

The Pennsylvania State University  
The Graduate School  
Department of Energy and Mineral Engineering

**EFFECTS OF SPATIAL HETEROGENEITY ON CALCITE DISSOLUTION RATES**

A Thesis in  
Energy and Mineral Engineering

by  
Mariya Skocik

© 2014 Mariya Skocik

Submitted in Partial Fulfillment  
of the Requirements  
for the Degree of

Master of Science

May 2014

The thesis of Mariya Skocik was reviewed and approved\* by the following:

Li Li

Assistant Professor in Petroleum & Natural Gas Engineering

Thesis Advisor

Mark S. Klima

Associate Professor of Mineral Processing and Geo-Environmental Engineering

Associate Department Head

William A. Groves

Associate Professor of Industrial Health and Safety

Luis F. Ayala

Associate Professor of Petroleum and Natural Gas Engineering

Associate Department Head for Graduate Education

---

\* Signatures are on file in the Graduate School

## ABSTRACT

The prediction of carbonate reservoirs behavior, including rock and fluid interactions, is challenging due to their complex mineralogy, porosity, and permeability heterogeneities. Calcite dissolution, one of the most important subsurface reactions, has been studied since late 19<sup>th</sup> century with a sole focus on homogeneous systems. First studies of more realistic heterogeneous systems started in the past couple of years.

This work examines the effects of geochemical heterogeneity on calcite dissolution rates with variable permeability contrasts, flow rates, and inlet pH. The investigation consisted of the two major parts: column experiments for dissolution data and reactive flow modeling by the use of CrunchFlow software that simulated the laboratory set-up. Two pairs of 10 cm long and 2.5 cm in diameter columns were wet packed with inert quartz and reactive calcite. The sets' permeability contrasts were 0.5 and 0.83. Each set contained a Mixed Column, representing a homogeneous system, and a One-Zone Column, a heterogeneous system with a cylindrical calcite insertion along the principal flow direction. The inlet solution was injected upwards through the columns at flow rates between 0.03 and 6.3 mL/min with pH at 4 and 6.7. The effluent samples were collected at the outlet of the column up to 10 residence times with variable time steps. The modeling was performed via CrunchFlow reactive flow software package. CrunchFlow simultaneously solves systems of differential transport equations for each grid block of the discretized system representation for each primary species. The reactive flow model was calibrated based on laboratory obtained calcite effluent breakthrough data for the slowest and fastest flow rates.

Under low flow rates where the system reaches equilibrium, the column scale bulk dissolution rates varied between 1.02 and  $1.55 \times 10^{-11}$  mol/ m<sup>2</sup>/s, producing effluent calcium concentrations between  $1.43$  and  $2.17 \times 10^{-4}$  mol/L. The rates of the Mixed Columns were on average 1.25 times higher than those of the corresponding One-Zone Columns. At higher flow rates, under prevalent kinetic regime with transport rates higher than reaction rates, the dissolution rates increased up to  $10^{-9}$  mol/ m<sup>2</sup>/s order of magnitude. The calcium concentration ranged between orders of magnitude  $10^{-5}$  mol/L for One-Zone Columns and  $10^{-4}$  mol/L for the Mixed Columns. The dissolution reaction occurred mostly at the interface of calcite and quartz the One-Zone Columns, leading to significantly lower rates than those in Mixed Columns, where all calcite and quartz grains were well-mixed. After matching the experimental data, more simulations were carried out under an array of flow rate conditions between 0.03 mL/min and 13 mL/min with permeability contrasts between 0.01 and 12. Model results showed that the discrepancy of the dissolution rate of One-Zone Columns in comparison to the corresponding Mixed Columns increased with increase in flow velocity. The simulations also showed that that under conditions where permeability of calcite zone is lower than that of the quartz and where flow rates are high, the calcite the interface is most influential in determining the dissolution rate.

The effective surface area of the system increased with increasing flow rate and permeability contrast, which occurred due to the increase in flow through the reactive calcite zone of the column. The simulations show that the dissolution rate strongly depend on effective surface area

instead of the total surface area of the columns. This proves that degree of system's heterogeneity directly affects its dissolution capacity.

These results imply that in heterogeneous carbonate formations, mineral spatial pattern must be taken into account during reservoir simulation or treatment design. The present study identified discrepancies in dissolution rates between homogeneous and heterogeneous systems on a relatively small spatial and time scales. These discrepancies are magnified in natural subsurface systems due to the systems' size and time of operation.

## TABLE OF CONTENT

|                                                                                                |            |
|------------------------------------------------------------------------------------------------|------------|
| <b>LIST OF FIGURES .....</b>                                                                   | <b>vii</b> |
| <b>LIST OF TABLES .....</b>                                                                    | <b>ix</b>  |
| <b>ACKNOWLEDGMENTS .....</b>                                                                   | <b>x</b>   |
| <b>Chapter 1.....</b>                                                                          | <b>1</b>   |
| <b>INTRODUCTION.....</b>                                                                       | <b>1</b>   |
| <b>1.1 Historic Overview of Mineral Dissolution Research .....</b>                             | <b>2</b>   |
| <b>1.2 Calcite Dissolution .....</b>                                                           | <b>4</b>   |
| <b>1.3 Factors Affecting Calcite Dissolution.....</b>                                          | <b>5</b>   |
| <b>PURPOSE .....</b>                                                                           | <b>9</b>   |
| <b>Chapter 2.....</b>                                                                          | <b>10</b>  |
| <b>METHODOLOGY.....</b>                                                                        | <b>10</b>  |
| <b>2.1 Column Experiments .....</b>                                                            | <b>10</b>  |
| <b>Material Preparation.....</b>                                                               | <b>11</b>  |
| <b>Column Packing Procedure.....</b>                                                           | <b>11</b>  |
| <b>Determination of Porosity and Mineral Volume Fraction in the One-zone Columns .....</b>     | <b>11</b>  |
| <b>Permeability Determination .....</b>                                                        | <b>14</b>  |
| <b>Bromide Tracer Study and Dispersivity Determination.....</b>                                | <b>14</b>  |
| <b>Dissolution Experiment .....</b>                                                            | <b>16</b>  |
| <b>2.2 Reactive Flow Modeling .....</b>                                                        | <b>16</b>  |
| <b>Reactions and Species.....</b>                                                              | <b>16</b>  |
| <b>Reactive Transport Equations.....</b>                                                       | <b>17</b>  |
| <b>Representation of the 3D Column by 2D Domain .....</b>                                      | <b>18</b>  |
| <b>2.3 Dissolution Rates at Different Scales .....</b>                                         | <b>19</b>  |
| <b>Local Dissolution Rates <math>r_{CaCO_3, i}</math>.....</b>                                 | <b>19</b>  |
| <b>Column-Scale Bulk Dissolution Rates <math>R_{CaCO_3, B}</math>.....</b>                     | <b>19</b>  |
| <b>Column-Scale BET Surface-area-normalized Dissolution Rates <math>R_{CaCO_3}</math>.....</b> | <b>19</b>  |
| <b>Damkohler Number, <math>Da_i</math> .....</b>                                               | <b>19</b>  |
| <b>Chapter 3.....</b>                                                                          | <b>21</b>  |
| <b>RESULTS AND DISCUSSIONS.....</b>                                                            | <b>21</b>  |
| <b>3.1 Porosity and Permeability .....</b>                                                     | <b>21</b>  |
| <b>3.2 Dispersivity .....</b>                                                                  | <b>21</b>  |
| <b>3.3 Calcium Breakthrough Curves.....</b>                                                    | <b>23</b>  |
| <b>3.4 Column-Scale Dissolution Rates: Effects of Flow Velocity and pH.....</b>                | <b>27</b>  |
| <b>3.5 Local Geochemistry and Dissolution Rates .....</b>                                      | <b>30</b>  |

|                                                                         |           |
|-------------------------------------------------------------------------|-----------|
| <b>3.6 Effective and Interface Surface Areas .....</b>                  | <b>34</b> |
| <b>3.7 Combined Effect of Permeability Contrast and Flow Rate .....</b> | <b>35</b> |
| <b>3.8 Column-Scale Rates and Damkohler Number .....</b>                | <b>38</b> |
| <b>Chapter 4.....</b>                                                   | <b>40</b> |
| <b>SUMMARY AND CONCLUSIONS .....</b>                                    | <b>40</b> |
| <b>REFERENCES .....</b>                                                 | <b>42</b> |

## LIST OF FIGURES

|                                                                                                                                                                                                                                                                                  |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1: Dependence of calcite dissolution on pH (Region 1: concave-up function, strong dependence on pH; Region 2: transition period, sharp discontinuity; Region 3: equilibrium state, concave-up function, no dependence on $P(\text{CO}_2)$ (Berner and Morse, 1974). ..... | 3  |
| Figure 2: Concentration distribution in relationship to packing patterns (Molins et al., 2012). Scales and axis labels in lower figures are identical to the top figure. ....                                                                                                    | 6  |
| Figure 3: Effects of pH on dissolution rate (Brantley, 2008). ....                                                                                                                                                                                                               | 7  |
| Figure 4: Temperature's effect on rate constant (Brantley, 2008). ....                                                                                                                                                                                                           | 8  |
| Figure 5: Columns packing patterns and cross-sections. ....                                                                                                                                                                                                                      | 10 |
| Figure 6: 2D Cross-section of the One-Zone Column. ....                                                                                                                                                                                                                          | 18 |
| Figure 7: A. Bromide breakthrough curve at 0.03mL/min and inlet pH=4; B. Bromide breakthrough curve at 6.3mL/min and inlet pH=4 .....                                                                                                                                            | 22 |
| Figure 8: Distribution of dispersivity ratio. ....                                                                                                                                                                                                                               | 23 |
| Figure 9: A. Ca(II) breakthrough curve at 0.03mL/min and inlet pH=4; B. Ca(II) breakthrough curve at 6.3mL/min and inlet pH=4. ....                                                                                                                                              | 24 |
| Figure 10: A. Ca(II) breakthrough curve at 0.03mL/min and inlet pH=6.7 B. Ca(II) breakthrough curve at 6.3mL/min and inlet pH=6.7. ....                                                                                                                                          | 24 |
| Figure 11: A. pH data at 0.03mL/min and inlet pH=4 B. pH data at 6.3mL/min and inlet pH=4.25                                                                                                                                                                                     |    |
| Figure 12: Comparison with Chao's experiment, 0.11 mL/min. ....                                                                                                                                                                                                                  | 26 |
| Figure 13: Comparison with Chao's experiment, 6.3mL/min. ....                                                                                                                                                                                                                    | 27 |
| Figure 14: A. Log of column-scale rates at Inlet pH=4; B. Ratio of One-Zone to Mixed Columns column-scale rates at Inlet pH=4. ....                                                                                                                                              | 28 |
| Figure 15: A. Column-scale rate at inlet pH=6.7; B. Ratio of One-Zone to Mixed Columns column-scale rates at inlet pH=6.7. ....                                                                                                                                                  | 29 |
| Figure 16: A. Log of column-scale rate at pH=6.7; B. Ratio of One-Zone to Mixed Columns column-scale rates at pH=6.7. ....                                                                                                                                                       | 29 |
| Figure 17: A. Ca(II) concentration distribution at 0.03mL/min and inlet pH=4; B. Ca(II) concentration distribution at 6.3/min and inlet pH=4. ....                                                                                                                               | 31 |
| Figure 18: A. pH distribution at 0.03mL/min and inlet pH=4; B. pH distribution at 6.3mL/min and inlet pH=4: .....                                                                                                                                                                | 31 |
| Figure 19: A. Log of dissolution rate distribution at 0.03mL/min and inlet pH=4; B. Log of dissolution rate distribution at 6.3mL/min and inlet pH=4. ....                                                                                                                       | 32 |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 20: A. Saturation Index distribution at 0.03mL/min and inlet pH=4; B. Saturation Index distribution at 6.3mL/min and inlet pH=4. ....                                                                                                                                                                                                                                                                                                                                                                                                                                          | 32 |
| Figure 21: Interface schematic: Mixed Column is on the left; One-Zone Column is on the right. ....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 34 |
| Figure 22: A. Ratios of Effective and Total Surface Areas in relationship to inlet pH; B. Ratios of Effective and Interface Surface Areas in relationship to inlet pH. On the left figure, the One-Zone LC and One-Zone HC data point for pH=4 is similar in value and is overlapped on the plot. On the right figure, LC and HC Mixed Columns points overlap. ....                                                                                                                                                                                                                   | 35 |
| Figure 23: A. Bulk dissolution ratio of One-Zone and corresponding Mixed Columns in relationship to flow rate and permeability contrast of the two mineral zones; B. Dissolution rate of One-Zone Columns in relationship to flow rate and permeability contrast of the two mineral zones; C. Ratio of Effective and Total Surface Areas of One-Zone Columns in relationship to flow rate and permeability contrast of the two mineral zones; D. Ratio of Interface and Effective Surface Areas in relationship to flow rate and permeability contrast of the two mineral zones. .... | 36 |
| Figure 24: Correlation of Effective Surface Area and Dissolution Rate. The points with effective area of zero are not plotted in this figure, since logarithm of zero does not exist. ....                                                                                                                                                                                                                                                                                                                                                                                            | 38 |
| Figure 25: Damkohler Number Distribution. Zones: 1- kinetic regime, 2 – transition state, and 3 – equilibrium state.....                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 39 |

## LIST OF TABLES

|                                                           |    |
|-----------------------------------------------------------|----|
| Table 1: Columns' properties. ....                        | 13 |
| Table 2: Experiment Schedule. ....                        | 14 |
| Table 3: Initial and Inlet Fluid Compositions. ....       | 15 |
| Table 4: Chemical reactions with kinetic parameters. .... | 17 |

## ACKNOWLEDGMENTS

I would like to express my gratitude towards to the Energy and Mineral Science Department of the Pennsylvania State University for allowing me to pursue the Master's of Science Degree in the Petroleum Engineering major. I would like to thank the committee members for taking the time to evaluate my work and listen to my defense presentation. Special thanks to my graduate advisor, Dr. Li Li, for taking me under her wing, instructing me through this process, and working within the posed time constraints. It has been a great honor and pleasure to pursue this research work with such dedicated, intelligent, and personable professor.

I am pleased to acknowledge the following technical staff of the University who provided valuable assistance throughout the research process: Randall L. Hale, Material Research Laboratory's experimental mechanic, Karol E. Confer, the laboratory manager of the Water Quality Laboratory, and Laura J. Liermann and Henry Gong, senior research assistants from Department of Geoscience. These staff members aided me during the experiment equipment preparation and effluent sample analysis.

This research work would not have been completed without help of my fellow graduate students: Jessie Tse-Hua Chao, Li Wang, Peyman Heidari, as well Fatemeh Salekhikoo and Rebecca Forgaty for their assistance in getting my experiment of the ground, sharing their technical knowledge, and providing valuable expertise in reactive flow simulations.

I greatly appreciate the flexible scheduling accommodations from my former employer, Herbert, Rowland, and Grubic, Inc., where I worked during four out of five semesters spent in graduate program. My former supervisors and colleagues provided me with great support by working around my class and research schedule.

Last, but definitely not the least, I would like to thank my family for their support in my decision to pursue a post-bachelor's degree, especially my husband, Corey Skocik, who manually crushed and sieved the minerals for my columns and kept me company during the late hours in the laboratory. Thank you all very much!

## Chapter 1

### INTRODUCTION

Energy is a driver of economic, business, and technological development in the modern world. In 2011, the United States of America consumed an equivalent of 97.3 quadrillion Btu of energy; 79.8 quadrillion Btu of which were derived from fossil fuels (EIA, 2012). Extraction of crude oil or natural gas from the formation to the surface plays a crucial role in the energy industry. Investigation of flow through porous media, such as petroleum production from the reservoir or treatment fluid injection into the formation, is the scientific basis behind all extraction and formation treatment processes. Often times, however, understanding of the physics of the flow itself is not sufficient for a complete design of the process. Flow through permeable medium can displace fluids originally contained in the formation; this process is utilized in the injection treatment. In addition, the fluid can react with the formation, effecting its composition and integrity. Therefore understanding of injection fluid's physical and chemical interactions with the formation is of crucial importance. The injection fluid must be compatible with the fluid originally contained in the medium but also with formation rock in order to ensure reservoirs production specifications (Bazin and Labrid, 1991). In addition, the flow can promote changes in the injected fluid; and it can change the formation itself (Bryant et al., 1986). Mineral reactions have a potential to affect structural properties of the formation during production (Pruess, 2008). Some subsurface chemical reactions induce formation of gaseous compounds such as carbon hydroxide, hydrogen sulfide, and etc. during steam injection procedure (Fan, 2003). Currently, it is widely recognized that the complexity of the subsurface processes requires multiphase flow models to be coupled with geochemical transport models through underground layering and fractures (Peszynska and Sun, 2002). Therefore there is a need for further investigation of subsurface fluid-rock interactions and their effects on integrity and production capabilities of the formation by the use of the reactive flow modeling.

All reservoir formations are primary sedimentary in nature and comprised of sandstone or carbonates. At least 60% of petroleum reservoirs occur in carbonate reservoirs (Morse and Mackenzie, 1990). It is challenging to predict the behavior and production of a carbonate reservoir mostly due to its highly heterogeneous porosity nature. Due to such complexity, a carbonate formation might contain a wide range of permeabilities at a constant porosity. In addition, carbonate succession is most common in vertical heterogeneous in laterally organized layers (Burchette, 2012). In order to better understand the behavior of complex carbonate reservoirs, this research analyzes its rock-fluid interactions. In particular, the focus of this work is on a calcite dissolution process, chemical reaction that finds its application in acidification reservoir treatment processes. In relationship to the porous media systems, the solid phase can be dissolved by the liquid phase. This results in increase of void fraction of the medium and subsequently increase in permeability, which in its turn facilitates increased oil/gas production (Kalia and Balakotaiah, 2009). In extreme cases, the entire porous medium matrix can be disintegrated (Békri et al., 1995).

## 1.1 Historic Overview of Mineral Dissolution Research

First attempts to qualify and quantify mineral dissolution occurred in late 19<sup>th</sup> century using marble specimens due to its availability and ease of preparation. Boguski first showed that the rate of marble solution is proportional to the molar concentration of acid used as solute (Boguski, 1876; Boguski and Kajander, 1877). In early 1900's it was also considered that the dissolution rate of marble is affected by the density of packing of calcite ions (Tammann and Krings, 1925). Early studies had also tried to link the dissolution rate with diffusion theory. Initial experiment with various acids showed that marble dissolves faster in strong inorganic acids; however, the dissolution rate was found to be erratic and slow in experiments with weak organic acids (Brunner, 1904). This was explained as incomplete reaction of neutralization on the mineral's surface. Subsequent investigations involved experiments with other minerals such as dolomite. It was noticed that different minerals dissolve at various rates; however, the diffusion rate theory still had issues explaining dissolution with weak acids due to the ion and neutral molecules complications (Ericson-huron and Palmaer, 1906).

By 1920's more experiments with weaker acids took place. It was found that the dissolution rate is greatly dependent on diffusion rate of carbonic acid from marble's surface and rate with which carbon dioxide escapes from the solution. It was also known that the carbonic acid dissociation reaction ( $H_2CO_3 = CO_2 + H_2O$ ) is pH dependent. The latter was quantified by several studies (Faurholt, 1924; Saal, 1928). The presence of carbonate and bicarbonate ions was considered to be of insignificant importance.

Later theories such as Nernst-Brunner theory stated that the dissolution was also correlated with acid/mineral interface as follows:

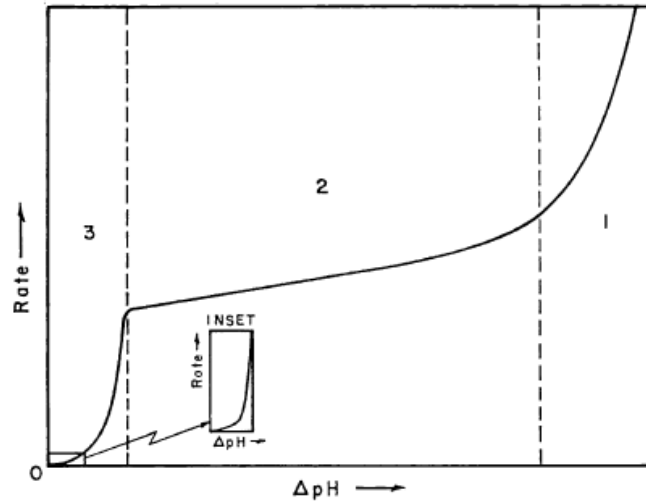
$$\frac{dx}{dt} = \frac{AD_{HCl}}{\delta_1} (C_0 - C_1)$$

where x is the dissolution, A is the exposed area, D is the diffusion coefficient of HCl,  $\delta_1$  is the thickness of the "diffusion layer",  $C_0$  is the bulk concentration of HCl, and  $C_1$  is the concentration of  $H^+$  next to the immediate surface of marble. This is an early attempt to correlate the inlet concentration of solute and mineral interface area.

In 1930's, the scientists started looking into effects of diffusion rate and viscosity of the solute on dissolution kinetics. The diffusion velocities were dependent on solution's viscosity. And since it was previously determined that the dissolution process is affected by the diffusion rate, it was concluded that the viscosity is a factor in dissolution kinetics (Tominaga et al., 1939). One step further was taken in 1950's, when the scientist started investigating the saturation parameter and its influence on the dissolution process (Weyl, 1958).

First mentioning of ion activity products (IAP's) found during literature review is dated 1967 (Berner, 1967). The referenced study experimentally determined IAP of calcite and dolomite in Florida Bay sediment, which were found to be  $10^{-8.97}$  and  $10^{-17}$ , respectively.

In 1970's, calcite dissolution studies become more involved and incorporate more than one parameter of interest. Several studies of calcite dissolution in sea water over a wide pH range, 3.9-7.5 and various degrees of saturation took place (Berner and Morse, 1974). The Figure 1 below summarizes the finding. Over the late 1970's and 1980's, scientists were attempting to quantify the dissolution dependence on temperature and overall reaction mechanism (Plummer et al., 1979; Sjöberg, 1978; Sjöberg and Rickard, 1983).



**Figure 1: Dependence of calcite dissolution on pH (Region 1: concave-up function, strong dependence on pH; Region 2: transition period, sharp discontinuity; Region 3: equilibrium state, concave-up function, no dependence on  $P(\text{CO}_2)$  (Berner and Morse, 1974).**

In 1979, Plummer et al., proposes that the forward rate reaction of calcite dissolution is a summation of reaction rate and ion activity products the following expression which, is widely utilized today:

$$R_f = k_1 \times a_{H^+} + k_2 \times a_{H_2CO_3^*} + k_3 \times a_{H_2O}$$

where  $R_f$  is the dissolution rate in forward direction (mole of dissolved calcite per  $\text{cm}^2$  per sec),  $k_1$ ,  $k_2$ , and  $k_3$  are temperature dependent rate constants, and  $a$  is the activity of corresponding species in bulk fluid.

During the late 1980's – 1990's time period, the majority of studies focused on coupling the dissolution process and the flow through the porous media models, resulting in development of reactive flow modeling (Murphy et al., 1989). The models were implemented for one-component, one-dimensional, and homogeneous systems under steady-state conditions and transient flow regimes.

It is important to highlight that the listed above studies primarily focused on homogeneous systems, and very little attention was paid to the effects of geochemical heterogeneity. Homogeneous systems are idealized theoretical systems and are non-existent in nature. It is also understood that accurate reservoir simulation and production management are impossible without investigation of the nature of reservoir's heterogeneity on various scales (Bagheri and

Biranvand, 2006). Only during the past decade, the mentioning of heterogeneity effects on dissolution, the focus of the present thesis work, appears in the literature. Several studies attempted to quantify the wormholes, the pathways within the specimen formed as a results of mineral's dissolution (Kalia and Balakotaiah, 2009). Other researched focused on mineral dissolution as a function of spatial heterogeneity, as well as flow rate, and reaction scale (Li et al., 2013; Salehikhoo et al., 2013).

## 1.2 Calcite Dissolution

As referenced above, the dissolution of carbonates such as calcite has been extensively studied in the past (Chou et al., 1989). Earlier research studies investigated dependency of the calcite dissolution based on the pH and saturation level of the solute (Berner and Morse, 1974). Subsequent studies also incorporated kinetic characteristics as factors influencing the dissolution process (Plummer et al., 1978, 1979). Nowadays, all listed above factors are considered during reactive flow modeling of the dissolution process. The following three simultaneous reactions were included in the model described in this study:



Each reaction prevails under certain conditions. Reaction 1 dominates within the overall geochemical reaction space at low pH levels. The rate of the second reaction acts as a limiting factor under moderate pH. And the last reaction prevails in absence of CO<sub>2</sub> and high pH levels (Chou et al., 1989).

The Transition State Theory (TST) –based rate law for these reactions is described by:

$$r_{CaCO_3} = (k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3) \times A \times \left(1 - \frac{IAP}{K_{eq}}\right) \quad (4)$$

The rate constant  $k_1$ ,  $k_2$ , and  $k_3$  (mol/m<sup>2</sup>/s) correspond to Equations (1) - (3).  $a_{H^+}$  and  $a_{H_2CO_3^*}$  characterize the activities (dimensionless) of hydrogen and carbonic acid respectively.  $A$  is the surface area (m<sup>2</sup>), refer to “Material Preparation” paragraph for details on Brunauer-Emmett-Teller (BET) surface area used in this study. *IAP is found using the following formula:*

$$IAP_{CaCO_3} = a_{Ca^{2+}} \times a_{CO_3^{2-}} \quad (5)$$

$K_{eq}$  is the equilibrium constant of reaction, described by Equation 3. The ratio of  $IAP$  and  $K_{eq}$  is the saturation index, a measure of the distance from equilibrium. The saturation index value varies between zero and one: one being the closest to equilibrium and zero – the furthest. Each of three reactions has the same saturation index, which can be proven by explicitly deriving the index for each pathway. As such, the rate law indicates that calcite dissolution reaction depends

---

<sup>2</sup>  $H_2CO_3^*$  is a common representation of  $H_2CO_3^0 + CO_2(aq)$ .

on three parameters: rate constants ( $k_1$ ,  $k_2$ , and  $k_3$ ), mineral's surface area ( $A$ ), and aqueous geochemistry ( $IAP$ ).

### 1.3 Factors Affecting Calcite Dissolution

As mentioned prior, the dissolution reaction is a reaction between a solid phase and a solute involving change in mass of solid and change in solute's concentration. The reaction consists of several physical and chemical processes (Morse, & Arvidson, 2002).:

1. Diffusion of reactants through solute to the solid surface;
2. Adsorption of the reactants on the solid surface;
3. Migration of the reactants on the surface to an "active" site;
4. The chemical reaction between the absorbed solute and solid
5. Migration of products away from the reaction dislocation
6. Desorption of the products to the solution
7. Diffusion of products away from the surface

The step that takes the least amount of time is the limiting factor during the dissolution reaction. In moving solutions relative to the solid phase, such as the experiment presented in this thesis work, advective transport is generally faster than the molecular diffusion. In these cases thickness of boundary layer between the solid phase and bulk turbulent solution can control the reaction rate, which is expressed in Fick's First Law.

Mineral interactions under homogenous conditions, when minerals are evenly distributed within the formation, have been studied in the past. Such investigations were performed via batch and column experiments (van Grinsven and van Riemsdijk, 1992). Homogenous conditions, however, are not indicative of oil and natural gas bearing shale formations. Shale is generally composed of stratified layers of multiple minerals packed in various spatial patterns (Dyni, 2005). On average, the Appalachian Basin's mineral content is broken down as following: 50% clay, 20% quartz, 25% calcite, 5% pyrite (Kepferle, 1993). Thus investigation of mineral interactions in heterogeneous conditions, conditions under which rock properties vary as a function of position (Dandekar, 2006), is more representative of the actual environment. "The term 'heterogeneity' is rarely defined and almost never numerically quantified although it is widely stated that carbonate heterogeneities are poorly understood" (P. Fitch, 2010). The focus of this paper is on a particular type of subsurface mineral reactions – mineral dissolution. Mineral dissolution is a crucial component of various physical, chemical, and biological processes in nature (Li et al., 2009). The rate of mineral dissolution has an effect on porosity in petroleum reservoirs (Brantley, 2008). Therefore the investigation of mineral dissolution under heterogeneous conditions plays an important role in understanding of formation's solid and fluid interactions and their effects on integrity and productivity of the formation (Kalia and Balakotaiah, 2009).

The exploration of carbonate containing reservoirs presents a challenge due to the heterogeneity occurring at all scales of observation. The heterogeneity is caused by variation in lithology, chemistry/mineralogy, pore types, and pore connectivity. At least 15 heterogeneity types are identified in carbonate reservoirs, which effects reservoir permeability and overall quality (P. Fitch, 2010). The permeability of carbonate reservoirs varies by approximately six orders of

magnitude (Ahr, 2008). According to the same source, the porosity of carbonate formations varies from less than 5% to over 20%. Although several sources studied the effects of dissolution process on the ability of formations to convey fluids (Filho and Ricardo, 2012; Reed, 1977), very few studies investigated the effects of spatial heterogeneity on mineral dissolution rates. In 2012, Molins et al. performed a series of CrunchFlow (the software shall be described in detail in “Methodology” chapter) simulations of porous media with 60% void space and various calcite spatial arrangements in order to analyze the effects of spatial heterogeneity on mineral dissolution. White grains in Figure 2 represent calcite grains that are being dissolved. Figure 2A depicts the distribution of dissolved calcite concentration throughout uniformly packed specimen. Figures 2B and 2C illustrate random and layered grain distributions respectively. The average geochemical parameters are equal for all three cases.

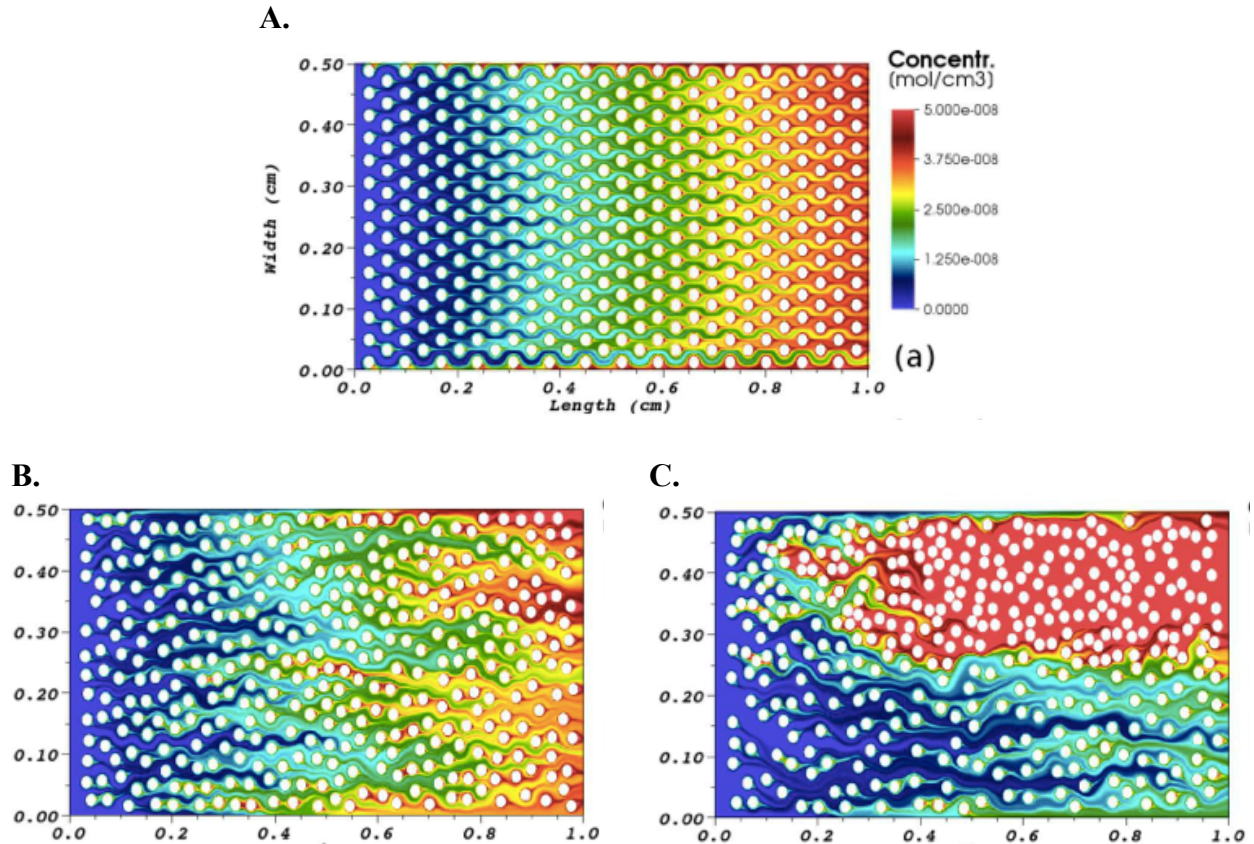


Figure 2: Concentration distribution in relationship to packing patterns (Molins et al., 2012). Scales and axis labels in lower figures are identical to the top figure.

The average dissolution rate of the sample with uniform calcite distribution was found to be  $7.79 \times 10^{-11}$  mol/m<sup>2</sup>/s, which is 7.5 and 12% higher than that of samples depicted in Figures 2B and 2C, respectively. It should also be noted that similar one-dimensional simulation resulted in dissolution rate of  $8.62 \times 10^{-11}$  mol/m<sup>2</sup>/s, approximately 10% higher than 2D simulation of uniform medium. This occurred because 1D modeled flow is uniform and does not account for the portions of domain not contributing to the dissolution. The described study concluded that the dissolution rates are dependent on flow pattern, which in its turn is dependent on spatial heterogeneity of the media.

In addition to heterogeneity, several other factors affect dissolution kinetics, such as flow rate, pH level, temperature, and saturation. Figure 3 depicts the relationship between the log of dissolution rate and pH level of solute. At lower pH (less than 3.5), the dependency is controlled by transport; the dissolution rate ranges between  $10^{-1}$  and  $10^{-6}$  orders of magnitude. However, at moderate and high pH levels the interaction is interface-controlled; and the rate variation stays within an order of magnitude.

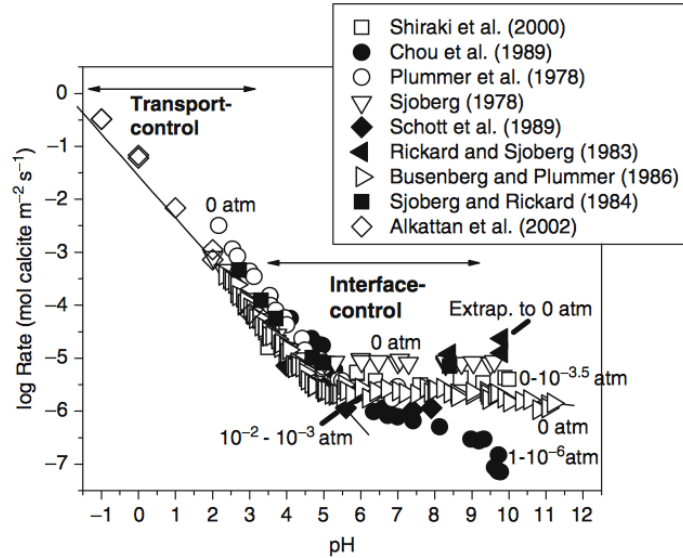


Figure 3: Effects of pH on dissolution rate (Brantley, 2008).

The dissolution's temperature dependency is generally expressed through activation energy. Figure 4 represents a schematic correlation between the rate limiting constant and temperature. With increase in temperature, the reaction may change from interface-limited to transport-limited, because the activation energy of interface reaction is generally higher than that of the transport. Overall, the temperature influence has not been investigated over a wide range. However, it is known that dissolution process becomes more pH sensitive with increased temperatures (Casey and Sposito, 1992).

Effects of flow rates on mineral dissolution kinetics have also been studied in the past (Salehikhoo et al., 2013). The referenced study quantified the dissolution kinetics of magnesite; the experimental and numerical simulation set-up was identical to the one presented in this paper. The source stated that the dissolved concentration of calcite increased with decrease in flow rate. The lower flow velocity and consequently longer residence time allows for an extended reaction time and therefore higher effluent concentration.

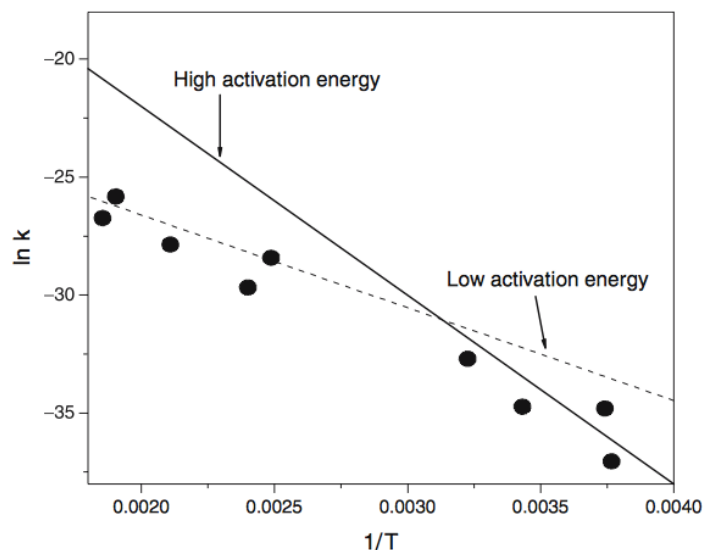


Figure 4: Temperature's effect on rate constant (Brantley, 2008).

Another crucial factor is dispersivity, which in its turn is a function of rock properties, flow rate, and pH. Dispersivity is a characteristic of mixing process. Laboratory-scale displacement scheme is well represented by dispersion coefficient, a product of the fluid velocity and dispersivity (Chesnut, 1994).

It is important to highlight the fact that all dissolution affecting factors listed above, including the figures and the described relationships, were studied for idealized homogeneous systems, which is not an accurate representation of natural mineral formations. In reality, the rock formations contain more than one type of heterogeneity; complicating the effects of pH, flow rate, and temperature. on the dissolution process. In addition to Molins' simulation study described above, two dissolution experimental studies investigated the effects of various factors on calcite (Chao, 2014) and magnesite (Salehikhoo et al., 2013) dissolution rates. Both research papers described the results of column dissolution and reactive flow simulations performed with CrunchFlow software. The magnesite dissolution study concluded that the reaction rates in columns experiments are three times higher than those based on homogeneous batch dissolution experiments. In addition, significant influence of flow rate and spatial distribution on dissolution rates was identified. Chao's calcite dissolution study had also recognized the discrepancies in dissolution rates of heterogeneous and well-mixed columns. Chao's observations will be presented and compared to the results of this thesis work in "Results and Discussion" section. As referenced above, the mineral dissolution has been studied for over a century; however, the first mentioning of heterogeneity effects appeared just one decade ago. Very few papers studying reactivity in heterogeneous systems were published to date; and, therefore this field requires further attention.

## **PURPOSE**

The intent of this study is to quantifiably analyze the calcite dissolution process via column experiments and numerical simulations. In addition, the study will provide a comparison of the dissolution process under various conditions. In particular, the influence of geochemical heterogeneity, such as contrast in particle sizes and mineral deposition patterns, flow velocity, and pH level on calcite dissolution is of interest.

Each case scenario will be executed in the laboratory and then modeled using CrunchFlow reactive flow modeling software package. The goal is to obtain the best match of experimentally obtained and modeled data sets and quantify parameters affecting the calcite dissolution process. Such parameters include transverse and longitudinal dispersivities, equilibrium constant, rate constants, and variety of surface areas. After the calibration, the reactive flow model will be further expanded to include a larger scale of conditions, such as flow velocity and permeability contrast, in order to analyze the combined effects of the factors as well as to determine where the heterogeneity has the most influence on the system.

## Chapter 2

### METHODOLOGY

The study consists of two major parts. Firstly, the calcite dissolution laboratory investigation was carried out in a form of column experiments under various conditions. Secondly, the numerical simulations, mimicking the laboratory set-up and a larger scale of conditions, were performed using CrunchFlow, reactive flow modeling software package. The final results and analysis of the study are based on the best match of the laboratory obtained and modeled data sets for real columns and a wide scale simulation of hypothetical columns. The results are also compared to another calcite dissolution study performed by Chao in 2013.

#### 2.1 Column Experiments

Four identical cylindrical columns with diameters of 2.5 cm and lengths of 10 cm were used in the study. Each column was packed with calcite (from Minas, Nuevo Leon, Mexico) and quartz (by Unimim Corporation) particles in two different patterns, as depicted in Figure 5. One-Zone Columns, Columns 1 and 3, were packed with quartz and a cylindrical insertion of calcite along the center of the column parallel to the main flow. Mixed Columns, Columns 2 and 4, contained homogeneous mixture of both minerals.

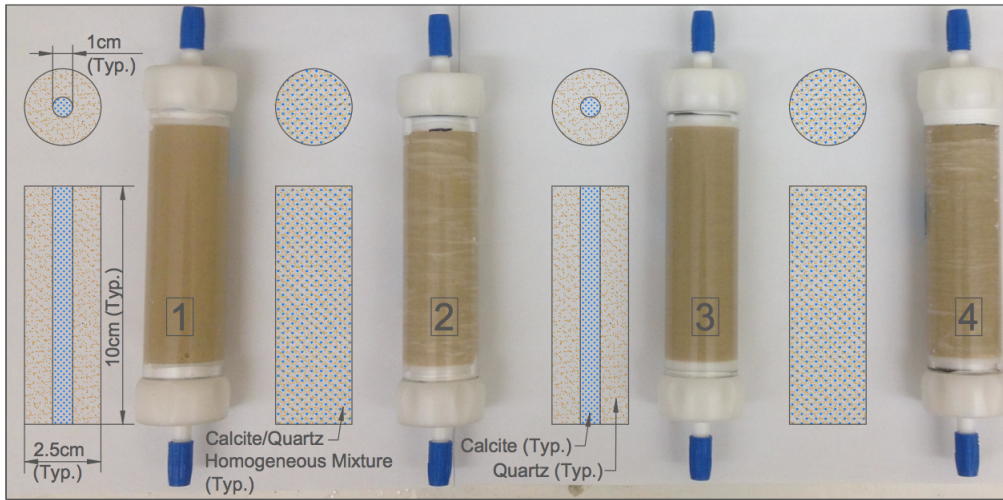


Figure 5: Columns packing patterns and cross-sections.

All columns were packed using the sample calcite particles with size between 125 and 150  $\mu\text{m}$ . Columns 1 and 2 contained quartz particles between 297 and 355  $\mu\text{m}$ , respectively. Columns 3 and 4 contained quartz particles between 420 and 500  $\mu\text{m}$ . Identical calcite sizes were chosen for equality of the dissolution comparison. Quartz sizes were varied to provide two cases of heterogeneity: low contrast (LC) in case of Columns 1 and 2 and high contrast (HC) in case of Columns 3 and 4. Initially smaller size calcite particles, between 45 and 74  $\mu\text{m}$  were intended to be used in the low heterogeneity contrast column set; however, the mineral dissolved during the washing procedure due to its size and was not used in the study. The column properties are summarized in Table 1.

### Material Preparation

The purity of the calcite utilized in the study was confirmed by X-ray Diffraction (XRD) analysis. In addition, Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES) test was performed, which identified the following insignificant contaminants: 0.17% of magnesite, 0.05% of sodium, 0.05% of strontium, and 0.001% of aluminum, manganese, and silicium.

The proper particle sizes were achieved by manual grinding of the minerals by the use of mortar and pestle and then sieving the material through the appropriate mesh manufactured by Fisher Scientific Company in accordance with A.S.T.M-11 Specification. Both minerals were washed with excessive amounts of deionized water. The calcite was also washed with a weak solution of hydrochloric acid. After the washing procedure, the samples were cleaned in an ultrasonic device, Branson 2210 model: calcite and quartz were treated for 20 and 40 minutes respectively.

After the samples were dried in the oven, they were analyzed for the Brunauer–Emmett–Teller (BET) surface areas. The estimated specific surface areas of the particles were based on its gas adsorption and were calculated via correlations from particles isotherms (Wolfson, 2012). The results of BET analysis are presented in Table 1.

### Column Packing Procedure

A “wet packing” procedure was utilized in column preparation (Minyard and Burgos, 2007). The bottom of the column was secured with an end cap lined with filter. The filter was produced by Ominifit Labware and contained opening of 10 µm. For the column with vertical calcite alignment surrounded by sand, a one cm diameter straw was temporary positioned in the center of the column. The calcite particles were dispensed inside of the column, and the quartz particles were arranged around the straw. The material was packed in approximately 1cm intervals with periodic tapping for better compaction and uniform distribution. After each interval, the straw was gently pulled up until, eventually; it was completely removed from the column. For the Mixed Columns, the two minerals were combined into a homogeneous mixture in a separate container and then packed into a column utilizing the above referenced procedure with the exception of the straw. It was intended to pack the two columns using the same amounts of the minerals. However, additional amounts of quartz, because it is a non-reactive component, were added to the mixed column to completely fill it. At the end of the packing procedure, the top end of the column was secured with another end cap.

### Determination of Porosity and Mineral Volume Fraction in the One-zone Columns

The overall porosity of the columns was determined by the ratio of the summation of the mineral volumes packed to the overall volume of the column, given by:

$$\phi = 1 - \frac{\frac{\text{Calcite Weight (g)}}{\text{Calcite Density (g/cm}^3\text{)}} + \frac{\text{Quartz Weight (g)}}{\text{Quartz Density (g/cm}^3\text{)}}}{\text{Column Volume (cm}^3\text{)}} \quad (6)$$

Porosity found using the above equation was used for the calculations relative to the Mixed Columns. In case of the One-zone Columns, the porosities of calcite and quartz individually are required for the calculations. The quartz zone was assumed to contain 100% quartz; amount of mixed in calcite is negligible. However, it is very likely that a small (but not negligible) amount

of quartz was introduced into the calcite zone due to the straw movement during the packing procedure. In order to estimate the porosities of individual zones and volume fraction of quartz in the calcite zone, the four mass balance equations with four unknowns were composed and solved:

$$M_{Ca} = V_{Ca} \times (1 - \varphi_{Ca}) \times VF_{Ca/Ca} \times \rho_{Ca} \quad (7)$$

$$M_{Qtz} = V_{Qtz} \times (1 - \varphi_{Qtz}) \times VF_{Qtz/Qtz} \times \rho_{Qtz} + V_{Ca} \times (1 - \varphi_{Ca}) \times VF_{Qtz/Ca} \times \rho_{Qtz} \quad (8)$$

$$\varphi_{overall} = \frac{V_{Qtz} \times \varphi_{Qtz} + V_{Ca} \times \varphi_{Ca}}{V_{total}} \quad (9)$$

$$VF_{Ca/Ca} + VF_{Qtz/Ca} = 1 \quad (10)$$

In above system of equations,  $M_{Ca}$  and  $M_{Qtz}$  are the measured masses of calcite and quartz in the column (g);  $\varphi_{Ca}$ ,  $\varphi_{Qtz}$ , and  $\varphi_{overall}$  are the porosities of calcite, quartz, and column's overall porosity (dimensionless);  $VF_{Ca/Ca}$  is the volume fraction of calcite in the calcite zone (dimensionless), similarly  $VF_{Qtz/Ca}$  is the volume fraction of quartz in calcite zone;  $VF_{Qtz/Qtz}$  is the volume fraction of quartz in quartz zone, assumed to be 100% (dimensionless);  $V_{total}$  is the total volume of the column (cm<sup>3</sup>).

The final porosity values and solids volume fractions for one-zone columns are provided in Table 1.

Table 1: Columns' properties.

| <b>Columns</b><br><b>Properties</b>             | <b>One-Zone<br/>LC</b> | <b>Mixed LC</b> | <b>One-Zone<br/>HC</b> | <b>Mixed HC</b> | <b>Chao's<br/>One-Zone</b> | <b>Chao's<br/>Mixed</b> |
|-------------------------------------------------|------------------------|-----------------|------------------------|-----------------|----------------------------|-------------------------|
| <b>Calcite (g)</b>                              | 12.57                  | 12.57           | 12.57                  | 12.57           | 14.97                      | 14.62                   |
| <b>Quartz (g)</b>                               | 74.61                  | 78.17           | 73.04                  | 81.37           | 76.8                       | 76.1                    |
| <b>aL (cm) at<br/>0.03mL/min</b>                | 0.03                   | 0.09            | 0.08                   | 0.3             | 0.2 <sup>3</sup>           | 0.09                    |
| <b>aL (cm) at 6.3mL/min</b>                     | 0.01                   | 0.04            | 0.05                   | 0.8             | 0.1                        | 0.09                    |
| <b>aT (cm) at<br/>0.03mL/min</b>                | 0.006                  | 0.006           | 0.007                  | 0.007           | 0.002 <sup>4</sup>         | 0.09                    |
| <b>aT (cm) at 6.3mL/min</b>                     | 0.006                  | 0.006           | 0.007                  | 0.007           | 0.036                      | 0.009                   |
| <b>BET Calcite (m<sup>2</sup>/g)</b>            | 0.5591                 | 0.5591          | 0.5591                 | 0.5591          | 0.1150                     | 0.1150                  |
| <b>BET Quartz (m<sup>2</sup>/g)</b>             | 0.3466                 | 0.3466          | 0.1038                 | 0.1038          | 1.8700                     | 1.8700                  |
| <b>Permeability Calcite<br/>(m<sup>2</sup>)</b> | 5.50E-13               | 6.5E-13         | 5.50E-13               | 8.5E-13         | 6.13E-14                   | 8.2E-14                 |
| <b>Permeability Quartz<br/>(m<sup>2</sup>)</b>  | 7.00E-13               |                 | 1.10E-12               |                 | 6.13E-14                   |                         |
| <b>Porosity Calcite</b>                         | 0.44                   | 0.37            | 0.44                   | 0.40            | 0.43                       | 0.40                    |
| <b>Porosity Quartz</b>                          | 0.33                   |                 | 0.36                   |                 | 0.42                       |                         |
| <b>Grain Size Calcite<br/>(μm)</b>              | 125-150                | 125-150         | 125-150                | 125-150         | 225-350                    | 225-350                 |
| <b>Grain Size Quartz</b>                        | 297-350                | 297-350         | 420-500                | 420-500         | 225-350                    | 225-350                 |

<sup>3</sup> Value estimated at 0.11mL/min, the slowest flow rate used in Chao's study.

<sup>4</sup> Value estimated at 0.11mL/min, the slowest flow rate used in Chao's study.

### Permeability Determination

The pressure gradients between the top and the bottom of each column were measured with Crystal Engineering differential pressure gauge (XP2i-2P) at three different flows: 0.3, 0.5, and 1.0 ml/min. Each flow rate was maintained constant for 15 minutes to achieve a stable pressure reading with maximum variation of 0.005 psi. Each measurement was taken in duplicate for accuracy. After the pressure differentials were obtained, Darcy's law (Equation 11) was used to estimate the effective permeability.

$$Q = \frac{kA(P_{top\ of\ the\ column} - P_{bottom\ of\ the\ column})}{\mu L} \quad (11)$$

The indirectly measured permeabilities were later confirmed or adjusted if needed (refer to "Results and Discussions" chapter) during reactive flow modeling. The permeabilities for each column are provided in Table 1.

### Bromide Tracer Study and Dispersivity Determination

The tracer study was conducted in order to determine the dispersivity coefficients, which will be used in the reactive flow modeling for the dissolution experiments. The tracer study was performed at room temperature and atmospheric pressure. The solution was pumped through the column in upwards direction by the use of a syringe pump, Harvard Apparatus. The experiment was repeated for three flow rates: 6.30, 1.23, and 0.11 mL/min, refer to Table 2 for experiment schedule.

Table 2: Experiment Schedule.

|              | Flow Rate, mL/min | Columns     |          |             |          |
|--------------|-------------------|-------------|----------|-------------|----------|
|              |                   | One-Zone LC | Mixed LC | One-Zone HC | Mixed HC |
| Tracer Study | 0.11              | ✓           | ✓        | ✓           | ✓        |
|              | 2.45              | ✓           | ✓        | ✓           | ✓        |
|              | 6.3               | ✓           | ✓        | ✓           | ✓        |
| pH=4         | 0.03              | ✓           | ✓        | ✓           | ✓        |
|              | 0.11              | ✓           | ✓        | ✓           | ✓        |
|              | 1.23              | ✓           | ✓        | ✓           | ✓        |
|              | 2.45              | ✓           | ✓        | ✓           | ✓        |
|              | 6.3               | ✓           | ✓        | ✓           | ✓        |
| pH=6.7       | 0.03              |             |          | ✓           | ✓        |
|              | 6.3               |             |          | ✓           | ✓        |

Prior to each run, the columns were flushed with 130mL of  $10^{-3}$  M sodium chloride solution in order to wash out any calcite cations. A solution bromide solution with concentration of  $1.2 \times$

$10^{-4}$  mol/L and pH of 9 was used as the experiment's inlet solution. The pH level of 9 was used to eliminate calcite dissolution during the tracer study. 15 samples were collected between 0.10 and 3.68 residence times. For the two faster flow rates (6.30 and 1.23 mL/min), the samples were collected manually. For the flow rate of 0.11 mL/min, automatic sampler collector Retriever 500 by Teledyne ISCO was used. Effluent bromide concentrations were measured using Dionex ICS2500 Ion Chromatography (IC). Local longitudinal and transverse dispersivities were determined for each column based by simulating the tracer study in the two – dimensional domain using CrunchFlow (Steefel and Lasaga, 1994) software, and matching modeled results and experimentally obtained data. The tracer study simulation was performed assuming no dissolution reactions took place. The porosity values, permeability ratio for one-zone columns, and dispersivities were treated as unknown and were varied until the modeled results converged with the experimental data. Due to a relatively short duration of the experiment, the porosity and BET surface area were assumed to remain constant. Table 3 provides a summary of initial and boundary chemical parameters.

**Table 3: Initial and Inlet Fluid Compositions.**

| <b>Species</b>                           | <b>Initial Concentration in the Column at t=0 (mol/L, except for pH)</b> | <b>Concentration of Inflowing Fluid (mol/L, except for pH)</b> |
|------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------|
| pH                                       | 9                                                                        | 4 and 6.7 depending on the run                                 |
| CO <sub>2</sub> (aq)/CO <sub>2</sub> (g) | 3.15E-4                                                                  | 5E-4 (LC) and 22E-4 (HC)                                       |
| Ca <sup>2+</sup>                         | Varies                                                                   | 0                                                              |
| SiO <sub>2</sub> (aq)                    | 1E-5                                                                     | 1E-5                                                           |
| Na <sup>+</sup>                          | 1E-3                                                                     | 1E-3                                                           |
| Cl <sup>-</sup>                          | 1E-3                                                                     | 1E-3                                                           |
| Br <sup>-</sup>                          | 1.26E-4                                                                  | 1.26E-4                                                        |

### **Total, Effective, and Interface Surface Areas**

This work references several types of surface areas. This section provides clarification on how each area is defined. The total reactive calcite surface area  $A_T$  (m<sup>2</sup>) is calculated as a product of calcite BET surface area (0.5591 m<sup>2</sup>/g) and total mass of calcite in the column (12.57 g).

Therefore  $A_T$  is a constant parameter since an identical size and amount of calcite was packed in each column for equal comparison.

The effective surface area  $A_e$  (m<sup>2</sup>) is the surface area of calcite, which effectively dissolves during the experiment. It represents the surface area of calcite with local dissolution rates significantly above zero.  $A_e$  was calculated as a product of BET area and effectively dissolved mineral mass. The latter was derived from CrunchFlow.

The interface surface area  $A_I$  (m<sup>2</sup>) is the effective area of calcite-quartz interface. For the mixed columns, Columns 2 and 4, the interface area is equal to the total effective surface area due to the assumption that all calcite particles are surrounded by quartz particles. In case of one-zone

columns, Columns 1 and 3,  $A_I$  was defined as effective surface area of grains lying within the first two grid block layers of the calcite zone. Thus the ratio of  $A_I/A_e$  represents the proportion of effective surface area at the interface of the two minerals.

### **Dissolution Experiment**

The set up of dissolution experiments is similar to the above described tracer study with a few variations. Five flow rates: 6.30, 3.45, 1.23, 0.11, and 0.03 mL/min were used in the experiment. Prior to each run the columns were flushed identically to the tracer study. The pH of the above described inlet solution was adjusted to 4 and 6.7 for the first and second sets of the experiment respectively. During each run, 15 samples with residence time fractions between 0.30 and 10 were collected from each of four columns and were preserved with 2% nitric acid. The samples were later analyzed for calcium, sodium, and strontium cations by the use of the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and plotted against corresponding residence time in order to obtain the trend of dissolution reaction progression.

## **2.2 Reactive Flow Modeling**

Two-dimensional (2D) reactive transport modeling was performed using the CrunchFlow code for all columns to represent one vertical slice of each column. The reactive transport models explicitly couples fluid flow and chemical reactions to facilitate quantitative simulations (Xiao and Jones, 2007) with a wide range of applications. These applications include mineral dissolution (Maher et al., 2006), reservoir flooding treatments (Pruess et al., 2006), and well performance analysis (Araque-Martinez and Lake, 2004).

### **Reactions and Species**

In addition to the calcite dissolution reactions taking place in the described experiment, other simultaneous chemical interactions occur between other species present in the columns. Such species include  $Ca^{2+}$ ,  $CaHCO_3^+$ ,  $CaCO_3(aq)$ ,  $H_2CO_3$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $H^+$ ,  $OH^-$ ,  $SiO_2(aq)$ ,  $CO_2(aq)$ ,  $Na^+$ ,  $Cl^-$ , and  $Br^-$ . For modeling purposes, all species are categorized as primary or secondary. The primary species are the main species comprising the chemistry of the system; the secondary species can be expressed in terms of the primary species (Lichtner, 1985). The  $Ca^{2+}$ ,  $H^+$ ,  $SiO_2(aq)$ ,  $Cl^-$ ,  $Br^-$ , and  $CO_2(aq)$  were designated as primary species; the remaining components were set as secondary species.

Table 4 provides a summary of chemical reactions and their kinetic parameters. The reaction equilibrium and rate constants were derived from EQ3/6 database (Wolery and al., 1990).

Table 4: Chemical reactions with kinetic parameters.

| Aqueous speciation (at equilibrium)                              | Log K <sub>eq</sub> | k (mol/m <sup>2</sup> /s)           | Specific Surface Area (m <sup>2</sup> /g, BET, measured) |
|------------------------------------------------------------------|---------------------|-------------------------------------|----------------------------------------------------------|
| $H_2O \rightleftharpoons H^+ + OH^-$                             | -14.00              | -                                   | -                                                        |
| $H_2CO_3^0 \rightleftharpoons H^+ + HCO_3^-$                     | - 6.35              | -                                   | -                                                        |
| $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$                     | -10.33              | -                                   | -                                                        |
| $CaHCO_3^- \rightleftharpoons Ca^{2+} + HCO_3^-$                 | -1.05               | -                                   | -                                                        |
| $CaCO_3(aq) \rightleftharpoons Ca^{2+} + CO_3^{2-}$              | -2.98               | -                                   | -                                                        |
| <b>Kinetic reactions (logK value is logK<sub>sp</sub> value)</b> |                     |                                     |                                                          |
| $CaCO_3(s) + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$           | -1.85               | $3.2 \times 10^{-5}$<br>(log=-4.50) | 0.5591                                                   |
| $CaCO_3(s) + H_2CO_3^0 \rightleftharpoons Ca^{2+} + 2HCO_3^-$    | -                   | $3.0 \times 10^{-6}$<br>(log=-5.50) | 0.55591                                                  |
| $CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$               | -8.48               | $2 \times 10^{-9}$<br>(log=-8.70)   | 0.5591                                                   |

### Reactive Transport Equations

The model utilizes reactive transport equations, which are derived in terms of total concentration of all primary species. Equation 4 is written for primary species  $Ca^{2+}$ :

$$\frac{\partial(C_{Ca^{2+}})}{\partial t} = D_L \frac{\partial^2(C_{Ca^{2+}})}{\partial z^2} + D_T \frac{\partial^2(C_{Ca^{2+}})}{\partial x^2} - \vartheta_z \frac{\partial(C_{Ca^{2+}})}{\partial z} - \vartheta_x \frac{\partial(C_{Ca^{2+}})}{\partial x} + r_{CaCO_3} \quad (8)$$

where  $C_{Ca^{2+}}$  is the total concentration of all  $Ca^{2+}$  - containing species (mol/m<sup>3</sup>);  $\vartheta$  is the flow velocity (in specified direction), where z is the direction of the main flow (m/s); t is time (s);  $r_{CaCO_3}$  is the dissolution rate (mol/s), represented by Equation 4;  $D_L$  and  $D_T$  are longitudinal and transverse dispersion coefficients (m<sup>2</sup>/s), which are defined by:

$$D_L = D^* + \alpha_L \vartheta_z \quad (9)$$

$$D_T = D^* + \alpha_T \vartheta_x \quad (10)$$

Here  $D^*$  is the effective diffusion coefficient in porous media (m<sup>2</sup>/s),  $\alpha_L$  and  $\alpha_T$  are the longitudinal and transverse dispersivities (m), which were determined during tracer study simulation.

### Numerical Simulation

For the modeling purposes, the 2D representation of the column was evenly discretized into 100 by 25 grid blocks; the size of each block was 1 by 1 mm. As determined in previous mineral dissolution studies (Salehikhoo et al., 2013), the 1 by 1 mm size is lowest resolution that generates the same results as grid block of smaller sizes. Experimentally measured and

confirmed via simulation parameters such as permeability, porosity, and flow rate along with the estimated dispersivities from the tracer study were utilized as known parameters in the reactive transport model. Kinetic parameters listed in Table 4 were also used as model's inputs. As the results of the numerical simulation of the reactive transport model, a spatial and temporal progression of the species concentrations was obtained. The output concentrations were then plotted against corresponding residence times using Matlab software by MathWorks.

### Representation of the 3D Column by 2D Domain

The 3D columns used in the described experiment are represented by the 2D domain in the reactive flow model. One 2D vertical radial slice of the one-zone column with the predominant flow depiction is presented in Figure 6. Mixed Columns, Columns 2 and 4, were assumed to be homogeneous; therefore the calculated velocities and flow rates were equal in both x and z directions. For the One-zone Columns, Column 1 and 3, there is a variation in flow and rate with the respect to the direction due to the columns' heterogeneity. In this case, the velocity and flow rate were calculated as a weighted average over the 2D cross-section of the column. The radial cross-section was further divided into 25 blocks in x-direction and 100 blocks in z-direction. For the one-zone columns, the 11 central horizontal blocks were assigned to be the calcite zone and the 7 blocks on each side of the central block were designated as the quartz zone.

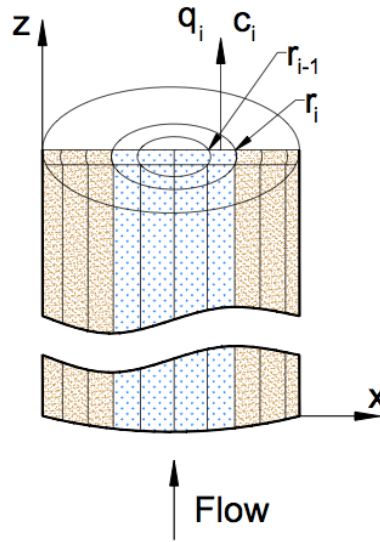


Figure 6: 2D Cross-section of the One-Zone Column.

The total radial cross-sectional area, total flow, and the concentration of the effluent were calculated using the following equations:

$$A_{C,T} = \sum_{i=1}^n A_{C,i} = \sum_{i=1}^n \pi(r_i^2 - r_{i-1}^2) \quad (11)$$

$$Q_T = \sum_{i=1}^n q_i = \sum_{i=1}^n \vartheta_i A_{C,i} \quad (12)$$

$$C_{effluent} = \frac{\sum_{i=1}^n c_i q_i}{Q_T} \quad (13)$$

In the equations, the  $r_i$  and  $r_{i-1}$  are the inner and outer radius of the  $i$ th circle from the center of the columns, as shown on Figure 6,  $A_{c,i}$ ,  $q_i$ ,  $v_i$ , and  $c_i$  are the corresponding cross-sectional area ( $\text{cm}^2$ ), flow rate ( $\text{cm}^3/\text{day}$ ), flow velocity ( $\text{cm}/\text{day}$ ), and effluent concentration ( $\text{mol}/\text{m}^3$ ), respectively. The same variables with subscript “T” designate total parameters.

## 2.3 Dissolution Rates at Different Scales

### Local Dissolution Rates $r_{CaCO_3,i}$

The local dissolution rate  $r_{CaCO_3,i}$  ( $\text{mol}/\text{L}$ ) was calculated using Equation 4 at a scale of each individual grid block. This parameter was estimated by the reactive flow model.

### Column-Scale Bulk Dissolution Rates $R_{CaCO_3,B}$

The steady-state column-scale reaction rate  $R_{CaCO_3,B}$  ( $\text{mol}/\text{s}$ ) is applicable when the columns reach steady-state conditions after approximately two and a half residence times. The parameters were calculated by:

$$R_{CaCO_3,B} = Q_T(c_{Ca^{2+}}(effluent) - c_{Ca^{2+}}(influent)) = \sum_{i=1}^n r_{CaCO_3,i} \quad (14)$$

The first part of the equality is a mass-balance expression for the column. The second part states that the dissolution rate at a column scale is equal to summation of local dissolution rates of each grid block derived using CrunchFlow.

### Column-Scale BET Surface-area-normalized Dissolution Rates $R_{CaCO_3}$

The column-scale BET surface area normalized dissolution rate  $R_{CaCO_3}$  ( $\text{mol}/\text{m}^2/\text{s}$ ) is found as a ratio of column-scale bulk dissolution rate and BET surface area of the mineral as:

$$R_{CaCO_3} = \frac{R_{CaCO_3,B}}{A_T} \quad (15)$$

### One-Zone to Mixed Columns Dissolution Rate Ratio, $\beta$

Beta is defined as a ratio of bulk-scale dissolution rates for One-Zone and corresponding Mixed Columns ( $R_B(\text{One-Zone})/R_B(\text{Mixed})$ ). The ratio ranges between zero and one. When beta is equal to one, the One-Zone and Mixed columns behave similarly in terms of dissolution rates. As the ratio decreases and approached zero, the difference between the two systems becomes more and more noticeable.

### Damkohler Number, $Da_1$

The Damkohler number is introduced to characterize the relative effects of advection and dissolution processes in the system. It determines where advection or chemical reaction are the dominant activity in the column. The parameter is a ratio of the residence time, advection characterization, and time required for the system to reach equilibrium conditions, and is calculated by:

$$Da_I = \frac{\tau_{adv}}{\tau_r} = \frac{\frac{L}{\vartheta}}{\frac{V_P C_{eq,Ca}}{R_{CaCO_3} A_T}} = \frac{L R_{CaCO_3} A_T}{\vartheta V_P C_{eq,Ca}} \quad (16)$$

The advection is defined as  $\tau_{adv} = \frac{L}{\vartheta}$ , where  $L$  is the length of the column (m) and  $\vartheta$  is the average flow velocity (m/d). The time denominator of Damkohler number equation is

$\tau_r = \frac{V_P C_{eq,Ca}}{R_{CaCO_3} A_T}$ , where  $V_P$  is the total pore volume in the column ( $m^3$ ),  $C_{CaCO_3}$  is the equilibrium concentration of calcium ( $mol/m^3$ ),  $R_{CaCO_3}$  is the column-scale BET-surface-area-normalized dissolution rate ( $mol/s/m^2$ ), and  $A_T$  is the BET surface area of calcite in the column ( $m^2$ ).

## Chapter 3

# RESULTS AND DISCUSSIONS

### 3.1 Porosity and Permeability

The average porosity of the columns varied between 0.37 and 0.40 as listed in Table 1. The effective permeability of the columns was in  $6.5 \sim 8.5 \times 10^{-13} \text{ m}^2$  range. The differences in both porosity and permeability were caused by variation of particle sizes and packing patterns. The two parameters are in direct correspondence with each other. The LC columns have lower porosity and subsequently lower permeability values; the HC columns have higher porosity and permeability values. These correlations indicate that due to spatial heterogeneity there is a variation in physical and hydrological properties.

It should be noted that the amplitude in properties variation was smaller than for the columns with LC of particle sizes (Columns 1 and 2). And the opposite was true for the columns with HC (Columns 3 and 4). The calcite to quartz permeability ratios were found to be 0.83 and 0.5, respectively for LC and HC columns.

### 3.2 Dispersivity

The bromide breakthrough curves for all four columns are exhibited in Figure 7. The Mixed Column from the low contrast set displays the breakthrough curve closest to the idealized homogeneous conditions: the change in concaveness occurs at approximately one residence time. The latter holds true for the Mixed Column from the high permeability contrast set; however, the transition from concave down to concave up state is smoother than that of the Mixed LC Column most likely due to contrast in particle size and subsequently porosity and permeability discrepancies between the two columns. The breakthrough curve of the LC One-zone is very similar to the corresponding Mixed Column's. Along with the similar local longitudinal dispersivity ( $\alpha_L$ ) values of 0.03 cm and 0.09 cm for Mixed and One-Zone Columns, respectively, alike behavior indicates that the chemical distribution within the system occurs in a similar manner. The local longitudinal dispersivity values of 0.08 cm and 0.3 cm were estimated for the HC columns. The variance in chemical distribution in HC set is better defined in comparison to the LC set. The HC One-Zone Column exhibits the most distinct tailing among all four columns, indicating the presence of low permeability zones within the column. A minor tailing is noted for the LC Columns as well, however, much less prevailing than in the corresponding HC Column. Although all columns transition from being concave down to concave up state at approximately one residence time, the upper and lower portions of the plot are not symmetrical: the tailing on the upper portion of the graph is much more distinct than the bottom.

The local dispersivity values were estimated by matching the experimentally attained and modeled bromide breakthrough data. During the simulation process, it was found that the key parameter for curve fitting of the Mixed Columns is the porosity value of the specimens. In the case of the One-Zone Columns, the permeability ratios of the individual mineral zones played a critical role in curve fitting in addition to the porosity specifications. The measured permeability

of quartz was found to be  $2.7 \times 10^{-12}$  and  $1.5 \times 10^{-12}$  for LC and HC sets, respectively. The One-zone columns' overall measured permeability was estimated at  $2.4 \times 10^{-12}$  and  $3.2 \times 10^{-12}$ . The measurement of large size quartz's (HC set) appears to be inaccurate, because it was expected to exceed the overall permeability of the column; in addition, it was expected to be higher than permeability of the large size quartz column. Therefore, the LC column data was used to estimate permeability of calcite zone and subsequently permeability ratio of the two zones. Assuming that the affecting permeability is a weighted average over the cross-sectional area of the column, the estimated permeability of calcite zone is  $8 \times 10^{-13}$ . The estimated ratio of calcite to quartz permeabilities is 0.30. The estimated ratio, however, did not reproduce the experimental data; and therefore, was adjusted. The best fit was reached with the LC ratio of 0.83 and HC ratio of 0.50, which intuitively are the more reasonable ratios. Permeability ratio is expected to be close to one when the two packed minerals are closer in size (LC set).

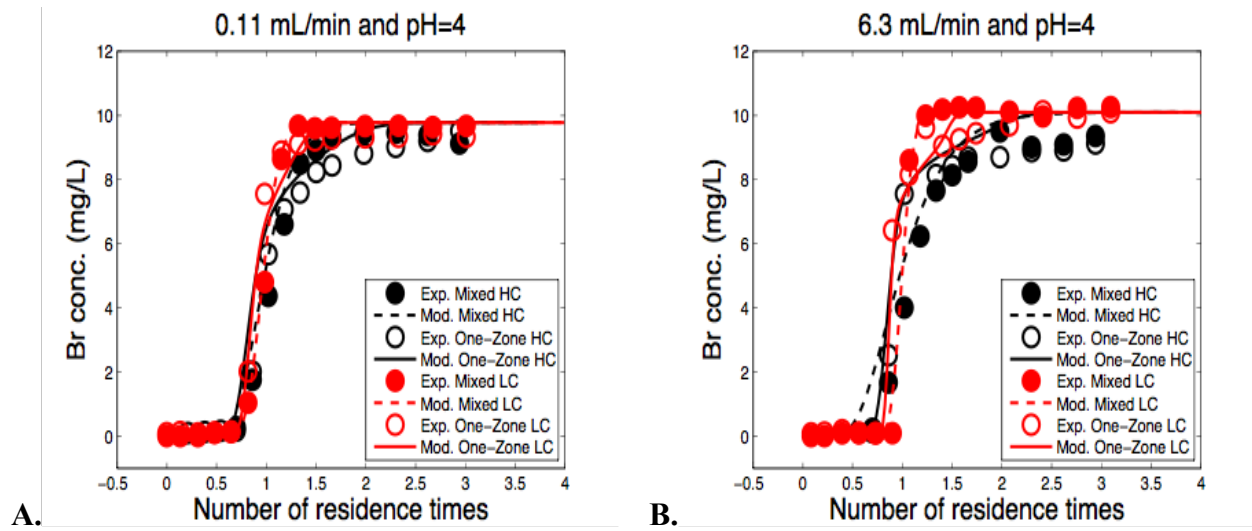
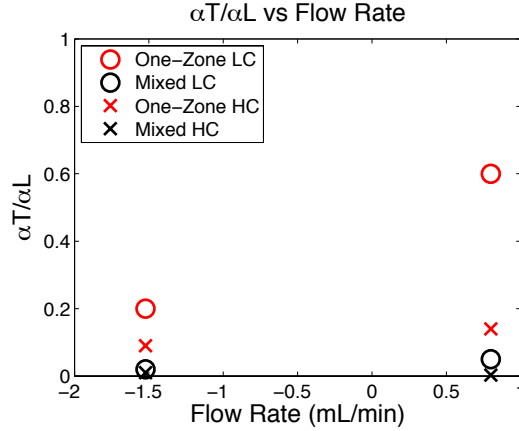


Figure 7: A. Bromide breakthrough curve at 0.03mL/min and inlet pH=4; B. Bromide breakthrough curve at 6.3mL/min and inlet pH=4

The goal of the tracer study was to confirm and/or adjust measured rock properties and to find longitudinal ( $\alpha_L$ ) and transverse ( $\alpha_T$ ) dispersivity values. The estimated longitudinal dispersivity varies between 0.01 and 0.3 cm. The lowest value belonged to One-Zone LC Column; the highest – to Mixed HC Column. Both sets of columns followed the trend: longitudinal dispersivities of Mixed Columns were higher than in the corresponding One-Zone Columns. The transverse dispersivities ranged between 0.002 and 0.007 cm. Figure 8 provides the distribution of transverse to longitudinal dispersivity ratio with respect to the flow rate at a constant pH of the solvent.



**Figure 8: Distribution of dispersivity ratio.**

As follows from Figure 8, the ratio increases with increase in flow rate, meaning that the contrast between dispersivity in horizontal and vertical directions amplifies with the flow rate increase.

Neither mixed columns were dependent on the transverse dispersivity. The transverse dispersivity of the One-zone columns was determined via matching of experimental data and simulation output. The obtained values for One-Zone Columns were assigned to the corresponding Mixed Columns.

### 3.3 Calcium Breakthrough Curves

The calcium breakthrough curves are presented in Figure 9. The initial concentration of calcite varied between  $0.375$  and  $2 \times 10^{-4}$  mol/L. This means that even though the columns were flushed with basic solution prior to performing the experiment, various amounts of dissolved calcite were present in the column at the beginning of the dissolution process. The steady-state was reached after approximately two residence times for all columns. From Figure 9, the steady-state calcite concentrations of Mixed Columns were higher than those of the corresponding One-zone Columns. In addition, the concentrations of HC Columns are higher than LC Columns as a set likely due to the higher permeabilities and porosities, since the dispersivity values were found to be quite similar for all four columns. These facts will be further discussed in consequent sections.

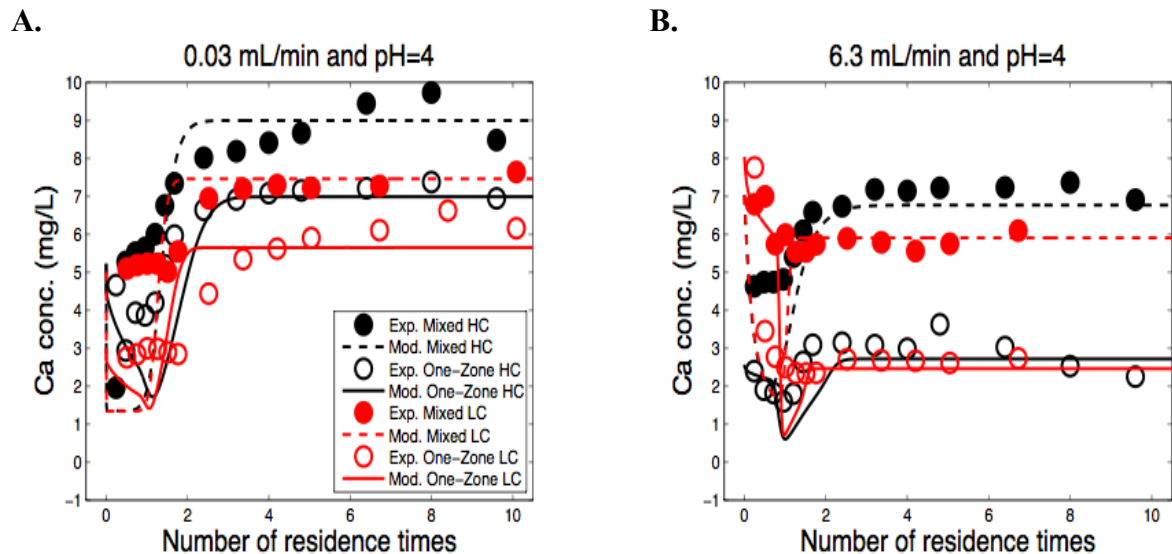


Figure 9: A. Ca(II) breakthrough curve at 0.03mL/min and inlet pH=4; B. Ca(II) breakthrough curve at 6.3mL/min and inlet pH=4

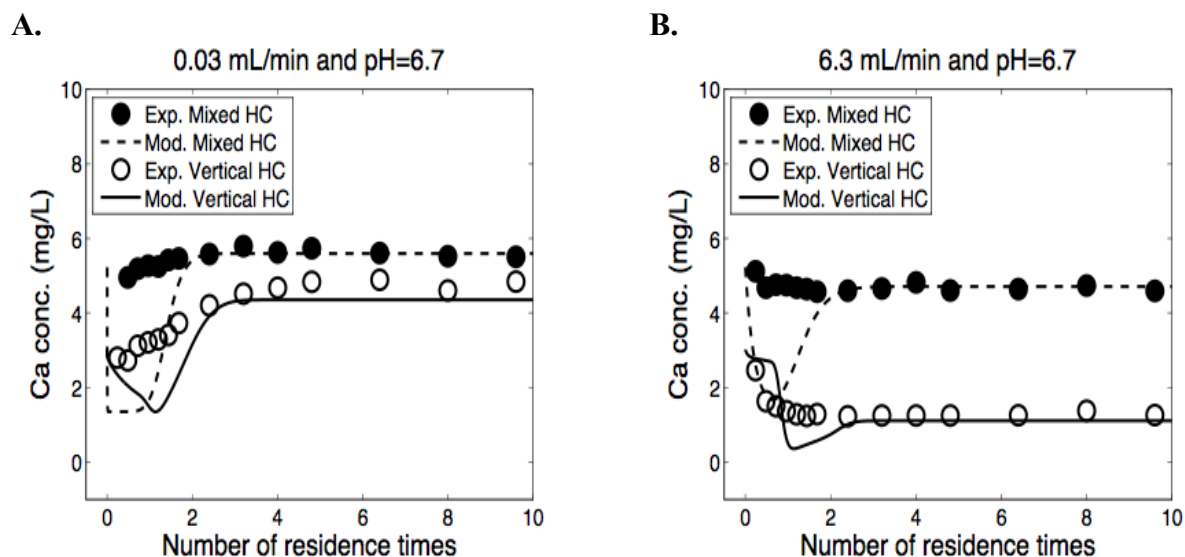


Figure 10: A. Ca(II) breakthrough curve at 0.03mL/min and inlet pH=6.7 B. Ca(II) breakthrough curve at 6.3mL/min and inlet pH=6.7

In order to fit the experimental data, parameters such as equilibrium constant ( $K_{eq}$ ), three rate constants ( $k_1$ ,  $k_2$ , and  $k_3$ ) specific to simultaneous reactions (1) – (3), and initial concentrations of all involved species were incorporated into the CrunchFlow model. In addition, the dispersivity properties were estimated during the tracer study.

For the slow flow rate of 0.03 mL/min and subsequently long duration residence time, the columns reached the equilibrium condition during the experiment. Therefore in this case, the rate constants did not have an effect on shape or position of the breakthrough curve. The software's default log of equilibrium constant equaled to 1.8487 was used unadjusted for the simulation.

Typically, a higher equilibrium constant results in higher effluent concentration. Curiously, another input parameter with significant influence on final calcite concentration was the concentration of carbon dioxide gas in the inlet solution.  $\text{CO}_2(\text{g})$  lowers the pH of the solution by forming carbonic acid with water; and lower pH in its turn results in higher calcium effluent concentration. Most likely, the carbon dioxide gas was introduced into the system when the inlet solution was being pulled into the syringe, which used in the syringe pump as described in the Methodology section. The large air bubbles collected at the tip of the syringe were discharged prior to the launch of the experiment. However, small size and even microscopic bubbles remained suspended within the syringe volume. In addition, a peristaltic pump that draws the solution out of an open container was used for high flow rates, which had a potential to contribute to introduction of carbon dioxide into the system. Thus, the amount of  $\text{CO}_2(\text{g})$  dissolved in the inlet solution needed to be adjusted to  $5 \times 10^{-4}$  and  $22 \times 10^{-4}$  mole/L for LC and HC column sets, respectively. Higher concentration of carbon dioxide gas in HC Column had also resulted in slightly lower pH levels of the effluent. Figure 11 depicts the measured and modeled pH concentration of collected HC samples. The pH level was expected to be around 9; however it is lower due to the presence of carbon dioxide gas. The  $\text{CO}_2(\text{g})$  influence findings are consistent with literature. (Brantley, 2008) states that under pH of 3.5 and higher, carbon dioxide gas does affect the dissolution breakthrough curve.

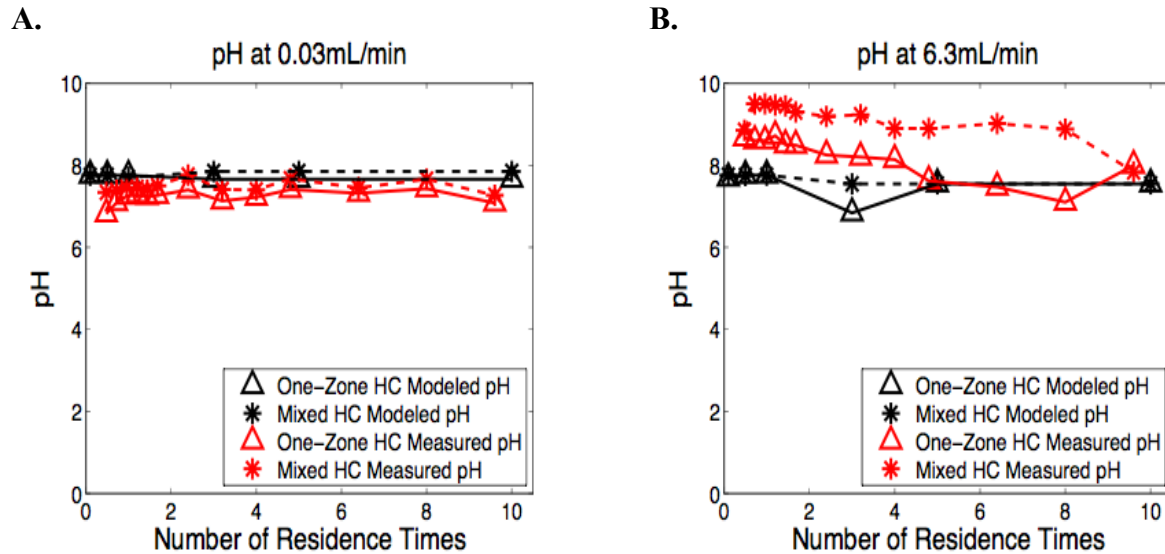


Figure 11: A. pH data at 0.03mL/min and inlet pH=4 B. pH data at 6.3mL/min and inlet pH=4.

The system did not reach equilibrium during the experiment with the fast flow rate of 6.3mL/min (and short residence time). The equilibrium constant as well as the  $\text{CO}_2(\text{g})$  concentration in the inlet solution were carried over from the slow flow rate simulation. Substantial influence of the rate constants is the distinguishable factor between the fast and slow rate conditions. According to the literature, each rate constant prevails under certain pH conditions:  $k_1$  – under low pH,  $k_2$  – under moderate pH, and  $k_3$  – under high pH levels and absence of carbon dioxide. The pH level is not constant throughout the column; it varies at each “slice” as the dissolution reaction progresses towards the outlet. Thus, the influence of the rate constants is not as straightforward. All three rates underwent adjustment in order to match the experimental and simulated data

points. The obtained best-fit combination is provided in Table 4. The estimated values are close to the rate constants reported in the literature (Chou et al., 1989). The first and third rate constants directly affected the magnitude of the dissolved calcite concentration under steady-state conditions. The second rate, however, influenced the effluent concentration prior to the achievement of the steady-state condition. In the case of  $k_1$  and  $k_3$ , the effluent calcite concentration increased with increase in rate constant. For  $k_2$ , the initial “dip” in the concentration deepens with an increase in the constant.

The study presented in this paper was compared to a study performed by Tse-Hua Chao (2014). In her study, Chao implemented a similar calcite dissolution experiment, using quartz particles with sizes between 255-350  $\mu\text{m}$ , which is close to the size used in LC columns and roughly one and a half time smaller than that used in HC columns. The calcite grain size also ranged between 225 and 350  $\mu\text{m}$ , two times larger than calcite particles size used in the present study. The calcium effluent concentrations from the two studies are presented in Figures 12 and 13 for flow rates of 0.11 and 6.3 mL/min, respectively.

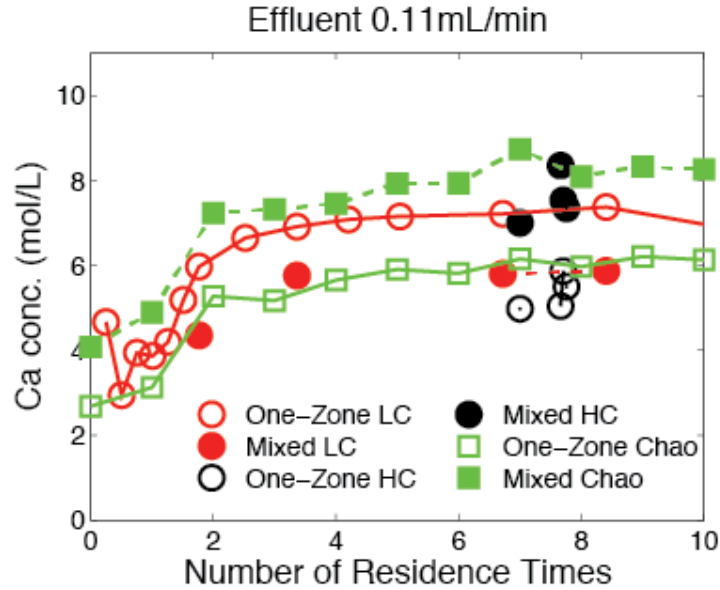


Figure 12: Comparison with Chao's experiment, 0.11mL/min.

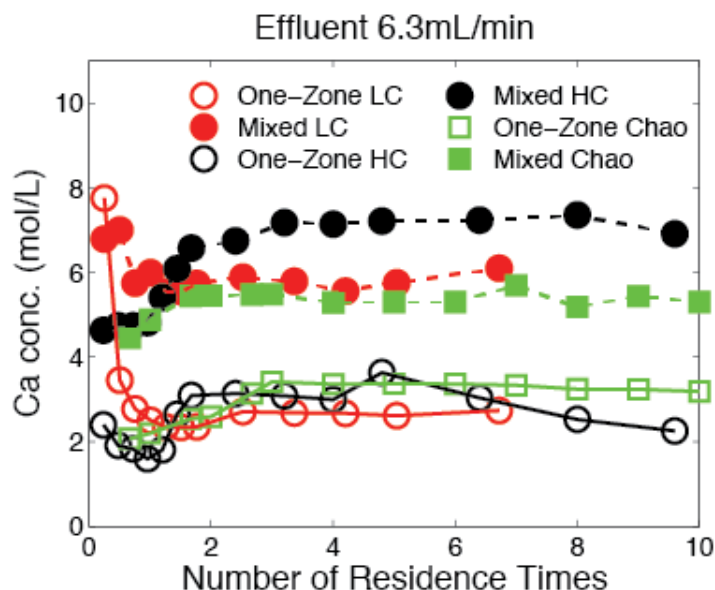


Figure 13: Comparison with Chao's experiment, 6.3mL/min.

From Figures 12 and 13, it is evident that at slower flow rate of 0.11 mL/min, all three Mixed and all three One-zone columns nearly overlap under the steady-state conditions. This indicates that at slow flow rate, when the system is approaching the equilibrium conditions, the dissolution rates are close in magnitude; and the mineral grain sizes as well as other property's deviations do not play a significant role. The effluent concentrations of different columns noticeably deviate from each other under fast flow rate conditions (6.3 mL/min). The fastest dissolution rate belongs to the Mixed HC Column; Chao's Mixed Column had the lowest rate. This trend, however, is not consistent for the One-zone Columns: Chao's column had the fastest dissolution rate, and One-zone LC had the slowest. The range of calcium effluent concentration was narrower for the One-zone Columns in comparison to the Mixed specimens, 2.5 – 3.5mg/L and 5.2 – 7.2 mg/L. This was expected, because, as discussed above, in One-zone Columns the reaction occurs at the calcite – quartz interface, which is similar for all three columns, since the same packing pattern and dimensions were utilized. In case of the Mixed Columns, the reaction is not limited to the minerals interface and takes place throughout the entire volume of the column; therefore there is a greater variance in outlet concentration.

### 3.4 Column-Scale Dissolution Rates: Effects of Flow Velocity and pH

The experimental data indicates that the dissolved concentration is inversely proportional to the flow rate and the pH level. The highest calcium concentration of  $2.5 \times 10^{-4}$  moles/L was observed for HC Mixed column at pH=4 and flow rate of 0.03mL/min. In opposite, the lowest calcium concentration of  $0.4 \times 10^{-4}$  moles/L occurred for HC One-Zone column at pH of 6.7 and flow rate of 6.3 mL/min. It should be noted that the effluent calcium concentration of LC columns was expected to be higher than that of the HC columns due to higher homogeneity of the LC set. However, the opposite occurred due to the increased carbon dioxide gas concentration in HC Column set. The experiment with inlet solutions' pH of 6.7 was only performed for HC Column set. Thus the amplitude of calcite concentration varied by a factor of ten among all conditions.

Another important finding is that the difference between the dissolved concentration for Mixed and One-zone Columns increased with increase in the flow rate. Slow flow velocity and subsequently longer residence time provides extended contact between calcite and solute allowing longer reaction time and even reaching of the equilibrium conditions. Therefore the variation in dissolved concentration was much more distinct than under fast flow rate. The steady-state concentrations of calcite are close in magnitude to the dissolved magnesite concentration described by magnesite study under similar conditions (Li et al., 2013).

Figures 14 and 15 depict distribution of column-scale dissolution rates with respect to the column permeability the contrast and flow rate. The rates of both mixed columns nearly overlapped for all flow rates. The latter had also occurred for the one-zone columns. Another observed trend is rate difference between Mixed and One-zone columns grows with an increase in flow rate. This behavior maintains under different pH conditions; and the difference becomes more substantial as pH level increases, refer to Figure 16.

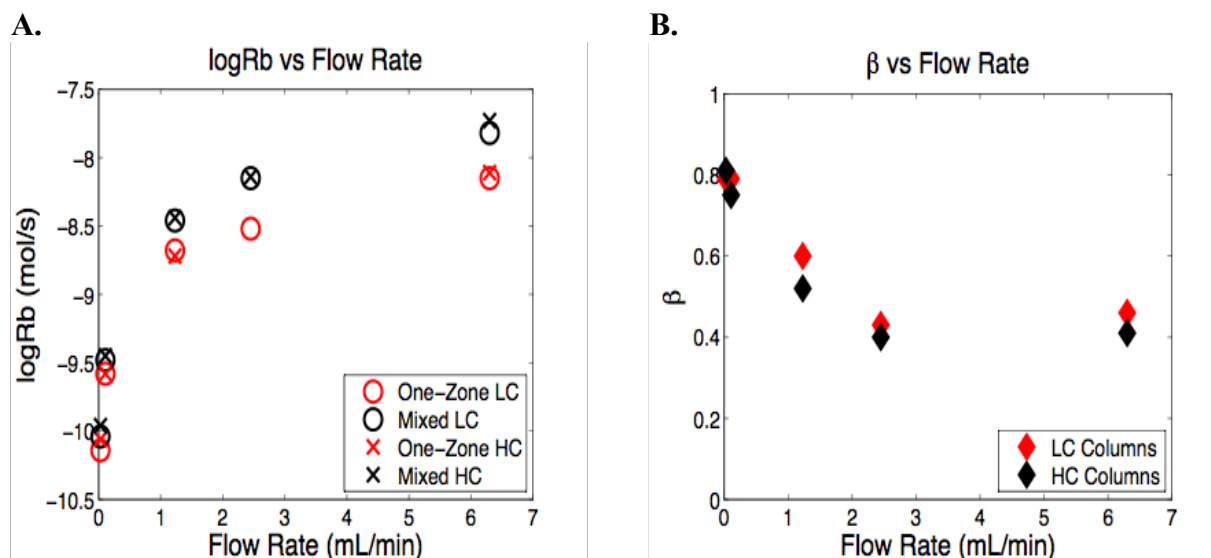


Figure 14: A. Log of column-scale rates at Inlet pH=4: B. Ratio of One-Zone to Mixed Columns column-scale rates at Inlet pH=4.

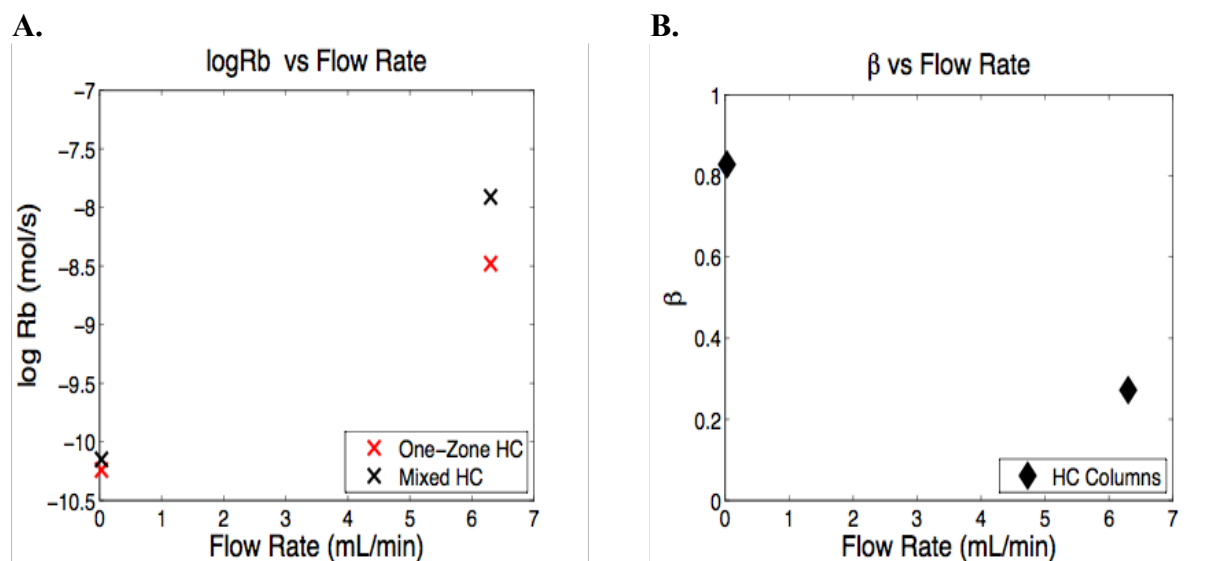


Figure 15: A. Column-scale rate at inlet pH=6.7; B. Ratio of One-Zone to Mixed Columns column-scale rates at inlet pH=6.7.

As expected, the dissolution rate was higher at lower pH levels. Figures 16 prove the latter statement. The trend is more obvious under slow flow rate conditions. For example, the difference in the log of dissolution rate between the mixed columns is 0.20 and 0.06 for 0.03 and 6.3mL/min, respectively.

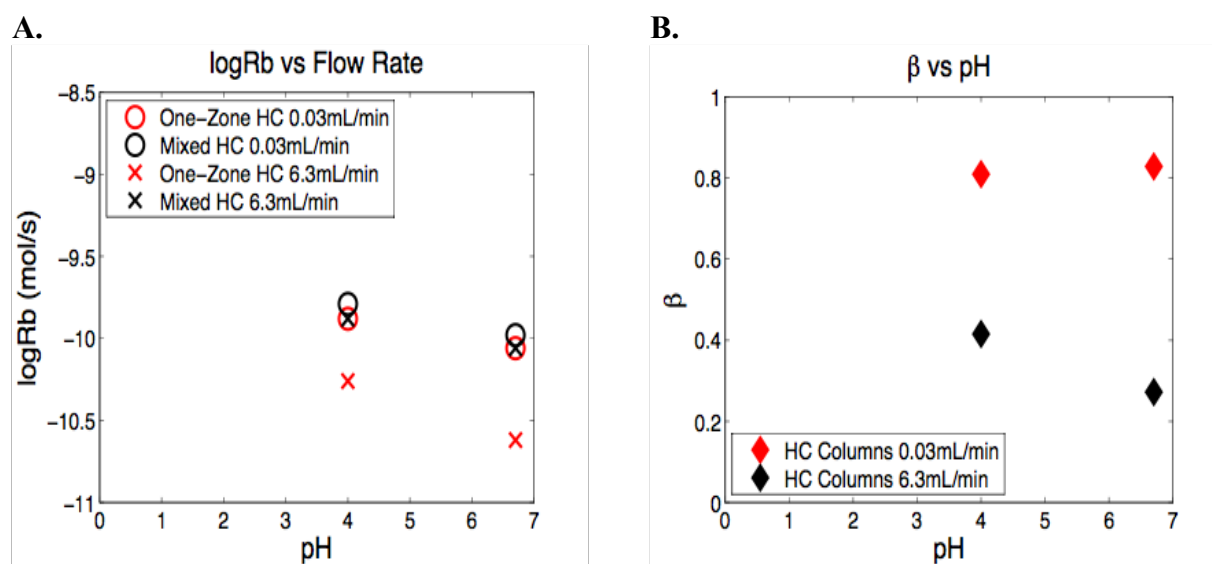


Figure 16: A. Log of column-scale rate at pH=6.7; B. Ratio of One-Zone to Mixed Columns column-scale rates at pH=6.7.

### 3.5 Local Geochemistry and Dissolution Rates

Figures 17 through 20 portray spatial profiles of Ca(II) concentration, pH level, ratio of ion activity product and equilibrium constant or saturation index ( $IAP/K_{eq}$ ), and location dissolution rate ( $r_{CaCO_3}$ ). Figures on the left were plotted under slow flow rate conditions (0.03mL/min); figures on the right – at fast flow rate (6.3mL/min). All plots resulted from simulation at pH=4 and after 11 residence times. These figures will aid in understanding of the property distribution within the columns during the dissolution process. Each spatial profile was plotted for all four columns in the following order: 1 – Mixed LC, 2 – One-Zone LC, 3 – Mixed HC, and 4 – One-Zone HC. The x- and y-axis's represent the width and the height of the columns in mm; a colorbar scale is provided on the right hand side.

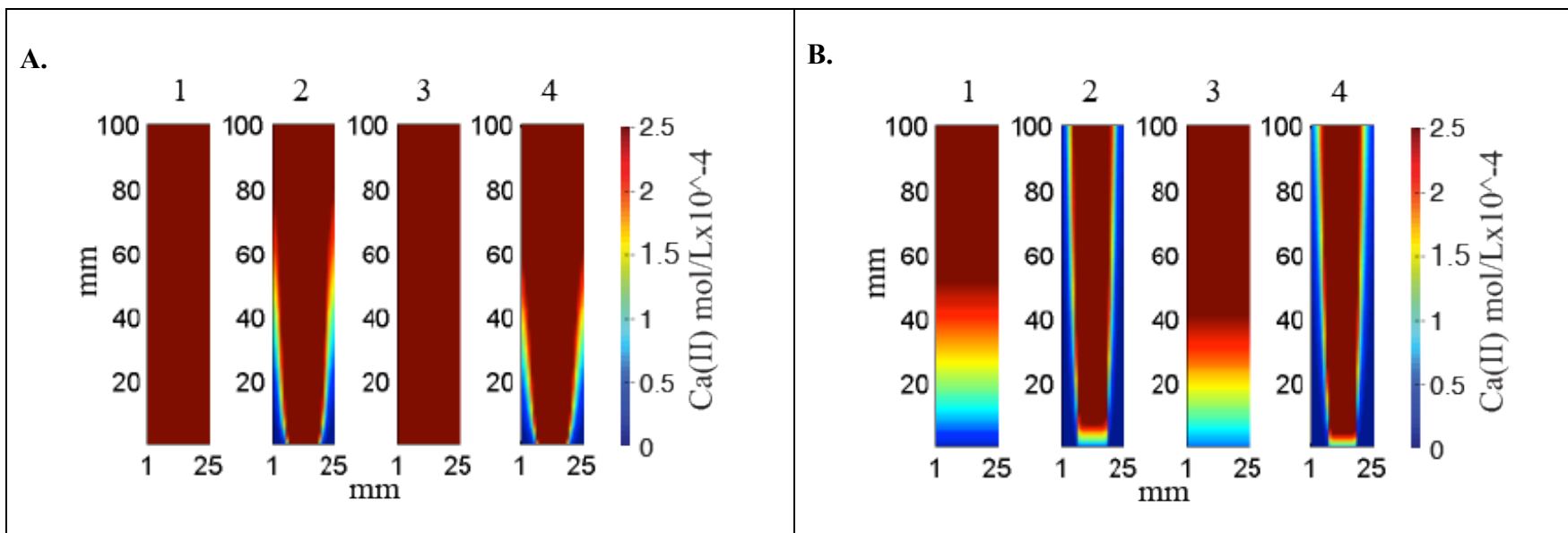


Figure 17: A. Ca(II) concentration distribution at 0.03 mL/min and inlet pH=4; B. Ca(II) concentration distribution at 6.3 mL/min and inlet pH=4.

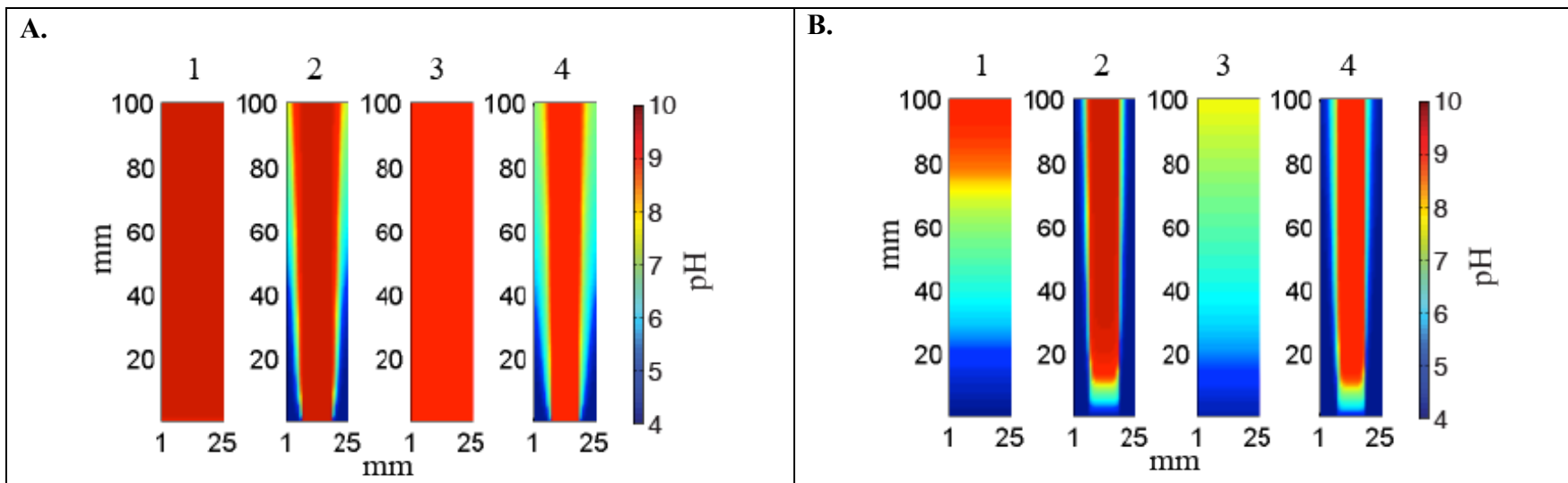


Figure 18: A. pH distribution at 0.03 mL/min and inlet pH=4; B. pH distribution at 6.3 mL/min and inlet pH=4.

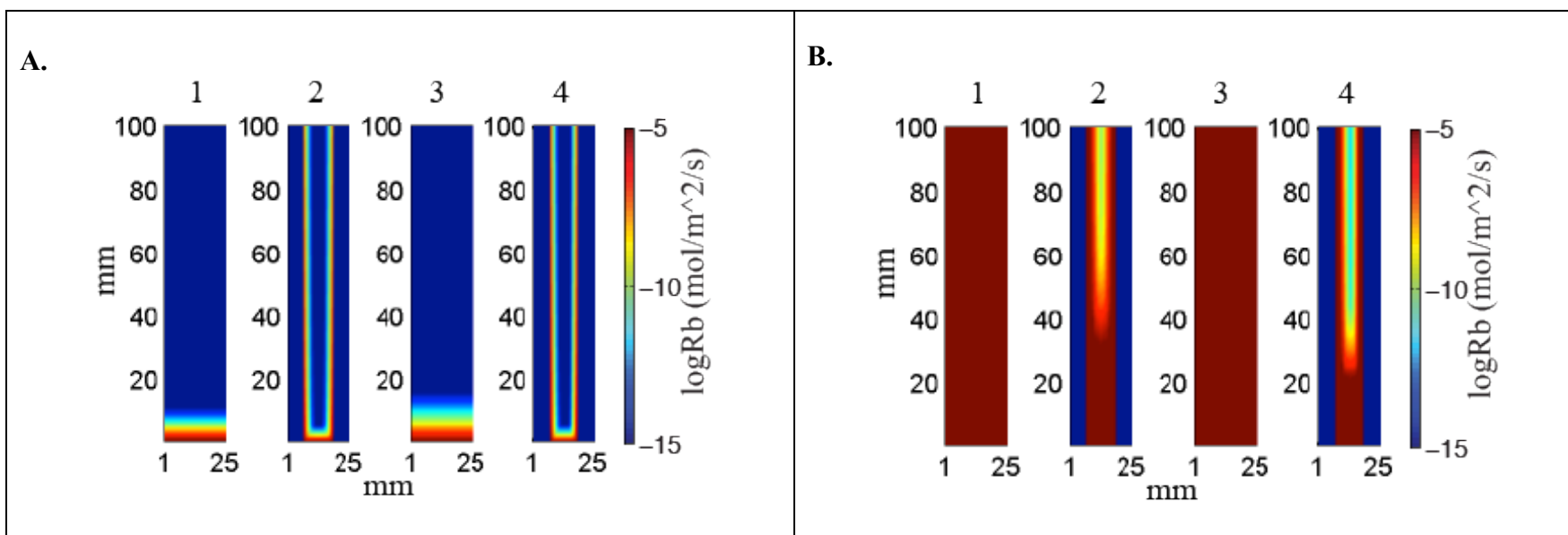


Figure 19: A. Log of dissolution rate distribution at 0.03mL/min and inlet pH=4; B. Log of dissolution rate distribution at 6.3mL/min and inlet pH=4.

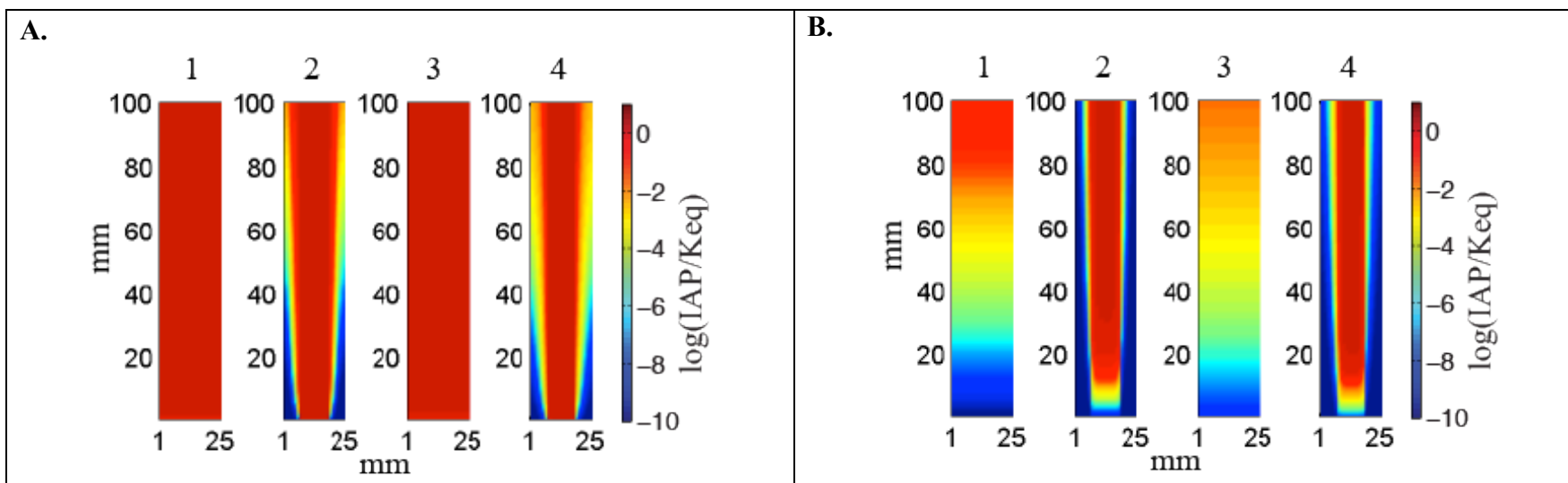


Figure 20: A. Saturation Index distribution at 0.03mL/min and inlet pH=4; B. Saturation Index distribution at 6.3mL/min and inlet pH=4.

As was mentioned during the breakthrough curve discussion, the systems reached the equilibrium state under slow flow velocity conditions. The two sets of spatial profiles (slow and fast rate) provide visual contrast between the system that reached equilibrium and one that is still in a process of doing so. The slow rate simulation will be detailed first. All four properties of the Mixed columns have “homogenized” by the end of the stimulation and are equal in magnitude and direction throughout the volume of the column. The same applies to the One-zone Columns; however, only to its reactive zone, the interface of calcite and quartz. Figure 17 depicts that the equilibrium calcite concentrations, ranging between  $1.43$  and  $2.17 \times 10^{-4}$  mol/L, had been reached; the effluent concentrations are consistent with those presented on the calcite breakthrough curves. The pH level reached 9, the initial pH of the column (Figure 19). The saturation of the reactive zones is one, which means that  $IAP$  is equal to the equilibrium constant. The  $IAP$  and  $K_{eq}$  are essentially the same parameter; the difference is that the equilibrium constant is a theoretical value of maximum dissolution and  $IAP$  is the actual value. Therefore the equality of the two is the most evident indicator of the system’s equilibrium. In addition to the above three parameters, the dissolution rate, depicted on Figure 19 is low, in the order of  $10^{-15}$  magnitude.

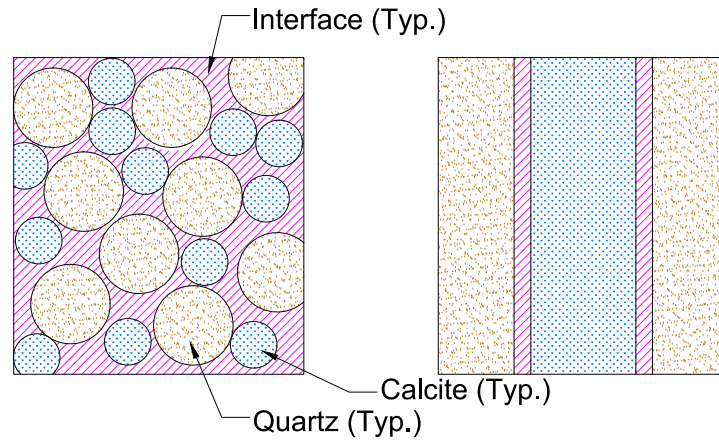
Next are the findings at fast rate, which provide information on dissolution process prior to the system at kinetic regime (prior to reaching equilibrium state). According to the spatial profile of calcium concentration, the reactivity in the Mixed Columns increases with flow progression: the concentration near the inlet is close to zero, but reaches equilibrium near the outlet. However, it is evident that the dissolution occurred throughout the entire volume of the column. In the case of One-zone Columns, the reaction only takes place at the interface of the two mineral zones. The concentration varied at the interface, proving that dissolution was occurring. As expected, the concentration of calcite was zero in the non-reactive quartz zone. Since the reaction occurred throughout the entire volume of system in the Mixed Columns and only in limited portion of volume in the One-zone Columns, the Mixed Columns produce higher dissolved calcite concentration in comparison to the corresponding One-zone systems. Therefore the spatial profiles are consistent with calcite breakthrough plots. This behavior was also confirmed with the by the spatial profile of the dissolution rate. The Mixed Columns had a higher dissolution rate, ranging between  $10^{-3} - 10^{-4}$  mol/m<sup>2</sup>/s; the calcite packed centers and quartz edge zone had rates of zero.

The described reactivity trends are applicable to both sets of columns; however, the increase in concentration and beginning of the equilibrium state itself were delayed in the HC set comparing to the LC set. It likely occurred due to the close calcite and quartz particle size in the LC set, which resulted in “higher” homogeneity of the set in comparison to HC Columns, where the size of particles varies by a factor of two.

The saturation index is in inverse correlation with the concentration values. The zones with saturation close to zero are the low reactive zones. In opposite, the areas with high saturation values are close to the equilibrium conditions.

### 3.6 Effective and Interface Surface Areas

It is known that the dissolution reaction takes places throughout the entire volume of the column in case of the mixed columns (homogeneous systems) but only at the interface of the two minerals in case of the one-zone columns (heterogeneous systems), as depicted on Figure 21. It is assumed that calcite grains are evenly distributed among quartz particles in mixed systems; and therefore it is also assumed that the interface surface area is comprised of the entire BET area, the surface area of calcite.



**Figure 21: Interface schematic: Mixed Column is on the left; One-Zone Column is on the right.**

Thus it is known that the interface area in Mixed columns is greater than that of the one-zone columns. In addition, it is expected that the effective surface area be in the same correlation as interface surface area. Both surface areas were computed for all four columns for the two flow rates, slow and fast, and two inlet pH levels described in this study. It was found that at 0.03mL/min, the effective surface area of all columns was zero. Once again, this was an indication that the systems were in equilibrium; and subsequently the rate of transport was much less than the reaction rate. Since the calculations were only performed for the two extreme flow rates, and the effective surface area was found to be zero at slow rate, the relationship between the surface areas and flow rates were not presented as a figure. Figure 22, however, illustrates the correlation between the ratio of effective and total surface areas and ratio of effective and interface surface areas for both sets of columns with inlet solution's pH level and fast flow rate of 6.3mL/min. In case of one-zone columns, the effective area was calculated based on the number of grid blocks participating in the dissolution reaction. The grid block was considered to be "effective" if its  $\frac{IAP}{K_{eq}}$  ratio was less than 0.1. The 0.1 value means that the grid block is far from equilibrium conditions, and therefore is contributing to the dissolution reaction. Similarly, the interface area was computed via interface grid blocks, which in addition to the  $\frac{IAP}{K_{eq}}$  ratio condition have to be located on the most outer one-block wide layer of calcite zone or most inner one-block wide layer of quartz. By definition the effective area was greater than interface area for one-zone columns. Figure 22A depicts the decreasing trend of effective surface area with respect to pH. This was expected, because lower pH level accelerates the dissolution reaction, as

was demonstrated in “Calcium Breakthrough” section of this paper. The difference between the effective surface areas in mixed and one-zone columns was more distinct at pH=6.7 than at pH=4, which is consistent with trends of effluent calcium concentration presented in breakthrough curves. Figure 22B illustrates how much reaction had occurred at the interface of the two minerals. The interface surface area is one of the limiting factors of the dissolution reaction in one-zone columns; and therefore its quantification is important. The next section of this paper more explicitly depicts the effects of flow rates and heterogeneity on effective and interface surface areas.

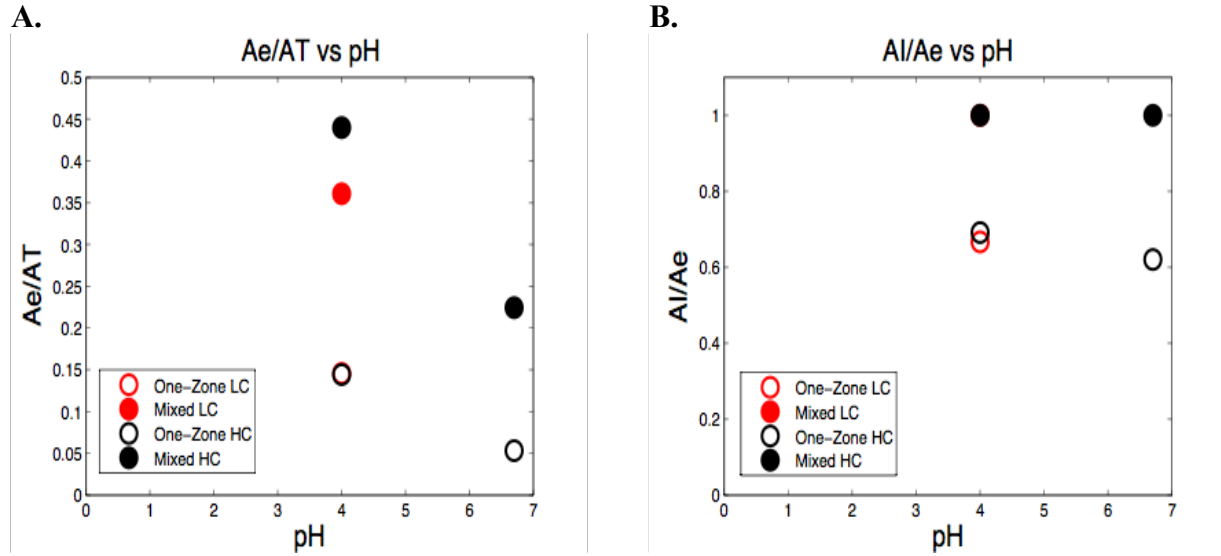


Figure 22: A. Ratios of Effective and Total Surface Areas in relationship to inlet pH; B. Ratios of Effective and Interface Surface Areas in relationship to inlet pH. On the left figure, the One-Zone LC and One-Zone HC data point for pH=4 is similar in value and is overlapped on the plot. On the right figure, LC and HC Mixed Columns points overlap.

### 3.7 Combined Effect of Permeability Contrast and Flow Rate

The effects of permeability contrast, flow rate, and pH on the calcite dissolution rate were discussed individually in the above sections of this paper. In order to analyze the combined effects of two key factors, permeability contrast and flow rate, the reactive flow model, calibrated using the laboratory obtained data, was used to map out the distribution of dissolution rates and effective areas with respect to the permeability contrast and flow rates. This analysis will further confirm and widen the scale of the previously described dissolution dependency trends. The input parameters of the simulation were taken from HC columns, which had an original permeability contrast of 0.5. The model was executed 36 times for One-Zone Columns with flow rate ranging between 0.03 and 13mL/min and permeability contrast between 0.01 and 12. The permeability contrast is the ratio between the permeabilities of calcite and quartz zones. Additional six runs with the same range of flow rates were performed for the Mixed Columns; the overall permeability was set to be constant and equal to the permeability of Mixed HC Column.

Figure 23A depicts the distribution of the dissolution rate with respect to the listed parameters. At slow flow rate, the rate of transport was much slower than the reaction rate and the system in the equilibrium; the dissolution rate was in order of  $10^{-10} - 10^{-10.5}$  range, the permeability contrast

had no effect. As flow rate increased, each of the permeability contrast maintained the same trend of dissolution rate increase: transport rate prevailed over the reaction rate. The ratios of bulk dissolution rates of One-Zone Columns and corresponding Mixed Columns are presented in Figure 23B.

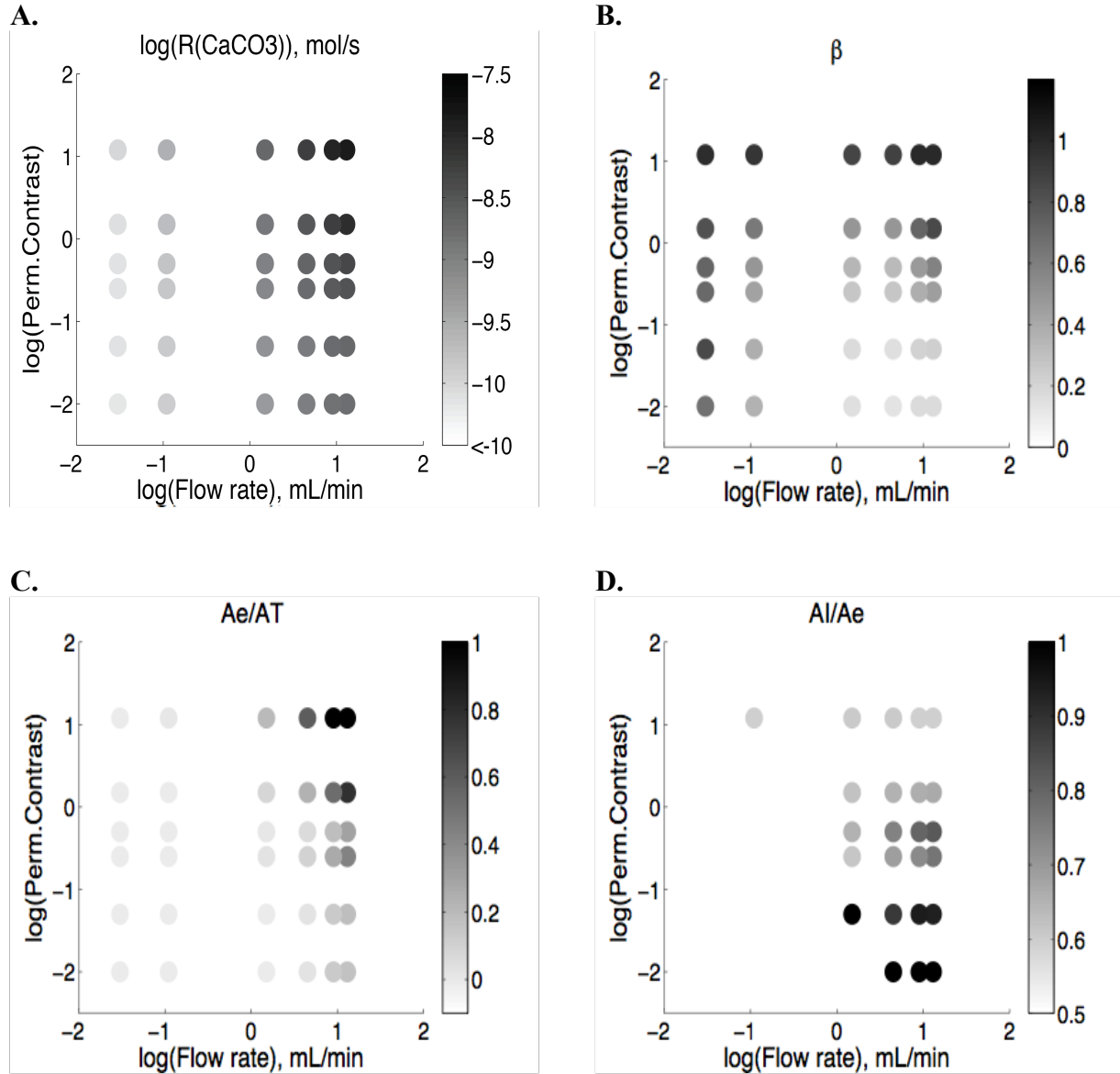


Figure 23: A. Bulk dissolution ratio of One-Zone and corresponding Mixed Columns in relationship to flow rate and permeability contrast of the two mineral zones; B. Dissolution rate of One-Zone Columns in relationship to flow rate and permeability contrast of the two mineral zones; C. Ratio of Effective and Total Surface Areas of One-Zone Columns in relationship to flow rate and permeability contrast of the two mineral zones; D. Ratio of Interface and Effective Surface Areas in relationship to flow rate and permeability contrast of the two mineral zones.

The ratio, ranging between zero and one, indicates that the rate is Mixed column was faster than in corresponding One-Zone column, and as a result produced higher effluent calcium concentrations. The effects of heterogeneity become less dominant as the bulk dissolution ratio approaches one. From the figure, the ratio is close to one at slow flow rates for all permeability contrasts. This indicated that the two columns behaved similarly; the same was observed during

the LC and HC columns simulations. The largest discrepancy was observed for low permeability contrast and high flow rates region. For medium flow rates and medium contrast, the ratio was almost constant at approximately 0.6. With increase in flow rates, it is expected that medium and high permeability contrast columns behaved closer to the corresponding homogeneous systems. The later occurred for contrasts between 0.25 and 1.5; however, it did not for the highest contrast of 12. The high permeability (PC=12) simulation series behave as expected until it reached moderately high flow rate of 4.5. This set acts less like a well-mixed case scenario between flow rates of 4.5 to 13 mL/min. This could have occurred because the flow travels through the less permeability calcite center of the column with less resistance than in other columns, and as result, the rate of transport supersedes the reaction rate more so that for other fast flow rate cases.

The surface areas illustrated in Figures 23C and 23D explain the variations in dissolution rates presented in Figures 23A and 23B. At equilibrium conditions, the effective area is equal to zero. Small effective area numbers were also observed across the entire permeability series. More grid blocks become effective as high permeability and high flow velocity conditions were being approached. Under the latter set-up, the flow was conveyed through the calcite center of the column rather than short-circuiting through the outer quartz layers. Figure 23D does not display points where the effective area equaled to zero, because zero cannot be divided by. The goal of this plot was to identify when the interface condition matter. From the figure, the interface plays a limiting factor role at low flow rates and low permeabilities. Under these conditions, the reactive flow is mainly going through the path at least resistance, the less permeable quartz zone. In these cases, only portion of the flow was in contact with the interface; and there was no flow through the middle calcite zone. In opposite, the interface was no longer a limiting parameter for the high contrast set-ups, since the middle calcite zone was more permeable, and flow was conveyed through the center of the column. The distribution of properties presented in Figure 23 highlights the significant influence of heterogeneity on column's behavior and differentiation from homogeneous conditions.

Figure 24 is plotted to quantify a relationship between the dissolution rate and the effective area of the columns. From this figure, it is confirmed that the dissolution rate increased with increase in effective surface area of the column. All points were in direct correlation; however, a straight line could be fitted for the data from the Mixed Columns with determination factor of 0.9992. The effective surface area is a characteristic of system's heterogeneity. Therefore Figure 24 depicts direct correlation between the system's heterogeneity and dissolution rates.

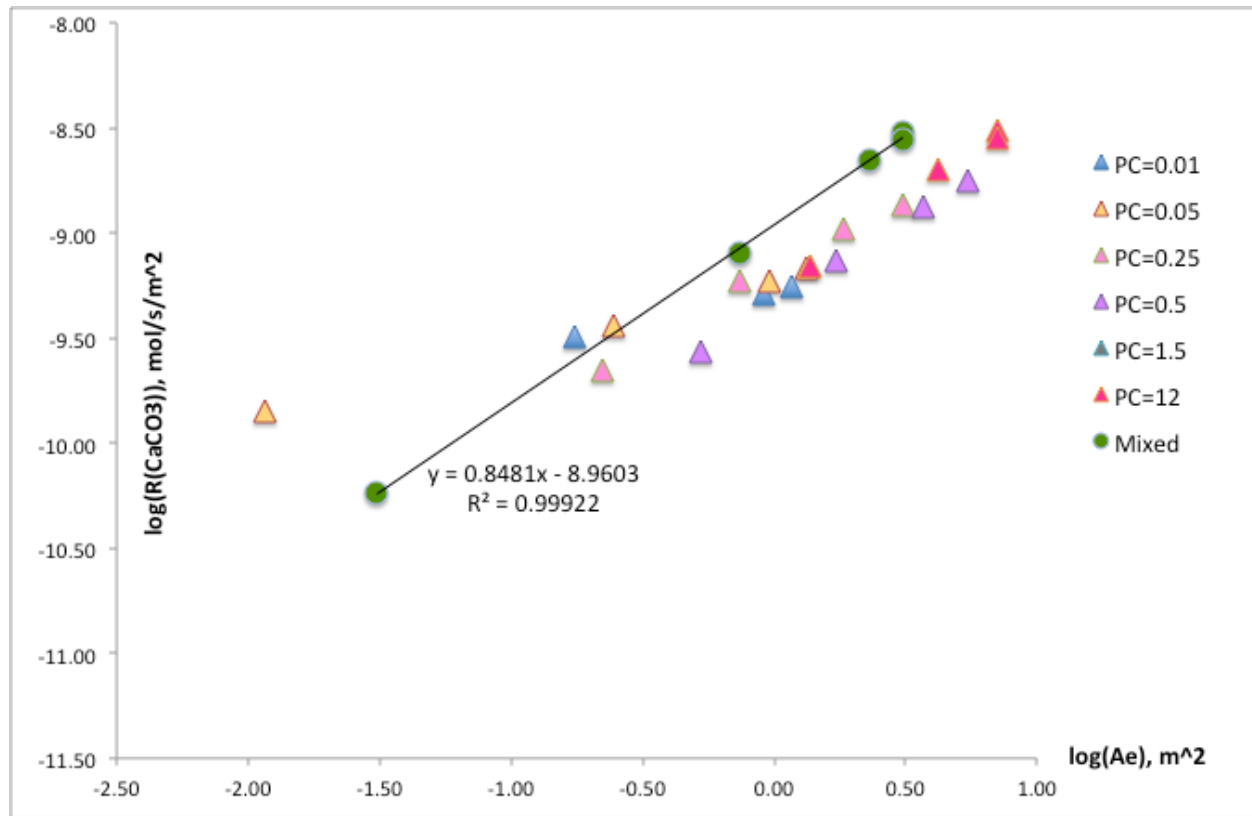


Figure 24: Correlation of Effective Surface Area and Dissolution Rate. The points with effective area of zero are not plotted in this figure, since logarithm of zero does not exist.

### 3.8 Column-Scale Rates and Damkohler Number

The Damkohler number is a ratio of turbulence travel time over reaction travel time. Essentially, it characterizes how quickly the turbulence moves with respect to the reaction progression. The distribution of Damkohler number with respect to the log of surface-area-normalized column-scale dissolution rate at pH=4 is depicted in Figure 25. The data presented is from the real columns, LC and HC sets, as well as the 42 simulated cases. The calculated Damkohler number ranged between approximately zero and 2.72. There is no clear trend present for the One-Zone Columns. However, three zones, depicted in Figure 25 can be observed for the Mixed Columns. The zone with prevailing kinetic regime is termed Zone 1 (Damkohler number < 2.13). Zone 2 designated system's transition state ( $2.13 < \text{Damkohler number} < 2.5$ ). Here, the Damkohler number is in direct linear correlation with the log of the dissolution rate. Finally, Zone 3 designated the equilibrium state (Damkohler number > 2.5).

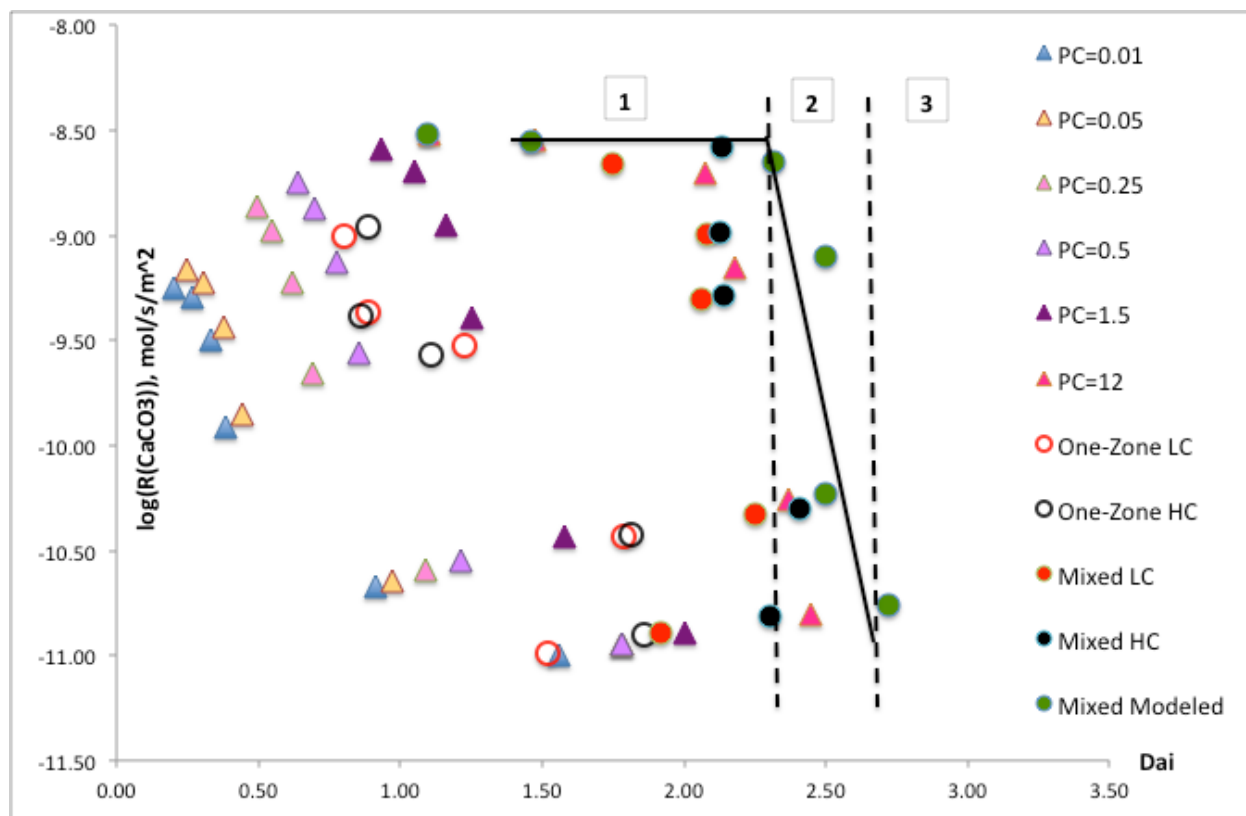


Figure 25: Damkohler Number Distribution. Zones: 1- kinetic regime, 2 – transition state, and 3 – equilibrium state.

## Chapter 4

### SUMMARY AND CONCLUSIONS

The goal of this research work was to compare the dissolution characteristics of calcite under various conditions and to quantify the effects of those conditions on the calcite dissolution rate. The variable factors included pH of inlet solution, flow rate, permeability contrast as well as the combined effects of the last two parameters. Furthermore, the effects were to be studied for a homogeneous and a variety of heterogeneous systems in order to analyze the behavioral differences of the theoretically idealized well-mixed system and more realistic heterogeneous system. In particular, the conditions under which the heterogeneity affects the systems the most was of interest.

All columns had reached equilibrium state at a slow flow rate of 0.03 mL/min. At this flow rate and inlet pH of 4, the column scale bulk dissolution rate normalized over the total surface area of the column ranged between 1.02 and  $1.55 \times 10^{-11}$  mol/s/m<sup>2</sup>. The rate of the Mixed LC and HC Columns was, respectively, 1.24 and 1.26 times faster than the corresponding One-Zone Columns. At fast flow rate of 6.3 mL/min, the dissolution rate varied from 1 to  $2.65 \times 10^{-9}$  mol/s/m<sup>2</sup>. Kinetics regime prevails under fast flow rate condition; this regime is characterized by faster transport rate in comparison to the reaction rate – the opposite of the equilibrium state. The rate of Mixed LC was 2.17 times faster than One-Zone LC; the rate of Mixed HC Columns, however, was 2.41 times faster than its corresponding One-Zone column. The wider cap is an indication that the HC columns contain higher degree of heterogeneity. Identical trends were identified for experiments and simulations with inlet pH of 6.7; the dissolution rates were slighter higher with the same corresponding order of magnitude. The calcite effluent concentration is a function of flow and dissolution rates; lower rates produce higher calcium concentrations and vice versa. Thus the dissolution rates increase with increase in flow rate and pH; consequently the effluent concentration of calcite has an opposite result. The amplitude of dissolution variance between the Mixed and One-Zone sets is greater for the HC systems; proving that heterogeneity of the system has significant effect on its behavior.

Spatial profiles of calcium concentration, pH level, saturation index, and dissolution rate show that under the slow flow conditions the parameters were uniformly distributed throughout the Mixed Columns; the same did not hold true for One-Zone Columns. In the latter columns, the properties were uniformly distributed throughout quartz zone and throughout the calcite zone, however, at different magnitudes. In addition, there were property variations at the interface of the two minerals. Under the kinetic regime, Mixed Columns' characteristics differed along the longitudinal direction and were generally uniform along transverse direction. In case of One-Zone Columns, the variation occurred in both directions, primary along the interface area. This was also confirmed with dispersivity values: the longitudinal dispersivity varied in both, homogeneous (Mixed Columns) and heterogeneous (One-Zone Columns) sets; the transverse dispersivity only influenced the latter systems. The local longitudinal dispersivity values were found to be between 0.03 and 0.3 cm at 0.03 mL/min and between 0.01 and 0.8 cm for 6.3 mL/min: the highest values belonged to Mixed HC Column, the lowest – to One-Zone LC Column for

both conditions. The transverse dispersivity was estimated at 0.006cm for LC set and 0.007cm for HC set; no change with flow rate increase. The values were in the same order of magnitude as previously performed Chao's study (comparison figures provided in Table 1).

After computing the parameters of interest for the laboratory columns, the model was expanded to include a wider range of flow rates and permeability contrasts. The increase in bulk dissolution rate with increase in flow rate trend was confirmed on the larger scale. It was also demonstrated that the One-Zone Columns behaved similar to the Mixed ones at low flow rates with no influence of the permeability contrast due to the equilibrium state. Under those conditions, the bulk dissolution ratio of the One-Zone to the corresponding Mixed Columns was close to one. For medium and high flow rates, the performance varied: the dissolution ratio generally increased with the increase in flow rate. The above analysis concluded that the various degrees of heterogeneity result in wide amplitude of system behaviors. The investigation of the interface surface area demonstrated that the available interface is one of the dissolution limiting parameters. The latter is particularly important for the low permeability kinetic region. The observed trends were consistent with a similar magnesite dissolution study (Salekhikoo, 2014).

It can be concluded that on the observed scale the permeability contrast (and therefore the degree heterogeneity of the system) had the most effect on the dissolution rates and consequently the calcium effluent concentration. The rate ranged by two orders of magnitude between all permeability contrasts options at the same flow rate and inlet pH. The flow rate only resulted in one order of magnitude variation while other factors were fixed. Lastly, the studied inlet pH had an outcome of no magnitude variation of the dissolution rate.

From the above-described findings, it can be concluded that the heterogeneity has a significant effect on the system's behavior. The flow rate, inlet solution's pH level, and permeability contrast result in various outcomes for a range of heterogeneous conditions. Higher degree of heterogeneity contributed to a higher deviation from the well-mixed systems behavior. The implications of this study imply that the natural heterogeneous systems cannot be assumed to homogenous for modeling and design purposes. The present study identified discrepancies in dissolution rates between homogeneous and heterogeneous systems on a relatively small spatial and time scales. These discrepancies are magnified in natural subsurface systems due to the systems' size and time of operation.

All conclusions were based on laboratory experiments and CrunchFlow simulations performed at standard conditions. Further investigation of the matter may include the execution and the analysis of the dissolution experiments with columns packed with more than one reactive mineral as well as systems packed under elevated pressures and temperatures, simulating more realistic reservoir conditions.

## REFERENCES

- Ahr, W.M. (2008) Carbonate Reservoir Rock Properties, *Geology of Carbonate Reservoirs*. John Wiley & Sons, Inc., pp. 13-55.
- Araque-Martinez, A. and Lake, L.W. (2004) Modeling Pressure and Temperature Effects on Reactive Flow and its Impact on Well Performance under Common Operational Conditions, SPE International Symposium and Exhibition on Formation Damage Control. Society of Petroleum Engineers, Lafayette, Louisiana.
- Bagheri, A.M. and Biranvand, B. (2006) Characterization of Reservoir Rock Types in a Heterogeneous Clastic and Carbonate Reservoir, Research Institute of Petroleum Industry (RIPI), 7 Hovaizeh Avenue, Tehran, Iran, pp. 29-38.
- Bazin, B. and Labrid, J. (1991) Ion Exchange and Dissolution/ Precipitation Modeling: Application to the Injection of Aqueous Fluids Into a Reservoir Sandstone. *SPE Reservoir Engineering* 6, 233-238.
- Békri, S., Thovert, J.F. and Adler, P.M. (1995) Dissolution of porous media. *Chemical Engineering Science* 50, 2765-2791.
- Berner, R.A. (1967) Comparative Dissolution Characteristics of Carbonate Minerals in the Presence and Absence of Aqueous Magnesium Ion. *American Journal of Science* 265, 45-70.
- Berner, R.A. and Morse, J.W. (1974) Dissolution Kinetics of Calcium Carbonate in Sea Water; IV, Theory of Calcite Dissolution. *American Journal of Science*.
- Boguski (1876) *Bcr.* 9.
- Boguski and Kajander (1877) *ibid.* 10, 34.
- Brantley, S.L. (2008) Kinetics of Mineral Dissolution, in: Brantley, S.L., Kubicki, J.D., White, A.F. (Eds.), *Kinetics of Water-Rock Interaction*. Springer New York, pp. 151-210.
- Brunner (1904) *Z. physik. Chcm.*, 47, 79.
- Bryant, S.L., Schechter, R.S. and Lake, L.W. (1986) Interactions of Precipitation/Dissolution Waves and Ion Exchange in FLOW Through Permeable Media, Department of Petroleum Engineering The University of Texas, Austin, TX.
- Burchette, T.P. (2012) Carbonate Rocks and Petroleum Reservoirs: a Geological Perspective from the Industry.
- Casey, W.H. and Sposito, G. (1992) On the temperature dependence of mineral dissolution rates. *Geochimica et Cosmochimica Acta* 56, 3825-3830.
- Chao, T. (2014) Calcite Dissolution Rates at Different Spatial Distribution: The Role of Mineral Spatial Distribution and Flow Velocity, Energy and Mineral Engineering. The Pennsylvania State University.
- Chesnut, D.A. (1994) Dispersivity in Heterogeneous Permeable Media. American Nuclear Society International High Level Radioactive Waste Management Conference.
- Chou, L., Garrels, R.M. and Wollast, R. (1989) Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. *Chemical Geology* 78, 269-282.
- Dandekar, A.Y. (2006) *Petroleum Reservoir Rock and Fluid Properties*. Taylor & Francis Group, LLC., Boca Raton, FL.
- Dyni, J. (2005) *Geology and Resources of Some World Oil-Shale Deposits*, Scientific Investigations Report 2005-5294. US Department of the interior, Reston, VA.
- EIA, U. (2012) *Primary Energy Consumption Estimates by Source, 1949-2011, Total Energy*. US Department of Energy, Washington, DC.

- Ericson-huron and Palmaer (1906) *ihid.*, 66, 689.
- Fan, H. (2003) The Effects of Reservoir Minerals on the Composition Changes of Heavy Oil During Steam Stimulation. *Journal of Canadian Petroleum Technology* 42.
- Faurholt, J. (1924) *J. chim.phys.*, 31, 400.
- Filho and Ricardo, D.G.d.F. (2012) Effects of Dissolution on the Permeability and Porosity of Limestone and Dolomite in High Pressure CO<sub>2</sub>/water Systems, 160911 - STU SPE Conference Paper.
- Kalia, N. and Balakotaiah, V. (2009) Effect of medium heterogeneities on reactive dissolution of carbonates. *Chemical Engineering Science* 64, 376-390.
- Kepferle, J.B.R.R.C. (1993) *Petroleum Geology of the Devonian and Mississippian Black Shale of Eastern North America*, US Geological Survey, Reston, VA.
- Li, Salehikhoo, Brantley and Heidari (2013) Spatial Zonation Limits Magnesite Dissolution in Porous Media. Resubmission to *Geochimica et Cosmochimica Acta*.
- Li, L., Carl, I.S. and Li, Y. (2009) Mineral Dissolution Kinetics at the Pore Scale, Earth and Mineral Science Division Lawrence Berkeley National Laboratory, Berkeley National Laboratory.
- Li, L., Steefel, C.I. and Yang, L. (2008) Scale dependence of mineral dissolution rates within single pores and fractures. *Geochimica et Cosmochimica Acta* 72, 360-377.
- Lichtner, P.C. (1985) Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochimica et Cosmochimica Acta* 49, 779-800.
- Maher, K., Steefel, C.I., DePaolo, D.J. and Viani, B.E. (2006) The mineral dissolution rate conundrum: Insights from reactive transport modeling of U isotopes and pore fluid chemistry in marine sediments. *Geochimica et Cosmochimica Acta* 70, 337-363.
- Minyard, M.L. and Burgos, W.D. (2007) Hydrologic Flow Controls on Biologic Iron(III) Reduction in Natural Sediments. *Environmental Science & Technology* 41, 1218-1224.
- Molins, S., Trebotich, D., Steefel, C.I. and Shen, C. (2012) An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation. *Water Resources Research* 48, W03527.
- Morse, J.W. and Mackenzie, F.T. (1990) *Geochemistry of sedimentary carbonates*. Elsevier, Amsterdam, New York, NY, USA.
- Murphy, W.M., Oelkers, E.H. and Lichtner, P.C. (1989) Surface reaction versus diffusion control of mineral dissolution and growth rates in geochemical processes. *Chemical Geology* 78, 357-380.
- P. Fitch, S.D., M. Lovell, T. Pritchard, & C. Sirju (2010) Heterogeneity in Carbonate Petrophysical Properties: application to fluid flow units and sampling strategies., SPWLA 51st Annual Logging Symposium. Society of Petrophysicists and Well Log Analysis, Perth, Australia.
- Peszynska, M. and Sun, S. (2002) Reactive Transport Model Coupled to Multiphase Flow Models, TICAM, University of Texas at Austin.
- Plummer, L.N., Wigley, T.M.L. and Parkhurst, D.L. (1978) The dissolution of calcite in CO<sub>2</sub>-water system at 5 to 60C and 0.0 to 1.0 atm CO<sub>2</sub>. *American Journal of Science*, 179-216.
- Plummer, L.N., Wigley, T.M.L. and Parkhurst, D.L. (1979) Critical review of the kinetics of calcite dissolution and precipitation. *American Journal of Science* 93, 537-573.
- Pruess, K. (2008) On production behavior of enhanced geothermal systems with CO<sub>2</sub> as working fluid. *Energy Conversion and Management* 49, 1446-1454.

Pruess, K., Xu, T., Birkle, P., Contreras-Lopez, E. and Diaz-Lopez, M. (2006) Using Laboratory Flow Experiments and Reactive Chemical Transport Modeling for Designing Waterflooding of the Agua Fria Reservoir, Poza Rica-Altamira Field, Mexico, First International Oil Conference and Exhibition in Mexico. Society of Petroleum Engineers, Cancun, Mexico.

Reed, M.G. (1977) Formation Permeability Damage by Mica Alteration and Carbonate Dissolution. 6009 - PA SPE Journal Paper.

Saal (1928) *Rec. trav.chim.*, 47, 264.

Salehikhoo, F., Li, L. and Brantley, S.L. (2013) Magnesite dissolution rates at different spatial scales: The role of mineral spatial distribution and flow velocity. *Geochimica et Cosmochimica Acta* 108, 91-106.

Salehikhoo, F. (2014) The role of spatial heterogeneity in determining dissolution rates in porous media: when does it matter?, *Energy and Mineral Engineering*. The Pennsylvania State University.

Sjoberg, E.L. (1978) Kinetics and Mechanism of Calcite Dissolution in Aqueous Solution at Low Temperatures. *Stockholm Contrib. Geol.* 32.

Sjoberg, E.L. and Rickard, D.T. (1983) The Influence of Experimental Design on the Rate of Calcite Dissolution. *Geochim. Cosmochim. Acta* 47, 2281-2285.

Steeffel, C.I. and Lasaga, A.C. (1994) A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems.

Tammann and Krings (1925) *anorg. Chem*, 146, 420.

Tominaga, H., Adzumi, H. and Isobe, T. (1939) Viscosity Effect on the Rate of Solution of Calcium Carbonate in Hydrochloric Acid. *Chemical Institute, Faculty of Science, Tohoku Imperial University, Sendai*, pp. 348-352.

van Grinsven, J.J.M. and van Riemsdijk, W.H. (1992) Evaluation of batch and column techniques to measure weathering rates in soils. *Geoderma* 52, 41-57.

Weyl, P.K. (1958) The Solution Kinetics of Calcite. *The Journal of Geology* 66, 163-176.

Wolery, T.J. and al., e. (1990) Current Status of the EQ3/6 Software Package for Geochemical Modeling.

Wolfson, R.L. (2012) Specifics on Surface Area. *Journal of GXP Compliance* 16, 22-33.

Xiao, Y. and Jones, G.D. (2007) Reactive Transport Models of Limestone-Dolomite Transitions: Implications for Reservoir Connectivity, *International Petroleum Technology Conference*. International Petroleum Technology Conference, Dubai, U.A.E.

# **APPENDIX A**

## **BET AREA ANALYSIS REPORT**

Sample: quartz  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-390.SMP

|                                          |                                                   |
|------------------------------------------|---------------------------------------------------|
| Started: 11/5/2013 9:06:18AM             | Analysis Adsorptive: N2                           |
| Completed: 11/5/2013 11:40:05AM          | Analysis Bath Temp.: 77.216 K                     |
| Report Time: 11/5/2013 11:40:06AM        | Thermal Correction: No                            |
| Sample Mass: 4.7461 g                    | Warm Free Space: 26.1237 cm <sup>3</sup> Measured |
| Cold Free Space: 81.1459 cm <sup>3</sup> | Equilibration Interval: 10 s                      |
| Ambient 22.00 °C                         | Low Pressure Dose: None                           |
| Temperature:                             |                                                   |
| Automatic Degas: Yes                     |                                                   |

### Summary Report

#### Surface Area

Single point surface area at P/Po = 0.299809896: 0.0862 m<sup>2</sup>/g

BET Surface Area: 0.1038 m<sup>2</sup>/g

Sample: quartz  
 Operator: Lymaris Ortiz Rivera  
 Submitter: Mariya Skocik  
 File: C:\2020\DATA\000-390.SMP

Started: 11/5/2013 9:06:18AM  
 Completed: 11/5/2013 11:40:05AM  
 Report Time: 11/5/2013 11:40:06AM  
 Sample Mass: 4.7461 g  
 Cold Free Space: 81.1459 cm<sup>3</sup>  
 Ambient 22.00 °C  
 Temperature:  
 Automatic Degas: Yes

Analysis Adsorptive: N2  
 Analysis Bath Temp.: 77.216 K  
 Thermal Correction: No  
 Warm Free Space: 26.1237 cm<sup>3</sup> Measured  
 Equilibration Interval: 10 s  
 Low Pressure Dose: None

### Isotherm Tabular Report

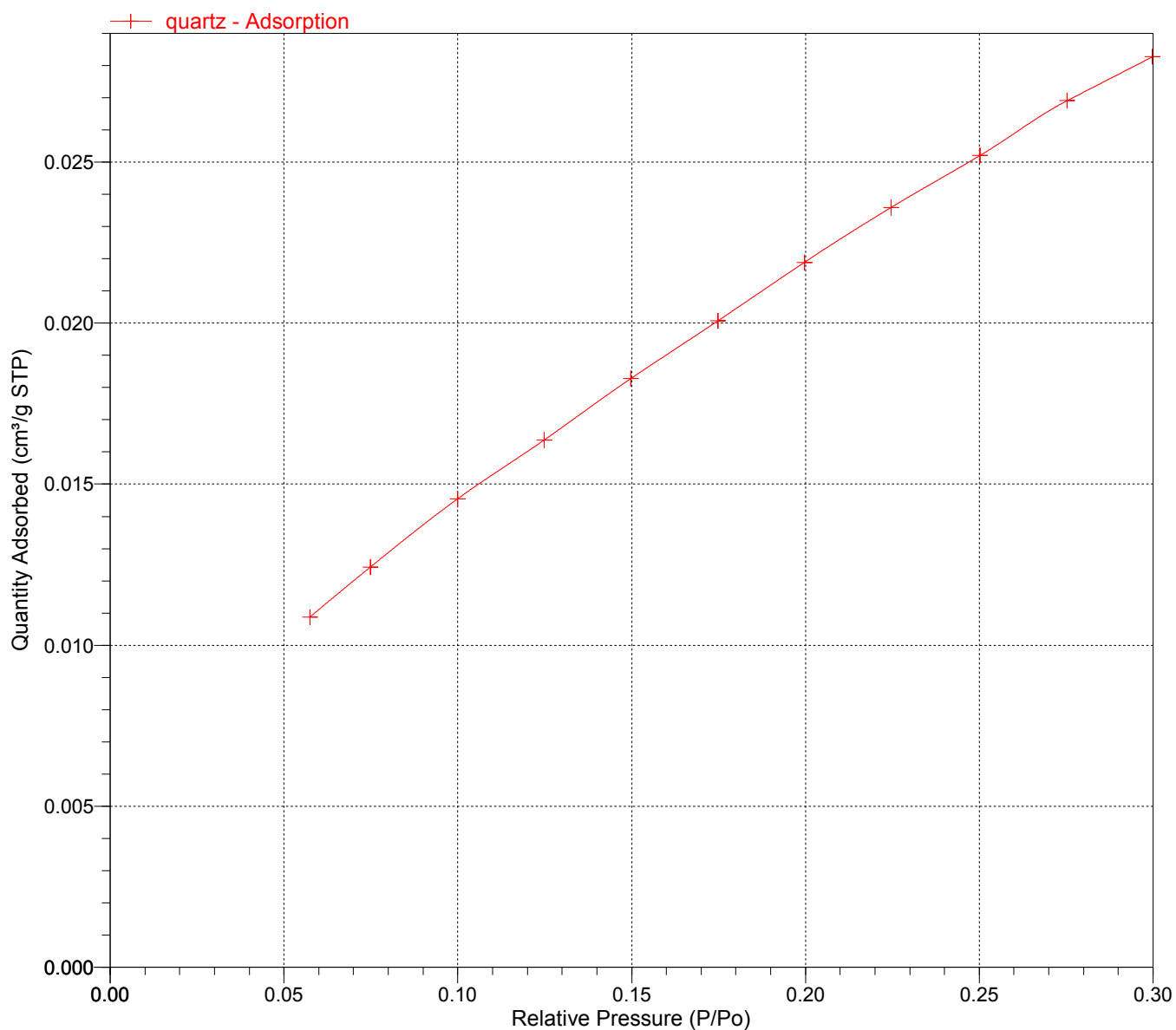
| Relative<br>Pressure (P/Po) | Absolute<br>Pressure<br>(mmHg) | Quantity<br>Adsorbed<br>(cm <sup>3</sup> /g STP) | Elapsed Time<br>(h:min) | Saturation<br>Pressure<br>(mmHg) |
|-----------------------------|--------------------------------|--------------------------------------------------|-------------------------|----------------------------------|
|                             |                                |                                                  | 01:44                   | 747.946289                       |
| 0.057489800                 | 42.999283                      | 0.0109                                           | 01:57                   |                                  |
| 0.074939978                 | 56.051079                      | 0.0124                                           | 01:59                   |                                  |
| 0.099885902                 | 74.709290                      | 0.0145                                           | 02:02                   |                                  |
| 0.124904983                 | 93.422218                      | 0.0164                                           | 02:04                   |                                  |
| 0.149806942                 | 112.047546                     | 0.0183                                           | 02:06                   |                                  |
| 0.174843435                 | 130.773499                     | 0.0201                                           | 02:08                   |                                  |
| 0.199706480                 | 149.369720                     | 0.0219                                           | 02:11                   |                                  |
| 0.224706313                 | 168.068253                     | 0.0236                                           | 02:13                   |                                  |
| 0.250234692                 | 187.162109                     | 0.0252                                           | 02:15                   |                                  |
| 0.275195192                 | 205.831223                     | 0.0269                                           | 02:17                   |                                  |
| 0.299809896                 | 224.241699                     | 0.0283                                           | 02:20                   |                                  |

Sample: quartz  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-390.SMP

Started: 11/5/2013 9:06:18AM  
Completed: 11/5/2013 11:40:05AM  
Report Time: 11/5/2013 11:40:06AM  
Sample Mass: 4.7461 g  
Cold Free Space: 81.1459 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.216 K  
Thermal Correction: No  
Warm Free Space: 26.1237 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Isotherm Linear Plot

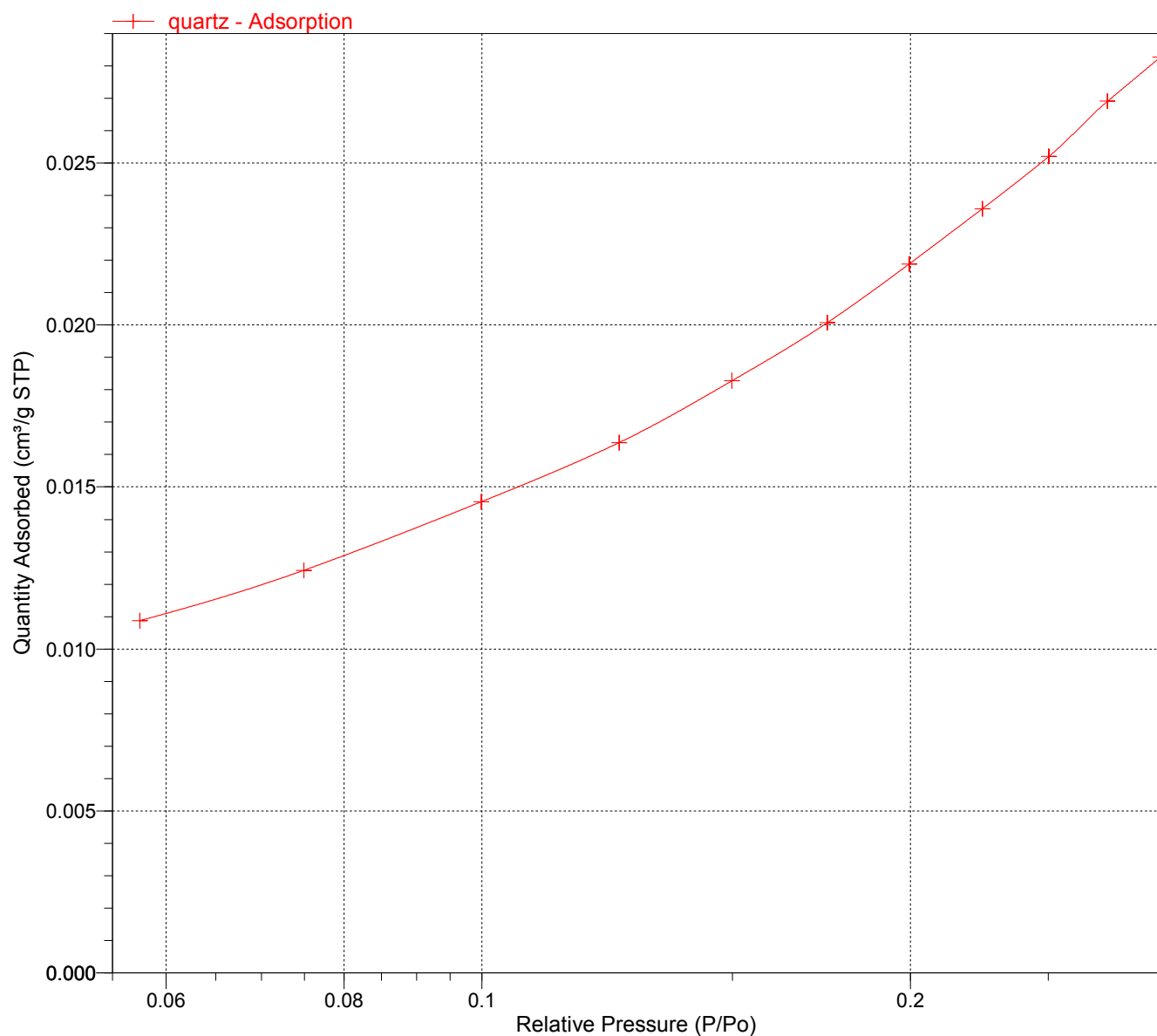


Sample: quartz  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-390.SMP

Started: 11/5/2013 9:06:18AM  
Completed: 11/5/2013 11:40:05AM  
Report Time: 11/5/2013 11:40:06AM  
Sample Mass: 4.7461 g  
Cold Free Space: 81.1459 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.216 K  
Thermal Correction: No  
Warm Free Space: 26.1237 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Isotherm Log Plot



Sample: quartz  
 Operator: Lymaris Ortiz Rivera  
 Submitter: Mariya Skocik  
 File: C:\2020\DATA\000-390.SMP

Started: 11/5/2013 9:06:18AM      Analysis Adsorptive: N2  
 Completed: 11/5/2013 11:40:05AM      Analysis Bath Temp.: 77.216 K  
 Report Time: 11/5/2013 11:40:06AM      Thermal Correction: No  
 Sample Mass: 4.7461 g      Warm Free Space: 26.1237 cm<sup>3</sup> Measured  
 Cold Free Space: 81.1459 cm<sup>3</sup>      Equilibration Interval: 10 s  
 Ambient 22.00 °C      Low Pressure Dose: None  
 Temperature:  
 Automatic Degas: Yes

### BET Surface Area Report

BET Surface Area:  $0.1038 \pm 0.0016$  m<sup>2</sup>/g  
 Slope:  $38.214175 \pm 0.631513$  g/cm<sup>3</sup>  
 STP  
 Y-Intercept:  $3.730675 \pm 0.121343$  g/cm<sup>3</sup> STP  
 C: 11.243234  
 Qm: 0.0238 cm<sup>3</sup>/g STP  
 Correlation Coefficient: 0.9987733  
 Molecular Cross-Sectional Area: 0.1620 nm<sup>2</sup>

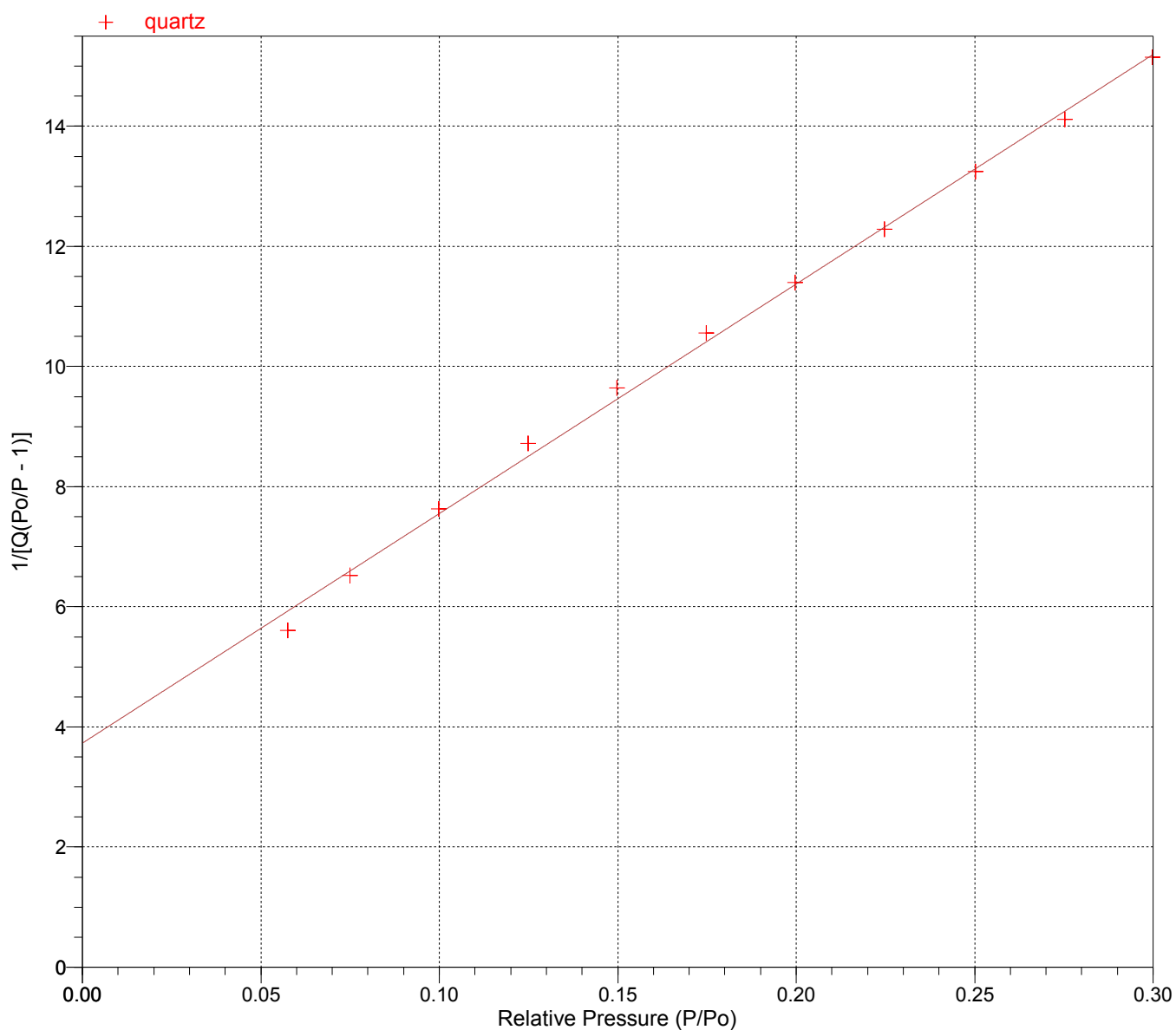
| Relative<br>Pressure<br>(P/Po) | Quantity<br>Adsorbed<br>(cm <sup>3</sup> /g STP) | 1/[Q(Po/P - 1)] |
|--------------------------------|--------------------------------------------------|-----------------|
| 0.057489800                    | 0.0109                                           | 5.608540        |
| 0.074939978                    | 0.0124                                           | 6.517800        |
| 0.099885902                    | 0.0145                                           | 7.629177        |
| 0.124904983                    | 0.0164                                           | 8.717943        |
| 0.149806942                    | 0.0183                                           | 9.640035        |
| 0.174843435                    | 0.0201                                           | 10.555152       |
| 0.199706480                    | 0.0219                                           | 11.399029       |
| 0.224706313                    | 0.0236                                           | 12.284423       |
| 0.250234692                    | 0.0252                                           | 13.241595       |
| 0.275195192                    | 0.0269                                           | 14.110138       |
| 0.299809896                    | 0.0283                                           | 15.145174       |

Sample: quartz  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-390.SMP

Started: 11/5/2013 9:06:18AM  
Completed: 11/5/2013 11:40:05AM  
Report Time: 11/5/2013 11:40:06AM  
Sample Mass: 4.7461 g  
Cold Free Space: 81.1459 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.216 K  
Thermal Correction: No  
Warm Free Space: 26.1237 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

BET Surface Area Plot



Sample: Calcite 125/150 washed and dried  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-289.SMP

|                                          |                                                   |
|------------------------------------------|---------------------------------------------------|
| Started: 8/8/2013 11:36:54AM             | Analysis Adsorptive: N2                           |
| Completed: 8/8/2013 2:15:23PM            | Analysis Bath Temp.: 77.075 K                     |
| Report Time: 8/9/2013 8:59:30AM          | Thermal Correction: No                            |
| Sample Mass: 0.6098 g                    | Warm Free Space: 28.1307 cm <sup>3</sup> Measured |
| Cold Free Space: 87.2963 cm <sup>3</sup> | Equilibration Interval: 10 s                      |
| Ambient 22.00 °C                         | Low Pressure Dose: None                           |
| Temperature:                             |                                                   |
| Automatic Degas: Yes                     |                                                   |

### Summary Report

#### Surface Area

Single point surface area at  $P/P_0 = 0.300282240$ : 0.4101 m<sup>2</sup>/g

BET Surface Area: 0.5591 m<sup>2</sup>/g

Sample: Calcite 125/150 washed and dried  
 Operator: Lymaris Ortiz Rivera  
 Submitter: Mariya Skocik  
 File: C:\2020\DATA\000-289.SMP

Started: 8/8/2013 11:36:54AM      Analysis Adsorptive: N2  
 Completed: 8/8/2013 2:15:23PM      Analysis Bath Temp.: 77.075 K  
 Report Time: 8/9/2013 8:59:30AM      Thermal Correction: No  
 Sample Mass: 0.6098 g      Warm Free Space: 28.1307 cm<sup>3</sup> Measured  
 Cold Free Space: 87.2963 cm<sup>3</sup>      Equilibration Interval: 10 s  
 Ambient 22.00 °C      Low Pressure Dose: None  
 Temperature:  
 Automatic Degas: Yes

### Isotherm Tabular Report

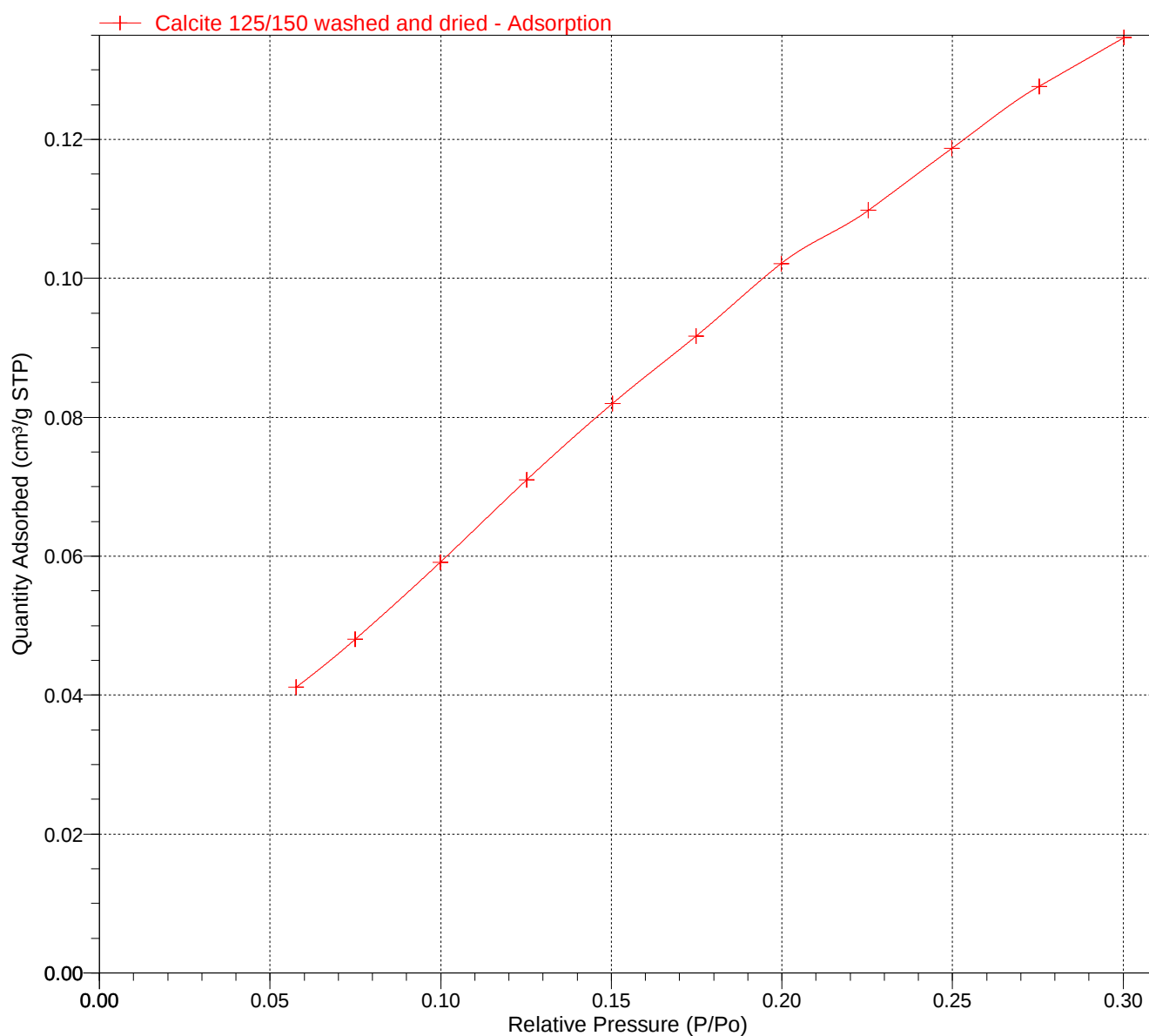
| Relative<br>Pressure (P/Po) | Absolute<br>Pressure<br>(mmHg) | Quantity<br>Adsorbed<br>(cm <sup>3</sup> /g STP) | Elapsed Time<br>(h:min) | Saturation<br>Pressure<br>(mmHg) |
|-----------------------------|--------------------------------|--------------------------------------------------|-------------------------|----------------------------------|
|                             |                                |                                                  | 01:42                   | 735.560730                       |
| 0.057624234                 | 42.386124                      | 0.0411                                           | 01:52                   |                                  |
| 0.074963529                 | 55.140228                      | 0.0480                                           | 01:54                   |                                  |
| 0.099930054                 | 73.504623                      | 0.0591                                           | 01:57                   |                                  |
| 0.125264274                 | 92.139481                      | 0.0710                                           | 01:59                   |                                  |
| 0.150280875                 | 110.540710                     | 0.0820                                           | 02:01                   |                                  |
| 0.174893334                 | 128.644669                     | 0.0917                                           | 02:03                   |                                  |
| 0.199751552                 | 146.929398                     | 0.1021                                           | 02:06                   |                                  |
| 0.225249840                 | 165.684937                     | 0.1098                                           | 02:08                   |                                  |
| 0.249778263                 | 183.727081                     | 0.1187                                           | 02:10                   |                                  |
| 0.275317811                 | 202.512970                     | 0.1277                                           | 02:12                   |                                  |
| 0.300282240                 | 220.875824                     | 0.1346                                           | 02:15                   |                                  |

Sample: Calcite 125/150 washed and dried  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-289.SMP

Started: 8/8/2013 11:36:54AM  
Completed: 8/8/2013 2:15:23PM  
Report Time: 8/9/2013 8:59:30AM  
Sample Mass: 0.6098 g  
Cold Free Space: 87.2963 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N<sub>2</sub>  
Analysis Bath Temp.: 77.075 K  
Thermal Correction: No  
Warm Free Space: 28.1307 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Isotherm Linear Plot

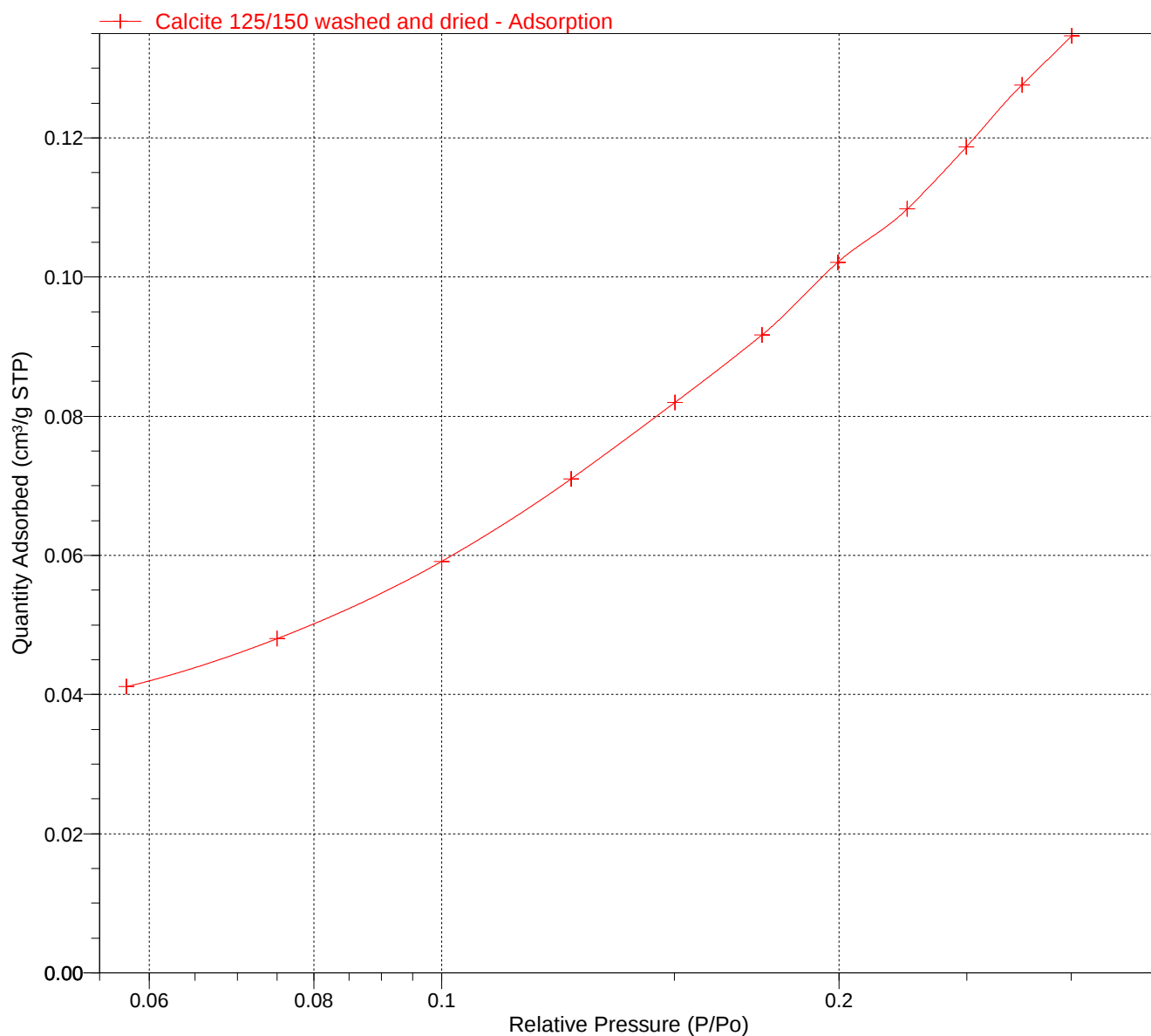


Sample: Calcite 125/150 washed and dried  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-289.SMP

Started: 8/8/2013 11:36:54AM  
Completed: 8/8/2013 2:15:23PM  
Report Time: 8/9/2013 8:59:31AM  
Sample Mass: 0.6098 g  
Cold Free Space: 87.2963 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N<sub>2</sub>  
Analysis Bath Temp.: 77.075 K  
Thermal Correction: No  
Warm Free Space: 28.1307 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Isotherm Log Plot



Sample: Calcite 125/150 washed and dried  
 Operator: Lymaris Ortiz Rivera  
 Submitter: Mariya Skocik  
 File: C:\2020\DATA\000-289.SMP

Started: 8/8/2013 11:36:54AM  
 Completed: 8/8/2013 2:15:23PM  
 Report Time: 8/9/2013 8:59:31AM  
 Sample Mass: 0.6098 g  
 Cold Free Space: 87.2963 cm<sup>3</sup>  
 Ambient 22.00 °C  
 Temperature:  
 Automatic Degas: Yes

Analysis Adsorptive: N2  
 Analysis Bath Temp.: 77.075 K  
 Thermal Correction: No  
 Warm Free Space: 28.1307 cm<sup>3</sup> Measured  
 Equilibration Interval: 10 s  
 Low Pressure Dose: None

### BET Surface Area Report

BET Surface Area:  $0.5591 \pm 0.0098$  m<sup>2</sup>/g  
 Slope:  $6.622432 \pm 0.134335$  g/cm<sup>3</sup> STP  
 Y-Intercept:  $1.163196 \pm 0.025833$  g/cm<sup>3</sup> STP  
 C: 6.693305  
 Qm: 0.1284 cm<sup>3</sup>/g STP  
 Correlation Coefficient: 0.9981535  
 Molecular Cross-Sectional Area: 0.1620 nm<sup>2</sup>

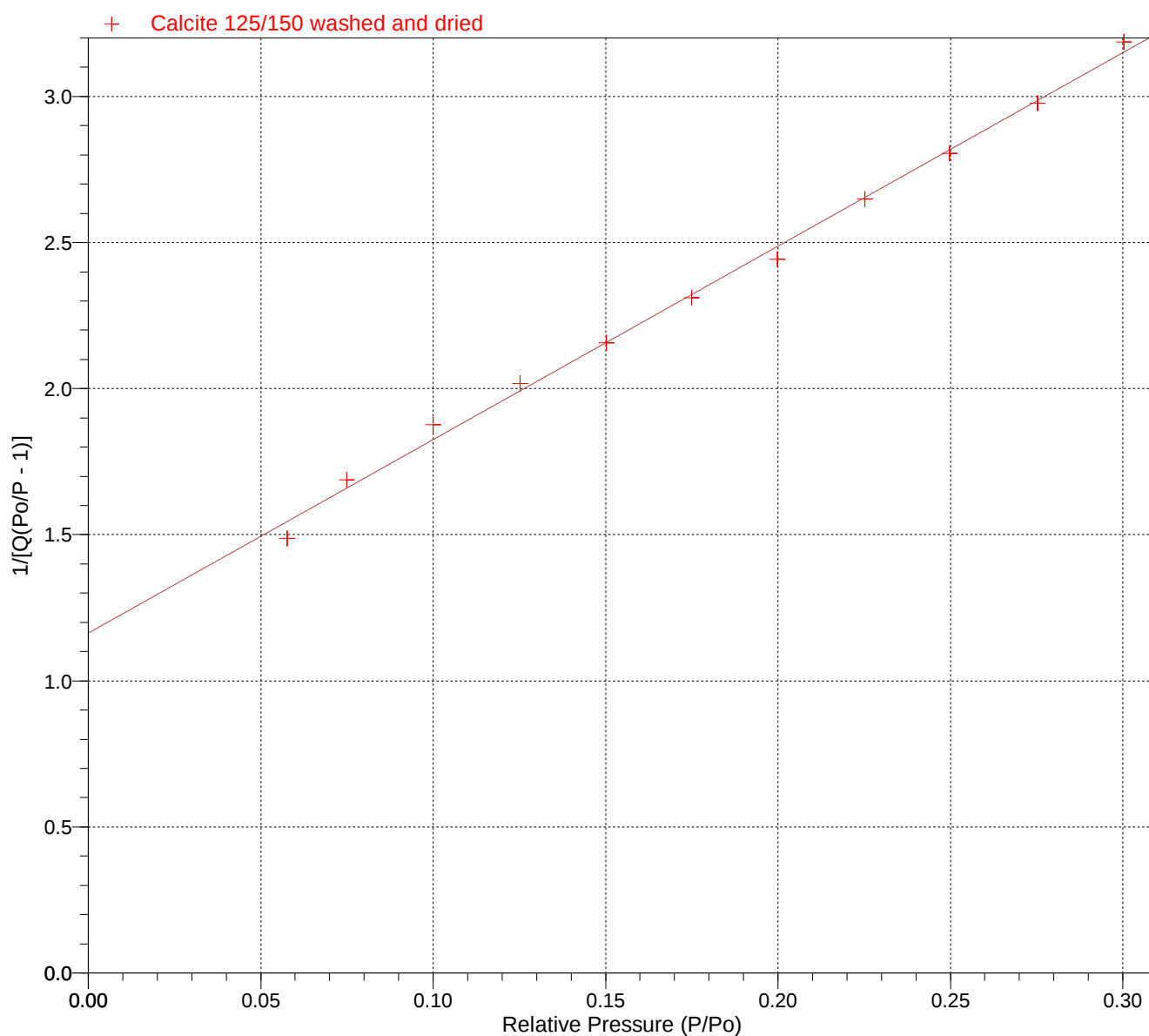
| Relative<br>Pressure<br>(P/Po) | Quantity<br>Adsorbed<br>(cm <sup>3</sup> /g STP) | 1/[Q(Po/P - 1)] |
|--------------------------------|--------------------------------------------------|-----------------|
| 0.057624234                    | 0.0411                                           | 1.487121        |
| 0.074963529                    | 0.0480                                           | 1.687249        |
| 0.099930054                    | 0.0591                                           | 1.877384        |
| 0.125264274                    | 0.0710                                           | 2.017050        |
| 0.150280875                    | 0.0820                                           | 2.157342        |
| 0.174893334                    | 0.0917                                           | 2.311966        |
| 0.199751552                    | 0.1021                                           | 2.443603        |
| 0.225249840                    | 0.1098                                           | 2.648543        |
| 0.249778263                    | 0.1187                                           | 2.804913        |
| 0.275317811                    | 0.1277                                           | 2.976103        |
| 0.300282240                    | 0.1346                                           | 3.187274        |

Sample: Calcite 125/150 washed and dried  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-289.SMP

Started: 8/8/2013 11:36:54AM  
Completed: 8/8/2013 2:15:23PM  
Report Time: 8/9/2013 8:59:31AM  
Sample Mass: 0.6098 g  
Cold Free Space: 87.2963 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.075 K  
Thermal Correction: No  
Warm Free Space: 28.1307 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

BET Surface Area Plot



Sample: MS sand  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-291.SMP

|                                          |                                                   |
|------------------------------------------|---------------------------------------------------|
| Started: 8/9/2013 9:05:23AM              | Analysis Adsorptive: N2                           |
| Completed: 8/9/2013 11:54:17AM           | Analysis Bath Temp.: 77.044 K                     |
| Report Time: 8/9/2013 11:54:18AM         | Thermal Correction: No                            |
| Sample Mass: 1.3030 g                    | Warm Free Space: 27.3421 cm <sup>3</sup> Measured |
| Cold Free Space: 88.0721 cm <sup>3</sup> | Equilibration Interval: 10 s                      |
| Ambient 22.00 °C                         | Low Pressure Dose: None                           |
| Temperature:                             |                                                   |
| Automatic Degas: Yes                     |                                                   |

### Summary Report

#### Surface Area

Single point surface area at  $P/P_o = 0.299822184$ : 0.2401 m<sup>2</sup>/g

BET Surface Area: 0.3466 m<sup>2</sup>/g

Sample: MS sand  
 Operator: Lymaris Ortiz Rivera  
 Submitter: Mariya Skocik  
 File: C:\2020\DATA\000-291.SMP

Started: 8/9/2013 9:05:23AM  
 Completed: 8/9/2013 11:54:17AM  
 Report Time: 8/9/2013 11:54:18AM  
 Sample Mass: 1.3030 g  
 Cold Free Space: 88.0721 cm<sup>3</sup>  
 Ambient 22.00 °C  
 Temperature:  
 Automatic Degas: Yes

Analysis Adsorptive: N2  
 Analysis Bath Temp.: 77.044 K  
 Thermal Correction: No  
 Warm Free Space: 27.3421 cm<sup>3</sup> Measured  
 Equilibration Interval: 10 s  
 Low Pressure Dose: None

### Isotherm Tabular Report

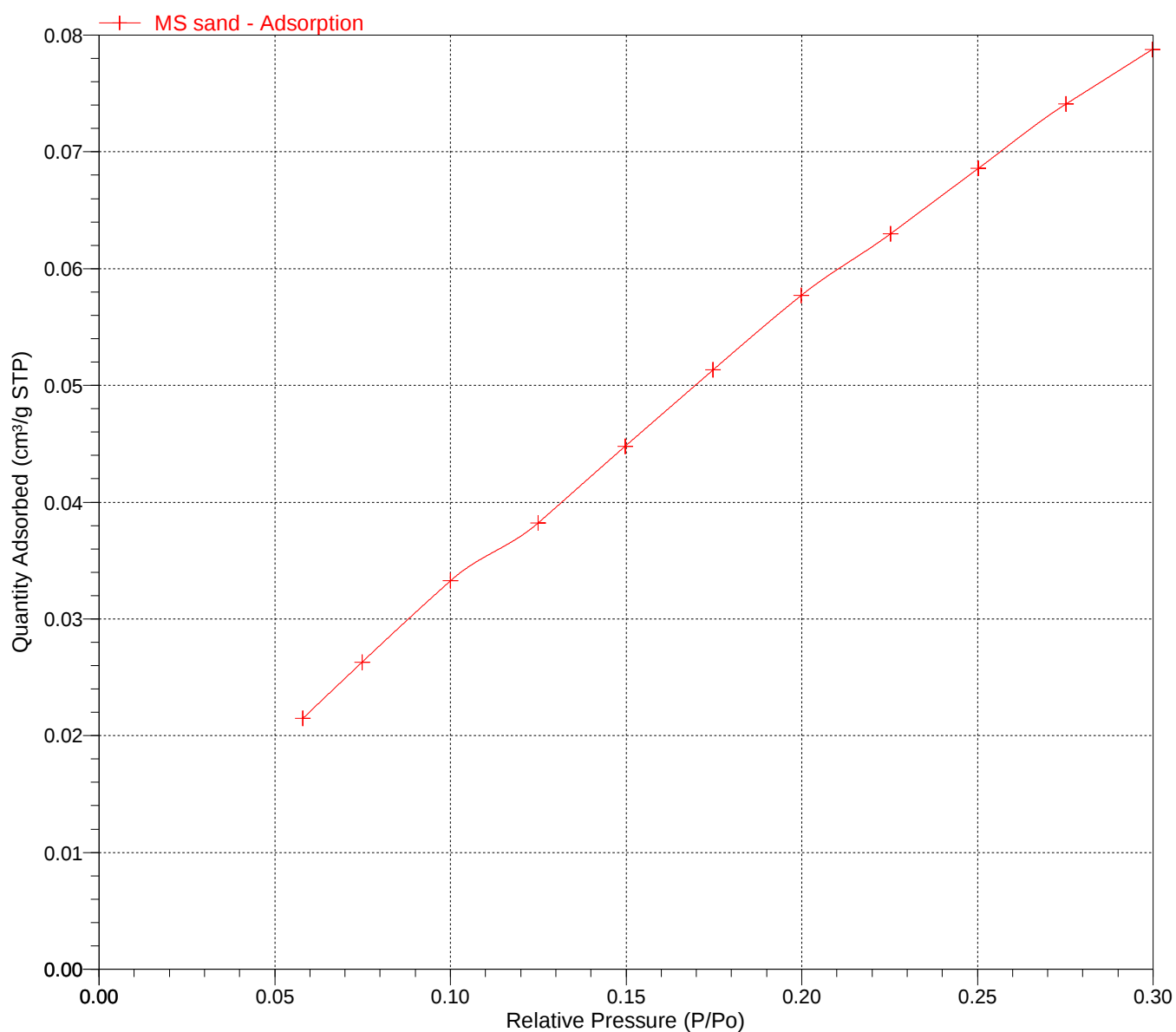
| Relative<br>Pressure (P/Po) | Absolute<br>Pressure<br>(mmHg) | Quantity<br>Adsorbed<br>(cm <sup>3</sup> /g STP) | Elapsed Time<br>(h:min) | Saturation<br>Pressure<br>(mmHg) |
|-----------------------------|--------------------------------|--------------------------------------------------|-------------------------|----------------------------------|
|                             |                                |                                                  | 01:45                   | 732.870911                       |
| 0.058036466                 | 42.533237                      | 0.0215                                           | 01:56                   |                                  |
| 0.074938608                 | 54.920326                      | 0.0263                                           | 01:58                   |                                  |
| 0.099967743                 | 73.263451                      | 0.0333                                           | 02:00                   |                                  |
| 0.124930043                 | 91.557594                      | 0.0382                                           | 02:02                   |                                  |
| 0.149817837                 | 109.797134                     | 0.0448                                           | 02:05                   |                                  |
| 0.174780324                 | 128.091415                     | 0.0513                                           | 02:07                   |                                  |
| 0.199797507                 | 146.425781                     | 0.0577                                           | 02:09                   |                                  |
| 0.225243032                 | 165.074066                     | 0.0630                                           | 02:11                   |                                  |
| 0.250312246                 | 183.446564                     | 0.0686                                           | 02:14                   |                                  |
| 0.275174441                 | 201.667343                     | 0.0741                                           | 02:16                   |                                  |
| 0.299822184                 | 219.730957                     | 0.0788                                           | 02:18                   |                                  |

Sample: MS sand  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-291.SMP

Started: 8/9/2013 9:05:23AM  
Completed: 8/9/2013 11:54:17AM  
Report Time: 8/9/2013 11:54:18AM  
Sample Mass: 1.3030 g  
Cold Free Space: 88.0721 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.044 K  
Thermal Correction: No  
Warm Free Space: 27.3421 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Isotherm Linear Plot

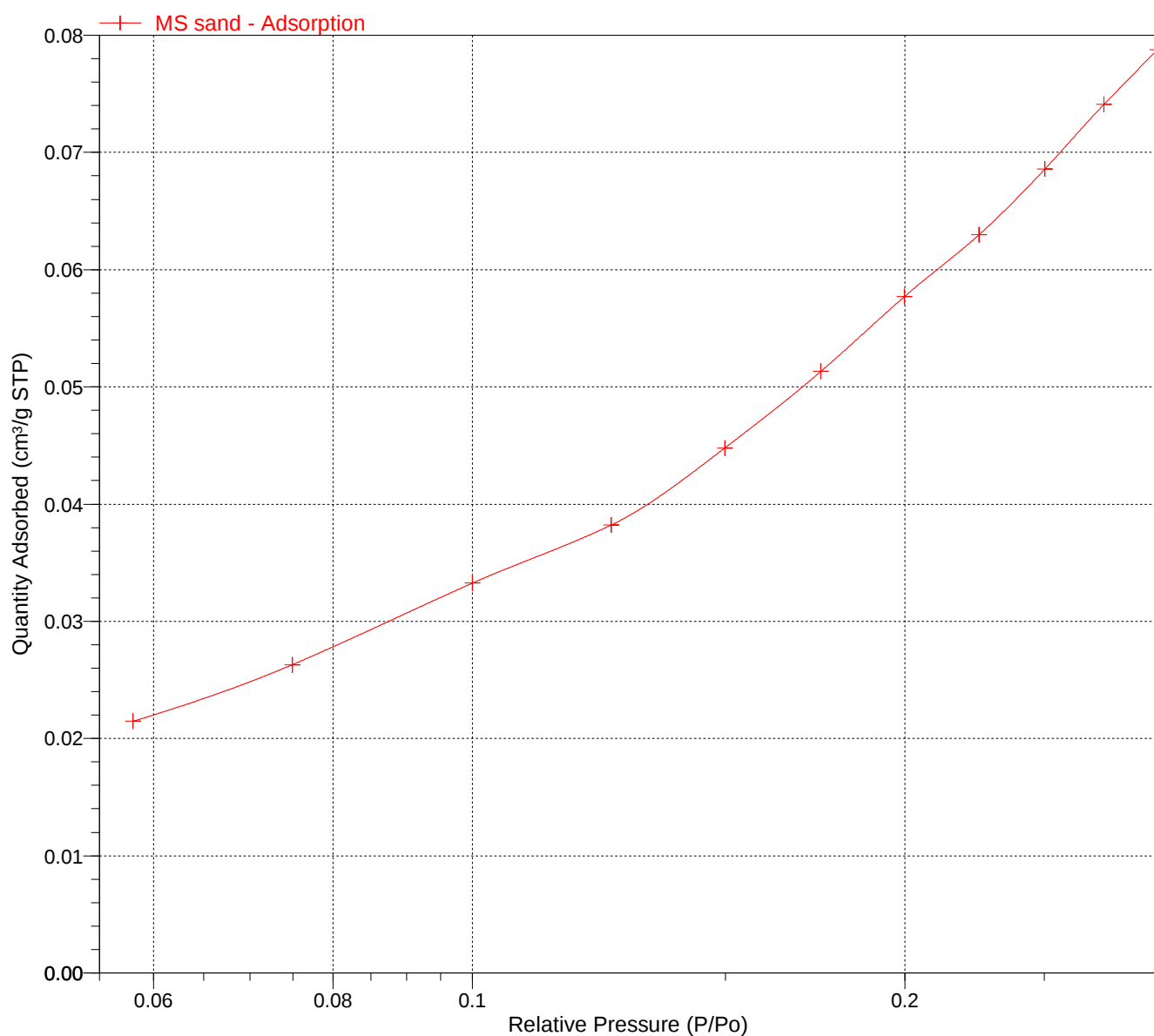


Sample: MS sand  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-291.SMP

Started: 8/9/2013 9:05:23AM  
Completed: 8/9/2013 11:54:17AM  
Report Time: 8/9/2013 11:54:18AM  
Sample Mass: 1.3030 g  
Cold Free Space: 88.0721 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.044 K  
Thermal Correction: No  
Warm Free Space: 27.3421 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

Isotherm Log Plot



Sample: MS sand  
 Operator: Lymaris Ortiz Rivera  
 Submitter: Mariya Skocik  
 File: C:\2020\DATA\000-291.SMP

Started: 8/9/2013 9:05:23AM  
 Completed: 8/9/2013 11:54:17AM  
 Report Time: 8/9/2013 11:54:18AM  
 Sample Mass: 1.3030 g  
 Cold Free Space: 88.0721 cm<sup>3</sup>  
 Ambient 22.00 °C  
 Temperature:  
 Automatic Degas: Yes

Analysis Adsorptive: N2  
 Analysis Bath Temp.: 77.044 K  
 Thermal Correction: No  
 Warm Free Space: 27.3421 cm<sup>3</sup> Measured  
 Equilibration Interval: 10 s  
 Low Pressure Dose: None

### BET Surface Area Report

BET Surface Area:  $0.3466 \pm 0.0062$  m<sup>2</sup>/g  
 Slope:  $10.223754 \pm 0.221280$  g/cm<sup>3</sup>  
 STP  
 Y-Intercept:  $2.336040 \pm 0.042538$  g/cm<sup>3</sup> STP  
 C: 5.376532  
 Qm: 0.0796 cm<sup>3</sup>/g STP  
 Correlation Coefficient: 0.9978986  
 Molecular Cross-Sectional Area: 0.1620 nm<sup>2</sup>

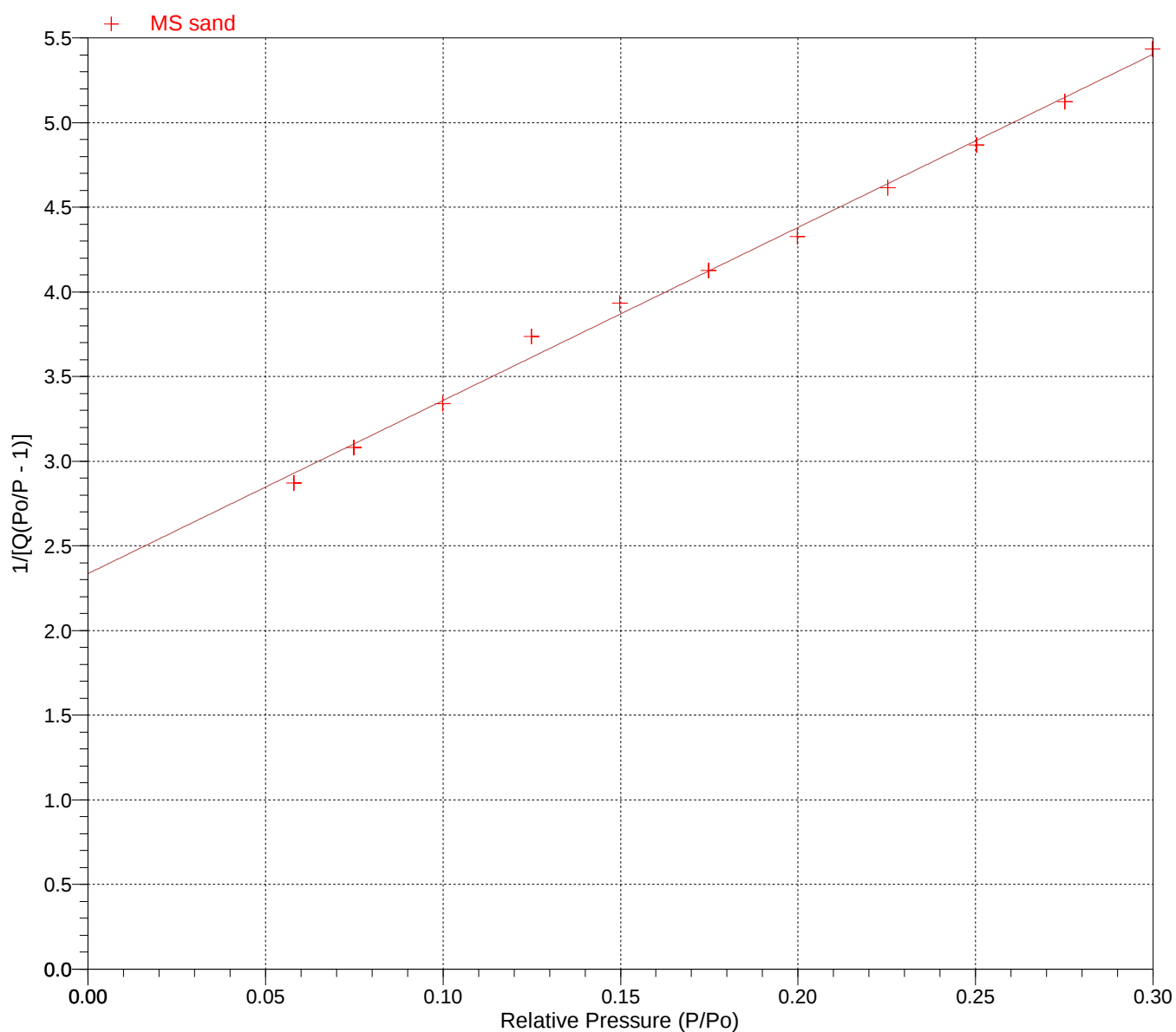
| Relative<br>Pressure<br>(P/Po) | Quantity<br>Adsorbed<br>(cm <sup>3</sup> /g STP) | 1/[Q(Po/P - 1)] |
|--------------------------------|--------------------------------------------------|-----------------|
| 0.058036466                    | 0.0215                                           | 2.869861        |
| 0.074938608                    | 0.0263                                           | 3.080057        |
| 0.099967743                    | 0.0333                                           | 3.339468        |
| 0.124930043                    | 0.0382                                           | 3.735807        |
| 0.149817837                    | 0.0448                                           | 3.933905        |
| 0.174780324                    | 0.0513                                           | 4.127368        |
| 0.199797507                    | 0.0577                                           | 4.327305        |
| 0.225243032                    | 0.0630                                           | 4.615816        |
| 0.250312246                    | 0.0686                                           | 4.868537        |
| 0.275174441                    | 0.0741                                           | 5.123758        |
| 0.299822184                    | 0.0788                                           | 5.435236        |

Sample: MS sand  
Operator: Lymaris Ortiz Rivera  
Submitter: Mariya Skocik  
File: C:\2020\DATA\000-291.SMP

Started: 8/9/2013 9:05:23AM  
Completed: 8/9/2013 11:54:17AM  
Report Time: 8/9/2013 11:54:18AM  
Sample Mass: 1.3030 g  
Cold Free Space: 88.0721 cm<sup>3</sup>  
Ambient 22.00 °C  
Temperature:  
Automatic Degas: Yes

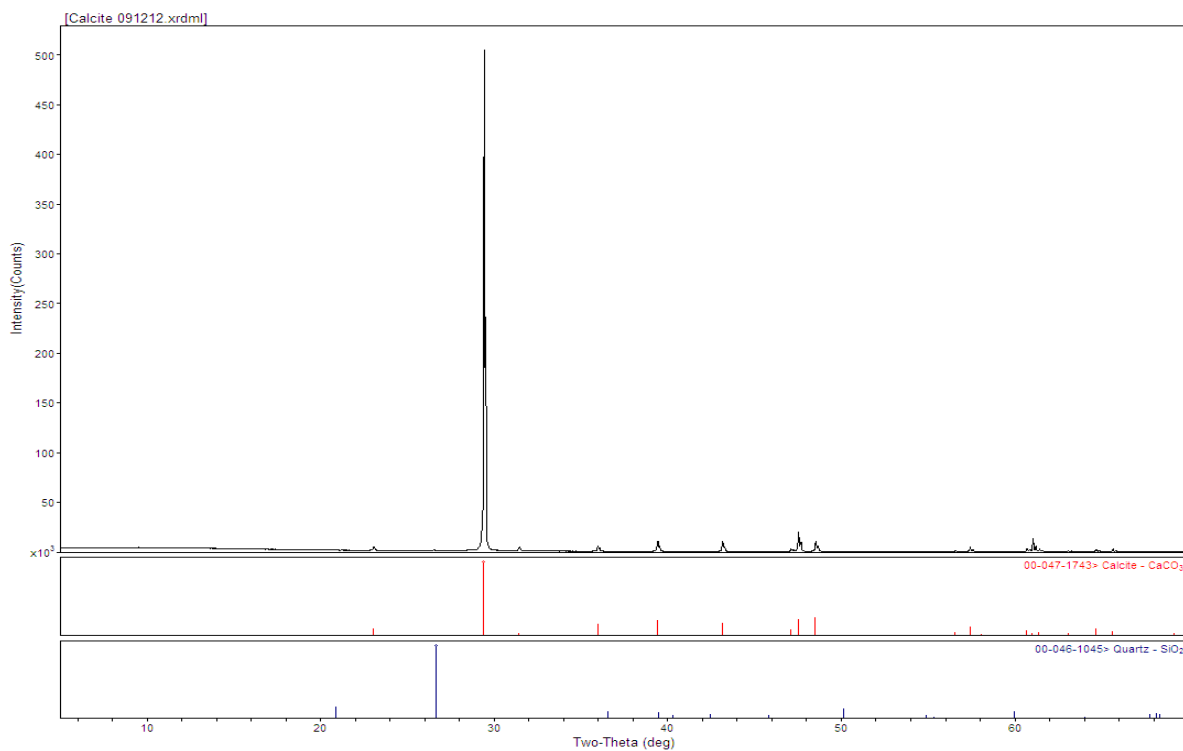
Analysis Adsorptive: N2  
Analysis Bath Temp.: 77.044 K  
Thermal Correction: No  
Warm Free Space: 27.3421 cm<sup>3</sup> Measured  
Equilibration Interval: 10 s  
Low Pressure Dose: None

BET Surface Area Plot



## **APPENDIX B**

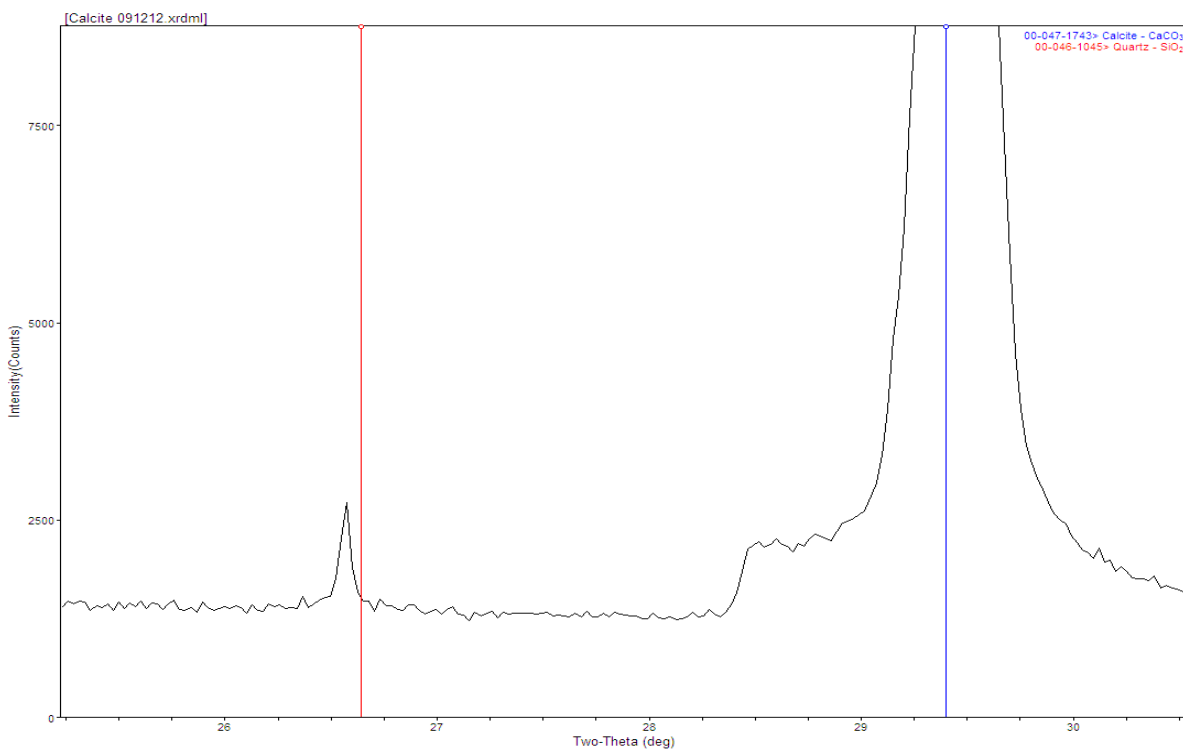
### **CALCITE PURITY ANALYSIS**



Penn State

[MRI-ANALYSIS3]jma1414M:\Penn State\Earth and Mineral Sciences\bx35 Li Li\Jesse Chao\ Wednesday, September 12, 2012 03:29p (MDI/JADE9)

#### PEAK ENLARGEMENT



Penn State

[MRI-ANALYSIS3]jma1414M:\Penn State\Earth and Mineral Sciences\bx35 Li Li\Jesse Chao\ Wednesday, September 12, 2012 03:33p (MDI/JADE9)