GEOLOGIC CARBON SEQUESTRATION IN DEEP SALINE AQUIFERS: BRINE ACIDIFICATION AND GEOCHEMICAL ALTERATIONS OF REACTIVE LEAKAGE PATHWAYS

BRIAN ROBERT ELLIS

A DISSERTATION
PRESENTED TO THE FACULTY
OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE
BY THE DEPARTMENT OF
CIVIL & ENVIRONMENTAL ENGINEERING
ADVISOR: CATHERINE A. PETERS

JUNE 2012
© Copyright by Brian Robert Ellis, 2012
All Rights Reserved
ABSTRACT

Of all geologic storage options, CO₂ injection into deep saline aquifers offers the largest potential storage opportunity, as these formations are nearly ubiquitous throughout the globe and have little to no economic value. However, CO₂ dissolution into formation brines will lead to acidification, which may promote acid-catalyzed mineral dissolution in both the injection formation and, more importantly, along reactive leakage pathways in overlying low permeability caprock formations. Understanding the extent of brine acidification likely to occur in these formations and its impact on caprock seal integrity is a necessary first step in evaluating leakage risk associated with geologic carbon sequestration in deep saline aquifers.

This dissertation examines several important issues related to the fate of stored CO₂ for the purpose of geologic carbon sequestration and offers insight into the risks of CO₂ leakage. Chapter 2 begins by addressing the degree of brine acidification that can be expected due to dissolution of CO₂ and the potential co-contaminant gas, SO₂. Model results demonstrate that due to SO₂ diffusion limitations within the supercritical CO₂ phase, co-injection of SO₂ may not lead to severe, rapid acidification as previously suggested by other researchers. This theoretical modeling study is followed by Chapters 3 and 4, which discuss the findings from a set of high-pressure experiments examining flow of CO₂-acidified brine through fractured carbonate caprock samples. The findings of Chapter 3 highlight the importance of mineral spatial heterogeneity in controlling the evolution of fracture permeability during flow of acidic fluids and emphasize the vulnerability of tight carbonate formations as long-term geologic seals for injected CO₂. In contrast to the findings of Chapter 3 where CO₂-acidified brine caused extensive erosion along the fracture, a near-replicate experiment presented in Chapter 4 exhibited a decrease in fracture permeability during flow of CO₂-acidified brine. This disparity in fracture permeability evolution
between two near-replicate experiments highlights the complexities of predicting fracture permeability evolution during a CO$_2$ leakage event. Chapter 5 extends the work presented in Chapters 3 and 4 through modeling efforts that investigate fracture permeability evolution for different mineral spatial heterogeneity scenarios.
Acknowledgements

It would seem that thanking everyone who has helped me along the way should be the easiest part of this thesis to write, yet I find myself struggling to find the right words to adequately acknowledge all those who have had an influence on the work presented here and my path to this point. I believe that it is fitting to begin with the two most influential people in my life, my Mom and Dad. Thank you both for always encouraging me to pursue my interests and for instilling in me the work ethic necessary to make it through such trying times as my general examination. I would not be enjoying the successes I have today without your constant love and support. I also want to thank the rest of my family including my siblings Brad, Hana, and Katie for their support over the years. I may never have been driven to achieve so much in school if not for my brother blazing such a prestigious academic path before me. I strived to be as successful as he was in school and this motivated me to always push myself academically and set my goals high. Katie, now on her way to a Ph.D. herself, has always helped keep me grounded and I have really enjoyed being able to share some of my grad school experiences with her as she charts her own path as a researcher. Lastly, I want to thank my in-laws, Steve and Kristen, for their love and support during my time in grad school and for welcoming me into their family.

My path to Princeton began in Virginia at Washington & Lee University when my freshman advisor, Chris Connors, convinced me to take his introductory field geology course. It was Chris’s influence and love of rocks that convinced me to pursue a degree in Geosciences, thereby forgoing my high school plans to get a business degree and make lots of money (yes, I had very noble aspirations as an eighteen year old). I transferred to the University of Michigan after my freshman year and it was there that I met Clara Castro in yet another introductory
geology course. Clara gave me an opportunity to join her research group and work with her graduate student, Lin Ma, over the summer. I wrote my senior thesis under her guidance and was able to contribute to my first peer-reviewed publication working with her and her collaborators. Finally, it was on her suggestion and strong encouragement alone that I applied to Princeton. She was and continues to be one of my biggest supporters and I attribute so much of my research success to her early guidance and continued support. Without her influence in my life I would not have ended up at Princeton and I would not be headed back to UofM in the fall. I want to thank her and the others in her group, including Chris Hall, Lin Ma and Tie Sun, for welcoming me into their research group and for giving me my first real taste of scientific research.

Clara did much to help get to me Princeton, but it was my advisor, Catherine Peters, who really brought me here. She literally had to walk across campus to personally collect my application from the Geosciences department – one of her favorite stories to tell about me – because I had applied to work with her via her adjunct position in that department believing I had no business applying to an engineering program (she obviously disagreed!). Catherine’s guidance and support as an advisor have been integral to my success at Princeton. I do not believe I could have had a better thesis advisor and cannot thank her enough for all she has done for me during my time at Princeton. She constantly challenged me in meetings and helped instill in me the confidence I have today. She also spent countless hours working with me through my first publication, telling me that she saw this time spent as an investment in my future and that this would be the one and only time that she would give my writing this much attention. I came a long way as a writer during this process and want to thank her for this invaluable contribution to my training as a researcher. I also want to thank the members of the Peters’ group for their friendship and support during my time at Princeton.
I must also recognize other influential faculty members and collaborators who have helped me over the past six years. Satish Myneni, Tullis Onstott, Mike Celia, and Jeff Fitts have all contributed substantially to my training and I want to thank them all for their support during my time at Princeton. As members of my Ph.D. committee, Satish and Tullis always brought up new perspectives from which to approach my research interests and really helped me grow as a geochemist. Mike was both a great teacher and a wonderful resource for all of my questions related to understanding flow in porous media and the physics of CO$_2$ sequestration in deep saline aquifers. Over the past two years Jeff has essentially been my co-advisor and I am very grateful for all the time he has spent helping me craft interesting stories from a few experiments that were less than perfect.

A large part of this thesis is based upon work that I completed at the Department of Energy’s National Energy Technology Laboratory in Morgantown, WV. I want to recognize and thank all of my NETL collaborators who helped make this possible including Grant Bromhal, Dustin McIntyre, Dustin Crandell, and Jinesh Jain. I also need to thank Bryan Tennant and Karl Jarvis for their help in building my flow-through apparatus. Thank you to Ben Myers and August Holtyn for taking me into their home during my first few visits to Morgantown and helping me get on my feet. Finally, I want to thank Ben Fancher for his friendship during my time in WV and for all the good times we had over a few cold PBRs.

I would like to acknowledge my many funding sources including Department of Energy grants DE-FG02-05ER15636 and DE-FE0000749, the ORISE professional internship program, and the ASCE Freeman Fellowship. I also acknowledge the use of PRISM Imaging and Analysis Center at Princeton University, which is supported in part by the NSF MRSEC program through the Princeton Center for Complex Materials (grant DMR-0819860). And a special thanks goes to
Jerry Poirier for all of his help during my time on the ESEM. I also want to thank PEI for financial support through the PEI-STEP fellowship that has allowed me to pursue my interests in public policy in addition to my Ph.D. work. I want to especially thank Denise Mauzerall for serving as my STEP advisor. Thank you to Pascale Poussart and Rob Socolow for your support during my time with the Princeton Energy and Climate Scholars group. And thank you to Joy Montero, Lisa Schreyer, and Olivia Martel for your friendship during my time as a Community Associate. Lastly, I must thank Tara McCartney and Elisabeth Dorman for all the great times we had together during my five-year tenure on the APGA reunions crew.

I attribute some of the greatest influences on my time at Princeton to all of the wonderful friendships I have made along the way. I want to thank all of the students in the CEE department for their friendship over the years and the many beers we have shared during Friday happy hours. In particular, I want to thank Luke and Trenton for helping connect me with all of the outside opportunities, such as being a CA and working reunions, which have enriched my Princeton experience. I also need to thank all of my office mates including Adam, Alex, Ben, Dan, Steve, and Stimit for putting up with me in close quarters for such a long time. It was the unexpected pranks, stories about turbulent cowboys and endless opportunities to interrupt my work for impromptu coffee breaks that helped keep me sane during the last six years. I also need to recognize and thank my good friends outside of the department including Tom Essinger-Hileman, Sam Bulow, the entire Little Family, Kim and Tyler and all of my other friends from PUB. Your friendship has really made my time at Princeton more enjoyable. And lastly, I want to thank my good friends Chris Hetrick and Craig Salveta for their continued friendship throughout the past years.
Finally, and most importantly, I would not be where I am today without the unwavering love and support of my wife, Karen. It is to her that I dedicate this thesis. She is my best friend and has seen me at my highest and lowest points throughout the past six years and has always been there to help me along the way. Whether it be just listening to me vent my frustration, dwell over a tough review, practice a presentation, or proofread my latest piece of writing, Karen has always been the constant positive force that kept me on track. I am so happy that she has chosen to spend her life with me and will never be able to thank her enough for the wonderful gift of my first child. I cannot wait to begin the next stage of our adventures together and am so looking forward to meeting our beautiful baby girl, who will hopefully join us after my defense!
Contents

Abstract iii
Acknowledgements v
List of Tables xiii
List of Figures xiv

1 Introduction 1
1.1 Background and motivation 1
  1.1.1 Geologic carbon sequestration 1
  1.1.2 CO₂-water-rock interactions: Studying the fate of CO₂ in deep saline aquifers 3
1.2 Chapter summaries 5
1.3 Putting my work into context, or “How I tell my Mom about my research” 9
1.4 Attribution of work for co-authored publications used as chapters 10

2 Limitations for brine acidification due to SO₂ co-injection in geologic carbon sequestration 12
2.1 Introduction 12
2.2 Methods 16
  2.2.1 SO₂ reaction scenarios 16
  2.2.2 Model system and conditions 17
  2.2.3 Geochemical model 19
  2.2.4 Phase equilibrium model 21
  2.2.5 Diffusion modeling 21
2.3 Results 23
2.4 Discussion 29
2.5 Conclusions 32
3 Deterioration of a fractured carbonate caprock exposed to CO₂-acidified brine flow

3.1 Introduction
3.2 Methods
   3.2.1 Sample characterization and brine composition
   3.2.2 Flow-through experiment
   3.2.3 X-ray computed tomography
   3.2.4 Sectioning and SEM imaging
3.3 Results
3.4 Discussion
3.5 Conclusions

4 Permeability evolution along a reactive CO₂ leakage pathway in a carbonate caprock

4.1 Introduction
4.2 Materials and methods
   4.2.1 Sample characterization
   4.2.2 Brine composition
   4.2.3 Flow-through experiment
   4.2.4 X-ray computed tomography
   4.2.5 Electron microscopy and spectroscopic imaging
4.3 Results
   4.3.1 Evolution of fracture permeability
   4.3.2 Electron microscopy and X-ray spectroscopic and diffraction imaging
   4.3.3 Effluent chemistry
   4.3.4 X-ray CT imaging
4.4 Discussion and conclusions

5 Simulation of permeability evolution in a variable aperture fracture

5.1 Introduction
5.2 Methods
   5.2.1 Two-dimensional steady state flow modeling
5.2.2 X-ray computed tomography and scanning electron microscopy imaging 77

5.3 Results 78
5.3.1 Mineral identification via combined µCT and EDS analysis 78
5.3.2 Modeling fracture permeability evolution 81
5.3.3 Geochemical alterations to fracture geometry and fluid flow hydrodynamics 84

5.4 Discussion and conclusions 86

6 Concluding remarks 88

References 91
List of Tables

2.1 Model brine composition. 19
2.2 Reactions considered in the geochemical model. 20
2.3 Diffusion coefficients. 22

3.1 Initial brine composition. 37
3.2 Thermodynamic constants (K) for acid-driven dissolution of calcite (eqn 3.1) and dolomite (eqn 3.2), and the solubility product constant (K_{sp}) for the dissolution of one mole of each mineral at 27°C and 10 MPa. Solution indices (SI) correspond to the solution conditions in the inlet brine. Reaction rates constants (k) are estimated following the work of Chou et al. (1981) for ambient pressure, 25°C and pH=4.4. 37

4.1 Initial brine composition. 58
List of Figures

2.1 Annual power plant emissions of SO$_2$ relative to CO$_2$ emissions for the highest SO$_2$-emitting plants in the United States (Miller and Van Atten, 2004). Lines represent ratios of molar quantities of SO$_2$ to CO$_2$.

2.2 Schematic diagram of model system showing the scCO$_2$ plume (light gray) and brine volume (dark gray): (a) SO$_2$ phase equilibrium between the CO$_2$ and brine phases; (b) diffusion-limited SO$_2$ dissolution with uniform sulfur distribution in an advecting brine phase; (c) diffusion-limited SO$_2$ dissolution with diffusive transport of SO$_2$ in a stagnant brine phase.

2.3 Phase equilibrium brine pH results for each of the three reactions and CO$_2$ alone for an initial alkalinity of 3.75x10$^{-2}$ M.

2.4 Phase equilibrium brine pH results for a range of values of initial brine alkalinity, for CO$_2$ alone and each of the three reaction scenarios.

2.5 Brine pH results for SO$_2$ hydrolysis and SO$_2$ oxidation reaction scenarios for diffusion-limited SO$_2$ dissolution into an advecting brine. For reference, pH results for the case of a pure CO$_2$ injection plume are also shown.

2.6 Cross section showing results from diffusion-limited SO$_2$ mass transport in both the scCO$_2$ and brine phases. For the case of SO$_2$ hydrolysis, contours show SO$_2$ concentration in the scCO$_2$ phase and pH in the brine phase after 500 and 1000 years. Shaded region denotes scCO$_2$ phase.

2.7 Cross section showing results from diffusion-limited SO$_2$ mass transport in both the scCO$_2$ and brine phases. For the case of SO$_2$ oxidation, contours show SO$_2$ concentration in the scCO$_2$ phase and pH in the brine phase after 500 and 1000 years. Shaded region denotes scCO$_2$ phase.

3.1 Simplified schematic of experimental design.

3.2 Diagram of fractured core with core dimensions and location of sections used for SEM analysis.

3.3 Six-day time series of medical CT scans of 2-mm section taken approximately 2 cm from core inlet. Scans from days 2 through 7 are shown, left to right. Consecutive scans are not precisely 24 hours apart, but show general progression of fracture erosion.
3.4 Fracture aperture maps of the fracture before (a) and after brine flow (b). The total change in aperture between the initial and final aperture measurements is shown in (c). Aperture width distributions are shown for the fracture before (d) and after brine flow (e). The average measured aperture along the length of the core is shown in (f).

3.5 (a) μCT scan of 2-cm section near the core inlet after brine flow. The initial fracture void is shown in white overlying the fracture after dissolution to highlight the changes in fracture aperture. Box 1 in (a) is enlarged and shown in (b) to emphasize the development of a degraded zone along the fracture surface.

3.6 BSE images of (a) area highlighted by box 2 in figure 3.5(a) showing preferential dissolution of calcite leading to non-uniform aperture increases, (b) area of section 2 showing homogenous mineral distribution and development of degraded zone along fracture wall, (c) area of section 2 showing non-uniform aperture increases, and (d) close-up view of clay-rich microporous zone highlighted by box in figure 6(c).

4.1 Change in measured pressure gradient across the core and corresponding best fit of permeability evolution. As the experimental flow conditions were switched from constant flow rate to constant pressure gradient at 28 hours, two separate linear fits were used to describe permeability evolution over these two distinct flow regimes.

4.2 (a) Schematic of fractured core showing core dimensions and location of subsection analyzed throughout Figure 4.2; (b) μCT scan showing evidence of fracture closure; (c) μXRF Ca elemental map of box highlighted in 4.2(b) showing locations of μXRD and μXANES analysis; (d) SEM BSE and EDS maps for Ca and Mg taken at the same location as 4.2(c); (e) Ca μXANES spectra for points A–D highlighted in 4.2(c). Calcite and dolomite end-member spectra are also shown along with estimates of dolomite:calcite from linear combination fits; (f) μXRD 1D integrated diffraction data for points A–D with corresponding calcite and dolomite peaks indicated.

4.3 Measured Ca concentration in brine effluent. Initial concentration (see Table 1) is shown at time = 0.

4.4 Aperture maps of the fracture before (a) and after (b) flow of the CO₂-acidified brine, as estimated from the μCT data. (c) shows the average mechanical aperture from core inlet (bottom) to outlet (top), demonstrating both the observed increase in fracture roughness after flow of CO₂-acidified brine and the trend of decreasing average aperture from core inlet to outlet.

5.1 (a) 2-D μCT scan showing variation in grayscale pixel intensity as a function of miner-specific X-ray attenuation; (b) BSE image of the inset shown in 5.1(a); (c) EDS elemental maps superimposed on the BSE image identifying locations where calcite (red), dolomite (blue), and quartz (green) are present at the surface.
5.2  (a) Reconstructed 2-D µCT scan of the Amherstburg core taken adjacent and parallel to the fracture; (b) Calcite-segmented binary image of 5.2(a). White area corresponding to positive calcite identification based on the segmentation algorithm presented in Figure 5.1.

5.3  Initial base case aperture distribution (a) and spatially non-uniform increases in fracture porosity of 20% (b), 40% (c), and 100% (d). Locations of aperture increase correspond to areas where calcite was identified to exist at the fracture surface (see Figure 5.2(b)).

5.4  Permeability as a function of the increase in total fracture porosity for uniform dissolution (blue) and non-uniform dissolution (green). Non-uniform dissolution assumes aperture increases only occur at locations where calcite is in contact with the fracture surface.

5.5  Normalized volumetric flow rates for the non-uniform dissolution scenario (see Figure 5.3 for corresponding aperture maps). Black lines represent flow streamlines drawn as the perpendicular to the velocity vector along the single path of travel for a theoretical particle released at the inlet. Flow direction is from bottom (inlet) to top (outlet) of figure.
Chapter 1

Introduction

1.1 Background and motivation

1.1.1 Geologic carbon sequestration

The increased emission of greenhouse gases (GHG), such as carbon dioxide (CO$_2$), is of great concern to both scientists and policy makers due to its implications for global warming. There has been a marked increase in the concentration of CO$_2$ in the atmosphere ever since the industrial revolution (IPCC, 2007). This imbalance in the global carbon cycle created by anthropogenic activity cannot be simply balanced by natural CO$_2$ sinks (Falkowski et al., 2000; IPCC, 2007). A primary source of anthropogenic GHG emissions comes from the burning of fossil fuels for energy, such as coal combustion for the production of electricity, which releases CO$_2$ into the atmosphere. As renewable energy strategies (e.g. wind and solar power) are not yet deployable to meet baseload energy demands, finding a near-term solution that reduces CO$_2$ emissions while still allowing for the continued use of fossil fuels is a necessary component in any effort seeking to slow the increase in atmospheric CO$_2$ concentration (Pacala and Socolow, 2004; Krey and Riahi, 2009).

One potential option for mitigating the release of CO$_2$ to the atmosphere is to store the gas deep below the subsurface, a process termed geologic carbon sequestration (GCS) (Bruant et al., 2002). Saline aquifers, which have little to no other economic value, provide the largest potential storage reservoirs and are nearly ubiquitous throughout the world. Furthermore, these reservoirs are in sedimentary basins that are often located under or very near many point-source
CO₂ emissions sites (Bergman and Winter, 1995; Gunter et al., 1996; Hitchon et al., 1999; Bachu, 2008).

The injected CO₂ is secured underground by overlying formations of very low permeability that serve as geologic seals or ‘caprocks’. When CO₂ is stored at depths greater than 800 km, temperature and pressure conditions are such that CO₂ will exist in a supercritical state (Van der Meer et al., 1992; Bachu et al., 1994). This guarantees maximum storage efficiency for the injected CO₂. However, the supercritical CO₂ phase is much less dense and less viscous than the resident brines. This causes the injected CO₂ to rise due to buoyant forces and skate along the bottom of the caprock due to its lower viscosity, eventually developing into a cone-shaped radial CO₂ plume (Nordbotten et al., 2005).

The success of geologic carbon sequestration requires that permanence of the injected CO₂ be assured. Ensuring permanence will require extensive site characterization of injection reservoirs and robust leakage risk assessments. At the CO₂-brine interface, CO₂ dissolution will lead to brine acidification due to generation of carbonic acid. Although carbonic acid is a weak acid, dissolved CO₂ concentrations may be on the order of 1 mol L⁻¹ at injection depths of 1 km (Duan and Sun, 2003) and the brine pH may be driven as low as 3 (Gunter et al., 2000). This brine acidification may lead to mineral dissolution within the aquifer and, potentially, along the base of the caprock formation threatening caprock seal integrity (e.g. Gaus et al. 2008). The existence of fractures within the caprock formation, whether preexisting or generated due to overpressure by CO₂ injection, may serve as leakage pathways for the injected CO₂ (Smith et al., 2011).
1.1.2 CO₂-water-rock interactions: Studying the fate of CO₂ in deep saline aquifers

Much of the earlier work studying the fate CO₂ in deep saline aquifers was focused on the potential for mineral sequestration of the injected CO₂ in the form of stable secondary carbonate mineral precipitates. One of the first studies to examine the fate of injected CO₂ for the purpose of carbon sequestration was published by Gunter et al. (1993). In this study the authors compared the potential for added CO₂ capacity for injection into carbonate versus siliciclastic formations and found that siliciclastic formations rich in Ca and Mg minerals had the greatest storage capacity due to an enhanced mineral trapping capability. Others have modeled CO₂ injection with interest in a formation’s ability to trap CO₂ in metal-carbonate precipitates and have seen that dawsonite and siderite are important carbonate trapping precipitates (Xu et al., 2003, 2005; Zerai et al., 2006). The implications of CO₂ injection with co-contaminant gases such as SOₓ, NOₓ, and H₂S, have also been studied, as these are commonly encountered emission species from point sources like coal-fired power plants (Gunter et al., 2000; Palandri and Kharaka, 2005; Knauss et al., 2005; Xu et al., 2007). The presence of these co-contaminants was shown to have a significant acidifying effect on the post-injection equilibrium brine pH due to the increased acidity caused by compounds such as H₂SO₄.

There have also been many experimental studies examining the CO₂-water-rock interactions likely to occur after CO₂ injection into deep saline aquifers. Most of this work has investigated the geochemical alterations within the injection formation (Shiraki and Dunn, 2000; Kaszuba et al., 2003, 2005; Bateman et al., 2005; Noiriel et al., 2004; Noiriel et al., 2005; Rosenbauer et al., 2005; Le Guen et al., 2007; Izgec et al., 2008; Luquot and Gouze, 2009; Luquot et al., 2012). These studies have demonstrated how the low pH created by CO₂ injection can lead to mineral dissolution and subsequent release of metal cations from carbonate and
aluminosilicate minerals. These metal cations may later combine with dissolved carbonate ions and truly ‘sequester’ the injected CO$_2$ in the form of stable carbonate precipitates.

There have been fewer experimental studies examining the impact of CO$_2$-acidified brine on the seal integrity of the caprock formations. The most notable investigations into the evolution of caprock integrity have examined flow of CO$_2$-acidified brine through reactive fractures (Gouze et al., 2003; Noiriel et al., 2007; Andreani et al., 2008). However, these studies tended to examine fairly homogeneous rock cores with simple mineralogy (e.g. clean limestones), thereby avoiding many of the complexities present in naturally heterogeneous rocks. It was the work of Gherardi et al. (2007), who presented model scenarios where the CO$_2$-water-rock interactions had the potential to lead to either degraded or enhanced sealing ability in caprock formations, that truly motivated the experimental work presented in this dissertation. In demonstrating the potential for mineral precipitation reactions to lead to improved caprock sealing ability, these authors have provided evidence of a scenario that would reduce the likelihood of CO$_2$ leakage. However, this was a modeling study and had not been verified experimentally. I saw this as an opportunity and set out in my dissertation studies to better understand the geochemical conditions that might lead to self-sealing behavior in a reactive fracture. Since leakage of CO$_2$ is most likely to occur along hydraulically connected flow pathways within the low permeability caprocks, it is crucial that we are able to predict the permeability evolution along these pathways. My goal was never to mirror the model scenarios presented by Gherardi et al. (2007), but my research directions have been greatly influenced by this particular study. The main thrust of this thesis is in examining the extent of brine acidification and in understanding the impact of CO$_2$-acidified brine on the seal integrity of reactive caprock formations.
1.2 Chapter summaries

This dissertation begins in Chapter 2 with a thorough discussion of brine acidification associated with GCS, since a fundamental issue facing the safe long-term storage of CO$_2$ in deep saline aquifers is the fact that CO$_2$ dissolution into formation brines will lead to brine acidification. This acidic brine has the potential to degrade the integrity of both the storage and caprock formations. Understanding the degree of brine acidification that can be expected after CO$_2$ injection will aid in the selection of suitable storage reservoirs and in the assessment of leakage risk. Although injection of a pure CO$_2$ stream may be desired, it is possible that contaminant gases may be co-injected with the CO$_2$. This may be due to either deliberate co-injection for economic purposes or due to the inability to strip these gases from the waste gas stream prior to geologic sequestration. One potential co-contaminant gas likely to be encountered is sulfur dioxide (SO$_2$), as sulfur is a common constituent in coal.

Co-injection of SO$_2$ during geologic carbon sequestration can cause enhanced brine acidification. The magnitude and timescale of this acidification will depend, in part, on the reactions that control acid production and on the extent and rate of SO$_2$ dissolution from the injected CO$_2$ phase. In Chapter 2, brine pH changes are predicted for three possible SO$_2$ reactions: hydrolysis, oxidation, or disproportionation. Also, three different model scenarios are considered, including models that account for diffusion-limited release of SO$_2$ from the CO$_2$ phase. In order to predict the most extreme acidification potential, mineral buffering reactions were not modeled. Predictions were compared to the case of CO$_2$ alone, which would cause a brine pH of 4.6 under typical pressure, temperature, and alkalinity conditions in an injection formation. In the unrealistic model scenario of SO$_2$ phase equilibrium between the CO$_2$ and brine phases, co-injection of 1% SO$_2$ is predicted to lead to a pH close to 1 with SO$_2$ oxidation or
disproportionation, and close to 2 with SO₂ hydrolysis. For a scenario in which SO₂ dissolution is diffusion-limited and SO₂ is uniformly distributed in a slowly advecting brine phase, SO₂ oxidation would lead to pH values near 2.5 but not until almost 400 years after injection. In this scenario, SO₂ hydrolysis would lead to pH values only slightly less than those due to CO₂ alone. When SO₂ transport is limited by diffusion in both the supercritical CO₂ and brine phases, enhanced brine acidification occurs in a zone extending only 5 m proximal to the CO₂ plume, and the effect is even less if the only possible reaction is SO₂ hydrolysis. In conclusion, the extent to which co-injected SO₂ can impact brine acidity is restricted by diffusion-limited dissolution from the CO₂ phase, and may also be limited by the availability of oxidants to produce sulfuric acid. These limitations for brine acidification suggest that the co-injection of SO₂ with CO₂ may be a viable option for the dual mitigation of these coal combustion byproducts.

Chapter 3 presents the initial results from a high pressure flow-through experiment that investigated the evolution of a fractured carbonate caprock during flow of CO₂-acidified brine. A core was taken from the Amherstburg limestone, a caprock formation overlying the Bois Blanc and Bass Islands formations, which have been used to demonstrate CO₂ storage in the Michigan basin. The inlet brine was representative of deep saline brines saturated with CO₂, resulting in a starting pH of 4.4. Experimental conditions were 27°C and 10 MPa. X-ray computed tomography and scanning electron microscopy were used to observe evolution of fracture geometry and to investigate mineralogical changes along the fracture surface. The initial brine flow corresponded to an average fluid velocity of 110 cm hr⁻¹. After one week, substantial mineral dissolution caused the average cross-sectional area of the fracture to increase from 0.09 cm² to 0.24 cm². This demonstrates that carbonate caprocks, if fractured, can erode quickly and
may jeopardize sealing integrity when hydrodynamic conditions promote flow of CO₂-acidified brine. However, changes to fracture permeability due to mineral dissolution may be offset by unaltered constrictions along the flow path and increases in surface roughness. In this experiment, preferential dissolution of calcite over dolomite led to uneven erosion of the fracture surface and an increase in roughness. In areas with clay minerals, calcite dissolution left behind a silicate mineral-rich microporous coating along the fracture wall. Thus, the evolution of fracture permeability will depend in a complex way on the carbonate content as well as the heterogeneity of the minerals and their spatial patterning.

Chapter 4 presents results from a near-replicate experiment to that presented in Chapter 3. Another sample of the Amherstburg limestone was artificially fractured and exposed to flow of CO₂-acidified brine at the same temperature and pressure conditions used in the previous chapter. However, in this subsequent run, fracture permeability was observed to decrease during flow of CO₂-acidified brine. This decrease is attributed to dissolution along the fracture pathway, which led to mobilization of less soluble mineral particles and subsequent clogging. Electron microscopy and synchrotron-based X-ray spectroscopic and diffraction imaging were used to examine the detrital occlusions, including the first application of microbeam Ca K-edge XANES to quantify calcite:dolomite ratios in consolidated geologic media. X-ray computed tomography was used to follow changes in fracture roughness. The outcome of this experiment is in contrast with a near-replicate experiment in which permeability increased. The disparity between these outcomes is attributed to the initial degree of calcite saturation in the brine and to differences in the dominant hydrodynamic processes controlling transport through the fracture. The decrease in fracture permeability despite a net increase in fracture void volume demonstrates a complex, non-intuitive relationship between fracture porosity and permeability evolution. The
experimental results presented in this chapter provide insight into some of the important mechanisms and geochemical conditions affecting fracture permeability evolution during flow of CO₂-acidified brine.

Chapters 2-4 have demonstrated how injection of CO₂ into deep saline aquifers will acidify formation brines and lead to complex CO₂-water-rock interactions that may alter caprock seal integrity. Chapter 5 presents a two-dimensional steady state model for flow in a variable aperture fracture with the purpose of evaluating the importance of mineral spatial arrangement as it relates to permeability evolution along reactive leakage pathways. Changes in local fracture aperture are evaluated for two different scenarios with equivalent increases in total fracture void volume, but with different spatial patterns of dissolution. Two-dimensional mineral spatial heterogeneity along the fracture surface is inferred from a novel analysis that combines X-ray computed tomography attenuation data with energy dispersive spectroscopic elemental mapping. Two different dissolution regimes are evaluated with one assuming uniform dissolution and the other assuming dissolution occurs only at locations where calcite is in contact with the fracture surface. The two model scenarios address the importance of accurately accounting for spatially variable dissolution along a fracture when predicting permeability evolution. Model results demonstrate that when dissolution is assumed to occur uniformly along the fracture, fracture permeability may be overestimated.

Chapter 6 summarizes the conclusions reached through the work presented in this dissertation and discusses the impact of these findings.
1.3 Putting my work into context, or “How I tell my Mom about my research”

When I introduce my research to my family or other non-scientists who ask the question, “So what do you study?”, I like to try to frame it in an accessible context. To begin, I introduce the concept of global warming followed by a brief discussion of CO$_2$ as a GHG. The image of a coal-combustion power plant with a smokestack spewing CO$_2$ into the atmosphere is always a great place to start. I then explain that one of the engineering strategies being considered to reduce CO$_2$ emissions to the atmosphere is to capture the CO$_2$ at a point source, such as a power plant, and re-inject it deep underground. This inevitably leads them to ask the question, “So what happens to the CO$_2$ after you inject it underground?”, which is where I smile and say, “That’s what I’m trying to figure out in my research!” Now, obviously, this is a gross over-simplification of my dissertation studies, but I believe this is exactly what makes doing basic science research with direct engineering application so exciting. I feel that I have successfully answered their question if I am able to convince them that what I have been doing for the past six years was not only interesting to me personally (an obvious pre-requisite for any Ph.D. project) but also has the potential to make a real impact beyond the scientific community. I would argue that the latter is (or at least should be) true for all published Ph.D. dissertations, but this can be a hard sell to your Mom without an easy connection to an accessible scientific question or societal problem (e.g. slowing global warming, curing cancer). Although I am under no illusions that my dissertation will singlehandedly lead to the large-scale implementation of GCS and a subsequent slowing of global warming, I do hope my efforts have helped to bring us at least one step closer to achieving such a noble goal.
1.4 Attribution of work for co-authored publications used as chapters

Chapters 2-4 of this dissertation are papers that have been published or are in review for publication in peer-reviewed scientific journals. Although these papers derived from collaborative efforts, the primary intellectual and writing contributions are attributed to the efforts of B.R. Ellis. The following makes clear the specific contributions of each of the co-authors.

The work presented in Chapter 2 is from the following published manuscript:


This paper was one part of a two part collaborative effort of the three authors, which resulted in this publication and a second paper, Crandell et al., 2010. The design of the study, the analysis, and the interpretation of the findings were performed by B.R. Ellis. The diffusion model used in this chapter was the product of the collaborative efforts of B.R. Ellis and L.E. Crandell. C.A. Peters played a supervisory role, and advised in the writing and editing of the manuscript.

The work presented in Chapter 3 is from the following published manuscript:


This manuscript was the product of an experiment designed and conducted by B.R. Ellis at the US Department of Energy’s National Energy Technology Laboratory. The analysis of all computed tomography data and the spectroscopic imaging presented are also solely attributed to the efforts of B.R. Ellis. C.A. Peters again contributed in a supervisory role and advised in the
writing and editing of the manuscript. J.P. Fitts and G.S. Bromhal advised in the writing and editing of the manuscript. D.L. McIntyre facilitated the experiment at the NETL facility. R.P. Warzinski and E.J. Rosenbaum collected the CT data.

The work presented in Chapter 3 is from a manuscript that has been submitted for publication and is currently in review:

Ellis, B. R.; Fitts, J. P.; Bromhal, G. S.; McIntyre, D. L.; Tappero, R.; Peters, C.


This paper presents results from a subsequent experiment, following the work presented in Chapter 3. The primary intellectual contribution, analysis, and writing are again attributed to B.R. Ellis. J.P. Fitts helped execute the synchrotron-based spectroscopic analyses and advised in the writing and editing of the manuscript. G.S. Bromhal and D.L. McIntyre advised in the editing of the manuscript. R. Tappero designed and performed the synchrotron Ca $\mu$XANES data collection. C.A. Peters served as the research supervisor and advised in the writing and editing of the manuscript.
Chapter 2

Limitations for Brine Acidification due to SO₂ Co-injection in Geologic Carbon Sequestration

1.1 Introduction

Geologic sequestration of carbon dioxide has come to the forefront of potential carbon mitigation strategies (Metz et al., 2005). Sequestration in deep saline formations is an especially attractive option due to the availability of injection sites, large potential storage capacity and technical feasibility of underground injection (Bruant et al., 2002; Bachu, 2008; Benson and Cole, 2008). One of the current challenges facing implementation of large-scale CO₂ injection projects is forming regulations or guidelines that specify the required purity of the injection stream (Pollak and Wilson, 2009). In a recent editorial, John Gale pointed out the need for sound policy concerning injection stream composition and a need for further research to better understand how co-injectants will impact the success of carbon capture and storage in geologic media (Gale, 2009).

This chapter focuses on co-injection of sulfur dioxide, an important environmental pollutant emitted from electric power plants, which will be a primary source of CO₂ for geologic carbon sequestration. The amount of SO₂ emitted from a plant is small relative to the amount of CO₂ emitted. Figure 2.1 shows the moles SO₂ emitted annually in relation to the moles of CO₂ emitted from 382 electric power plants in the United States. In 2002, these plants accounted for
99.5% of all \( \text{SO}_2 \) power plant emissions and, collectively, released more than eight million tonnes of \( \text{SO}_2 \) to the atmosphere (Miller and Van Atten, 2004).

To regulate \( \text{SO}_2 \) emissions, the U.S. EPA uses a market-based approach through Title IV of the 1990 Clean Air Act Amendments. The total size of the \( \text{SO}_2 \) emissions allowance market in the United States is on the order of $5 billion, based on a snapshot of the market in mid 2007 (EPA, 2009). It is generally believed that the collective costs are far smaller than the net benefits of \( \text{SO}_2 \) regulation in light of protection of human health and the environment (Chestnut and Mills, 2005). However, the fact remains that the power industry deems it economically favorable to, collectively, spend billions of dollars for the right to emit \( \text{SO}_2 \) rather than to control it. With the emergence of carbon capture and geologic sequestration, and the possibility of \( \text{SO}_2 \) co-injection, the economic favorability of emitting \( \text{SO}_2 \) to the atmosphere could change.

![Figure 2.1. Annual power plant emissions of \( \text{SO}_2 \) relative to \( \text{CO}_2 \) emissions for the highest \( \text{SO}_2 \)-emitting plants in the United States (Miller and Van Atten, 2004). Lines represent ratios of molar quantities of \( \text{SO}_2 \) to \( \text{CO}_2 \).](image)

A primary concern surrounding geologic carbon sequestration is the potential for brine acidification. Injection of \( \text{CO}_2 \) alone would lead to the formation of carbonic acid and cause
brine acidification. This will lead to acid-catalyzed mineral dissolution and subsequent precipitation (Gunter et al., 1993; Baines and Worden, 2004; Pearce et al., 2004; Xu et al., 2004; Giammar et al., 2005; Li et al, 2006; Zerai et al., 2006; Gaus et al., 2008; Peters, 2009). Dissolution of minerals containing divalent metal cations can lead to mineral trapping of the injected carbon in the form of stable carbonate precipitates (Xu et al., 2003; Soong et al., 2004; Xu et al., 2005). These reactions will alter formation permeability and porosity and may be deleterious to formation integrity (Kaszuba et al., 2005). However, mineral dissolution may also lead to pH buffering as has been observed in the CO\(_2\) injection into the Frio formation (Kharaka et al., 2006). If formation mineralogy has insufficient buffering capacity, acidified brine may degrade cements of nearby abandoned wells or alter the integrity of the caprock, thereby increasing the probability of CO\(_2\) leakage to the surface (Gaus et al., 2005; Nordbotten et al., 2005; Carey et al., 2007; Duguid et al., 2007; Gherardi et al., 2007; Kutchko et al., 2007).

The presence of co-injectants, such as SO\(_2\), may lead to further brine acidification through the formation of stronger acids. Both SO\(_2\) and H\(_2\)S have been previously studied as co-injectants in the context of geologic carbon sequestration (Gunter et al., 2000; Knauss et al., 2005; Palandri and Kharaka, 2005; Xu et al., 2007). Knauss et al. (2005) predicted that co-injection of even a small amount of SO\(_2\) (10\(^{-6}\) bar partial pressure) would lead to a brine pH of unity and enhanced mineral dissolution. This extreme acidification was attributed to the formation of sulfuric acid. Supporting evidence for extreme brine acidification due to co-injection of SO\(_2\) was predicted by Xu et al. (2007) whose reactive transport simulations demonstrated that SO\(_2\) co-injection into a quartzose lithic arkose formation would lead to near-zero pH values within a radial distance exceeding 100 m from the point of injection.
Although previous studies have demonstrated that co-injection of SO$_2$ is likely to cause enhanced brine acidification, the rate of dissolution of the injected SO$_2$ has never been assumed to be a limiting factor for brine acidification. Injected SO$_2$ will exist within a separate supercritical CO$_2$ (scCO$_2$) phase in the formation. As SO$_2$ is much more soluble in water than CO$_2$, it has the potential to extensively partition into the brine phase. This explains how small amounts of SO$_2$ can cause significant brine acidification as previously predicted (Knauss et al., 2005; Xu et al., 2007). However, the work of Crandell et al. (2010) has shown that mass transfer limitations of SO$_2$ through the scCO$_2$ phase may be important. That work demonstrated that SO$_2$ within the scCO$_2$ plume near the phase boundary is quickly depleted. This establishes a thick zone of depletion, which creates resistance to further SO$_2$ mass transfer, resulting in less than a third of the injected SO$_2$ dissolving into the brine phase after 1000 years.

The goal of the modeling effort presented in this chapter is to gain a more thorough understanding of the magnitude and time scale of brine acidification for the case of SO$_2$ co-injection during geologic carbon sequestration in deep saline formations. The potential for brine acidification is investigated for three different SO$_2$ reaction scenarios: hydrolysis, oxidation, and disproportionation, to investigate the effects of different sulfur-bearing acids. The model scenarios that are studied describe the situation in which SO$_2$ mass transport to the brine phase is limited by diffusion in the scCO$_2$ phase. One model describes rapid dispersion of SO$_2$ in a slowly advecting brine phase. The other model investigates diffusive transport of SO$_2$ in a stagnant brine phase. These represent extreme end cases for transport limitations and are meant to provide bounding estimates of brine acidification, as in reality, a combination of advective and diffusive transport in the aqueous phase will exist. For comparison, we model the case of SO$_2$ phase equilibrium between the entire volumes of scCO$_2$ and brine, which represents the maximum
potential basin-scale acidification. To predict brine pH, we developed a geochemical model that simulates aqueous speciation and thermodynamic phase equilibrium of injected CO₂ and SO₂ with brine from a Mississippian carbonate formation in the Alberta Basin, Canada.

2.2 Methods

2.2.1. SO₂ reaction scenarios

Three different scenarios for reaction in the brine phase were investigated. The first is that of SO₂ hydrolysis,

\[ \text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3 \]  

(2.1)

This reaction produces only the weak acid, sulfurous acid. If this is the only reaction occurring, it represents the case of there being no mechanism for oxidation of SO₂. When oxidizing conditions exist, SO₂ is oxidized following the reaction,

\[ \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{SO}_4 \]  

(2.2)

This produces sulfuric acid, a very strong acid. While this reaction is written with molecular oxygen as the oxidant, a typical oxygen fugacity in deep saline formations is on the order of \(10^{-63}\) bar (Helgeson et al., 1993). It is unlikely that this is sufficient to drive the SO₂ oxidation reaction to completion, so here, molecular oxygen as a reactant is intended to be representative of all potential oxidants. Strong oxidants, such as MnO, are likely to exist in sufficient quantities to oxidize the small amount of injected SO₂. This assumption is in line with the work of Knauss et al. (2005).

The third scenario that is modeled is SO₂ disproportionation,

\[ \text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \frac{3}{4}\text{H}_2\text{SO}_4 + \frac{1}{4}\text{H}_2\text{S} \]  

(2.3)
In this reaction scenario, the sulfur in SO$_2$ is both oxidized to sulfate and reduced to sulfide in a ratio of 3:1. In the context of SO$_2$ co-injection during geologic carbon sequestration, disproportionation has been previously modeled as the dominant mechanism of acid formation (Palandri and Kharaka, 2005; Xu et al., 2007). This reaction is typically associated with hydrothermal systems. Holland (1965) demonstrated through thermochemical modeling that nearly all SO$_2$ of magmatic origin is consumed via disproportionation. As magmatic gases are cooled, SO$_2$ reacts with condensed water vapor to form sulfuric acid and the weaker acid, hydrogen sulfide (Holland, 1965; Rye et al., 1992; Kusakabe et al., 2000; Symonds et al., 2001).

2.2.2. Model system and conditions

To estimate the impact of SO$_2$ on brine chemistry, a two-phase system was modeled consisting of a scCO$_2$ phase containing a small amount of SO$_2$ and a brine phase. Consistent with the simplified geometry used by Crandell et al. (2010), the injected gas phase was modeled as a cone-shaped plume (Figure 2.2). The cone radius of 2.8 km corresponds to a formation with 20% porosity and a thickness of 75 m. Together with the brine phase under the cone, the system is a cylinder of diameter equal to that of the scCO$_2$ cone and height corresponding to the formation thickness. The injection formation is assumed to be bounded on the top and bottom by impermeable formations. Model simplifications, including the absence of CO$_2$ flow and the absence of residual brine, are discussed along with the implications in Crandell et al. (2010).
Figure 2.2. Schematic diagram of model system showing the scCO₂ plume (light gray) and brine volume (dark gray): (a) SO₂ phase equilibrium between the CO₂ and brine phases; (b) diffusion-limited SO₂ dissolution with uniform sulfur distribution in an advecting brine phase; (c) diffusion-limited SO₂ dissolution with diffusive transport of SO₂ in a stagnant brine phase.

System conditions were 40°C and 127 bar, which correspond to an injection depth of 1.2 km assuming a pressure gradient of 105 bar km⁻¹, a thermal gradient of 25°C km⁻¹ (Van der Meer, 1993; Bachu, 2000), and a surface temperature of 10°C. Under these conditions, CO₂ will exist as a supercritical fluid. The total volume of the injected CO₂-SO₂ mixture was 1.2x10⁸ m³.
This was determined based upon a 50-year injection period at a rate of 1.83 Mtonne yr\(^{-1}\) (Wilson and Monea, 2004) and a mixture density of 774 kg m\(^{-3}\) (Crandell et al., 2010).

The mixture composition was chosen to be 99% CO\(_2\) and 1% SO\(_2\), as this is within the range of relative CO\(_2\) to SO\(_2\) emissions shown in Figure 2.1. Initial conditions for both diffusive models were such that SO\(_2\) was assumed to be uniformly distributed throughout the scCO\(_2\) plume. The initial brine composition used in all modeling is shown in Table 2.1; it is taken from an analysis of a Mississippian carbonate aquifer from the Alberta sedimentary basin, Canada, (Michael, 2002). The analysis is an uncorrected well-head formation fluid measurement.

<table>
<thead>
<tr>
<th>Species</th>
<th>[mol L(^{-1})]</th>
<th>[mg L(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>8.65 x 10(^{-1})</td>
<td>19900</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>8.61 x 10(^{-1})</td>
<td>30500</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>9.98 x 10(^{-3})</td>
<td>400</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>6.99 x 10(^{-3})</td>
<td>170</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>3.44 x 10(^{-4})</td>
<td>33</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>3.75 x 10(^{-2})</td>
<td>2290</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

Source: Michael (2002)

The phase equilibrium and diffusive transport models developed for this chapter are coupled with a geochemical model describing instantaneous reaction and speciation in the aqueous phase. All model codes were written in Matlab\textsuperscript{®} (Version 7.6.0.324 R2008a, The MathWorks\textsuperscript{TM}).

2.2.3 Geochemical model

In the geochemical model, an iterative process was used to compute aqueous speciation of carbonates, sulfates, sulfites and hydrogen sulfide. As needed, aqueous speciation was coupled with phase equilibrium of SO\(_2\) and CO\(_2\). The SO\(_2\) reactions were examined individually, such that in a given simulation only one of the three possible reaction scenarios was modeled. For the
case of SO₂ oxidation, oxygen fugacity was held constant at 10⁻² bar to represent full oxidation of the injected SO₂. The brine pH was determined by convergence on a solution for conservation of mass and balance of charge.

All aqueous speciation reactions are assumed to be instantaneous and are shown with their equilibrium constants in Table 2.2. Reaction equilibrium constants were adjusted for high temperature and pressure conditions using SUPCRT92 (Johnson et al., 1992). Also shown in Table 2.2 are the equilibrium constants for aqueous solubility of SO₂ and CO₂. For SO₂, the value shown is the pressure- and temperature-adjusted Henry’s Law constant estimated by Crandell et al. (2010) for a 1 M NaCl solution at 40°C and 127 bar. The SO₂ fugacity coefficient in the scCO₂ was determined following the method of Tarakad and Danner (1977). The semi-empirical model of Duan and Sun (2003) was used to calculate CO₂ solubility. Aqueous species activity coefficients were calculated via the extended Debye-Huckel formalism of Helgeson and Kirkham (1974).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log($K_{eq}$)</th>
<th>log($K_{H}$ [mol L⁻¹ bar⁻¹])</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_{2(aq)}$ + H$_2$O ↔ H$_2$SO$_3$</td>
<td>-0.042</td>
<td></td>
</tr>
<tr>
<td>SO$_3^{2-}$ + $\frac{1}{2}$O$_2$(g) ↔ SO$_4^{2-}$</td>
<td>42.86</td>
<td></td>
</tr>
<tr>
<td>SO$_{2(aq)}$ + H$_2$O ↔ $\frac{3}{4}$HSO$_4^{-}$ + $\frac{3}{4}$H$^+$ + $\frac{1}{4}$H$<em>2$S$</em>{(aq)}$</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td>H$_2$CO$_3$ ↔ HCO$_3^{-}$ + H$^+$</td>
<td>-6.27</td>
<td></td>
</tr>
<tr>
<td>HCO$_3^{-}$ ↔ CO$_3^{2-}$ + H$^+$</td>
<td>-10.16</td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_3$ ↔ HSO$_3^{-}$ + H$^+$</td>
<td>-1.93</td>
<td></td>
</tr>
<tr>
<td>HSO$_3^{-}$ ↔ SO$_3^{2-}$ + H$^+$</td>
<td>-7.24</td>
<td></td>
</tr>
<tr>
<td>HSO$_4^{-}$ ↔ SO$_4^{2-}$ + H$^+$</td>
<td>-2.12</td>
<td></td>
</tr>
<tr>
<td>H$_2$O ↔ OH$^{-}$ + H$^+$</td>
<td>-13.49</td>
<td></td>
</tr>
<tr>
<td>SO$<em>{2(scCO2)}$ ↔ SO$</em>{2(aq)}$</td>
<td>-0.23&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>CO$_{2(scCO2)}$ + H$_2$O ↔ H$_2$CO$_3^*$</td>
<td>-1.99</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>From Crandell et al. (2010)
In order to predict the most extreme acidification potential, mineral buffering reactions were not included in any of the simulations performed in this study. For further simplicity, aqueous complexation reactions were also not included.

2.2.4 Phase equilibrium model

In the phase equilibrium model scenario, all the brine is assumed to be in equilibrium with the SO$_2$ and CO$_2$ in the entire scCO$_2$ phase (Figure 2.2(a)). According to the system geometry, the ratio of the volumes of brine to scCO$_2$ phases is 2:1. Initial brine alkalinity was varied to test the sensitivity of equilibrium pH to initial brine composition under each of the three reaction scenarios. Brine alkalinity was modeled as bicarbonate and ranged from $1 \times 10^{-3}$ M to 1 M.

2.2.5 Diffusion modeling

The first diffusion model considers SO$_2$ diffusion limitations in the scCO$_2$ phase and uniform sulfur distribution in a slowly advecting brine phase (Figure 2.2(b)). This model is meant to simulate rapid dispersion in the aqueous phase. Fresh brine is introduced at each time step to simulate advective flow within the brine portion of the model system. Flow rates of 1 m yr$^{-1}$ and 0.1 m yr$^{-1}$ were modeled by computing a residence time using the diameter of the cylindrical model system as the length scale for advective flow. At each time step SO$_2$ and CO$_2$ are allowed to reach saturation at the brine phase boundary and are then uniformly distributed throughout the brine phase. This model assumes a constant total system volume allowing for increasing brine volume as the scCO$_2$ phase is depleted.

The second diffusion model considers diffusion in both phases (Figure 2.2(c)) and is meant to simulate the case of a stagnant brine phase. In the brine phase at a distance of 1 km beyond the radial extent of the scCO$_2$ plume, a constant concentration boundary condition was
set to be equal to the background sulfate and bicarbonate concentrations shown in Table 2.1. \( \text{SO}_2 \) and \( \text{CO}_2 \) concentrations in the brine phase at the plume boundary were determined by solubility limitations. For \( \text{CO}_2 \), this effectively represents a constant concentration boundary condition for the brine-side of the system.

### Table 2.3 – Diffusion Coefficients

<table>
<thead>
<tr>
<th>Species</th>
<th>Diffusion Coefficient [m(^2)/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2\text{(scCO}_2) (^a)</td>
<td>(2.49 \times 10^{-8})</td>
</tr>
<tr>
<td>( \text{SO}_2\text{(aq)} )</td>
<td>(2.31 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_3 )</td>
<td>(2.31 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{HSO}_3^- )</td>
<td>(1.62 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{SO}_3^- )</td>
<td>(1.01 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4^- )</td>
<td>(1.45 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} )</td>
<td>(1.12 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{CO}_2\text{(aq)} )</td>
<td>(2.73 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>(1.24 \times 10^{-9})</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} )</td>
<td>(9.68 \times 10^{-10})</td>
</tr>
</tbody>
</table>

\(^a\text{From Crandell et al. (2010)}\)

In both cases, the diffusion modeling builds upon the modeling presented in Crandell et al. (2010) by including brine phase transport and geochemical reactions. All diffusion modeling uses a time step of 0.25 years. See Crandell et al. (2010) for further detail regarding model equations and the numerical discretization scheme. Previously, \( \text{SO}_2 \) flux to the brine phase was calculated assuming no build-up of sulfur in the brine phase (Crandell et al., 2010); however, in this study \( \text{SO}_2 \) concentration in the brine is governed by both solubility constraints and the thermodynamics of each \( \text{SO}_2 \) reaction scenario. Diffusive flux of \( \text{SO}_2 \) into the brine phase was determined by simultaneously solving for phase partitioning and thermodynamic equilibrium of the aqueous geochemical reactions via an iterative process at each boundary cell. No flux boundaries are imposed at the top and bottom of the injection formation in both diffusive models, corresponding to the injection formation being bounded by impermeable caprocks.
The diffusion coefficient for SO\textsubscript{2} within the scCO\textsubscript{2} phase was taken from Crandell et al. (2010). For the second diffusion model, aqueous diffusion coefficients for neutral species were determined via the Wilke-Chang equation (Wilke and Chang, 1955) using an updated association parameter for water from Hayduk and Laudie (1974). Aqueous diffusion coefficients for ionic species were determined via the Nernst-Haskell equation (Robinson and Stokes, 1965; Vanysek, 2009). Diffusion coefficients are given in Table 2.3.

### 2.3 Results

The brine pH results from the phase equilibrium model scenario are shown in Figure 2.3 for an initial brine alkalinity of 3.75x10\textsuperscript{-2} M. For all three SO\textsubscript{2} reaction scenarios, mass balance modeling showed that equilibrium partitioning would cause more than 99.8% of the SO\textsubscript{2} to partition into the brine phase. All three scenarios are predicted to produce significant acidification beyond a pH of 4.6 that would result from dissolution of pure CO\textsubscript{2}. SO\textsubscript{2} oxidation is predicted to cause the most severe brine acidification with a pH of 1.1. SO\textsubscript{2} disproportionation causes a similar degree of acidification. While SO\textsubscript{2} hydrolysis produces a weaker acid, it would still significantly reduce the pH.
Figure 2.3. Phase equilibrium brine pH results for each of the three reactions and CO$_2$ alone for an initial alkalinity of $3.75 \times 10^{-2}$ M.

Figure 2.4 shows how variation in initial brine alkalinity is predicted to impact equilibrium pH. In the case of pure CO$_2$, the brine pH varies gradually from 3.2 for $10^{-3}$ M alkalinity to 6.1 for 1 M. For each of the three SO$_2$ reaction scenarios, an inflection in the brine pH curve is predicted indicating the alkalinity at which the acidity would be titrated. The absence of a distinct titration point for the case of pure CO$_2$ is due to the fact that it remains in excess, whereas only a limited amount of acid is generated from the dissolved SO$_2$. For the case of SO$_2$ hydrolysis, titration occurs at a lower alkalinity than for the other two reactions because hydrolysis is less thermodynamically favorable and produces less acid.
Figure 2.4. Phase equilibrium brine pH results for a range of values of initial brine alkalinity, for CO$_2$ alone and each of the three reaction scenarios.

Brine pH results from the diffusion model investigating rapid brine phase dispersion are displayed in Figure 2.5, for two brine flow rates. The results from SO$_2$ disproportionation are very similar to those for oxidation, so only results for SO$_2$ oxidation and SO$_2$ hydrolysis are shown. For reference, brine pH evolution for the case of a pure CO$_2$ injection plume is also shown. The system brine reaches CO$_2$ saturation after 150 years, for a flow rate of 1 m yr$^{-1}$. As CO$_2$ dissolves, the scCO$_2$-brine boundary moves inward a few meters, corresponding to a 12% reduction in the total scCO$_2$ volume after 1000 years.
Figure 2.5. Brine pH results for SO₂ hydrolysis and SO₂ oxidation reaction scenarios for diffusion-limited SO₂ dissolution into an advecting brine. For reference, pH results for the case of a pure CO₂ injection plume are also shown.

The case of SO₂ oxidation is again predicted to cause the most severe brine acidification, but hundreds of years would need to pass before this is manifested. Enhanced brine acidification beyond a pH of 4.6, caused by CO₂ alone, is not predicted to occur until after 25 years for the case of SO₂ oxidation. Brine pH values below 3 are not predicted to occur until after nearly 200 years when SO₂ is oxidized to sulfuric acid. At 200 years, only 20% of the total injected sulfur is predicted to have dissolved. At the end of the 1000-year simulation, brine pH values near 2 and 4 are predicted for the cases of SO₂ oxidation and hydrolysis, respectively. Slightly higher pH
values are predicted for a higher brine flow rate due to the increased rate of flushing from the system. After 1000 years, just over 35% of the injected sulfur is predicted to have dissolved.

Diffusion modeling results for the case of a stagnant brine phase are shown in Figures 2.6 and 2.7. The results are presented at snapshots in time as a cross section drawn from the center of the scCO₂ plume to 200 m beyond the radial extent of the plume. The figures show pH contours within the brine phase and SO₂ concentration contours within the scCO₂ phase. As the results for SO₂ oxidation and disproportionation are again very similar, only results for SO₂ oxidation and hydrolysis are presented. Figure 2.6 shows simulation results for SO₂ hydrolysis after 500 and 1000 years. Here, pH values near 2 are predicted to occur adjacent to the plume boundary; however, enhanced brine acidification beyond that caused by CO₂ alone (pH = 4.6) is not predicted to occur beyond 4 meters of the plume boundary. Build-up of dissolved SO₂ at the plume boundary causes a significant reduction in the flux of SO₂ from the scCO₂ phase, resulting in less than 10% of the injected sulfur dissolving after 1000 years.
Figure 2.6. Cross section showing results from diffusion-limited SO\(_2\) mass transport in both the scCO\(_2\) and brine phases. For the case of SO\(_2\) hydrolysis, contours show SO\(_2\) concentration in the scCO\(_2\) phase and pH in the brine phase after 500 and 1000 years. Shaded region denotes scCO\(_2\) phase.

Figure 2.7 shows the results for the case of SO\(_2\) oxidation. Brine pH values near zero are predicted proximal to the scCO\(_2\)-brine phase boundary, but enhanced acidification beyond a pH of 4.6 is not predicted to occur beyond 5 meters of the plume boundary. In this simulation, dissolved SO\(_2\) does not substantially build-up adjacent to the plume boundary as SO\(_2\) is readily oxidized to sulfuric acid. In fact, the SO\(_2\) concentration profile is effectively identical to the case of a zero concentration of SO\(_2\) adjacent to the plume boundary simulated by Crandell et al. (2010). Compared to SO\(_2\) hydrolysis, the case of oxidation results in a greater flux of SO\(_2\) from the scCO\(_2\) phase leading to approximately 27% of the injected SO\(_2\) dissolving after 1000 years.
Figure 2.7. Cross section showing results from diffusion-limited SO\textsubscript{2} mass transport in both the scCO\textsubscript{2} and brine phases. For the case of SO\textsubscript{2} oxidation, contours show SO\textsubscript{2} concentration in the scCO\textsubscript{2} phase and pH in the brine phase after 500 and 1000 years. Shaded region denotes scCO\textsubscript{2} phase.

2.4 Discussion

The results from this study confirm that SO\textsubscript{2} co-injection will lead to increased brine acidification relative to the case of injection of pure CO\textsubscript{2}, but the magnitude depends on the rate of SO\textsubscript{2} dissolution, redox conditions in the formation, hydrodynamic conditions controlling the zone of influence, and buffering potential of the formation. For the scenario of instantaneous and complete phase equilibrium across the entire system, extensive partitioning of SO\textsubscript{2} to the brine phase and significant brine acidification is predicted. However, this scenario is unrealistic due to
the absence of fast fluid flows that would produce rapid mixing and extensive contact between the two phases. It is more likely that SO$_2$ mass transfer to the formation brine will be limited by slow diffusion through the scCO$_2$ phase (Crandell et al., 2010). Our modeling results show that when this is the case, SO$_2$ co-injection will not lead to brine acidification as severe as has been previously predicted (Knauss et al., 2005; Xu et al., 2007). Diffusion limitations will slow the rate at which SO$_2$ will dissolve into the brine. To a large extent, SO$_2$ is predicted to remain in the scCO$_2$ plume even after 1000 years. This means that acidification will persist for a long time, but the magnitude of this acidification is not nearly as severe as that predicted when SO$_2$ mass transport to the brine is not a limiting factor.

All three SO$_2$ reaction scenarios predicted enhanced brine acidification, but consistently, SO$_2$ oxidation caused the most severe acidification. This is not surprising given that, for this reaction, the SO$_2$ is oxidized to the very strong acid, sulfuric acid. This will occur only if oxidizing conditions exist in the injection formation. If SO$_2$ is not oxidized, only the weak acid, sulfurous acid, is produced via SO$_2$ hydrolysis. This acid will cause less severe acidification and is more easily titrated by brine alkalinity, SO$_2$ hydrolysis alone would create the minimum potential for brine acidification, and SO$_2$ oxidation would create the maximum potential. In this chapter, these have been modeled in isolation but in reality it is likely that the fate of dissolved SO$_2$ will not be determined by a combination of the different possible SO$_2$ reaction scenarios.

If SO$_2$ disproportionation occurs, it will lead to a similar degree of brine acidification to that of full SO$_2$ oxidation, providing supporting evidence to the work of Xu et al. (2007) who established that disproportionation of co-injected SO$_2$ will lead to significant brine acidification. As SO$_2$ disproportionation occurs via simultaneous oxidation and reduction of the sulfur in SO$_2$, the favorability of this reaction is not dependent on the availability of other oxidants.
implies that this reaction has the potential to occur regardless of the local redox conditions and if it occurs, it will likely occur coincidentally with either SO$_2$ hydrolysis or oxidation.

The models in this study present pH estimates for bounding aqueous transport-limiting scenarios, however, in reality SO$_2$ will be dispersed via a combination of advective and diffusive transport. Regardless of aqueous transport conditions, slow diffusion in the scCO$_2$ will reduce the potential for brine acidification due to SO$_2$ co-injection. Slow diffusion of SO$_2$ in the scCO$_2$ prevents basin-wide brine acidification from occurring for several centuries. In this same timeframe, pH-buffering mineral dissolution reactions are likely to occur. These reactions have the potential to buffer much of the acid generated by SO$_2$ dissolution as long as the recipient formation has sufficient carbonate, basic silicate or basic aluminosilicate minerals (Gunter et al., 2000).

It is most likely that potential injection formations will have very slow-moving brines and diffusion will play a major role in determining aqueous phase transport. This would suggest that acidification of the injection formation brine will occur over a similar spatial and temporal scale as that predicted for the case of a stagnant brine phase. Here, even after 1000 years, brine acidification below a pH of 4.6 is not predicted to occur beyond 5 m of the injection plume boundary. This is a much smaller zone of extreme acidification than the roughly 100 m zone predicted by Xu et al. (2007) for a 1-D system which allowed for both advection and diffusion in the brine. As demonstrated by Xu et al. (2007), severe mineral dissolution within this highly acidified zone may be likely. Enhanced mineral dissolution due to SO$_2$ co-injection may eventually lead to enhanced mineral trapping of injected CO$_2$ in the form of secondary carbonate mineral precipitates (Knauss et al., 2005; Palandri and Kharaka, 2005; Xu et al., 2007).
2.5 Conclusions

This study has demonstrated that SO\textsubscript{2} co-injection during geologic carbon sequestration has the potential to cause enhanced brine acidification, but that the magnitude, onset, and spatial extent of this acidification may not be significant. When SO\textsubscript{2} mass transfer limitations are not accounted for, brine pH values near unity are predicted. However, we predict that diffusion limitations can cause 73 to 90% of the injected SO\textsubscript{2} to remain within the scCO\textsubscript{2} phase after 1000 years. Furthermore, if potential oxidants are not present, severe brine acidification will occur only if SO\textsubscript{2} disproportionation is favorable. Even for the case of rapid aqueous phase dispersion, pH values below 3 are not reached for several hundred years. As mineral dissolution and resultant pH buffering is likely to occur during this same timeframe, the potential for brine acidification would be further reduced.

In conclusion, the co-injection of a small amount of SO\textsubscript{2} is not predicted to cause rapid, severe widespread brine acidification. This suggests that co-injection may be a viable option for mitigating SO\textsubscript{2} emissions from power plants and should be considered in future policy regarding injection stream purity.

The results presented in this chapter highlight the potential disparity in estimating brine pH if dissolution limitations are not accounted for. As brine pH will impact water-rock interactions, the manner in which SO\textsubscript{2} dissolution is modeled is an important consideration in any geochemical modeling effort investigating SO\textsubscript{2} co-injection.
Chapter 3

Deterioration of a Fractured Carbonate Caprock Exposed to CO$_2$-acidified Brine Flow

3.1 Introduction

Secure geologic carbon sequestration requires a caprock that is able to contain carbon dioxide for long periods of time. Subsurface injection of large volumes of CO$_2$ may lead to conditions that generate new fractures in the caprock or reopen existing fractures (Rutqvist et al., 2008; Shukla et al., 2010). Fractures, regardless of their origin, may serve as conduits for flow if they are hydraulically connected to an overlying aquifer (Smith et al., 2011).

CO$_2$ that dissolves in water will acidify formation brines (Ellis et al., 2010). Carbonate minerals, such as calcite and dolomite, are known to be reactive when in contact with CO$_2$-acidified brines (Pokrovsky et al., 2009). Therefore some degree of erosion is expected along flow paths where CO$_2$-acidified brine contacts carbonate rock, such as in hydraulically-connected fractures in carbonate caprocks. Characterizing and modeling coupled fluid flow and reaction in fractures is challenging due to the interrelationship of these processes and the effects of spatial heterogeneities in fracture geometry and mineral distributions (Berkowitz, 2002; Dijk et al., 2002; Detwiler, 2008). Reaction-induced changes in fracture geometry can alter intrinsic permeabilities and relative permeabilities in ways that are difficult to predict. It is well known that flow permeability increases with fracture aperture (Snow, 1969), but flow is hindered with increasing roughness of fracture surfaces (Brown et al., 1998; Crandall et al., 2010).
Furthermore, while mineral dissolution may enlarge the flow path, it is also possible that fracture permeability may decrease due to removal of the asperities holding the fracture open (Polak et al., 2003). Finally, mineral dissolution may lead to clogging of the flow path caused by particle decohesion (Noiriel et al., 2007). Therefore, predictions of long-term seal integrity require an understanding of how the complex interplay of \( \text{CO}_2 \)-water-rock interactions and fluid transport will impact fracture evolution.

This chapter presents results from an experimental study designed to investigate the micrometer- to centimeter-scale evolution of fracture geometry in an artificially-fractured limestone caprock exposed to flow of \( \text{CO}_2 \)-acidified brine. Experiments conducted at this scale are needed to determine the importance of complexities such as mineral spatial heterogeneity in controlling flow along fracture pathways. To investigate a relevant case, a caprock specimen was sampled from the drilling core of the injection well at one of the \( \text{CO}_2 \) injection demonstration sites of the U.S. Department of Energy. The site is the Midwest Regional Carbon Sequestration Partnership’s project located in Otsego County, Michigan. Approximately 60,000 tons of \( \text{CO}_2 \) have been injected into the Bass Islands Dolostone between 2008 and 2009. This formation is overlain by the Bois Blanc formation, a cherty carbonate, and above that by the Amherstburg formation, a dense fossiliferous dolomitic limestone. The Amherstburg formation is considered the primary caprock for this injection site (MRCSP, 2008). This is one of three existing deep saline formation \( \text{CO}_2 \) injection projects that rely on a carbonate caprock as the primary seal for securing the injected \( \text{CO}_2 \) (Michael et al., 2010).

A seven-day core-flooding experiment was conducted in which \( \text{CO}_2 \)-acidified brine flowed through an artificially-fractured Amherstburg core sample. The brine composition was selected to represent a brine that has had time to react with the injection formation minerals.
under CO\textsubscript{2}-saturated conditions prior to contact with the core. Temperature and pressure conditions were 27\textdegree C and 10 MPa. Under these conditions and at equilibrium with CO\textsubscript{2}, the brine had a pH of 4.4. The evolution of fracture aperture was monitored in real-time using an X-ray computed tomography (CT) scanner. Before and after the experiment, 3-D reconstructions of the fracture geometry, aperture, and surface roughness were examined at higher resolution via micro X-ray CT (\textmu CT). Finally, the cores were sectioned and examined with scanning electron microscopy (SEM). The combination of high resolution \textmu CT and SEM analysis provides valuable insight into the mineralogy-dependent alterations of fracture geometry due to flow of reactive fluids (Noiriel et al., 2007; Gouze et al., 2003; Andreani et al., 2008).

3.2 Methods

3.2.1 Sample characterization and brine composition

The Amherstburg sample used in this study came from a 4” diameter core that had been collected at a depth of 928 m during the drilling of the injection well at the Otsego County project site. A similar specimen from the Bois Blanc was also obtained, and used to estimate mineralogy of that formation. A 1” diameter vertical core was cut from the Amherstburg sample using a water-jet cutter to prevent unwanted mechanical degradation of the sample. The sample was artificially fractured prior to the experiment to enable flow. The fracture was induced under normal stress compression with dual knife-edge chisels perpendicular to the horizontal (XY) plane of the core. Prior to fracturing, the core was stabilized by coating the exterior in epoxy. This technique was successful in producing a fracture that propagated the length of the core. After the core was fractured another coat of epoxy was applied to the core exterior, leaving only the ends exposed, to ensure the integrity of the epoxy coating and prevent lateral flow along the outer boundary during brine flow.
The Amherstburg caprock specimen is primarily composed of calcite and dolomite, in roughly equal proportions. Together, these minerals comprise >90% of the bulk sample, with the remaining rock containing a mixture of quartz, K-feldspar, clay minerals, and pyrite. The Bass Islands formation is predominately composed of dolomite with <10% other minerals including, in descending order of proportion, calcite, anhydrite, quartz, K-feldspar, and clay minerals. To determine these mineral compositions, X-ray diffraction was used to identify the primary minerals present. Then, a section of each sample was cut and polished for SEM analysis. Back-scattered electron (BSE) microscopy was used to differentiate mineral material from pore space, and where possible, differentiate between minerals. These BSE images were then combined with energy dispersive spectroscopy (EDS) elemental maps, such as those for calcium and magnesium. Specific minerals and their percent contribution to the sample area were identified using an algorithm that overlays the BSE gray-scale images with the EDS elemental maps. For example, the BSE images can be used to separate calcite from dolomite. Dolomite is assigned to regions of the EDS map where calcium and magnesium co-occur, with no other metals present, and where the BSE map has a gray-scale intensity corresponding to the range assigned to dolomite. These area estimates are used as a proxy for the percent volume contribution of each mineral and represent a semi-quantitative estimate of bulk mineralogy. Several 2-D images were taken at random locations on the polished section. The analysis of the BSE images builds upon the work of Peters (2009). The samples were examined at the Image Analysis Center at Princeton University using a Bruker X-ray diffractometer and a Quanta environmental scanning electron microscope.

The experimental brine composition shown in Table 3.1 was selected to represent CO₂-saturated brine that had already reacted with minerals in the injection formation. Specifically, the
composition mimicked a CO$_2$-saturated 1 M NaCl brine reacted with dolomite, calcite and anhydrite with saturation indices of approximately -2. Temperature and pressure conditions of 40°C and 10 MPa were chosen to represent those occurring at a depth of approximately 1 km, which is at the interface between the Amherstburg and the Bois Blanc formations. Brine pH and mineral saturation calculations were made using PHREEQC with the Pitzer.dat database (Parkhurst and Appelo, 1999). Aqueous activity coefficients were estimated using the Pitzer model (Pitzer, 1973). CO$_2$ solubility was estimated to be 0.98 mol L$^{-1}$ following the work of Duan et al. (2006). Thermodynamic constants shown in Table 3.2 were determined through the use of SUPCRT92 to account for system pressure and temperature conditions (Johnson et al., 1992).

<table>
<thead>
<tr>
<th>Species (total)</th>
<th>[mol L$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>$1.0 \times 10^0$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>$1.0 \times 10^0$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>$6.4 \times 10^{-3}$ to $3.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$1.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>CO$_2$(aq)</td>
<td>$9.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>pH</td>
<td>4.4 to 4.9</td>
</tr>
</tbody>
</table>

**Table 3.2.** Thermodynamic constants (K) for acid-driven dissolution of calcite (eqn 3.1) and dolomite (eqn 3.2), and the solubility product constant (K$_{sp}$) for the dissolution of one mole of each mineral at 27°C and 10 MPa. Solution indices (SI) correspond to the solution conditions in the inlet brine. Reaction rates constants (k) are estimated following the work of Chou et al. (1989) for ambient pressure, 25°C and pH=4.4.
3.2.2 Flow-through experiment

Figure 3.1 shows a simplified depiction of the experimental system that was constructed in the core-flow experimental facility at DOE NETL in Morgantown, WV. The fractured sample was placed in a rubber jacket that was inserted into a TEMCO triaxial carbon-fiber core holder. A confining pressure of 14 MPa was applied to the exterior of the rubber jacket to prevent lateral flow along the core exterior.

![Figure 3.1. Simplified schematic of experimental design.](image)

A batch of the synthetic brine was prepared in the brine reservoir by mixing deionized water and salts: NaCl (extra pure, Acros Organics), CaCl₂ (>96% pure, Acros Organics), MgCl₂·4H₂O (reagent grade ACS, Acros Organics), NaOH (>97% pure, Acros Organics), and Na₂SO₄ (>99% pure, Fisher). Then, two separate high-pressure syringe pumps (Teledyne Isco, Inc., Lincoln, NE) delivered CO₂ (99.5% pure, Airgas) and brine to the high-pressure mixing vessel where they were allowed to equilibrate at 40°C and 10 MPa. The resulting CO₂ saturation in the brine was checked by comparing the measured pH to the predicted equilibrium pH. The
measured pH values were within the expected range of model pH values shown in Table 3.1. Inlet brine samples were taken at the beginning of the experiment (higher calcium concentration, higher pH) and after three days (lower calcium concentration, lower pH). Precipitates, likely calcium-bearing, were visible in the brine reservoir early on in the experiment. As such, the day-3 composition is believed to be most representative of the fluid flowed through the fracture over the course of the experiment and is therefore used throughout this chapter for the purpose of discussion. The pH measurements were made at system temperature and pressure conditions with use of high-pressure, high-temperature pH probes (Corr Instruments, LLC, San Antonio, TX. Brine samples were treated with nitric acid and diluted before being analyzed via ICP-OES on a Perkin Elmer Optima 3000 XL.

To start the flow experiment, the CO₂ valve was closed and the brine pump was used to push the CO₂-saturated brine through the core. The experiment was designed to have a constant flow rate of 10 mL hr⁻¹, which was chosen such that the pumps would be refilled once every two days. This corresponded to an average initial fluid velocity of 110 cm hr⁻¹, which was calculated as the volumetric flow rate divided by the average initial cross-sectional area of the fracture. The system pressure was controlled at 10 MPa by a back pressure regulator located near the outlet. Under the flow conditions of the experiment, there was no measureable pressure differential across the core and as such, there is no discussion of changes in core permeability presented in this chapter. A temperature of 40°C was successfully maintained in the mixing vessel; however, the average temperature measured at the core was 27°C. This lower core temperature was due to safety limitations in heating of the core holder exterior coupled with heat losses along the upstream flow path and at the core holder end caps.
3.2.3 X-ray computed tomography

X-ray computed tomography was used in two ways to perform non-destructive imaging of the fractured core before, during, and after the experiment. X-ray attenuation at beam energies greater than 100 keV corresponds to material density with a characteristic CT number that can distinguish mineral and void space (Wildenschild et al., 2002; Cai et al., 2009). The flow-through experiment was conducted within a Universal Systems HD-350E medical CT scanner. This allowed for real-time scans to be taken without disturbing the experiment. Scans were taken twice daily with a beam energy of 140 keV for the duration of the experiment providing information on fracture evolution. The medical scanner produces a series of 2-D slices with a voxel resolution of 250 µm in the plane of the slice and a thickness of 2 mm. This leads to data being averaged over the 2 mm depth of a single slice causing some blurring along areas where the fracture aperture changes within this length. It also means that a fracture aperture of less than 250 µm will only be positively identified as a void space due to a reduction in the CT number for the voxel that captures the fracture.

The fractured core was also imaged prior to and after completion of the experiment with a MicroXCT-400 scanner (Xradia, Inc., Pleasanton, CA). The core was scanned dry and under ambient temperature and pressure conditions. Unlike the medical CT that scans a stationary sample while rotating the X-ray source and detector array, the µCT obtains a series of 2-D images with the sample rotating in a stepwise fashion between a stationary source and detector. Xradia utilizes a proprietary arrangement of scintillators, optics, and high-resolution detector to achieve high-resolution, high-contrast X-ray images (Feser et al., 2008). The large size of the core required that the sample be imaged in three sections of approximately 27 mm in length, allowing for some overlap between consecutive sections. The sample was scanned with an X-ray
beam energy and power of 150 keV and 10 W, respectively, at rotational increments of 0.06° for the top section and 0.14° for the bottom two sections. The selected optics provided a 3-D reconstructed image with a voxel resolution of 27 µm, representing an order of magnitude improvement in resolution when compared to that achieved by the medical scanner.

The medical CT scans were adjusted using the image processing Java application, ImageJ, in order to provide a uniform gray-scale image for the given range of CT numbers generated in the reconstruction. This also allowed for balancing of the contrast between consecutive scans, which then made it possible for cross-scan comparison of single 2 mm slices.

Two-dimensional slices of the reconstructed µCT scans were exported as jpeg files and ImageJ was again used to align and uniformly contrast these images. Each 2-D slice contained square pixels (27 µm x 27 µm) and represented a thickness (z-direction) of 27 µm. The field-of-view for these images was 27 x 27 mm, which is slightly larger than the core diameter. At these settings, the angle of the cone-beam of the µCT X-ray source introduces a wedge-shaped artefact at the top and bottom of the reconstructed images. This artefact can be seen at the top of Figure 3.5(a), the bottom of which was cropped for this figure. If detailed whole-core information was required, more sections could have been scanned to provide sufficient overlap between sections to enable elimination of the wedge-shaped artefacts during stitching of the stacked sections. This was not necessary for the purposes of the research reported here. The three sections that were scanned of the 7.06-cm core still yielded ~6.5 cm (92%) of good µCT data for image analysis.

Prior to fracture aperture analysis, the fracture area of the entire set of 2-D images was isolated and the gray-scale contrast enhanced. The gray-scale images were then segmented using a thresholding algorithm in ImageJ based on a normalized histogram of the entire set of images. Fracture aperture was measured as the width of the fracture at every pixel column spanning the
fracture. In areas where there were multiple fractures, a volumetric average was calculated to estimate an effective fracture aperture.

3.2.4 Sectioning and SEM imaging

To examine mineralogical alterations of the fracture surface, the core was sectioned and prepared for SEM imaging. After the experiment was finished and the core had been scanned, the core was dried and flooded with epoxy to allow for sectioning and further analysis with the SEM. To do this, the core was first flushed with ethanol and then dried via continuous flow of desiccated air. The core was flooded with epoxy with vacuum-assisted flow.

Figure 3.2 depicts the fracture orientation and identifies where samples were taken for SEM analysis. The core was sectioned along three planes. Section 1 was taken approximately 15 mm from the core inlet. Section 2 was taken approximately 8 mm from the outlet end of the core. The 15 mm section (core inlet to section 1) was then cut in the flow (Z) direction to bisect the fracture perpendicular to its propagation in the XY plane. The sections were then polished and analyzed using the BSE/EDS image analysis technique previously described in Section 2.1 to identify the minerals adjacent to the fracture.
Figure 3.2. Diagram of fractured core with core dimensions and location of sections used for SEM analysis.

3.3 Results

Results from both the medical and μCT scans show evidence of an increase in fracture aperture throughout the core. Figure 3.3 shows a series of scans taken near section 1 with the medical CT scanner over the duration of the experiment. Even with the relatively low resolution of the medical CT images, an increase in fracture aperture is observed.

Figure 3.3. Six-day time series of medical CT scans of 2-mm section taken approximately 2 cm from core inlet. Scans from days 2 through 7 are shown, left to right. Consecutive scans are not precisely 24 hours apart, but show general progression of fracture erosion.
Figure 3.4 contains aperture maps for the fracture before (a) and after (b) flow of the CO$_2$-acidified brine. The difference in aperture is shown in Figure 3.4(c). Figure 3.4(f) shows the average fracture aperture along the length of the core from the core inlet to the outlet. Initially, the fracture aperture was largest near the inlet with an average aperture of ~480 µm and smallest near the outlet with an average aperture of 160 µm. The largest increase in aperture occurred in the one third of the core near the outlet. This section of the core represents not only the area of largest absolute change in aperture but also the area with the largest average final aperture of 1100 µm. Figures 3.4(d) and 3.4(e) show the distribution of fracture apertures before and after flow, respectively. Initially, the median aperture of the fracture was 270 µm. The distribution of fracture apertures changed significantly after flow of the CO$_2$-acidified brine, resulting in a median aperture of 860 µm.

Along the 6.5 cm length, fracture void volume prior to flow of CO$_2$-acidified brine was ~0.6 ml and the average cross-sectional area was 0.09 cm$^2$. After seven days of exposure to the flowing CO$_2$-acidified brine, the fracture had a void volume of ~1.6 ml and average cross-sectional area of 0.24 cm$^2$. This represents an increase in flow area of ~2.7 times, resulting in a reduction in average flow velocity from 110 to 42 cm hr$^{-1}$, and a reduction in flushing from ~17 to ~6 fracture pore volumes hr$^{-1}$. In the field, a constant pressure gradient is more likely to exist, in which case the increase in flow area would increase the volumetric flow rate.
Figure 3.4. Fracture aperture maps of the fracture before (a) and after brine flow (b). The total change in aperture between the initial and final aperture measurements is shown in (c). Aperture width distributions are shown for the fracture before (d) and after brine flow (e). The average measured aperture along the length of the core is shown in (f).

Close examination of the µCT images shows evidence that the fracture wall was eroding in a non-uniform manner. Figure 3.5 focuses on the one third of the core near the fluid inlet. Figure 3.5(a) shows the fracture after the experiment overlain with the initial fracture void shown in white. The µCT images show intermittent regions adjacent to the fracture void space that are slightly blurred. These are partially degraded zones. The zone highlighted by Box 1 is focused upon in Figure 3.5(b), and is on the order of 300-400 µm in thickness. It appears to be of a fairly
uniform thickness, suggesting that transport in this degraded zone may have been a limiting factor controlling the continued dissolution of the fracture surface.

Figure 3.5. (a) µCT scan of 2-cm section near the core inlet after brine flow. The initial fracture void is shown in white overlying the fracture after dissolution to highlight the changes in fracture aperture. Box 1 in (a) is enlarged and shown in (b) to emphasize the development of a degraded zone along the fracture surface.

The BSE and EDS analysis of sectioned segments of the core shed light on the mineralogical content of the fracture boundary and within the degraded zones observed in the µCT images. Along the fracture, calcite dissolved to a much greater extent than the other minerals present in the sample. The non-uniform degradation along the fracture wall is a result of the mineral spatial heterogeneity of the rock. Figures 3.6(a) and 3.6(c) show that the largest increases in fracture aperture occurred at points where calcite is in direct contact with the flowing brine. Figure 3.6(a) is the BSE image corresponding to Box 2 shown in Figure 3.5(a). The smallest increases in fracture aperture correspond to areas where there are silicate minerals. In areas where calcite is intermixed with dolomite and other silicate minerals the dissolution of calcite leads to the formation of degraded zones along the fracture boundary as observed in the µCT images. Figure 3.6(b) provides a good example of preferential calcite dissolution in an area
with homogenous mineral distribution. Figure 3.6(d), which is a close-up of the clay-rich zone in Figure 3.6(c) highlighted within the box, demonstrates how calcite dissolution in an area of higher clay content can leave behind a continuous microporous silicate matrix.

The non-uniform change in average aperture along the length of the core, as shown in Figure 3.4(f), is most consistent with an uneven distribution of calcite along the length of the core. Figure 3.6(c) is from section 2 (see Figure 3.2), which is the segment of the core that experienced the largest increase in aperture. Large grains of calcite are observed adjacent to the fracture wall. Here, there was erosion at a much faster rate than the surrounding rock of mixed calcite, dolomite, and clay mineral composition. There appears to be a distinct dissolution front along these calcite grains, which suggests the large increases in fracture aperture in this section are due to extensive dissolution and not grain plucking.
Figure 3.6. BSE images of (a) area highlighted by box 2 in figure 3.5(a) showing preferential dissolution of calcite leading to non-uniform aperture increases, (b) area of section 2 showing homogenous mineral distribution and development of degraded zone along fracture wall, (c) area of section 2 showing non-uniform aperture increases, and (d) close-up view of clay-rich microporous zone highlighted by box in figure 6(c).

3.4 Discussion

The results of this experimental study demonstrate that for a carbonate caprock significant fracture erosion is possible when CO$_2$-acidified brine is able to flow continuously through the fracture. In the context of geologic carbon sequestration, this would increase the likelihood of leakage of CO$_2$ through the caprock, but predicting the extent and time frame of this increased risk is complicated by how the fracture geometry evolves. In this discussion section, we put the findings from this experiment in context with comparable studies, and we use
the collective findings of these studies to frame a discussion on how flow through caprock fractures may be influenced by geochemical alteration of fracture geometry. We also interpret the finding of the disproportionate dissolution rates of calcite and dolomite.

The rate and extent of geochemically-driven evolution of caprock fractures will depend in a coupled way on fluid transport conditions (advective and diffusive mass transport), fluid composition (pH and mineral saturation conditions), caprock mineralogy (carbonates and silicates), and mineral spatial heterogeneity (mixed or banded). In this experiment, advective flow was dominant over diffusion. If mass transport in the fracture is diffusion-limited then the erosion of the fracture surface will occur at a significantly reduced rate, as dissolution kinetics would be limited by the rate of diffusion of species away from reactive mineral surfaces. Diffusion of CO$_2$-acidified brines into the higher pH native fluids within the caprock may produce conditions that favour carbonate mineral precipitation, and thereby enhance the sealing capacity of the caprock (Gherardi et al., 2007). In laboratory experiments involving reactive flow in fractured carbonate rocks, it was found that dissolution was favoured in advection-dominated fractures and precipitation (of sulfates) was favoured in diffusion-limited fractures (Singurindy and Berkowitz, 2005). Another relevant scenario is the coupled flow of acidified brine with advection- and buoyancy-driven flow of supercritical CO$_2$ (Bryant et al., 2008). Andreani et al. (2008) studied the impact of alternating brine and CO$_2$ gas flow through a fractured claystone caprock. They observed calcite dissolution during CO$_2$-acidified brine flow and an increase in fracture aperture which was attributed to a cyclic process of clay decohesion during CO$_2$ gas flow followed by clay removal during subsequent brine flow. Upon further investigation of these results, Pèpe et al. (2010) suggested that during CO$_2$ gas flow the interstitial fluids within the microporous clay matrix become highly acidified leading to clay particle decohesion.
The evolution of caprock fractures will also depend strongly on the mineralogy of the caprock. In this study, there was substantial erosion of the fracture wall where there was calcite, and to a lesser but measurable extent where there was dolomite. The clay minerals, which are less reactive, remained and possibly inhibited the dissolution of the carbonate minerals by slowing the transport of reaction products to the bulk brine phase. The slower rate of aperture growth in clay-rich regions of the fracture surface is particularly evident in Figure 3.6(d). This implies that the presence of clay minerals may reduce the concomitant fracture aperture growth in a carbonate rock. This observation also suggests that weathered fracture surfaces, which can have significant clay mineral deposits, may experience lower aperture growth rates relative to freshly created fracture surfaces. In a similar study, Noiriel et al. (2007) investigated acidic water flow through an existing fracture in an argillaceous limestone, and reported that the preferential dissolution of calcite led to the development of a microporous clay coating along the fracture wall. Formation of the microporous clay coating was correlated with an increase in surface roughness, and an overall reduction in fracture permeability was primarily attributed to clay particle transport and accumulation within the fracture.

The mineralogical composition of the rocks used in the current study differed significantly from the rocks used in the studies by Noiriel et al. (2007) and Andreani et al. (2008). All three studies observed preferential dissolution of calcite within fractures of carbonate and carbonate-rich rocks; however, the clay mineral content of the three rock samples varied considerably. Noiriel et al. (2007) used a limestone containing roughly 25% clay minerals, and Andreani et al. (2008) used a carbonate-rich shale containing 45% clay minerals. The Amherstburg core used in the current study contained less than 10% non-carbonate minerals with an estimated clay mineral content of 2 to 5% of the bulk rock. The low percentage of clay
minerals within the Amherstburg rock core, in addition to the fact that the fracture was fresh and not weathered, meant that the fracture surfaces would provide substantial contact with carbonate minerals.

Finally, the evolution of caprock fracture geometry is strongly dependent on the mineral spatial heterogeneity and configuration, as evidenced in Figure 3.6(a-c), particularly as it relates to the fracture surfaces. The preferential dissolution of calcite coupled with non-uniform mineral distribution along the fracture led to increases in fracture surface roughness. This uneven fracture erosion is similar to that found by Gouze et al. (2003) for a fractured limestone containing 10% dolomite. It is well known that fracture roughness can substantially reduce hydraulic flow through a fracture relative to what would be predicted from the average fracture aperture (Zimmerman and Bodvarsson, 1996). Additionally, the non-uniform dissolution of the fracture surface may lead to conditions that promote the development of preferential flow paths and possible wormhole formation along the fracture pathway (Szymczak and Ladd, 2009).

In this experiment, it was also observed that fracture aperture growth was negligible where the fracture intersected a silicate-rich band, as shown near the top of Figure 3.6(a). The flow resistance through this unaltered silicate band may ultimately dominate the system flow even though it is only a small portion of the total fracture geometry. According to the principles of critical path analysis in percolation theory, flow rate is largely dominated by the most resistive paths (Berkowitz and Balberg, 1993).

In summary, for reactive flow through fractures in mineralogically heterogeneous rocks, the effect of increased fracture aperture may be offset by the effect of increased fracture roughness, and may even be negated if unaltered narrow restrictions remain.
In the remainder of the discussion section, we seek to explain the observed preferential dissolution of calcite over dolomite. Three factors are considered: mineral solubility, thermodynamic driving forces, and dissolution kinetics. The acid-driven mineral dissolution reactions for calcite and dolomite are, respectively,

\[ CaCO_3(s) + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \quad (3.1) \]
\[ CaMgCO_3(s) + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \quad (3.2) \]

Table 3.2 contains the temperature- and pressure-adjusted equilibrium constants, \( K \), for these reactions, along with the solubility product (\( K_{sp} \)) for the dissolution of one mole of each mineral. Although calcite is slightly more soluble than dolomite, the differences in solubility alone unlikely account for the observed preferential dissolution of calcite in this experiment. Values of the saturation index (SI), the logarithm of the ratio of the ion activity product to \( K \) for each of the reactions shown above are given in Table 3.2. These minerals were at nearly equal saturation states, and in fact dolomite was slightly further from thermodynamic equilibrium. Thus thermodynamic forces were not the determining factor leading to preferential calcite dissolution.

The preferential dissolution of calcite over dolomite in these experiments is therefore attributed primarily to the differences in the reaction rate kinetics. Reaction rate constants for each mineral are also given in Table 3.2, based on literature-reported values for ambient pressure, 25°C and pH=4.4 (Chou et al., 1989). The reaction rate constant for calcite dissolution is nearly one order of magnitude greater than that of dolomite, and therefore, dissolution kinetics was likely the primary driving force of the observed preferential calcite dissolution.
3.5 Conclusions

The experimental results from this study suggest that if hydraulically-connected fractures exist in carbonate caprocks, flow of CO$_2$-acidified brine may lead to rapid dissolution along fracture pathways. The deterioration of the fracture in this experiment was due primarily to calcite dissolution and resulted in an increase in fracture cross-sectional area of ~2.7 times. This finding is not unexpected scientifically, but in the context of geologic sequestration of CO$_2$ it highlights the vulnerability of carbonate formations as caprocks for securing CO$_2$ underground, and it underscores the need to carefully evaluate their suitability during site selection. This study also demonstrates the complex manner in which fracture geometry can evolve under reactive flow conditions, making it difficult to predict the actual impact on fracture permeability. The differential dissolution rates of calcite and dolomite led to an uneven erosion of the fracture surface, which caused a substantial increase in surface roughness. The existence of unaltered silicate-rich bands along the fracture flow path and the increase in surface roughness may offset the effect of increases in average fracture aperture. This finding highlights the importance of understanding mineral spatial heterogeneity when trying to predict fracture evolution and ultimately, caprock seal integrity when in contact with CO$_2$-acidified brine.

Because of the extreme degree and rate of fracture deterioration in this experiment, it is important to summarize the extent to which the scenario is plausible and representative. Several factors make this a plausible scenario including that the fractured specimen is from a real caprock from an actual CO$_2$ injection site, one that presumably satisfied numerous site selection criteria. In addition, the brine composition and experimental temperature and pressure conditions are representative of typical subsurface conditions. Finally, fractures in sedimentary rocks can exist, there is uncertainty in their detection, and fracture propagation can result from
perturbations in fluid pressures, rapid expansions, and thermal gradients. The co-existence of several unique conditions also contributed to the observed rapid fracture deterioration. First, the carbonate caprock used contained only a small amount of non-carbonate minerals and was therefore, quite susceptible to acid-driven dissolution. Second, the mineral surfaces along the fracture wall were not weathered since the fracture was fresh. Third, the brine was undersaturated with respect to calcium. Fourth, the flow rate may be high relative to what might occur in the field (although we have no basis for comparison). Therefore, this finding is representative of what could happen if several plausible events co-occurred.
Chapter 4

Permeability Evolution along a Reactive CO₂ Leakage Pathway in a Carbonate Caprock

4.1 Introduction

The success of geologic carbon sequestration in deep saline formations will rely heavily on our ability to estimate the leakage risks associated with underground storage of large quantities of a buoyant fluid. The existence of potential CO₂ leakage pathways and estimates of CO₂ leakage have been discussed extensively in the literature (Metz et al., 2005; Damen et al., 2006; Hawkes et al., 2005; Lewicki et al., 2007; Celia and Nordbotten, 2009; Pruess, 2008; Zhang et al., 2010b). However, current leakage risk assessment models (e.g. LeNeveu, 2008; Viswanathan et al., 2008) do not account for geochemical alterations of potential leakage pathways in caprock formations. Instead, leakage pathways are assumed to either exist or not exist, and pathway permeability is assumed to be constant over time. Assessments that do not account for permeability evolution may estimate inaccurate CO₂ or brine leakage rates along a reactive pathway such as that of a fractured carbonate caprock (Ellis et al., 2011).

Although geochemical reactions that alter caprock integrity may take place over the course of hundreds to thousands of years due to slow reaction kinetics (e.g. Gaus et al., 2008), important reactions may also occur over much shorter time periods, as demonstrated in bench-scale experimental investigations (Shiraki and Dunn, 2000; Kaszuba et al., 2005; Andreani et al., 2008; Wigand et al., 2009; Detwiler, 2010; Shao et al., 2010; Ellis et al., 2011). Experiments conducted at injection temperature and pressure conditions on actual caprock samples offer an
opportunity to elucidate some of the complexities controlling caprock integrity and permeability evolution of reactive leakage pathways.

We know that CO$_2$ injection into deep saline aquifers will cause acidification of formation brines (Ellis et al., 2010) and that carbonate minerals are susceptible to acid-driven dissolution (Pokrovsky et al., 2009). Therefore, understanding the potential alterations in reactive, carbonate mineral-rich caprocks due to contact with CO$_2$-acidified brine is a necessary first step toward predicting leakage through these formations. Previous studies have demonstrated the complex behavior of fractured limestones when exposed to flow of acidic fluids, including observations of dissolution of critical fracture asperities (Polak et al., 2003), non-uniform aperture alterations along the fracture surface (Gouze et al., 2003; Ellis et al., 2011), and particle clogging along the fracture (Noiriel et al., 2007).

This chapter discusses results from a high-pressure core flow-through experiment in which CO$_2$-acidified brine flowed through a fractured carbonate caprock sample, extending the work presented in Chapter 3. The experiment was carried out at the US Department of Energy’s National Energy Technology Laboratory. The core sample used in this study is from the Amherstburg limestone, which serves as the primary caprock for a CO$_2$ injection demonstration project in northern Michigan. This experiment is a near-replicate of the previous experiment (Chapter 3), including the use of a rock specimen from the same formation. The primary difference is in the solution chemistry and initial fracture geometry. These experiments were designed to examine how small changes in brine chemistry and core-scale mineral heterogeneity may control whether pre-existing fractures will be widened or will self-seal during a CO$_2$ leakage event. The experimental design allowed for measurement of the pressure gradient over time, and inference of the evolution of permeability. A combination of spectroscopic imaging techniques
and X-ray computed tomography (CT) were used to follow changes in fracture geometry and mineralogical alterations along the fracture surface. This included the development of new procedures for microbeam Ca K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy at the National Synchrotron Light Source (NSLS).

### 4.2 Materials and methods

#### 4.2.1 Sample characterization

The Amherstburg sample used in this study was collected at a depth of 928 m during the drilling of the injection well for the Michigan Regional Carbon Sequestration Partnership CO$_2$ injection demonstration project in Otsego County, Michigan. A 2.54 cm diameter, 3.8 cm long sub-core was taken from the drilling core sample, oriented vertically. The sample was artificially fractured using dual knife-edge chisels prior to the experiment to enable flow. Prior to and after fracturing, the core was stabilized in epoxy, minimizing artificial displacement between the fracture surfaces. This method is in contrast to methods used by other researchers in which fracture surfaces are propped apart to negate mechanical displacement under pressure (e.g. Noiriel et al., 2007) or are simply mated within a sealing jacket to allow for unconstrained mechanical closure (e.g. Polak et al., 2003).

The Amherstburg is a fossiliferous carbonate formation composed primarily of calcite and dolomite, in roughly equal proportions. Together, these minerals make up >90% of the bulk sample, with the remaining rock containing quartz, K-feldspar, clay minerals, and pyrite. For details on the mineral identification procedure, see Section 3.2.1. The estimated porosity and permeability of the unfractured sample were on the order of 1% and $10^{-21}$ m$^2$, respectively.
4.2.2 Brine composition

The experimental brine composition shown in Table 4.1 was selected to represent CO₂-saturated brine that had already reacted with minerals in the target injection formation, the Bass Islands dolostone. Specifically, the initial brine was modelled to mimic a CO₂-saturated 1 M NaCl brine reacted with anhydrite, calcite, and dolomite to an initial calcite saturation index (SI) of -0.8. This brine was more than an order of magnitude closer to calcite saturation when compared to the brine used previously, which had an initial calcite SI of -2 (see Table 3.2). A small amount of Sr was added for the intended purpose of distinguishing any new calcite precipitates from the host calcite. Brine pH and mineral saturation calculations were made using PHREEQC with the Pitzer.dat database (Parkhurst and Appelo, 1999). Aqueous activity coefficients were estimated using the Pitzer model (Pitzer, 1973). CO₂ solubility was estimated to be 0.98 mol L⁻¹ following the work of Duan et al. (2006).

<table>
<thead>
<tr>
<th>Species (total)</th>
<th>[mol L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.0 x 10⁰</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.0 x 10⁰</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.9 x 10⁻²</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.6 x 10⁻³</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1.2 x 10⁻²</td>
</tr>
<tr>
<td>CO₂(aq)</td>
<td>9.8 x 10⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>4.6</td>
</tr>
</tbody>
</table>

4.2.3 Flow-through experiment

A modified version of the flow-through setup described in Section 3.2.2 (see Figure 3.1) was used to inject CO₂-saturated brine through the fractured core. Temperature and pressure conditions of 40ºC and 10 MPa were chosen to represent those occurring at a depth of
approximately 1 km, which is near the interface between the Amherstburg and the top of the CO₂ storage reservoir. A TEMCO triaxial carbon-fiber core holder was used with a confining pressure of 14 MPa. The CO₂-acidified brine was generated using two separate high-pressure syringe pumps (Teledyne Isco, Inc., Lincoln, NE) that delivered CO₂ (99.5% pure, Airgas) and brine to the high-pressure mixing vessel and allowed to equilibrate at 40°C. The measured pH was within ±0.2 of the modeled pH of 4.6, demonstrating that the brine was at or near equilibrium with the supercritical CO₂ phase. A key difference between this and the previous work is that the CO₂-saturated brine was transferred directly from the high-pressure mixing vessel to a syringe pump prior to flow through the fractured core, removing the need for a separate brine reservoir upstream of the mixing vessel. Inlet brine compositions were measured at the beginning of the experiment and after two days, with the average shown in Table 4.1. Inlet pH was measured using high-pressure, high-temperature pH probes (Corr Instruments, LLC, San Antonio, TX). Brine samples were acidified and diluted before being analyzed via ICP-OES on a Perkin Elmer Optima 3000 XL.

The experiment was designed to have a constant flow rate of 3 mL hr⁻¹; however, this constant flow rate was only held for the first 28 hours of the experiment. After this, the flow was controlled by a constant pressure gradient of ~2.2 MPa due to a predetermined upper limit of 12.2 MPa for the inlet pore pressure. (This upper limit was set to ensure that the pore pressure did not exceed the confining pressure of 14 MPa). A temperature of 40°C was successfully maintained in the mixing vessel but the average temperature measured inside the core was 30°C and is therefore the temperature used to estimate brine viscosity.
4.2.4 X-ray computed tomography

X-ray CT is a valuable tool for performing non-destructive analysis of porous materials as X-ray attenuation corresponds to material density with a characteristic CT number that can distinguish mineral and void space (Ketcham and Carlson, 2001; Cai et al., 2009). The flow-through experiment was conducted within a Universal Systems HD-350E medical CT scanner, allowing for real-time scans to be taken during active injection. However, the scan resolution of 250 µm in the lateral directions was too coarse to capture changes in fracture aperture during the experiment. The fractured core was also imaged prior to and after completion of the experiment with a MicroXCT-400 (µCT) scanner (Xradia, Inc., Pleasanton, CA). The core was scanned dry and under ambient temperature and pressure conditions. The sample was scanned with an X-ray beam energy and power of 150 keV and 10 W, respectively, at rotational increments of 0.14°. The selected optics provided a 3-D reconstructed image with a voxel resolution of 27 µm, representing an order of magnitude improvement in resolution when compared to that achieved by the medical scanner. See Section 3.2.3 for details on methods of analysis of the µCT data.

4.2.5 Electron microscopy and spectroscopic imaging

After the experiment was finished and the core had been scanned, the core was flushed with ethanol, dried with desiccated air, and then impregnated with epoxy using methods described by Crandell et al. (2012). This allowed for sectioning and 2-D imaging. Sections were taken perpendicular to the direction of flow along the core.

At Princeton University, the samples were examined at the Image Analysis Center using a Quanta environmental scanning electron microscope (SEM). Back-scattered electron (BSE) imaging and energy dispersive spectroscopy (EDS) were used to examine alterations in fracture surface mineralogy at an incident beam energy of 15 keV.
Additional X-ray measurements were performed at the NSLS at Brookhaven National Lab using the X-ray microprobes at beamlines X27A and X26A. X-ray fluorescence maps were collected by raster ‘fly-scanning’ the approximately 7x10 (VxH) micron beam at 17.5 keV over regions of interest within the sample. Element maps for Ca, Fe, and Sr were generated by processing their Kα emission lines. Microbeam Ca K-edge XANES spectra were collected at points of interest of the thin section. Beam energy was controlled with a Si(111) monochromator. Background subtraction, normalization and Linear Combination Fits (LCF) were performed using Athena software (Ravel and Newville, 2005). X-ray diffraction point spectra were collected at 17.479(2) keV incident beam energy using either a Bruker or Rayonix CCD. The diffraction images were background subtracted and integrated into 1-D intensity versus 2-theta using FIT2D (Hammersley, 1998).

4.3 Results

4.3.1 Evolution of fracture permeability

Based on observed pressure changes, fracture permeability decreased during the course of the experiment. After confining stress was applied and flow commenced, the initial fracture permeability of 10^{11.7} m^2 decreased steadily during the first 28 hours of flow. Fracture permeability, \( k \), was calculated by first relating the measured differential pressure, \( \Delta P \), to an equivalent hydraulic aperture, \( b_h \), according to the cubic law for flow between two parallel plates (Zimmerman and Bodvarsson, 1996)

\[
b_h = \left( \frac{12 \mu Q}{L \Delta P} \right)^{1/3}
\]

where \( Q \) is the volumetric flow rate \( \text{[L}^3\text{T}^{-1}] \), \( \mu \) is the viscosity of the fluid \( \text{[M L}^{-1}\text{T}^{-1}] \), \( L \) is the length of the fracture \( \text{[L]} \), and \( w \) is the fracture width \( \text{[L]} \). A brine viscosity of 0.90 mPa s^{-1} was
calculated following the theoretical relationship presented by (Phillips et al., 1981) for the core temperature of 30°C. This hydraulic aperture was then used to estimate fracture permeability by combining the cubic law with Darcy’s law

\[ k = \frac{b^2}{12} \quad (4.2) \]

The measured change in \( \Delta P \) is shown in Figure 4.1 along with the corresponding evolution of fracture permeability. There were two distinct periods of flow during the experiment, the first 28 hours when the flow rate was held constant and the final 51 hours when the flow was controlled with a constant pressure gradient. As such, there are two trends in the differential pressure data. A linear regression fit to the differential pressure data for the first 28 hours of flow indicates a rate of change in \( \Delta P \) of 0.074 MPa hr\(^{-1}\). This \( \Delta P \) evolution provides an estimate of permeability evolution during the first 28 hours. The rate of brine effluent collection was instead used to estimate permeability evolution during the final 51 hours of the experiment. Over the course of the entire experiment fracture permeability decreased more than an order of magnitude from an initial value of \( 10^{-11.7} \) m\(^2\) to a final value of \( 10^{-13.4} \) m\(^2\).
Figure 4.1. Change in measured pressure gradient across the core and corresponding best fit of permeability evolution. As the experimental flow conditions were switched from constant flow rate to constant pressure gradient at 28 hours, two separate linear fits were used to describe permeability evolution over these two distinct flow regimes.

4.3.2 Electron microscopy and X-ray spectroscopic and diffraction imaging

Results from one particular core cross-section are presented in Figure 4.2. A schematic of the fractured core is shown in Figure 4.2(a) with the gray region identifying the section analysed. Figures 4.2(b-d) provide evidence of mobilized detrital occlusions between the fracture walls. Figure 4.2(b) is a two-dimensional µCT cross-section, Figure 4.2(c) is a µXRF Ca element map showing points where µXANES and µXRD analyses were performed, and Figure 4.2(d), from left to right, shows a BSE scan of the fracture and EDS elemental maps for Ca and Mg. Closer examination of the fracture occlusions observed in Figure 4.2(d) identified two common particle sizes, with approximate mean diameters of 3 µm and 30 µm for the smaller and larger occlusions, respectively.
Ca µXANES and EDS were used to identify the mineralogy of the detrital occlusions along the fracture pathway. The Ca µXANES spectra for the subset of points labelled A-D are shown in Figure 4.2(e) along with the end-member spectra of calcite and dolomite used in the linear combination fitting (LCF) to determine calcite:dolomite ratios. The end-member spectra were collected at points on the thin section where µXRD independently confirmed only the single crystalline phase was present. While the end-member spectra are consistent with the spectral shapes of standard spectra collected on powdered calcite and dolomite samples, their amplitude envelopes do not match due to the self absorption which is inherent to spectroscopic imaging of concentrated elements in thin section samples. The end-member spectra were used in the LCF because this strategy fit the unknown spectra without the use of amplitude corrections for self-absorption (Sarret et al., 2007).
Figure 4.2. (a) Schematic of fractured core showing core dimensions and location of sub-section analyzed throughout Figure 4.2; (b) μCT scan showing evidence of fracture closure; (c) μXRF Ca elemental map of box highlighted in 4.2(b) showing locations of μXRD and μXANES analysis; (d) SEM BSE and EDS maps for Ca and Mg taken at the same location as 4.2(c); (e) Ca μXANES spectra for points A-D highlighted in 4.2(c). Calcite and dolomite end-member spectra are also shown along with estimates of dolomite:calcite from linear combination fits; (f) μXRD 1-D integrated diffraction data for points A-D with corresponding calcite and dolomite peaks indicated.

The four points of comparison highlighted by the grey arrows in Figure 4.2(e) show how calcite and dolomite spectra can be clearly distinguished qualitatively. The spectrum at point D is consistent with the calcite end-member, and therefore is consistent with calcite being the dominant mineral in the limestone. In contrast, the spectrum at point A shares the spectral features of the dolomite end-member spectrum. LCF was used to estimate the relative
composition of calcite and dolomite at each point. The ratio of calcite to dolomite contribution as estimated from LCF is shown to the right of each point spectrum in Figure 4.2(e). The LCF analysis shows a clear difference in the Ca \(\mu\)XANES spectra of the larger occlusions (site A) and those of the smaller occlusions (sites B and C). The smaller occlusions have a signal most similar to that of calcite, while there is a stronger contribution of dolomite in the larger occlusions. EDS analysis of the occlusions (Figure 4.2(d)) does not show a strong magnesium signal in the larger grain occlusions. The disparity between this observation and that of the Ca \(\mu\)XANES analysis, which identified a dolomite signature in the larger occlusions, can be attributed to differences in the greater penetration depth of Ca \(\mu\)XANES relative to the Mg EDS. Mg fluorescence originates from the first 1 to 2 \(\mu\)m from the surface, whereas Ca fluorescence is detectable from depths of up to 30 \(\mu\)m (Ravel and Newville, 2005). Figure 4.2(f) shows the diffraction spectra for the four points A-D identified in Figure 4.2(c). This \(\mu\)XRD evidence further supports the conclusion that the smaller occlusions (A-B) contain only calcite while the larger occlusions (A) contain a combination of calcite and dolomite.

4.3.3 Effluent chemistry

Analysis of the change in Ca concentration in the collected brine effluent is given in Figure 4.3. There is an initial increase in Ca concentration followed by a decrease in concentration after cessation of the constant flow rate. The error bars represent the 95% confidence interval of the standard analytical error of 2.8% calculated from duplicate analysis of several brine effluent samples. The decrease in measured Ca concentration during the latter half of the experiment suggests that calcite precipitation may have occurred within the fracture. Although Sr was added to the inlet brine to help identify any secondary calcite precipitation in the fracture, \(\mu\)XRF analysis could not be used to definitively identify calcite precipitation by
looking for evidence of elevated Sr in the occlusions. This is because even though EDS detected no strong Sr signal with a 20 keV incident beam energy, µXRF analysis of the fractured core demonstrated a significant Sr background signal throughout a majority of the core.

![Figure 4.3](image)

**Figure 4.3.** Measured Ca concentration in brine effluent. Initial concentration (see Table 1) is shown at time = 0.

### 4.3.4 X-ray CT imaging

The µCT images were processed as described previously in Section 3.2.3, and mechanical apertures of the fracture were inferred. Figure 4.4(a-b) portrays the resulting fracture aperture maps before and after the experiment. Figure 4.4(c) shows the average aperture along the length of the core for before and after the experiment. The increased variation in average aperture after the experiment can be interpreted as an increase in fracture surface roughness.

The initial mechanical aperture averaged over the entire fracture was 150 µm, while the initial hydraulic aperture derived from the initial pressure measurement was estimated to be 5 µm. This discrepancy arises because the mechanical aperture was measured under conditions without confining stress, while the hydraulic aperture was measured under confined conditions.
Figure 4.4. Aperture maps of the fracture before (a) and after (b) flow of the CO$_2$-acidified brine, as estimated from the µCT data. (c) shows the average mechanical aperture from core inlet (bottom) to outlet (top), demonstrating both the observed increase in fracture roughness after flow of CO$_2$-acidified brine and the trend of decreasing average aperture from core inlet to outlet.

Although the aperture maps derived from the µCT data, which were recorded at ambient pressure, do not represent the absolute magnitude of fracture apertures during the flow experiment, the measurements do record net changes in fracture aperture because it can be reasonably assumed that due to the epoxy coating the fracture relaxed uniformly after the confining stress was removed. Comparison between Figures 4.4(a) and 4.4(b) clearly depicts a region on the right side of the fracture that experiences a net decrease in fracture aperture, but the total fracture void volume increased by an estimated 12%. A preferential flow path formed on the left side of the fracture where a net increase in fracture aperture is observed. Presence of detrital occlusions within the fracture, which occur predominantly on the right side of the fracture after flow, appear in the µCT scans as voxels with X-ray attenuation values similar to that of the rock matrix (see Figure 4.2(b)) and may be interpreted as contacting asperities or localized reductions in fracture aperture.

The fact that the estimated hydraulic aperture is two orders of magnitude smaller than the µCT-estimated average mechanical aperture does not necessarily mean that the average aperture
under confining stress was on the order of 5 µm. This is because the hydraulic aperture is an effective parameter that is an estimate of the equivalent aperture for flow between two parallel plates of length $L$ and width $w$ (Zimmerman and Bodvarsson, 1996). First, as fracture widths narrow, the cubic law assumption used in equation 1 tends to underestimate the effective aperture (Crandall et al, 2010). Second, the principles of critical path analysis in percolation theory dictate that the most resistive paths will control the flow rate along a leakage pathway (Berkowitz and Balhberg, 1993). Because we know that the fracture surfaces were not exactly parallel, it is possible that after confining stress was applied the mechanical aperture at the outlet was the same order of magnitude as the estimated hydraulic aperture and was restricting flow, while larger apertures remained upstream of the outlet. Existence of apertures greater than 30 µm is supported by evidence of particle clogging.

4.4 Discussion and conclusions

For reactive flows, decreases in fracture permeability can be primarily attributed to three possible mechanisms: dissolution of critical fracture asperities, particle clogging along the fracture pathway, and mineral precipitation. In this experiment, we have found evidence for all three of these mechanisms, but they were not operative at the same time.

Based on the measured increase in Ca concentration of the brine effluent observed during the early stages of the experiment, we believe that initial dissolution of critical asperities along the fracture pathway led to mechanical compression of the fracture and the observed steady reduction in fracture permeability. Analysis of the fracture occlusions supports a scenario where dissolution of calcite may have also led to decohesion of larger less reactive grains that were then redeposited along the fracture, further impeding the flow of the CO$_2$-acidified brine. It is possible that particles were also generated as a result of the mechanical compression along the fracture
surfaces. The combination of these two processes led to clogging of the fracture pathway and continued reductions in permeability.

It is our contention that after the constant flow rate was switched to a constant pressure gradient, which resulted in an approximate 80% reduction in flow rate, localized conditions favoring calcite precipitation developed along the occluded fracture pathway. The decrease in fracture aperture and clogging caused by the detrital occlusions along the right side of the fracture may have generated a localized flow regime where mass transport became diffusion-controlled. A diffusion-controlled transport regime would allow longer residence times for the CO$_2$-acidified brine. As the inlet brine was already near calcite equilibrium, it is reasonable to expect that the brine in the occluded flow region may have reached calcite saturation. We have sufficient evidence in the form of effluent chemistry and spectroscopic analysis to support the conclusion that calcite precipitation along the fracture may have contributed to the observed decrease in fracture permeability. This is a very interesting finding from the standpoint of predicting CO$_2$ leakage evolution, as the occurrence of self-sealing along reactive CO$_2$ leakage pathways would be a favorable outcome.

The process of particle decohesion along reactive fracture pathways has been previously documented in the literature (Noiriel et al., 2007; Andreani et al., 2008). As particle clogging proved to have a substantial impact on fracture flow in this experiment, it may be necessary to include particle transport in reactive transport simulations for CO$_2$ leakage risk assessment (Sbai and Azaroual, 2011). Furthermore, the dissolution of critical fracture asperities resulting in closure of the fracture due to mechanical stresses has been observed in hydrothermal flow-through experiments (Polak et al., 2003; Yasuhara et al. 2006). Accounting for potential mechanical closure of the fracture following the approach of the thermal-hydrologic-mechanical-
chemical modeling employed for the study of geothermal reservoirs (e.g. Taron and Elsworth, 2009) should also lead to more robust CO$_2$ leakage risk assessments.

In the context of geologic carbon sequestration Gherardi et al. (2007) demonstrated the possibility for enhanced sealing at the caprock-reservoir interface when mass transport of reactive fluids is limited by slow diffusion into the caprock. Similar self-sealing behavior was seen in wellbore cements (Huerta et al., 2011). Conditions that favor carbonate mineral precipitation within advective-controlled leakage pathways may require mixing of higher pH interstitial waters with calcium- and carbonate-enriched reservoir brines (Zhang et al., 2010a). If the combination of mineral dissolution and particle clogging are able to create stagnant flow zones within leakage pathways, it may be possible for self-sealing conditions to develop along reactive CO$_2$ leakage pathways in the absence of low probability mixing conditions.

The results of this experiment are in stark contrast to those of the near-replicate experiment presented in Chapter 3. The two key differences between the two experiments is that in the first experiment the inlet brine was further from calcite equilibrium and the initial average aperture of the fracture was much larger. The important observations presented in Chapter 3 relate to the impact of small-scale mineral heterogeneity on fracture surface roughness and the potential importance of non-reactive constrictions in controlling fracture permeability. The observation that acidic brine far from calcite equilibrium led to calcite dissolution along the fracture pathway in a very short timeframe was not a surprising result. It is surprising, however, that in the subsequent near-replicate experiment presented in this chapter far less calcite dissolution was observed and fracture permeability decreased after flow of the CO$_2$-acidified brine. This observation is attributed to the combination of a higher initial calcite saturation and
an initially tighter fracture leading to particle clogging and the development of stagnant transport zones within the fracture.

The fact that two very similar experiments performed on nearly identical rock cores resulted in opposite outcomes for fracture permeability evolution suggests that the chemical and physical processes controlling fracture aperture are very complex. A third replicate CO₂-acidified brine flow-through experiment, not presented here but also performed on a fractured Amherstburg sample, resulted in only a small amount of dissolution along the fracture pathway with minimal alteration of fracture permeability. Given the disparity in findings between similar experiments, it is a fair assumption that further replicate experiments performed on samples of the same rock would each result in a unique outcome. This conclusion brings into question, for the case of naturally heterogeneous rocks, the reliability of using only a few bench-scale experiments to validate models that estimate fracture permeability evolution, as each experiment may be unique due to µm-cm scale variability in mineralogy and fracture hydrodynamics. Deciding how to upscale these small-scale heterogeneities in modeling efforts that examine large-scale leakage through reactive pathways is still an open research question. Furthermore, we may need to decide whether accounting for mineral heterogeneity at the scale of microns to centimeters is even necessary in models whose resolution is at the scale of meters – i.e. what is the representative elementary volume for capturing the important geochemical alterations along reactive leakage pathways?

Experiments that highlight the complexities (mineralogy, fluid chemistry, hydrodynamics) controlling fracture permeability evolution of natural rocks are needed not because the findings are necessarily broadly applicable or easily replicated in modeling efforts, but because they may draw our attention to important processes such as geochemically-induced
particle decohesion that may not be captured in current models. They also elucidate findings, such as that of this work, that demonstrate that net dissolution along a reactive CO₂ leakage pathway might not always correspond to a net increase in fracture permeability. This means that traditional porosity-permeability relationships for porous media (e.g. Kozeny-Carman equation) may not be appropriate for estimating fracture permeability evolution in 1-D models used to assess CO₂ leakage risk.
Chapter 5

Simulation of Permeability Evolution in a Variable Aperture Fracture

5.1 Introduction

Due to the inherent low matrix permeability of caprock formations, any leakage of CO$_2$ through these formations is likely to occur through fractures or existing wellbores. It is therefore paramount to leakage risk assessment that we understand and be able to predict permeability evolution along these pathways during leakage of CO$_2$-acidified brine. As evidenced in the previous two chapters, predicting the impact on fracture permeability due to geochemical alterations of fracture geometry is not trivial and is influenced in a complex way by mineralogy, fluid chemistry, and initial fracture hydrodynamics. Leakage through existing wellbores is not covered here, but for a thorough discussion see Nordbotten et al. (2009) and references therein.

The study of fluid flow in fractured geologic media has been of great interest to researchers investigating the storage of hazardous waste and contaminant transport in fracture-dominated subsurface systems (e.g. Berkowitz, 2002). Researchers interested in examining contaminant transport in fractured media have also considered the importance of colloidal transport and deposition along fractures (Adbel-Salam and Chrysikopoulos, 1995; Ibaraki and Sudicky, 1995; Grindrod, 1993; James and Chrysikopoulos, 2000; Boutt et al., 2006). Nearly all of these studies use the assumption that flow in a single rough-walled fracture can be modeled according to the cubic law, which is a simplification of the Navier-Stokes equations for laminar flow between two smooth parallel plates (Witherspoon et al., 1980). As natural fractures are not
truly two smooth parallel surfaces, there is a need to account for fracture roughness and contacting asperities. Different methods have been proposed for accounting for fracture surface roughness, including transport laws for based on the concept of tortuosity (Brown, 1987; Piggot and Elsworth, 1992; Zimmerman et al., 1992; Nicholl et al., 1999). Further application of the cubic law to variable aperture fractures led to the introduction of channel flow models (Tsang and Tsang, 1987; Tsang and Tsang 1989) and two-dimensional generalizations of the bottleneck approximation (Talon et al., 2010). These types of studies, although not originally designed to examine leakage of CO₂, have laid the foundation for the modeling of permeability evolution in variable aperture fractures exposed to CO₂-acidified brine.

The work presented in this chapter investigates the evolution of permeability in a single fracture with spatially variable aperture. The fracture presented in Chapter 4 is reexamined here for the case of reactive flow leading to mineral dissolution along the fracture pathway. Changes in local fracture aperture are evaluated for two different scenarios with equivalent increases in total fracture void volume, heretofore referred to as fracture porosity. In the first case, dissolution is assumed to occur uniformly throughout the entire fracture. The second case employs a novel combination of X-ray computed micro-tomography (µCT) and energy dispersive spectroscopy (EDS) to identify two-dimensional mineral spatial heterogeneity. This mineral identification procedure allows for translation of three-dimensional mineral spatial information into two-dimensional mapping of fracture surface mineralogy. Experimental results presented in Chapter 3 have demonstrated that the largest increases in fracture aperture will occur at locations where calcite is the dominant mineral in contact with the fracture surface. Using this knowledge, all dissolution in the second scenario is assumed to occur at locations where calcite is identified to exist at the fracture surface. Thus, the two model scenarios address the importance of accurately
accounting for spatial variability of dissolution along a fracture when predicting permeability evolution.

5.2 Methods

5.2.1 Two-dimensional steady state flow modeling

Following the work of James and Chrysikopoulos (2000), two-dimensional single-phase steady state flow in a variable aperture fracture was modeled. Both theoretical aperture distributions and measured fracture apertures from the experiment presented in Chapter 4 are studied. The µCT scans prior to flow of CO₂-acidified brine were used to estimate the initial aperture field of the fracture with a grid cell resolution of 162 µm in both the x and y directions. This represents a 6-fold reduction in resolution from the original µCT data voxel resolution of 27 µm and was chosen for improved computational efficiency within the model.

Fluid flow in a variable aperture fracture can be described by (Chrysikopoulos and Abdel-Salam, 1997)

\[
\frac{\partial}{\partial x} \left[ b^3(x,y) \frac{\partial h(x,y)}{\partial x} \right] + \frac{\partial}{\partial y} \left[ b^3(x,y) \frac{\partial h(x,y)}{\partial y} \right] = 0 \tag{5.1}
\]

Where \( b(x,y) \) is the local fracture aperture [L] and \( h \) is the piezometric head [L]. Here again, it is assumed that flow in the fracture can be effectively modeled by use of the cubic law for incompressible laminar flow between two parallel plates (Witherspoon et al., 1980). Flow is induced by setting constant pressure boundary (Dirichlet) conditions at the inlet and outlet of the fracture so as to create a constant pressure drop across the fracture. No flow boundary (Neumann) conditions are assigned to the lateral boundaries of the fracture and along the fracture walls, since it is also assumed that there is no flow into or out of the rock matrix along the fracture surface. The equivalent aperture between neighboring grid cells is estimated as the
harmonic mean of the two individual apertures. The pressure head at each grid cell is calculated by solving the governing flow equation through use of a five-point central finite difference numerical approximation. First order finite difference forms of the following expressions

\[
U_x = -\frac{\gamma b^2(x,y) \partial h(x,y)}{12\mu} \frac{\partial}{\partial x}, \\
U_y = -\frac{\gamma b^2(x,y) \partial h(x,y)}{12\mu} \frac{\partial}{\partial y},
\]

are used to calculate the average velocity components in the x and y directions, where \(\gamma\) is the fluid specific weight \([\text{M L}^{-2} \text{T}^{-2}]\) and \(\mu\) is the fluid dynamic viscosity \([\text{M L}^{-1} \text{T}^{-1}]\). The velocity within each grid cell is assumed constant (i.e. there is no development of a parabolic velocity field). A brine viscosity of 0.90 mPa s\(^{-1}\), which is calculated for the brine composition shown in Table 4.3 at a temperature of 30°C following the work of Phillips et al. (1981), is used in all flow calculations presented in this chapter.

Fracture permeability is calculated following the assumptions and equations presented in section 4.3.1. The cubic law is first used to estimate an effective hydraulic aperture, which is then combined with Darcy’s Law to estimate the corresponding fracture permeability (Witherspoon et al., 1980; Zimmerman and Bodvarson, 1996).

5.2.2 X-ray computed tomography and scanning electron spectroscopy imaging

Micro X-ray computed tomography (\(\mu\)CT) offers the ability for high-resolution non-destructive three-dimensional visualization of geologic samples. Easier access to and availability of CT scanners have led to increased use of CT scanning as a means for conducting analysis of geologic media over the past two decades (Johns et al., 1993; Keller, 1998; Ketcham and Carlson, 2001; Wildenschild et al., 2002; Gouze et al., 2003; Noiriel et al., 2007; Luquot and Gouze, 2009; Cai et al., 2009; Ketcham et al., 2011). For CT analysis of geologic media, X-ray
attenuation corresponds closely with mineral density (Ketcham and Carlson, 2001). This means that void space in a rock sample will have very low X-ray attenuation, allowing for it to be easily discerned from the rock matrix. Specifically, X-ray mass attenuation coefficients for individual elements vary based on atomic number, with greater X-ray attenuation corresponding to higher atomic number. For elemental compounds (e.g. calcite: CaCO₃) the attenuation is additive according to the individual elements’ proportion by weight in the mineral (Seltzer, 1993). Differences in mineral-specific attenuation values allow for visual separation of different mineral species within the rock matrix. This is demonstrated in Figure 5.1(a) where the mineral calcite is discernable from the surrounding dolomite-quartz matrix by its lighter grayscale pixel value, which corresponds to it having higher X-ray attenuation.

The mineral identification procedure used for this study utilizes the mineral identification procedure described in Section 3.2.1 to inform the µCT grayscale data to generate a 2-D representation of mineral spatial location along the fracture. For details regarding the µCT scanning procedures, see Sections 3.2.3 and 4.2.4. All scanning electron microscopy (SEM) imaging was performed at the Image Analysis Center at Princeton University using a Quanta environmental SEM with an incident beam energy of 15 keV.

5.3 Results

5.3.1 Mineral identification via combined µCT and EDS analysis

Figure 5.1 demonstrates the mineral identification process by first showing a µCT scan in Figure 5.1(a) in which the mineral heterogeneity is easily discernable. The core sub-section examined in 5.1 corresponds to the same approximate location as that highlighted in Figure 4.2(a). Figure 5.1(b) is a back-scattered electron (BSE) image of the subsection identified by the box in 5.1(a). Figure 5.1(c) shows the mineral spatial arrangement of calcite (red), dolomite
(blue), and quartz (green) as identified via EDS elemental maps. A ‘smart’ algorithm for segmenting the µCT data to isolate locations where calcite was in contact with the fracture surface was created by combining the information gained through the combined BSE/EDS mineral identification procedure with the µCT X-ray attenuation data. This process is demonstrated in Figure 5.2 where 5.2(a) shows a reconstructed 2-D µCT scan of the core taken adjacent and parallel to the fracture, with the subsequent calcite-segmented binary image shown in 5.2(b). The white area in 5.2(b) corresponds to positive calcite identification.
Figure 5.1. (a) 2-D μCT scan showing variation in grayscale pixel intensity as a function of miner-specific X-ray attenuation; (b) BSE image of the inset shown in 5.1(a); (c) EDS elemental maps superimposed on the BSE image identifying locations where calcite (red), dolomite (blue), and quartz (green) are present at the surface.
Figure 5.2. (a) Reconstructed 2-D μCT scan of the Amherstburg core taken adjacent and parallel to the fracture; (b) Calcite-segmented binary image of 5.2(a). White area corresponding to positive calcite identification based on the segmentation algorithm presented in Figure 5.1.

5.3.2 Modeling fracture permeability evolution

As discussed in the chapter introduction, two dissolution scenarios were modeled for an equivalent total increase in fracture porosity. Each scenario began with the same initial variable aperture field based on the μCT-estimated apertures shown in Figure 4.4(a). This variable aperture field is referred to throughout this chapter as the base (or initial) fracture. The location of fracture dissolution was modeled differently for each of the two cases in an attempt to evaluate the importance of accurately capturing and accounting for mineral spatial heterogeneity along the fracture pathway. The first model scenario assumes that, for a given increase in fracture porosity, the fracture experiences uniform dissolution throughout the entire aperture field. The second model scenario assumes all dissolution takes place at locations along the
fracture where calcite is identified through the combined µCT-EDS image analysis shown in Figure 5.2(b). These two scenarios are referred to throughout this chapter as the uniform and non-uniform dissolution scenarios, respectively.

Fracture permeability is estimated following the methods presented in Section 5.2.1 using the 2-D steady state flow model. Dissolution is represented in the model by accounting for increases in local fracture apertures from the base case for given percentage increases in total fracture porosity of 10, 20, 40, and 100 percent. Figure 5.3 shows the initial fracture (a) and the subsequent variable aperture fields for non-uniform, calcite-specific dissolution of 20 (b), 40 (c) and 100 (d) percent increases in fracture porosity.

The important difference in the uniform and non-uniform dissolution scenarios is in the allocation of aperture increase due to mineral dissolution. Figure 5.4 shows the estimated increase in fracture permeability for each of the two model scenarios for the equivalent increases in total fracture porosity. Fracture permeability is estimated to be as much as 40% greater for the case of uniform dissolution when compared to the non-uniform dissolution case for the same total increase in fracture porosity. This demonstrates the potential error in prediction of fracture permeability if mineral spatial heterogeneity is not considered or accurately captured in the modeling effort.
Figure 5.3. Initial base case aperture distribution (a) and spatially non-uniform increases in fracture porosity of 20% (b), 40% (c), and 100% (d). Locations of aperture increase correspond to areas where calcite was identified to exist at the fracture surface (see Figure 5.2(b)).
Figure 5.4. Permeability as a function of the increase in total fracture porosity for uniform dissolution (blue) and non-uniform dissolution (green). Non-uniform dissolution assumes aperture increases only occur at locations where calcite is in contact with the fracture surface.

5.3.3 Geochemical alterations to fracture geometry and fluid flow hydrodynamics

2-D steady state flow modeling results are presented in Figure 5.5 for the non-uniform dissolution scenario, which assumes dissolution occurs only at points of contact with calcite as identified in white in Figure 5.2(b). The streamlines shown as black lines in Figure 5.5 are drawn as the perpendicular to the velocity vector along the single path of travel for a theoretical particle released at the inlet. These flow paths are superimposed over the normalized volumetric flow rates through the fracture. Closer examination of Figure 5.5(b-d) demonstrates how calcite dissolution alters fracture geometry and impacts fluid flow through the fracture. As fluid flows through the fracture it deviates to follow the paths of least resistance. These preferential flow pathways are generated along areas of greatest calcite dissolution and represent a similar process to that of wormhole generation during dissolution in limestone formations (Hoefner and Fogler, 1988; Detwiler, 2008).
Figure 5.5. Normalized volumetric flow rates for the non-uniform dissolution scenario (see Figure 5.3 for corresponding aperture maps). Black lines represent flow streamlines drawn as the perpendicular to the velocity vector along the single path of travel for a theoretical particle released at the inlet. Flow direction is from bottom (inlet) to top (outlet) of figure.
5.4 Discussion and conclusions

The previous two chapters in this dissertation have shown a complex relationship between mineralogy, solution chemistry, and initial fracture geometry in controlling fracture permeability evolution. In particular, the preferential dissolution of calcite observed in Chapter 3 (see Figure 3.6) demonstrates the potential importance for accurate accounting of mineral spatial locations when predicting changes in fracture permeability during reactive flows. This experimental observation motivated the modeling work presented here with the goal of ascertaining the importance of accounting for spatially variable mineral dissolution when predicting fracture permeability evolution. The results of this modeling effort have demonstrated that there is a non-linear relationship between changes in fracture porosity and fracture permeability and that the spatial distribution of mineral dissolution may strongly influence this relationship.

This finding has important implications for modeling leakage of CO$_2$ in that it highlights the influence that 2-D mineral spatial variability may have in determining fracture permeability evolution. The two model scenarios examined in this chapter had the same total increase in fracture porosity and the same average mechanical aperture. If traditional methods (e.g. the cubic law with known $\Delta P$ and $Q$) were used to estimate fracture permeability given this information, it is possible that fracture permeability would be substantially overestimated. The existence of bands of less-reactive minerals, such as is observed in Figure 3.6(a), provides anecdotal evidence for continued low fracture permeability even for the case of substantial dissolution along the majority of the fracture. The model results shown in Figure 5.4 provide additional evidence for the influence of these less-reactive bands in controlling fracture permeability. Furthermore, the results of this modeling exercise support the contention that traditional porosity-permeability
relationships for porous media may be unable to accurately capture fracture permeability evolution based simply on accounting for changes in total fracture porosity.

The novel application of combining μCT X-ray attenuation data with EDS elemental maps for the purpose of ascertaining 2-D mineral spatial information along a fracture establishes an exciting new use of CT for the study of geologic media. Previous researchers have discussed the ability to identify minerals by their different X-ray attenuations (e.g. Ketcham and Carlson, 2001), however, the direct assessment of mineral spatial data for the purpose of modeling the impact of mineral-specific dissolution in fractured media represents a new extension in the use of CT data. Although the results presented here are only a first-order attempt at using CT data for this purpose, they do demonstrate the potential usefulness of this new application.

Because EDS elemental mapping is a time-consuming process it is not easily applied at scales larger than a few millimeters. CT scanning, on the other hand, is an automated process capable of scanning samples at length scales of several centimeters. If EDS elemental mapping is used to accurately associate grayscale X-ray attenuation data with specific minerals, then this technique offers the possibility for obtaining cm-scale 3-D mineral spatial data in a fairly rapid, non-destructive manner. Achieving a high level of confidence in determining mineralogy based on a combined μCT-EDS analysis will require further effort and will benefit from additional measurements such as dual-energy μCT scanning to better separate individual mineral attenuation data. When CT scanning artifacts like the cone-beam ‘hour glass’ observed in the CT data presented in Chapter 3 exist in the reconstructed CT grayscale intensity data the CT data will cease to reliably represent true mineral-specific X-ray attenuation. Therefore, careful application of this combined analysis for mineral identification is advised, as not all CT data may be suitable for this purpose.
Chapter 6

Concluding Remarks

The body of work presented in this dissertation provides a thorough discussion on the fate of CO$_2$ injected into deep saline aquifers for the purpose of mitigating CO$_2$ emissions to the atmosphere. The primary objective of this work was to investigate the CO$_2$-water-rock interactions likely to impact the risk of CO$_2$ leakage back to the surface and gain a better understanding of the important processes and initial conditions that should be considered when evaluating potential injection sites. These objectives were achieved through a combination of theoretical modeling efforts, experimental observations, and novel imaging analyses.

In Chapter 2 I demonstrate that, from the standpoint of pH alone, the co-injection of CO$_2$ and SO$_2$ may be a viable solution for the dual mitigation of these atmospheric pollutants. Furthermore, I discuss the importance of reservoir brine chemistry, which is going to be closely tied to reservoir mineralogy, in determining the degree of brine acidification to be expected after CO$_2$ injection. These findings will aid in the selection of CO$_2$ injection reservoirs, as the post-injection brine pH will be an important factor to consider when selecting potential injection reservoirs.

Chapters 3 and 4 present results from a flow-through experiment that examined the impact of geochemical alterations on fracture permeability in a fractured carbonate caprock. There have been few studies that examine naturally heterogeneous rock samples, so my work has exposed some important processes that may have been otherwise neglected in simplified modeling efforts. These processes include: (1) the preferential dissolution of calcite leading to
increased fracture roughness due to non-uniform spatial distribution of mineralogy along the fracture, and (2) the potential for decohesion of less-reactive mineral particles leading to clogging along the fracture and a reduction in fracture permeability. The increased fracture roughness may negate, to some degree, increases in fracture permeability due to mineral dissolution along the fracture. The observation of particle transport and its potential for clogging the fracture pathway suggest that reactive transport models may need to consider a combination of geochemical and physical processes to accurately capture changes in fracture permeability during a CO$_2$ leakage event. Lastly, I have highlighted the importance of bands of less-reactive minerals that exist perpendicular to the direction of fracture flow. These bands may persist even when there is substantial dissolution along the fracture and may serve to constrict flow through the fracture, thereby controlling fracture permeability. The work presented in Chapter 5 confirms this possibility and emphasizes the importance of accurately accounting for mineral spatial distribution in two-dimensional reactive transport modeling efforts.

Modeling leakage of CO$_2$ along reactive leakage pathways in caprock formations is complicated by many factors including the potential existence of a two-phase flow regime, rapid expansion of CO$_2$ due to changes in pressure and temperature with depth, and poorly understood geology, to name only a few important considerations. Therefore, it is necessary to make simplifications and assumptions in nearly all modeling efforts, not only for computational efficiency but also due to a lack of perfect information. Incorporating geochemical reactions into basin-scale CO$_2$ injection models by coupling geochemical reactions to changes in formation flow properties has been previously viewed as unnecessary due to a the belief that all important geochemical reactions will occur over very long timescales (>1000 years) (Celia and Nordbotten, 2009). However, I hope that through my work in this dissertation I have convinced the reader
that some geochemical reactions can be very rapid and may indeed be necessary inclusions in CO₂ leakage risk assessments. I also hope that I have made it clear that I believe that tight carbonate caprocks should be a choice of last resort when selecting favorable CO₂ injection reservoirs.
References


Midwest Regional Carbon Sequestration Partnership (MRCSP). Factsheet for partnership field validation test. NETL Cooperative Agreement DE-FC26-05NT42589. September **2008**.


