, top), it has the higher column-scale rates by approximately 1.2 order of magnitude than the magnesite case does under the same flow velocity. This observation is consistent with the higher effluent Ca(II) concentration in the calcite case (1.86 x 10^{-4} M) and lower effluent Mg(II) concentration in the magnesite case (1.61 x 10^{-4} M) shown in Figure 17 and Equation 10. In other words, high effluent reactive mineral concentrations lead to higher values in column-scale rates under the same flow velocities.

Figure 17 B shows the $\alpha$ values, which is the ratios of rates of the zonation columns and the mixed column. The $\alpha$ values are all lower than 1, suggesting lower rates in the zonation columns compared to those in the mixed column for both calcite and magnesite dissolution case. Also, we can also find that the deviation of $\alpha$ from 1 for both cases, is lower when the flow velocity is slow, indicating less difference among the columns. This could be caused by the long residence time and the increasing importance of the concentration fields under the low flow velocity condition. Plus, low flow velocities can bring to local equilibrium conditions, making the reaction kinetics less relevant and therefore thermodynamics becomes more dominant. The $\alpha$ values of magnesite dissolution case are smaller than the calcite dissolution case by approximately 0.1 at two flow velocities, which is very small. Even though the difference of $\alpha$ values between the calcite and magnesite case is not significant, the deviation of $\alpha$ is much lower than 1 when the number of zones gets smaller for both cases, which suggesting the influence of mineral spatial distribution on dissolution rates is getting more important with the decreasing number of zones for both calcite and magnesite cases.
Figure 17 A comparison of (A) the logarithm of column dissolution rate (log R) ;(B) the ratios (α) of the rates of the zonation columns and the mixed column; as a function of the number of reactive mineral zones for the calcite (top row) and magnesite (Li et al., 2013) (bottom row) case under different flow velocities.

Figure 18 shows a comparison of the predicted 2D steady-state spatial profiles for magnesite (top) and calcite case (bottom) at flow velocity of 3.6 m/d. In the mixed column of these two cases (the left figure of each pair), the dissolution happens everywhere and leads to the reactive mineral concentration homogeneously distributed in the mixed column. The dissolution results in the increases in pH, reactive mineral concentration (Mg(II) and Ca(II)), and IAP/Keq along the main flow direction. Correspondingly, the local dissolution rates decrease by approximately 1-10 orders of magnitude, depending on the reactive mineral. The reactive mineral concentration and pH in calcite case are more homogeneously distributed than in magnesite case, and it is likely because calcite dissolution reaction reaches the steady-state condition faster than magnesite dissolution reaction, which leads to the longer residence time by an order of magnitude in calcite case. The longer residence time in calcite
Comparing the middle zone in the 1-cylinder column of the two cases, because both reactive mineral grains are distributed in the middle zone that reactive mineral concentrations, pH, IAP/Keq have the great increases in the middle zone than the rest parts of the column. The local dissolution rates in these local equilibrium regions for the magnesite and calcite case are respectively 2-4, 1-5 orders of magnitude lower than the maximum dissolution rates close to the inlet. Considering the saturation degree shown in the figure of IAP/Keq, only the magnesite grains close to the inlet and at the magnesite-quartz interface are dissolving. In the calcite case, on the other hand, the high homogeneously distributed Ca(II) concentrations in the middle zone lead to the local equilibrium conditions with IAP/Keq close to 1, suggesting that the calcite grains are not dissolving in the middle zone except for the calcite-quartz interface regions. For the concentration and rate gradients along the x direction in the two cases, the area of the gradients in the calcite case is wider than in the magnesite case. The difference in the area of concentrations and rate gradients along the x direction in the two cases, is likely due to the different in $\alpha_T$ values. The $\alpha_T$ value of magnesite and calcite case is 0.0072 and 0.036, respectively. A small $\alpha_T$ value leads to the small mass transport rate at the reactive mineral-quartz interface. As such, Mg(II) is confined to the middle zone due to the smaller $\alpha_T$ that results in smaller mass transport rate compared to Ca(II). The calcite case, however, has a larger $\alpha_T$ value that results in a faster mass transport rate in the x direction.

In conclusion, calcite dissolution generally has a higher values in effluent Ca(II) concentrations at steady-state because of the higher residence time compared to magnesite dissolution. As such, the column-scale rates of calcite dissolution is higher by approximately 1.2 order of magnitude than the rates of magnesite dissolution. The longer residence time also lead to the fact that almost everywhere in the middle zone of the calcite case reaches the local equilibrium conditions, while only the end of the middle zone in the magnesite case reaches the local equilibrium conditions. Plus, from the difference in the area of concentration and rate gradients, demonstrating that the mass transport in x direction of the calcite case is faster compared to the magnesite case due to the larger values in transverse dispersivity.
**Figure. 18** A comparison of spatial profiles for the magnesite (bottom row) and calcite case (top row) at flow velocity of 3.6 m/d. The figure on the left of each pair is the mixed column, and the one on the right represents the 1-cylinder column. (A) Reactive mineral concentration (mol/L), (B) pH, (C) IAP/Keq, (D) local dissolution rates (mol/m²/s). The vertical axis is the distance along with the column (0-10 cm), and the horizontal axis is the diameter of the column (0-2.5 cm).
CHAPTER 5. CONCLUSION

This work investigates the effects of mineral spatial distribution on dissolution rates by using experimental and modeling data. We measured the calcite dissolution rates by using column experiments, which packed the same amount of calcite but different distributed patterns within quartz-sand columns (the mixed, 2-cylinder, 1-cylinder column). The mixed column is packing by homogeneously distributed calcite and quartz, and the 1-cylinder/2-cylinder column is placing calcite in the middle zones that are parallel to the flow injection. Experimental data show that column-scale rates in the 1-cylinder column are lower by 0.2~0.75 order of magnitude compared to the homogeneously distributed mixed column. Also, rates are lower by 1.2 to 1.5 order of magnitude under slow flow velocity (0.31 m/day) compared to fast flow velocity (18.5 m/day). The column-scale rates become higher with the increasing flow velocities.

To better understand the impact of mineral spatial distribution under variable geochemical conditions at column scale, the 2-D spatial profile modeling is applied to illustrate the variations in column-scale effluent Ca(II), pH, saturation, and dissolution rates at grid block scale (1 mm). We find that the large local dissolution rates (\(> 10^{-10} \, \text{mol/m}^2\text{s}\)) are located in the middle calcite-distributed zone. This suggests the local dissolution rates are limited by transverse mass transport between calcite-quartz interface in the middle calcite-distributed zone. Moreover, transverse dispersivity \((\alpha_T)\) is the crucial factor determining the mass transport rate at the calcite-quartz interface. The \(\alpha_T\) values determine the amount of dissolving calcite at calcite-quartz interface, as well as flow velocity. Larger transverse dispersivity leads to the faster transverse mass transport and therefore a wider range of dissolving calcite at the calcite-quartz interface.

The idea of different measures in approaching effective surface area is introduced to understand how local dissolutions are affected by transverse mass transport: (1) total surface area \((A_T)\); (2) effective surface area \((A_e)\). In the mixed column, all the calcite are dissolving and therefore the effective surface area equals to total calcite surface area. In the 1-cylinder/2-cylinder column, the effective surface area is equals to the region with IAP/Keq < 0.5 at calcite-quartz interface surface and inlet area. In addition, we observed that \(A_e\) values increases with the increasing flow velocities and increasing \(\alpha_T\) values. Therefore, \(\alpha_T\) values and flow velocity are the key factors controlling effective surface area. The experimental and modeling data demonstrate that column-scale bulk rates increase in the 1-cylinder/2-cylinder column with the increasing effective surface area \((A_e)\), but they are independent of the total surface area \((A_T)\). This observation indicates that \(A_e\) is important in determining the
column-scale bulk rates. The different approaches of the effective surface area lead to the discrepancies between field and laboratorial measured rates. To estimate calcite dissolution rate under natural subsurface conditions, this work minimizes the discrepancies by using the effective surface area rather than the traditional BET surface area. That is, the surface area of dissolving calcite at the interface of calcite and other non-reactive minerals needs be measured first, and then the rate constant (mol/m²/s) obtained in laboratory work can be applied to infer the rates.

The work also compares with the literature (L. Li, Salehikhoo et al., 2013) with the same experimental procedures but different reactive mineral, magnesite. The column-sale rates in this work are about 1.2 order of magnitude larger than in the magnesite case. The transverse mass transport rates in the calcite case is faster than the magnesite case due to the larger transverse dispersivity of the calcite case. In the 1-cylinder column of the calcite case, the saturation and local dissolution spatial profile modeling demonstrate that the total effective surface area of the calcite case is mostly contributed by the interface surface area. In the magnesite case, however, the dissolving magnesite is found near the column inlet and the magnesite-quartz interface, which contributes to the total effective surface area. The interface magnesite surface area accounts for 60~70% of effective magnesite surface area, and the rest of the effective surface area is contributed by the inlet dissolving magnesite. As such, the effective area estimation also depends on different reactive minerals.

To sum up, we infer that the discrepancies between laboratory and field measured rates are likely caused by slow flow velocities, mineral spatial distribution that results in the different effective surface area calculations. This work helps to reduce the potential discrepancies among the laboratory measured rates and rates in natural subsurface system with heterogeneously distributed minerals everywhere. Consequently, it will decrease the errors in the mineral compositions evaluation for aquifers or reservoirs.
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Appendix

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Submitter: Jessie Chao  
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Ambient: 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.019 K  
Thermal Correction: No  
Warm Free Space: 15.7600 cm$^3$ Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Summary Report

Surface Area

Single point surface area at P/Po = 0.300354261: 0.0872 m$^2$/g  
BET Surface Area: 0.1150 m$^2$/g

Sample: calcite  
Operator: Lyman Ortino Rivera  
Submitter: Jessie Chao  
File: C:\2020\DATA\000-186.SMP

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Automatic Degas: Yes

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Thermal Correction: No  
Warm Free Space: 15.7600 cm$^3$ Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

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BET Surface Area Report

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Correlation Coefficient: 0.9979045
Molecular Cross-Sectional Area: 0.1620 nm$^2$

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