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To my wife Jung Hyun Hong and daughter Sua Kim
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SUMMARY

Global energy consumption will increase in the next decades and it is expected to largely rely on fossil fuels. The use of fossil fuels is intimately related to CO$_2$ emissions and the potential for global warming. Geological CO$_2$ storage aims to mitigate the global warming problem by sequestering CO$_2$ underground. Coupled hydro-chemo-mechanical phenomena determine the successful operation and long term stability of CO$_2$ geological storage.

This research explores various coupled phenomena, identifies different zones in the storage reservoir, and investigates their implications in CO$_2$ geological storage. Spatial patterns in mineral dissolution and precipitation are examined based on a comprehensive mass balance formulation. CO$_2$-dissolved fluid flow is modeled using a novel technique that couples laminar flow, advective and diffusive mass transport of species, mineral dissolution, and consequent pore changes to study the reactive fluid transport at the scale of a single rock fracture. The methodology is extended to the scale of a porous medium using pore network simulations to study both CO$_2$ reservoirs and caprocks. The two-phase flow problem between immiscible CO$_2$ and the formation fluid (water or brine) is investigated experimentally. Plug tests on shale and cement specimens are used to investigate CO$_2$ breakthrough pressure. Sealing strategies are explored to plug existing cracks and increase the CO$_2$ breakthrough pressure. Finally, CO$_2$-water-surfactant mixtures are evaluated to reduce the CO$_2$-water interfacial tension in view of enhanced sweep efficiency. Results can be used to identify optimal CO$_2$ injection and remediation strategies to maximize the efficiency of CO$_2$ injection and to attain long-term storage.
CHAPTER 1

INTRODUCTION

Fossil fuels have been a major energy source since the Industrial Revolution. The dependency on fossil fuels is expected to continue for the next several decades, until alternative energy sources satisfy anticipated energy demands. Carbon capture and sequestration CCS has emerged as a potential option for the more sustainable use of fossil fuels in the near future. In CCS, carbon dioxide $\text{CO}_2$ is captured at carbon emission sources and injected into geological formations. Two key criteria for the successful operation of geological $\text{CO}_2$ storage are injectivity and long-term system integrity. Both require careful understanding of complex hydro-chemo-mechanically coupled phenomena.

This thesis addresses emergent hydro-chemo-mechanically coupled phenomena, their implications on $\text{CO}_2$ geological storage, and the development of engineered $\text{CO}_2$ injection methods to improve sweep efficiency and storativity. The research approach is based on analytical solutions, numerical simulations, and complementary experimental studies. The research is organized into seven stand-alone chapters, followed by a chapter where global conclusions are identified.

Chapter 2 explores geotechnical concepts and implications of $\text{CO}_2$ geological storage. A comprehensive review of the water-$\text{CO}_2$-mineral system, reservoir conditions, and the fundamentals of $\text{CO}_2$ geological storage is followed by the identification of various hydro-chemo-mechanically coupled processes that may lead to emergent phenomena and increase the probability of geotechnical hazards. This chapter was developed in collaboration with D.N. Espinoza.
Chapter 3 identifies distinct regions in a CO\textsubscript{2} storage reservoir and their characteristic geochemical conditions. Each region is analyzed at equilibrium. Mass balance formulations that account for temperature, pressure, brine salinity, mineralogy, and porosity provide insight into the system response in different scenarios. The discussion addresses the impact of dissolution and precipitation on injectivity and system integrity.

Chapter 4 uses kinetic rate laws to investigate the evolution of a saline aquifers following CO\textsubscript{2} injection. The finite element method is used to simulate reactive fluid transport where CO\textsubscript{2}-dissolved water flows through a rock fracture plane. The simulation couples laminar flow, selective mass transport of species, mineral dissolution, and consequent channel enlargement. Results help us understand the interactions between processes and parameters such as advection, diffusion, species concentration, and geometry at the pore scale during reactive fluid transport. The model can be readily extended to larger porous systems.

Chapter 5 develops a network simulation code for a reservoir system based on mineral dissolution and kinetic rate laws to upscale pore/joint scale results obtained in Chapter 4. Simulations examine CO\textsubscript{2}-dissolved fluid transport through a porous reservoir for different Damköhler numbers, Peclet numbers, and heterogeneity of the porous network. Network simulations provide information such as the distribution of species concentration, the evolution of channel diameter, flow rate, pressure field, and permeability. Simulation results suggest that the reservoir may experience either compact dissolution or localized channel formation, depending on injection conditions.

Chapter 6 extends the previous study to the low-permeability cap rock layer. Preliminary analyses show that transversely homogeneous diffusive transport prevails over advective transport, hence, simulations are restricted to 1-D conditions. Simulations are conducted for two different mineralogies with end-member reactivities for typical
field situations: calcium carbonate and kaolinite. Simulation results and analyses highlight the interplay between mineral reactivity/dissolution and diffusive transport.

Chapter 7 reports an experimental study designed to examine the transport of CO\(_2\) through formations selected as barriers. Plugs cut from shale or prepared with well cement are tested to gain information on CO\(_2\)-breakthrough pressures and the main transport mechanisms. We devise a remediation method to seal discontinuities in the shale that can otherwise act as preferential paths for CO\(_2\) leakage. Pressure tests after remediation treatments demonstrate that micron-size particles can fill cracks and increase the CO\(_2\)-breakthrough pressure.

Chapter 8 explores engineering CO\(_2\) injection strategies to prevent viscous fingering and to improve sweep efficiency. This chapter begins with the evaluation of modified interfacial tension between CO\(_2\) and water when adding surfactants. Pore-scale CO\(_2\) injection experiments use a micro-model to provide insights on parameters that affect the sweep efficiency and the interface between the two fluid phases. Complementary network simulations support experimental observations and show different CO\(_2\) displacement topologies.

Finally, salient observations from this thesis are summarized in Chapter 9.
CHAPTER 2

CO₂ GEOLOGICAL STORAGE – GEOTECHNICAL IMPLICATIONS

2.1 Introduction

Quality of life, in terms of education, infant mortality, and life expectancy, correlates with energy consumption. Global energy consumption will increase dramatically in the next decades, and it is expected to largely rely on fossil fuels because of the available reserves, their low cost, the investment in current infrastructure, and the still limited development of renewable energy. Currently, 90% of the total primary energy sources in the world are fossil fuels, and more than 85% in the USA (DOE, 2010).

The use of fossil fuels is intimately linked to the emission of CO₂ into the atmosphere. The current concentration of CO₂ in the atmosphere is ~385 ppm (parts per million), which is almost twice the concentration before the Industrial Revolution (200 ppm - IPCC, 2001). Anthropogenic CO₂ global emissions add to ~7 GtC/year (see Figure 2.1). The USA releases 1.59 GtC/yr and China 1.78 GtC/yr – 2007 data (CDIAC, 2009). Power plants account for ~40% of total CO₂ emissions. Once released into the atmosphere, CO₂ enters into the global carbon cycle and interacts with the ocean and terrestrial sinks as shown in Figure 2.2.

The estimated net annual increase of CO₂ concentration in the atmosphere is problematic since CO₂ is a greenhouse gas. The mean surface temperature has increased ~0.6±0.2°C since the industrial revolution, and atmospheric models forecast as much as a ~3°C increase by 2100 if anthropogenic CO₂ emissions continue current trends (Figure 2.3).
Figure 2.1  Annual CO₂ emissions per person as a function of Gross Domestic Product (adjusted for inflation) for different countries. Data from the Carbon Dioxide Information Analysis Center (www.cdiac.ornl.gov) and (www.gapminder.org).

Figure 2.2  Anthropogenic perturbation of the carbon dioxide cycle – Values show the annual contribution of various components (data from: Global-Carbon-Project, 2010).
The UN Framework Convention on climate change has suggested that the atmospheric concentration of CO₂ should not exceed 450ppm to prevent a major impact on climate conditions. Several technologies have been proposed for mitigating the emission of CO₂ into the atmosphere (Table 2.1). Two clear options call for reducing the combustion of fossil fuels, and capturing the generated CO₂ followed by permanent sequestration.
Table 2.1  CO₂ Emission Mitigation Technologies

<table>
<thead>
<tr>
<th>CO₂ emission mitigation technology</th>
<th>Advantages</th>
<th>Difficulties</th>
<th>Capacity and certainty of execution</th>
</tr>
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</table>
| DIRECT - capture, transport, and final sequestration of CO₂ generated from fossil fuel power plants, | - Available injection technology  
- Large capacity  
- May give additional revenue by enhanced hydrocarbon production | - Cost: it needs additional energy consumption ~20% for carbon capture and storage (1)  
- Monitoring, contamination, and liability | - Large capacity: 10³~10⁴ GtCO₂, mostly in saline aquifers (2) |
| CO₂ geological storage coupled or not with fuel switching | - Easy and relatively inexpensive.  
- No porous media involved | - Water acidification and effects on aquatic life (3)  
- Transportation to the site | - Very large capacity >> 10¹ GtCO₂ (volume of the ocean deeper than ~3,000m) |
| Ocean storage | - Thermodynamically stable | - Expensive and labor intensive | - Very limited; for example: annual production of concrete is ~15Gt concrete |
| Chemical carbonation | - Almost C-free  
- Available technology | - Nuclear waste  
- Non-commercial use of nuclear power technology | - Currently provide 4% of the energy demand (4) |
| Biofuels | - Consume bio-products in excess, e.g. sugar cane and corn | - Competes with food supply | - In Brazil ethanol accounts for less than 5% of the energy production (5) |
| Alternative energy sources | - Small contribution to the energy portfolio | - Currently provide 6% of the energy demand (4) |
| Renewables, Solar, Wind, Geothermal | - Nuclear waste  
- Non-commercial use of nuclear power technology | - Efficient implementation could reduce carbon emissions from the building sector to levels equivalent to those 20 years ago. |
| Nuclear fission | - Almost no cost | - Requires time and policy | - Some countries are already highly efficient. |
| Change in people’s habits - e.g. promote mass transit | - In progress | - It needs market-transforming policies (6) | |
| More efficient end-use energy technologies and appliances - HVAC | - Relatively inexpensive | - Difficult to increase natural sinks (trees, algae)  
- Uncertainties about land use in the future (7) | - Currently at maximum  
- Uptake about ~20% of total emissions. |
| CO₂ surface uptake | | | |
| Terrestrial uptake | | | |

(1) Heddle et al., 2003; Dooley et al., 2006; (2) IPCC, 2005; (3) Golomb, 1993; House et al., 2006; (4) IEA, 2009; (5) World-Resources-Institute, 2010; (6) Brown and Southworth, 2006; (7) Jaccard, 2005

Suggested minimum storage time for CO₂ geological storage ranges between 1,000 and 10,000 years. This requirement is less demanding than for nuclear waste in part
due to the expectation that future technological developments might find other methods to mitigate global warming, and because of natural climate fluctuations such as the average glacial cycle period of 28,000 years (Augustin et al., 2004). Figure 2.4 shows a comparison of time scales for different processes related to human activities and geologic processes relevant to energy. The dramatic contrast between political, engineering, and geological time scales add difficulty to short-time decision making.

Figure 2.4 Time scales of relevant energy-related activities and processes (Note: (1) Estimation based on the capacity of forest to absorb carbon in the atmosphere, 0.17GtC/yr; from IPCC, 2001).

The purpose of this manuscript is to explore geotechnical concepts relevant to carbon dioxide geological storage. First, we review the chemo-physical properties of water-CO$_2$-mineral systems, reservoir conditions, and the fundamentals of CO$_2$ geological storage. Next, we explore various hydro-chemo-mechanical coupled processes that may lead to emergent phenomena and increase the probability of geotechnical hazards. Finally, we investigate potential geophysical strategies to monitor the evolution of CO$_2$ storage projects.
2.2 CO₂ Geological Storage and Reservoir Conditions

2.2.1 Volume Estimation

The injected CO₂ displaces the original fluids that fill the voids in geological formations. The volume of the geological formation \( V_{\text{bulk}} \) affected by the injection of a volume of CO₂ \( V_{\text{CO₂}} \) is a function of the average porosity of the reservoir \( n \):

\[
V_{\text{bulk}} = \frac{1}{\psi} \frac{V_{\text{CO₂}}}{n}
\]

(1)

where the displacement efficiency coefficient is \( \psi \approx 0.6 \) in media with spatially correlated random porosity and can be very low \( \psi < 0.1 \) if fingered invasion takes place. Let’s assume a target sequestration of 4GtC/year (for a flat trend based on present data – Figure 2.3). The total amount of CO₂ to be sequestered in the next 50 years is 200 GtC or 730 GtCO₂. In a compressed state (\( \rho_{\text{CO₂}} \approx 0.7 \) tonnes/m³), this mass would occupy a volume \( V_{\text{CO₂}} = 1,050 \) km³. The geological volume for storage would be \( V_{\text{bulk}} \approx 27,500 \) km³ for a porosity \( n \approx 0.2 \), and displacement efficiency \( \psi = 0.5 \). A 100m thick reservoir would extend \( \approx 325 \) km in each direction.

2.2.2 CO₂ Trapping

The trapping mechanisms to keep CO₂ within deep geological formations rely on physical as well as chemical processes (IPCC, 2005; Jaccard, 2005; Dooley et al., 2006). Physical trapping mechanisms include structural and stratigraphic trapping by cap rocks, hydrodynamic trapping by slow aquifer currents, and capillary trapping by interfacial forces. Chemical trapping mechanisms include dissolution of CO₂ in water, mineralization, CO₂ adsorption on coal and rich-organic shales, and CO₂ hydrate formation. Most trapping mechanisms and safe disposal conditions are found and favored at depth. We note that there are natural accumulations of CO₂ in the Earth’s upper crust.
where CO$_2$ has been contained for geological times such as the Ladbroke Grove and Katnook Gas Fields in southeastern Australia (Watson et al., 2004).

### 2.2.3 Geological Formations

Stable sedimentary basins facilitate CO$_2$ storage, particularly when they are near emission points. These basins are found in most continents (IPCC, 2005). The USA, Canada and Australia have extensive storage capacity (Dooley et al., 2006).

Favorable storage sites must have a thick accumulation of permeable sediments to maximize storage capacity and injectivity, overlain by a highly impermeable seal or cap rock (generally shale and evaporites).

The increase in effective stress with depth $z$ leads to low porosity fine grained sediment barriers. Pore size depends on porosity and specific surface. In high specific surface montmorillonitic shales, the mean pore size can be in the order of $10^{-8}$ m (Hildenbrand et al., 2002; Armitage et al., 2010). High pore fluid pressure at depth also lowers the mass density difference between water and CO$_2$, increases the solubility of CO$_2$ in water, and increases the adsorption of CO$_2$ in coal.

The geological system should be structurally simple. Candidate storage sites are assessed for reservoir size, depth and hydrogeology, geology and petrophysical characteristics of the reservoir and the seal cap rock, surface temperature and geothermal gradient, tectonic stability and faulting intensity, accessibility, infrastructure, and proximity to major CO$_2$ sources.

Figure 2.5 shows schematic diagrams of various formations for CO$_2$ geological storage. The principal targets for CO$_2$ injection are deep saline aquifers and depleted/semi-depleted hydrocarbon reservoirs (which inherently include physical barriers and cap rocks). Injection into coal seams benefits from the co-production of CH$_4$. Similarly, hydrate-bearing sediments can also be used to sequester CO$_2$ while at the same time releasing CH$_4$ (a pilot test in the Alaska North Slope is planned for 2011, US DOE-
Deep saline aquifers are most abundant and could store 110 to 2700 GtC (Gale, 2004).

Figure 2.5  CO₂ storage alternatives. (a) Deep saline aquifers. (b) Depleted hydrocarbon reservoirs. (c) CO₂-enhanced oil recovery. (d) CO₂-enhanced gas recovery from coal bed methane. (e) CO₂-CH₄ replacement in hydrate bearing sediments. Depths shown for selected pilot projects.

2.2.4 Pilot Projects

There are more than 50 CO₂ injection projects reported worldwide (NETL, 2010). Figure 2.6 shows the mean pressure-temperature conditions at these storage sites. Most projects involve supercritical CO₂ and relatively small volumes.

2.2.5 Implementation

The injection of CO₂ underground can be implemented with technology developed for petroleum and gas production. In fact, acid gas injection is routinely done in Alberta, and CO₂-enhanced oil recovery is a common practice in oil reservoirs around the world, and there are more than ~5,000km of CO₂ pipelines in North America (Dooley et al., 2006). Still, the systematic geological storage of CO₂ will require improvements in
risk assessment, adequate evaluation of regional capacity and reservoir integrity, matching emission sources with sinks, and enhanced monitoring technology (Gale, 2004). In addition to these technical difficulties, economical, political, and legal obstacles have hindered the adoption of carbon capture and sequestration (CCS) technologies.

Figure 2.6  Pressure-temperature dependent CO$_2$ phases. Pilot CO$_2$ injection projects are superimposed on this plot. Unless reported in the original sources, the PT conditions are estimated as: $P = g \rho_w z$, $T = T_0 (4^\circ C) + 30^\circ C/km \cdot z$. (CO$_2$ hydrate phase boundary from: Takenouchi and Kennedy, 1965; Sloan and Koh, 2008).
2.3 Underlying Concepts and Implications

2.3.1 Geochemical Concepts

Properties of CO$_2$. The combustion of fossil fuels yields CO$_2$ among other byproducts. For example, burning methane produces

$$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad (2)$$

The physical properties of CO$_2$ depend on pressure-temperature P-T conditions. The CO$_2$ phase diagram is shown in Figure 2.6. CO$_2$ is a gas at normal temperature and pressure, it turns into liquid at moderate pressures $\sim$6.4MPa at 298K, and becomes supercritical when the temperature is higher than 304.1K and the pressure is greater than 7.38 MPa. The mass density $\rho$ of CO$_2$ varies widely, in fact, CO$_2$ is heavier than seawater at pressures above $\sim$28MPa at 277.15K ($\rho$$_{CO2}$=1.035kg/m$^3$). Mass density can be approximated with a cubic equation of state (Peng and Robinson, 1976) or using more accurate but complex equations (Span and Wagner, 1996). The mass densities of water and CO$_2$ are plotted in Figure 2.7 for typical P-T conditions present in onshore and offshore applications.

Other important P-T dependent properties of CO$_2$ include high bulk compressibility, typically an order of magnitude higher than that of water (Span and Wagner, 1996), and very low viscosity, typically 10 times lower than that of water as shown in Figure 2.7 ($\mu$$_{CO2}$=10$^{-4}$ Pa·s at 10MPa and 280K - Fenghour et al., 1998).

Water-CO$_2$ interaction and properties. CO$_2$ dissolves in water to form aqueous carbon dioxide CO$_2$(aq). The solubility of CO$_2$ in water $x_{CO2}$ [mol/L] can be estimated using Henry’s law

$$x_{CO2} = k_H \varphi P_{CO2} \quad (3)$$

where the Henry's coefficient is approximately $k_H$$\approx$10$^{-1.46}$=0.0347 and the fugacity coefficient $\varphi$$\leq$1 can be estimated with an equation of state. Water at room temperature and at 0.1MPa contains $x_{CO2}$$\approx$0.03-to-0.04 mol/L. That solubility increases by two orders
of magnitude \( x_{\text{CO}_2} \approx 1\text{-}2 \text{ mol/L} \) as pressure and temperature increase to reservoir conditions, i.e., one to two moles of CO\(_2\) per liter of brine (Figure 2.8).

**Figure 2.7** Density and viscosity of CO\(_2\) and water as a function of depth, both on-shore and off-shore (for an assumed seabed at 500 m). \( P_c \) and \( T_c \) are the critical pressure and temperature for CO\(_2\). Note: the density of liquid CO\(_2\) exceeds the density of deep seawater when the seabed is deeper than 3000m.

**Figure 2.8** CO\(_2\) solubility in water and pH. (a) CO\(_2\) solubility in 1m NaCl aqueous solution (Note: an increase in salinity reduces CO\(_2\) solubility). (b) pH as a function of dissolved CO\(_2\) (Note: Solubility data from Duan and Sun, 2003).
Part of the aqueous carbon dioxide mixes with water to produce carbonic acid and ionizes stepwise:

\[ \text{CO}_2(g) = \text{CO}_2(aq) \quad \text{Henry’s law} \quad (4) \]

\[ \text{CO}_2(aq) + \text{H}_2\text{O}(l) = \text{H}_2\text{CO}_3(aq) = \text{H}^+ + \text{HCO}_3^-(aq) \quad \log K_{eq} = -6.35 \]

\[ \text{HCO}_3^-(aq) = \text{H}^+ + \text{CO}_3^{2-}(aq) \quad \log K_{eq} = -10.33 \]

The final result of adding CO\(_2\) to water is the production of ion bicarbonates, an increase in H\(^+\), and a decrease in pH. At reservoir conditions, CO\(_2\) dissolution in water yields a pH \(\approx 3\) (Figure 2.8).

Other relevant properties of the water-CO\(_2\) system include (a) solubility of water in liquid and supercritical CO\(_2\) (~0.05 mol of water per kg of liquid CO\(_2\) at 10MPa and 285K - Spycher et al., 2003), (b) high diffusivity of water into liquid CO\(_2\) \((D=2\text{-}20\times 10^{-8}\text{m}^2/\text{s} \text{ at } 7\text{-}25\text{MPa and } 305\pm10\text{K} - \text{Espinoza and Santamarina, 2010})\), and (c) CO\(_2\) hydrate formation at high pressure and low temperature (Figure 2.6; Sloan and Koh, 2008).

**Water-CO\(_2\)-Mineral interaction.** Table 2.2 summarizes representative chemical reactions, typical reaction rates and related comments. The equilibrium constant for dissolution reaction denotes the concentration of produced species relative to the concentration of reactant species at steady state conditions, i.e., a function of mineral solubility. The solubility of minerals in water depends on pH (Stumm et al., 1996). Furthermore, the reaction rate of minerals in CO\(_2\)-water depends on temperature, pressure (i.e., CO\(_2\) solubility and pH), and the concentration of other species (Fredd and Fogler, 1998; Pokrovsky et al., 2005; Renard et al., 2005; Algive et al., 2009). Dissolution rates for calcite Ca\(_{CO_3}\), anorthite Ca\(_{Al_2Si_2O_8}\), and kaolinite Al\(_2Si_2O_5(OH)_4\) are plotted as a function of pH in Figure 2.9. Silicates yield more dissolved cations (pH up to 8) than carbonates (pH up to 5) but the reaction rate is much slower (Gunter et al., 2000). Consider 1 mm spheres of calcite, anorthite, and kaolinite submerged into water acidified
by 1 mole of dissolved CO$_2$ per liter (pH~3). Using dissolution rates in Figure 2.9 and assuming that the system is far from equilibrium, the time required to dissolve each sphere is 4 hours for calcite, 16 years for anorthite, and 226 years kaolinite.

Table 2.2  Mineral reactions with CO$_2$-acidified water

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Typical reaction</th>
<th>Reaction rate</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Silicates$^a$</td>
<td>SiO$_2$(s) + 2H$_2$O $\rightleftharpoons$ H$_4$SiO$_4$ $\rightleftharpoons$ H$^+$ + H$_2$SiO$_4^-$ $\rightleftharpoons$ H$^+$ + H$_2$SiO$_4^{2-}$</td>
<td>1.26×10$^{-14}$ mol·m$^{-2}$·s$^{-1}$ (White et al., 2005)</td>
<td>-Solubility of quartz does not change with concentration of dissolved CO$_2$</td>
</tr>
<tr>
<td>2) Aluminosilicates$^b$</td>
<td>Anorthite: CaAl$_2$Si$_2$O$_8$(s) + 8H$^+$ $\rightleftharpoons$ Ca$^{2+}$ + 2Al$^{3+}$ + 2H$_2$SiO$<em>4$, $K</em>{eq}$ = 10$^{-21.7}$ Kaolinite: Al$_2$Si$_2$O$_5$(OH)$_4$(s) + 6H$^+$ $\rightleftharpoons$ 2Al$^{3+}$ + 2H$_2$SiO$_4$ + H$<em>2$O, $K</em>{eq}$ = 10$^{-3.8}$</td>
<td>Anorthite: 1.2×10$^{-5}$ mol·m$^{-2}$·s$^{-1}$ Oligiocalse: 1.2×10$^{-8}$ mol·m$^{-2}$·s$^{-1}$ Albite: 3.6×10$^{-9}$ mol·m$^{-2}$·s$^{-1}$ Kaolinite: 10$^{-14}$-to-10$^{-15}$ mol·m$^{-2}$·s$^{-1}$ (Gaus et al., 2005)</td>
<td>-Include feldspars, micas, and clays. -Reaction rate is slow. -Yields more dissolved cations than carbonate. -Results in pH up to 8.</td>
</tr>
<tr>
<td>3) Carbonates$^c$</td>
<td>CaCO$_3$(s) + H$^+$ $\rightleftharpoons$ Ca$^{2+}$ + HCO$<em>3^-$, $K</em>{eq}$ = 10$^{-1.85}$</td>
<td>Calcite: 1.6-to-3.2×10$^{-5}$ mol·m$^{-2}$·s$^{-1}$ (Brosse et al., 2005)</td>
<td>-Faster than aluminosilicates. -Solubility depends on T, P, Salinity, ionic concentration, and pH. -Dissolution rate is fast, but overall amount of reaction is small. -Results in pH from 3 to 5</td>
</tr>
</tbody>
</table>

Sources: (a) Drever, 1997; (b) Li et al., 2006; (c) Stumm et al., 1996; Fredd and Fogler, 1998; Renard et al., 2005; Algive et al., 2009

$CO_2$ adsorption on organic surfaces. Coal and organic shales adsorb CO$_2$ (Larsen, 2004; NETL, 2010). Langmuir-type sorption isotherms are commonly used to characterize the kinetics of the reaction at pressures <10MPa (Ceglarska-Stefanska and Zarebska, 2002; Mazumder et al., 2006). For reference, about ~1.6 moles of CO$_2$ can be adsorbed per kg of coal at 3MPa and 298K (37 cm$^3$ of gas CO$_2$ at normal pressure and temperature per gram of coal). A higher fluid pressure promotes higher and faster uptake.
Figure 2.9 Reaction rate log \( (k_d \text{[mol/m}^2\text{/s}]) \) for dissolution of calcite \( \text{CaCO}_3 \), anorthite \( \text{CaAl}_2\text{Si}_2\text{O}_8 \), and kaolinite \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \) at temperature \( T=40^\circ\text{C} \) and fixed concentration of aqueous carbon dioxide \( [\text{CO}_2(aq)] = 1\text{mol/L} \). For calcite, \( k_d = k_1[H^+] + k_2[H_2\text{CO}_3^*] \) where \( k_1 = 0.745\text{mol/m}^2\text{/s} \), \( k_2 = 8.6 \times 10^{-4} \text{mol/m}^2\text{/s} \) at \( T=40^\circ\text{C} \) (Fredd and Fogler, 1998; Pokrovsky et al., 2005; Renard et al., 2005; Algive et al., 2009). For anorthite, \( k_d = k_H[H^+]^{1.5} + k_{H_2O} + k_{OH}[OH]^0.33 \) where \( k_H = 6.883 \times 10^{-4} \text{mol/m}^2\text{/s} \), \( k_{H_2O} = 3.58 \times 10^{-12} \text{mol/m}^2\text{/s} \), and \( k_{OH} = 4.51 \times 10^{-14} \text{mol/m}^2\text{/s} \) at \( T=40^\circ\text{C} \) (Li et al., 2006). For kaolinite, \( k_d = k_H[H^+]^{0.4} + k_{OH}[OH]^0.3 \) where \( k_H = 2.79 \times 10^{-11} \text{mol/m}^2\text{/s} \) and \( k_{OH} = 3.51 \times 10^{-16} \text{mol/m}^2\text{/s} \) at \( T=40^\circ\text{C} \) (Li et al., 2006).

**Summary.** High fluid pressure and temperature bring \( \text{CO}_2 \) into liquid or supercritical phases and promote \( \text{CO}_2 \) solubility in water and adsorption onto organic surfaces. In the presence of \( \text{CO}_2 \), water acidifies and more intense and faster mineral dissolution takes place. Liquid and supercritical \( \text{CO}_2 \) exhibit much lower viscosity than water.
2.3.2 Mixed Fluid Conditions

*Pressure dependent $T_s$ and $\theta$.* The water-CO$_2$ interfacial tension decreases from $T_s \approx 72$ to 25mN/m as the pressure increases from 0.1MPa to 6.4MPa at $\sim$298K, eventually $T_s$ reaches a plateau at $T_s \approx 25\pm 5$mN/m in the supercritical state (Kvamme et al., 2007; Espinoza and Santamarina, 2010). Furthermore, the contact angle formed by the CO$_2$-water interface on mineral surfaces varies with fluid pressure in response to changes in CO$_2$-water interfacial tension: as the fluid pressure increases, the contact angle increases on non-wetting surfaces such as oil-wet quartz and coal and slightly decreases in water-wet quartz and calcite surfaces (Chi et al., 1988; Dickson et al., 2006; Chiquet et al., 2007; Chalbaud et al., 2009; Espinoza and Santamarina, 2010).

Changes in interfacial tension $T_s$ and contact angle $\theta$ will affect the capillary pressure, the evolution of flooding, the residual saturation, relative permeabilities, and capillary effects. In its simplest form, capillary pressure $\Delta P_c$ [Pa] is estimated from Laplace’s equation:

$$\Delta P_c = P_{CO_2} - P_w = \frac{2T_s \cos \theta}{r}$$

(5)

*Breakthrough pressure.* The breakthrough pressure $P^{*}_{thru}$ when CO$_2$ percolates through a porous medium depends on the mean pore size expressed in terms of specific surface $S_s$ and void ratio $e = e_{1kPa} - C_c \log(p'/1kPa)$, the wettability of the minerals in the presence of water and CO$_2$, and the standard deviation in pore size distribution. We can extend Laplace’s capillary pressure equation to obtain the following expression for the breakthrough pressure (Espinoza and Santamarina, 2010):

$$P^{*}_{thru} = \psi \frac{S_s \rho T_s \cos \theta}{e_{1kPa} - C_c \log \frac{p'}{1kPa}}$$

(6)

where $p'$ is the in situ effective stress, and the factor $\psi$ depends on clay fabric and grain size distribution; a value of $0.04 \leq \psi \leq 0.08$ applies to smectite clay barriers. The sealing capacity of cap rocks will depend on this breakthrough pressure; thereafter, the leak rate
will be determined by the cap rock permeability to CO$_2$ (Fleury et al., 2010; Pusch et al., 2010).

**Differences in mass density – Convection and self mixing.** CO$_2$ is lighter than water or brine at reservoir P-T conditions (Figure 2.7). The Bond number $B$ quantifies gravity-driven CO$_2$ migration as a function of the mass density difference ($\rho_w - \rho_{CO2}$) relative to capillary forces $T_s \cdot \cos \theta$ (Pennell et al., 1996):

$$B = \frac{(\rho_w - \rho_{CO2}) g k k_{CO2}}{T_s \cos \theta}$$

(7)

The mass density of the water with CO$_2$ in solution $\rho_{sol}$ [kg/m$^3$] is slightly heavier than the formation water and can be estimated from the mass density of pure water $\rho_w$ [kg/m$^3$] and the concentration of CO$_2$ in water $x_{CO2}$ [mol/m$^3$] as:

$$\rho_{sol} = \rho_w + m_{CO2} x_{CO2} - x_{CO2} \rho_w V_\varphi$$

(8)

where $m_{CO2}$[kg/mol] is the molecular weight of CO$_2$, and $V_\varphi$ [m$^3$/mol] is the apparent molar volume of dissolved CO$_2$ as a function of temperature, $V_\varphi = 37.51 - 9.585 \cdot 10^{-2}T + 8.740 \cdot 10^{-4}T^2 - 5.044 \cdot 10^{-7}T^3$ (Garcia, 2001). For example, there is an increase in density $\Delta \rho \sim 10$kg/m$^3$, for water saturated with CO$_2$ at 10MPa and 313K ($x_{CO2} \sim 1,230$ moles/m$^3$). Dissolution-densification and gravity-driven flow will cause convective transport which will accelerate CO$_2$ mixing in the reservoir water (Riaz et al., 2006; Kneafsey and Pruess, 2010).

**Differences in viscosity: Fingering.** Two dimensionless numbers control the pattern of fluid displacement: (1) the ratio of viscosities $M$ between the invading fluid $\mu_{CO2}$ and the displaced fluid $\mu_w$, and (2) the capillary number $C$ which is the ratio between viscous and capillary forces:

$$M = \frac{\mu_{CO2}}{\mu_w}$$

(9)

$$C = \frac{q \mu_{CO2}}{T_s \cos \theta}$$

(10)
where \( q [m^3/s/m^2] \) is the injection rate, \( T_s [N/m] \) is the interfacial tension between water and CO\(_2\), and \( \theta \) is the contact angle formed by the water-CO\(_2\) interface and the mineral surface. Stable displacement takes place when \( M > 1 \) and \( C > 1 \), viscous fingering when \( M << 1 \), and capillary fingering when \( C << 1 \) (Lenormand et al., 1988). Since the viscosity of CO\(_2\) is at least one order of magnitude lower than that of water at reservoir P-T conditions (Figure 2.7), CO\(_2\) may displace water from the pore space in the form of viscous fingers; in this case, the bulk volume of sediment \( V_{bulk} \) involved in storage will increase dramatically (Equation 1).

**CO\(_2\) lowers the viscosity of oil.** CO\(_2\) dissolves in crude oil (typically alkanes with less than 13 carbon atoms at reservoir conditions with \( P > 10\text{MPa} \) and \( T > 320\text{K} \)), lowers the viscosity of the crude oil, and favors oil recovery (Blunt et al., 1993).

**Summary.** Interfacial tension and the capillary entry pressure for CO\(_2\) into a water saturated seal cap rock decrease with pressure. The dissolution of CO\(_2\) in water increases the density of water, promote gravity-driven flow and accelerate mixing. Pronounced differences in viscosity between liquid or supercritical CO\(_2\) and water tend to promote viscous fingering during CO\(_2\) injection.

### 2.3.3 Chemo-Hydro-Mechanical Coupling

*Increased fluid pressure and fault reactivation.* The increase in pore fluid pressure during CO\(_2\) injection can reactivate nearby faults if the state of effective stress approaches failure conditions (Rutqvist and Tsang, 2002; Streit and Hillis, 2004).

*Capillary-driven deformation.* The invasion of immiscible CO\(_2\) in a water saturated reservoir gives rise to capillary forces and can cause significant volumetric deformation in fine-grained sediments (Delage et al., 2008).

*Fluid-driven fracture formation.* Hydraulic fracture can take place in both cohesive-cemented and cohesionless-frictional sediments (Bjerrum et al., 1972; Jaworski et al., 1981; Zhai and Sharma, 2005). Particle-scale mechanisms compatible with the effective-
stress dependent strength of sediments take into consideration capillary forces induced by the tensile membrane between CO$_2$ and water, seepage drag forces, and skeletal forces to explain particle displacement and localization (Shin and Santamarina, 2010).

**Effects of pH and permittivity on interparticle electrical forces – Changes in clay fabric.**

Two fluid-mineral interactions anticipate changes in interparticle forces after CO$_2$ injection: (1) water acidification changes the mineral surface charge, and (2) the low permittivity of CO$_2$ ($\kappa'\sim 2$ to $3$) compared to water ($\kappa'= 80$) implies changes in van der Waal’s attraction (Obriot et al., 1993; Palomino and Santamarina, 2005; Israelachvili, 2011). These fluid-mineral phenomena will alter the equilibrium between van der Waal’s attraction and double layer repulsion forces at the clay platelet scale, cause changes in clay fabric, and affect the seal capacity of cap rocks.

**Reactive fluid transport – Wormholes.** Acidified water dissolves minerals and enlarges pores along transport channels (Emberley et al., 2004; Watson et al., 2004; Kaszuba et al., 2005). The hydraulic conductivity may increase by a factor of 10-to-100 (Verdon and Woods, 2007), with even small changes in global porosity, as can be predicted using the Kozeny-Carman model. Two dimensionless numbers control the evolution of dissolution patterns: Damköhler number represents the ratio between advection and reaction times $Da = \kappa l / \nu$ (reaction rate $\kappa [1/s]$, characteristic length $l [m]$, velocity $\nu [m/s]$), while the Peclet number is the ratio between advection and diffusion time $Pe = \nu l / D$ (diffusion coefficient $D [m^2/s]$). The process is mass-transfer limited if a chemical reaction is very fast compared to mass-transfer kinetics $Da >> 1$ (e.g., more likely in the dissolution of carbonates). Otherwise, the process is reaction-rate limited $Da << 1$ (e.g., more likely if the dissolution of aluminosilicates is involved). The dissolution pattern during reactive transport can be categorized as face/global dissolution ($Da > 10^3$, $Pe < 10^3$), dominant wormholes ($Da > 10^3$, $Pe > 10^3$), or uniform dissolution ($Da < 10^3$) (Golfier et al., 2002). A rapid mineral dissolution rate combines with the inherent sediment heterogeneity to
facilitate a dominant wormholes tendency (Fredd and Fogler, 1998). Wormhole formation would lead to marked CO$_2$ leakage.

*Dissolution – Horizontal effective stress $k_0$ – Shear and tensile fractures.* Complementary analytical, numerical (DEM and FEM), and experimental techniques show the effects of mineral dissolution and ensuing particle-level volume contraction on the evolution of the state of stress under constant overburden at zero-lateral strain boundary conditions during mineral dissolution. In particular, the stress ratio at zero lateral strain $k_0=\sigma'_h/\sigma'_v$ (Jaky, 1944; Mayne and Kulhawy, 1982) experiences a pronounced decrease during mineral dissolution, and it may reach the Rankine active failure condition $k_a$ on the Coulomb failure plane (Shin and Santamarina, 2009). Strain localization along shear planes may follow (Shin et al., 2008). Furthermore, mineral dissolution causes sediment compaction, and the cap rock may experience bending and tensile failure.

*Coal swelling pressure.* Coal swells, its fluid conductivity decreases, and the effective stress increases with the adsorption of CO$_2$ (Somerton et al., 1975; Pekot and Reeves, 2002; Mazumder et al., 2006). Eventually, CO$_2$-CH$_4$ replacement in coal may become self-limiting because of coal swelling and reduced fracture porosity (Ceglarska-Stefańska and Zarębska, 2002).

*Summary.* The trapping mechanisms of CO$_2$ in geological formations rely on physical, chemical, and mechanical processes identified above. Each has different time and spatial scales. We summarize potential implications on CO$_2$ storage in Table 2.3.
Table 2.3  Coupling and emergent phenomena

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<td></td>
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</tr>
<tr>
<td>Chemo-Hydro-Mechanical</td>
<td>- Combination of previous phenomena</td>
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</tbody>
</table>

2.4 Monitoring Strategies and Risk Assessment

CO$_2$ leakage from storage sites back into the atmosphere decreases the efficiency of CO$_2$ storage. Faults and abandoned wells are preferential flow paths that add to the slow transport and diffusion through otherwise continuous strata (Calabrese et al., 2006; Dooley et al., 2006; Leuning et al., 2008). Monitoring is required to assess the movement of CO$_2$ and to detect leaks. The design of a monitoring strategy must consider the large areal extent of CO$_2$ storage reservoirs (on the order of ~km$^2$) and account for spatial and temporal variability.

Potential monitoring methods, most of them already available for other applications, are summarized in Table 2.4. These monitoring methods take advantage of differences between physical properties (mass density, bulk stiffness, electrical resistivity...
and dielectric permittivity, and thermal characteristics), the detection of byproducts from chemical reactions, or coupled process effects such as subsidence or micro-seismicity. Tracers such as $\delta^{13}C$ and SF$_6$ may be included in the injected CO$_2$ to facilitate detection (Leuning et al., 2008). The most common subsurface geophysical methods for deep reservoir applications are based on elastic wave propagation and electrical resistivity (Kiessling et al., 2010; Nakatsuka et al., 2010). The following analysis expresses their applicability to CO$_2$ geological storage. The bulk modulus $B_{mix}$ of the sediment can be estimated from the Biot-Gassman equation:

$$B_{mix} = B_{sk} + \left(1 - \frac{B_{sk}}{B_g}\right) n \left(\frac{S_w + S_{CO2}}{B_w + B_{CO2}}\right) + \frac{1 - n}{B_g} \left(\frac{B_{sk}}{B_g}\right)^2$$ \hspace{1cm} (11)

where subindices represent the skeleton $sk$, the mineral that makes the grains $g$, the water $w$, and the CO$_2$. The density of the mixture is:

$$\rho_{mix} = (1-n)\rho_s + n(S_{CO2}\rho_{CO2} + S_w\rho_w)$$ \hspace{1cm} (12)

Then, the compressional $V_P$ and shear $V_S$ wave velocities are:

$$V_P = \sqrt{\frac{B_{mix} + \frac{4}{3}G_{sk}}{\rho_{mix}}} \hspace{1cm} (13)$$

$$V_S = \sqrt{\frac{G_{sk}}{\rho_{mix}}} \hspace{1cm} (14)$$

where $G_{sk}$ is the shear modulus of the mineral skeleton.

The electrical conductivity of a geological formation depends on the concentration and mobility of hydrated ions in the pore fluid and the volume fraction of fluid in the formation (Santamarina, 2001). The injection of CO$_2$ displaces the electrolyte (conductivity $\sigma_{fl}$) and the formation conductivity can be estimated using the Archie's equation (Mavko et al., 2009):

$$\sigma_{form} = \sigma_{\beta} [n(S_{perc} - S_{CO2})]^\beta$$ \hspace{1cm} (15)
where $S_{CO2} \leq S_{perc}$, the maximum saturation of CO$_2$ at percolation. Figure 2.10 shows the variation of P-wave velocity $V_p [\text{m/s}]$ and electrical conductivity $\sigma_{form}$ as a function of the CO$_2$ saturation $S_{CO2}$. Because CO$_2$ is non conductive and has a much lower bulk modulus than water, both $\sigma_{form}$ and $V_p$ decrease as the relative saturation $S_{CO2}$ increases. While forward predictions show a clear effect of CO$_2$ on $V_p$ and $\sigma_{form}$, the inverse analysis is hindered by measurement errors and error propagation. Hence, the estimation of $S_{CO2}$ from field measurements remains challenging.

Figure 2.10 Reduction of P-wave velocity and electrical conductivity $\sigma_{form} = 1/\rho_{form}$ with CO$_2$ saturation for a sediment with porosity $n=0.42$. Ratio of P-wave velocity computed with $V_p(\text{Brine}) = 1540\text{m/s}$, $V_p(\text{CO}_2) = 268\text{m/s}$ (at $T=40^\circ\text{C}$ and $P=10\text{MPa}$), $V_p(\text{dry sediment}) = 1000\text{m/s}$, and $\nu_{sk}=0.1$. Electrical conductivity computed with an exponent $\beta=2$ for relative saturation and porosity, and a percolation threshold $S_{perc}=0.7$. 
Table 2.4  CO₂ monitoring techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Property measured</th>
<th>Principle, comments and issues</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. SUBSURFACE MONITORING</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porewater geochemistry (1)</td>
<td>CO₂, HCO₃⁻, CO₃²⁻, DIC, major ions, pH, alkalinity, salinity, and isotopes</td>
<td>CO₂ dissolves in water and changes water geochemistry</td>
</tr>
<tr>
<td>Seismic techniques (2)</td>
<td>P-wave velocity and amplitude</td>
<td>The bulk modulus of CO₂ is one order of magnitude lower than that of water</td>
</tr>
<tr>
<td>Electromagnetic techniques (3)</td>
<td>Resistivity and electromagnetic waves</td>
<td>High impedance mismatch of electrical conductivity and dielectric permittivity between CO₂ and formation water.</td>
</tr>
<tr>
<td>Temperature signal (4)</td>
<td>Temperature</td>
<td>CO₂ causes non-isothermal events such as expansion induced cooling of CO₂ and thermal heat dissipation from CO₂ dissolution</td>
</tr>
<tr>
<td>Infrared monitoring (5)</td>
<td>Infrared absorption</td>
<td>CO₂ gas shows characteristic absorption spectrum for infrared waves.</td>
</tr>
<tr>
<td><strong>2. NEAR SURFACE MONITORING</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis of near-surface water (6)</td>
<td>Isotopic composition, tracers, bulk gas composition, and DIC</td>
<td>CO₂ dissolves in water. A meaningful analysis requires a thorough understanding of the geochemical cycle at the site.</td>
</tr>
<tr>
<td>Surface analysis of soil gas (7)</td>
<td>Composition of gas fluxes through the soil</td>
<td>CO₂ leaks would eventually percolate through the soil. Point measurements &lt;1m² are accurate but they lack spatial resolution</td>
</tr>
<tr>
<td>Near surface analysis of air composition (8)</td>
<td>CO₂ concentration in the near surface by infrared gas analyzer, eddy correlation tower, and light detection and ranging measure</td>
<td>CO₂ from leaks readily mix with other atmospheric gases. Local changes in turbulence and biological sources and sinks of CO₂ make the identification difficult.</td>
</tr>
<tr>
<td><strong>3. ON-SURFACE MONITORING</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time-lapse 3D reflection seismic imaging (9)</td>
<td>P-wave velocity and amplitude</td>
<td>Takes advantage of low bulk modulus of CO₂. It is routinely used in the petroleum industry and can track the plume subsurface movement.</td>
</tr>
<tr>
<td>Gravity (10)</td>
<td>Mass density</td>
<td>CO₂ is generally lighter than water</td>
</tr>
<tr>
<td>Ground displacements (11)</td>
<td>Subsidence and heave, vertical displacement</td>
<td>CO₂ injection alters pore pressure and effect on effective stress, and therefore strata compressibility</td>
</tr>
<tr>
<td>Surface analysis of carbon content in soil (12)</td>
<td>Carbon content by Inelastic Neutron Scattering INS</td>
<td>Increased CO₂ levels asphyxiate aerobic organisms.</td>
</tr>
<tr>
<td>Remote sensing of air composition (15)</td>
<td>CO₂ atmospheric concentration by hyperspectral remote sensing of vegetative stress and long open path infrared absorption</td>
<td>Applicable at large scales</td>
</tr>
</tbody>
</table>

(1) Gunter et al., 2000; Emberley et al., 2004; Newell et al., 2008; (2) laboratory studies (Xue et al., 2005; Shi et al., 2007; Lei and Xue, 2009) and pilot tests (Daley et al., 2007; Daley et al., 2008; Onishi et al., 2009; Bohnhoff et al., 2010); (3) Gasperikova and Hoversten, 2006; Nakatsuka et al., 2010; (4) Bielinski et al., 2008; (5) Charpentier et al., 2009; (6) Oldenburg et al., 2003; (7) Oldenburg et al., 2003; Leuning et al., 2008; (8) Strazisar et al., 2009; (9) Arts et al., 2004; (10) Alnes et al., 2008; (11) Alnes et al., 2008; Kempka et al., 2008; (12) Wielopolski and Mitra, 2010
2.5 Conclusions

The volume of the geological formation that is affected by the injection of CO$_2$ depends on geometric boundaries, spatial variability, flow conditions, and the emergence of viscous fingering. The physical properties of CO$_2$ such as density, viscosity, interfacial tension, and bulk compressibility vary with pressure and temperature conditions, and must be properly modeled in numerical simulations of CO$_2$ geological storage. In particular, the CO$_2$-water interfacial tension decreases with fluid pressure. Lower interfacial tension reduces the capillary entry pressure for CO$_2$ into a water saturated seal cap rock.

High CO$_2$ injection pressures can induce fluid driven fractures and trigger displacements along preexisting faults. The solubility of CO$_2$ in water is high under reservoir pressure conditions. The density of water increases with dissolved CO$_2$, and convective self-mixing takes place. Water acidification in the presence of CO$_2$ enhances mineral dissolution and alters the sediment fabric when clay minerals prevail. Silicates have solubility higher than calcite but the reaction rate is much slower. The evolution of dissolution and ensuing dissolution patterns depend on the interplay between the rates of advection, diffusion, and dissolution. Dissolution may cause settlement, change in effective stress, and the formation of preferential channels for fluid flow, particularly in carbonates.

The presence of CO$_2$ decreases the fluid bulk modulus, mass density, and electrical conductivity. These changes support the application of geophysical methods based on elastic and electromagnetic waves to monitor deep storage reservoirs. While forward predictions are manageable, inverse analysis is hindered by measurement difficulties and error propagation. Hence, the monitoring of CO$_2$ geological storage remains challenging.
3.1 Introduction

The injectivity of CO$_2$ and the integrity of the reservoir-caprock system are affected by mineral precipitation and dissolution (Gaus et al., 2008). Mineral precipitation reduces porosity, lowers permeability, and hinders the injectivity of CO$_2$. The CO$_2$ injection pressure can be increased to overcome the compromised injectivity, but this approach may cause hydraulic fractures in the reservoir (Rutqvist and Tsang, 2002; Streit and Hillis, 2004; Shin and Santamarina, 2010). On the other hand, mineral dissolution triggered by CO$_2$ driven brine acidification will increase permeability, change the state of stresses in the reservoir (Shin and Santamarina, 2009), and cause caprock bending.

In this manuscript, different zones in the reservoir around injection wells are identified in terms of the prevailing conditions and phenomena. Then, we analyze key phenomena in each zone taking into account parameters such as temperature, pressure, brine salinity, mineralogy, and porosity. These zone-specific storage reservoir analyses provide robust guidelines to understand short and long-term reservoir performance.

3.1.1 Zones

The CO$_2$ reservoir can be analyzed into four different zones around a CO$_2$ injection well (Figure 3.1 - modified from an early zonation by Azaroual et al. 2007). The far-field Zone I is not affected by the CO$_2$ injection, and brine saturation is $S_b=1$. Acidified brine dominates Zone II and mineral dissolution prevails over precipitation;
loaded with dissolved CO$_2$ and minerals, denser brine experiences convection and sustains further dissolution in this zone (Weir et al., 1996; Riaz et al., 2006; Hassanzadeh et al., 2007; Kneafsey and Pruess, 2010). The ionic strength in brine increases as water is removed by the injected CO$_2$, and salt precipitation may occur in Zone III; in fact, brine acidification and brine dissolution into CO$_2$ coexist in the transition Zone III and there is partial compensation between mineral dissolution and precipitation. The CO$_2$ saturation approaches $S_{CO2} \approx 1$ near the injection well (Zone IV) where the continuous influx of “dry” CO$_2$ first displaces and dries all the residual brine and causes salt precipitation.

### 3.1.2 Geological Formations

Sandstones and carbonates are common candidate formations for CO$_2$ geological storage (Gale, 2004; Dooley et al., 2006). Table 3.1 summarizes the mineralogical composition of sandstone and carbonate formations being considered for CO$_2$ storage. Sandstone reservoirs are made of oxides (e.g., quartz and hematite), and some aluminosilicates (e.g., various feldspars, micas, and clays) and carbonates (e.g., calcite, dolomite, and siderite). The dominant mineral in the carbonate reservoirs is calcite, followed by a small fraction of aluminosilicates and clays.
Figure 3.1 Zones around a CO$_2$ injection well (modified from Azaroual et al., 2007). $M$: Mineral, $B$: Brine, $S_{CO2}$: saturation of CO$_2$, $S_B$: saturation of brine.
Table 3.1  Mineralogical compositions (volume percentage) of reservoir sites for the CO$_2$ geological storage

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sandstone (1)</th>
<th>Sandstone (2)</th>
<th>Sandstone (3)</th>
<th>Sandstone (4)</th>
<th>Sandstone (5)</th>
<th>Sandstone (6)</th>
<th>Carbonate (7)</th>
<th>Carbonate (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>58</td>
<td>70</td>
<td>77</td>
<td>60</td>
<td>75</td>
<td>80</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.93</td>
<td>8</td>
<td>1.3</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0</td>
<td>13.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Siderite</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.02</td>
<td>1</td>
<td>2.25</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Illite</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Oligoclase</td>
<td>19.8</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>8.2</td>
<td>5</td>
<td>0.6</td>
<td>3</td>
<td>13</td>
<td>1</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Albite</td>
<td>0</td>
<td>1</td>
<td>0.6</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Anorthite</td>
<td>0</td>
<td>0</td>
<td>0.66</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na-smectite</td>
<td>4</td>
<td>0</td>
<td>2.25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Chlorite</td>
<td>4.55</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Hermitate</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

(Data source: (1) Gulf Coast, Frio (Xu et al., 2005), (2) Rose Run, Ohio (Zerai et al., 2006), (3) Colorado Plateau, Utah (White et al., 2005), (4) & (7) Arno River Plain, Italy (Biagi et al., 2006), (5) Utsira, Sleipner (Hellevang, 2006), (6) Hettangium and Contorta, Germany (Meyer et al., 2008), (8) Dogger, France (André et al., 2007))

3.2 Geochemical Analyses

Let’s analyze the four different zones that develop around injection wells at CO$_2$ storage sites (Figure 3.1), starting with the composition of the formation water.

3.2.1 Far-Field Zone I

The formation water in a geologic basin originates from the subaerial evaporation of sea water, the subsurface dissolution of minerals including evaporates, membrane filtration, and dilution by meteoric water (Land and Prezbindowski, 1981; Connolly et al., 1990; Pauwels et al., 1993; Hanor, 1994; Kharaka et al., 2006). The resulting formation water is either a Na-Cl or a Na-Ca-Cl type at most candidate sites for CO$_2$ storage (Figure 31
3.2). The pore fluid evolves towards equilibrium with the formation minerals, but the time interval may be insufficient for complete equilibrium in relatively active systems (Pauwels et al., 1993; Baines and Worden, 2004; Lagneau et al., 2005). In general, the formation water is: (1) under-saturated in terms of evaporate minerals such as halite and anhydrite, and (2) either under-saturated or in equilibrium with other minerals in the formation (Connolly et al., 1990 – see estimation in Xu et al., 2005).

![Figure 3.2](image)

<table>
<thead>
<tr>
<th>Number</th>
<th>Site</th>
<th>Pressure [MPa]</th>
<th>Temperature [°C]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Frio</td>
<td>20</td>
<td>75</td>
<td>Xu et al., 2005</td>
</tr>
<tr>
<td>2</td>
<td>Sleipner</td>
<td>10</td>
<td>37</td>
<td>Gaus et al., 2005</td>
</tr>
<tr>
<td>3</td>
<td>Rose Run</td>
<td>22</td>
<td>75</td>
<td>Zerai et al., 2006</td>
</tr>
<tr>
<td>4</td>
<td>Colorado Plateau</td>
<td>10</td>
<td>40</td>
<td>White et al., 2005</td>
</tr>
<tr>
<td>5</td>
<td>Paradox Valley</td>
<td>30</td>
<td>120</td>
<td>Rosenbauer et al., 2005</td>
</tr>
</tbody>
</table>

Figure 3.2 Chemical composition of formation water for candidate CO$_2$ sequestration sites.

In this analysis, we consider a single mineral formation, calcite $CaCO_3$, and assume that equilibrium has been reached (Lasaga, 1984; Baines and Worden, 2004). The
formation water retains its original halite NaCl concentration ranging from Sal=0 to 6 [mol/kg-water] and is in equilibrium with the formation CaCO₃. The resulting geochemical composition of the pore fluid is under-saturated with halite NaCl and saturated with calcite CaCO₃ (Computation details in Chart 3.1). Two assumptions are made to formulate the mass balance calculations: 1) the initial system consists of mineral and brine only and there is no entrapped gas, and 2) water salinity is controlled by the initial concentration of halite NaCl. All symbols and conditions relevant to the mass balance analysis are listed in Table 3.2.

### 3.2.2 Zone II – Mixing and Mineral Dissolution

The CO₂ phase that reaches Zone II is water saturated. In the proximity of fresh brine, CO₂ dissolves into the brine and acidifies it; mineral dissolution follows. The concentrations of species in brine at equilibrium when CO₂ and mineral dissolves to its maximum solubility are evaluated based on the initial composition, pressure, and temperature (Computation details in Charts 3.2 to 3.4). The new equilibrium condition is used to compute the change in pH, density, and volume (Figure 3.3; Charts 3.5 to 3.7).

*pH*. Without any buffering by mineral dissolution, the dissolution of CO₂ acidifies brine to pH~3 (computed using CO₂ solubility and acidity constant $K_{a1}$ for the dissociation of total $H_2CO_3^{*}\leftrightarrow H^+ + HCO_3^-$ where the total dissolved $H_2CO_3^{*}$ is the summation of aqueous carbon dioxide $CO_2(aq)$ and true carbonic acid $H_2CO_3$; for a depth~1km, pressure $P\approx$10MPa, temperature $T\approx40°C$ - Figure 3.4; computation details in Chart 3.3). The drop in pH is more pronounced when the brine salinity is low. If mineral dissolution is accounted for, the pH of brine converges to around 5 for the same $P$-$T$ condition (computed in PHREEQC with the input of concentration of dissolved CO₂ and ambient calcite environment; for a depth~1km, pressure $P\approx$10MPa, temperature $T\approx40°C$ - Figure 3.4; computation details in Chart 3.4). Throughout all these calculations, brine remains under-saturated in terms of halite NaCl.
Table 3.2  Symbols used in the geochemical analysis

<table>
<thead>
<tr>
<th>Notations</th>
<th>Subscripts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium constant</td>
<td>K [-]</td>
</tr>
<tr>
<td>Fugacity</td>
<td>Φ [-]</td>
</tr>
<tr>
<td>Ionic concentration</td>
<td>C [mol/kg]</td>
</tr>
<tr>
<td>Mass</td>
<td>M [kg]</td>
</tr>
<tr>
<td>Mass density</td>
<td>ρ [kg/m³]</td>
</tr>
<tr>
<td>Mass fraction in aqueous phase</td>
<td>X [-]</td>
</tr>
<tr>
<td>Mass fraction in gaseous phase</td>
<td>Y [-]</td>
</tr>
<tr>
<td>Mole fraction in aqueous phase</td>
<td>x [-]</td>
</tr>
<tr>
<td>Mole fraction in gaseous phase</td>
<td>y [-]</td>
</tr>
<tr>
<td>Amount of substance</td>
<td>n [mol]</td>
</tr>
<tr>
<td>Molality</td>
<td>b [mol/kg]</td>
</tr>
<tr>
<td>Molar volume</td>
<td>Vm [m³/mol]</td>
</tr>
<tr>
<td>Molar mass</td>
<td>m [kg/mol]</td>
</tr>
<tr>
<td>Pressure</td>
<td>P [Pa]</td>
</tr>
<tr>
<td>Porosity</td>
<td>ϕ [-]</td>
</tr>
<tr>
<td>Salinity</td>
<td>Sal [mol/kg]</td>
</tr>
<tr>
<td>Saturation</td>
<td>S [-]</td>
</tr>
<tr>
<td>Solubility</td>
<td>Sol [mol/kg]</td>
</tr>
<tr>
<td>Temperature</td>
<td>T [°K]</td>
</tr>
<tr>
<td>Universal gas constant</td>
<td>R [J/K/mol]</td>
</tr>
<tr>
<td>Volume</td>
<td>V [m³]</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Superscript</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference state</td>
<td>&lt;0&gt;</td>
</tr>
<tr>
<td>Right after CO₂ injection</td>
<td>&lt;1&gt;</td>
</tr>
<tr>
<td>At equilibrium</td>
<td>&lt;2&gt;</td>
</tr>
<tr>
<td>Ensuing event</td>
<td>&lt;3&gt;</td>
</tr>
<tr>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Equations</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass density of water&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>f(P,T)</td>
</tr>
<tr>
<td>Mass density of brine&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>f(P,T,Sal)</td>
</tr>
<tr>
<td>Mass density of CO₂&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>f(P,T)</td>
</tr>
</tbody>
</table>

**Geochemistry**

- Mineral dissolution (calcite):
  \[ \text{CaCO}_3(s) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}; \quad K_M = 10^{-8.48} \]

<sup>(1)</sup> Bachu and Adams, 2003,  <sup>(2)</sup> Duan and Sun, 2003,  <sup>(3)</sup> Spycher et al., 2003,  <sup>(4)</sup> Sawamura et al., 2007
Figure 3.3  Mass balance formulation for Zone II. Symbols are $M$: Mass, $V$: Volume, $C$: Ionic concentration, $S$: Saturation, $\phi$: Porosity, $\rho$: Density, $P$: Pressure, $T$: Temperature; Subscript – $M$: Mineral, $B$: Brine, $W$: Water ($\text{H}_2\text{O}$), $T$: Total, $S$: Salt (Halite, $\text{NaCl}$); Superscript – <0>: Reference state, <1>: Right after $\text{CO}_2$ injection, <2> At equilibrium, $\text{CO}_2$: In $\text{CO}_2$ phase, $B$: In brine phase, $T$: Total, $S$: Salt (Halite, $\text{NaCl}$).

**Brine and $\text{CO}_2$ density.** The detailed computation of the brine and $\text{CO}_2$ densities is summarized in Chart 3.5. The density of brine increases as $\text{CO}_2$ and mineral dissolution takes place (Figure 3.5-a). The ratio between the increase in density and the initial density is higher when the brine salinity is lower because the solubility of $\text{CO}_2$ decreases with increasing brine salinity (Figure 3.5-b). For conditions occurring at a 1km storage depth...
(\(P\approx 10\text{MPa}\) and \(T\approx 40^\circ\text{C}\)), the maximum increase in brine density is \(~1.2\%\) (computation details in Chart 3.5; Figure 3.5-b – see also Pruess and Zhang, 2008). The denser brine can trigger convection and the dissolution-transport sequence persists.

![Figure 3.4](image1.png)

**Figure 3.4** Acidity in Zone II of a CO\(_2\) geological storage reservoir. Initial pH value in the calcite environment, pH after CO\(_2\) dissolves in the brine, and pH after both CO\(_2\) dissolution and consequent mineral dissolution occur (\(P=10\text{MPa}, T=40^\circ\text{C}\)).

![Figure 3.5](image2.png)

**Figure 3.5** Brine density in Zone II of a CO\(_2\) geological storage reservoir: (a) Change in the brine density and (b) the percentage of change in brine density with respect to the brine salinity (a storage depth~1km; \(P=10\text{MPa}, T=40^\circ\text{C}\)).
Water also dissolves in the CO\(_2\) phase, but its solubility is very low. Figure 3.6 shows the mutual solubility of CO\(_2\) and water, as a function of brine salinity, for typical reservoir conditions (pressure \(P\approx10\text{MPa}\), temperature \(T\approx40^\circ\)). The increase in the density of supercritical CO\(_2\) due to water dissolution is only \(~0.08\%\) for the same \(P-T\) conditions (computation details in Chart 3.5).

![Figure 3.6](image)

*Figure 3.6*  Mutual solubility in Zone II: (a) CO\(_2\) solubility in brine and (b) water solubility in CO\(_2\) with respect to the brine salinity (at Pressure \(P=10\text{MPa}\) and Temperature \(T=40^\circ\)). Results are obtained using formulae from Duan and Sun (2003), Spycher et al. (2003), and Hassanzadeh et al. (2008).

**Porosity.** Minerals are the dominant phase in CO\(_2\) geological storage. The computation of the mineral volumetric change in outlined in Charts 3.6 to 3.7. The maximum decrease in the normalized mineral volume is \(\Delta V_M/V_M\approx0.2\%\), corresponds to zero brine salinity (for a depth~1km - Figure 3.7). This volumetric contraction in the combined solid-fluid mixture may cause geomechanical implications such as change in effective stress and shear failure.
Normalized change in mineral volume $\Delta V_M/V_M^{<1>}$ for Zone II. Note: Maximum CO$_2$ solubility is considered (applied to $P=10$MPa, $T=40$°C).

3.2.3 Zone III – Transition Zone: Brine Displacement

Water saturated CO$_2$ displaces brine in Zone III. The residual brine fraction $V_B^{<1>}/V_T^{<0>}=\phi^{<0>}\cdot S_B$ immediately after CO$_2$ injection is a function of the initial porosity $\phi^{<0>}$ and the residual fluid saturation $S_B$ (Figure 3.3). The evolution of species thereafter can be evaluated based on the initial composition, pressure, and temperature including: total dissolved carbonic acid $H_2CO_3^*$ and other dissolved ions, the mole fraction of water in CO$_2$ ($y_w$), and of CO$_2$ in brine ($x_{CO2}$).

3.2.4 Zone IV – Water Drying Near the Injection Well

The residual brine phase gradually dries when exposed to the continuous influx of dry CO$_2$ near the injection well. Mineral precipitation (e.g., halite and other minerals dissolved in the brine phase) increases the mineral volume fraction. The maximum amount of calcite and halite precipitation are computed from initial equilibrium condition
(refer to Zone II – Computation details in Chart 3.8). Clearly, the increase in the mineral volume fraction after the water dries is more pronounced at higher initial brine saturation $S_B$ and brine salinity $Sal$ [mol/kg-water] (Figure 3.8). The contribution of initial salinity to the precipitated mass prevails over the contribution of dissolved carbonates in most cases because the amount of ions produced from brine acidification and carbonate dissolution is much lower than salts contained in the brine. The maximum increase in mineral volume is 5% for an initial salinity of $Sal=4$mol/kg-water and porosity $\phi^{<0>}=0.286$ under a depth~1km ($P\approx 10$MPa, $T\approx 40^\circ$C). This increase in mineral volume will hinder the injectivity of CO$_2$.

![Figure 3.8](image_url)  
**Figure 3.8** Normalized change in mineral volume $\Delta V_M/V_M^{<1>}$ for Zone IV as water is removed by dry CO$_2$ flushing ($P=10$MPa, $T=40^\circ$C, and initial porosity $\phi^{<0>}=0.286$).
3.3 Hydro-Geomechanical Analyses

Hydro-geomechanical implications associated to geochemical process identified above are addressed next.

3.3.1 Reservoir and CO$_2$ Plume Thickness

The quasi-static lateral spread of the CO$_2$ plume in the absence of geometric or stratigraphic features is determined by the balance between the excess buoyant pressure in the CO$_2$ and the capillary pressure required to invade the storage reservoir. Therefore, the CO$_2$ plume thickness $H_{CO2}$ [m] is a function of the interfacial tension between CO$_2$ and brine $T_s$ [mN/m], the characteristic pore radius in the storage reservoir $R_{pore}$ [m], and the unit weights of CO$_2$ $\gamma_{CO2}$ [N/m$^3$] and brine $\gamma_w$ [N/m$^3$]:

$$H_{CO2} \leq \frac{2T_s}{R_{pore} \left( \gamma_w - \gamma_{CO2} \right)}$$

(1)

For example, the plume thickness cannot exceed $H_{CO2}=2.5m$ in a reservoir with characteristic pore size $R_{pore}=10\mu m$ (assumed: $T_s=50mN/m$ and $\gamma_w-\gamma_{CO2}=4kPa/m$). In general, we can anticipate that the thickness of CO$_2$ plumes in flat layered sediments will be smaller than $H_{CO2}<10m$ in most cases. Thicker accumulations will require geometric traps.

3.3.2 State of Stress

Zone I. Consider a brine-saturated geological basin with an initial effective stress ratio $K_0=\sigma_{h0}/\sigma_{v0}$. Vertical total and effective stresses can be determined from formation depth $z$ [m], unit weight of saturated media $\gamma_{sat}$ [N/m$^3$], and unit weight of brine $\gamma_w$ [N/m$^3$]. Thus, initial value of vertical total stress is $\sigma_{v0}$ [Pa]=$\gamma_{sat}z$, pore-brine pressure is $u_w$ [Pa]=$\gamma_wz$, and vertical effective stress is $\sigma_{v0}'$ [Pa]=$(\gamma_{sat}-\gamma_w)z$. The horizontal effective stress is obtained from initial stress ratio $\sigma_{h0}'$ [Pa]=$K_0(\gamma_{sat}-\gamma_w)z$. Finally, the horizontal total stress is $\sigma_{h0}$ [Pa] = $K_0(\gamma_{sat}-\gamma_w)z+\gamma_wz$. 
Zone II. Convection-sustained mineral dissolution causes a decrease in the horizontal effective stress \( \sigma_{h0}' \rightarrow \sigma_h' \) while the vertical effective stress and pore-brine pressure may remain almost constant \( \sigma_v' \sim \sigma_{v0}' \) and \( u \approx u_w \). Therefore, Mohr circle enlarges leftwards, approaching the Coulomb failure criterion (Figure 3.9-a). The ratio of effective stress \( \sigma_h'/\sigma_v' \) also approaches the active pressure coefficient \( K_a \) (Shin et al., 2008).

Zone III. CO\(_2\) partially displaces brine; the residual brine saturation is \( S_B \) in Zone III. Associated stress changes have been previously explored (Rutqvist and Tsang, 2002; Streit and Hillis, 2004; Rutqvist et al., 2007; Rutqvist et al., 2008; Shi and Durucan, 2009; Soltanzadeh and Hawkes, 2009; Ferronato et al., 2010; Vidal-Gilbert et al., 2010). The vertical effective stress \( \sigma_v' \) and horizontal effective stress \( \sigma_h' \) after CO\(_2\) injection are a function of the unit weight of the saturated medium \( \gamma_{sat} \), the unit weight of brine \( \gamma_w \), depth \( z \), brine saturation \( S_B \), capillary pressure \( u_c = u_{CO2} + u_w \), and the initial stress ratio \( K_0 \); following Bishop’s effective stress approach:

\[
\sigma_v' = \sigma_v - (S_B u_w + (1 - S_B) u_{CO2}) = (\gamma_{sat} - \gamma_w)z - (1 - S_B)u_c
\]  

(2)

\[
\sigma_h' = (\sigma_h - u_w) - (1 - S_B)u_c = K_a(\gamma_{sat} - \gamma_a)z - (1 - S_B)u_c
\]  

(3)

To estimate changes in effective stresses as a result of CO\(_2\) storage, we couple the saturation of brine \( S_B \) with the capillary pressure \( u_c \) (van Genuchten, 1980):

\[
S_B = \left[ 1 + \left( \frac{u_c}{u_a} \right)^{\frac{1}{\lambda}} \right]^{-\lambda}
\]  

(4)

The model parameter \( u_a \) [Pa] is taken as the CO\(_2\) entry pressure, and the parameter \( \lambda \) [-] relates to the sediment pore structure. Finer and denser sediments imply higher \( u_a \) and lower \( \lambda \) values. These simple analytical calculations can provide first-order estimation for changes in the state of stresses as a result of CO\(_2\) injection. Note that this approach might not be applicable for the event of localized displacement such as viscous fingering.

Zone IV. During CO\(_2\) injection, excess pressure is applied to cause the required pressure gradient. The excess injection pressure gradually vanished once injection stops. The
asymptotic CO$_2$ pressure remaining above the brine pressure due to buoyancy and it is maintained by capillarity at the boundaries: $\Delta u=(\gamma_w-\gamma_{CO2})H_R \leq 2\cdot T_s/R_{pore}$, where $H_R$ [m] is the thickness of storage reservoir. Thus, the vertical effective stress in Zone IV $\sigma_v' = \sigma_{v0} - u_w - \Delta u$ is lower than in Zone I. Capillarity pushed the lateral boundary away and the effective horizontal stress in Zone IV decreases by as much as $\Delta \sigma \leq 2\cdot T_s/R_{pore}$, but limited by the stress ratio $\sigma_h'/\sigma_v' \geq K_a$ (note: the formation strains away from the injection well, i.e., $\varepsilon_h>0$). Therefore, Figure 3.9-b shows anticipated stress path in Zone IV.

Figure 3.9  Geomechanical analysis - Change in the state of stresses: (a) in Zone II (Convection of CO$_2$-dissolved brine sustains mineral dissolution, which results in decrease in the horizontal effective stress $\sigma_h'$ while vertical effective stress remains same; ratio of effective stress $\sigma_h'/\sigma_v'$ approaches the active pressure coefficient $K_a$), and (b) in Zone IV (At equilibrium, CO$_2$ pressure is higher than initial pore brine pressure $u_w$ because of buoyancy and capillary effect $\Delta u=(\gamma_w-\gamma_{CO2})H_R \leq 2\cdot T_s/R_{pore}$. The effective horizontal stress decreases by as much as $\Delta \sigma \leq 2\cdot T_s/R_{pore}$, but limited by the stress ratio $\sigma_h'/\sigma_v' \geq K_a$ (note: the formation strains away from the injection well, i.e., $\varepsilon_h>0$).
3.3.3 Implications of Dissolution (Zone II)

Convection. Rayleigh number $Ra$ compares convective and diffusive transport. For a storage reservoir thickness $H_R$ [m] with permeability $k$ [md], diffusivity $D$ [m$^2$/s], and fluid with viscosity $\mu$ [Pa·s] and density difference $\Delta \rho$ [kg/m$^3$] the Rayleigh number is (Hassanzadeh et al., 2007):

$$Ra = \frac{k \cdot \Delta \rho \cdot g \cdot H_R}{\mu \cdot D}$$  \hspace{1cm} (5)

Denser CO$_2$-dissolved brine triggers instability when $Ra > 4\pi^2$ (Kneafsey and Pruess, 2010). Persistent convective flow may sustain CO$_2$ dissolution in brine, its acidification, and ensuing mineral dissolution. The time for convection is $t_{conv}=H_R/v_{conv}$ where the Darcy velocity $v_{conv}$ [m/s] = $k \cdot \Delta \rho \cdot g / \mu$ can be computed from the driving gradient and the hydraulic conductivity:

$$t_{conv} = \frac{\mu \cdot H_R}{k \cdot \Delta \rho \cdot g}$$  \hspace{1cm} (6)

For a typical storage reservoir with permeability $k$=200md, thickness $H_R$=10m, and density difference $\Delta \rho$=20kg/m$^3$, the Rayleigh number is $Ra=4.4 \times 10^3 > 4\pi^2$, convective fingering will take place, and convective fingers will touch the bottom of the reservoir after $t_{convection}\approx 9$ years. The mineral flux rate due to convection is in the order of $\Delta V_M \cdot \rho_M / t_{conv}$. Therefore, while the mineral dissolution may be low, short convection time may cause substantial mineral flux rate in Zone II.

Compaction-Driven Shear Failure. Convection-sustained mineral dissolution causes settlement and change in the state of stress under constant overburden stress conditions. In particular, the ratio between horizontal effective stress to vertical effective stress at zero-lateral strain $K_0=\sigma_h'/\sigma_v'$ (Jaky, 1944; Mayne and Kulhawy, 1982) may decrease as a result of mineral dissolution, and cause the system to meet the Rankine active failure condition $K_a$ (Shin and Santamarina, 2009; Shin et al., 2010; Cha, 2012). In fact, mineral dissolution may cause shear failure within the reservoir in Zone II (Figure 3.1).
Caprock Bending Failure. In addition, convective flow and sustained dissolution may result in an poorly supported span beneath the caprock (Figure 3.10-a). Let’s consider a uniformly-distributed load on a 2D beam overlying an elastic foundation (Hetényi and Michigan, 1946). The maximum tensile stress $\sigma_{\text{max}}$ [kPa] that develops at the bottom of the caprock in the middle of the softer span is a function of the average density of the overlying layer $\rho_c$ [kg/m$^3$], the depth of caprock $z_c$ [m], the thickness $H_c$ [m] and yield strength of the caprock $\sigma_y$ [kPa], the length of the free span $L_{\text{free}}$ [m]. The characteristic length scale of the system is $\lambda$ [m$^{-1}$] = $\frac{4}{k_r} \sqrt{\frac{k_r}{4E_cI_c}}$, where $k_r$ [kPa] is the stiffness of the reservoir, $E_c$ [kPa] the Young’s modulus of caprock, and $I_c$ [m$^4$] the moment of inertia of caprock. Then, assuming lateral boundaries at infinite, the maximum tensile stress in the caprock is (Hetényi and Michigan, 1946):

$$\frac{\sigma_{\text{max}}}{\sigma_y} = 3\pi_1\pi_2 \left( \frac{1}{4} \pi_2 + \frac{6 - (\pi_2 \pi_3)^2}{6\pi_3 (2 + \pi_2 \pi_3)} \right),$$

where $\pi_1 = \frac{\rho_c g z_c}{\sigma_y}$, $\pi_2 = \frac{L_{\text{free}}}{H_c}$, and $\pi_3 = \frac{\lambda H_c}{H_c}$. (7)

Figures 3.10-b and c suggest the maximum free span length to avoid bending failure of the caprock for conditions that resemble the Frio project (USA; Doughty et al., 2008) and the Weyburn project (Canada; White et al., 2004). Results suggest that the free span cannot exceed 20% of the caprock thickness, $L_{\text{free}}/H_c \leq 0.2$. 
3.3.4 Porosity and Permeability Change due to Dissolution (Zone II) and Precipitation (Zone IV)

Mineral precipitation decreases porosity and lowers the fluid permeability. The Kozeny-Carman formula defines a power-law relationship between normalized porosity $\varphi/\varphi_0$ and normalized permeability $k/k_0$ (Carman, 1956): $k/k_0 = (\varphi/\varphi_0)^{\alpha}$ where $\varphi_0$ and $k_0$ are initial values for porosity and permeability. The analysis of Zone IV (the complete
evaporation of water) shows that the mineral volume can increase by \( \leq 5\% \). The exponent \( \alpha \) has been reported to be at least larger than \( \alpha \geq 3 \) (e.g., \( \alpha \sim 3.4 \) from Wellman et al., 2003; \( \alpha = 5 \sim 6 \) from Mohamed and Nasr-El-Din, 2012). A value of \( \alpha = 3 \) yields a 16\% decrease in permeability. Note that the power law represents the average value of porosity and permeability. Since a geological formation consists of heterogeneous porous media, the reduction in permeability could be locally different.

For a more rigorous analysis, consider a porous medium where CO\(_2\) breaks through from one end to the other while residual brine remains (Figure 3.11-a). We simplify this structure into a parallel arrangement in which one phase is CO\(_2\) and the other is brine (Figure 3.11-b). For this arrangement, the maximum attainable CO\(_2\) permeability \( k_{CO2} \) [m\(^2\)] is:

\[
k_{CO2} = S_{CO2} \cdot k_c + (1 - S_{CO2}) \cdot k_f \tag{8}
\]

where \( k_c \) is the permeability of CO\(_2\) layer and \( k_f \) the permeability of brine layer in Figure 3.11-b. Salt precipitation is likely to occur mostly in the brine layer, so the permeability of the brine layer will become \( k_f^{m} \) (computed using Kozeny-Carman formula). Then, the maximum attainable CO\(_2\) permeability is (Figure 3.11-c):

\[
k_{CO2}^{m} = S_{CO2} \cdot k_c + (1 - S_{CO2}) \cdot k_f^{m} \tag{9}
\]

Figure 3.11-d suggests that the decrease in the maximum attainable CO\(_2\) permeability is minor. Indeed, CO\(_2\) will invade and displace brine from the larger interconnected pores and then dry the water from residual brine patches; salt precipitation in the pore space of these patches will not significantly decrease the maximum attainable CO\(_2\) permeability. In summary, salt precipitation will not cause clogging if continuous pumping occurs (i.e., channels remain open), and only a minor decrease in CO\(_2\) permeability is anticipated.

Mineral dissolution increases porosity and enhances the fluid permeability in Zone II. A similar analysis predicts a very small increase in permeability <1\% when the normalized decrease in the mineral volume is \( \sim 0.2\% \). However, convection-sustained
mineral dissolution could cause more pronounced changes in permeability within the storage time.

Figure 3.11  Change in the permeability of CO$_2$ after salt precipitation. (a) CO$_2$ invases and residual brine in the pore space. (b) Simplification into a parallel arrangement. (c) Original evolution of CO$_2$ permeability $k_{CO2}$ with respect to CO$_2$ saturation $S_{CO2}$ and modified CO$_2$ permeability after salt precipitation. and (d) Ratio of modified maximum attainable CO$_2$ permeability $k_{CO2}^m = S_{CO2} \cdot k_c + (1-S_{CO2}) \cdot k_f^m$ to original maximum attainable CO$_2$ permeability $k_{CO2} = S_{CO2} \cdot k_c + (1-S_{CO2}) \cdot k_f$ with respect to the initial CO$_2$ saturation $S_{CO2}$ right before salt precipitation takes place, assuming parallel arrangement (solid line), and lower boundary when assuming series arrangement (dotted line) ($k_c = 10 \cdot k_f$; $k_f^m$ is obtained from Kozeny-Carman formula with exponent $\alpha = 3$ and normalized porosity change $\phi/\phi_0 = 0.95$).
3.4 Conclusions

Four different zones are identified in the storage reservoir around injection wells. Mass balance calculations show the extent of mineral dissolution and precipitation. Density changes, fluid convection, and hydro-geomechanical analyses lead to the following conclusions.

- The formation water is under-saturated in terms of evaporate minerals such as halite and anhydrite and either under-saturated or in equilibrium with other minerals in the formation.
- In leveled sediments (i.e., no geometric trap), the CO$_2$ pool thickness may be limited by lateral capillary trapping rather than by the sediment layer thickness. Typical pools will be only a few meters thick in the absence of geometric traps.
- Brine densifies as CO$_2$ and mineral dissolve. Density changes are more pronounced when the brine salinity is low; the maximum increase in brine density is ~1.2%. The maximum decrease in mineral volume at equilibrium is $\Delta V_M/V_M \leq 0.2\%$ for the worst zero brine salinity case. The associated increase in permeability is <1%.
- The continuous influx of dry CO$_2$ dries the residual brine near the wellbore. The precipitation of secondary minerals increases the mineral volume by a maximum of 5%. A minor decrease in CO$_2$ permeability is anticipated.
- The time for convection may be as low as few years in pervious reservoirs. Short convection times will aggravate dissolution consequence in relatively short storage time. Convection-sustained mineral dissolution in the proximity of fresh brine causes a decrease in the horizontal effective stress $\sigma_{h0} \rightarrow \sigma_{ha}'$. Either compaction-driven shear failure (system satisfies the Rankine active failure condition) or caprock bending failure (gradual development of a poorly supported span beneath the caprock) may occur as a result of mineral dissolution. In particular, the unsupported free span of the caprock cannot exceed 20% of the caprock thickness.
Computation Charts

Chart 3.1 Initial pore fluid composition (Zone I)

Only mineral and brine exists in the far-field Zone I, Volume terms are:

• Volume of mineral: $V_M^{<0>} = (1-\phi^{<0>}) \cdot V_T^{<0>}$ (C.1)

• Volume of brine: $V_B^{<0>} = \phi^{<0>} \cdot V_T^{<0>}$ (C.2)

where $\phi^{<0>}$ is the initial porosity, and $V_T^{<0>}$ is total volume.

• Concentration of salt NaCl in brine: $b_{NaCl}^{<0>}$ [mol/kg-water]$=Sal$ (C.3)

where salinity is preset between $0 \leq Sal \leq 6$ [mol/kg-water]

• Concentration of calcite in brine: $b_{Ca}^{<0>}$ [mol/kg-water]$=\sqrt{K_M}=10^{-4.24}$ (C.4)

• Mass of brine: $M_B^{<0>}=\rho_B^{<0>} \cdot \phi^{<0>} \cdot V_T^{<0>}$ (C.5)

Brine density $\rho_B^{<0>}$ is computed as a function of pressure, temperature, and dissolved species (expressions in Bachu and Adams, 2003):

• Water density: $\rho_w^{<0>}$ [g/cm$^3$] = $1+10^{-5} \cdot (-80T - 3.3T^2 + 0.00175T^3 + 489P$

\[ - 2TP + 0.161T^2 P - 1.3 \cdot 10^{-5} T^3 P - 0.333 P^2 - 0.002 TP^2 \] (C.6)

• Brine density: $\rho_B^{<0>}$ [g/cm$^3$] = $\rho_w^{<0>} + C_{SM} \cdot (0.668 + 0.44C_{SM} + 10^{-6} \cdot (300P$

\[ - 2400 PC_{SM} + T \cdot (80 - 3T - 3300 C_{SM} - 13 P + 47 PC_{SM}) ) \] (C.7)

where temperature $T$ in [°C], pressure $P$ in [MPa], and Concentration of dissolved species (salt+calcite) $C_{SM}$ in ppt (parts per thousand).

• Mass of mineral = Solid phase mineral + Mineral dissolved in brine

\[ M_M^{<0>} = M^{<0,M>} + M^{<0,B>} = \rho_M^{<0>} \cdot (1-\phi^{<0>}) \cdot V_T^{<0>} + m_M \cdot b_{Ca}^{<0>} \cdot \rho_B^{<0>} \cdot \phi^{<0>} \cdot V_T^{<0>} \] (C.8)

where the mineral mass density is $\rho_M^{<0>}=2700$kg/m$^3$, and the mineral molar mass is $m_M=100$g/mol.

• Mass of salt dissolved in brine: $M_S^{<0,B>} = Sal \cdot \rho_B^{<0>} \cdot \phi^{<0>} \cdot V_T^{<0>}$ (C.9)
Chart 3.2 Zone II: Before equilibrium

There are three phases. The corresponding volumes are:

- **Volume of mineral:** \( V_M^{<1>} = (1 - \phi^{<0>}) \cdot V_T^{<0>} \)  
  \[ \text{(C.10)} \]
- **Volume of CO\(_2\):** \( V_{CO2}^{<1>} = \phi^{<0>} \cdot (1 - S_B) \cdot V_T^{<0>} \)  
  \[ \text{(C.11)} \]
- **Volume of residual brine:** \( V_B^{<1>} = \phi^{<0>} \cdot S_B \cdot V_T^{<0>} \)  
  \[ \text{(C.12)} \]

where \( S_B \) denotes residual saturation of brine.

The mass of CO\(_2\), brine, mineral, and salt NaCl follow:

- **Mass of CO\(_2\):** \( M_{CO2}^{<1>} = \rho_{CO2}^{<0>} \cdot \phi^{<0>} \cdot (1 - S_B) \cdot V_T^{<0>} \)  
  \[ \text{(C.13)} \]

where CO\(_2\) density \( \rho_{CO2}^{<0>} \) is computed from formulae by Duan and Sun (2003).

- **Mass of brine:** \( M_B^{<1>} = \rho_B^{<0>} \cdot \phi^{<0>} \cdot S_B \cdot V_T^{<0>} \)  
  \[ \text{(C.14)} \]

- **Mass of mineral**
  \[ M_M^{<1>} = M_M^{<1,M>} + M_M^{<1,B>} = \rho_M^{<0>} \cdot (1 - \phi^{<0>}) \cdot V_T^{<0>} \cdot \rho_B^{<0>} \cdot \phi^{<0>} \cdot S_B \cdot V_T^{<0>} \]  
  \[ \text{(C.15)} \]

- **Mass of salt:** \( M_S^{<1,B>} = Sal \cdot \rho_B^{<0>} \cdot \phi^{<0>} \cdot S_B \cdot V_T^{<0>} \)  
  \[ \text{(C.16)} \]

- **Concentration of salt NaCl in brine:** \( b_{NaCl}^{<1>} \) \([\text{mol/kg-water}]=Sal\)  
  \[ \text{(C.17)} \]

- **Concentration of mineral in brine:** \( b_{Ca}^{<1>} \) \([\text{mol/kg-water}]=\sqrt{K_M} \times 10^{-4.24}\)  
  \[ \text{(C.18)} \]

Chart 3.3 Dissolution of supercritical CO\(_2\)

- The solubility of supercritical CO\(_2\) in brine \( Sol_{CO2} \) is obtained from the semi-empirical formulae proposed by Duan and Sun (2003):
  \[ Sol_{CO2} = \exp \left[ \ln(y_{CO2} \cdot P) - \frac{\mu_{CO2}^{(0)}}{RT} + \ln \Phi_{CO2} - \sum_c 2 \lambda_{CO2,c} \cdot n_c - \sum_a 2 \lambda_{CO2-a} \cdot n_a - \sum_c \sum_a \zeta_{CO2,c-a} \cdot n_c \cdot n_a \right] \]  
  \[ \text{(C.19)} \]

where symbol \( \mu \) represents chemical potential, symbols \( \lambda \) and \( \zeta \) denote dimensionless standard chemical potentials, and subscript \( c \) and \( a \) mean cations and anions, respectively. All expressions are described in Duan and Sun (2003).
• Concentration of total dissolved CO$_2$:

\[ b^{>}_{CO2} \text{ [mol/kg - water]} = \min \left( Sol_{CO2}, \frac{M^{<>}_{CO2} / m_{CO2}}{M_B^{<>}} \right) \]  

where the molar mass of CO$_2$ is $m_{CO2}=44 \text{g/mol}$. We compare $Sol_{CO2}$ with the present concentration of CO$_2$ to account for the maximum amount of dissolvable CO$_2$.

• Concentration of hydrogen ion H$^+$:

\[ b^<_{H} \text{ [mol/kg-water]} = \sqrt{(K_{a1} \cdot b^{<>}_{CO2})}; \text{ acidity constant } K_{a1}=10^{-6.35} \]  

(C.21)

• pH=$-\log b^<_{H}$  

(C.22)

**Chart 3.4 Mineral dissolution and concentrations of species at equilibrium**

• The concentration of dissolved CO$_2$ $b_{CO2}^{<>}$ and the presence of calcite CaCO$_3$ are input to PHREEQC software (Parkhurst et al., 1999) to compute chemical reactions. The output values are the concentrations of species such as $H_2CO_3^*$, $H^+$, $Ca^{2+}$, $HCO_3^-$, and $CO_3^{2-}$ at equilibrium - $b_{CO2}^{<2>}$, $b_H^{<2>}$, $b_{Ca}^{<2>}$, $b_{HCO3}^{<2>}$, and $b_{CO3}^{<2>}$ in [mol/kg-water].

• pH=$-\log b^{<2>}_{H}$  

(C.23)

• The mass fraction of CO$_2$ $X_{CO2}$ in the aqueous brine phase:

\[ X_{CO2} = \frac{b^{<2>}_{CO2} \cdot m_{CO2}}{b_{CO2}^{<2>} \cdot m_{CO2} + 1 + Sal \cdot m_S + b^{<2>}_{Ca} \cdot m_M} \]  

(C.24)

where the molar mass of salt NaCl is $m_S=58 \text{g/mol}$.

• The mass fraction of brine $X_B$ in the aqueous brine phase:

\[ X_B = \frac{1 + Sal \cdot m_S}{b_{CO2}^{<2>} \cdot m_{CO2} + 1 + Sal \cdot m_S + b^{<2>}_{Ca} \cdot m_M} \]  

(C.25)

• The mass fraction of mineral $X_M$ in the aqueous brine phase:

\[ X_M = \frac{b^{<2>}_{Ca} \cdot m_M}{b_{CO2}^{<2>} \cdot m_{CO2} + 1 + Sal \cdot m_S + b^{<2>}_{Ca} \cdot m_M} \]  

(C.26)
The mole fraction of water \( y_w \) in the CO\(_2\) phase:

\[
y_w = \frac{K_w^0 (1 - x_{CO2})}{\Phi_w P} \exp \left( \frac{(P - P^0) V_w}{RT} \right)
\]  
(C.27)

Equation C.25 is proposed by Spycher et al. (2003). Detailed calculations of molar fraction \( y_w \) can be found in Spycher et al. (2003) and Hassanzadeh et al., 2008).

The molar fraction of CO\(_2\) \( y_{CO2} \) in the supercritical CO\(_2\) phase:

\[
y_{CO2} = 1 - y_w
\]  
(C.28)

The mass fraction of CO\(_2\) \( Y_{CO2} \) in the supercritical CO\(_2\) phase:

\[
Y_{CO2} = \frac{y_{CO2} \cdot m_{CO2}}{y_{CO2} \cdot m_{CO2} + y_w \cdot m_w}
\]  
(C.29)

where the molar mass of water is \( m_w = 18 \text{g/mol} \).

The mass fraction of water \( Y_w \) in the supercritical CO\(_2\) phase:

\[
Y_w = \frac{y_w \cdot m_w}{y_{CO2} \cdot m_{CO2} + y_w \cdot m_w}
\]  
(C.30)

**Chart 3.5 Density estimation**

Density of brine: \( \rho_B^{<CO2>} = \left( \frac{X_w^{W}}{\rho_B^{W}} + \frac{X_{CO2}^{W}}{\rho_{CO2}^{W}} + \frac{X_M^{W}}{\rho_M^{W}} \right)^{-1} \) (ref: Spycher et al., 2003)  
(C.31)

\( \rho_{CO2}^{W} \) denotes density of CO\(_2\) dissolved in water: \( \rho_{CO2}^{W} = \frac{m_{CO2}}{V_{\phi}} \)  
(C.32)

\( V_{\phi} \): apparent molar volume of CO\(_2\) dissolved in water (see - Garcia, 2001).

For simplicity, density of minerals dissolved in water is \( \rho_M^{W} = \rho_M^{<CO2>} \).

Density of CO\(_2\): \( \rho_{CO2}^{<CO2>} = \left( \frac{Y_{CO2}^{W}}{\rho_{CO2}^{W}} + \frac{Y_w^{W}}{\rho_w^{W}} \right)^{-1} \)  
(C.33)

\( \rho_w^{CO2} \) denotes density of water dissolved in CO\(_2\): \( \rho_{CO2}^{W} = \frac{m_w}{V_{w\phi}} \)  
(C.34)

\( V_{w\phi} = 18.1 \text{cm}^3/\text{mol} \): average value for the partial molar volume of water (Hassanzadeh et al., 2008).
Chart 3.6 Mass balance of CO$_2$ and brine

- Mass of CO$_2$ dissolved in brine $M_{CO2}^{<2,B>}$: $M_{CO2}^{<2,B>} = X_{CO2} \cdot M_B^{<2>}$ (C.35)
- Mass of CO$_2$ in CO$_2$ $M_{CO2}^{<2,CO2>}$: $M_{CO2}^{<2,CO2>} = Y_{CO2} \cdot M_{CO2}^{<2>}$ (C.36)
- Mass of water dissolved in CO$_2$ $M_W^{<2,CO2>}$: $M_W^{<2,CO2>} = Y_W \cdot M_{CO2}^{<2>}$ (C.37)
- Mass of water in brine $M_B^{<2,B>}$: $M_B^{<2,B>} = X_B \cdot M_B^{<2>}$ (C.38)

where $M_{CO2}^{<2>}$ denotes the total mass of CO$_2$ at equilibrium, and $M_B^{<2>}$ the total mass of brine at equilibrium.

- Mass conservation of CO$_2$: $M_{CO2}^{<2>} = M_{CO2}^{<2,B>} + M_{CO2}^{<2,CO2>}$ (C.39)
- Mass conservation of brine: $M_B^{<2>} = M_B^{<2,B>} + M_W^{<2,CO2>}$ (C.40)
- Total mass of brine $M_B^{<2>}$: $M_B^{<2>} = \frac{\rho_{CO2}^{<0>} \cdot \phi^{<0>} \cdot (1 - S_B) \cdot V_T^{<0>} \cdot Y_B - \rho_B^{<0>} \cdot \phi^{<0>} \cdot S_B \cdot V_T^{<0>} \cdot Y_{CO2}}{Y_W \cdot X_{CO2} - Y_{CO2} \cdot X_B}$ (C.41)
- Total mass of CO$_2$ $M_{CO2}^{<2>}$: $M_{CO2}^{<2>} = \frac{\rho_{CO2}^{<0>} \cdot \phi^{<0>} \cdot (1 - S_B) \cdot V_T^{<0>} \cdot X_B - \rho_B^{<0>} \cdot \phi^{<0>} \cdot S_B \cdot V_T^{<0>} \cdot X_{CO2}}{X_B \cdot Y_{CO2} - X_{CO2} \cdot Y_W}$ (C.42)

Equations C.40 and C.41 are derived by rearranging Equations C.11~12 and C.35~40.

- Total mass of mineral $M_M^{<2>}$: $M_M^{<2>} = M_M^{<2>} - m_M \cdot (b_{Ca}^{<2>} - b_{Ca}^{<0>}) \cdot M_B^{<2>}$ (C.43)
- Total mass of salt $M_S^{<2,B>}$: $M_S^{<2,B>} = S_{al} \cdot \rho_B^{<0>} \cdot \phi^{<0>} \cdot S_B \cdot V_T^{<0>}$ (C.44)

Chart 3.7 Volume changes

- Volume of brine $V_B^{<2>}$: $V_B^{<2>} = \frac{M_B^{<2>}}{\rho_B^{<2>}}$ (C.45)
- Volume of CO$_2$ $V_{CO2}^{<2>}$: $V_{CO2}^{<2>} = \frac{M_{CO2}^{<2>}}{\rho_{CO2}^{<2>}}$ (C.46)
- Volume of mineral $V_M^{<2>}$: $V_M^{<2>} = \frac{M_M^{<2>}}{\rho_M^{<2>}}$ (C.47)
Chart 3.8 Mineral precipitation (Zone IV)

- Amount of calcium ion $Ca^{2+}$ in brine $n_{Ca}^{\prec}\prec$ [mol] = $D_{Ca}^{\prec}\prec \cdot M_{B}^{\prec}\prec$ (C.48)

- Amount of salt $NaCl$ in brine $n_{S}^{\prec}\prec$ [mol] = $M_{S}^{\prec\prec}$ (C.49)

If we assume all $Ca^{2+}$ and $NaCl$ species precipitate as a result of complete evaporation, a corresponding volume increase $\Delta V$ is:

- Precipitation of calcite $\Delta V_M$: $\Delta V_M = n_{Ca}^{\prec}$ $\cdot Vm_M$ (C.50)

- Precipitation of halite $\Delta V_S$: $\Delta V_S = n_{S}^{\prec}$ $\cdot Vm_S$ (C.51)

where the molar volume of calcite is $Vm_M = 3.7\times10^{-5}$ m$^3$/mol, and the molar volume of halite is $Vm_S = 2.7\times10^{-5}$ m$^3$/mol.

- Increase in the mineral volume $\Delta V_M^{\prec\prec}$: $\Delta V_M^{\prec\prec} = \Delta V_M + \Delta V_S$ (C.52)
CHAPTER 4
CO₂ GEOLOGICAL STORAGE: PORE-SCALE REACTIVE FLUID TRANSPORT (ROCK JOINT AND PORES)

4.1 Introduction

Quality of life is correlated with energy consumption. The anticipated increase in both quality of life and energy demand in the coming decades will largely rely on fossil fuels because of readily available reserves, low cost, prevailing infrastructure, and insufficient energy production from renewable sources (EIA, 2010; Espinoza et al., 2011; Pasten and Santamarina, 2012). Currently, 90% of the world’s consumption and more than 85% of the energy consumed in the USA comes from fossil fuels (DOE, 2010). Fossil fuel combustion produces CO₂. When released into the atmosphere, CO₂ acts as a greenhouse gas and it is believed to be a main cause for global warming (IPCC, 2005). In this context, carbon capture and geologic sequestration emerges as an important alternative to mitigate global warming.

Supercritical CO₂ conditions are preferred to minimize CO₂ storage volume (temperature $T > 304.1$K and pressure $P > 7.38$MPa; Span and Wagner, 1996; Kaldi and Gibson-Poole, 2008). The injection of supercritical CO₂ triggers: advection of CO₂ (Saripalli and McGrail, 2002; Nordbotten et al., 2005; Ennis-King and Paterson, 2007), buoyancy in response to CO₂-brine density difference (Bachu and Adams, 2003; Bielinski et al., 2008; Okwen et al., 2010), convection of CO₂-dissolved water (Weir et al., 1996; Riaz et al., 2006; Hassanzadeh et al., 2007; Kneafsey and Pruess, 2010), diffusion and dissolution of CO₂ into the water phase (Gaus et al., 2005; Berne et al., 2010; Li et al., 2011), viscous fingering of CO₂ (Homsy, 1987; Fenghour et al., 1998; Cinar et al., 2007), capillary trapping of the immiscible CO₂ by the water-saturated
porous formation (Juanes et al., 2006; Kopp et al., 2009; Saadatpoor et al., 2009), and reactive fluid transport due to the acidification of water following CO$_2$ dissolution (Li et al., 2008; Solomon et al., 2008; Szymczak and Ladd, 2009; Figure 4.1). We note that reactive fluid transport through a porous medium generates positive feedback and may lead to the formation of wormholes (Golfier et al., 2002).

![Figure 4.1](image.png)

**Figure 4.1** Schematic illustration of the CO$_2$ geological storage and consequent CO$_2$ invasion and flow of CO$_2$-dissolved fluid through rock joints/pores. Reactant species such as hydrogen ions $H^+$ and aqueous carbon dioxide $CO_2(aq)$ cause chemical reactions to occur at mineral surfaces as reactive fluid flows through rock joints/pores.
Preferred formations for CO$_2$ geological storage are either sandstones or carbonates (Gale, 2004; Dooley et al., 2006). Previous studies show that the overall amount of surface reaction between carbonates and acidified water is smaller than that between sandstones and the solute, but the reaction rate between carbonates and acidified fluid is much faster than that for sandstones (Stumm et al., 1996; Gunter et al., 2000; Gaus et al., 2005).

Injection could be engineered to prevent or minimize some of the negative consequences of CO$_2$ geological storage. However, a proper pore-scale understanding of reactive fluid transport is required when fluids are rich in total carbonic acid $H_2CO_3$* and hydrogen ions $H^+$. The kinetics of injected CO$_2$ is analyzed first followed by 2-D simulations of CO$_2$-dissolved fluid injection in a pore.

### 4.2 CO$_2$ Injection: Kinetic Rates

Injected carbon dioxide CO$_2$ dissolves in the formation water or brine to sequentially form aqueous carbon dioxide $CO_2(aq)$ and carbonic acid $H_2CO_3$, which consequently dissociates into bicarbonate ions $HCO_3^-$ and hydrogen ions $H^+$ (Stumm et al., 1996; IPCC, 2005):

\[
CO_2(g) \overset{k_e}{\leftrightarrow} CO_2(aq) ; \quad K_H = \frac{k_e}{k_{a_2}} = 10^{-1.47} \quad \text{(Henry’s constant)} \tag{1}
\]

\[
CO_2(aq) + H_2O \overset{k_{CO_2}}{\leftrightarrow} H_2CO_3 ; \quad K = \frac{k_{H_2CO_3}}{k_{CO_2}} \tag{2}
\]

\[
H_2CO_3 \overset{k_{fast}}{\leftrightarrow} HCO_3^- + H^+ ; \quad K_{H_2CO_3} = \frac{k_{12}}{k_{21}} \tag{3}
\]

where capital $K$ represents an equilibrium constant for each chemical reaction. The hydration reaction $CO_2(aq)+H_2O\rightarrow H_2CO_3$ (Equation 2) is first order with respect to aqueous $CO_2(aq)$ (Stumm et al., 1996). Likewise, dehydration $H_2CO_3\rightarrow CO_2(aq)+H_2O$
(Equation 2) is first order with respect to carbonic acid $H_2CO_3$. Assuming that the reaction between carbonic acid and bicarbonate ion is linear, the following kinetic laws are obtained for the chemical reactions above:

$$\frac{d[CO_{2(g)}]}{dt} = -k_\text{g}[CO_{2(g)}] + k_\text{aq}[CO_{2(aq)}]$$  \hspace{1cm} (4)  

$$\frac{d[CO_{2(aq)}]}{dt} = k_\text{g}[CO_{2(g)}] - k_\text{aq}[CO_{2(aq)}] - k_\text{CO}_2[CO_{2(aq)}] + k_{H2CO3}[H_2CO_3]$$  \hspace{1cm} (5)  

$$\frac{d[H_2CO_3]}{dt} = k_\text{CO}_2[CO_{2(aq)}] - k_{H2CO3}[H_2CO_3] - k_{12}[H_2CO_3] + k_{21}[HCO_3^-][H^+]$$  \hspace{1cm} (6)  

$$\frac{d[H^+]}{dt} = \frac{d[HCO_3^-]}{dt} = k_{12}[H_2CO_3] - k_{21}[HCO_3^-][H^+]$$  \hspace{1cm} (7)  

where square brackets around species name indicates concentrations of the species. The reaction rate constants for hydration and dehydration reactions are: $k_{CO2} = 0.04s^{-1}$ at 25°C with the activation energy $E_a = 15kcal/mol$, and $k_{H2CO3} = 20s^{-1}$ at 25°C with $E_a = 16kcal/mol$ (Stumm et al., 1996). The rate constants $k_{CO2}$ and $k_{H2CO3}$ permit the calculation of the equilibrium constant $K$ (Equation 2). Then, we can obtain equilibrium constant $K_{H2CO3}$ from $K$ (Stumm et al., 1996):

$$K_{H2CO3} = K_1(1 + K)$$  \hspace{1cm} (8)  

$K_1$ denotes the first acidity constant for the reaction in which $H_2CO_3^*$ dissociates to bicarbonate and hydrogen ion (the asterisk denotes combining both aqueous carbon dioxide and carbonic acid; Stumm et al., 1996). The value of the acidity constant is $K_1 \approx 10^{-6.35}$ under standard conditions ($T=25°C$ and $P=0.1MPa$). The rate constants are: $k_{12} \approx 10^7s^{-1}$ at ~40°C for the dissociation of carbonic acid (Zhang, 2008), $k_{21} = k_{12}/K_{H2CO3}$ for the reversed reaction (Equation 3), $k_\text{g} \approx 5x10^{-3}s^{-1}$ at 40°C for the dissolution of gaseous carbon dioxide ($4.6x10^{-3}s^{-1}$ at 25°C; Sposito, 1994), and $k_\text{aq} = k_\text{g}/K_H$ for the reversed reaction (Equation 1). These rate constants are summarized in Table 4.1.
### Table 4.1 Parameters used in simulations

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$5 \times 10^3 \text{ s}^{-1}$</td>
<td>Rate constant of CO$_2$(g) → CO$_2$(aq)</td>
</tr>
<tr>
<td>$k_{a1}$</td>
<td>$k_g / K_H$</td>
<td>Rate constant of CO$_2$(g) ↔ CO$_2$(aq)</td>
</tr>
<tr>
<td>$k_{CO2}$</td>
<td>$0.135 \text{ s}^{-1}$</td>
<td>Rate constant of CO$_2$(aq) → H$_2$CO$_3$</td>
</tr>
<tr>
<td>$k_{H2CO3}$</td>
<td>$72.982 \text{ s}^{-1}$</td>
<td>Rate constant of H$_2$CO$_3$ ↔ H$_2$CO$_3$</td>
</tr>
<tr>
<td>$k_{12}$</td>
<td>$10^3 \text{ s}^{-1}$</td>
<td>Rate constant of H$_2$CO$_3$ → H$^+$ + HCO$_3^-$</td>
</tr>
<tr>
<td>$k_{21}$</td>
<td>$4.1 \times 10^{10} \text{ s}^{-1}$</td>
<td>Rate constant of H$_2$CO$_3$ ↔ H$^+$ + HCO$_3^-$</td>
</tr>
<tr>
<td>$K_H$</td>
<td>$10^{-1.47}$</td>
<td>Henry’s constant</td>
</tr>
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</table>

#### Calcite fracture plane

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[H^+]_{\text{inlet}}$</td>
<td>$10^6 \text{ mol/L}$ to $10^3 \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[H_2CO_3^{aq}]_{\text{inlet}}$</td>
<td>$10^{-3} \text{ mol/L}$ to 1 mol/L</td>
<td></td>
</tr>
<tr>
<td>$[Ca^{2+}]_{\text{inlet}}$</td>
<td>$1.36 \times 10^3 \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[HCO_3^-]_{\text{inlet}}$</td>
<td>$6.68 \times 10^4 \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[OH^-]_{\text{inlet}}$</td>
<td>$1.50 \times 10^{-11} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[Cl^-]_{\text{inlet}}$</td>
<td>$2.72 \times 10^{-3} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[H^+]_{\text{initial}}$</td>
<td>$1.0 \times 10^{-8} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[H_2CO_3^{aq}]_{\text{initial}}$</td>
<td>$1.0 \times 10^{-8} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[Ca^{2+}]_{\text{initial}}$</td>
<td>$1.59 \times 10^{-3} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[HCO_3^-]_{\text{initial}}$</td>
<td>$4.47 \times 10^{-4} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[OH^-]_{\text{initial}}$</td>
<td>$1.0 \times 10^{-6} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[Cl^-]_{\text{initial}}$</td>
<td>$2.72 \times 10^{-3} \text{ mol/L}$</td>
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#### Anorthite fracture plane

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[H^+]_{\text{initial}}$</td>
<td>$1.0 \times 10^{-8} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[H_2CO_3^{aq}]_{\text{initial}}$</td>
<td>$1.0 \times 10^{-8} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[Ca^{2+}]_{\text{initial}}$</td>
<td>$4.47 \times 10^{-4} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[Cl^-]_{\text{initial}}$</td>
<td>$4.35 \times 10^{-3} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[Al^{3+}]_{\text{initial}}$</td>
<td>$3.51 \times 10^{-8} \text{ mol/L}$</td>
<td></td>
</tr>
<tr>
<td>$[H_2SiO_4^{aq}]_{\text{initial}}$</td>
<td>$9.67 \times 10^{-13} \text{ mol/L}$</td>
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</tbody>
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### Additional Parameters

<table>
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<tr>
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_0$</td>
<td>$10^3 \text{ cm/s}$</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>$10^3 \text{ Pa.s}$</td>
<td>Viscosity of fluid</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>$1100 \text{ kg/m}^3$</td>
<td>Density of fluid</td>
</tr>
<tr>
<td>$S_s$</td>
<td>$0.06 \text{ m}^2/\text{g}$</td>
<td>Specific surface of calcite and anorthite</td>
</tr>
<tr>
<td>$M_m$</td>
<td>$100 \text{ g/mol}$</td>
<td>Molar mass of calcite</td>
</tr>
<tr>
<td>$V_m$</td>
<td>$3.7 \times 10^8 \text{ m}^3/\text{mol}$</td>
<td>Molar volume of calcite</td>
</tr>
<tr>
<td>$D$</td>
<td>$2.0 \times 10^8 \text{ m}^2/\text{s}$</td>
<td>Average diffusion coefficient for all species</td>
</tr>
</tbody>
</table>

(Rate constants are computed for temperature $T=40^\circ C$ from: (1) Sposito, 1994, (2) Stumm et al., 1996, (3) Zhang, 2008; species concentrations are computed for: (4) pH=3.18, (5) pH=8 and $K_{tot}=10^{-6.7}$, (6) pH=8 and $K_{tot}=10^{-6.7}$, (7) Renard et al., 2005; Wigand et al., 2008; Algive et al., 2009, (8) Li et al., 2006, (9) Gaus et al., 2005)
We can numerically examine the evolution of species concentrations with these kinetic rate laws. For instance, the solution of differential Equations 4 to 7 (using 4th order Runge-Kutta method in the Matlab) shows that the concentration of hydrogen ions \([H^+]\) converges to \(10^{-3.28}\) mol/L and the acidity level drops to pH\(=3.28\) under a partial pressure of CO\(_2\) \(P_{CO2}=10\) MPa and temperature \(T=40\)°C.

### 4.3 Mineral Dissolutions: Kinetic Rates

Let’s consider two representative minerals: calcite \(CaCO_3\) (its dissolution may provide preferential leakage paths), and anorthite \(CaAl_2Si_2O_8\) (it exhibits the fastest reaction rate among aluminosilicates). While the dissolution of aluminosilicates is much slower than that of calcite, aluminosilicates yield more dissolved cations in the long term: higher solubility (Gunter et al., 2000); therefore, aluminosilicates are good candidates for mineral trapping.

#### 4.3.1 Calcite Dissolution

Calcite can act as a buffering agent when CO\(_2\) is injected into a carbonate reservoir. Three chemical reactions involve calcite and occur in parallel albeit with different rate constants (Plummer et al., 1978):

\[
CaCO_3(s) + H^+ \overset{k_{1f}}{\rightleftharpoons} Ca^{2+} + HCO_3^-; \quad \log K_{eq}=1.85 \tag{9}
\]

\[
CaCO_3(s) + CO_2(aq) + H_2O \overset{k_{3f}}{\rightleftharpoons} Ca^{2+} + 2HCO_3^-; \quad \log K_{eq}=-4.50 \tag{10}
\]

\[
CaCO_3(s) \overset{k_{3f}}{\rightleftharpoons} Ca^{2+} + CO_3^{2-}; \quad \log K_{eq}=-8.48 \tag{11}
\]

The rate constants are: \(k_{1f}=5.1\times10^{-1}\) mol/m\(^2\)/s, \(k_{2f}=3.4\times10^{-4}\) mol/m\(^2\)/s, and \(k_{3f}=1.1\times10^{-6}\) mol/m\(^2\)/s at 20°C with the activation energy of \(E_1=14.5\) kJ/mol, \(E_2=35.4\) kJ/mol, and \(E_3=23.5\) kJ/mol (Chou et al., 1989; Renard et al., 2005; Wigand et al., 2008; Algive et al.,
2009). The third reaction (Equation 11) has a much smaller rate and equilibrium constants, hence, it is ignored and only the first two reactions are captured in the numerical simulation (Equations 9 and 10). One reaction consumes $H^+$ and produces $Ca^{2+}$ and $HCO_3^-$ (Equation 9). The other reaction consumes one mole of $CO_{2(aq)}$ in exchange for one mole of $Ca^{2+}$ and two moles of $HCO_3^-$ (Equation 10). The Transition State Theory enables us to express the overall dissolution rate $R_d$ as follows (Lasaga, 1984; Li et al., 2008):

$$R_d = \left(k_{1f}[H^+] + k_{2f}[CO_{2(aq)}]\right) \left(1 - \frac{\Omega}{K_{eq}}\right)$$

where

$$\Omega = \frac{[Ca^{2+}]^2[HCO_3^-]^3}{[H^+][CO_{2(aq)}]}$$

and the overall equilibrium constant becomes $logK_{eq}=1.85-4.50=-2.65$ (refer to Equations 9 and 10).

4.3.2 Anorthite Dissolution

We adopt the model by Li et al. (2006) to represent the dissolution of anorthite. The reaction consumes eight moles of $H^+$ to produce one mole of $Ca^{2+}$, two moles of $Al^{3+}$, and two moles of $H_4SiO_4$:

$$CaAl_2Si_2O_8(s) + 8H^+ \leftrightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4$$

(13)

Again, the overall dissolution rate is described as a function of rate constants, concentrations of reactant species and saturation:

$$R_d = \left(k_H[H^+]^{1.5} + k_{H_2O} + k_{OH}[OH^-]^{0.33}\right) \left(1 - \frac{\Omega}{K_{eq}}\right)$$

where

$$\Omega = \frac{[Ca^{2+}][Al^{3+}]^2[H_4SiO_4]^2}{[H^+]^8}$$

and $logK_{eq}=21.7$, $k_H=10^{-3.32}$ mol/m$^2$/s, $k_{H_2O}=10^{-11.6}$ mol/m$^2$/s, $k_{OH}=10^{-13.5}$ mol/m$^2$/s at 25°C (Li et al., 2006). We omit the term $k_{OH}[OH^-]^{0.33}$ during the numerical simulation because both the rate constant and the concentration of hydroxide $[OH^-]$ are negligible. Figure 4.2 compares the overall mineral dissolution rates $R_d$ when we fix the concentration of the total carbonic acid $H_2CO_3*$ at $[H_2CO_3*]=1$mol/L as a consequence of CO$_2$ geological storage. Results show that the concentration of hydrogen ions $[H^+]$ controls the reaction.
rate of calcite up to pH~4 beyond which high concentration of total carbonic acid \([H_2CO_3^\ast]\) takes control of it. Reaction rate of anorthite decreases gradually as \([H^+]\) decreases until the acidity level drops to pH~6. Reaction rate of calcite is several orders of magnitude higher than that of anorthite in the range of 2<pH<7 (Figure 4.2).

![Graph showing reaction rate log \(k_d/\text{[mol/m}^2\text{/s]}\) for dissolution of calcite \(CaCO_3\), anorthite \(CaAl_2Si_2O_8\), and kaolinite \(Al_2Si_2O_5(OH)_4\) at temperature T=40°C and fixed concentration of total dissolved carbon dioxide \([H_2CO_3^\ast]\)=1mol/L. For calcite, \(k_d=k_1[H^+]+k_2[H_2CO_3^\ast]\) where \(k_1=0.745\text{mol/m}^2\text{/s}\) and \(k_2=8.6\times10^{-4}\text{mol/m}^2\text{/s}\) at T=40°C (Fredd and Fogler, 1998; Pokrovsky et al., 2005; Renard et al., 2005; Algive et al., 2009). For anorthite, \(k_d=k_H[H^+]^{1.5}+k_{H_2O}+k_{OH}[OH]^{0.33}\) where \(k_H=6.883\times10^{-4}\text{mol/m}^2\text{/s}\), \(k_{H_2O}=3.58\times10^{-12}\text{mol/m}^2\text{/s}\), and \(k_{OH}=4.51\times10^{-14}\text{mol/m}^2\text{/s}\) at T=40°C (Li et al., 2006). For kaolinite, \(k_d=k_H[H^+]^{0.4}+k_{OH}[OH]^{0.3}\) where \(k_H=2.79\times10^{-11}\text{mol/m}^2\text{/s}\) and \(k_{OH}=3.51\times10^{-16}\text{mol/m}^2\text{/s}\) at T=40°C (Li et al., 2006).

4.4 Numerical Simulation of Reactive Fluid Flow
A numerical simulation study is implemented to explore the coupling between hydro-chemical phenomena during the transport of reactive CO\textsubscript{2}-acidified water through a pore in a mineral system. Governing dimensionless ratios are introduced first.

### 4.4.1 Dimensionless Ratios

Consider a reactive fluid advecting with velocity \( v \) [m/s] through a rock joint (i.e., 2-D pore) driven by a pressure difference between inlet and outlet boundaries a distance \( l \) [m] from each other. Reactant species are transported towards the mineral surface by molecular diffusion so that the joint aperture \( d \) [m] and the diffusion coefficient \( D \) [m\textsuperscript{2}/s] determines the characteristic time for the transverse diffusion. Mineral dissolution at the fracture surface produces species that are carried away by both advection (downstream) and diffusion (towards the center).

Two dimensionless ratios capture the interplay between governing processes. The Damköhler number \( Da \) is the ratio between the advection time and the chemical reaction time (Fredd and Fogler, 1998). The Peclet number \( Pe \) compares the time for transverse diffusion to the time for longitudinal advection (Golffier et al., 2002):

\[
Da = \frac{t_{\text{advection}}}{t_{\text{reaction}}} = \frac{k d}{v} \quad (15)
\]

\[
Pe = \frac{t_{\text{diffusion}}}{t_{\text{advection}}} = \frac{d^2 v}{4 l D} \quad (16)
\]

where the kinetic rate \( \kappa \) [1/s] = \( k_r S_s M_m \) is a function of the rate constant for mineral dissolution \( k_r \) [mol/m\textsuperscript{2}/s], the mineral specific surface \( S_s \) [m\textsuperscript{2}/g], and the mineral molar mass \( M_m \) [g/mol].

### 4.4.2 Simulation Method

Consider a slice of a rock joint or a long pore with length \( l \) much longer than the aperture \( d \), i.e., \( l \gg d \), subjected to reactive fluid transport by the forced advection of CO\textsubscript{2}-acidified water. The problem is simulated using the moving mesh function in COMSOL.
to reproduce the joint enlargement (COMSOL, 2008). Figure 4.3 summarizes the simulation scheme. Flow satisfies the Navier-Stokes’ law; species experience both advective and diffusive transport. Mineral dissolution occurs at the interface between the fluid and the joint walls with dissolution rate $R_d$ [mol/m$^2$/s]. The moving mesh function adjusts the mesh outwards or inwards according to the volume of dissolved mineral $R_d (\nu_s/\nu) V_m$ [m/s], where $(\nu_s/\nu)$ denotes the stoichiometric ratio of dissolved mineral to reactant species and $V_m$ [m$^3$/mol] is the molar volume of the mineral.

While results will be summarized in dimensionless form, the numerical simulation is implemented in a dimensional physical space to facilitate model validation and to add clarity to the discussion of results. Let’s set the pore length $l=100\mu$m (Note: the channel length in Fontainebleau and Berea sandstones ranges from 20$\mu$m to 600$\mu$m - Lindquist et al., 2000; Dong and Blunt, 2009). The pore aperture varies from $d=2\mu$m to 28$\mu$m (Bachu and Bennion, 2008). The inlet velocity is varied from $v_0=1$cm/s to $10^{-3}$cm/s. The inlet concentration of $H^+$ ranges from $[H^+]_{\text{inlet}}=10^{-3}$mol/L to $10^{-6}$mol/L, and for $H_2CO_3^*$ between $[H_2CO_3^*]=1$mol/L and $10^{-3}$mol/L. Initial concentrations of all species are assigned so that the system is in thermodynamic-equilibrium and satisfies electroneutrality at pH=8. Zero pressure is imposed at the outlet, and free flux of species is allowed to simulate an infinite boundary (Figure 4.3). Computations are conducted for every 0.001s until the total simulation time equals 10 times of advection time $10\cdot l/v_0$. All parameters used for numerical simulations are summarized in Table 4.1.
Figure 4.3  Numerical simulation scheme and governing equations for reactive fluid flow through a rock joint/pore problem. Physics models used in COMSOL: 1) Incompressible Navier-Stokes (\(\eta\): dynamic viscosity of fluid, \(\rho\): density of fluid, \(\mathbf{v}\): velocity field, \(p\): pressure, \(\mathbf{F}\): volume force field such as gravity; gravity is disregarded in the simulation), 2) Convection and diffusion (\(c_i\): concentration of species \(i\), \(D\): coefficient of molecular diffusion), and 3) Moving mesh (\(R_d\): overall dissolution rate of mineral at the wall, \(k_i\): reaction rate of reactant species \(i\), \(\Omega\): ionic concentration product, \(K_{eq}\): equilibrium constant, \(d\): joint aperture, \(V_m\): mineral molar volume, \(\nu_s/\nu\): stoichiometric ratio between reactant species and dissolved mineral); Number of elements: 1,608 (when length \(l=100\mu m\) and joint aperture \(d=10\mu m\)). Type of mesh: triangle. Linear system solver: Direct (PARDISO).

4.4.3 Validation

We verify the numerical simulation scheme by comparing COMSOL simulation results with a closed-form solution. There is no analytical solution for reactive fluid
transport in a two-dimensional pore, so we compare a 1-D analytical solution with 1-D numerical results obtained with COMSOL. The governing equation for the one-dimensional transport of reactive fluid is:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \kappa c$$

(17)

For a single reactant species at an initial concentration $c(x,0)=0$ for $x>0$ and boundary conditions $c(0,t)=c_0$ and $c(\infty,t)=0$ for $t\geq0$, the solution for the variation of the species concentration in space and time is (Boudreau, 1997):

$$\frac{c}{c_0} = \frac{1}{2} \exp(\xi_2) \left[ \exp(-\xi_1)erfc\left(\frac{2\xi_1 - \tau}{2\sqrt{\tau}}\right) + \exp(\xi_1)erfc\left(\frac{2\xi_1 + \tau}{2\sqrt{\tau}}\right) \right]$$

where $\beta^2 = \left(\frac{v^2}{4D^2} + \frac{\kappa}{D}\right)$, $\xi_1 = \beta x$, $\xi_2 = \frac{vx}{2D}$, $\tau = \frac{(v^2 + 4\kappa D)t}{D}$

(18)

Figure 4.4 shows that 1-D numerical simulation results are in excellent agreement with results from the analytical solution. Note that two outlet boundary conditions are simulated for the finite length numerical system as compared to the infinite length analytical solution: 1) free flux, and 2) maintain the initial outlet concentration fixed $c=0$. Results bound the theoretical solution (Figure 4.4-b).

4.5 Results and Discussion

Numerical simulation results for the 2-D case relevant to CO$_2$ geological storage are presented herein in terms of species concentrations in space and time, the enlargement of the rock joint, and the effect of pore geometry.

4.5.1 Species Concentrations

Mineral dissolution couples with advection and diffusion to generate a concentration gradient across and along the pore/joint aperture (Li et al., 2006). Figure 4.5 shows a snap-shot of concentrations for all relevant species along a joint in calcite.
Low advection velocity allows for diffusion and homogenization across the aperture and for the consumption of most reactant species near the inlet (Figure 4.5-a). In contrast, when the advection velocity is high, diffusion fails to homogenize the concentration field across the joint, and mineral dissolution takes place uniformly along the joint length (Figure 4.5-b). The longitudinal drop in reactant species is much lower in the less reactive anorthite for the same advection velocities (Figure 4.6). For both mineralogies, a higher advection velocity yields higher concentrations of residual reactant species at the outlet due to the lower residence time.

Figure 4.4  Comparison of the numerical simulation with a closed-form solution for 1-D reactive solute transport model. Assumption: homogeneous reaction of single species $CO_{2(aq)}$ for reaction $CO_{2(aq)} + H_2O \rightarrow H_2CO_3$ where $k_{CO2}=0.135 s^{-1}$. Insert in (b) shows discrepancy between the closed-form solution and numerical solution for two boundary conditions: free flux or fixed initial concentration at the outlet. Fixed inlet concentration of $CO_{2(aq)} [CO_{2(aq)}]_{(x=0)}=1\text{mol/L}$, initial concentration of $CO_{2(aq)} [CO_{2(aq)}]_{(x>0)}=0$, fixed inlet velocity $v_0=0.01\text{cm/s}$, diffusion coefficient $D=2*10^{-9} \text{m}^2/\text{s}$, and length $l=100\mu\text{m}$.

The fluid acidity evolves as the numerical simulation proceeds. During the flow of acidified fluid along the rock joint, the pH near the inlet drops while the area near the outlet remains at the initial pH~8. The entire pore space acidifies and the area near the
outlet converges to an asymptotic value pH~5 as advection continues and the system becomes saturated in terms of mineral dissolution (Figure 4.7-a). Electro-neutrality is maintained during the numerical simulation (Figure 4.7-b).

Figure 4.5 Reactive fluid transport along a joint/pore in calcite. Concentration of reactants ($H^+$ and $H_2CO_3^*$) and produced species ($Ca^{2+}$ and $HCO_3^-$). Joint aperture $d=10\mu m$ and length $l=100\mu m$. The flow velocity is: (a) $v_0=10^{-3} cm/s$ ($Da=9.6*10^1$, and $Pe=2.7*10^4$) and (b) $v_0=1cm/s$ ($Da=9.6*10^{-2}$, and $Pe=2.7*10^1$). Concentration results are shown after: (a) 50 seconds ($=l/v_0*5$) and (b) 10 seconds ($=l/v_0*1,000$). Unit of species concentration in the graph is $[mol/m^3]$. All parameters are summarized in Table 4.1.

Figure 4.8 summarizes species concentrations along the centerline and at the outlet for different inlet velocities. Clearly, $H^+$ is readily consumed in a calcite-dominant environment, the system reaches chemical equilibrium, and $H_2CO_3^*$ passes through the
rest of the joint plane unconsumed. The residual $H_2CO_3$ at the outlet may react with minerals and induce additional mineral dissolution in successive flow channels. In contrast to the calcite case, the low reaction rate of $H^+$ with anorthite ($Da<1$) allows more than two-thirds of $H^+$ species to reach the outlet (Figure 4.8). In general, mineral dissolution will influence a larger area in sandstones than in carbonates, under the same flow regime.

Figure 4.6 Reactive fluid transport along a joint/pore in anorthite. Concentration of reactant ($H^+$) and produced species ($Ca^{2+}$, $Al^{3+}$, and $H_4SiO_4$). Joint aperture $d=10\mu m$ and length $l=100\mu m$. The flow velocity is: (a) $v_0=10^{-3}$ cm/s ($Da=5.7*10^{-2}$, and $Pe=2.7*10^{-4}$) and (b) $v_0=1$ cm/s ($Da=5.7*10^{-3}$, and $Pe=2.7*10^{-1}$). Concentrations results are shown after: (a) 5 seconds ($=l/v_0*0.5$) and (b) 1 seconds ($=l/v_0*100$). Unit of species concentration in the graph is [mol/m$^3$]. All parameters are summarized in Table 4.1.
Figure 4.7 Evolution of pH in time and space. (a) pH along the joint length with respect to the normalized time \( t/(l/v_0) \). (b) Verification of electro-neutrality along the joint length. Note: \( v_0 = 10^{-3} \text{cm/s} \); \( Da \approx 5.7 \times 10^{-3} \) and \( Pe \approx 2.7 \times 10^{-3} \); beyond \( t/(l/v_0) \approx 1 \), pH distribution reaches quasi-steady state.
Variation of reactant species concentration: (a) along the centerline for different times \( (v=0.01 \text{cm/s}) \) and (b) at the outlet for different flow velocities. All parameters are summarized in Table 4.1.

### 4.5.2 Enlargement

The rock joint aperture increases as the reactive fluid passes through the joint plane (Figures 4.5 & 4.6). The effect of advective velocity and reactivity are explored in Figures 4.9 and 4.10. Results show that pore enlargement may decrease either exponentially or linearly along the flow path. In all cases, the normalized enlargement \( \Delta d/d \) in anorthite is three orders of magnitude lower than that of calcite (Figure 4.9). Figure 4.10 compiles all results in terms of dimensionless numbers, \( Da \) and \( Pe \). For any \( Pe \) value, a lower \( Da \) causes the flow channel to experience a more uniform enlargement of the aperture along the joint.
4.5.3 Time to Reach Quasi Steady-State Condition

The time to reach a quasi steady-state concentration at the outlet $t_{qc}$ is determined when species concentrations at the outlet $c$ reach 95% of the equilibrium value $c_\infty$ at $t=\infty$ (Figure 4.11-a). Figures 4.11-(b) and (c) indicate that the time to reach quasi steady-state $t_{qc}$ is between the advection time $l/v_0$ and two-folds of it $(2\cdot l/v_0)$. This implies that mineral dissolution and channel enlargement cause the system to reach quasi steady-state condition later than the advection time. Results when $Pe<1$ for the joint/pore in anorthite deviate from the general trend ($Da<<1$; Figures 4.10 & 4.11-c). When $Da<1$ and $Pe<1$, diffusion takes control over advection and dissolution, and quasi steady-state is reached faster than the advection time $l/v_0$. 

Figure 4.9 Normalized enlargement $\Delta d/d_0$ by mineral dissolution along the joint/pore wall at the moment of quasi steady-state for different velocities $v$: (a) calcite and (b) anorthite. Note: orders of enlargement are different between (a) and (b). Original joint aperture is $d_0=10\mu m$. 

(a) Calcite
(b) Anorthite
Figure 4.10  Dissolution patterns in the Da - Pe space. The sketches show dissolution patterns observed in numerical simulations of joints in either calcite or anorthite.

Figure 4.11  Determination of time to reach quasi steady-state of concentration \( t_{qs} \) at the outlet (95\% of \( c_{\infty} / c_{inlet} \), where \( c_{inlet} \) is inlet concentration). The time to reach quasi steady-state of concentration at the outlet \( t_{qs} \) is normalized by the advection time \( l/v \) based on the joint length \( l \) and velocity \( v \) for (b) in calcite and (c) in anorthite.
5.4 Initial Joint Slenderness

Finally, let’s examine the effect of joint slenderness by varying the aperture-to-length ratio $d/l$. When the aperture-to-length ratio $d/l$ is very small $d/l \leq 0.035$, diffusive transport homogenizes species concentrations across the joint, and centerline concentrations resemble the 1-dimensional theoretical solution (Figure 4.12). An increased aperture-to-length ratio slows the diffusive transport of reactant species to the mineral surface ($t_{\text{diff}} \approx d^2/D$), and higher reactant concentrations remain along the centerline (Figure 4.12). Therefore, scaling must take into consideration both the joint length and its slenderness (see also Li et al., 2008).

![Figure 4.12](image)

Figure 4.12  Effect of joint slenderness $d/l$. Variation of the normalized concentration of hydrogen ions $[H^+]/[H^+]_{\text{inlet}}$ at quasi steady-state for joints in calcite with different slenderness $d/l$ (Note: length $l=100\mu$m, velocity $v=0.01\text{cm/s}$, $[H^+]_{\text{inlet}}=10^{-3}\text{mol/L}$). The theoretical 1-D solution is shown for comparison. All parameters are summarized in Table 4.1.
4.6 Conclusions

Numerical simulations for the reactive fluid transport through a rock joint/pore in calcite and anorthite were conducted taking into consideration all kinetic rate laws relevant to CO$_2$ geological storage including CO$_2$ dissolution and mineral buffering. The species concentrations at equilibrium can be tracked by numerically solving these kinetic rate laws. A novel simulation technique was used to couple laminar flow, mass transport of species, mineral dissolution, and subsequent pore enlargement. This 2-D simulation enables us to investigate interactions among governing parameter, including advection, diffusion, species concentration, and geometry during reactive fluid transport at the pore scale. Results show:

• Hydrogen ions H$^+$ are readily consumed in a calcite-dominant environment, the system becomes saturated, and H$_2$CO$_3^*$ passes through the rest of the joint plane unconsumed. In contrast, the low reaction rate of H$^+$ with anorthite (Da<$10^{-2}$) allows more extensive H$^+$ transport along the joint/pore.

• Pore enlargement may decrease either exponentially or linearly along the flow path. For any Pe value, a lower Da causes the flow channel to experience a more uniform enlargement of the aperture along the joint. Dissolution patterns define a consistent trend in the Da - Pe space.

• Mineral dissolution and pore enlargement extend the time to reach quasi steady-state, unless diffusion takes control over advection and dissolution when Da<1 and Pe<1.

• When the aperture-to-length ratio d/l is small d/l≤0.035, the system resembles the 1-D problem. An increased aperture-to-length ratio slows the diffusive transport of reactant species to the mineral surface ($t_{diff}$≈d$^2$/D), and higher reactant concentrations remain along the centerline. Therefore, upscaling must take into consideration both the joint length and its slenderness.

• The simulation environment can be extended to 2-D pore networks and heterogeneous porous media. The extension, limited only by computer capacity, provides insightful
results for reactive fluid flow through porous media of particular relevance to CO$_2$
geological storage.

Figure 4.13 Application of the coupled reactive fluid flow simulation to (a) a two-channel model, (b) a channel network model, and (c) a scanned geometry of a porous medium (pore geometry obtained from: http://www.comsol.com).
CHAPTER 5

REACTIVE FLUID FLOW IN CO₂ STORAGE RESERVOIRS –
PORE NETWORK MODEL STUDY

5.1 Introduction

Global energy consumption is projected to increase by 50% in the next 30 years (EIA, 2010; This is the status-quo scenario in Pasten and Santamarina, 2012). In the short term, this increased demand will largely rely on fossil fuels because of available reserves, low cost, the available infrastructure, and the relatively low energy production from other sources (Chapter 2). Carbon storage in geological saline aquifers is being considered to mitigate carbon emissions in the atmosphere.

CO₂ enters supercritical state when temperature and pressure condition exceed $T>304.1\text{K}$ and $P>7.38\text{MPa}$ (Span and Wagner, 1996), i.e., typically at reservoir depths greater than $\sim800\text{m}$. The solubility of supercritical CO₂ in water can reach 1–2 moles/L (White et al., 2004; Gaus et al., 2005; Kharaka et al., 2006) and water acidifies to pH~3 while it retains two reactant species, hydrogen ions $H^+$ and aqueous carbon dioxide $CO_2(aq)$ (Chapter 3 - Stumm et al., 1996). The ensuing reactive fluid flow depends on mineral reactivity, advection, and diffusion.

Injected CO₂ displaces brine (two-phase flow) and CO₂-dissolved acidic water advances as a single-phase flow (Solomon et al., 2008). This study focuses on single-phase acidic water flow at the boundary between CO₂ and water in deep saline aquifers (Azaroual et al., 2007; Gaus et al., 2008) including the boundary between the aquifer and the caprock where migrating CO₂ accumulates (Figure 5.1). A pore network model is used herein to investigate reactive fluid flow within the storage reservoir. Previous studies are reviewed first.
Figure 5.1 Zones around the injection well – Prevalent processes (modified from Azaroual et al., 2007). M: Mineral, B: Brine, $S_{CO2}$: saturation of CO$_2$, and $S_B$: saturation of brine.

5.2 Previous Studies

Reactive fluid flow through porous media has been studied using equivalent continuum models (Liu et al., 1997; Golfier et al., 2002; Panga et al., 2005; Xu et al., 2006; Kalia and Balakotaiah, 2007), single-flow channel or wormhole models (Hung et al., 1989; Buijse, 2000; Li et al., 2008), lattice Boltzmann pore-scale models (Kang et al., 2010), and network models. The equivalent continuum approach requires pore-scale information such as the relationship between porosity and permeability (Liu et al., 1997;
Panga et al., 2005; Xu et al., 2006). Alternatives to the equivalent continuum model include discrete fracture network models (Pashin et al., 2008) and multiple continuum models (Steefel et al., 2005).

Network models allow us to capture pore-scale phenomena in order to study their effect on macro-scale flow conditions (Dillard and Blunt, 2000). Network models have two main drawbacks: 1) scale limitations and 2) hydro-mechanical decoupling. Reactive fluid flow involves dissolution, which adds complexity to the network simulation code, and only a few attempts have been reported (Hoefner and Fogler, 1988; Daccord et al., 1993; Daccord et al., 1993; Fredd and Fogler, 1998; Egermann et al., 2005; Li et al., 2006; Li et al., 2007; Algive et al., 2009). Published results show that the dissolution pattern varies with the ratio between advection and reaction times (2D-Fredd and Fogler, 1998); that the exponent of the Kozeny-Carman equation changes for different dissolution scenarios, including uniform dissolution, compaction dissolution, and wormhole formation (3D-Egermann et al., 2005; Algive et al., 2009); that and reaction rates are affected by the spatial distribution of minerals (3D-Li et al., 2006; Li et al., 2007).

5.3 Development of the Network Simulation Code

The new network simulation code presented here was created to investigate fluid-mineral interaction when CO$_2$-dissolved water flows through a porous network, such as the CO$_2$ storage reservoir where advective transport prevails. Relevant chemical formulae and the algorithm are presented next.
5.3.1 Mineralogy and Mineral Dissolution

Let’s consider a porous medium in a calcium carbonate formation (mineral with fastest reaction rate in saline reservoirs). Two parallel reactions prevail because of the low pH and the high concentration of aqueous CO$_2$ (Plummer et al., 1978):

\[
\begin{align*}
\text{CaCO}_3(s) + H^+ & \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \\
\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O} & \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-
\end{align*}
\]

Let’s assume first-order reactions with rate laws:

\[
\begin{align*}
- \frac{d[H^+]}{dt} &= \frac{d[Ca^{2+}]}{dt} = \frac{d[HCO_3^-]}{dt} = \kappa_1[H^+] \\
- \frac{d[H_2CO_3^*]}{dt} &= \frac{d[Ca^{2+}]}{dt} = \frac{1}{2} \frac{d[HCO_3^-]}{dt} = \kappa_2[H_2CO_3^*]
\end{align*}
\]

where square brackets indicate species concentration, $\kappa_i$ denotes the kinetic rate for each chemical reaction, and total carbonic acid $H_2CO_3^*$ denotes the summation of aqueous carbon dioxide $CO_2(aq)$ and true carbonic acid $H_2CO_3$. Reactions stop when the system reaches equilibrium and the ionic concentration product $\Omega$ [-] equals the equilibrium constant $K_{eq}$ [-]:

\[
\Omega = \frac{[Ca^{2+}]^2[HCO_3^-]^3}{[H^+][H_2CO_3^*]} = K_{eq} = 10^{-2.65}
\]

Table 5.1 summarizes equations and parameters. Note that mineral precipitation is not considered in this study.
Table 5.1  Calcite dissolution by CO₂-dissolved water. Summary of properties used in network simulations.

(a) Equations for mineral dissolution and properties

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical equation for mineral dissolution</th>
<th>Rate constant ([\text{mol/m}^2\text{s}])</th>
<th>Equilibrium constant</th>
<th>Ionic concentration product, (\Omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>(\text{CaCO}_3(s) + H^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-)</td>
<td>(k_1=0.745 (1))</td>
<td>(K_{eq}=10^{1.85 (1)})</td>
<td>([\text{Ca}^{2+}]^2[\text{HCO}_3^-]^3)</td>
</tr>
<tr>
<td></td>
<td>(\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-)</td>
<td>(k_2=8.6*10^{-4 (1)})</td>
<td>(K_{eq}=10^{-4.5 (1)})</td>
<td>([\text{H}^+][\text{H}_2\text{CO}_3])</td>
</tr>
</tbody>
</table>

(b) Boundary condition: Concentrations of species at the inlet

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration ([\text{mol/L}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{H}^+])_{inlet}</td>
<td>6.68*10^{-4}</td>
</tr>
<tr>
<td>([\text{H}_2\text{CO}<em>3]^*)</em>{inlet}</td>
<td>1mol/L</td>
</tr>
<tr>
<td>([\text{HCO}<em>3^-])</em>{inlet}</td>
<td>6.68*10^{-4}</td>
</tr>
<tr>
<td>([\text{Ca}^{2+}])_{inlet}</td>
<td>1.361*10^{-3}</td>
</tr>
<tr>
<td>([\text{OH}^-])_{inlet}</td>
<td>1.50*10^{-11}</td>
</tr>
<tr>
<td>([\text{Cl}^-])_{inlet}</td>
<td>2.72*10^{-3}</td>
</tr>
</tbody>
</table>

Note: \(S_s\): mineral specific surface, \(M_m\): mineral molar mass, \(V_m\): mineral molar volume; kinetic rate is \(\kappa_i (1/s) = k_i S_s M_m\) where \(k_i\) is a rate constant; Rate constants are computed for \(T=40^\circ\text{C}\) in this study; total equilibrium constant for calcite \(K_{eq}=K_{1eq} K_{2eq}\) (Reference: (1) Plummer et al., 1978; Fredd and Fogler, 1998; Pokrovsky et al., 2005; Renard et al., 2005; Algive et al., 2009, and (2) Gaus et al., 2005).

5.3.2 Network Construction

The 2-D square network consists of tubes that intersect at nodes, where incoming species mix thoroughly. Tube diameters \(d [\text{m}]\) are log-normally distributed with mean value \(\bar{d}_0\) and variance \(var\). All tubes have identical length \(L_{ch} [\text{m}]\). The limitation in network size NxM is partially overcome by assuming periodic longitudinal boundary conditions. Flow is driven by the pressure difference between the inlet \(P_{in}\) and the outlet \(P_{out}\) (Figure 5.2 - Network details in Table 5.2).
### Table 5.2  Network model and simulation parameters.

<table>
<thead>
<tr>
<th>Entity</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network size (NxM)</td>
<td>50x50</td>
</tr>
<tr>
<td>Mineralogy</td>
<td>Calcite</td>
</tr>
<tr>
<td>Mean of tube diameters, $\bar{d}_0$</td>
<td>20µm</td>
</tr>
<tr>
<td>Distribution of tube diameters</td>
<td>Log-normal distribution</td>
</tr>
<tr>
<td>Coefficient of Variation, COV</td>
<td>0.4, 1, and 1.5</td>
</tr>
<tr>
<td>Tube length, $L_{ch}$</td>
<td>200µm</td>
</tr>
<tr>
<td>Hydraulic gradient $i_h$ applied at the model</td>
<td>10, 100, and 1000</td>
</tr>
<tr>
<td>Flushed pore volume during one cycle</td>
<td>$10 \cdot V_p$ ($V_p$: one network pore volume)</td>
</tr>
<tr>
<td>Number of cycle (repetition)</td>
<td>100</td>
</tr>
<tr>
<td>Total flushed network pore volume</td>
<td>$1000 \cdot V_p$</td>
</tr>
</tbody>
</table>

**CO₂-dissolved water**

\[ \text{pH} = 3.18 \]

Fixed concentration

\[ \text{[H}^+\text{]} = 6.68 \times 10^{-4} \text{mol/L} \]
\[ \text{[H}_2\text{CO}_3\text{]} = 1 \text{mol/L} \]
\[ \text{[HCO}_3\text{]} = 6.68 \times 10^{-4} \text{mol/L} \]
\[ \text{[Ca}^{2+}\text{]} = 1.36 \times 10^{-3} \text{mol/L} \]
\[ \text{[OH}^-\text{]} = 1.50 \times 10^{-1} \text{mol/L} \]
\[ \text{[Cl}^-\text{]} = 2.72 \times 10^{-3} \text{mol/L} \]

**Figure 5.2**  Pore network model: geometry, initial, and boundary conditions.
5.3.3 Governing Parameters

The time scales for advection $t_{adv}$, diffusion $t_{diff}$, and reaction $t_{rxn}$ can be combined to form two dimensionless ratios, i.e., the Damköhler $Da$ and Peclet $Pe$ numbers:

$$Da = \frac{t_{adv}}{t_{rxn}} = \frac{\kappa L_{ch}}{v_{ave}}$$

$$Pe = \frac{t_{diff}}{t_{adv}} = \frac{v_{ave} L_{ch}}{D}$$

where the kinetic rate $\kappa$ [1/s] = $k_r S_s M_m$ is a function of the rate constant $k_r$ [mol/m$^2$/s], the mineral specific surface $S_s$ [m$^2$/g], and the mineral molar mass $M_m$ [g/mol]. The average pore velocity is $v_{ave}$ [m/s], and $D$ [m$^2$/s] denotes the molecular diffusion coefficient. The simulation is designed for advection-controlled situations such as those that prevail in the reservoir formation during CO$_2$ injection (Damköhler number $Da \leq 10^{-3}$; Peclet number $Pe > 10^2$; and hydraulic gradient $i_h \geq 10$ - Table 5.2). A small Damköhler number $Da << 1$, i.e., advection much faster than reaction, permits convenient simplifications.

5.3.4 Numerical Simulation – Algorithm

General Formulation

Velocity. Nodal fluid pressures are computed by writing the continuity equation at all nodes and solving the system of equations (details in Jang et al., 2011):

$$\sum q_i = 0$$

The pressure difference $\Delta P$ [Pa] between two adjacent nodes is then used to compute the tube flow velocity $v$ [m/s] and flow rate $q$ [m$^3$/s] for each tube using Poiseuille’s law as a function of the tube diameter $d$ [m], length $L_{ch}$ [m], and the fluid viscosity $\mu$ [Pa·s]:

$$\text{Velocity: } v = \frac{\Delta P d^2}{32 \mu L_{ch}}$$
Flow rate: 
\[
q = \frac{\Delta P \pi d^4}{128 \mu L_{ch}}
\]  
(10)

*Evolution of the species concentration.* Mineral dissolution in a given tube lowers the concentration of reactant species and increases the concentration of produced species at the next node until saturation is reached and dissolution stops. The concentration \(c_{i+1,j+1}\) for reactant species \(H^+\) and \(H_2CO_3^*\) at location \(x_{i+1} = x_i + \Delta x\) and time \(t_{j+1} = t_j + \Delta t\) in a tube in direction \(x\) is determined by the chemical reaction rate \(\kappa\), the residence time of species inside a tube \(L_{ch}/v\), and the concentration of reactant species \(c_{i,j}\) at location \(x_i\) and time \(t_j\).

For a 1-D tube aligned in \(x\):

\[
[H^+]_{i+1,j+1} = [H^+]_{i,j} - \kappa_1 \cdot [H^+]_{i,j} \cdot \left(1 - \frac{\Omega_{i,j}}{K_{eq}}\right) \frac{L_{ch}}{v_{i,j}}
\]

(11)

\[
[H_2CO_3^+]_{i+1,j+1} = [H_2CO_3^+]_{i,j} - \kappa_2 \cdot [H_2CO_3^+]_{i,j} \cdot \left(1 - \frac{\Omega_{i,j}}{K_{eq}}\right) \frac{L_{ch}}{v_{i,j}}
\]

(12)

where the parameter \(\Omega_{i,j}\) is the ionic concentration product, and \(v_{i,j}\) the velocity at location \(x_i\) and time \(t_j\). The concentration of produced species \(Ca^{2+}\) and \(HCO_3^-\) are determined from the consumption of reactant species and the stoichiometric ratio between reactant and produced species. For a 1-D tube aligned in \(x\):

\[
[Ca^{2+}]_{i+1,j+1} = [Ca^{2+}]_{i,j} + \left(\kappa_1[H^+]_{i,j} + \kappa_2[H_2CO_3^+]_{i,j}\right) \left(1 - \frac{\Omega_{i,j}}{K_{eq}}\right) \frac{L_{ch}}{v_{i,j}}
\]

(13)

\[
[HCO_3^-]_{i+1,j+1} = [HCO_3^-]_{i,j} + \left(\kappa_1[H^+]_{i,j} + 2\kappa_2[H_2CO_3^+]_{i,j}\right) \left(1 - \frac{\Omega_{i,j}}{K_{eq}}\right) \frac{L_{ch}}{v_{i,j}}
\]

(14)

These equations presume that advective transport prevails over diffusive transport \((Pe>1)\) and is valid for advection-dominant regimes.

**Initial and Boundary Conditions**

The first column \((i=1)\) is the inlet of \(CO_2\)-dissolved water; it has fixed concentration of reactant species. The concentration of total carbonic acid \([H_2CO_3^*]\) is
determined using expressions proposed by Duan and Sun (2003) as shown in Chapter 3. Concentrations of hydrogen \([H^+]\), hydroxide \([OH^-]\), and bicarbonate \([HCO_3^-]\) are obtained from the thermodynamic equilibrium of a carbonate system \(H_2CO_3 \leftrightarrow H^+ + HCO_3^-\) at \(T=40^\circ C\) and \(P=10\) MPa. Concentrations of other species, such as \(Ca^{2+}\) and \(Cl^-\) at the inlet boundary are determined to satisfy electro-neutrality (Figure 5.2).

A free flux condition is used for the outlet \(i=M\) in order to simulate an infinite boundary \(c_{M-2,j}=c_{M-1,j}=c_{M,j}\). Figure 5.2 summarizes initial and boundary conditions.

Chemical conditions must be initiated within the network to avoid numerical instabilities. We assume that the transport of species along transverse tubes is initially negligible because flow velocities are typically much lower than along longitudinal tubes. We also assume that changes in tube diameters are negligible during the initial moments. Then, the initial “pseudo-steady state” concentration field of reactant species along 1-D longitudinal tubes can be estimated by numerically solving the differential equation for reactive fluid transport (Boudreau, 1997):

\[
\frac{dc}{dt} - \nu \frac{dc}{dx} - \kappa x = 0
\]  

This equation is expressed in finite difference form (central approximation functions).

\[
-\frac{\nu}{2\Delta x} c_{i+1} - \kappa \cdot c_i + \frac{\nu}{2\Delta x} c_{i-1} = 0
\]  

where \(c_i\) \([\text{mol/m}^3]\) denotes species concentration at location \(x_i\), and the space interval is taken as the distance between adjacent nodes \(\Delta x=L_{ch}\). In matrix form,

\[
A \cdot c = B
\]  

where matrix \(A\) contains coefficients in Equation 16 (that is \(-\nu/2\Delta x\), \(-\kappa\), and \(\nu/2\Delta x\)), and the vector \(B\) captures boundary conditions, i.e., fixed concentration \(c_{inlet}\) at the inlet node \(i=1\) and free flux at the outlet node \(i=M\). For example, the matrix \(A\) and vector \(B\) for \(M=6\) nodes are:
The sought concentration field \( \vec{c} \) of reactant species \( H^+ \) and \( H_2CO_3^* \) at all nodes at the initial pseudo-steady state condition is obtained by inverting the system of equations to recover the vector \( \vec{c} = A^{-1} \cdot \vec{b} \). Pseudo-steady state concentration for other species, such as \( Ca^{2+} \), \( HCO_3^- \), \( OH^- \), and \( Cl^- \), are determined to satisfy both equilibrium in the carbonate system and electro-neutrality with the concentrations of \( H^+ \) and \( H_2CO_3^* \) at each node.

Complementary computations

**Enlargement of tube diameters.** The solid mineral dissolution \( \Delta c_{i,j}^m \) [mol/m\(^3\)] between location \( x_i \) and \( x_{i+1} \) from time \( t_j \) to \( t_{j+1} \) is computed from the consumption of reactant species \( H^+ \) and \( H_2CO_3^* \) and their stoichiometric ratios (1:1 for both reactant species). For a 1-D tube aligned in \( x \):

\[
\Delta c_{i,j}^m = \left( \kappa_1[H^+]_{i,j} + \kappa_2[H_2CO_3^*]_{i,j} \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \frac{L_{ch}}{V_{i,j}}
\]

The increase in tube diameter \( \Delta d_{i,j} \) [m] between locations \( x_i \) and \( x_{i+1} \) from time \( t_j \) to \( t_{j+1} \) is proportional to flow rate \( q_{i,j} \), the solid mineral dissolution \( \Delta c_{i,j}^m \), the mineral molar volume \( V_m \) [m\(^3\)/mol], and the elapsed time \( \Delta t \) [s]. For a 1-D tube aligned in \( x \):

\[
\Delta d_{i,j} = \frac{2V_m \Delta t \cdot q_{i,j} \cdot \Delta c_{i,j}^m}{\pi d_{i,j} \cdot \Delta t_{ch}}
\]

As noted earlier, mineral dissolution is much slower than advection in most problems of reactive fluid transport related to CO\(_2\) geological storage \((Da \ll 1)\). Thus, the enlargement
of tube diameters, for one replaced network pore volume $V_p$, is minute, and we select the
time interval $\Delta t$ for one iteration step to be several times $\beta$ the overall advection time
$L_{\text{total}}/v_{\text{ave}}$ across the network $L_{\text{total}}=L_{\text{ch}}*(M-1)$:

$$\Delta t = \beta \frac{L_{\text{total}}}{v_{\text{ave}}} \quad (21)$$

Updated Nodal Concentrations. The new nodal concentration $c_{i+1,j+1}^{\text{new}}$ at location $x_{i+1}$ at
time $t_{j+1}$ is computed assuming instantaneous mixing at the node:

$$c_{i+1,j+1}^{\text{new}} = \frac{\sum_k q_{k,j} \cdot c_{k+1,j+1}}{\sum_k q_{k,j}} \quad (22)$$

Algorithm

One cycle in the network simulation corresponds to the time interval $\Delta t$, and
involves the following steps: (1) estimate the evolution of species concentration at the
end of every tube based on species concentrations, velocity, and kinetic rates – Equations
11 to 14, (2) compute the enlargement of tube diameter $\Delta d$ for every tube – Equations 19
to 21, (3) update concentration of species at all nodes – Equation 22, and (4) update nodal
pressure, velocity and flow rate based on change in tube diameters – Equations 8 to 10.
We repeat this cycle until the total flushed volume reaches $1000 \cdot V_p$ (Table 5.2). The
algorithm is summarized in Figure 5.3.
Figure 5.3  Network model simulation scheme for the advection-dominant reactive transport in the CO$_2$ reservoir (Notation corresponds to a tube aligned in the $x$-direction).

Species:
- $H^+$
- $H_2CO_3^*$
- $Ca^{2+}$
- $HCO_3^-$
- $OH^-
- Cl^-$

CaCO$_3$ + $H^+$ $\rightarrow$ Ca$^{2+}$ + HCO$_3^-$; kinetic rate $\kappa_1$
CaCO$_3$ + CO$_2$(aq) + H$_2$O $\rightarrow$ Ca$^{2+}$ + 2HCO$_3^-$; kinetic rate $\kappa_2$

Equilibrium constant for the mineral dissolutions: $K_{eq}$

Ionic concentration product $\Omega_{ij}$ at $x_i$ and time $t_j$:
$$\Omega_{ij} = \frac{[Ca^{2+}]^{\frac{L}{v}} [HCO_3^-]^{\frac{L}{v}}}{[H^+] [H_2CO_3^*]}$$

Concentration of reactant species at $x_{ij} = x_i + \Delta x$ and $t_{ij} = t_j + \Delta t$:

$H^+$:  
$$[H^+]_{i,j+1} = [H^+]_{i,j} - \kappa_1 [H^+]_{i,j} \left(1 - \frac{\Omega_{ij}}{K_{eq}}\right) \frac{L_{ch}}{v_{ij}}$$

$CO_2$(aq):  
$$[H_2CO_3^*]_{i,j+1} = [H_2CO_3^*]_{i,j} - \kappa_2 [H_2CO_3^*]_{i,j} \left(1 - \frac{\Omega_{ij}}{K_{eq}}\right) \frac{L_{ch}}{v_{ij}}$$

Concentration of produced species at $x_{ij} = x_i + \Delta x$ and $t_{ij} = t_j + \Delta t$:

$Ca^{2+}$:  
$$[Ca^{2+}]_{i,j+1} = [Ca^{2+}]_{i,j} + \kappa_1 [H^+]_{i,j} + \kappa_2 [H_2CO_3^*]_{i,j} \left(1 - \frac{\Omega_{ij}}{K_{eq}}\right) \frac{L_{ch}}{v_{ij}}$$

$HCO_3^-$:  
$$[HCO_3^-]_{i,j+1} = [HCO_3^-]_{i,j} + \kappa_1 [H^+]_{i,j} + 2\kappa_2 [H_2CO_3^*]_{i,j} \left(1 - \frac{\Omega_{ij}}{K_{eq}}\right) \frac{L_{ch}}{v_{ij}}$$

Time interval for one iteration:
$$\Delta t = \beta \frac{L_{ch}}{v_{av}}$$

Enlargement of a tube:
$$\Delta d_{ij} = \frac{2V_{ij} \Delta t}{\rho_{ch}} \frac{q_{i,j}}{d_{ij}} \left(\kappa_1 [H^+]_{i,j} + \kappa_2 [H_2CO_3^*]_{i,j} \right) \left(1 - \frac{\Omega_{ij}}{K_{eq}}\right) \frac{L_{ch}}{v_{ij}}$$

Instantaneous mixing:
$$c_{i+1,j}^{new} = \sum_{i} q_{i,j} c_{i+1,j}^{old}$$

Updates on nodal pressure, velocity, and flow rate
5.4 Results

Reservoir parameters and pressure conditions are selected in view of CO₂ storage reservoirs. Parameters and results are discussed next.

5.4.1 Selected Parameters

Distribution of tube diameters. The mean tube diameter $\bar{d}_0$ is selected to satisfy typical reservoir permeabilities $k_{perm}$ [md]. Given the following empirical expression (Bachu and Bennion, 2008),

$$\frac{k_{perm}}{1\text{md}} = 0.37 \cdot \left( \frac{\bar{d}_0}{1\mu m} \right)^{2.05}$$

we select a value $\bar{d}_0 \approx 20 \mu m$ for a reservoir permeability of $k_{perm} \approx 172 \text{md}$ which is in the range for carbonate porous rocks (Brosse et al., 2005; Egermann et al., 2005). Pore diameters are log-normally distributed with a coefficient of variation COV=0.4 for sediments (Phadnis and Santamarina, 2011); we also test COV=1.0 and 1.5 that correspond to fractured rocks (Shapiro, 2010).

In-situ hydraulic gradient. The injection pressure is limited to prevent hydraulic fracture. The hydraulic gradient $i_h$ is highest near the injection well and diminishes inversely proportional to distance from the well. In this study, we test three different hydraulic gradients $i_h=10$, 100, and 1000.

5.4.2 Results

Concentration. The spatial distributions of species concentration ($H^+$, $H_2CO_3^*$, $Ca^{2+}$, and $HCO_3^-$) are monitored during fluid flow (Figure 5.4). When the advection time is much longer compared to the reaction time ($Da>10^{-4}$), the concentration of reactant species (i.e., $H^+$ and $H_2CO_3^*$) rapidly decreases near the inlet. However, reactant species migrate towards the outlet and ramify as the hydraulic gradient increases and $Da<10^{-4}$. The lower consumption of reactant species with higher hydraulic gradients makes the pH converge.
to lower values away from the inlet (Figure 5.5-a). Electro-neutrality is satisfied during the numerical simulation (Figure 5.5-b).

![Figure 5.4](image)

Figure 5.4  Distribution of species concentration after 1000 network pore volumes have been flushed through the system: (a) $H^+$, (b) $H_2CO_3^*$, (c) $Ca^{2+}$, and (d) $HCO_3^-$ ($i_h=1000$, $Da=1.5*10^{-5}$, $Pe=6.8*10^{3}$).

**Pore Diameter.** Tube diameter enlargement prevails near the inlet when the hydraulic gradient $i_h$ is low ($i_h<100$; $Da>10^{-3}$ Figure 5.6-a), but it extends towards the outlet as the advection velocity increases (Figure 5.6-b). Figure 5.6 shows tube diameter enlargement after 1000 network pore volumes $V_p$ have been flushed (Note: when $i_h=1000$ ($Da~10^{-5}$), the corresponding total simulation time is two orders of magnitude longer than
characteristic time for calcite dissolution by hydrogen ions $H^+$). For a given number of network pore volumes flushed, the higher the advection velocity the lower the eroded mass within a given model space (Figure 5.6-c).

![Graph](image)

**Figure 5.5** Evolution of pH in space and time. (a) The average pH along the network model after 1000 network pore volumes have been flushed through the system. (b) Verification of electro-neutrality along the network model. Note: Damköhler number decreases from $Da=1.5\times10^{-3}$ to $Da=1.5\times10^{-4}$ and $Da=1.5\times10^{-5}$ as hydraulic gradient increases from $i_h=10$ to $i_h=100$ and $i_h=1000$.  

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Flow rate. Reactive flow tends to preferentially enlarge tubes with high flow velocity. Figure 5.7 compares the normalized change in flow rate $\Delta q/q_{0,max}$ after 1000 network pore volumes under different hydraulic gradients: the initial pore size distribution (COV=0.4) evolves towards localized flow and wormhole formation. The flow pattern clearly shows that initially dominant channels experience most of the increase in the flow rate during reactive fluid flow at high gradients (Figure 5.7-b and c), however, flow remains more homogeneous after 1000·$V_p$ when the hydraulic gradient is low ($i_h=10$; $Da\sim10^{-3}$, Figure 5.7-a).

Figure 5.6 Evolution in tube diameters during reactive fluid transport. Line thickness represents normalized diameter growth $(\Delta d/d_0)*50$ (top), and cumulative distribution of initial tube diameters and tube diameters after 1000 network pore volumes have been flushed is shown in bottom (coefficient of variation COV=0.4): (a) $i_h=10$ ($Da=1.5*10^{-3}$, $Pe=6.8*10$), (b) $i_h=100$ ($Da=1.5*10^{-4}$, $Pe=6.8*10^2$), and (c) $i_h=1000$ ($Da=1.5*10^{-5}$, $Pe=6.8*10^3$).
**Pressure.** The pressure field in the porous medium changes with preferential tube enlargement. At low hydraulic gradients, high dissolution at the inlet transfers high inlet pressures further into the medium (Figure 5.8-a). As the hydraulic gradient $i_h$ increases, dissolution extends further into the medium and pressure follows the pre-dissolution trend closer (Figures 5.8-b~d).

![Figure 5.7 Evolution in flow rate across the network model. Line thickness represents normalized flow rate increase ($Δq/q_{0,max}$)*100 after 1000 network pore volumes have been flushed (COV=0.4): (a) $i_h=10$ ($Da=1.5*10^{-3}$, $Pe=6.8*10$), (b) $i_h=100$ ($Da=1.5*10^{-4}$, $Pe=6.8*10^2$), and (c) $i_h=1000$ ($Da=1.5*10^{-5}$, $Pe=6.8*10^3$).](image)

**Porosity-permeability.** Enlargement in tube diameters increases both porosity and permeability. The Kozeny-Carman equation (Carman, 1956) suggests a power relationship between relative porosity $φ/φ_0$ and relative permeability $k/k_0$:

$$\frac{k}{k_0} = \left(\frac{φ}{φ_0}\right)^\alpha$$  \hspace{1cm} \text{(24)}$$

where $φ_0$ and $k_0$ are selected reference values. Consider a cylindrical tube in representative elementary volume. A change in pore diameter $Δd$ corresponds to change in porosity $Δφ$: 

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\[
\frac{\Delta d}{d_0} = \left(1 + \frac{\Delta \phi}{\phi_0} - 1\right)
\]  
(25)

For small changes in normalized porosity $\Delta \phi/\phi_0 \ll 1$, Equation 25 approaches:

\[
\frac{\Delta d}{d_0} \approx \frac{1}{2} \frac{\Delta \phi}{\phi_0}
\]
(26)

Thus, changes in porosity are proportional to changes in pore diameter. Equations 24 and 25 (or 26) link micro-scale change in pore size to macro-scale changes in permeability.

Figure 5.8  Pressure field after 1000 network pore volumes have been flushed (COV=0.4): (a) $i_h=10$ ($Da=1.5*10^{-3}$, $Pe=6.8*10$), (b) $i_h=100$ ($Da=1.5*10^{-4}$, $Pe=6.8*10^2$), (c) $i_h=1000$ ($Da=1.5*10^{-5}$, $Pe=6.8*10^3$), and (d) normalized average pressure with respect to the distance from inlet (initial graph is identical to the normalized average pressure when $i_h=1000$).
When the hydraulic gradient is high $Da<10^{-4}$ ($i_h>100$), the normalized mean tube diameter $\overline{d}/d_0$ is linearly related to the normalized flow rate $q/q_0$ (Figure 5.9-a). However, when the hydraulic gradient is low $Da\sim10^{-3}$ ($i_h=10$), the trend $q/q_0$ vs. $\overline{d}/d_0$ deviates from linearity and reaches a plateau, even though the normalized mean tube diameter continues increasing; this apparent paradox is explained by the localized dissolution near the inlet (Figure 5.6-a). Figure 5.10 compares the normalized flow rate and the normalized mean tube diameter for the first layer of tubes next to the inlet. When the hydraulic gradient is high $Da\sim10^{-5}$ ($i_h=1,000$), the relationship approaches the upper bound where every tube grows in proportion to its initial diameter. As the hydraulic gradient $i_h$ decreases, the relationship moves downwards until it hits the plateau. Results in Figures 5.9 and 5.10 highlight the inherent bias when “average trends” are analyzed in reactive fluid flow.

![Figure 5.9](image-url)  

Figure 5.9  Evolution in flow rate normalized by the original total flow rate $q/q_0$ with respect to: (a) normalized mean tube diameter $\overline{d}/d_0$, and (b) flushed pore volume for different Damköhler number $Da$ (COV=0.4). Note: Damköhler number is $Da=1.5\times10^{-3}$ for hydraulic gradient $i_h=10$, $Da=1.5\times10^{-4}$ for $i_h=100$, and $Da=1.5\times10^{-5}$ for $i_h=1000$. 

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Figure 5.10 Evolution in flow rate normalized by the original total flow rate $q/q_0$ with respect to the normalized mean tube diameter $d/d_0$ for the first layer next to the inlet (COV=0.4, up to 1000 flushed network pore volumes), and the theoretical bound in which all tubes grow proportional to their original diameter values (solid line). Note: Damköhler number is $Da=1.5 \times 10^{-3}$ for $i_h=10$, $Da=1.5 \times 10^{-4}$ for $i_h=100$, and $Da=1.5 \times 10^{-5}$ for $i_h=1000$. 
5.5 Discussion

5.5.1 Dissolution Pattern

We use the numerical algorithm described above to explore dissolution patterns in the context of CO$_2$ injection projects (for $Da$<<1). The summary plot in terms of the Damköhler number $Da$ in Figure 5.11 shows that the reactive flow of water with dissolved CO$_2$ yields either compact dissolution near the inlet ($Da$>10$^{-4}$) or several branches of localized flow paths ($Da$<10$^{-4}$). These results agree with previous studies that show a transition from compact dissolution to uniform dissolution at around $10^{-4}$<Da<10$^{-3}$ (injection tests of under-saturated salt solution in a porous medium made of salt grains - Golfier et al., 2002).

![Diagram of dissolution pattern](image-url)

Figure 5.11 Dissolution pattern as a function of the Damköhler number $Da$, for 1000 flushed network pore volumes: CO$_2$-dissolved fluid flow through porous media during CO$_2$ geological storage. Note: network simulations were conducted for various hydraulic gradients $i_h$=10 ($Da$=1.5*10$^{-3}$), 20,…, 200 ($Da$=3*10$^{-4}$), and 1000 ($Da$=1.5*10$^{-5}$).
5.5.2 Effect of Initial Pore Size Variability

The coefficient of variation COV in pore size is larger in jointed rock masses than in sediments (compare Phadnis and Santamarina, 2011 and Shapiro, 2010). Let’s examine the role of pore size variability on the evolution of mean tube diameter and flow rate by running additional simulations with COV=1.0 and 1.5. Results in Figure 5.12-a show that the normalized flow rate increases faster with higher COV values for a given increase in the normalized mean tube diameter. Hence, the exponent for the Kozeny-Carman equation $\alpha$ (Equation 24) increases with pore-size variability. Moreover, the range in the exponent $\alpha$ widens as the coefficient of variation in pore size COV increases (Figure 5.12-b): a porous medium with a higher COV is likely to have more localized fluid flow whereby few channels are responsible for most of the flow.

![Figure 5.12](Fig5.12.png)

Figure 5.12 Dependency of the mean tube diameter-flow rate evolution on pore-size variability: (a) typical mean tube diameter-flow rate evolution with respect to different coefficient of variations COV, and (b) comparison of exponent $\alpha$ for $\left(\frac{q}{q_0}\right) = \left(\frac{d}{d_0}\right)^\alpha$; all simulations were conducted up to 1000 flushed network pore volumes with hydraulic gradient $i_h=1000$ ($Da=1.5x10^{-5}$).
5.6 Conclusions

Reactive fluid flow prevails near the CO$_2$-water boundary, and it displaces during CO$_2$ injection (Figure 5.1). The dissolution rate between minerals and reactant species in the case of CO$_2$-dissolved water is relatively low. At the same time, the CO$_2$ front displaces at low velocity because injection pressure are limited to prevent hydraulic fracture.

A new network simulation code was written to investigate fluid-mineral interaction when CO$_2$-dissolved water flows through a calcitic porous network near the CO$_2$-water boundary. Simulation results include the distribution of reactive species and reaction product concentrations, the evolution of tube diameters, pressure field, and the relationship between mean tube diameter and flow rate as a result of the CO$_2$-dissolved reactive fluid flow. Results show:

- The concentration of reactant species rapidly decreases near the inlet when the hydraulic gradient is low and Damköhler number exceeds $Da>10^{-4}$. Reactant species migrate towards the outlet and ramify as the hydraulic gradient increases and the Damköhler number drops $Da<10^{-4}$.
- At low hydraulic gradients ($Da>10^{-4}$; $i_h<100$), tube diameter enlargement prevails near the inlet, flow remains more homogeneous, and high inlet pressure is gradually transferred further into the formation. As hydraulic gradients increase ($Da<10^{-4}$; $i_h>100$), pore enlargement extends towards the outlet and reactive flow tends to preferentially enlarges tubes with high flow rate.
- Results show that calcite storage reservoir will experience either compact dissolution near the inlet ($Da>10^{-4}$) or localized flow paths ($Da<10^{-4}$) as a result of CO$_2$-dissolved reactive fluid flow.
- Both the Damköhler number and pore-size variability affect the relationship between mean tube diameter and flow rate. Changes in Damköhler number result in inherent bias between average and local trends. The exponent of the Kozeny-Carman equation
\( q_l/q_0 = (\psi/\psi_0)^\alpha \) increases with the coefficient of variation COV in pore size. Both the Damköhler number and pore-size variability should be accounted in field-scale FEM models.
CHAPTER 6

REACTIVE FLUID FLOW THROUGH THE CAPROCK

OVERLYING CO₂ STORAGE RESERVOIRS

6.1 Introduction

More than 80% of the electric power in the USA is produced by burning fossil fuels (DOE, 2010), resulting in CO₂ emissions into the atmosphere. The geological storage of CO₂ has been suggested to mitigate the potential consequences of CO₂ emissions (IPCC, 2005), whereby large quantities of CO₂ are injected typically deeper than 800m to attain supercritical CO₂ conditions in order to minimize the affected volume (Note: supercritical temperature \( T \geq 304.1K \) and pressure \( P \geq 7.38MPa \)). Supercritical CO₂ migrates upwards due to buoyancy and accumulates underneath the caprock.

Most sites considered for CO₂ storage involve low-permeability clay-rich water-saturated caprocks \( (10^{-22}m^2 < k_{perm} < 10^{-19}m^2 \) - Katsube and Williamson, 1994; Horseman et al., 1999; Armitage et al., 2010). The solubility of CO₂ in water can be as high as 1-to-2 moles/L under the P-T conditions in deep reservoirs (Duan and Sun, 2003). Therefore, water with high-CO₂ concentration may diffuse through the caprock even when small pores prevent CO₂ invasion and advective transport (Figure 6.1; Gaus et al., 2005). Dissolved CO₂ acidifies the formation water, changes the surface charge in clay minerals, and causes mineral dissolution (Chapter 3; Gherardi et al., 2007; Berne et al., 2010; Espinoza and Santamarina, 2012). Furthermore, discontinuities in the caprock such as cracks or faults favor localized fluid migration and erosion (Chapter 4; Bildstein et al., 2010). These observations suggest that a proper understanding of reactive fluid flow in the caprock is critical to the analysis of the long-term integrity of geologic seals in CO₂ storage projects.
Figure 6.1  CO₂ geological storage and coupled processes: four zones around a CO₂ injection well (modified from Azaroual et al., 2007). The focal area for this study is within the rectangular frame. CO₂ plumes migrate upwards by buoyancy and accumulate underneath the caprock, and sustain the diffusion of dissolved CO₂ into the caprock (M: Mineral, B: Brine, $S_{CO₂}$: saturation of CO₂, and $S_B$: saturation of brine).

Recent studies related to geochemical changes in caprocks following the accumulation of CO₂ plumes have shown that: the diffusion of dissolved CO₂ may negatively affect the porosity and sealing capacity of the caprock (Gaus et al., 2005; Johnson et al., 2004); the primary mineral composition of the caprock determines the CO₂ trapping capacity (Xu et al., 2005); buffering and mineral precipitation may preserve
the sealing capacity of the caprock in a diffusion-controlled regime (Gherardi et al., 2007); and that the impact of mineral dissolution and precipitation on porosity changes may be limited to a narrow zone in the caprock next to the reservoir (Bildstein et al., 2010).

This study analyzes transport conditions in the caprock and examines the consequences of reactive CO$_2$-dissolved fluid flow. Simulation results are used to investigate changes in hydraulic properties in the caprock as a result of CO$_2$ injection. Caprock transport conditions are analyzed first, followed by a detailed description of the numerical algorithm.

6.2 Transport Conditions in the Caprock

Fluid pressure and hydraulic gradient. Injected CO$_2$ migrates upwards by buoyancy and accumulates underneath the caprock due to capillary trapping (Chapter 3; Kopp et al., 2009). The excess fluid pressure $\Delta P$ [Pa] at the bottom of the caprock due to presence of buoyant CO$_2$ is a function of the thickness of the CO$_2$-filled storage reservoir $H_R$ [m], and the unit weight of CO$_2$ $\gamma_{CO2}$ [N/m$^3$] and water $\gamma_w$ [N/m$^3$] as shown in Figure 6.2:

$$\Delta P = H_R \cdot (\gamma_w - \gamma_{CO2})$$  \hspace{1cm} (1)

The total head difference $\Delta h_T$ across the caprock thickness $H_C$ [m] is computed from the pressure head difference $\Delta h_p = h_p^I - h_p^{II} = \Delta P/\gamma_w$ and the elevation head difference $\Delta h_e = h_e^I - h_e^{II}$:

$$\Delta h_T = (h_p^I - h_p^{II}) + (h_e^I - h_e^{II}) = \frac{\Delta P + H_C \gamma_w}{\gamma_w} - H_C = H_R \frac{\gamma_w - \gamma_{CO2}}{\gamma_w}$$ \hspace{1cm} (2)

Therefore, the hydraulic gradient $i_h$ across the caprock is:

$$i_h = \frac{\Delta h_T}{H_C} = \left( \frac{H_R}{H_C} \right) \cdot \left( \frac{\gamma_w - \gamma_{CO2}}{\gamma_w} \right)$$ \hspace{1cm} (3)

The CO$_2$ density can vary from 200kg/m$^3$ to 800kg/m$^3$ under storage conditions that cover both cold ($i_T \leq 20^\circ$C/km) and warm geothermal gradients ($i_T \geq 45^\circ$C/km-IPCC, 2005).
Figure 6.2  Trapping, and hydraulic gradient $i_h$ for the upward flow through caprock with different $CO_2$ densities $\rho_{CO2}$ [kg/m³]. Parameters: storage reservoir thickness $H_R$ [m], caprock thickness $H_C$ [m], unit weight of brine $\gamma_w$ [N/m³], unit weight of CO₂ $\gamma_{CO2}$ [N/m³], total head $h_T$ [m], pressure head $h_p$ [m], elevation head $h_e$ [m], CO₂ entry pressure $P_{CEP}$ [Pa], interfacial tension between CO₂ and brine as a function of fluid pressure $T_s(u)$ [N/m], characteristic pore diameter $d_{pore}$ [m].

(a) Excess fluid pressure at the bottom of caprock

\[ \Delta P = \left( \gamma_w - \gamma_{CO2} \right) H_R \]

(b) Condition for capillary trapping

\[ \Delta P \leq P_{CEP} = \frac{4T_s(u)}{d_{pore}} \]

(c) If capillary trapping fails, advecting gradient is as follows:

Head difference:

\[ \Delta h_r = h'_r - h''_r \]

\[ = \left( h'_p - h''_p \right) + \left( h'_e - h''_e \right) \]

\[ = \frac{\Delta P + H_C \gamma_w - H_C}{\gamma_w} \]

\[ = \frac{\Delta P + H_C \gamma_w - H_C}{\gamma_w} \]

\[ = H_R \left( \frac{\gamma_w - \gamma_{CO2}}{\gamma_w} \right) \]

\[ \Rightarrow i_h = \frac{\Delta h_r}{H_C} = \left( \frac{H_R}{H_C} \right) \left( 1 - \frac{\gamma_{CO2}}{\gamma_w} \right) \]

\[ \begin{array}{c}
\text{Hydraulic gradient, } i_h \\
\end{array} \]

\[ \begin{array}{c}
\text{Ratio of reservoir/caprock thickness, } H_R/H_C \\
\end{array} \]

\[ \begin{array}{c}
\rho_{CO2} \text{[kg/m}^3] = 400 \\
600 \\
800 \\
\end{array} \]
For these conditions, the potential hydraulic gradient is quite small (Equation 3), in fact, it is $i_h < 10$ for most sites currently under consideration (Figure 6.2).

**Reactive transport regime.** The time scales for advection $t_{adv}$, diffusion $t_{diff}$, and reaction $t_{rxn}$ can be combined to form two dimensionless ratios, i.e., the Damköhler number $Da$ and Peclet’s number $Pe$:

$$Da = \frac{t_{adv}}{t_{rxn}} = \frac{\kappa H_c}{v_{ave}}$$

$$Pe = \frac{t_{diff}}{t_{adv}} = \frac{v_{ave} H_c}{D}$$

where $D$ [m$^2$/s] denotes the coefficient of molecular diffusion. The kinetic rate $\kappa$ [1/s] = $k_r S_s M_m$ is a function of the rate constant for mineral dissolution $k_r$ [mol/m$^2$/s], the mineral specific surface $S_s$ [m$^2$/g], and the mineral molar mass $M_m$ [g/mol].

If advective flow develops across the caprock, the average flow velocity $v_{ave}$ [m/s] would be a function of the hydraulic gradient $i_h$ across the caprock (Equation 3) according to Darcy’s law:

$$v_{ave} = K_{con} \cdot i_h$$

The hydraulic conductivity $K_{con}$ [cm/s] ranges between $10^{-10}$cm/s and $10^{-13}$cm/s for typical seal rocks in the absence of discontinuities (Note: hydraulic conductivity $K_{con}=k_{perm} \rho_w g/\mu_w$ is computed from the absolute permeability $10^{-22}$m$^2 < k_{perm} < 10^{-19}$m$^2$, water density $\rho_w = 1000$kg/m$^3$, and water viscosity $\mu_w = 10^{-3}$Pa·s). The resulting Peclet’s number is much smaller than one, $10^{-6} < Pe < 10^{-3}$ for the anticipated hydraulic gradients $i_h < 10$. Therefore, diffusive transport prevails over advective transport in the caprock.

**Capillary trapping.** A laplacian interface between water and CO$_2$ develops at pore throats size $d_{pore}$ [m] and can sustain a CO$_2$–water pressure difference that is proportional to the interfacial tension $T_s \approx 35$mN/m (Espinoza and Santamarina, 2010):
The trapping number $\pi_c$ is the ratio between the capillary entry pressure $P_{CEP}$ and the pressure difference at the caprock-reservoir interface $\Delta P = H_R \cdot (\gamma_w - \gamma_{CO2})$ as shown in Equation 1,

$$\pi_c = \frac{4 \cdot T_s}{d_{pore} \cdot H_R \cdot (\gamma_w - \gamma_{CO2})}$$

The pore size is $d_{pore} \leq 0.1 \mu m$ for most seal rocks without discontinuities, and anticipated reservoir thickness will be less than $H_R \leq 100 m$ in most cases. Therefore, $\pi_c \geq 3.6$ and capillary trapping is anticipated in CO$_2$ storage projects.

**Conclusion.** Capillary trapping concurs with the prevalent diffusive transport to define a diffusion-controlled reactive transport condition in the caprock.

### 6.3 Numerical Simulation Model for Diffusion-Controlled Reactive Transport

The governing pore-scale equations for diffusion-dominant reactive transport are numerically solved to analyze the caprock evolution in CO$_2$ storage projects.

#### 6.3.1 Mineralogy and Dissolution

The dissolution of CO$_2$ in water produces hydrogen ions $H^+$ and aqueous carbon dioxide CO$_{2(aq)}$; both species cause mineral dissolution. Calcite and kaolinite are selected to analyze a worst-case scenario and a more common mineralogy frequently encountered in potential reservoir caprock.

**Calcite.** Carbonate content in shales varies from 1% to 65% (Guéguen and Palciauskas, 1994; Wollenweber et al., 2010). The two dominant calcium carbonate dissolution reactions at high $H^+$ and CO$_{2(aq)}$ concentrations are (Plummer et al., 1978):
CaCO$_3$(s) + H$^+$ → Ca$^{2+}$ + HCO$_3^-$ \hspace{1cm} (9)

CaCO$_3$(s) + CO$_2$(aq) + H$_2$O → Ca$^{2+}$ + 2HCO$_3^-$ \hspace{1cm} (10)

**Kaolinite.** Kaolinite is selected to examine clayey caprocks. We adopt the model by Li et al. (2006) to represent the dissolution of kaolinite. The reaction consumes six moles of $H^+$ to produce two moles of $Al^{3+}$ and two moles of $H_4SiO_4$:

$$Al_2Si_2O_5(OH)_{4(s)} + 6H^+ → 2Al^{3+} + 2H_4SiO_4 + H_2O$$ \hspace{1cm} (11)

**First-order kinetics.** The formulation assumes first-order kinetics:

$$-\frac{d[\text{react}]}{dt} = \frac{V_{\text{produced}}}{V_{\text{react}}} \frac{d[\text{produced}]}{dt} = \kappa [\text{react}]$$ \hspace{1cm} (12)

where square brackets indicate species concentration, $V_{\text{produced}}/V_{\text{react}}$ defines stoichiometric ratio between produced and reactant species, and $\kappa$ [1/s] denotes the kinetic rate for each chemical equation. The system reaches equilibrium and mineral dissolution stops when the ionic concentration product $\Omega$ [-] equals the equilibrium constant $K_{eq}$ [-]:

$$\Omega = \frac{\Pi[\text{produced}]^\nu}{\Pi[\text{react}]^\nu} = K_{eq}$$ \hspace{1cm} (13)

where $\Pi$ indicates product of components in series. Mineral precipitation is not considered in this study. All parameters and rate constants are summarized in Table 6.2.

<table>
<thead>
<tr>
<th>Table 6.1 Parameters used for numerical simulations and analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Number of nodes, $N$</td>
</tr>
<tr>
<td>Length between nodes, $\Delta x$</td>
</tr>
<tr>
<td>Mineralogy</td>
</tr>
<tr>
<td>Courant number, $D\Delta t/(\Delta x)^2$ ($D$ [m$^2$/s]; coefficient of diffusion)</td>
</tr>
<tr>
<td>Characteristic time for diffusion, $t_{ch}$</td>
</tr>
<tr>
<td>Initial porosity, $\phi_0$</td>
</tr>
<tr>
<td>Mean pore diameters, $d_0$</td>
</tr>
<tr>
<td>Interfacial tension between CO$_2$ and water, $T_i$</td>
</tr>
<tr>
<td>Thickness of reservoir, $H_R$</td>
</tr>
<tr>
<td>Density difference between CO$_2$ and water, $\Delta\rho$</td>
</tr>
</tbody>
</table>
Table 6.2  Chemical properties for calcite and kaolinite used in the numerical simulation

(a) Equations for mineral dissolution and properties

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical equation for mineral dissolution</th>
<th>Rate constant [mol/m^2/s]</th>
<th>Equilibrium constant</th>
<th>Ionic concentration product, Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃(s) + H⁺ → Ca²⁺ + HCO₃⁻</td>
<td>kᵢ=0.745 (1)</td>
<td>Kₑq=10⁻⁸⁵ (1)</td>
<td>[Ca²⁺][HCO₃⁻]³/([H⁺][H₂CO₃])</td>
</tr>
<tr>
<td></td>
<td>CaCO₃(s) + CO₂(aq) + H₂O → Ca²⁺ + 2HCO₃⁻</td>
<td>kᵢ=8.6*10⁻⁴ (1)</td>
<td>Kₑq=10⁻₄₅ (1)</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₄Si₂O₅(OH)₄(s) + 6H⁺ → 2Al³⁺ + 2H₂SiO₄ + H₂O</td>
<td>kᵢ=2.79*10⁻¹¹</td>
<td>Kₑq=10⁻³₈₀ (1)</td>
<td>[Al³⁺][H₂SiO₄]²/[H⁺]₆</td>
</tr>
</tbody>
</table>

(b) Boundary condition: Concentrations of species in calcite-dominant environment

<table>
<thead>
<tr>
<th>Inlet concentration</th>
<th>Initial concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H⁺]_inlet=6.68*10⁻⁴mol/L</td>
<td>[H⁺]_initial=1.0*10⁻⁸mol/L</td>
</tr>
<tr>
<td>[H₂CO₃⁺]_inlet=1mol/L</td>
<td>[H₂CO₃⁺]_initial=1.0*10⁻⁵mol/L</td>
</tr>
<tr>
<td>[HCO₃⁻]_inlet=6.68*10⁻⁴mol/L</td>
<td>[HCO₃⁻]_initial=4.47*10⁻⁴mol/L</td>
</tr>
<tr>
<td>[Ca²⁺]_inlet=1.36*10⁻³mol/L</td>
<td>[Ca²⁺]_initial=1.59*10⁻³mol/L</td>
</tr>
<tr>
<td>[OH⁻]_inlet=1.50*10⁻¹¹mol/L</td>
<td>[OH⁻]_initial=1.0*10⁻¹⁰mol/L</td>
</tr>
<tr>
<td>[Cl⁻]_inlet=2.72*10⁻³mol/L</td>
<td>[Cl⁻]_initial=2.72*10⁻³mol/L</td>
</tr>
</tbody>
</table>

(c) Boundary condition: Concentrations of species in kaolinite-dominant environment

<table>
<thead>
<tr>
<th>Inlet concentration</th>
<th>Initial concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H⁺]_inlet=6.68*10⁻⁴mol/L</td>
<td>[H⁺]_initial=1.0*10⁻⁸mol/L</td>
</tr>
<tr>
<td>[H₂CO₃⁺]_inlet=1mol/L</td>
<td>[H₂CO₃⁺]_initial=1.0*10⁻⁵mol/L</td>
</tr>
<tr>
<td>[HCO₃⁻]_inlet=6.68*10⁻⁴mol/L</td>
<td>[HCO₃⁻]_initial=4.47*10⁻⁴mol/L</td>
</tr>
<tr>
<td>[OH⁻]_inlet=1.50*10⁻¹¹mol/L</td>
<td>[OH⁻]_initial=1.0*10⁻¹⁰mol/L</td>
</tr>
<tr>
<td>[Al³⁺]_inlet=8.91*10⁻¹²mol/L</td>
<td>[Al³⁺]_initial=8.91*10⁻¹²mol/L</td>
</tr>
<tr>
<td>[H₂SiO₄]_inlet=8.91*10⁻¹²mol/L</td>
<td>[H₂SiO₄]_initial=8.91*10⁻¹²mol/L</td>
</tr>
<tr>
<td>[Na⁺]_inlet=1.0*10⁻¹²mol/L</td>
<td>[Na⁺]_initial=4.48*10⁻¹⁰mol/L</td>
</tr>
</tbody>
</table>

(d) Coefficient of molecular diffusion: D=2.0*10⁻⁹m²/s

Note: Sᵢ: mineral specific surface, Mᵢ: mineral molar mass, Vᵢ: mineral molar volume; kinetic rate is kᵢ[1/s]=kᵢSᵢMᵢ where kᵢ is a rate constant; Rate constants are computed for T=40°C in this study; total equilibrium constant for calcite Kₑq=Kₑq*Kₑq. References/comments: (1) Plummer et al., 1978; Fredd and Fogler, 1998; Pokrovsky et al., 2005; Renard et al., 2005; Algive et al., 2009, (2) Li et al., 2006, (3) Xu et al., 2006, (4) The average molecular diffusion coefficient is selected to satisfy electro-neutrality.)
6.3.2 Numerical Simulation – Algorithm

Reactants. The equation for diffusion-dominant reactive transport predicts, the concentration \( c \) [mol/m\(^3\)] of reactant species (i.e., \( H^+ \) and \( H_2CO_3^* \); total carbonic acid \( H_2CO_3^* \) denotes the summation of aqueous carbon dioxide \( CO_2(aq) \) and true carbonic acid \( H_2CO_3 \)) in the caprock in the absence of advection (Peclet’s number \( Pe<<1 \) and trapping number \( \pi_c>1 \)); for one-dimensional transport:

\[
\frac{dc}{dt} + \kappa c = D \frac{d^2c}{dx^2}
\]  
(14)

Let’s add a saturation criterion \((1-\Omega/K_{eq})\) into Equation 14 in terms of the ratio between the ionic concentration product \( \Omega \) and the equilibrium constant \( K_{eq} \):

\[
\frac{dc}{dt} + \kappa \left( 1 - \frac{\Omega}{K_{eq}} \right) = D \frac{d^2c}{dx^2}
\]  
(15)

Equation 15 is expressed in finite difference form to estimate the species concentration \( c_{i,j+1} \) at location \( x_i \) and time \( t_{j+1} = t_j + \Delta t \) with information of species concentrations at location \( x_i \), \( x_{i-1} = x_i - \Delta x \), and \( x_{i+1} = x_i + \Delta x \) at time \( t_j \) (Note: \( \Omega_{ij} \) is the ionic concentration product at location \( x_i \) and time \( t_j \)):

\[
c_{i,j+1} = c_{i,j} \left( 1 - \kappa \cdot \Delta t \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \right) + D \frac{\Delta t}{\Delta x^2} \left( c_{i-1,j} - 2 \cdot c_{i,j} + c_{i+1,j} \right)
\]  
(16)

Thus, the concentrations of \( H^+ \) and \( H_2CO_3^* \) are computed as follows:

for calcite dissolution

\[
[H^+]_{i,j+1} = [H^+]_{i,j} \left( 1 - \kappa_1 \cdot \Delta t \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \right) + D \frac{\Delta t}{\Delta x^2} \left( [H^+]_{i-1,j} - 2[H^+]_{i,j} + [H^+]_{i+1,j} \right)
\]  
(17)

\[
[H_2CO_3^*]_{i,j+1} = [H_2CO_3^*]_{i,j} \left( 1 - \kappa_2 \cdot \Delta t \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \right) + D \frac{\Delta t}{\Delta x^2} \left( [H_2CO_3^*]_{i-1,j} - 2[H_2CO_3^*]_{i,j} + [H_2CO_3^*]_{i+1,j} \right)
\]  
(18)

for kaolinite dissolution
\[ [H^+]_{i,j+1} = [H^+]_{i,j} \left( 1 - \kappa_H \cdot \Delta t \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \right) + D \frac{\Delta t}{\Delta x^2} \left( [H^+]_{i-1,j} - 2[H^+]_{i,j} + [H^+]_{i+1,j} \right) \]

(19)

**Products.** The concentrations of produced species (i.e., \(Ca^{2+}\) and \(HCO_3^-\) in calcite and \(Al^{3+}\) and \(H_4SiO_4\) in kaolinite) are determined from the consumption of reactant species in terms of stoichiometric ratios between reactant and produced species. Furthermore, they are subjected to diffusion as well, hence:

for \(Ca^{2+}\):\[
[Ca^{2+}]_{i,j+1} = [Ca^{2+}]_{i,j} + \left( \kappa_1[H^+]_{i,j} + \kappa_2[H_2CO_3^+]_{i,j} \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \Delta t
\]

\[ + D \frac{\Delta t}{\Delta x^2} \left( [Ca^{2+}]_{i-1,j} - 2[Ca^{2+}]_{i,j} + [Ca^{2+}]_{i+1,j} \right) \]

(20)

for \(HCO_3^-\):\[
[HCO_3^-]_{i,j+1} = [HCO_3^-]_{i,j} + \left( \kappa_1[H^+]_{i,j} + 2\kappa_2[H_2CO_3^+]_{i,j} \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \Delta t
\]

\[ + D \frac{\Delta t}{\Delta x^2} \left( [HCO_3^-]_{i-1,j} - 2[HCO_3^-]_{i,j} + [HCO_3^-]_{i+1,j} \right) \]

(21)

for \(Al^{3+}\):\[
[Al^{3+}]_{i,j+1} = [Al^{3+}]_{i,j} + \left( \frac{\kappa_H[H^+]_{i,j}}{3} \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \Delta t
\]

\[ + D \frac{\Delta t}{\Delta x^2} \left( [Al^{3+}]_{i-1,j} - 2[Al^{3+}]_{i,j} + [Al^{3+}]_{i+1,j} \right) \]

(22)

for \(H_4SiO_4\):\[
[H_4SiO_4]_{i,j+1} = [H_4SiO_4]_{i,j} + \left( \frac{\kappa_H[H^+]_{i,j}}{3} \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \Delta t
\]

\[ + D \frac{\Delta t}{\Delta x^2} \left( [H_4SiO_4]_{i-1,j} - 2[H_4SiO_4]_{i,j} + [H_4SiO_4]_{i+1,j} \right) \]

(23)

**Boundary conditions.** The first node \(i=1\) represents the interface between the caprock and the reservoir, and it has a fixed concentration of reactant species. The concentration of total carbonic acid \([H_2CO_3^\leftrightarrow]\) is determined using expressions proposed by Duan and Sun (2003). Concentrations of hydrogen \([H^+]\), hydroxide \([OH^-]\), and bicarbonate \([HCO_3^-]\) are obtained from the thermodynamic equilibrium of carbonate system \(H_2CO_3^\leftrightarrow \leftrightarrow H^+ + HCO_3^-\).
at reservoir conditions $T=40^\circ C$ and $P=10\text{MPa}$. The initial concentration of other species ($Ca^{2+}$, $Al^{3+}$, $H_4SiO_4^-$, and $Cl^-$) at the inlet boundary $i=1$ at time $j=1$ are determined to satisfy electro-neutrality; thereafter values $c_{i=1,j}$ are allowed to change to prevent the backward diffusion of dissolved species (i.e., $c_{1,j}=c_{2,j}$ for time step $j>1$).

Three different boundary conditions are considered at the outlet $i=N$: a) fixed initial concentration $c_{N,j}=c_{N,1}$ for all $j>1$, b) free flux to simulate an infinite boundary $c_{N,j-1}-c_{N,j}=c_{N-1,j}-c_{N,j}$, and c) closed boundary by forcing $c_{N,j}=c_{N-1,j}$ to impose a null exit gradient.

Initial concentrations of species in the 1-D space are determined to be in thermodynamic-equilibrium and to satisfy electro-neutrality at pH=8, except the inlet ($2\leq j \leq N$). Species concentrations evolve as the numerical simulation proceeds (Equations 17 to 23). Tables 6.1 and 6.2 summarize parameters and geochemical values used in numerical simulations and analyses hereafter.

**Mineral dissolution.** The mineral mass consumption during the time interval $t_j$ to $t_{j+1}$ between location $x_i$ and $x_{i+1}$ is computed from the consumption of reactant species and the corresponding stoichiometric ratios:

$$
\Delta c_{i,j}^m = \left( \kappa_1[H^+]_{i,j} + \kappa_2[H_2CO_3]^+_{i,j} \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \Delta t ; \text{ calcite dissolution} \quad (24)
$$

$$
\Delta c_{i,j}^m = \left( \kappa_3[H^+]_{i,j} / 6 \right) \left( 1 - \frac{\Omega_{i,j}}{K_{eq}} \right) \Delta t ; \text{ kaolinite dissolution} \quad (25)
$$

**Algorithm stability.** The algorithm is summarized in Figure 6.3 for calcite and in Figure 6.4 for kaolinite. This formulation is stable when the diffusion coefficient $D$, kinetic rate $\kappa$, and the time and space intervals satisfy $D \Delta t / \Delta x^2 << 1$ and $\kappa \Delta t << 1$; thus, we set the time interval $\Delta t = 0.01 \cdot \Delta x^2 / D \leq 0.1 / \kappa$. One cycle in the numerical simulation implies a finite time interval $\Delta t$ and results in updated species concentrations and mass consumption at all nodes. We repeat this cycle until the total simulation time reaches $t = 10 \cdot L_{\text{total}}^2 / D$. 

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Figure 6.3  One-dimensional numerical simulation scheme for diffusive reactive transport in calcium carbonate caprocks.

\[ \text{CaCO}_3 \rightarrow \text{H}_2\text{CO}_3^* + \text{H}^+ \] kinetic rate \( \kappa_1 \)

\[ \text{CaCO}_3 + \text{CO}_2(aq) + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \] kinetic rate \( \kappa_2 \)

Equilibrium constant for the mineral dissolutions: \( K_{eq} \)

Ionic concentration product \( \Omega_{ij} \) at location \( x_i \) and time \( t_j \):

\[ \Omega_{ij} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}^+][\text{H}_2\text{CO}_3^*]} \]

Governing equation:

\[ \frac{dc}{dt} + \kappa_i \left( 1 - \frac{\Omega}{K_{eq}} \right) = D \frac{d^2c}{dx^2} \]

Concentration of reactant species at location \( x_i \) and time \( t_{j+1} = t_j + \Delta t \):

\[ [\text{H}^+]_{i,j} = [\text{H}^+]_{i,j-1} \left( 1 - \kappa_i \cdot \Delta t \left( 1 - \frac{\Omega_{ij}}{K_{eq}} \right) \right) + D \frac{\Delta \text{t}}{\Delta x^2} ([\text{H}^+]_{i+1,j-1} - 2[\text{H}^+]_{i,j} + [\text{H}^+]_{i-1,j}) \]

Concentration of produced species at location \( x_i \) and time \( t_{j+1} = t_j + \Delta t \):

\[ [\text{Ca}^{2+}]_{i,j} = [\text{Ca}^{2+}]_{i,j-1} \left( 1 - \kappa_i \cdot \Delta t \left( 1 - \frac{\Omega_{ij}}{K_{eq}} \right) \right) + D \frac{\Delta \text{t}}{\Delta x^2} ([\text{Ca}^{2+}]_{i+1,j-1} - 2[\text{Ca}^{2+}]_{i,j} + [\text{Ca}^{2+}]_{i-1,j}) \]

\[ [\text{HCO}_3^-]_{i,j} = [\text{HCO}_3^-]_{i,j-1} \left( 1 - \kappa_i \cdot \Delta t \left( 1 - \frac{\Omega_{ij}}{K_{eq}} \right) \right) + D \frac{\Delta \text{t}}{\Delta x^2} ([\text{HCO}_3^-]_{i+1,j-1} - 2[\text{HCO}_3^-]_{i,j} + [\text{HCO}_3^-]_{i-1,j}) \]

Mass consumption of mineral:

\[ \Delta \varepsilon_{ij} = \kappa_i [\text{H}^+]_{i,j} + \kappa_i [\text{H}_2\text{CO}_3^*]_{i,j} \left( \frac{\Omega_{ij}}{K_{eq}} \right) \Delta t \]
Figure 6.4  One-dimensional numerical simulation scheme for diffusive reactive transport in kaolinitic caprocks.
6.3.3 Verification

The numerical simulation code was verified with a closed-form solution for 1-dimensional reactive fluid transport (initial concentration condition \( c(x,0)=0 \) for \( x>0 \), and boundary conditions \( c(0,t)=c_{\text{inlet}} \) and \( c(\infty,t)=0 \) for \( t\geq 0 \); Boudreau, 1997):

\[
\frac{c}{c_{\text{inlet}}} = \frac{1}{2} \exp(\xi_2) \left[ \exp(-\xi_1) \text{erfc}\left(\frac{2\xi_1 - \tau}{2\sqrt{\tau}}\right) + \exp(\xi_1) \text{erfc}\left(\frac{2\xi_1 + \tau}{2\sqrt{\tau}}\right) \right]
\]

where \( \beta^2 = \left(\frac{v^2}{4D^2} + \frac{\kappa}{D}\right), \xi_1 = \beta x, \xi_2 = \frac{v x}{2D}, \tau = \frac{(v^2 + 4kD)t}{D} \) (26)

Results in Figure 6.5 corroborate the numerical simulation code. Differences at the tail of the simulation reflects the simulated boundary conditions for a finite length system \( L_{\text{total}}=N \Delta x \) as compared to the infinite length analytical solution. The following section presents numerical results for multiple species, stoichiometry, and boundary conditions that are relevant to CO\(_2\) geological storage.

6.4 Results

The numerical code was used to study the distribution of all reactant and produced species during diffusion-controlled transport when either calcite or kaolinite dominates the caprock.

Species concentration. Due to the high calcite reactivity, the simulation must be restricted to very short total length \( L_{\text{total}}=10\text{mm} \) to satisfy numerical stability and to observe the interplay between reaction and diffusion. Hence, a free-flux outlet boundary condition is selected for this very-short length calcite simulations. This close look highlights that reactant species are readily consumed near the caprock-reservoir interface. On the other hand, all three boundary conditions are explored for kaolinite mineralogy since the length represents a typical full caprock thickness \( L_{\text{total}}=10\text{m} \).
Figure 6.5 Verification of the numerical simulation code. Comparison of results from the numerical simulations and the closed-form solution for 1-dimensional diffusive transport after $t/t_{ch}=0.1$. Solid line: closed-form solution, Open circle: numerical simulation. Inserted graph zooms in discrepancies with the closed-form solution for two boundary conditions: free flux and no flux at the outlet (Note: saturation criterion $(1-\Omega/K_{eq})$ is disregarded during simulations, and reaction rate varies from $\kappa=10^{-2}\text{s}^{-1}$ to $10^{-3}\text{s}^{-1}$ and $10^{-4}\text{s}^{-1}$; characteristic time ratio of diffusion to mineral dissolution $Da\cdot Pe=\kappa\cdot L_{total}^2/D=5$ ($\kappa=10^{-2}\text{s}^{-1}$), 0.5 ($\kappa=10^{-3}\text{s}^{-1}$), 0.05 ($\kappa=10^{-4}\text{s}^{-1}$); fixed inlet concentration $[c]_{\text{inlet}}=0.001\text{mol/L}$; initial concentration $[c]_{(x>0)}=0$; diffusion coefficient $D=2\times10^{-9}\text{m}^2/\text{s}$; and total length $L_{total}=10\text{mm}$).
Figures 6.6 and 6.7 show the concentration of reactant species ($H^+$ and $H_2CO_3^*$) and produced species ($Ca^{2+}$, $HCO_3^-$, $Al^{3+}$, and $H_4SiO_4$) in calcite and kaolinite-rich caprocks. The characteristic diffusion time is $t_{ch}\approx 3$ hr for calcite ($L_{total}=10$ mm) and $t_{ch}\approx 340$ yr for kaolinite ($L_{total}=10$ m). The concentration of reactant species $H^+$ in the calcite caprock rapidly decreases near the inlet due to the high reactivity and slow diffusive transport (Figure 6.6-a). The other reactant species $H_2CO_3^*$ in calcite and $H^+$ in kaolinite caprock evolve towards a linear gradient as the simulation time prolongs beyond the diffusive characteristic time $t_{ch}=L_{total}^2/D$ when the free flux outlet condition is imposed (Figures 6.6-b and Figure 6.7-a). The concentrations of produced species also evolve towards a constant gradient when the free flux condition is set at the outlet (Figures 6.6-c, d and Figure 6.7-b). Forcing the initial concentration to remain constant at the outlet is similar to the free flux boundary condition and leads to similar results. However, when the boundary is closed (i.e., null gradient at the outlet), both reactant and produced species eventually distribute homogeneously along the entire length as the system reaches saturation (Figures 6.7-c and d). Note that the closed boundary yields acidification throughout the entire caprock.
Figure 6.6  Distribution of species concentrations normalized by their saturation concentrations in calcite. (a) Reactant species $\text{H}^+$ (Free flux at outlet) (b) Reactant species $\text{H}_2\text{CO}_3^*$ (Free flux at outlet) (c) Produced species $\text{HCO}_3^-$ (Free flux at outlet) (d) Produced species $\text{Ca}^{2+}$ (Free flux at outlet) (Note: free flux condition at the outlet; total length is $L_{\text{total}}=10\text{mm}$; characteristic diffusion time is $t_{ch}=L_{\text{total}}^2/D\approx3\text{hr}$).
Figure 6.7  Distribution of species concentrations normalized by their saturation concentrations in kaolinite. (a) Reactant species $H^+$ (Free flux at outlet), (b) produced species $Al^{3+}$ (Free flux at outlet), (c) reactant species $H^+$ (No flux at outlet), and (d) produced species $Al^{3+}$ (No flux at outlet). Note: total length $L_{total}=10$ m; characteristic diffusion time $t_{ch}=L_{total}^2/D \approx 340$ yr.
The mineral dissolution rate and boundary conditions affect the evolution of pH in the caprock. In the calcite caprock, the acidity near the inlet increases rapidly to pH~5 and converges to pH=8 near the outlet where free flow condition is imposed. Mineral dissolution buffers the solution within a narrow thickness next to the caprock-reservoir interface (Figures 6.8-a and b). In contrast, acidity drops to values lower than pH~5 along the entire kaolinitic caprock as the simulation time extends beyond the diffusive characteristic time (Figure 6.9-a). Acidification is more pronounced when the outlet boundary is closed (Figure 6.9-b). Electro-neutrality is maintained during the numerical simulation (Figures 6.8-c, 6.9-c, and d).

**Figure 6.8** Evolution of pH in calcitic caprocks. (a) pH along the entire model length, (b) pH – zoomed in to $x=1$mm from the caprock-reservoir interface, and (c) electro-neutrality along the model (Note: free flux condition at the outlet; total length is $L_{\text{total}}=10$mm; characteristic diffusion time is $t_{\text{ch}}=L_{\text{total}}^2/D\approx3$hr).
6.5 Analyses and Discussion

Porosity. The change in pore volume $\Delta V_p$ [m$^3$] as a consequence of mineral dissolution can be computed from the mass consumption of mineral per pore volume $\Delta c^m$ [mol/m$^3$] and the initial pore volume $V_p^0$ [m$^3$]:

$$\Delta V_p = \Delta c^m \cdot V_m \cdot V_p^0$$  \hspace{1cm} (27)
where $V_m [\text{m}^3/\text{mol}]$ is the mineral molar volume. The change in porosity $\Delta \phi [-]$ due to the increase in pore volume $\Delta V_p$ is a function of the initial total volume $V_{T0} [\text{m}^3]$ and the initial porosity $\phi_0 [-]=V_p^0/V_{T0}^0$:

$$\Delta \phi = \frac{\Delta V_p}{V_{T0}^0} = \frac{\Delta c^m \cdot V_m \cdot V_p^0}{V_{T0}^0} = \Delta c^m \cdot V_m \cdot \phi_0$$

(28)

**Pore diameter.** The change in pore diameter $\Delta d [\text{m}]$ can be estimated assuming that only one cylindrical flow channel exists in the representative elementary volume REV. The initial porosity $\phi_0 [-]$ with initial pore diameter $d_0 [\text{m}]$, and the new porosity $\phi_1 [-]$ after the pore diameter increases by $\Delta d$ in a REV of length $l [\text{m}]$ are:

$$\phi_0 = \frac{\pi d_0^2}{4l^2}$$

(29)

$$\phi_1 = \frac{\pi (d_0 + \Delta d)^2}{4l^2}$$

(30)

Combining Equations 29 and 30, the change in pore diameter $\Delta d$ as a function of the change in porosity $\Delta \phi$ is:

$$\Delta d = \left( \frac{1}{\sqrt{1 + \frac{\Delta \phi}{\phi_0}}} - 1 \right) \cdot d_0$$

(31)

**Permeability.** Convective flow of denser CO$_2$-dissolved water can eventually expose the caprock to water once again (Zone III - Figure 6.1) after it experienced mineral dissolution while in contact with CO$_2$. The initial permeability $k_0 [\text{m}^2]$ for cylindrical flow channels is a function of the pore diameter $d_0 [\text{m}]$ as predicted by the Hagen-Poiseuille’s equation:

$$k_0 = \frac{d_0^2}{32}$$

(32)

Increase in pore diameter $\Delta d$ causes the permeability to increase to:

$$k_1 = \frac{(d_0 + \Delta d)^2}{32} = \frac{d_0^2}{32} \cdot \left( 1 + \frac{\Delta d}{d_0} \right)^2 = \frac{d_0^2}{32} \cdot \left( 1 + \frac{\Delta \phi}{\phi_0} \right)$$

(33)
And the permeability ratio $k_1/k_0$ is a function of the change in porosity:

$$\frac{k_1 - k_0}{k_0} = \frac{\Delta \phi}{\phi_0} \quad (34)$$

*Change in caprock properties.* These analyses can be combined with the results of diffusion-controlled reactive transport to anticipate changes in caprock properties. Consider calcite: porosity, pore diameter, and permeability change within $x=0.2\text{mm}$ ($x/L_{\text{total}}<0.02$) from the caprock-reservoir interface. Beyond $x=0.2\text{mm}$, the system reaches saturation and mineral dissolution no longer takes place. Near the caprock-reservoir interface, the increase in porosity is $\Delta \phi \sim 0.06$, the normalized increase in pore diameter is $\Delta d/d_0 \sim 0.6$, and the normalized increase in permeability is $(k_1-k_0)/k_0 \sim 1.5$ within the first 15 hrs (Figure 6.10). In other words, there is a very rapid erosion of a skin-layer at the interface. Further erosion can take place if dissolution products are removed by diffusion, advection, or convection in the reservoir. If skin removal is localized, the caprock may experience an unsupported free span and break in tension if the length of the free span is about 20% of the caprock thickness (Chapter 3).

In the case of kaolinite, mineral dissolution extends to about $x=1\text{m}$ ($x/L_{\text{total}}<0.1$) 3400 years after CO$_2$ injection in the reservoir. Changes in porosity, pore diameter, and permeability are shown in Figure 6.11. Estimated changes in porosity $\Delta \phi \sim 5\times10^{-5}$, normalized increase in pore diameter $\Delta d/d_0 \sim 6\times10^{-4}$, and normalized increase in permeability $(k_1-k_0)/k_0 \sim 0.001$ are quite small even 3400 years after CO$_2$ injection when the upper caprock boundary is open and allows for free flux (Figures 6.11-a, b, and c). These changes are even smaller when the upper caprock boundary is closed (no flux at the outlet; Figures 6.11-d, e, and f). Based on these results, we can anticipate that capillary trapping will be stable in long-term CO$_2$ storage projects when clayey caprocks are involved.

In both cases, mineral dissolution is restricted to a region near the bottom of the caprock as the system reaches saturation in diffusion-controlled reactive transport.
Figure 6.10 Evolution of calcite caprock properties with respect to the distance from the caprock-reservoir interface (zoomed in to $x=1\text{mm}$): (a) change in porosity $\Delta \phi = \Delta c^m \cdot V_m \cdot \phi_0$ (initial porosity is assumed $\phi_0=0.04$), (b) 1D cylindrical model to estimate change in pore diameter $\Delta d/d_0 = (1+\Delta \phi/\phi_0)^{0.5} - 1$, (c) normalized change in pore diameter $\Delta d/d_0$, and (d) normalized change in permeability $(k_1-k_0)/k_0 = \Delta \phi/\phi_0$ (Note: all changes are computed based on the mass consumption of mineral $\Delta c^m$ [mol/m$^3$]; total length is $L_{\text{total}}=10\text{mm}$, simulation proceeds until time reaches $t\approx 15\text{hr}$).
Figure 6.11  Evolution of kaolinite-rich caprock properties with respect to the distance from the caprock-reservoir interface (zoomed in to $x=1\text{m}$): (a) change in porosity $\Delta \phi$ (initial porosity is $\phi_0=0.04$), (b) normalized change in pore diameter $\Delta d/d_0$, and (c) normalized change in permeability $(k_1-k_0)/k_0$ (Note: free flux condition at the outlet), (d) change in porosity $\Delta \phi$, (e) normalized change in pore diameter $\Delta d/d_0$, and (f) normalized change in permeability $k_1/k_0$ (Note: no flux condition at the outlet; all changes are computed based on the mass consumption of mineral $\Delta c^m$ [mol/m$^3$]; total length is $L_{\text{total}}=10\text{m}$; simulation proceeds until time reaches $t \approx 3400\text{yr}$).
**Governing parameters.** The multiplication of the Damköhler and Peclet’s numbers \( Da \cdot Pe = \kappa H_C^2 / D \) defines the ratio between the characteristic times for diffusion and mineral dissolution. In calcite, \( Da \cdot Pe > 10^8 \) for a caprock thickness \( H_C = 10 \)m, hence, mineral dissolution prevails over diffusion. In contrast, the much lower kinetic rate for kaolinite results in \( 10^{-1} < Da \cdot Pe < 1 \) for a clayey caprock of thickness \( H_C = 10 \)m; this confirms that there is full coupling between diffusion and dissolution in a kaolinite-rich caprock.

**6.6 Conclusions**

Capillary trapping prevents the invasion of liquid or supercritical CO\(_2\) into the caprock, and diffusion governs the transport of dissolved species in the caprock. The evolution of caprock properties as a result of the diffusion-dominant reactive transport is critical to determine the caprock long-term integrity. We wrote a 1-D numerical simulation code to investigate the transport of dissolved species through the caprock, taking into account the saturation state. Results show the evolution of species concentrations, mass consumption, and hydro-mechanical implications. Salient observations follow:

- The concentration of species evolves towards a constant gradient as the simulation time extends beyond the characteristic diffusion time for both calcite and kaolinite when free flux is allowed at the outlet. In contrast, species eventually distribute homogeneously along the entire length as the system reaches saturation when the boundary is closed.
- Acidity near the inlet increases rapidly to pH~5 and mineral dissolution buffers the solution within a narrow thickness next to the calcite-rich caprock. In contrast, acidity drops to values lower than pH~5 along the entire kaolinitic caprock as the simulation time extends beyond the diffusive characteristic time; acidification is more pronounced when the outlet boundary is closed.
- Changes in porosity, pore diameter, and permeability as a consequent of diffusive reactive transport can be estimated from the mineral mass consumption. Results for calcite anticipate a change in porosity $\Delta\varphi \sim 0.06$, normalized increase in pore diameter $\Delta d/d_0 \sim 0.6$, and normalized increase in permeability $(k_1-k_0)/k_0 \sim 1.5$ within $x=0.2$mm from the caprock-reservoir interface and the first 15hrs after injection. The dissolved skin may leave the caprock locally unsupported and bending-tensile cracks may form. Further erosion can take place if dissolution products are removed by diffusion, advection, or convection in the reservoir.

- Diffusion and dissolution are fully coupled in the kaolinite-rich caprock. Mineral dissolution extends to about $x=1$m from the caprock-reservoir interface after more than 3000 years. Capillary trapping will continue performing in long-term CO$_2$ storage projects judging by the small changes in porosity and absolute permeability computed in this study.
CHAPTER 7

CO₂ BREAKTHROUGH AND LEAK - SEALING EXPERIMENTS
ON SHALE AND CEMENT

7.1 Introduction

Geologic carbon sequestration can be used to avoid CO₂ emissions that result from burning fossil fuels. Injected CO₂ migrates upward and accumulates underneath the caprock (Bielinski et al., 2008; Okwen et al., 2010). Caprocks and cement plugs should prevent CO₂ leakage for thousands of years (Chapter 2; Gaus et al., 2008).

The breakthrough pressure seals can sustain $P_{bt}$ must exceed the pressure difference between the CO₂ phase $P_{CO₂}$ and the water phase $P_w$, $P_{bt} > P_{CO₂} - P_w$ (Chapter 6; Fig 7.1-a; Kopp et al., 2009; Saadatpoor et al., 2009; Ehlig-Economides and Economides, 2010; Bergmo et al., 2011). The breakthrough pressure $P_{bt}$ depends on the formation pore radius $r_p$ and the interfacial tension $T_s$ between water and CO₂, $P_{bt} \approx 2 \cdot T_s/r_p$. The characteristic pore radius in shale caprocks is $5 \text{nm} < r_p < 100 \text{nm}$ (Katsube and Williamson, 1994; Bachu and Bennion, 2008; Armitage et al., 2010), therefore, the estimated CO₂ breakthrough pressure is between 0.1MPa and 5MPa in a fracture-free formation (Hildenbrand et al., 2002; Hildenbrand et al., 2004; Li et al., 2005; Wollenweber et al., 2010). Most candidate sites for CO₂ geological storage satisfy this condition in the absence of discontinuities (White et al., 2004; Gaus et al., 2005; Bachu and Bennion, 2008; Doughty et al., 2008; Sharma et al., 2009).

Discontinuities are inherent to caprocks and reflect the formation history such as bedding planes, faults, fractures, and joints (Hoek and Brown, 1990). Discontinuities lower the CO₂ breakthrough pressure because of their larger pore size (Downey, 1984).
and become preferential conduits for CO₂ leakage (Bildstein et al., 2010; Dooley et al., 2010; Figure 7.1-b).

![Figure 7.1: Capillary trapping at the interface between caprock and CO₂ storage reservoirs.](image)

(a) Ideal condition in which intact caprock overlies CO₂ storage reservoirs (characteristic pore radius of caprock is orders of magnitude smaller than that of storage reservoir), (b) undesirable condition in which caprock retains a crack that can provide leakage path for CO₂ injected in the storage reservoir, and (c) proposed solution that plugs the crack with sub-micron particles and recovers the initial pore radius.

Similarly, the well cement that fills the annulus between borehole and casing must have a high CO₂ breakthrough pressure to prevent CO₂ leakage (Benson and Hepple, 2005; IPCC, 2005), and there must be discontinuities within the cement plugs or at the cement-caprock interface (Kutchko et al., 2007; Viswanathan et al., 2008; Wigand et al., 2009). Clearly, the role of the cement fill is most critical during injection when the CO₂ pressure is highest.

Several strategies have been proposed to address the risk of CO₂ leakage (Réveillère et al., 2012): 1) control overpressure of CO₂, 2) enhance CO₂ immobilization in the form of dissolution or capillary trapping, 3) form a hydraulic barrier in the overlaying layer, and 4) modify the fracture hydraulic properties. Several attempts have
been made to control hydraulic properties, such as microbial clogging (Bryant and Britton, 2008; Cunningham et al., 2009) and the injection of polymer gels (Sydansk et al., 2005).

In this research, we investigate the CO₂-breakthrough pressure for caprock shales and cement specimens, and seek to find feasible strategies to effectively plug discontinuities (Fig 7.1-c).

7.2 Experimental Study

Breakthrough and sealing tests are conducted on core plugs using a uniquely designed device to apply high fluid pressure under constant effective stress.

7.2.1 Experimental Device

The high-pressure cell \( (P \leq 20 \text{MPa}) \) has an enclosed steel spring to apply a vertical effective stress \( \sigma_v' \leq 3 \text{MPa} \) (Figure 7.2-a; Espinoza, 2011). The test is designed for radial flow to minimize the preferential leaks between the specimen and the chamber in conventional 1-D plug tests (Figure 7.2-b). The outlet pipe connects to a pipet to measure flowthrough water and to observe CO₂ leaks. The high-pressure cell is modified to run sealing tests and houses two inlet ports, one for CO₂ and the other to inject the sealing solution as needed (Figure 7.2-a).

7.2.2 Materials – Specimens

Cores of the shale caprock at a Kansas CO₂ pilot test site (Southern Kansas, Watney and Bhattacharya, 2011) were drilled, cut, and surface polished to prepare the annular specimens (outside diameter \( d_c \sim 40 \text{mm} \), inside diameter \( d_p \sim 3.17 \text{mm} \), and height \( 25 \text{mm} < h < 35 \text{mm} \)). The specimens exhibited horizontal hairline cracks in the form of layer separation, probably due to stress relaxation during coring and recovery (Figures 7.3-a and b).
Figure 7.2 Experimental device. (a) Entire setup of CO₂-breakthrough test and sealing treatment where the internal spring applies effective stress on a specimen, CO₂ enters the inside of the cell through a upper tube, sealing solution (suspension) enters the inside of the cell through a lower one, and CO₂ and water come out and stay in a collection pipet and (b) detail (1) in (a) where CO₂ infiltrates the specimen from its outside and reaches the tube in the center, which is connected to the collection pipet.

Figure 7.3 Shale rock specimen. (a) Core prepared for the CO₂-breakthrough test and (b) microscopic image of interlayer crack that might develop during coring and core recovery.
Cement specimens were prepared using class-A well-cement at a water-cement ratio w/c=0.4 and cured under 100% humidity for 28 days. The estimated porosity is around $\varphi=0.4$ (computed from saturated and dry weights).

7.2.3 Sealing Strategy

Fine migration and accumulation at pore throats can clog and seal porous media (oil recovery: Sharma and Yortsos, 1987; Khilar and Fogler, 1998. Bio-processes: Lee et al., 2004; Trask et al., 2007). We attempt to seal cracks using sub micron-size particles in order to decrease the characteristic pore radius $r_p$ within cracks. The test procedure includes suspension injection under reservoir $P$-$T$ conditions followed by the re-injection of CO$_2$ (Figure 7.4-a). The selected water-based suspensions are prepared with bentonite (1gram of GEL-PureGold bentonite, and 20ml of water) and kaolin (1gram SA1-Wilkinson kaolin, 1gram dispersant, and 20ml of water).

7.2.4 Test Procedure – Data Interpretation

Saturated shale specimens were stored in a 100% humidity box for one month to reach equilibrium. The specimen was mounted into the high-pressure cell with epoxy at bottom boundary and grease on the top to prevent boundary leaks between the specimen and stainless steel caps (Figure 7.2-b). A vertical stress $\sigma_v \sim 1$MPa was applied in all tests using the internal steel spring. Initially, water fills the annulus around the specimen.

Two inlet pressure histories are imposed in this study (Note: the outlet pressure is atmospheric in all cases). One involves the gradual step-wise increase in CO$_2$ pressure until the breakthrough is reached and CO$_2$ continuously comes out (b-1 in Figure 7.4-b). The other pressure history starts by imposing a CO$_2$ pressure 3~4 times higher than the anticipated breakthrough value; and closing the inlet valve. Then, CO$_2$ escapes through the outlet port until the pressure drops to the specimen’s shut-off pressure $P_d$ as water re-imbibition closes pores starting with the smallest pores first (Hildenbrand et al., 2002; b-2...
in Figure 7.4-b; Note: water-saturated CO$_2$ must be used in this case to prevent drying the formation). Breakthrough and shut-off pressures reflect the smallest pore along the percolating path. Figure 7.5 illustrates water drainage and re-imbibition. The shut-off pressure $P_d$ will be lower than the breakthrough pressure $P_{bt}$ if water re-imbibition does not take place (Hildenbrand et al., 2002), therefore the shut-off pressure is a conservative estimate for the sealing capacity of the caprock.

Figure 7.4  CO$_2$-breakthrough test and sealing treatment. (a) Schematic of sealing treatments where suspension is injected prior to the CO$_2$ injection. Following the suspension, CO$_2$ is re-injected, and pressurized CO$_2$ displaces the suspension on the inside of the specimen and causes sub-micron particles in the suspension to fill in cracks and (b) typical graph of pressure history - (b-1): Initial CO$_2$-breakthrough test. When CO$_2$ percolates, its pressure starts to decline. The highest value of CO$_2$ pressure defines a breakthrough pressure $P_{bt}$. (b-2): Sealing treatment. With excess pressure, CO$_2$ starts to percolate the specimen, and the excess pressure of CO$_2$ gradually decreases. When the last inter-connected path of CO$_2$ is shut off, no more CO$_2$ comes out of the system. At the moment, the shut-off pressure $P_d$ denotes the largest effective pore radius, and this value compares to the breakthrough pressure.
7.3 Experimental Results and Discussion

We measure the initial CO\textsubscript{2}-breakthrough pressure \( P_{bt} \) in the annular plugs, followed by sealing treatments and shut-off pressure measurement. Post-test forensic analyses provide insight into crack sealing and transport mechanisms.

7.3.1 Shale Plugs

*Initial CO\textsubscript{2} injection.* The three shale specimens exhibited very low CO\textsubscript{2}-breakthrough pressure \( P_{bt} \approx 20\text{kPa-to-30kPa} \) (Figures 7.6-a and c, Table 7.1). This pressure range...
corresponds to 4\(\mu\)m–6\(\mu\)m pore radius (from \(r_p = 2T_s/P_{bt}\) where the interfacial tension is assumed as \(T_s = 60\text{mN/m}\) under pressure \(P < 1\text{MPa}\)), which is much larger than the nanometer pore radius expected for intact shales.

Figure 7.6  Test results for shale specimens. (a) Initial CO\(_2\)-breakthrough test for specimen #1 results in the breakthrough pressure \(P_{bt} \sim 20\text{kPa}\), (b) sealing treatments for specimen #1 in which the residual pressure difference \(P_d\) (shut-off pressure) is measured. The dotted line is from the first treatment and the solid line from the second treatment; both treatments involve the injection of bentonite slurry before the re-injection of CO\(_2\). The first and second treatments yield \(P_d \sim 1.05\text{MPa}\) and \(P_d \sim 1.25\text{MPa}\), respectively, (c) initial CO\(_2\)-breakthrough test for specimen #2 results in \(P_{bt} \sim 30\text{kPa}\), and (d) sealing treatments for specimen #2. The dotted line is from the first treatment: injecting bentonite slurry. The solid line is from the second treatment: injecting kaolin slurry before the re-injection of CO\(_2\). The first and second treatments yield \(P_d \sim 0.31\text{MPa}\) and \(P_d \sim 0.55\text{MPa}\), respectively.
Cracks. While visual inspection does not reveal cracks (Figure 7.3-a), careful examination under the microscope shows the presence of hairline cracks parallel to the bedding planes in all plugs (Figure 7.3-b). These cracks are parallel to the imposed flow direction in these tests and may have developed during coring and stress relaxation.

Sealing treatment. Clay slurries were injected (~8ml) under constant vertical effective stress ($\sigma_v'$~1MPa) to fill the annular gap (4ml) between the test specimen and the high-pressure cell (Figure 7.4-a). Then, CO$_2$ was re-pressurized above the anticipated breakthrough pressure to determine the new shut-off pressure. Specimens underwent a series of bentonite or kaolin slurry treatments and CO$_2$ re-injections:

- Shale specimen #1 (Figures 7.6-a and b): before treatment $P_{bt}$=0.02MPa; after first bentonite treatment $P_d$~1.05MPa; after second bentonite treatment $P_d$~1.25MPa. A lower pressure decline rate was observed: 0.12MPa/hr for the first treatment vs. 0.01MPa/hr for the second treatment.
- Shale Specimen #2 (Figures 7.6-c and d): before treatment $P_{bt}$=0.02MPa; after first bentonite treatment $P_d$~0.31MPa; after second kaolin treatment $P_d$~0.55MPa. The leak-off rate and excess pressure drop decreased after the following treatment as well: 0.11MPa/hr for the first treatment vs. 0.004MPa/hr for the second treatment.
- Shale Specimen #3: before treatment $P_{bt}$=0.01MPa; after first bentonite treatment $P_d$~0.50MPa; after second bentonite treatment $P_d$~0.58MPa.

The water displaced during plug tests is shown in Figure 7.7 (Specimen #2, during ~45hours for the first treatment and ~1200hours for the second treatment). The flow rate is highest during the initial period of CO$_2$ leakage. Displaced water is transparent, without clays in suspension.
**Figure 7.7** Displaced water during plug tests after sealing treatments – Water comes out of the shale specimen as pressurized CO\textsubscript{2} displaces both the suspension outside of the specimen and the water inside of it. Displaced water is transparent: no sub-micron particle in suspension. After the pressure difference between CO\textsubscript{2} and the outlet $P_d$ stabilizes, a small amount of water enters back into the specimen. This observation supports the occurrence of water re-imbibitions as the excess pressure of CO\textsubscript{2} gradually diminishes. (a) first sealing treatment (bentonite slurry) and (b) second sealing treatment (kaolin slurry) for specimen #2.

**Forensic analyses.** Forensic studies after disassembly were conducted using microscopy and XRD analysis. The microphotograph in Figure 8 shows that hairline cracks filled with sub-micron particles (compare Figures 7.8-a with 7.3-b). Exposed fracture surfaces (forced to open in tension) show clay deposition and the formation of clogging rings (Figure 7.8-b). XRD analysis confirms the presence of bentonite along cracks in bentonite treated specimen #2 (Figure 7.8-c). There is no evidence of new minerals that may have formed during these short-time plug tests (Figure 7.8-c).
Figure 7.8  Post-test forensic analyses for shale specimens. (a) A microphotograph shows that a crack in the shale specimen is filled with sub-micron clay particles (bentonite) after sealing treatments, (b) sub-micron particles deposited in the gap between cracks after sealing treatments, (c) XRD analysis for original shale specimen and bentonite, and shale and bentonite after the sealing treatments.
Table 7.1  Summary of the CO₂ breakthrough tests and sealing treatments on the shale and cement specimens

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$P_{bt}$ [MPa] or $P_d$ [MPa]*</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale #1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.05*</td>
<td>1st sealing attempt (with bentonite slurry)</td>
</tr>
<tr>
<td></td>
<td>1.25*</td>
<td>2nd sealing attempt (with bentonite slurry)</td>
</tr>
<tr>
<td>Shale #2</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.31*</td>
<td>1st sealing attempt (with bentonite slurry)</td>
</tr>
<tr>
<td></td>
<td>0.55*</td>
<td>2nd sealing attempt (with kaolin slurry)</td>
</tr>
<tr>
<td>Shale #3</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50*</td>
<td>1st sealing attempt (with bentonite slurry)</td>
</tr>
<tr>
<td></td>
<td>0.58*</td>
<td>2nd sealing attempt (with bentonite slurry)</td>
</tr>
<tr>
<td>Cement #1</td>
<td>6.15*</td>
<td>Shut-off pressure</td>
</tr>
<tr>
<td>Cement #2</td>
<td>0.93*</td>
<td>Shut-off pressure</td>
</tr>
<tr>
<td>Cement #3</td>
<td>1.85*</td>
<td>Shut-off pressure</td>
</tr>
</tbody>
</table>

Figure 7.9  Test results for cement specimen #1. CO₂ is pressurized up to 20MPa. The excess pressure of CO₂ gradually decreases, eventually stabilizing around $P_d$~6.15MPa. During the pressure decline, the amount of displaced water is less than 0.2ml. Therefore, a very small fraction of pore space ($\sim 10^{-3}$) was used for the CO₂ flow.
7.3.2 Cement Plugs

Three cement specimens were tested to assess their sealing capacity (Table 7.1). The specimens show no cracks after curing.

Breakthrough pressure. The “cement #1” plug showed no CO$_2$ leakage at $P\sim5$MPa for two months. Then, we increased the pressure to 20MPa and closed the CO$_2$-inlet valve. The CO$_2$ pressure gradually dropped and stabilized around $P_d\sim6.15$MPa after two weeks. The CO$_2$ pressure no longer decreased for the next three weeks. This shut-off pressure $P_d\sim6.15$MPa yields a characteristic pore radius $r_p\sim11$nm (assuming $T_s\approx35$mN/m at $P_d\sim6.15$MPa). CO$_2$ percolated the other two specimens under $P\sim4$MPa, and the shut-off pressures were $P_d\sim0.93$MPa and $P_d\sim1.85$MPa (Table 1); these values correspond to characteristic pore radius $r_p\sim75$nm and $r_p\sim38$nm, respectively, in agreement with reported mean pore radius for cement pastes $r_{mean}=40$nm–50nm (Reinhardt and Gaber, 1990; Rimmelé et al., 2008).

Forensic analyses. Microscopy and XRD analyses reveal extensive coloration along the specimen periphery as a result of cement carbonation (orange color in Figure 7.10-a & XRD analysis in Figure 7.10-c). Diffusive transport limits the carbonation front to a certain skin thickness (Kutchko et al., 2007; Rimmelé et al., 2008; Brandvoll et al., 2009). Diffusion of CO$_2$ to mineral boundaries also resulted in reaction rims around grains (Figure 7.10-b). The reaction rims consist of silica gel SiO$_2.nH_2O$ and/or calcium carbonate CaCO$_3$ as a result of reactions from calcium silicate hydrate C-S-H and calcium hydroxide Ca(OH)$_2$ with hydrogen ions $H^+$ and bicarbonate $HCO_3^-$ (Wigand et al., 2009; Duguid et al., 2011; Liteanu and Spiers, 2011).

Discussion. Volumetric shrinkage 3–5% may take place in well cements during curing (Sabins and Rozieres, 1995). If we assume a radial shrinkage strain $\varepsilon_r=0.01$ for an annulus thickness $t_a=10$mm, the resulting gap is $t_{gap}=t_a.\varepsilon_r=100$µm. This value is much larger than the characteristic pore radius of cements in this study, and the gap becomes the preferential leakage path with a breakthrough pressure $P_{gap}=T/t_{gap}\approx1$kPa. Indeed,
4~19% of the production wells were reported to experience gas leakage in Canada and North Sea (Nygaard, 2010). Therefore, emphasis should be placed on breakthrough pressure and sealing strategies for probable gaps between the cement and the caprock.

Figure 7.10  Post-test forensic analyses for cement specimens. (a) Carbonation front on the specimen periphery (orange color), (b) reaction rim around a grain, and (c) XRD analysis for the original cement and the reaction front.
7.4 Conclusions

Caprock and well-cement must confine the CO$_2$ injected in storage reservoir. We investigated the CO$_2$-breakthrough pressure for shale caprocks and cement specimens, and explored a viable sealing strategy to correct CO$_2$ leakage. Salient observations follow:

- While pores in shale are in the nm-scale and can sustain MPa-scale capillary pressures, orders of magnitude lower breakthrough pressures are measured when discontinuities are aligned with the pressure gradient. We anticipate that this conclusion applies to fractures parallel to the bedding planes, transverse tensile fractures due to unsupported span (Chapter 3), or shear fractures in compression (Chapter 3).

- Sub-micron clay particles can be injected to fill cracks. Sealing treatments cause a marked increase in shut-off pressure. The permeability to CO$_2$ decreased as the specimen experienced successive sealing treatments.

- Intact cement plugs can generate a shut-off pressure as high as $P_d$~6MPa. Extensive carbonation with orange color and reaction rims around grains were observed on the plug surface.

- The cement-rock gap that results from cement contraction is the preferential flow path.
CHAPTER 8

ENGINEERED CO₂ INJECTION FOR GEOLOGICAL STORAGE

8.1 Introduction

Fossil fuels account for ~85% of all energy consumption and result in 30Gton of CO₂ emissions per year worldwide (Tsouris et al., 2010). Our dependency on fossil fuels will continue for the coming decades, until alternative energy sources can satisfy both current and anticipated demands (EIA, 2010; Pasten and Santamarina, 2012). In the meantime, carbon capture and storage allows for a more sustainable use of fossil fuels (Baines and Worden, 2004; Dooley et al., 2006).

Geological formations that are candidates for CO₂ geological storage include depleted hydrocarbon reservoirs, oil reservoirs (as part of enhanced oil recovery), unminable coal seams, salt caverns, and deep saline aquifers (IPCC, 2005). The use of depleted hydrocarbon reservoirs and salt caverns for CO₂ storage competes with natural gas storage, and does not necessarily match the geographic distribution of CO₂ sources (EIA, 2004; Pusch et al., 2010). Deep saline aquifers are most promising because of their large storage capacities (~10³ and 10⁴ GtCO₂), their ubiquitous presence in the USA, and their advantageous proximity to stationary CO₂ emission sources (such as coal power plants-IPCC, 2005).

The CO₂ storage capacity \( G_{CO₂} \) [Gton] is a function of the storage reservoir’s areal extent \( A_t \) [km²], the mean storage thickness \( h_g \) [m] \(< H_R \) (where \( H_R \) [m] is the thickness of the reservoir layer; Chapter 3), porosity \( \phi \) [-], CO₂ density \( \rho_{CO₂} \) [kg/m³], and a storage efficiency factor \( E \) [-] (NETL, 2010): \( G_{CO₂} = A_t \cdot h_g \cdot \phi \cdot \rho_{CO₂} \cdot E \). Typically, the storage efficiency factor is low and ranges between \( E=0.005 \) and 0.055 (NETL, 2010; Okwen et al., 2010), and formation porosities range between \( \phi=0.1 \) and 0.3 (IPCC, 2005; Bachu
and Bennion, 2008). Let’s consider that the worldwide mass of CO₂ emissions over the next 50 years \(G_{CO2}=730\) GtCO₂ (Chapter 2) will be injected under supercritical conditions (density \(\rho_{CO2}=600\) kg/m\(^3\)) with a storage thickness \(h_g=10\) m with porosity \(\varphi=0.2\). Assuming the maximum storage efficiency factor \(E=0.055\) results in a ~1,000,000 km\(^2\) storage area, similar to the area of Texas, USA or France. Large areal extent increases the probability of unexpected phenomena such as leaks along intersecting faults, hydro-chemo-mechanical effects, fault erosion and reactivation, and induced seismicity, among others. Therefore, the goal of this study is to identify viable CO₂-injection strategies to optimize the efficiency of CO₂ storage in the pore space of deep saline reservoirs. This will minimize residual brine saturation, salt precipitation and injection difficulties, water acidification and mineral dissolution, as well as the possibility of piping, internal shear, and differential settlement. Engineered injection will also hinder long-term convective flow, and further enhance the long-term geological storativity of CO₂.

### 8.2 Underlying Concepts

Let’s start with the identification of processes that may affect CO₂ storage projects (refer to Chapter 2 and subsequent Chapters).

#### 8.2.1 Coupled Processes

*Viscous fingering*. The viscosity of supercritical CO₂ at reservoir conditions is more than ten times lower than that of water or brine (Fenghour et al., 1998), and results in unstable injection fronts and the formation of viscous fingers (Chapter 2). Viscous fingering yields high residual water saturation, a large water-CO₂ interface, poor sweep efficiency \((E \leq 0.055)\), and large reservoir volumes. Consequently, monitoring strategies must cover large areas, compensation must include additional property owners (Gresham et al., 2010), and the probability of encountering potential leakage paths increases.
**Acidification and mineral dissolution.** Injected CO$_2$ dissolves into brine and decreases pH. In turn, acidified water prompts mineral dissolution (Kharaka et al., 2006). Extensive experimental evidence, discrete element simulations, and network model simulations show that mineral dissolution can cause: 1) a pronounced decrease in lateral stresses, so that the sediment reaches failure under zero lateral strain and extensive shear planes develop (Shin and Santamarina, 2009), 2) localized reactive fluid transport and internal piping (Fredd and Fogler, 1998), 3) skin erosion below the caprock (Chapter 6), and 4) differential settlement of the cap rock that may lead to bending failures and open mode discontinuities (Chapter 3). Shear, tensile, and piping discontinuities will facilitate CO$_2$ leakage.

**Fluid convection.** The dissolution of CO$_2$ and minerals in water increases the water density, and induces convective fluid circulation that sustains persistent coupled hydro-chemo-mechanical phenomena (Chapter 3; Pruess and Zhang, 2008).

**Injectivity.** As water in the residual brine diffuses into supercritical CO$_2$, excess salts precipitate (e.g., calcite, halite, and anhydrate), the formation conductivity decreases, and injectivity is compromised (Zone IV – Chapter 3; André et al., 2007).

### 8.2.2 Governing Ratios

The mobility number $M$ is the ratio of the viscosity of CO$_2$ $\mu_{CO_2}$ to that of water $\mu_w$:

$$M = \frac{\mu_{CO_2}}{\mu_w}$$

(1)

Supercritical CO$_2$ storage yields a mobility number $10^{-1}<M<10^{-2}$ (Adams and Bachu, 2002), where viscous fingering may prevail (Lenormand et al., 1988). The capillary number $C$ defines the ratio between viscous and capillary forces:

$$C = \frac{q\mu_{CO_2}}{T\cos\theta}$$

(2)
where $q$ is flow rate [$m^3/s/m^2$], $T_s$ [N/m] interfacial tension, and $\theta$ [deg] contact angle (Lenormand et al., 1988). The bond number $B$ is the ratio of gravity-driven CO$_2$ migration $(\rho_w-\rho_{CO2})gkk_{CO2}$ to capillary force $T_s\cos\theta$, where $\rho_i$ [kg/m$^3$] is the density of each phase, $k$ [m$^2$] is permeability, and $k_{rCO2}$ [-] is relative permeability of CO$_2$ (Pennell et al., 1996):

$$B = \frac{(\rho_w - \rho_{CO2})gkk_{rCO2}}{T_s \cos \theta}.$$

Low bond number $B$ and high capillary number $C$ leads to high CO$_2$ storage capacity (Kopp et al., 2009).

### 8.2.3 Concepts relevant to Engineered CO$_2$ Injection

Following the previous analysis, we seek to engineer the injection of CO$_2$ to prevent viscous fingering and to improve sweep efficiency. Engineered CO$_2$ injection can be based on the following strategies, used individually or in combination.

**Increased CO$_2$ viscosity.** Higher CO$_2$ viscosity is needed to promote a more homogeneous displacement pattern. Previous CO$_2$ viscosity control studies have been targeted at CO$_2$-enhanced oil recovery, and considered (1) emulsification/foams using surfactants (Kam and Rossen, 2003; Kovscek and Bertin, 2003; Levitt et al., 2009) and (2) thickening agents such as polymers (Huh and Rossen, 2008; Alvarado and Manrique, 2010; Enick et al., 2010). These efforts were reported to increase the ratio of oil recovery up to 80% (Lake and Venuto, 1990; Levitt et al., 2009).

**Sequential fluid injection.** Viscous fingering can be minimized and CO$_2$ displacement enhanced by the intermediate injection of fluid with density, viscosity, and wetting properties that are between the properties of brine and CO$_2$ (Alvarado and Manrique, 2010). Furthermore, the intermediate fluid could be miscible in both brine and CO$_2$. For example, acetone could act as intermediate fluid (viscosity$\approx 0.3$mPa·s at $T=30^\circ$C and $P=0.1$MPa, density$\approx 780$kg/m$^3$ (at $T=35^\circ$C and $P=0.1$MPa - Kinart et al., 2002), and it is
miscible with water and CO₂ (Tanaka et al., 1987; Pečar and Doleček, 2005; Liu and Kiran, 2007)). A properly selected/engineered intermediate fluid injected prior to or simultaneously with CO₂ will alter the fluid displacement topology and improve storage efficiency. For example, the intermediate injection of water enhances oil recovery by 50% (Lake and Venuto, 1990).

**Bio-clogging.** Microbial activity can be stimulated in water-filled flow paths (Bryant and Britton, 2008) as long as pore exceeds a $d_{pore}\sim 1\mu m$ size (Rebata-Landa and Santamarina, 2006). Bio-clogging will cause flow to divert to low-permeability channels. Compiled results suggest that bio-clogging will be most effective in sediments with permeability $10\text{md} \leq k \leq 10\text{Darcy}$ (Rebata-Landa and Santamarina, 2012).

**Decreased interfacial tension.** The CO₂-H₂O interfacial tension $T_s$ impedes CO₂ invasion into small pores, and contributes to residual water saturation (Suekane et al., 2005; Chalbaud et al., 2009). The CO₂-H₂O interfacial tension can be modified with surfactants such as pluronic block copolymers, PDMS-g-PEO-PPO copolymers, PEPE, PFPE, Ethoxylated acetylenic surfactants, and methylated branched hydrocarbon surfactants (da Rocha et al., 1999; Ryoo et al., 2003; Stone et al., 2004; Dickson et al., 2005). The interface can be altered by actively imposing electromagnetic fields as well (Francisca et al., 2008). The use of surfactants is explored next.

### 8.3 This Study: Interfacial Tension Control

Let’s explore the conditions for interfacial tension control and implications. First, we measure water-CO₂ interfacial tension with and without surfactants. Then we conduct fluid displacement experiments within a porous micro-model. Finally, we complement and extend experimental results using numerical network model simulations.
8.3.1 Surface Tension Control

Surfactant. The surfactant selected for this study is SURFONIC POA-25R2 (HUNTSMAN), which is a reversed block copolymer composed of hydrophilic polyoxyethylene and CO2-philic polyoxypropylene (Figure 8.2). The selected surfactant was reported to lower CO2-water interfacial tension at a ~0.1% volumetric concentration of surfactant, temperature \( T = 45^\circ \text{C} \), and pressure \( P = 27 \text{MPa} \) (da Rocha et al., 1999). This surfactant is a water soluble, nonionic surface active agent, and has hydrophilic/lipophilic balance HLB=6.3. The nonionic surfactant molecules diffuse in water, adsorb at interface, and change the local electric field as they partition between two phases (De Gennes et al., 2004). The anticipated variation of surface tension \( \sigma \) as a function of surfactant concentration \( C_s \) [mol/m³] and surface excess concentration \( \Gamma \) [mol/m²] is captured in Gibbs adsorption equation (Dickson et al., 2005):

\[
\frac{d\sigma}{d \log C_s} = -\Gamma RT \tag{4}
\]

Test procedure – Interfacial tension measurement. We use the device described in Espinoza and Santamarina (2011) to investigate the change in CO2-water interfacial tension as a function of pressure, with and without the surfactant. The high-pressure chamber is first subjected to three cycles of vacuum and CO2 flushing (99.99% purity) to remove air. Then water or water mixed with surfactant is injected using a high-pressure syringe to form a droplet that hangs at the tip of a stainless steel needle at a CO2 pressure \( P \approx 0.1 \text{MPa} \). The system is pressurized with CO2 in steps, from the initial 0.1MPa pressure to 10MPa. We use a high-resolution camera to capture the shape of the pendent drop through a sapphire window (Figure 8.1-a). Recorded images are analyzed using Laplace’s equation in parametric form to determine interfacial tension \( T_s \) (Rotenberg et al., 1983):

\[
T_s \left( \frac{d\phi}{ds} + \frac{\sin \phi}{x} \right) = \frac{2T_s}{R_0} + \Delta \rho gz \tag{5}
\]
where $R_0$ denotes the curvature at the droplet apex, and $\Delta \rho$ density difference between droplet and surrounding fluid (Figure 8.3-a). The density difference $\Delta \rho$ between CO$_2$ and water is computed using expressions in Duan and Sun (2003). The inverted interfacial tension $T_s$ is the value that minimizes the square error between the theoretical droplet shape and the experimentally captured image. The error surface is a function of the two unknowns, interfacial tension $T_s$ and maximum curvature $R_0$; it is convex as shown in Figure 8.4. Figure 8.4 also shows the sensitivity in the determination of the interfacial tension $T_s \pm 0.2$ mN/m.

**Results.** The effect of surfactant is readily seen in the shape of the pendent drop (Figure 8.5-a). The interfacial tension of CO$_2$-water-surfactant decreases from ~50 mN/m (at 0.1 MPa) to ~4 mN/m along the liquid-gas boundary (Figure 8.5-b). The trend parallels the interfacial tension for CO$_2$-water but is lower by an almost constant shift of 25~35 mN/m.
Figure 8.2 Molecular structure of: (a) H$_2$O, (b) CO$_2$, and (c) selected surfactant that consists of central hydrophilic chain of polyoxyethylene and two flanked hydrophobic chains of polyoxypropylene (Surfonic POA-25R2, $a=22$, $b=38$; molecular structure is inspired from: Prasad et al., 1979, Kozlov et al., 2000; visualization of molecular structure is in courtesy of Zhao, Q.).
Figure 8.3  Surface tension, contact angle, and surfactant. (a) Definition of the coordinate system for a pendant drop (from Rotenberg et al., 1983), (b) equilibrium state. Components: surrounding fluid $f$, liquid droplet $l$, and solid substrate $s$, (c) distribution of surfactant molecules in the system of partially wetting droplet, and (d) distribution of surfactant molecules in the tube that is partially filled with liquid (water) and fluid (CO$_2$).
Figure 8.4  Sensitivity analysis. Error surfaces as a function of interfacial tension $T_s$ and the curvature radius at the apex of a pendent drop $R_0$. Images show both the theoretical shape of a pendent drop that corresponds to conditions in the graph and the shape of an actual pendent drop that was obtained from a test (Pressure $P=5.4$MPa, temperature $T=25^\circ$C, density of water $\rho_{\text{water}} \approx 998.4$kg/m$^3$, and density of CO$_2$ $\rho_{\text{CO}_2} \approx 154.6$kg/m$^3$; the density of CO$_2$ is calculated based on formulae that is proposed by Duan and Sun, 2003).
Figure 8.5  The effect of surfactant and pressure on interfacial tension $T_s$. (a) Images: sessile and pendent droplets of water (Left, $P=5.79$MPa, and $T=24.5^\circ$C) and water+surfactant (POA-25R2; $wt=0.4$%; Right, $P=5.4$MPa, and $T=25^\circ$C). Note: The substrate is quartz (SiO$_2$). (b) Fluid pressure effect on interfacial tension: triangle=brine, square=water (from Espinoza and Santamarina, 2010), and circle=water+surfactant; POA-25R2, $wt=0.4$%).
8.3.2 Water Displacement by CO₂ Injection in a Pore Micro-model

*Test procedure.* We conducted water displacement studies by injecting CO₂ into a pore micro-model saturated with water with and without surfactant. The original device described in Jang (2011) was modified for this study to allow for separate water and CO₂ injections (Figure 8.1-b). The micro-model was prepared through photo-fabrication and glass etching processes to create a regular pattern of 0.3mm high cylindrical glass pillars and a porous network with 0.4mm pore size; a flat glass plate is glued above. The micro-model rests inside the high-pressure chamber. First, all air is evacuated by three cycles of vacuum followed by CO₂ flushing (99.99% purity). Then, we fill the micro-model with water (or water with surfactant) while the chamber is under vacuum. While we pressurize the chamber with CO₂, CO₂ bubbles trapped inside the micro-model dissolve in the water. At the target fluid pressure, we inject water (or water with surfactant) again into the micro-model using a high-pressure syringe to attain almost full water saturation in the micro-model. Finally, we inject CO₂ through the center of the micro-model. A high resolution camera is used to capture invasion patterns.

*Results.* Figure 8.6-a shows images captured at four different conditions: 1) Gaseous CO₂ displaced water at ~0.1MPa, 2) gaseous CO₂ displaced water in the presence of surfactant at ~0.1MPa, 3) liquid CO₂ displaced water at ~7MPa, and 4) liquid CO₂ displaced water in the presence of surfactant at ~7MPa. Menisci at CO₂-water interfaces within the micro-model confirm that interfacial tension $T_s$ decreases as fluid pressure increases and in the presence of the surfactant: the interface curvature between CO₂ and water becomes flatter as the test condition varies from 1 to 4 (Figure 8.6-a), in agreement with the decrease in interfacial tension reported in Figure 8.5.
Figure 8.6 The interface of a CO\textsubscript{2}-water system in the micro-model. (a) CO\textsubscript{2} injection: (a-1) log\(M\approx-2.0\), log\(C\approx-6.2\), (a-2) log\(M\approx-1.3\), log\(C\approx-5.3\), (a-3) log\(M\approx-1.1\), log\(C\approx-4.9\), and (a-4) log\(M\approx-0.4\), log\(C\approx-3.4\) (\(T\approx25^\circ\text{C}\) for all conditions, \(M=\mu_{\text{CO}_2}/\mu_w\), and \(C=q\mu_{\text{CO}_2}(T\cos\theta)\); variation of contact angle was disregarded in estimating the capillary number \(C\), \(\cos\theta=1\)) and (b) water imbibition.
The sweep efficiency \( E \) in this 2-D model can be estimated as the ratio of area occupied by CO\(_2\) to the area of the entire micro-model. At a low pressure (~0.1 MPa), gaseous CO\(_2\) \((T_s \sim 70 \text{ mN/m})\) fingers through the micro-model displacing water in a very small area with a measured \( E < 0.1 \). The other extreme corresponds to water with surfactant and at high pressure \((T_s \sim 5 \text{ mN/m})\), and shows that liquid CO\(_2\) displaces water evenly until it eventually breaks through the model perimeter resulting in a sweep efficiency that surpasses \( E > 40\% \). Figure 8.7 summarizes sweep efficiencies as a function of interfacial tension \( T_s \).

![Figure 8.7](image.png)

**Figure 8.7** Comparison of the sweep efficiency \( E \) with respect to interfacial tension \( T_s \). Note: as interfacial tension \( T_s \) decreases, capillary number \( C = \frac{q u_{CO2}}{(T_s \cos \theta)} \) increases from \( \log C \approx -6.2 \) to -5.3, -4.9, and -3.4 (variation of contact angle was disregarded in this analysis, \( \cos \theta = 1 \)).
8.3.3 Numerical Study – Network Model

We run network model simulations to further investigate the effect of interfacial tension on CO\textsubscript{2} displacement patterns and sweep efficiency trends. The network simulation algorithm was developed for the case of immiscible drainage where a non-wetting fluid is injected into a medium saturated with a wetting fluid (Lenormand et al., 1988; Aker et al., 1998; Ferer et al., 2003).

Network construction. The 2-D square network model consists of tubes that intersect at nodes. Tube diameters \( d \) are log-normally distributed with mean value \( \bar{d}_0 = 20 \mu m \) and coefficient of variation \( \text{COV}=0.4 \). All tubes have identical length \( L_{ch} = 200 \mu m \). The limitation in network size 10x10 is partially overcome by assuming periodic conditions for the longitudinal boundaries. The network is filled with water at the beginning of the simulation.

Initial condition. A pressure difference between the inlet and the outlet \( \Delta P_{tot} \) [Pa] is imposed to compute initial nodal pressures in the network and the water saturated total flow rate \( q_{tot} \). Nodal fluid pressures are computed by writing the continuity equation at all nodes and solving the system of equations (details in Jang et al., 2011):

\[
q_a + q_b + q_l + q_r = 0
\]  

(6)

where \( q_a \) denotes flow rate to center from above, \( q_b \) flow rate to center from below, \( q_l \) flow rate from left to center, and \( q_r \) flow rate from right to center. The pressure difference \( \Delta P \) between two adjacent nodes is then used to compute the initial flow velocity \( v_0 \) [m/s] and flow rate \( q_0 \) [m\(^3\)/s] for each tube using Poiseuille’s law as a function of the tube diameter \( d \) [m], length \( L_{ch} \) [m], and the fluid viscosity \( \mu \) [Pa\cdot s]:

Initial velocity: \( v_0 = \frac{\Delta P d^2}{32 \mu L_{ch}} \)  

(7)

Initial flow rate: \( q_0 = \alpha_w \cdot \Delta P \); initial conductance \( \alpha_w = \frac{\pi d^4}{128 \mu L_{ch}} \)  

(8)
where \( \alpha_w \) denotes the initial conductance of a tube that is filled with water. The water saturated flow rate \( q_{tot} \) is obtained by summing all flow rates for tubes in the first layer.

**CO\textsubscript{2} invasion.** The non-wetting CO\textsubscript{2} is injected at the inlet with the same constant flow rate \( q_{tot} \) computed for the water saturated network (under the imposed \( \Delta P_{tot} \)). We assume that both water and CO\textsubscript{2} are incompressible.

The non-wetting CO\textsubscript{2} invades a tube only if the pressure difference between the two fluids \( P_{CO2} - P_w \) exceeds the tube’s capillary pressure \( P_c = 4 \cdot T_s \cdot \cos \theta / d \). As the non-wetting CO\textsubscript{2} displaces the wetting water, the pressure drops along the tube due to both viscous loss (Lenormand et al., 1988) and capillary pressure (Aker et al., 1998). The flow rate \( q \) through the tube is computed based on Poiseuille’s law and the total pressure drop across the tube, from node \( i-1 \) to node \( i \):

\[
q = \alpha_{eff} \left( P_{CO2}^{i-1} - P_w^i - P_c \right) ; \text{ effective conductance } \alpha_{eff} = \frac{\pi d^4}{128 \mu_{eff} L_{ch}} \tag{9}
\]

where \( \mu_{eff} \) denotes the effective viscosity, which is the average of the two viscosities weighted with the length fraction of each fluid in the tube (Lenormand et al., 1988). The positive sign in Equation 9 denotes a positive value, in other words, the flow rate is \( q = 0 \) if the pressure difference between the two fluids \( P_{CO2}^{i-1} - P_w^i \) is smaller than the tube’s capillary pressure \( P_{CO2}^{i-1} - P_w^i < P_c \).

**Nodal pressure.** The pressure field in the network model is updated based on mass conservation, i.e., continuity: the pressure \( P_{center} \) at a central node \( center \) in the 2-D porous network is obtained by complying the mass conservation from all adjacent tubes (Ferer et al., 2003):

\[
\left( \alpha_{eff}^a + \alpha_{eff}^b + \alpha_{eff}^l + \alpha_{eff}^r \right) P_{center} = \left( \alpha_{eff}^a P_a + \alpha_{eff}^b P_b + \alpha_{eff}^l P_l + \alpha_{eff}^r P_r \right) + \left( f^a \alpha_{eff}^a P_c^a + f^b \alpha_{eff}^b P_c^b + f^l \alpha_{eff}^l P_c^l + f^r \alpha_{eff}^r P_c^r \right) \tag{10}
\]

where \( P_a \) denotes pressure at a node above, \( P_b \) pressure at a node below, \( P_l \) pressure at a left node, and \( P_r \) pressure at a right node. Superscripts for the effective viscosity \( \alpha_{eff} \) and
factor $f$ represent tubes connected to the central node: $a$ for a tube above, $b$ for a tube below, $l$ for a left tube, and $r$ for a right tube. The factor $f$ is zero $f=0$ if no meniscus exists in a tube and one $f=1$ if meniscus exists in the tube. The system of equation is iteratively resolved simultaneously updating the position of menisci within tubes until equilibrium is reached.

**Invasion.** The evolution of invasion uses a hybrid algorithm to avoid numerical instability. First, a flow-controlled condition is computed where fluids advance in each tube for a pre-selected time interval $\Delta t$ and at a velocity that is computed with the known nodal pressures. The time interval $\Delta t$ is determined so that maximum advance of any meniscus is less than 10% of the tube length $\Delta t \leq 0.1 L_{ch} / v_{max}$. Second, equilibrium is re-established by re-computing nodal pressures while enforcing equal nodal pressures at the inlet and at outlet nodes. We repeat each $\Delta t$-cycle until CO$_2$ reaches outlet nodes (details in Ferer et al., 2003).

**Results.** We varied the capillary factor $T_{s} \cos \theta = 35$ mN/m (liquid CO$_2$-water condition) to $T_{s} \cos \theta = 5$ mN/m and 1 mN/m (liquid CO$_2$ and water with surfactant) to compare the effect of capillarity $T_{s} \cos \theta$ on sweep efficiency $E$. As capillarity decreases, viscous drag prevails over capillarity, CO$_2$ invades more evenly and the sweep efficiency $E$ increases (Figure 8.8). The pattern of CO$_2$ invasion exhibits a transition from localized displacement or fingering along large tubes to a more homogeneous pattern of stable displacement when the capillarity approaches $T_{s} \cos \theta \sim 5$ mN/m.
8.4 Discussion

Surfactant, pressure, and interfacial tension. The interfacial tension between CO₂ and water decreases from ~70mN/m to 25mN/m as the fluid pressure increases, and reaches a
constant value ~30mN/m beyond the CO₂ gas-liquid boundary (studies at 278K-to-373K and up to ~70MPa can be found in: Massoudi and King, 1975; Chun and Wilkinson, 1995; Dickson et al., 2006; Kvaamme et al., 2007; Sutjiadi-Sia et al., 2007; Espinoza and Santamarina, 2010). As pressure increases, the CO₂ densifies as well as the concentration of dissolved CO₂ near the CO₂-water interface increases, and the interfacial tension decreases (Massoudi and King, 1975; Chun and Wilkinson, 1995; Espinoza and Santamarina, 2010).

Surfactant molecules align at the polar/non-polar interface between CO₂ and water and fold (Figures 8.3-c and d - Prasad et al., 1979), modify local electric field, and weaken the surface tension by adding repulsion forces at the surface. The interfacial CO₂-water tension in the presence of surfactant decreases from ~50mN/m to ~4mN/m as pressure increases from 0.1MPa to ~7MPa, and reaches a constant value ~4mN/m across the CO₂ gas-liquid boundary (Figure 8.5). The trend parallels the results for CO₂-water without surfactant but with an almost constant shift between ~30mN/m. Apparently, the surfactant concentration at the interface remains constant with pressure.

**Contact angle and interfacial tension.** The Young-Dupre equation relates the contact angle to interfacial tensions (Figure 8.3-b):

\[
\cos \theta = \frac{\sigma_{fs} - \sigma_{ls}}{T_s}
\]

(11)

Therefore, the factor \(T_s \cos \theta = \sigma_{fs} - \sigma_{ls}\) is not a function of the CO₂-water interfacial tension. Yet, experimental results show consistent difference in invasion topology when the interfacial tension \(T_s\) is modified (Figure 8.7). This observation implies either \(\sigma_{fs}\) and/or \(\sigma_{ls}\) must change with pressure and surfactant as well.

Indeed, the interfacial tension \(\sigma_{fs}\) between CO₂ and solid mineral decreases as CO₂ pressure increases from 0.1MPa to ~7MPa (Dickson et al., 2006; Sutjiadi-Sia et al., 2008). On the other hand, while the interfacial tension \(\sigma_{ls}\) between water and mineral remains relatively constant as the fluid pressure increases (Dickson et al., 2006; Espinoza and
Santamarina, 2010), it increases as the concentration of surfactant increases probably due to hydrogen bonding between the CO$_2$-philic (or hydro-phobic) tail of nonionic surfactant molecules and adsorbent glass SiO$_2$ (Szymczyk and Jańczuk, 2008). Thus, the factor $T_s \cdot \cos \theta$ effectively decreases as the interfacial tension $T_s$ decreases.

**Size of surfactant.** The selected surfactant, pluronic block copolymer has a molecular weight $mw=4224$g/mol and an estimated molecular size of $\sim 20$nm (Figure 8.2). The two hydro-phobic tails repel each other as the surfactant concentration at the interface increases. This long molecule could resist invading pores of 2nm–3nm diameter, perhaps as large as 10nm. The fraction of pores $d_{pore} < 1$nm is very small in most shale (<1% - Bachu and Bennion, 2008).

**Sweep efficiency in 3-D.** Investigation of the sweep efficiency in this chapter has been based on 2-D micro-model experiments and 2-D network model simulations. As the pore coordination number increases in 3-D, so do the degrees of freedom during invasion, and lower 3-D sweep efficiencies are anticipated.

### 8.5 Conclusions

Efficient injection and the long-term stability of saline aquifers could be negatively affected by emergent hydro-chemo-mechanically coupled phenomena, such as viscous fingering, acidification and mineral dissolution, mineral precipitation, and fluid convection. We can engineer CO$_2$ injection to prevent these negative effects. Possible alternatives include: increased CO$_2$ viscosity, sequential fluid injection, bio-clogging, and decreased interfacial tension. In this study, we attempted to lower the interfacial tension. Salient observation follows:

- Surfactants that have hydrophilic heads and CO$_2$-philic tails can lower the interfacial tension between CO$_2$ and water. In this study, a long-chain nonionic surfactant (weight percent $wt \approx 0.4\%$) lowered the CO$_2$-water interfacial tension from $T_s \sim 50$mN/m to
$T_s \sim 4\text{mN/m}$ at a pressure of $P \geq 7\text{MPa}$. The parallelism in $T_s$-$P$ trends with and without surfactants suggests a pressure-independent concentration of surfactants at the interface.

- Capillarity, governed by the product of CO$_2$-water interfacial tension $T_s$ and contact angle $\theta$ is independent of $T_s$ as per Young’s equation $T_s \cdot \cos \theta = \sigma_{fs} - \sigma_{ls}$. However, pressure and surfactants also affect the force between $\sigma_{fs}$ mineral-CO$_2$ and $\sigma_{ls}$ water-mineral interfacial tension.

- Experimental CO$_2$ injection tests in pore micro-models and parallel network model simulations demonstrate that the sweep efficiency of CO$_2$ invasion can be effectively enhanced by lowering the interfacial tension. In fact, the sweep efficiency can surpasses $40\%$ in 2-D systems (lower values are expected in 3-D systems).

- Engineered CO$_2$ injection methods such as the use of surfactants can minimize emergent hydro-chemo-mechanically coupled phenomena and improve the long-term integrity of storage sites, enhance the injectivity of CO$_2$, and optimize pore space occupancy underground.
CHAPTER 9
CONCLUSIONS

This research addresses emergent hydro-chemo-mechanically coupled phenomena, their implications on CO\textsubscript{2} geological storage, and engineered CO\textsubscript{2} injection method. The scope of the work included data compilation from published studies, geochemical analysis based on mass balance calculations and geomechanical analysis for different zones, pore-scale reactive fluid transport, upscale of the reactive fluid flow in both CO\textsubscript{2} reservoirs (2-D network model) and overlying caprock (1-D simulation), sealing capacity of shale-caprock and well-cement and sealing strategy, and engineered injection strategy to improve sweep efficiency. Complementary analyses, numerical simulations, and experimental works support the applicability of the results in each section. The main observations are presented separately for each study.

\textit{CO\textsubscript{2} Geological Storage – Geotechnical Implications}

- The physical properties of CO\textsubscript{2} such as density, viscosity, interfacial tension, and bulk compressibility depend on the pressure and temperature conditions.
- Geometric boundaries, spatial heterogeneity, flow conditions, and the emergence of viscous fingering affect the volume of the geological formation injected with CO\textsubscript{2}.
- Water acidification in the presence of CO\textsubscript{2} enhances mineral dissolution, and denser CO\textsubscript{2}-dissolved water triggers self-mixing.
- Complex hydro-chemo-mechanical interactions, which lead to emergent phenomena, may hinder the storativity of injected carbon dioxide.
- The contrasting physical properties of CO\textsubscript{2} and water support the application of geophysical monitoring methods based on elastic and electromagnetic waves.
**CO₂ Geological Storage: A Mass Balance Analysis and Implications**

- Four different zones in the reservoir around injection wells are identified, starting from far-field zone I, to intermediate zone II and III, and to near-well zone IV.
- In leveled sediments, the CO₂ pool thickness may be limited by lateral capillary trapping rather than by the sediment layer thickness. Typical pools will be only a few meters thick in the absence of geometric traps.
- The time for convection may be as low as few years in pervious reservoirs. Short convection times will aggravate dissolution consequence, and either compaction-driven shear failure or caprock bending failure may occur. In particular, the unsupported free span of the caprock cannot exceed 20% of the caprock thickness.
- The continuous influx of dry CO₂ dries the residual brine near the wellbore. The precipitation of secondary minerals increases the mineral volume by a maximum of 5%. A minor decrease in CO₂ permeability is anticipated.

**CO₂ Geological Storage: Pore-Scale Reactive Fluid Transport (Rock Joint and Pores)**

- Newly devised simulation technique enables us to investigate interactions among governing parameters, including advection, diffusion, species concentration, and geometry.
- Reactant species are readily consumed in a calcite-dominant environment, while low reaction rate allows more extensive transport of them in sandstones.
- Pore enlargement may decrease either exponentially or linearly along the flow path. Dissolution patterns define a consistent trend in the $Da - Pe$ space.
- An increased aperture-to-length ratio slows the diffusive transport to the mineral surface. Upscaling must take into consideration both the joint length and its slenderness.
Reactive Fluid Flow in CO$_2$ Storage Reservoirs – Pore Network Model Study

- We develop a new network simulation code to investigate fluid-mineral interaction when CO$_2$-dissolved water flows through a porous network near the CO$_2$-water boundary. The new code provides results including the distribution of species concentration, tube diameters, flow rate, and pressure field.
- Porous media in a calcite formation will experience either compact dissolution near the inlet ($Da>10^{-4}$) or localized flow paths ($Da<10^{-4}$) as a result of CO$_2$-dissolved reactive fluid flow.
- Both the Damköhler number and pore-size variability affect the relationship between mean tube diameter and flow rate. Changes in Damköhler number result in inherent bias between average and local trends. Both the Damköhler number and pore-size variability should be accounted in field-scale FEM models.

Reactive Fluid Flow Through the Caprock Overlying CO$_2$ Storage Reservoirs

- Capillary trapping prevents the invasion of liquid or supercritical CO$_2$ into the caprock, and diffusion governs the transport of dissolved species in the caprock.
- Most reactant species are consumed within ~0.2mm from the caprock-reservoir interface in the calcite environment. Estimated increases in porosity $\Delta\phi$~0.06 and permeability ($k_1/k_0$~1.5 for the first 15hrs are significant. The dissolved skin may leave the caprock locally unsupported and bending-tensile cracks may form.
- Diffusion and dissolution are fully coupled in the kaolinite-rich caprock. Mineral dissolution extends to about ~1m from the caprock-reservoir interface. Capillary trapping will continue performing in long-term CO$_2$ storage projects judging by the small changes in porosity and permeability.
**CO₂ Breakthrough and Leak - Sealing Experiments on Shale and Cement**

- Very low CO₂-breakthrough pressure $P_{bt} \sim 20$ kPa are measured when discontinuities are aligned with the pressure gradient. This observation applies to fractures parallel to bedding planes, transverse tensile fractures due to unsupported span, or shear fractures in compression.

- Sub-micron clay particles can be injected to fill cracks. Sealing treatments cause a marked increase in shut-off pressure $P_d \sim 1$ MPa. The CO₂ permeability decreases as the shale specimen experiences successive sealing treatments.

- Intact cement plugs can generate a shut-off pressure as high as $P_d \sim 6$ MPa. Extensive carbonation with orange color and reaction rims around grains were observed on the plug surface.

- Emphasis should be placed on breakthrough pressure and sealing strategies for probable gaps between the cement and the caprock that result from cement contraction.

**Engineered CO₂ Injection for Geological Storage**

- The selected long-chain nonionic surfactant lowers the CO₂-water interfacial tension to $T_s \sim 4$ mN/m at pressure $P \geq 7$ MPa. The parallelism in $T_s-P$ trends with and without surfactants suggests a pressure-independent surfactant concentration at the interface.

- Pressure and surfactants also affect the force between mineral and CO₂ and interfacial tension between water and mineral.

- Experimental CO₂ injection tests in pore micro-models and parallel network model simulations demonstrate that the sweep efficiency of CO₂ invasion $E$ can be effectively enhanced to $E \sim 40\%$ in 2-D systems by lowering the interfacial tension.

- Engineered CO₂ injection methods such as the use of surfactants can minimize emergent hydro-chemo-mechanically coupled phenomena, enhance the injectivity of CO₂, and optimize pore space occupancy underground.
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