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Investigation On the Effect of Supercritical CO_2 Treatment On Shale Properties: Implications for CO_2 Sequestration

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DECLARATION OF AUTHORSHIP

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

Date: July, 2022.

DEDICATION

In the name of Allah, the Most Gracious, the Most Merciful.

All thanks and praise are due to Allah almighty and peace and blessings be upon His Messenger.

I truly dedicate this thesis to all those people who are the source of my motivation.

To my beloved parents (F&F), for their encouragement, help and support throughout my entire life, who's taught me to be responsible and loyal to my belief.

To my wife, Mawadh, for your unconditional support, love and kindness, and for all the inspiration and sacrifices that kept me going. Without your support, it would have been difficult to complete this thesis. Thank you from the bottom of my heart.

To my lovely daughter, Larin. You always give me a reason to smile after long hours in the office and the lab.

To my sister, Eman; my brother, Mohammed; and all my friends for their support, prayers and inspiration.

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In The Name of Allah, The Most Gracious, The Most Merciful

In the beginning, I must admit that I have been waiting to write this page more than any other page of this entire thesis because I finally had the opportunity to publicly acknowledge the help and the support of numerous people who made this work possible. This Ph.D. journey was one of the most challenging –yet enjoyable- experiences I have had in life, and I am so grateful for the lessons learned, the skills gained, and the achievement made during this journey.

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I end with the quote by Nelson Mandela “***Education is the most powerful weapon which you can use to change the world”, “It is in your hands to make a better world for all who live in it***”.

ABSTRACT

Carbon capture and storage (CCS) is an innovative technology to reduce the impact of Carbon Dioxide (CO_2) emissions into the atmosphere, resulting from fossil fuels and other industrial activities. CO_2 is one of the most abundant and harmful greenhouse gases compared to other gases such as Methane gas (CH_4) or Nitrous Oxide (N_2O), contributing into 70-75% of the total global emissions of greenhouse gases. Therefore, by storing CO_2 into deep geological formations, the effects of greenhouse gases on climate change can be significantly reduced. Shale formations hold a promising potential to utilize CCS projects due to their wide availability and high CO_2 adsorption capacity. However, the associated alterations in shale properties caused by CO_2/shale geochemical interaction play key roles in the efficiency and the successful application of CO_2 geological sequestration shales. When CO_2 contacts with the shale formation water, it forms carbonic acid, which leads to alter the petro-physical and chemical properties of the shale formations, and affects the overall CO_2 storage capacity. This study focuses on evaluating the impact of CO_2 treatment on shale properties, and addresses the overall implications on storage capacity and seal integrity. Specifically, the alterations in mineral composition, surface morphology, functional groups, pore structure system and wettability were evaluated. To achieve this goal, different types of shales with various mineralogy were collected from Eagle Ford, Mancos and Wolfcamp formations, and treated with Supercritical (SC)CO_2 under various experimental conditions; i.e. different durations (1-30 days), pressures (9-24 MPa) and temperatures (40-90^o C). Various analytical methods were applied such as X-Ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transfer infrared (FTIR) spectroscopy, low-pressure N_2 adsorption test, and contact angle measurements on the shale samples before and after the treatment. Moreover, simplified one-dimensional reactive transport models were constructed using PHREEQC-interactive software, to simulate the reaction kinetics of CO_2 with shale at geological time scales. The results indicated that the mineral composition has an important role to define the changes in shales properties. The ability of $SCCO_2$ to extract and dissolve clay and carbonate minerals in shales promotes the release of H^+ ions during CO_2/shale interactions, which led to altering the surface morphology and surface structure. Clay-rich shale samples collected from Eagle Ford field were more affected by CO_2 injection compared to quartz-rich shales (collected from Mancos field) due to the effect of clay-swelling that may reduce the CO_2 adsorption capacity of the former in the long term, and affect the sealing integrity. The analysis of the functional groups revealed that aromatic hydrocarbons had minor changes compared to aliphatic hydrocarbons, due to the higher extraction behavior of aliphatic contents by $SCCO_2$. Moreover, the contents of the oxygen-containing groups increased after $SCCO_2$ treatment, which proved the high CO_2 adsorption capacity in shales. The changes in the pore structural system were mainly caused by the adsorption-induced expansion by $SCCO_2$ on the shale surface. This resulted in narrowing the pores between the grains and reduced the overall pore volume of Eagle Ford shales. While the development of micro-cracks in Mancos shale increased the pore volume and provided the potential for creating new pores in the shale matrix. Moreover, the low-pressure N_2 adsorption test results indicated that the fractal dimensions and the specific surface area had a positive linear correlation. The specific surface area of Eagle Ford shale was reduced by 35.46% after the $SCCO_2$ treatment, which reduced surface roughness and complexity. On the other hand, the specific surface area was increased by 27.4% in Mancos shale, leading to increasing the surface roughness and complexity. Clay-rich shales such as Eagle Ford and Wolfcamp displayed a possible turn in wetting behavior to CO_2-wet with extending treatment time and increasing the treatment pressure and temperature beyond 20MPa and 80^o C respectively, which may reduce the sealing integrity in the long term. Conversely, quartz-rich shales such as Mancos, remained strongly hydrophilic (water-wet) after various $SCCO_2$ treatment conditions, which suggested better sealing integrity and higher CO_2 storage potential. The equilibrium and kinetic models had revealed that the geochemical interactions caused minerals dissolution and precipitation, which confirmed the high reactivity of shales to the injection of CO_2. The kinetic model indicated that carbonate and clay minerals can be significantly dissolved in the presence of CO_2, and enhance the mineral trapping as an effective sealing mechanism of CO_2. This outcome is confirming the high feasibility of CO_2 sequestration applications in shales. In summary, the finding of this work

enhanced the knowledge of the impact of CO_2/shale interaction on shale properties and provided a better understanding of the feasibility of sub-surface CO_2 storage in shales.

LIST OF PUBLICATIONS INCLUDED AS PART OF THE THESIS

The following published peer-reviewed publications are included as part of this thesis:

1. **CHAPTER 2**: **Fatah, A.**; Bennour, Z.; Ben Mahmud, H.; Gholami, R.; Hossain, M.M. A Review on the Influence of CO_2/Shale Interaction on Shale Properties: Implications of CCS in Shales. Energies, 13, 3200 (**2020**). DOI: https://doi.org/10.3390/en13123200

2. **CHAPTER 3**: **Fatah, A.**; Ben Mahmud, H.; Bennour, Z.; Hossain, M.M; Gholami, R. Effect of Supercritical CO_2 Treatment on Physical Properties and Functional Groups of Shales. FUEL, 303, 121310 (**2021**). DOI: https://doi.org/10.1016/j.fuel.2021.121310

3. **CHAPTER 4**: **Fatah, A.**; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. Geochemical and physical alteration of clay-rich shales under supercritical CO_2 conditions, Applied Geochemistry, 140, 105291 (**2022**). DOI: https://doi.org/10.1016/j.apgeochem.2022.105291

4. **CHAPTER 5**: **Fatah, A.**; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. The Impact of Supercritical CO_2 On the Pore Structure and Storage Capacity of Shales. Journal of Natural Gas Science and Engineering, 98, 104394 (**2022**). DOI: https://doi.org/10.1016/j.jngse.2021.104394

5. **CHAPTER 6**: **Fatah, A.**; Bennour, Z.; Ben Mahmud, H.; Gholami, R.; Hossain, M.M. Surface Wettability Alteration of Shales Exposed to CO_2: Implication for Long-term Integrity of Geological Storage Sites. International Journal of Greenhouse Gas Control, 110, 103426 (**2021**). DOI: https://doi.org/10.1016/j.ijggc.2021.103426

6. **CHAPTER 7**: **Fatah, A.**; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. Geochemical Modelling of CO_2 Interactions with Shale: Kinetics of Mineral Dissolution and Precipitation on Geological Time Scales. Chemical Geology, 592, 120742 (**2022**). DOI: https://doi.org/10.1016/j.chemgeo.2022.120742

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Date: July, 2022.

STATEMENT OF CONTRIBUTION OF OTHERS

This thesis is presented as a series of six peer-reviewed papers (either published or under review). These papers are linked together by a general introduction and a conclusion chapters. The author of this present thesis (***Ahmed Fatah***) was involved primarily in the main conceptualization of the research methods and methodology, investigation, data visualization and collection, formal analysis and interpretation, validation, and writing the original drafts of the papers (Appendix II contains the attribution of authorship agreements).

Ahmed Fatah is the first author in all publications, and the thesis supervisors were directly involved in the publications arising from this research and significantly contributed to improving the quality of the publications. The main contribution of the co-authors is outlined below.

Associate Professor Hisham Ben Mahmud contributed as the main supervisor of this project. He was directly involved in the research activities including project conceptualization, methodology design, discussing the results, project administration, funding acquisition, and review & editing. He also contributed to reading drafts and making suggestions for improvements to all publications.

Dr. Ziad Bennour contributed as a co-supervisor of this project. He was directly involved in the research activities including project conceptualization, methodology design, discussing the results, project administration, validation, and review & editing. Besides contributing to reading drafts and making suggestions for improvements to all publications.

Professor Raoof Gholami contributed as a co-supervisor of this project. He was directly involved in the research activities including project conceptualization, methodology design, discussing the results, providing resources, and review & editing. Besides contributing to reading drafts and making suggestions for improvements to all publications.

Professor Mofazzal Hossain contributed as an associate supervisor of this project. He was involved in the research activities including project conceptualization, discussing the results, and review & editing. He also contributed to reading drafts and providing suggestions for improvements to all publications.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

AP	Acidification Potential
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
BI	Brittleness Index
BSS	Brazilian Splitting Strength
CCS	Carbon Capture and Storage
CO_2	Carbon Dioxide
CH_4	Methane Gas
CGS	Carbon Geo-Sequestration
CED	Cumulative Energy Demand
EF	Eagle Ford
EP	Eutrophication Potential
EDS	Energy Dispersive Spectrometer
ESGR	Enhanced Shale Gas Recovery
EDF	Extended Depth of Focus
EOS	Equation of State
EIA	Energy Information Administration
FHH	Frenkel-Halsey-Hill
FPS	Frames Per Second
FTIR	Fourier Transform Infrared Spectroscopy
GWP	Global Warming Potential
Gt	Gigatonnes
HRXCT	High-Resolution X-Ray Computed Tomography

IGCC	Integrated Gasification Combined Cycle
ICDD	International Centre for Diffraction Data
IR	Infra-Red
IUPAC	International Union of Pure and Applied Chemistry
KBr	Potassium Bromide
LCA	Life Cycle Assessment
MAN	Mancos
MPa	Mega Pascal
NGCC	Natural Gas Combined Cycle
NMR	Nuclear Magnetic Resonance
PSD	Pore Size Distribution
POCP	Photochemical Ozone Creation Potential
PC	Pulverized Coal Combustion
$SCCO_2$	Supercritical CO_2
SSA	Specific Surface Area
SEM	Scanning Electron Microscopy
TOC	Total Organic Carbon
TPV	Total Pore Volume
UCS	Uniaxial Compressive Strength
WF	Wolfcamp
XRD	X-Ray Diffraction

SYMBOLS

Symbol	**Description**	**Units**
D	Fractal Dimension	Dimensionless
E	Young's Modulus	N/m^2
R_o	Vitrinite Reflectance	% Percentage
V	Adsorbed N_2 volume	cm^3
P_o	Saturated vapor pressure	MPa
P	Equilibrium pressure	MPa
γ	Interfacial tension	mN/m
γ_{sv}	Solid/gas interfacial tension	mN/m
γ_{sl}	Solid/liquid interfacial tension	mN/m
γ_{lv}	Liquid/gas interfacial tension	mN/m
P_c	Capillary Pressure	MPa
r	Capillary inner radius	cm
θ	Contact angle	° degree
B	Apex	Dimensionless
R_0	Radius at the apex	cm
$\Delta\rho$	Air/water density difference	g/m^3
g	Gravitational acceleration	m/s^2
r	Minerals precipitation/dissolution rate	mol/m^3.s
k	Kinetic rate constant	mol/m^2.s
A	Reactive surface area	m^2
Q	Ionic activity product	Dimensionless

K_{eq}	Chemical equilibrium constant	Dimensionless
T	Temperature	^oK
R	Ideal gas constant	$J \cdot K^{-1} \cdot mol^{-1}$
$\Delta H^{\ominus}$	Standard enthalpy change	kj/mol
V_m	Molar volume	m^3/mol
M	Molecular weight	g/mol
ρ	Density	g/m^3
V_s	Volume of 1 grain of mineral	m^3
A	Surface area of 1 gram of mineral	m^2/g
r	Grain radius	m

CHAPTER 1

INTRODUCTION AND OVERVIEW

1.1 Research Background

Carbon capture and storage is an innovative technology to reduce the impact of CO_2 emissions into the atmosphere, resulting from fossil fuels and other industrial activities [1]. CO_2 is particularly regarded as one of the most abundant and harmful greenhouse gases compared to other gases such as Methane gas (CH_4) or Nitrous Oxide (N_2O), contributing into 70-75% of the total global emissions of greenhouse gases (**FIGURE 1-1**) [2]. The continuous increase of CO_2 emissions comes from the growing energy demands for electricity production worldwide. The International Energy Agency [2] estimated that the total production of electricity in 2019 exceeded 20×10^6 GWh, and it is expected to increase by more than 35% by the year 2030, reaching 31×10^6 GWh worldwide. This increase in electricity production can lead to release more than 60 Gigatonnes (Gt) of CO_2 by the year 2030. Therefore, storing CO_2 into deep geological formations can contribute to minimizing climate change effects, and provide the potential to enhance CH_4 recovery [3–5].

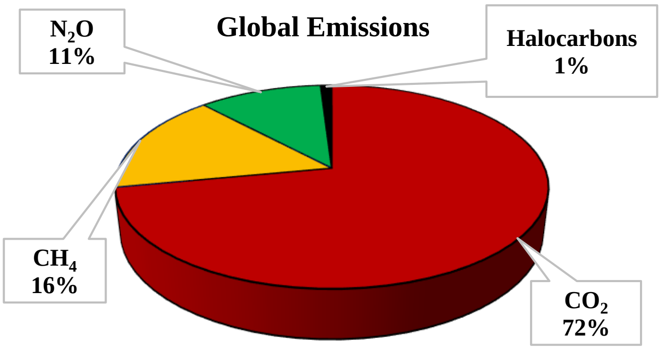

Figure 1-1. Global emissions for main greenhouse gas [2]

Currently, shales are considered as suitable targets for CO_2 storage applications [6], due to their low permeability and wide availability worldwide [7–13]. Compared to conventional geo-sequestration formations, shale gas fields are more abundant and provide a higher potential for carbon geo-sequestration (CGS) projects [7]. The strong adsorption capacity of CO_2 allows for more displacement of methane gas from the formation, which also provides an opportunity for enhanced shale gas recovery (ESGR) process to be applied [10,13–16]. Carbon dioxide is highly reactive to shale formations, when injected, it will be dissolved into brine and cause minerals dissolution and precipitation during CCS and ESGR process [1,17]. The interaction between the CO_2 and shales can significantly impact the efficiency and viability of CCS in shales, besides altering the shale petrophysical properties, which may affect the storage capacity, rock geometry, and fluid transportation [18,19].

The literature reported that the dissolution behavior of CO_2 in clay minerals and organic matter causes the formation of carbonic acid within the porous medium, which results in noticeable changes in shale properties [20,21]. Considerable studies were conducted to understand the interactions between CO_2 and shales and the implications on CCS applications. However, the knowledge of the alteration in shale properties associated with CO_2 treatment is evolving, and more studies are required for better utilization of CCS projects in shales in terms of the technical feasibility and economic viability [7,22,23]. In this regard, this research tends to investigate the alterations in some of the main physical, and chemical properties for different types of shales after CO_2 exposure, and evaluate the implications on CO_2 storage capacity. The outcomes of this study present a wide understanding of CO_2/shale interaction and its impact on CCS projects.

1.2 Literature Review

1.2.1 CO_2/Shale Interaction

The geochemical interactions between CO_2 and shales cause uncertainty for the long-term CO_2 sequestration, these interactions lead to mineral dissolution, gas adsorption, and changes in porous medium [18,24,25]. Due to shales heterogeneity, the storage capacity and the stability of targeted shales should be evaluated on a case-by-case basis for efficient CCS application. Several factors were reported to have a direct impact on the alteration of shale properties, including but not limited to mineralogy, wettability, maturity of total organic carbon (TOC) content, pressure, temperature, surface morphology, and geometry [8,18,26–28]. Addressing these factors will assist in evaluating the CO_2 storage feasibility in the targeted formation. However, the possible alteration of shale properties caused by the CO_2/shale interaction has recently motivated many researchers to study the effect of CO_2 treatment on shale properties [18,21,26,29–43]. **CHAPTER 2** provides comprehensive coverage and a critical review of the relevant literature on the effect of CO_2/shale interaction on shale properties.

The CO_2/shale interaction can alter the pore and surface structural system, as CO_2 can dissolve and extract clay minerals [20,21], which results in wide variations of minerals' dissolution and precipitation such as kaolinite, silica, and gypsum [24,38]. Shale sedimentary and mineralogy play decisive roles in the potential changes of the pore structure system parameters including specific surface area (SSA), fractal dimension, total pore volume (TPV) and pore size distribution (PSD) [18,40–42,44,45]. In this regard, researchers reported a reduction in SSA of shales after CO_2 treatment, which could reduce CO_2 adsorption capacity and storage efficiency in the long-term [18,39,41,42,44,45]. Additionally, extending CO_2 treatment time and increasing treatment pressure were found to increase shale porosity and SSA, due to the high dissolution of organic matter and carbonate minerals such as Ca^{++} and Mg^{++}, which can decrease the sealing integrity of the shale-caprock [44–46].

Shale mineralogy is influenced by the reactivity of shales to CO_2, the presence of carbonate minerals such as calcite and dolomite was found to increase the reactivity of shales to CO_2 compared to clay minerals such as kaolinite and illite, which results in significant precipitation of carbonate solids [37,40,47]. Recent studies indicated that CO_2 exposure in shales may result in increasing quartz content and reducing carbonate and clay minerals, caused by CO_2-induced swelling and CO_2 adsorption [18,38,39,41,42]. Similarly, the reactivity of shales to CO_2 causes relative changes in surface chemistry and functional groups after CO_2 treatment, due to the presence of oxygen-containing groups on the shale surface [18,48], which can affect the overall CO_2 adsorption and storage capacity [38].

The shale's surface wettability is also influenced by the CO_2/shale interaction due to the presence of clay and non-clay contents on the surface [49,50]. In the presence of CO_2, the shale's surface wettability could be altered towards CO_2-wet, which leads to reduce the CO_2 storage capacity and affect the sealing integrity [9,30]. Several studies reported that the presented minerals in the shale surface play the main role in influencing the hydrophilicity of shales at high pressures [29,33,51–53], for instance, Iglauer et. al. [29] reported an intermediate-wetting behavior of caprock due to the exposure of CO_2, which would reduce the sealing efficiency, while a strong water-wet behavior of CO_2/brine/silty shale caprock can form good sealing barriers and prevent CO_2 capillary breakthrough [31]. This variation in wetting behavior is related to the different mineralogy that existed on the shale surface [30]. However, factors such as salinity, pressure and TOC may have an additional impact on CO_2/brine/shale wettability system [9,31].

The dissolution and precipitation of minerals after CO_2 exposure can cause a notable degradation in shales' mechanical properties, affecting the stress behavior and the overall stability of the long-term CO_2 sequestration [54]. The development of compression strain within the pores may lead to weakening the shale, decreasing its brittleness, and increasing its plasticity and toughness [37,40,54]. Recent studies reported significant reductions in shale's triaxial compressive strength, tensile strength, and elastic modulus after CO_2 exposure, due to the dissolution and precipitation of carbonate and clay minerals [14,20,37,42,54,55]. The reduction in shale strength caused by CO_2/shale interaction could be a result of the expansion of shale pores caused by CO_2 dissolution, which in return destroys shale skeleton density, reduce mesopores volume, and weakens the shale [42].

1.2.2 CO_2 Sequestration in Shales

Carbon dioxide storage feasibility in shales was studied by multiple researchers, confirming the high potential of shales to store CO_2 [56–59]. Marcellus shales can store between 10.4 and 18.4 Gt of CO_2 by the year 2030 [58], this amount represents more than

50% of total U.S. CO_2 emissions over the same time [60]. Similarly, Edwards et al. [56] presented an initial assessment on the CO_2 storage capacity of Barnett shale and found that between 2.1-3.1Gt could be stored. The high storage capacity of shales provides economic benefits for CCS compared to conventional formations [12,13,16]. Liu et al. [7] presented a numerical study on Yanchang shale in China, indicating that the long-term CO_2 storage capacity is controlled by the CO_2/shale interaction and gas adsorption behavior, however, the presence of chlorite and smectite minerals may gradually increase the dissolution of CO_2, thus increasing the CO_2 storage capacity in the mineral phase.

Although these initial results are promising, the rate between CO_2 injection and capture should be systematically assessed to achieve a cost-effective sequestration project. To date, the technical demonstration of CCS in shales is promising, while the economic aspects to the cost of CO_2 capture, transport, and storage prevents CCS to be applied commercially [22,59]. Therefore, considering the petro-physical characteristics for shales, the storage site cost and infrastructure cost would provide a better assessment of the feasibility of CO_2 storage in shales [61,62]. **FIGURE 1-2** illustrates the latest reported global development of the current CCS projects [63]. Shales deserve more attention, and the knowledge of CO_2/shale interaction and its influence on CCS projects needs additional studies. The technical and commercial feasibility of CCS in shales needs to be evaluated through systematic studies for better utilization of this evolving technology [59].

Figure 1-2. Current commercial CCS facilities worldwide [63].

1.3 Problem Statement and Research Gap

Due to the complex structure and heterogeneity of shales, the understanding of the mechanism of CO_2/shale interaction in the long-term is not fully established. Many factors could directly impact the nature of CO_2/shale interaction and affect the stability and the efficiency of CCS in shales. Further investigations are required to evaluate the alteration in shale properties, such as shale mineralogy, pore structure and wetting behavior, as to date only limited literature exists in this area [31,37,38,40]. Moreover, the impact of CO_2 treatment time, pressure, and temperature will have an additional impact on altering shale properties. In regard, this research presents comprehensive investigations on the effect of CO_2 exposure on some of the major physical and chemical properties of shales and evaluates the associated implications on CO_2 storage capacity. Our main argument is that different types of shale formations will indicate different behavior of CO_2/shale interactions, due to shale heterogeneity, thus the alteration of shale properties will vary based on the mineral composition and pore structure for each shale. Addressing these alterations in shale properties will instantly help to assess the functionality of the targeted shale formation to host CO_2 for extended periods. As pointed earlier in this chapter, the knowledge of the impact of CO_2/shale interaction on shale properties is evolving; yet the accomplishments achieved in this study provide a wide understanding of the CO_2/shale interaction and its impact on CCS projects.

1.4 Research Questions

This study aims to investigate the potential interactions caused by CO_2 exposure and evaluate the associated alteration in shale properties and overall storage capacity for different types of shales. Accordingly, several questions were arisen to narrow the research gap and gain an in-depth understanding of the factors that influence the nature of the CO_2/shale interaction and the subsequent impact on CCS applications. This study tends to answer the following questions:

- How CO_2 injection affects the mineral composition of different types of shales? And what is the effect of mineralogy alteration on the shale surface structure?

- What is the impact of CO_2 treatment on the surface chemistry and chemical functional groups of shales? And what role does the CO_2 treatment pressure play?

- What is the relationship between shale mineralogy and the alteration of the pore structure system after CO_2 treatment?

- What is the influence of CO_2 treatment on the water wettability of shales? And how the sealing integrity is affected?

- What is the nature of the CO_2/brine/shale geochemical reactions in the long-term? And what are the kinetics that controls the dissolution and precipitation of minerals at geological time scales?

1.5 Research Hypotheses

In this study, several experimental hypotheses were set to examine the overall impact of CO_2/shale interaction on shale properties and storage capacity. The presence of clay and carbonate minerals in a high percentage on the shale surface after CO_2 treatment will result in increasing the SSA and pore volume of shales. Similarly, the dissolution of clay minerals will cause an increase in the oxygen-containing groups of the shale surface chemistry. However, a high possibility of content increasing in non-clay minerals such as quartz is expected, which then increases the CO_2 storage capacity. If the pore volume increases after CO_2 treatment, then an increase in shale-water contact angle will occur, and the surface water wettability will be shifted towards CO_2-wet. This will result in a possible CO_2 leakage and capillary breakthrough in the long term. There is a direct correlation between the time and pressure of CO_2 exposure, and the changes in shale properties, however in static lab experiments an equilibrium state is expected to occur within a short period, yet in the long-term, the CO_2 storage capacity will decrease with CO_2 migration possibility. These hypotheses were the guidance to answer the research questions, and by achieving the research objectives they will be either supported or denied.

1.6 Research Objectives

The main aim of this study was to investigate the interactions between CO_2 and shale formations and evaluate the resulted alteration on shale properties, and storage feasibility. To achieve this aim, the following specific objectives were formulated:

1. To evaluate the reactivity of shales to CO_2 exposure through investigating the alteration in mineral composition, surface structure and chemical properties for different types of shales.
2. To identify the role of CO_2 treatment pressure in the alteration of clay-rich shale properties and the impact on overall storage capacity.
3. To investigate the complexity and roughness of macropore and mesopore structure of shales, by addressing the variations in pore structure system parameters including specific surface area, pore size distribution, and fractal dimension.
4. To address the seal integrity of shales before and after CO_2 treatment, through the evaluation of surface wettability and surface tension.
5. To evaluate the reaction kinetics of CO_2 with shale at geological time scales, and address the impact on minerals dissolution/precipitation.

1.7 Research Significance

The efficient application of CCS projects in shales requires knowledge about the fundamentals of CO_2/shale interaction. Hence, the outputs of this study will contribute to the overall understanding of the CO_2/shale interaction, through investigating and analyzing the possible changes in different types of shales after $SCCO_2$ treatment. Besides, this study assists to understand the relationship between shale mineral composition and the changes in pore structure surface morphology and functional groups caused after CO_2 treatment. The study also provides new insights on the alteration of shale-water contact angles and surface wettability at various $SCCO_2$ treatment conditions. These findings provide a technical assessment for the feasibility of CCS application in shales based on the associated alteration in shale properties.

1.8 Research Framework and Methodology

1.8.1 Research Framework

FIGURE 1-3 shows the thesis's framework to address the knowledge gaps related to the CO_2/shale interactions, and the main objectives of this thesis. Generally, the research focuses on evaluating the effect of CO_2 treatment on some of the main physical and chemical properties of shales and addressing the impact on CO_2 storage capacity and seal integrity. This study begins with addressing the reactivity of different types of shales to CO_2 treatment and the implications on mineral composition, surface morphology and chemical functional groups (gaps #1 and #2). Then, the research examines the alterations in the complexity and roughness of macropore and mesopore structure of shales (gap #3). Particularly, addressing the variations in pore structure system parameters including, specific surface area, pore size distribution, and fractal dimension. After that, the thesis studies the impact of wettability alterations on the seal integrity for the water/shale system after CO_2 treatment (gap #4). Specifically, the alteration in water/shale contact angles and surface tension caused by CO_2 treatment can negatively affect the seal integrity, and provide the potential for a capillary breakthrough. Finally, geochemical models were constructed on a core scale to validate the outcomes from the experimental work and assist in understanding the reaction kinetics of CO_2 with shale at geological time scales (gap #5).

1.8.2 Methodology

The research methods and approaches that were applied in this research are described in detail throughout **CHAPTERS 3-7**. Both experimental and simulation methodologies were applied. In the experimental approach, the alterations in shale properties after CO_2 treatment were evaluated with different analytical methods. X-Ray Diffraction (XRD) was used to evaluate the changes in mineral composition; Scanning Electron Microscopy (SEM) and thin section analyses were applied to evaluate the alteration on the surface morphology; Fourier Transform Infrared (FTIR) Spectroscopy was applied to address the impact on the surface chemistry and functional groups; low-pressure N_2 adsorption method assisted to evaluate the alteration in the pore structural system of shales; and lastly, contact angle measurements were used to evaluate the alteration in wettability system.

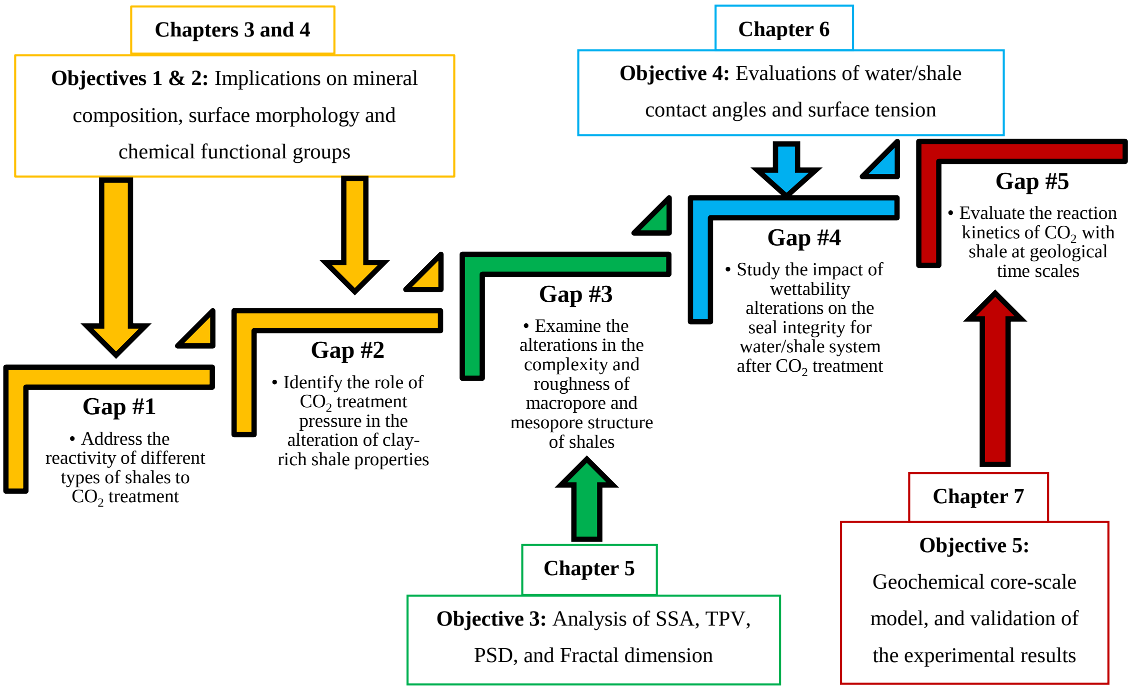

Figure 1-3. Research Framework

Simplified one-dimensional reactive transport models were constructed using PHREEQC-interactive software, to simulate the CO_2/brine/shale interaction at geological time scales. The equilibrium models were performed at the isothermal conditions of 70 ^{o}C, while the injected volume of CO_2 (1L) was assumed to fill the pore spaces at a pressure of 177 atm (18MPa). The concept of the kinetic model considers a constant CO_2 pressure source (177atm), supplying abundant CO_2 to the aqueous system during the simulation. Both models assume no-flow boundaries, as the model was built on a core scale. The selection of the methods was based on the consistent results obtained from previous studies, which provide the most reliable and valid data [18,20,26,37,38,40,42,44,64–66].

1.9 Thesis Structural Review and Organization

This thesis contains eight chapters that explains the background, outcomes, and conclusion of this research. The format of this thesis follows the current presentation of doctoral research. **CHAPTER 1** provides a brief background on the status and the gaps in knowledge on CO_2/shale interaction and the impact on shale properties and storage capacity. The chapter presents the research problem, questions, objectives, and significance, besides providing an overview of the research design and the thesis structure.

In **CHAPTER 2,** a comprehensive review of the existing literature on the alteration of shale properties caused by CO_2 is provided. The fundamentals of CO_2/shale interactions in altering the pore structure, chemical properties wettability and mechanical properties were discussed. The chapter outlined the development of shale formations and the potential for long-term CO_2 storage applications. This chapter also highlighted the environmental evaluation and the economic viability of CCS in shales. This chapter has been published in ***Energies*** by ***MDPI***, as a review paper titled: A Review on the Influence of CO_2/Shale Interaction on Shale Properties: Implications of CCS in Shales.

CHAPTER 3 addresses the impact of CO_2/shale interactions on mineralogy, surface morphology and functional groups of shales. Samples from Eagle Ford and Mancos were treated with $SCCO_2$ for 30 days at 70^o C and 18 MPa, and analyzed by XRD, thin sections and FTIR methods. In this chapter, both qualitative and quantitative analyses were performed. This chapter has been published in ***FUEL*** by ***Elsevier***, as a technical paper titled: Effect of Supercritical CO_2 Treatment on Physical Properties and Functional Groups of Shales.

In **CHAPTER 4**, the effect of $SCCO_2$ treatment pressures on mineralogy, surface morphology and functional groups of Eagle Ford shales was investigated. The abstract of this chapter was presented at the *6th International Conference on Oil & Gas Engineering and Technology (ICOGET)*, and the full paper has been published in ***Applied Geochemistry*** by ***Elsevier***, as a technical paper titled: Geochemical and Physical Alteration of Clay-Rich Shales under Supercritical CO_2 Conditions.

CHAPTER 5 presents an experimental investigation on Eagle Ford and Mancos shales to evaluate the relationship between the alterations of pore structural system and mineralogy, after $SCCO_2$/shale interaction. The assessment of pore structure parameters including specific surface area, pore size distribution, total pore volume and fractal dimension plays a crucial role in determining the feasibility of long-term CO_2 geological storage in shales. This chapter has been published in ***Journal of Natural Gas Science and Engineering*** by ***Elsevier***, as a technical paper titled: The Impact of Supercritical CO_2 On the Pore Structure and Storage Capacity of Shales.

CHAPTER 6 discusses the alterations of surface wettability and surface energy of Eagle Ford, Mancos and Wolfcamp shales after various CO_2 treatment durations, pressures and temperatures. This chapter also discusses the implications of wettability alteration on sealing integrity and trapping mechanisms in the long-term. A copy of this chapter has been published in ***International Journal of Greenhouse Gas Control*** by ***Elsevier***, as a technical paper titled: Surface Wettability Alteration of Shales Exposed to CO_2: Implication for Long-term Integrity of Geological Storage Sites.

In **CHAPTER 7**, geochemical modeling for the CO_2/brine/shale interaction was performed to address the kinetics of mineral dissolution and precipitation in the long-term. Both equilibrium and kinetic models were constructed using PHREEQC-interactive software. This chapter also discusses the potential of mineralization to occur during CO_2 storage as an effective trapping mechanism in shales. This chapter has been published in ***Chemical Geology*** by ***Elsevier***, as a technical paper titled: Geochemical Modelling of CO_2 Interactions with Shale: Kinetics of Mineral Dissolution and Precipitation on Geological Time Scales.

CHAPTER 8 concludes the thesis with a general discussion reviewing the research objectives and the main findings, besides addressing the research limitations and future work recommendations.

Note: **CHAPTERS (2-7)** have been published in peer-reviewed journals, and are reproduced in this thesis as individual chapters (**APPENDIX I** contains the relevant copyright agreements between the author and the respective journals).

The presented format of this thesis makes the repetition of some details between the journal papers inevitable. Below points can assist the reader in; i) navigating throughout this thesis to ensure a full and coherent narrative without unnecessary repetition. ii) identifying the contribution of each paper to the overall research questions and objectives. iii) summarizing the research methodology and methods. In this regard, it is suggested to consider the following points while reading the thesis:

1. The background of this research is briefly explained in **CHAPTER 1**. However, the reader can also choose to read the introduction part of any of the following chapters to understand the general concept of the research area (**CHAPTERS 3-7**).

2. If the reader wishes to gain a comprehensive coverage of the relevant literature and the previous studies about the research, then it is advised to read **CHAPTER 2**.

3. The research results are presented and discussed extensively through **CHAPTERS 3-7**, and the reader can freely navigate to the desired results and discussion sections of each chapter. The discussion part of the papers represents the core arguments of the research hypothesis. A short introductory paragraph is given at the beginning of each paper, to highlight the connection and the contribution of the chapter to the overall objectives of the thesis.

4. Each chapter which is a paper (**CHAPTERS 3-7),** includes a conclusion section that highlights its findings and contributions to the research objectives. However, the reader can get the major conclusions of the research findings in **CHAPTER 8**. The reader may also find the recommendations useful for future directions.

5. Referencing style was unified to fit the thesis format, and the reference list is given at the end of this thesis. Besides, all abbreviations were defined at first appearance in this thesis.

CHAPTER 2

A REVIEW ON THE INFLUENCE OF CO_2/SHALE INTERACTION ON SHALE PROPERTIES: IMPLICATIONS OF CCS IN SHALES

This chapter provides a comprehensive, critical and systematic review of the literature on the influence of CO_2/shale interaction on shale properties and discusses the implications of the overall CO_2 storage capacity of shales during carbon capture and storage (CCS) applications. The alteration in some of the main physical and chemical properties of shales was discussed including; mineral composition, pore structure, chemical properties, wettability and mechanical properties. Moreover, the environmental evaluation and economic viability of CCS in shales were outlined. This chapter has been published in ***Energies*** by **MDPI**, open access in **2020**, as a review paper.

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Abstract: Carbon capture and storage (CCS) is a developed technology to minimize CO_2 emissions and reduce global climate change. Currently, shale gas formations are considered as a suitable target for CO_2 sequestration projects predominantly due to their wide availability. Compared to conventional geological formations including saline aquifers and coal seams, depleted shale formations provide larger storage potential due to the high adsorption capacity of CO_2 compared to methane in the shale formation. However, the injected CO_2 causes possible geochemical interactions with the shale formation during storage applications and CO_2 enhanced shale gas recovery (ESGR) processes. The CO_2/shale interaction is a key factor for the efficiency of CO_2 storage in shale formations, as it can significantly alter the shale properties. The formation of carbonic acid from CO_2 dissolution is the main cause for the alterations in the physical, chemical and mechanical properties of the shale, which in return affects the storage capacity, pore properties, and fluid transport. Therefore, in this paper, the effect of CO_2 exposure on shale properties is comprehensively reviewed, to gain an in-depth understanding of the impact of CO_2/shale interaction on shale properties. This paper reviews the current knowledge of the CO_2/shale interactions and describes the results achieved to date. The pore structure is one of the most affected properties by CO_2/shale interactions; several scholars indicated that the differences in mineral composition for shales would result in wide variations in pore structure system. A noticeable reduction in specific surface area of shales was observed after CO_2 treatment, which in the long-term could decrease CO_2 adsorption capacity, affecting the CO_2 storage efficiency. Other factors including shale sedimentary, pressure and temperature can also alter the pore system and decrease the shale “caprock” seal efficiency. Similarly, the alteration in shales’ surface chemistry and functional species after CO_2 treatment may increase the adsorption capacity of CO_2, impacting the overall storage potential in shales. Furthermore, the injection of CO_2 into shales may also influence the wetting behavior. Surface wettability is mainly affected by the presented minerals in shale, and less affected by brine salinity, temperature, organic content, and thermal maturity. Mainly, shales have strong water-wetting behavior in the presence of hydrocarbons, however, the alteration in shale’s wettability towards CO_2-wet will significantly minimize CO_2 storage capacities, and affect the sealing efficiency of caprock. The CO_2/shale interactions were also found to cause noticeable degradation in shales’ mechanical properties. CO_2 injection can weaken shale, decrease its brittleness and increases its plasticity and toughness. Various reductions in tri-axial compressive strength, tensile strength, and the elastic modulus of shales were observed after CO_2 injection, due to the dissolution effect and adsorption strain within the pores. Based on this review, we conclude that CO_2/shale interaction is a significant factor for the efficiency of CCS. However, due to the heterogeneity of shales, further studies are needed to include various shale formations and identify how different shales’ mineralogy could affect the CO_2 storage capacity in the long-term.

Keywords: shale gas; CO_2 injection; CO_2 sequestration; CO_2 storage capacity; CO_2/shale interaction

2.1 Introduction

The development of carbon capture and storage (CCS) stands as a suitable technology to reduce the massive increase in CO_2 emissions in recent decades, as global climate change is becoming a serious concern to the public environment and economic growth [1]. CO_2 geological sequestration was proposed as a reliable technique to mitigate the emissions of greenhouse gas from fossil fuels into the atmosphere, by injecting CO_2 for long-term storage and enhancing gas recovery [3–5]. Conventional geological formations with high pore volume, including saline aquifers, depleted oil and gas fields, and un-minable coal seams, were utilized as suitable candidates for CCS projects [67]. However, some concerns related to these formations, including cost and long-term storage, prevent efficient CO_2 storage [58]. The trapping mechanism during CO_2 storage is usually associated with the CO_2/rock interactions in the porous medium, including CO_2 absorption, minerals dissolution, dissolution trapping, capillary trapping, rock heterogeneity and physical adsorption [12]. The trapping mechanism in deep saline aquifers, for instance, is mainly driven by structural trapping; when the injected CO_2 diffuses into the formation, it reaches the top layer due to the buoyance factor, hence CO_2 would be trapped by an impermeable caprock [1]. Coal seams that have been proven to have economic potential for CCS projects at extremely deep locations are driven by an adsorption trapping mechanism, yet the injection of CO_2 is more likely to cause high swelling rates and many environmental issues [68]. In depleted reservoirs, gas absorption and structural trapping effectively work as CO_2 trapping mechanisms. The injected CO_2 will be absorbed by the immobile residual oil causing multiple-contact miscibility [12].

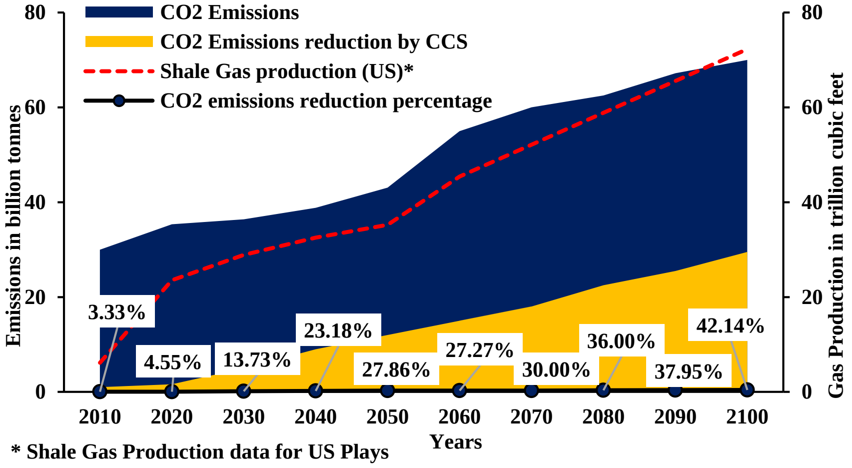
2.1.1 Development of Shale Formations

The success in developing shale formations in recent decades has shifted attention towards shale reservoirs, and considered them as promising candidates to store CO_2 for extended periods [6], mainly because shales with their ultralow permeability play a major role as barriers or seals in a petroleum reservoir system, and also due to their wide availability worldwide [7–13]. The breakthrough made in technology to utilize CO_2 (instead of slick-water) in developing shale formation during drilling, fracturing, and enhanced shale gas recovery (ESGR) processes leads to minimizing many environmental issues during the operations, i.e., minimizing the amount of produced wastewater and increasing the production efficiency of gas while sequestering the adsorbed CO_2 simultaneously [38,69,70]. These developed technologies, including hydraulic fracturing and horizontal drilling make commercial development of shale formations possible. In the US, shale gas production has increased since 2010 from about 6.16 trillion cubic feet to exceeding 20 trillion cubic feet in 2020, and is expected to reach about 35 trillion cubic feet in 2050. Forty-nine percent of the total US gas production is expected to come from shale reservoirs by 2035 [71], securing the gas production for the upcoming decades and providing the potential for CCS projects [72,73]. As illustrated in **FIGURE 2-1**, CCS applications hold good promise in reducing CO_2 emissions in the coming decades, despite the increase in energy demands. However, effective utilization of depleted shale gas formations as storage sites for CO_2 can significantly contribute to minimizing CO_2 emissions, assuming good connectivity between induced and existing fractures and no pore space collapse [60].

2.1.2 Adsorption Capacity of CO_2 in Shales

Carbon dioxide is a non-toxic fluid that is present at the reservoir in the supercritical phase when the temperature and pressure exceed 31.8 °C and 7.38 MPa, respectively. Supercritical CO_2 ($SCCO_2$) has low viscosity and no surface tension, with a high adsorption capacity relative to methane gas (CH_4) to the shale formation [60,74]. CO_2 sorption on clay and kerogen in partially depleted wells allows the displacement of CH_4 and stores more CO_2 [16,75,76]. As noted by many studies [10,13–16], the high CO_2 adsorption capacity is the main derive mechanism for CO_2 storage in shale formation after production phase, as injecting CO_2 continuously leads to the release of the natural pre-adsorbed CH_4 during CO_2 fracturing stimulation due to the displacement mechanism and higher chemical potential. Nuttall et al. [13] presented the adsorption isotherms between CO_2 and CH_4 in Devonian shale formations, showing stronger CO_2 adsorption than CH_4, providing the potential for CO_2 sequestration in shales (**FIGURE 2-2**). A study conducted by Kang et al. [12] on Barnett shales confirmed the strong adsorption capacity of CO_2, which was 5–10 times higher compared to CH_4. The adsorption of CO_2 in most shales in the US indicated a similar tendency of higher adsorption than

CH_4, by 2–3 times [77]. The strong CO_2 capacity provides high storage security in shale formation due to the existence of stable in-place CH_4 in the reservoir, which can be related to the fact that five CO_2 molecules can displace one CH_4 molecule, which allows the CO_2 to occupy the porous medium, providing the potential for storage application [15]. Later research has come to a similar conclusion from measuring the adsorption behavior of CO_2 and CH_4 on different shale formations, indicating that shale formations favor adsorbing CO_2, enhancing the recovery of CH_4, preventing massive leakage risks and reducing storage costs [40,77,78]. Tao and Clarens [58] estimated that Marcellus shale could store a total mass of CO_2 ranging between 10.4 and 18.4 gigatonnes (Gt) (1 Gt = 10^{12} kg), offering the potential to store around 50% of CO_2 emissions in the US by 2030 [60]. Similarly, Edwards et al. [56] presented that Barnett Shale has a CO_2 storage capacity ranging between 2.1–3.1 Gt. These studies provide a strong foundation for the investigation of the feasibility of CCS projects in shale formations, confirming the high possibility of storage capacity in shale formations by multiple trapping mechanisms [7,56–58].



* Shale Gas Production data for US Plays

Figure 2-1. Carbon capture and storage (CCS) contribution percentage in CO_2 emission reduction from 2010 to 2100 [63,79–81].

2.1.3 CCS in Shales

The injection of CO_2 into depleted shale formations may help to recover additional hydrocarbons through the ESGR process, which provides economic benefits in CCS compared to conventional storage sites. Shale formations are very promising targets for CCS, however, the rate of CO_2 injection into the shale formation should be coupled with the rate of CO_2 capture from industrial processes such as fossil fuels in power plants, ensuring the storage safety, stability and economic feasibility [5,56,57]. CO_2 is a relatively reactive substance; once injected into the shale formation, it will be trapped in the adsorbed phase. In the long-term, formation brine will dissolve the injected CO_2 and causes reactions with the shale rock, leading to mineral precipitation and dissolution which may affect the shale storage capacity [1,17]. The CO_2/shale interaction is a key factor for the efficiency of CCS in shale formations; it can significantly alter the shale properties, which in return affect the rock geometry, fluid transportation, and storage capacity [18,19]. The presence of organic and inorganic components in a heterogeneous porous medium such as shale permits the injected CO_2 to interact with clay minerals and organic matter through chemical dissolution [18]. This dissolution behavior of CO_2 can be related to the creation of carbonic acid when meeting a brine formation, leading to major changes in the shale properties [20,21].

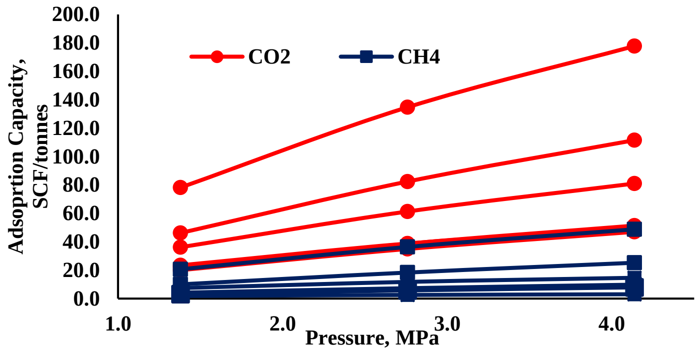


Figure 2-2 Adsorption capacities for CO_2 and CH_4 in Devonian shales at different pressures [13].

In the last decade, enormous work was directed towards understanding the fundamentals of the CO_2–shale interaction at reservoir conditions for better CCS applications [21,26,43,29–31,33,37,39,41,42], by evaluating the impact of CO_2 injection on shales. Earlier in 2008, Busch et al. [25] found that the rock properties of Muderong shale in Australia were affected by the dissolution behavior of $SCCO_2$. These findings were supported later by several studies [44,45,82], confirming that $SCCO_2$ can significantly alter the pore structure system of shale, leading to changes in the porosity and the specific surface area. Some recent studies have related the effect of CO_2/shale interaction on shale properties to the mineral composition and specific reservoir conditions, including temperature, pressure, and CO_2 phase states [18,26–28]. However, the knowledge of CO_2–shale interaction is still evolving, and more investigations are needed to successfully apply CCS technology in shale formations technically and economically. It is crucial to address the potential interactions between CO_2 and shale formation, and their influence on CCS, to ensure the longevity of CO_2 containment [7].

In this regard, the related literature of CO_2/shale interaction and its effect on shales are comprehensively reviewed, to gain a wide understanding of the effect of CO_2 injection on shale properties. The overall assessment of CCS viability in depleted hydrocarbon shale formations depends on its reliability in terms of technical feasibility, long-term CO_2 containment and economic viability. Several studies [7,56–58] have supported the functionality of shales to host CO_2, related to CO_2 injectivity, storage capacity, methane gas recovery and CO_2/shale interactions. However, this paper focuses on reviewing the existing knowledge of CO_2-shale interactions and describing the results achieved to date. Therefore, the following sections address this issue and evaluate the implications of the overall storage capacity. This review also highlights the topics on Life Cycle Assessment (LCA) and the economic viability of CCS applications in shales.

2.2 CO_2-Shale Interaction

Long-term CO_2 sequestration in shale formations causes CO_2/shale geochemical interactions, such as mineral dissolution, gas adsorption and changes in pore structure, which affect the sealing integrity of the shale [18,24,25]. Because of the heterogeneity of shale, it is crucial to address several factors that could have a direct influence on shale properties for the specific shale formation, such as shale mineralogy, total organic carbon (TOC) content, surface morphology, geometry, pressure, and temperature [8]. This will help to evaluate the functionality of the targeted shale formation to host CO_2 for extended periods. Recently, characterization of shale formation associated with CO_2 injection has received much attention in the literature, for its importance in applying a cost-effective CCS project [49,83]. Many characterization methods, i.e., *X*-ray diffraction, scanning electron microscopy, *X*-ray fluorescence, low-pressure gas adsorption, Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) are being widely applied to investigate the effect of CO_2/shale interactions on physical and chemical properties of shales [18,37,38].

For this paper, and according to the nature of shale, the shale properties can be categorized under physical, chemical and mechanical properties; this classification is made based on the potential changes caused by CO_2 injection. This review discusses the impact of CO_2 exposure on some of the major shale properties, which are: (1) Pore structure, (2) Mineral composition, (3) Chemical properties, (4) Surface wettability and (5) Mechanical properties.

2.2.1 Pore Structure

The pore structure is one of the most affected properties of shale formation by CO_2 injection, therefore, any changes in pore structure may impact the efficiency of CO_2 storage capacity. This may lead to affect the economic feasibility of the CCS application. The ability of CO_2 to dissolve and extract clay minerals is the main cause of the changes in the pore morphology, this dissolution behavior of CO_2 can be attributed to the creation of carbonic acid and the chemical reaction with the formation water [20,21]. Generally, when the CO_2 is injected into the shale, it is stored as free gas in the macropores structure; over time, the CO_2–shale interaction takes place within the nanopore system, which in return affects the pore structure and its specific surface area (SSA), fractal dimension, total pore volume (TPV) and pore size distribution (PSD) [18]. Several studies have discussed the alteration of pore structure parameters when shales are exposed to CO_2, confirming that the alteration of pore structure system is affected by multiple factors including, the type of shale sedimentary, the presence of clay and non-clay mineral in the formation, and reservoir's pressure and temperature [18,40–42,44,45]. The alteration in the pore structure system during CO_2 injection is mainly influenced by the minerals' dissolution and precipitation. Shales are usually composed of clay minerals, quartz, carbonate, and fragments of other minerals. Several studies have characterized different shale formations and provided their typical mineral composition, as illustrated in **FIGURE 2-3** [18,84–86]. Liu et al. [24] reported that the CO_2 has a limited impact on the caprock due to the miner dissolution of K-feldspar and anhydrite, along with low precipitation of illite, smectite (a mineral that contains Ca^{++} and Mg^{++}), and siderite. On the contrary, Armitage et al. [87] reported an increase in the porosity and permeability of mudstone, due to the high dissolution of chlorite and siderite by CO_2. This indicates that the differences in mineral composition for shales would result in wide variations in the pore structure system.

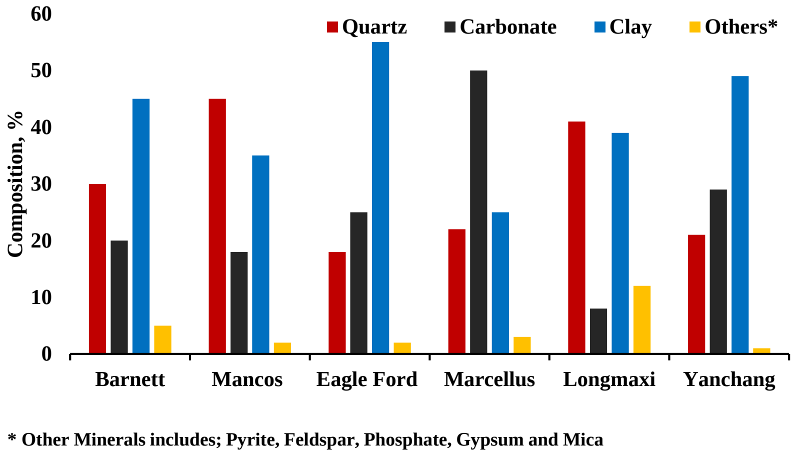


Figure 2-3. Typical mineral compositions of some shale formations.

Lahann et al. [44] addressed the mineralogical and petrophysical alteration of New Albany shales associated with the CO_2 injection, indicating that various alterations in Brunauer–Emmett–Teller (BET)-specific surface area of the mesopore and micropore structure system could occur. At high pressure and temperature (24 MPa and 150 °C, respectively), the BET-SSA of both mesopore and micropore has increased with extended CO_2 injection treatment time, mainly because of the gradual increase in CO_2 solubility to dissolve carbonate minerals such as Ca^{++} and Mg^{++} at high pressures (**FIGURE 2-4; FIGURE 2-5**). A later study by Jiang et al. [45] has confirmed that $SCCO_2$ injection led to increasing SSA and porosity of Longmaxi shales with extending the treatment time, due to the extraction of organic matter from shale by $SCCO_2$, which can be related to the grain size of shale. Moreover, with increasing the pressure, the $SCCO_2$ density rises, permitting more organic matter to be dissolved in shale, thus increasing shale porosity [46,88–90]. **FIGURE 2-6** shows the relationship between SSA and porosity at different $SCCO_2$ treatment pressures.

Recent studies [18,37–42] have further investigated the changes in the structural system of shales associated with $SCCO_2$ injection, and following points can be concluded: (1) the extraction of organic matter and the dissolution of carbonate minerals by $SCCO_2$ are the main causes for altering the pore structure system of shales, with a significant effect on micropores' and mesopores structure. (2) In the long-term, high pressure and temperature could result in more extraction of organic matter in shale, which in return reduces the CO_2 storage capacity. (3) The changes in shale's SSA and TPV are strongly related to the type of shale formation in term of surface mineralogy, surface morphology, and TOC; for instance, organic-rich shales are more likely to exhibit an increase in pore system [39,42,44,45], while the porosity and SSA of silty and low thermal maturity shales may decrease after $SCCO_2$ treatment [18,37,38,40].

The CO_2–shale interaction can also affect the shale's fractal dimensions after $SCCO_2$ exposure. Shales generally have complex inner porosity and irregular surface morphology, and the fractal dimension (D) index is used to quantitatively evaluate the structural complexity and surface roughness of solids [91]. Yin et al. [40] reported a reduction in the shale surface roughness caused by the CO_2 adsorption-induced swelling, which gradually transformed the surface morphology of shales from an irregular-complex structure to a smooth-regular structure. Consistently, Pan et al. [18] concluded that the extraction of organic matter in shales is the main mechanism for reducing the fractal dimensions of micropores structure after $SCCO_2$ treatment. However, a recent study by Luo et al. [41] reported opposite results, indicating an increase in the fractal dimensions and surface roughness of shale, which increases the complexity of the pore structure. This can be related to the dissolution of clay and carbonate minerals, which results in increasing the micropores' structure. This disagreement in results shows that the mineral genesis, mineral composition and sedimentary environment of shale could influence the fractal dimensions and surface roughness of shale.

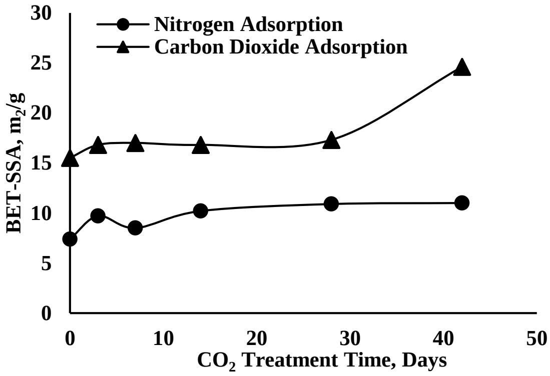


Figure 2-4. The effect of CO_2 treatment time on specific surface area (SSA) of New Albany shale at 150 °C [44].

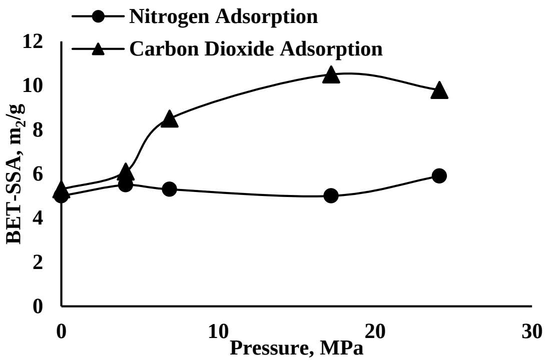


Figure 2-5. The effect of CO_2 treatment pressure on SSA of New Albany shale at 150°C [44].

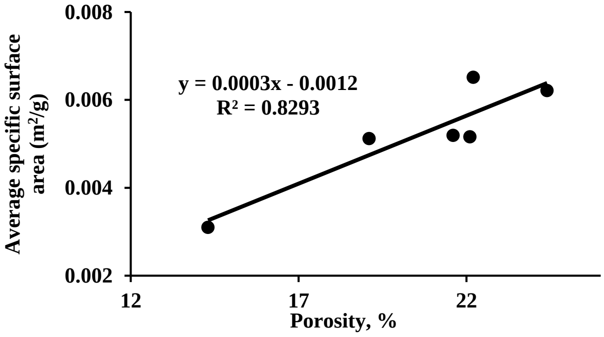


Figure 2-6. The relationship between SSA and porosity at different SC-CO_2 treatment pressures [45].

In the long-term, the alteration in pore structure can affect the hydrocarbon transport during ESGR process, the sealing mechanism, and lead to lower CO_2 adsorption capacity [45]. The dynamic sealing efficiency of shales after $SCCO_2$ exposure was examined by Rezaee et al. [39], over time, a possible CO_2 leakage could occur due to the increase in pore volume, and the reduction in the capillary threshold pressure. This alteration in pore structure and capillary pressure is caused by the dissolution and precipitation of kaolinite, silica, and gypsum, which results in decreased CO_2 adsorption capacity, which is not favorable for CO_2 sequestration [38]. Alteration of pore structure during $SCCO_2$ injection could have a direct impact on other shale properties, including chemical and mechanical properties, as explained later in this paper. Therefore, it is crucial to examine the changes in shale pore structure associated with $SCCO_2$ injection. The related literature has addressed the significant impact of pore structure alteration on CO_2 storage capacity and hydrocarbon flow pattern during ESGR, however, a different type of shales will indicate various alterations on pore structure, thus each shale formation should be evaluated separately before CCS projects

[8]. **TABLE 2-1** summarizes several studies that highlighted the effect of CO_2 injection on pore structure system.

Table 2-1. Summary of recent studies highlighting the effect of CO_2 injection on pore structure.

Author(s)	**Alteration % in Pore Structure Parameters**	**Name and Type of Shale Formation**	**Exposure Pressure, Temperature and Time**	**Main Findings**
Lahann et al. [44]	SSA (49.05%)	New Albany (Organic-rich)	4–24 MPa 150 °C 3–42 Days	They concluded that at high pressures, CO_2 solubility in water increases due to the high dissolution of carbonate minerals. This is the main cause of increasing the SSA of the mesopore and micropore structure.
Jiang et al. [45]	SSA (99.39%); Porosity (58.33%)	Longmaxi (silty/organic-rich)	8–18 MPa 40–90 °C 1–5 Days	This study showed that both shale porosity and SSA are increased with increasing $SCCO_2$ treatment time and pressure, due to the increase in $SCCO_2$ density and dissolving capability to extract organic matter in shale.
Yin et al. [40]	SSA (−60.52%); TPV (−28.25%); D (−4.18%); R_A (82.01%)	Longmaxi (organic/low thermal maturity)	16 MPa 40 °C 30 Days	In this study, a significant reduction in SSA, TPV and shale’s fractal dimensions was observed after 30 days of $SCCO_2$ treatment, while the average pore size increased. This behavior is related to organic matter dissolution in micropores by $SCCO_2$.
Ao et al. [37]	SSA (−70.27%)	Longmaxi (organic)	15 MPa 35 °C 5–20 Days	The specific surface area of shale was reduced after $SCCO_2$ treatment. Shale deformation was caused by $SCCO_2$ adsorption and gas pressure, which further affects the strength of shales.
Rezaee et al. [39]	Porosity (4.0%); Capillary Pressure (−52.74)	Latrobe Group (mix of mudstone/organic-rich)	15.17 MPa 66 °C 60 Days	They reported that the increase in pore structure and the reduction in capillary threshold pressure could decrease the caprock seal efficiency, and cause a possible CO_2 leakage
Pan et al. [18]	For Longmaxi: SSA (−42.91%); D (−5.99%) For Yanchang: SSA (94.09%); D (2.37%)	Yanchang (mix of mudstone/organic-rich) and Longmaxi (organic-rich with low thermal maturity)	15 MPa 80 °C 10–30 Days	They studied the changes in shale surface morphology and CO_2 adsorption. They found that at high temperatures (80 °C), $SCCO_2$ can dissolve and extract organic matter on the surface. Leading to the formation of carbonic acid, which in return causes the alteration of SSA and pore volume in nanopores structure.

Hui et al. [38]	For Longmaxi: SSA (−52.05%); TPV (−10.34%) For Yanchang: SSA (23.99%); TPV (−16.67%)	Yanchang (mix of mudstone/organic-rich), Longmaxi (organic-rich) and Wufeng (organic-rich)	18 MPa 60 °C 10 Days	It was found that the high-pressure CO_2 adsorption resulted in a significant reduction in SSA, affecting the structural and geochemical properties of shale. After CO_2 treatment, the CO_2 adsorption capacity decreased which is not favorable for CO_2 sequestration.
Luo et al. [41]	SSA (115.1%); TPV (24.78%); D (4.43%)	Yanchang (mudstone)	10 MPa 50 °C 50 Days	This study confirms that CO_2–shale interactions have a strong influence on the micropores of shale, indicating an increase in SSA and pore volume. It was also found that fractal dimensions of shale have increased due to the dissolution of the clay and carbonate minerals.

2.2.2 Mineral Composition

Researchers initially explained the influence of mineralogical composition on the reactivity of shales during CO_2 injection. $SCCO_2$ has high diffusivity and acts as an organic solvent to extract some organic and inorganic minerals, which may lead to an increase in the porosity of shale [45,48]. Previous studies indicated that the alteration in shale mineralogy after $SCCO_2$ treatment is mainly caused by the geochemical reaction with the formation brine in the presence of carbonate minerals such as dolomite and calcite [18,37–40,47]. Alemu et al. [47] found that carbonate-rich shales have high reactivity to CO_2 compared to clay-rich shales, due to the dissolution of carbonate minerals and the formation of smectite, which results in a significant increase in calcite concentration. The diffusion of carbonic acid leads to a significant reduction in the pH [25,44,92], leading to changes in the mineral contents of shale through a series of chemical reactions and reversible reactions [37,54], mainly including:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

$$CaCO_3 + H^+\ HCO_3^- \leftrightarrow Ca^{2+} + CO_2 + H_2O$$

$$MgCO_3 + H^+\ HCO_3^- \leftrightarrow Mg^{2+} + CO_2 + H_2O$$

$$Al_2O_3 + H^+\ HCO_3^- \leftrightarrow 2Al^{3+} + CO_2 + H_2O$$

Few scholars [40,45] have analyzed the surface microstructure of shale and indicated various changes in clay minerals such as kaolinite montmorillonite, illite, and anorthite after $SCCO_2$ treatment, caused by the extraction and dissolution of the in situ substance by $SCCO_2$. Non-clay minerals such as quartz, pyrite, and feldspar are most likely to exhibit a relative increase in content after $SCCO_2$ treatment because silicate minerals are rich in Ca^{+2}, Mg^{+2} and Al^{+3},and have high dissolving potential in acidified water during CO_2 injection, which leads to precipitation as carbonate solids [37,40]. This is favorable for mineral trapping mechanisms during long-term CO_2 storage. The phenomenon of mineral alteration in shales after $SCCO_2$ treatment was reported by the latest studies [18,38,39,41,42], indicating a high possibility for increasing quartz percentage and reduction in carbonate and clay minerals contents caused by CO_2-induced swelling, which affects CO_2 adsorption behavior.

During CO_2 injection, carbonic acid can also mobilize major and trace elements, affecting the physical structure of shales [93–95]. Recently, a study by Luo et al. [41] concluded that the hydrolysis and carbonation of silicate minerals is the main cause of element mobilization; minerals such as calcite, calcium, magnesium, sodium, potassium, and aluminum could face varying degrees of mobilization, which is controlled by the mineral composition and occurrence. However, it is important to consider the minerals' alteration for shale formation before CCS projects, as some elements with a high mobility such as zinc, cobalt, barium, and strontium may cause severe groundwater contamination [41]. The mineralogical alteration after $SCCO_2$ injection can cause major changes in the petro-physical properties of shales; as reported in the literature, the possible increase in micropore volumes might be beneficial for CCS and ESGR applications. Moreover, the long-term geochemical reactions provide a significant opportunity for mineralization trapping in shale formations, which plays an important role in increasing CO_2 storage capacity. However, further studies are required to capture the long-term mineral trapping mechanisms, especially mineral carbonation associated with CO_2 injection, and address the involved factors such as mineral type, pressure, and temperature [54].

2.2.3 Chemical Properties

Understanding the chemical reactions between CO_2, shales and formation water are very crucial for the practical application of CO_2 geological sequestration. The reactivity of shales to CO_2 depends mainly on the rock mineralogy, which eventually affects the chemical properties of the shale. Additionally, the fluid chemistry of CO_2 controls the dissolution and precipitation processes, and significantly impact the pore structure [47]. The alteration in shale chemical properties during CO_2 injection can be understood by evaluating the surface chemistry of the shale and its functional groups' distribution through FTIR and *X*-ray photoelectron spectroscopy analysis [96]. Several studies [18,24,38,40,97] have reported that the presence of oxygen-containing groups on the shale surface such as −COOH, −H and −OH bonds, would have a severe impact for both CO_2 and CH_4 adsorptions on carbonate minerals at high pressures.

Carbon dioxide (CO_2) injection causes a reduction in the intensity of C-O bonds in shales as well as aliphatic hydrocarbon (C-H) groups, which is related to the extraction of organic matter [18,48]. Yin et al. [40] suggested that some inorganic vibrational bands of quartz and illite (Si-O, Al-O-H and Si-O-Al bonds) can exhibit high absorption in shales similar to calcite and dolomite. Additionally, a noticeable reduction in aliphatic hydrocarbon groups was observed after CO_2 treatment, which confirms the associated changes in mineral contents. Recently, Pan et al. [18] proved that CO_2 injection can decrease the adsorption of the aliphatic hydrocarbon group, caused by the ability of CO_2 to dissolve the non-polar aliphatic and polar aromatic hydrocarbons. These alterations in hydroxyl functional groups (groups with oxygen) could increase CO_2 adsorption and affect the overall storage capacity.

Similarly, Hui et al. [38] confirmed that the chemical reactions between $SCCO_2$ and shales could decrease the oxygen-containing functional groups (C-O, O-C-O, C=O, COO−), and relatively increase the hydrogen groups (C-C/C-H) due to the ability of $SCCO_2$ to extract organics from the shale surface. This conclusion was based on the results obtained from three different shale formations after being treated with $SCCO_2$ as shown in

Table 2-2. These relative alterations in oxygen and hydrogen functional groups can be explained by two points, (1) the evaporation and extraction behavior of $SCCO_2$ [38], and (2) the ability of $SCCO_2$ to extract organic matter and dissolve the polar kerogen moieties from shale surface [48,98]. As mentioned before, this alteration in surface chemistry and functional species after CO_2 injection could increase the CO_2 adsorption capacity in shales, thus more investigations are required to clarify the impact of chemical properties' alteration on the sequestration potential of CO_2 in shales.

Table 2-2. Changes in Hydrogen and Oxygen Functional Groups after $SCCO_2$ saturation [38].

Formation	**Treatment Time, Hours**	**Hydrogen Functional Groups {C-C/C-H}, (%)**	**Increasing %**	**Oxygen Functional Groups {C-O, CO_3^{-2}, C=O, COO-}, (%)**	**Reduction %**
Yanchang	0	74.11	6.06	25.89	17.34
	240	78.60		21.40	
Marine Longmaxi	0	57.41	11.18	42.59	15.07
	240	63.83		36.17	
Marine Wufeng	0	52.36	3.53	47.64	3.88
	240	54.21		45.79	

2.2.4 Surface Wettability

Shales' surface wettability is one of the major petro-physical properties that is affected by CO_2 injection. Wettability is defined as the affinity of the rock surface to a particular fluid; it is mainly affected by the rock surface mineralogy and temperature [99,100]. Understanding the wettability of shales is important as it controls the capillary forces, the relative permeability and hydrocarbon production [50]. Characterizing the wettability of shales can be challenging because of the nano-Darcy permeability, the porous medium heterogeneity and the presence of clay minerals with the variety of organic and inorganic matrix [101]. Hence, it is necessary to address the complex nature of shales' wettability and analyze the factors involved, i.e., pressure, temperature, pH, mineral composition and TOC [102]. Several studies were conducted to evaluate the wetting behavior of different types of shales at the presence of different fluids, by using different methods and techniques, such as equilibrium contact angle (sessile drop) [33,103–107], NMR [108], spontaneous imbibition [109–113], and liquid–liquid extraction [104].

Based on the related literature, it was reported that (1) shales usually have a mixed wettability, which can be related to the presence of organic matter [103], (2) the shale surface is originally hydrophilic at atmosphere pressure, due to the existence of clay minerals and other non-clay minerals such as quartz, feldspar, and dolomite in high fragments [49,50], and (3) the contact angle between CO_2 and shales increases with increasing pressure and temperature [33]. A recent review by Siddiqui et al. [102] claimed that under in situ conditions, the wettability system of hydrocarbon/brine/shale is preferentially water-wet, regardless of the mineral composition and type of hydrocarbon. The strong water-wetting behavior of shales in the presence of hydrocarbons works in favor of storage applications, as it increases the structural storage capacity. However, in the presence of CO_2, several studies suggested that pure minerals in the caprock are not entirely water-wet and highly influenced by the CO_2–rock interactions [21,29,31,32]. A high possibility of CO_2 migration may occur when shales become CO_2-wet; CO_2 could escape back into the atmosphere or the overlying aquifers [9]. This alteration in wettability will dramatically minimize CO_2 storage capacities, and reduce the sealing efficiency, which is the main sealing mechanism [9,30].

During the first decades of CO_2 storage, a possibility of CO_2 leakage may occur, when the capillary threshold pressure is reached; this may lower the structural trapping capacity and the overall efficiency of CO_2 sequestration [29,30,114]. Although shales display ultra-low permeability, they might still have a possibility of CO_2 breakthrough depending on the presented minerals [21,43]. It is important to highlight the primary trapping mechanisms for CO_2 sequestration in shales, which are: (1) structural trapping, where shale formations act as a caprock [87,115]; (2) residual trapping, where capillary forces restrict the movement of CO_2 in the shale pores [116,117]. However, during ESGR processes, mineral trapping may also occur in some shale formations, due to the interactions between CO_2 and shale mineralogy; this mineral dissolution allows the CO_2 to enter the reservoir interlayers, and increases the CO_2 storage capacity [19,30].

In the last decade, several scholars have investigated the factors affecting the CO_2 wettability behavior of caprocks [9,26,29–31,51,114,118,119]. Mineral composition and surface chemistry were found to have significant influences on the structural trapping capacity, besides other factors including organic matter, brine salinity, pressure and temperature.

Iglauer et al. [29] found that CO_2 wettability of caprock increases with increasing pressure, indicating a poor water-wet or intermediate-wet, which may affect the sealing efficiency. Chaudhary et al. [51] also reported a high contact angle between CO_2 and shale at 22.8 MPa, indicating a mixed-wet behavior. On the contrary, low contact angles between CO_2 and silty shales were reported by Kaveh et al. [31], which indicate a strong hydrophilic caprock system even at high pressures. When the contact angles between CO_2 and shale are low, CO_2 becomes immobilized by the high capillary forces in the pore structure of the shale. However, increasing the contact angles decreases the capillary force and allows CO_2 to move upward by the buoyancy forces, and thus increases the chances of capillary breakthrough. Surface wettability is mainly affected by the shale's mineralogical composition, therefore different wetting behaviors could occur for different shale geometries [30]. Factors including brine salinity, temperature, organic content and thermal maturity, were found to have minor impacts on CO_2/shale contact angles. Strong water-wet behavior was observed in several studies despite the high concentrations of organic content, brine salinities and thermal maturities [9,31].

The injection of CO_2 into shales was also found to increase the contact angle between brine and shales, and reduce the shale surface hydrophilicity [26]. This can be related to the release of water content from clay minerals during CO_2 treatment. Moreover, the increase in shale-water contact angles causes a relative reduction in the surface tension between shale and water. This can be attributed to the adsorption capacity of solid surfaces and the CO_2 diffusion into the shale matrix after CO_2 treatment. **FIGURE 2-7** shows the relationship between the $SCCO_2$ treatment time and pressure on the shale–water contact angle. Accurate characterization of CO_2 wettability of shales is useful to estimate CO_2 storage capacity, and essential to determine the technical feasibility for CO_2 sequestration and hydrocarbon flow dynamics during the ESGR process [60]. Despite the progress achieved in the related literature on CO_2 wetting in shales, the knowledge on wettability alteration is still evolving, and more insights are required to answer some decisive questions, i.e., what is the wetting behavior of different shales at various length scales? What mineral composition will prevent CO_2 capillary leakage [9]? **TABLE 2-3** highlights the related work on the changes in shales' contact angles values associated with CO_2 injection at different operating parameters, and the subsequent impact on shales' wettability.

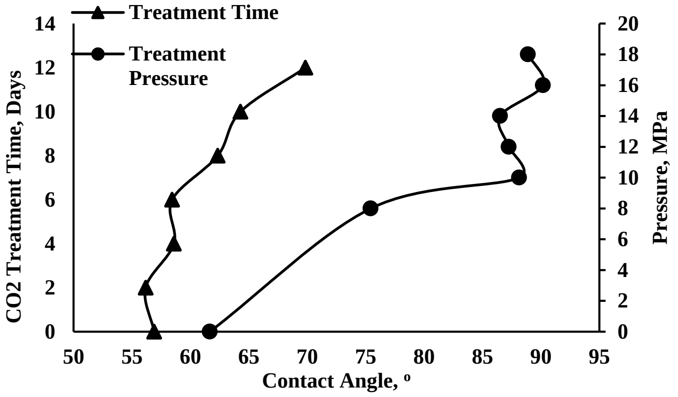


Figure 2-7. The changes in contact angle with extending SCCCO₂ treatment time (at 10 MPa, and 50 °C) and increasing treatment pressure (after 4 days at 50 °C) [26].

Table 2-3. Summary of related work on the effect of CO₂ injection on wettability and contact angle.

Author(s)	**Wettability System**	**Contact Angle Measurement Method**	**Pressure and Temperature**	**Main Findings**	**Effect on Storage Capacity and CO₂ Leakage Possibility**
Chiquet et al. [21]	CO_2/Brine/(Mica-Quartz)	Contact angle (captive-drop)	3.5–11 MPa Unknown temperature	Contact angle measurements were conducted on shale caprock minerals (mica and quartz), indicating that the presence of CO_2 significantly increases the contact angle. This behavior altered the wettability from water-wet to intermediate-wet at high pressures, caused by the CO_2 dissolution and brine pH reduction.	Decreasing in CO_2 storage capacity. CO_2 leaks more easily due to the increase in contact angles and IFTs.
Zhu et al. [50]	CO_2/Brine/Rock	Contact angle (Wilhelm plate method)	Atmospheric pressure 50, 70 °C	This study indicated that tight rocks' wettability can be altered after CO_2–brine–shale interactions, due to the dissolution and precipitation of the minerals. The contact angles increases after the CO_2 injection with increasing CO_2 treatment pressure at 50 °C.	Continuous dissolution of carbonate minerals may increase the percentage of some elements (O and Si) on the shale surface, which reduces the possibility of CO_2 leakage.
Iglauer et al. [29]	CO_2/Brine/Rock	Tilted plate method	10–20 MPa 50 °C	In this study, the CO_2 wettability of several natural caprock samples was tested at various pressures. They found that CO_2 wettability of caprock increased at high pressure of 20Mpa, indicating an intermediate-wet to poor-wet behavior.	Noticeable reduction in the sealing efficiency implies possible CO2 leakage. Structural trapping capacity is reduced significantly.

Chaudhary et al. [51]	CO_2/brine/Organic Shale	High-resolution X-ray computed tomography (HRXCT)	13.8–22.8 MPa 60–71 °C	In this study, the authors presented a new method to measure the contact angle and wettability behavior of minerals at reservoir conditions. This method is based on the usage of X-ray imaging and radiography. They reported an increase in the contact angle at a pressure of 22.8 MPa. This confirms the ability of CO_2 to alter minerals wettability due to dissolution behavior.	The contact angle in organic-rich shale increased to (59°). However, the shale surface indicated a water-wet behavior. This implies stronger storage capacity and low leakage potential.
Kaveh et al. [31]	CO_2/water/Silty Shale	Contact angle (pendant-drop)	0.2–15 MPa 45 °C	They examined the wettability of silty shale with CO_2 and water under various temperatures and pressures. The results showed that the silty shale remains hydrophilic at high pressures. They also found that the wettability system slightly increases with decreasing temperature.	Silty shales show strong water-wet behavior, indicating a low possibility of CO_2 capillary breakthrough, and high storage capacity.
Guiltinan et al. [9]	brine/CO_2/organic-rich shale	X-ray computer tomography scanning	13.79 MPa 20,40,60 °C	This study investigated the effect of organic matter and thermal maturity on the CO_2 wettability of shales. The results showed that the wettability system remains strong water-wet despite the changes in concentrations of organic content and thermal maturities.	This behavior has no major influence on the efficiency of structural trapping (low leakage potential) and is favorable for CO_2 sequestration.
Qin et al. [26]	Water/shale contact angles	Contact angle (pendant-drop)	Atmospheric pressure 25 °C	In this study, treatment time and pressure led to a significant increase the contact angles, due to the decrease in carbonate mineral content and the release of water content from clay minerals during the treatment.	The hydrophilicity of the shale surface decreases, which may result in CO_2 leakage and lower capacity.

2.2.5 Mechanical Properties

The dissolution and precipitation of minerals after CO_2 injection causes significant alterations in the mechanical properties of shales, which raises stability concerns for the long-term CO_2 sequestration. Generally, the changes in pore structure and mineral content caused by CO_2 injection reflect the possible deformation and weakening in the strength of caprocks, and thus reduces the overall CO_2 adsorption capacity [54]. Several studies were conducted to investigate the effect of CO_2 injection on rocks' mechanical properties, and evaluate the associated factors including treatment time, pressure, CO_2 phase state, and bedding angles [14,20,54,55]. The injection of acid gases such as CO_2 and H_2S together with carbonated water was found to alter the physical properties of chalk, and affect the displacement behavior under in situ conditions, which eventually reduced the chalk strength and ductility [120,121]. Similarly, deformation in sandstone and siltstone formations was observed after the injection of $SCCO_2$ [122], which led to increasing the porosity and precipitation of calcite [123,124]. This deformation behavior in caprock can be attributed to the changes in effective stress and crack propagation, which increases the potential of CO_2 leakage.

The alteration of coal mechanical properties is affected by pressure and CO_2 phase state [125–129]. Coal seams are significantly weakened by the injection of $SCCO_2$ compared to gaseous and Sub-critical CO_2. Viete and Ranjith reported a reduction of 13% and 26% in both compressive strength and elastic modulus, respectively, after $SCCO_2$ injection [126]. Such an effect is caused by the high $SCCO_2$ adsorption in coals and the permeability increase under in situ conditions. Shale formations have a strong ability to adsorb CO_2, and such behavior causes a reduction in effective stress, increasing the compression and raising the pore pressure within the formation [37,130]. This results in shale swelling, decreasing strength and brittleness, and eventually damaging the shale formations. Few recent scholars have investigated the effect of different factors on shale mechanical properties after CO_2 injection [14,20,37,42,54,55]. The analysis of uniaxial compressive strength (UCS) and Young's modulus (E), are commonly used to evaluate the stress conditions of shales through conducting uniaxial and triaxial compression tests [131].

Increasing the CO_2 treatment time of black shale was found to reduce both UCS and E values drastically by 66.05% and 56.32%, respectively, after 30 days [54]. This also results in decreasing the shale's brittleness index, and increasing its plasticity and toughness. When CO_2 interacts with black shale, carbonate minerals precipitate as calcite and cause a reduction in the stress in the formation. Besides, the dissolution of clay minerals exhibits possible damage in shale macroscopic structure, which, as a result, increases the initial compaction and reduces shale strength [42]. CO_2 phases and saturation pressure were also found to affect shale mechanical properties. Saturating organic-rich shales with $SCCO_2$ for 10 days reduced UCS and E by 22.86% and 23.10%, respectively [20]. $SCCO_2$ has a stronger ability to increase the crack initiation pressure compared to gaseous CO_2, and thus reduce the crack damage stress. This results in shale swelling and creating more micro-cracks within the shale formation, and subsequently reduces the strength [14,20]. Moreover, increasing saturation pressure beyond 12 MPa showed a minor impact on reducing UCS and E due to the compression effect of fluid [42]. The mechanical properties of shales could also be influenced by the bedding orientation and the various forces generated, i.e., normal, shear, and compressive stresses along the bedding plane [55]. The direction of normal and shear stresses is dependent on the bedding angle, which results in differences in the degree of deformation in shale. At a bedding angle of 0°, only normal stress exists, which promotes the development of tensile failure [55]. In such a case, the cracks deviate through the damaged bedding direction which causes shale weakening. However, increasing the bedding angle beyond 45° sustains the shale strength and the resistance to crack propagation, which is related to the development of both tensile and shear failures.

The weakening of shales was further clarified by later studies [14,37,42,55], which reported various reductions in mechanical strength after $SCCO_2$ injection, due to the dissolution effect and adsorption strain within the pores. It should be highlighted that the resulted physical changes in shales after CO_2 injection, were found to have a significant impact on the shale strength [42]. The associated reduction in mesopores volume can partially destroy the shale skeleton density and weakens the shale. Based on the related literature, it is apparent that CO_2-shale interaction may significantly reduce the mechanical parameters and weaken strength and brittleness of the shales. This degradation in shale mechanical properties is caused by several factors, which require further assessment in the future. Because of the heterogeneity of shale, it is essential to characterize each shale formation on a case-by-case basis to ensure the stability of shale formations during CCS.

TABLE 2-4 summarizes recent studies that highlighted the effect of CO_2 injection on mechanical properties.

Table 2-4. Summary of recent studies highlighting the effect of CO_2 injection on mechanical properties.

Author(s)	**Reduction % in Measured Parameters**	**Name and Type of Shale Formation**	**Exposure Pressure, Temperature and Time**	**Main Findings**
Lyu et al. [54]	UCS (66.05%); *E* (56.32%); BI (50%)	Longmaxi (Black shale)	9 MPa 40 °C 10–30 Days	This study evaluated the effect of different $SCCO_2$ saturation time on UCS and Young's modulus of black shales. They observed a clear reduction in shale strength and brittleness index, after 10 days of saturation, due to the dissolution of clay minerals, with more reduction after 30 days.
Ao et al. [37]	Tensile Strength (22.7%); Tri-axial compressive strength (15.3%); *E* (29.56%)	Longmaxi (organic)	15 MPa 35 °C 5–20 Days	They reported a gradual reduction in tensile strength and triaxial compressive strength of the shales with increasing $SCCO_2$ treatment time.
Yin et al. [20]	UCS (22.86%); *E* (23.10%)	Longmaxi (organic-rich)	4–16 MPa 38 °C 10 Days	This study reported the impact of saturation pressure and CO_2 phase on shale mechanical properties. The results showed that $SSCO_2$ has more influence on UCS and E than $subCO_2$, due to the high adsorption and dissolution capacity for $SCCO_2$. Consistently, a noticeable increase was observed in the Crack initiation pressure and a reduction in crack damage stress, which indicates the creation of more micro-cracks by $SCCO_2$.
Lyu et al. [14]	UCS (30%); *E* (38%)	Sichuan Basin (low-clay)	9 MPa 40 °C 10–30 Days	The ability of CO_2 adsorption in weakening the shale strength and increasing its ductility was addressed. A clear reduction in UCS and E was found on the $SCCO_2$ treated shale samples, with a noticeable increase in crack initiation and the decrease in crack damage.

Feng et al. [55]	Brazilian splitting strength (BSS) (46%); Absorbed energy (U) (50%); *E* (22%)	Sichuan Basin (Black shale)	10 MPa 40 °C 10–60 Days	This study investigated the effect of $SCCO_2$ saturation time and bedding orientation on shale strength. They concluded that the damage caused by $SCCO_2$ in the pore structure is the key cause of mechanical degradation. Noticeable changes were observed in shale strength with changing the bedding angles (θ); both tensile and shear failure could occur affecting the shale resistance and cracking propagation.
Lu et al. [42]	UCS (31%); *E* (10%)	Yanchang (mudstone)	12 MPa 50 °C 8 Days	This study found a strong connection between the damage in pore structure and the weakening of shale strength. The possible damage in shale macroscopic structure increases the stress–strain in the initial compaction stage, which results in reducing shale strength.

2.3 Environmental Evaluation of CCS

The environmental consequences of CCS are often evaluated through Life Cycle Assessment (LCA) studies. LCA is proven to provide a complete analysis of all environmental effects of applying CCS to power plants. Such studies are detailed and time-consuming and vary in scope, methodology and outcomes, but they provide a suitable assessment of many environmental effects, including global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), photochemical ozone creation potential (POCP) and cumulative energy demand (CED) [132]. Several studies have performed LCA on different CCS power plants [133–137], and the majority of these studies indicated a clear reduction in GWP, regardless of the technology used in transport, injection and storage of CO_2 [132]. Generally, there are three main factors incorporated to influence the environmental effects from the CCS systems [138]: (1) efficiency energy penalty, (2) purity and capture efficiency of CO_2, and (3) origin and composition of the fuel. However, CO_2 capturing is out of the scope of the current study.

Energy penalties are associated with the capture technology, generally, pre-combustion processes produce lower energy penalties compared to pre-combustion and oxyfuel processes [133,134]. For instance, 29.6% of post-combustion thermal efficiency for hard coal was reported by Schreiber et al. [136], while 48% thermal efficiency was reported with pre-combustion process [134]. This variation can be attributed to the different types of fuel composition (natural gas, coal), assumptions in time scale, and the different energy sources (gas, hard coal, bituminous, lignite) [138]. For an electricity production process, CO_2 is produced in different purities and captured by the different systems. Therefore by minimizing the consumption of electricity for the CO_2 capture, the energy penalty is reduced, and thus reduces the environmental effects from the CCS system [138]. Hard coal is considered as a valuable and wide available fuel to capture CO_2; one LCA study shows that the power generation from hard coal has significantly reduced the GWP, indicating about 13% contribution to the total GWP for post-combustion [137]. Similarly, the power generation from lignite power plant reduces the GWP, with lower share to the global total GWP compared to hard coal [135], due to the production of mono-ethanolamine during the capture process. However, natural gas implies higher efficiency in capturing process compared to hard coal and lignite, with a reported thermal efficiency of 49.6% and 44.7% in post-combustion and oxyfuel processes, respectively [136]. This results in lowering the GWP of power plants and increases the efficiency in CO_2 capture.

Other environmental effects including AP, EP, POCP and CED showed inconsistent results for different energy power plants and capture technology [138]. For instance, post-combustion hard coal power generation systems indicated an increase in the EP compared with the power plants without CCS [138], while a 15% reduction in EP was reported at the lignite oxyfuel system. This inconsistency between hard coal and lignite can be related to the capture technology used (post-combustion and oxyfuel, respectively), and long transport distance required in hard coal systems [138]. However, for natural gas systems, the EP usually increases, as it is mainly dominated by emissions from operation regardless of the capture technology [132]. An increase in EP by 266%–403% was reported for natural gas systems when using a steam integrated system for CO_2 delivery [132]. Similarly, a range between a 15% and 50% increase in EP was reported in several studies [133,135–137]. Therefore, no solid conclusion can be made regarding the assessment of EP and other environmental effects, due to the lack of sufficient data in the literature. In LCA studies, the selection of the time scale is crucial for reliable evaluation. Considering the present and future power plants for extended duration allows us to predict the main production processes and consider future modification [2,134]. Moreover, sensitivity analysis on the time scale could help to assess the storage process and identifying possible leakage [133,135]. However, it is not clear how possible storage leakage will impact the environmental effects, as it is difficult to perform climate conditions forecasts. Other factors are considered in LCAs, including compression, pipeline transport, injection and storage of CO_2 indicate almost negligible impacts for all environmental effects [132].

In summary, LCA studies vary in the technologies used for the CO_2 capture and storage, and the existing literature is too scarce to draw a solid conclusion. However, LCA still provides an idea of the impact of CCS on environmental performance, and a general understanding of the influence of capture efficiency, energy penalty and fuel composition. In future LCA studies, several aspects shall be considered, including techniques for CO_2 capture, modeling leakage potential and incorporating both conventional and renewable energy resources [138].

2.4 Economic Viability of CCS in Shales

Shale formations hold a promising potential to utilize CCS projects in terms of their technical feasibility. By combining ESGR operations with long-term CO_2 storage applications, CH_4 production can be maximized due to the strong adsorption capacity of CO_2. However, the economic viability of CCS in shales has yet to be proven, as the related literature on this topic is limited. Considering the associated costs of CO_2 capture, transport, and storage, together with infrastructure cost and petro-physical characteristics of shales could make CCS project costly [61,62]. Therefore, in this paper, we briefly highlight the main challenges facing the economic viability of CCS in shales. The costs of CO_2 capture were studied and analyzed earlier in the 21st century, and enormous reports were presented based on the plant type (source) and capture technique (**TABLE 2-5**). Mainly, there are two components of the cost of CO_2 capture. First is the cost of removing CO_2 from industrial emissions, as, currently, chemical adsorption of CO_2 is believed to be the best available technology [139]. Secondly, the cost of equipment and chemicals, as they increase the overall capture capital cost. CO_2 capture is more of a technical factor, and innovative technologies are needed to reduce the costs of CO_2 capture and deliver stable long-term benefits [63].

The costs of CO_2 injection and transportation are dominant factors affecting the economic viability of CCS in shales. These costs are controlled by the potential revenue form CH_4 production and other factors including well spacing, CO_2 separation, and bottom-hole pressure [23]. The CO_2 injection cost is related directly to the CO_2 injectivity approach used, i.e., the applied huff-n-puff processes in the Big Sinking Field showed an increase in injection cost by USD 0.35/metric tonnes [140]. Although CO_2 injection is costly, integrated CCS systems in shales estimated a reduction of 30% on the average of the CO_2 injection cost, with an average of USD 5–10/metric tonnes lower cost compared to saline aquifer [22]. The main reasons behind this are as follows: one is the gradual reduction in pore pressure during CO_2 injection in shales and the production of CH_4; two is the large storage potential for shales.

However, the added cost of CO_2 transportation is large compared to injection and capture costs. A study on Marcellus shales estimated a cost of USD 60–70/metric tonnes to transport CO_2 from industrial source to the site, added to the USD 22.4/metric cost of for CO_2 injection [23]. These results indicate that using shorter pipeline transport distances with smaller diameters could be a suitable method to reduce the transport cost, which eventually implies high incremental capital costs. Moreover, utilizing high bottom-hole pressure wells with a short distance between producer and injector wells could reduce the total cost of CCS to USD 39/metric tonnes and provide more storage potential due to high injection pressure. The cost of infrastructure—which includes CO_2 storage hubs and pipelines—is less costly compared to CO_2 injection, transport and capture, nevertheless, they should be carefully assessed and included in economic viability studies.

Table 2-5. Early studies on estimated CO_2 capture cost from different plants [23].

Author(s)	**CO_2 Capture Cost, $/Metric Tonnes**	**Plant Type (Source)**
Smith et al. [141]	21–62	Coal-based Integrated gasification combined cycle (IGCC)
Heddle et al. [142]	14.55	N/A
Rubin et al. [143]	29–44	Pulverized coal combustion (PC)
	11–32	Coal-based Integrated gasification combined cycle (IGCC)

	28–57	Natural gas combined cycle (NGCC)
Holloway [144]	18–72	Power Plant
Finkenrath [145]	43–62	N/A

Apart from the consideration of the fixed costs, the application of CCS is derived by other factors, mainly related to the concerns regarding carbon price and carbon tax revenues [146]. Addressing this topic is within the gaps between the economic theory and reality that prevents CCS to have an international breakthrough [147]. Another concern about integrated CCS systems is how they can be utilized for large-scale fossil fuel power plants instead of refining industries only. However, reviewing and discussing these factors is out of the scope of this paper, yet it is reliable for generally highlighting these economic drivers and their impact on CCS deployment (**TABLE 2-6**). In summary, more studies are needed to provide clear assessments of economic viability of CCS in shales. Although the application of CCS in shales is encouraging, the lack of available knowledge regarding storage capacity, reservoir data for best sequestration settings and the effect of long-term CO_2/shale interaction can affect its economic viability.

Table 2-6. Economic drivers for CCS projects [147].

Environmental Policy	**Cost of CCS**	**Fossil Fuel Energy Costs**	**Clean Energy Sources**
This is the main driver for CCS technology, as it controls the economic market and energy generation. The demand for CCS will depend on the employed strategy that targets carbon emissions through "carbon tax" revenues. When carbon emissions are optimally taxed, this allows for the non-energy cost of CCS to drop, and thus lowers the emissions tax [146]. In this case, a lower carbon tax provides the opportunity for companies to apply CCS projects.	For the CCS project to be cost-effective, the unit cost to capture, transport and storage has to be lower than the emitting CO_2 and pay the carbon price. A more advanced CCS technology will lead to an increase in energy generation from fossil fuels and reduce the unit cost of CCS. Moreover, the availability of geological sequestration sites will also result in a higher level of CCS.	Fossil fuel resources are limited in nature, and the increase of generating fossil fuel energy costs will affect the level of fossil fuel energy, carbon emissions, and overall CCS activity. Therefore, due to the exhaustibility and scarcity rent cost, renewable resources should be considered as a possible alternative for fossil fuels, which may help to achieve a higher level of CCS [148].	There is an approach to utilize carbon-free resources i.e., solar energy, wind and nuclear electric power to replace or at least contribute to energy generated from fossil fuels. It will be ideal to employ clean energy sources only, as generating energy cost is low, which puts CCS in high demand, but the full replacement of fossil fuels is not expected soon. As of today, 80% of the global energy needs are supplied by fossil fuels, however, by combining both sources with optimal timing, the cost of energy generation can be reduced, and thus increases the level of CCS [149].

2.5 Conclusions

CO_2/shale interaction is a significant factor for the efficiency and the success of CCS technology in depleted shale formations, for its noticeable impact on altering shale physical, chemical, and mechanical properties. This paper presented the current knowledge of CO_2/shale interactions and provided a comprehensive review of the impact of CO_2 exposure on shale properties and the subsequent implications on CO_2 storage. The accomplishments achieved through laboratory experiments confirm that the physical structure and surface chemistry of shales are highly influenced by CO_2 injection, due to the formation of carbonic acid within shales, which, in the long-term, might reduce CO_2 adsorption capacity and storage potential. Shale-sealing efficiency is also affected by the injection of CO_2, as the presented minerals on the shale surface could decrease the shale surface hydrophilicity. Furthermore, CO_2 injection causes a massive degradation in shale mechanical properties, and a noticeable reduction in shale brittleness and increases in its plasticity and toughness were observed, which results in shale weakening. The knowledge of CO_2/shale interaction and its implications on CCS requires further study; systematic studies are in need to evaluate the feasibility of CCS in shales technically and commercially. With this evolving technology comes many technical and economical unknowns, which shall be addressed in future work.

CHAPTER 3

EFFECT OF SUPERCRITICAL CO_2 TREATMENT ON PHYSICAL PROPERTIES AND FUNCTIONAL GROUPS OF SHALES

In this chapter, the impact of $SCCO_2$ treatment on some of the main physical and chemical properties of shales was discussed. This chapter provides both qualitative and quantitative analysis on the alteration of mineral composition, surface morphology and functional groups of shales, and addresses the impact on overall CO_2 adsorption. Samples from Eagle Ford and Mancos shales were treated with $SCCO_2$ for 30 days at 70^o C and 18 MPa, and analyzed by XRD, thin sections and FTIR methods. The changes in contact angles were also analyzed after the treatment. This chapter has been published in ***FUEL*** by **Elsevier,** in **2021**, as a technical paper.

Fatah, A.; Ben Mahmud, H.; Bennour, Z.; Hossain, M.M; Gholami, R. Effect of Supercritical CO_2 Treatment on Physical Properties and Functional Groups of Shales. FUEL, 303, 121310 (2021).

DOI: https://doi.org/10.1016/j.fuel.2021.121310

Received 17 December 2020, Revised 26 May 2021, Accepted 19 June 2021, Available online 30 June 2021.

Abstract: The influence of Supercritical CO_2 ($SCCO_2$) on geochemical interaction is considered a key factor affecting CO_2 storage capacity in shales. To address this issue, samples from Eagle Ford and Mancos shales were treated with $SCCO_2$ for 30 days at 70°C and 18MPa. Analytical methods including *X*-ray diffraction (XRD), optical microscope, and Fourier Transform Infrared spectroscopy (FTIR) were used. The alteration in shale/water contact angles was evaluated based on Sessile drop method. The results show that $SCCO_2$ treatment can alter the mineral composition of shales. Quartz content generally increased, while clay and carbonate minerals' contents decreased. Evaluating the dissolution of carbonate minerals, in particular, is beneficial to form an effective mineral carbonation trapping for long-term CO_2 storage. The changes in surface morphology suggest that clay-rich shales are more affected by $SCCO_2$ treatment compared to sandy/quartz-rich shales. The aromatic hydrocarbons showed minor changes after $SCCO_2$ treatment compared to the aliphatic hydrocarbons. The increase in oxygen-containing groups after $SCCO_2$ treatment proves the high adsorption capacity of CO_2 in shales. However, hydroxyl functional groups showed various trends after $SCCO_2$ treatment, depending on the clay content. Eagle Ford shales displayed a possible turn to CO_2-wet behavior, while the surface of Mancos shales remained strongly hydrophilic. In conclusion, quartz-rich shales could be favorable for CO_2 adsorption and providing more storage capacity.

Keywords: CO_2/shale interaction, Mineral composition, Functional groups, CO_2 sequestration, Wettability alteration, Thin sections microscopy.

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CHAPTER 4

GEOCHEMICAL AND PHYSICAL ALTERATION OF CLAY-RICH SHALES UNDER SUPERCRITICAL CO_2 CONDITIONS

The previous chapter evaluated the alteration in shale properties for different types of shale samples after $SCCO_2$ treatment. The purpose of this chapter is to extend the experimental conditions and further evaluate the impact of $SCCO_2$ treatment pressures on shale properties for clay-rich shales. Several samples from Eagle Ford shale were subjected to various $SCCO_2$ treatment pressures (10-24 MPa), and the alteration in properties was analyzed by XRD, thin sections and FTIR methods. The results supported the hypothesis of the research and further confirmed the reported outcomes from the previous chapter. The abstract of this chapter was presented at the 6th International Conference on Oil & Gas Engineering and Technology (ICOGET), and the full chapter has been published in ***Applied Geochemistry*** by **Elsevier**, in **2022,** as a technical paper.

Fatah, A.; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. Geochemical and physical alteration of clay-rich shales under supercritical CO_2 conditions, Applied Geochemistry, 140, 105291 (2022).

DOI: https://doi.org/10.1016/j.apgeochem.2022.105291

Received 20 December 2021, Revised 29 March 2022, Accepted 30 March 2022, Available online 9 April 2022.

Abstract: The injection of Carbon Dioxide (CO_2) into shale gas formations is a promising approach that not only reduces the impact of greenhouse gas on climate change but also enhances the gas recovery due to geochemical interactions between CO_2 and clay minerals. However, these geochemical interactions have not been fully explored and changes in the petrophysical properties of shales have been reported over time. This paper evaluates the geochemical reactions and physical changes caused by the injection of supercritical carbon dioxide ($SCCO_2$) on the properties of clay-rich shales. Samples from the Eagle Ford formation were collected and exposed to $SCCO_2$

at different pressures ranging from 10 to 24 MPa at 70° C. Analytical methods such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thin-section microscopy were used to characterize the $SCCO_2$-treated samples. The results showed dissolution of clays and precipitation of quartz with increasing $SCCO_2$ treatment pressure. The content of carbonate minerals was also reduced at high pressure, which can be attributed to the reactions of the dolomite with H^+ to form magnesium carbonate. The percentage of absorption of aromatic hydrocarbons and oxygenated groups gradually increased with increasing pressure, which can be attributed to the increase in CO_2 adsorption. On the other hand, the absorption of aliphatic and hydroxyl groups decreased after treatment. $SCCO_2$ treatment pressure is an important factor to evaluate the CO_2 adsorption capacity of clay-rich shales. The presented results enrich the understanding of the interactions between CO_2 and shale under different pressures, which may be helpful to determine the feasibility of long-term injection and storage in shale.

Keywords: CO_2 sequestration, shale, Supercritical CO_2, Eagle Ford, Mineral composition

CHAPTER 5

THE IMPACT OF SUPERCRITICAL CO_2 ON THE PORE STRUCTURE AND STORAGE CAPACITY OF SHALES

In Chapters 3 and 4, the changes in surface morphology and structure were evaluated after various $SCCO_2$ treatment conditions. However, these alterations were evaluated qualitatively. The purpose of this chapter is to provide a quantitative analysis of alteration in the pore structure system after $SCCO_2$ treatment. Analyses of macropores and mesopores structures were performed on various shales using SEM and low-pressure N_2 adsorption isotherms techniques. Moreover, the alterations in the specific surface area, total pore volume, pore size distribution, and fractal dimensions were also evaluated. This chapter has been published in ***Journal of Natural Gas Science and Engineering*** by **Elsevier**, as a technical paper.

Fatah, A.; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. The Impact of Supercritical CO_2 On the Pore Structure and Storage Capacity of Shales. Journal of Natural Gas Science and Engineering, 98, 104394 (**2022**).

DOI: https://doi.org/10.1016/j.jngse.2021.104394

Received 6 August 2021, Revised 20 November 2021, Accepted 23 December 2021, Available online 27 December 2021.

Abstract: Injection of supercritical CO_2 ($SCCO_2$) causes significant changes in the petrophysical properties of shales and affects the integrity of geological storage sites. The alteration of mineralogy and pore structure plays a major role in defining the fluid transport in pours media of shale gas during CO_2 storage. In this study, a series of $SCCO_2$ treatment experiments were performed on different types of shales to evaluate the alterations of the pore structure and mineralogy. Two types of shales from Eagle Ford and Mancos fields were treated with $SCCO_2$ and analyzed with scanning electron microscope, X-ray diffraction, and low-pressure nitrogen adsorption before and after 30 days at 70°C and 18MPa. The experimental results indicated that $SCCO_2$ affected the mineral composition and changed the macropore structure of shales, due to the adsorption-induced expansion effect. The pore structure of clay-rich shales samples was more affected by CO_2 treatment compared to quartz-rich shales, due to the dissolution of clay contents in the former, which reduced the overall pore volume by 24% in Eagle Ford shales. Conversely, the development of micro-cracks in Mancos shale surface created new pores and increased the pore volume by more than 13%. The results from nitrogen adsorption isotherms indicated a prominent alteration in the mesopores structure. The specific surface area and total pore volume of Eagle Ford shale reduced by 35.46% and 11.86% respectively after the $SCCO_2$ treatment, while the specific surface area and total pore volume of Mancos shale increased by 27.4% and 25.92% respectively. A positive correlation was reported between the fractal dimension and specific surface area. It appeared that the surface roughness was reduced in Eagle Ford shale and relatively increased in Mancos shales after the treatment. The obtained results suggested that the adsorption capacity of clay-rich shales could be reduced after the CO_2 treatment, while quartz-rich shales displayed a uniformed pore size distribution profile, indicating a possible increase in the adsorption capacity. These findings can provide technical support to further understand the effect of CO_2 on the pore structure and mineralogical alteration of shale during geological storage.

Keywords: Pore structure, CO_2 sequestration, Mineral composition, Shales, Geological storage.

CHAPTER 6

SURFACE WETTABILITY ALTERATION OF SHALES EXPOSED TO CO_2: IMPLICATION FOR LONG-TERM INTEGRITY OF GEOLOGICAL STORAGE SITES

The alterations in mineral compositions and pores structure system discussed in the previous chapters (**CHAPTER 3 AND CHAPTER 5**) may have a direct impact on the wetting behavior and surface wettability after $SCCO_2$ treatment. The alterations in surface wettability and surface tension of shales associated with $SCCO_2$ treatment are discussed in this chapter. Samples from Eagle Ford, Mancos and Wolfcamp shale formations were treated with $SCCO_2$ at different durations, pressures and temperatures, and the changes in water/shale contact angles were measured. This chapter provides new insights into the integrity of shales to store CO_2 for long periods and outlines the relationship between shale wettability, mineral composition and pore structure. This chapter has been published in ***International Journal of Greenhouse Gas Control*** by **Elsevier**, in **2021**, as a technical paper.

Fatah, A.; Bennour, Z.; Ben Mahmud, H.; Gholami, R.; Hossain, M.M. Surface Wettability Alteration of Shales Exposed to CO_2: Implication for Long-term Integrity of Geological Storage Sites. International Journal of Greenhouse Gas Control, 110, 103426 (2021).

DOI: https://doi.org/10.1016/j.ijggc.2021.103426

Received 13 February 2021, Revised 24 May 2021, Accepted 2 August 2021, Available online 9 August 2021.

Abstract: Surface wettability is a key factor controlling the CO_2 seal capacity and defines the CO_2 storage potential. Limited studies have addressed the shale/water wettability behavior during CO_2 injection, thus considerable attention is needed to understand this concept. In this paper, an ample number of supercritical CO_2 exposure experiments were conducted to evaluate the alteration of shale/water contact angles. Different types of shales with various mineralogy from Eagle Ford, Wolfcamp, and Mancos fields, were exposed to $SCCO_2$ at different durations, pressures, and temperatures. Shale mineralogy and surface were analyzed using *X*-ray diffraction and scanning electron microscope. The results indicated a strong relationship between mineral composition and the alteration in shale/water wettability. Clay-rich shales displayed a possible turn in wetting behavior to CO_2-wet with extending the $SCCO_2$ treatment time and increasing the treatment pressure, caused by $SCCO_2$ dissolution of clay and carbonate minerals. While the wettability of high-quartz contents shales remained strongly hydrophilic after various $SCCO_2$ treatment conditions. Increasing the temperature accelerated the CO_2/shale interactions, and a minor effect was observed on the shale hydrophilicity. Increasing the cohesive energy density of CO_2 promotes a favorable CO_2 wetting environment, which reduced the hydrophilicity of the surface and reduces the surface energy. In conclusion, shales with high quartz contents exhibit strong water wetting behavior after $SCCO_2$ treatment, which leads to better sealing capacity, more efficient integrity of geological storage sites, and higher potential for CO_2 containment.

Keywords: Wettability alteration, contact angle, SEM, surface energy, supercritical CO_2, Geological Storage.

CHAPTER 7

GEOCHEMICAL MODELLING OF CO_2 INTERACTIONS WITH SHALE: KINETICS OF MINERAL DISSOLUTION AND PRECIPITATION ON GEOLOGICAL TIME SCALES

Previous **CHAPTERS (3-6)** provided various experimental approaches to evaluate the changes in shale properties caused by CO_2/shale interactions, and address the implications on CO_2 storage capacity and seal integrity. However, the study of the reaction kinetics of CO_2 with shale at a laboratory scale is subject to a limited treatment time. Numerical modeling can help to extrapolate these kinetics to a larger time scale. Therefore, in this chapter, the geochemical kinetics of the CO_2/brine/shale interactions are investigated. A simplified one-dimensional reactive transport model was constructed using PHREEQC-interactive software. Both equilibrium and kinetic models were applied to simulate the CO_2/brine/shale interaction at geological time scales. The models were built on core-scale, and the alterations in minerals dissolution/precipitations during CO_2 storage were evaluated. The results were verified/validated with the experimental outcomes explained in **CHAPTERS (3-6)**, confirming the high potential for shales to store CO_2 in the long-term. This chapter has been published in ***Chemical Geology*** by **Elsevier**, in **2022**, as a technical paper.

Fatah, A.; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. Geochemical Modelling of CO_2 Interactions with Shale: Kinetics of Mineral Dissolution and Precipitation on Geological Time Scales. Chemical Geology, 592, 120742 (**2022**).

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Received 17 August 2021, Revised 23 January 2022, Accepted 27 January 2022, Available online 1 February 2022.

Abstract: The research on Carbon Capture and Storage (CCS) has become fruitful as energy-intensive industries are working towards transitioning to low carbon energy industry. Shale gas reservoirs have been recently considered as suitable geological targets for carbon dioxide (CO_2) storage. However, due to the high reactivity of shales to CO_2, the mineralogical changes after CO_2/brine/shale interactions play a decisive role in defining the sealing properties of shales at geological time scales. Up to date, this issue is rarely investigated; therefore, in this study, a simplified 1-D reactive transport model was constructed based on the properties obtained from Eagle Ford and Mancos shales. PHREEQC software was utilized to simulate equilibrium and kinetic behavior and evaluate the alterations in minerals at 177 atm and 70° C. The equilibrium model indicated that calcite and clay minerals dissolved in CO_2-saturated brine, while quartz grains precipitated, due to the formation of carbonic acid. This behavior confirmed the high reactivity of shales to the injection of CO_2-saturated brines. The kinetic model indicated that the geological time scale for CO_2/brine/shale interaction can be divided into three phases. Primary minerals alterations occurred during the first 10 years, however, the main alteration in mineralogy occurred between 10 and 100 years, whereas the reactants continued to dissolve in low portions until the equilibrium state was reached beyond 100 years. The model showed that carbonate and clay minerals dissolved during the CO_2/brine/shale interaction, which could provide the potential for mineral trapping as an effective sealing mechanism in the middle phases of the storage lifetime in shales, confirming the high potential of shales for CO_2 containment. The main observations and conclusions obtained from this work can be easily extrapolated to other shale formations with similar mineral compositions.

Keywords: Geological storage, PHREEQC, Shale, Mineralogy, Geochemical modelling

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CHAPTER 8

CONCLUSION AND RECOMMENDATION

8.1 Conclusion

The innovative technology of carbon capture and storage is a reliable method in reducing the impact of greenhouse gas emissions into the atmosphere, assisting in the transition to low-carbon energy. Shale formations hold a promising potential to utilize CCS projects due to their wide availability and high CO_2 adsorption capacity. However, the associated alterations in shale properties caused by CO_2/shale interaction play key roles in the efficiency and the successful application of CO_2 geological sequestration shales. This thesis investigated the alteration in some of the major physical and chemical properties of shales after CO_2 treatment and evaluated the impact on CO_2 storage capacity. Different types of shale samples were treated with CO_2 at various durations, pressures and temperatures.

This thesis evaluated the alterations in mineral composition of shales after CO_2 treatment and defined the relationship between the shale mineralogy and the changes in pore structural system, surface structure, and functional groups. This thesis also provided new insights on the alteration of water-wettability, shale/water contact angles and surface tension after CO_2 treatment, and the possible implications on sealing integrity and capillary breakthrough. Moreover, this thesis advanced the understanding of the nature of the long-term geochemical kinetics of CO_2/brine/shale interactions, and the impact on mineral dissolution/precipitation at geological time scales for CO_2 storage. A simplified one-dimensional reactive transport model was built using PHREEQC-interactive software, in which both equilibrium and kinetic models were constructed to simulate CO_2/brine/shale interactions. Generally, the finding of this thesis enhanced the knowledge of the impact of CO_2/shale interaction on shale properties and provided a better understanding of the feasibility of sub-surface CO_2 storage in shales. The main conclusions and contributions of this thesis are as follow:

1. The mineral composition has an important role to define the changes in shales properties. Clay and carbonate contents for all shale samples (Eagle Ford, Mancos, and Wolfcamp) were reduced by an average of 15% and 27% respectively after 30 days of $SCCO_2$ treatment, which is related to the ability of $SCCO_2$ to extract and dissolve clay and carbonate minerals in shales. This behavior promoted the release of H^+ ions during CO_2/shale interactions and led to altering the surface morphology and surface structure accordingly. On the other hand, quartz contents increased after the treatment by an average of 37%, due to the production of quartz minerals as byproducts from the dissolution of Illite, Kaolinite and K-feldspar minerals.

2. Shales with high contents of clay minerals such as Eagle Ford were more affected by $SCCO_2$ treatment compared to shales that were dominated by quartz minerals such as Mancos. Thin section and histogram profiles analysis revealed that non-clay contents increased by 9.51% for Eagle Ford samples, while an increase of 6.3% was reported for Mancos samples. This is related to the possible effect of clay-swelling that may reduce the CO_2 adsorption capacity in clay-rich shales in the long term, which could also affect the sealing integrity.

3. The alteration in surface chemistry and functional groups proved the changes in shale mineralogy and assisted in evaluating the adsorption capacity and storage potential of shales. Aromatics hydrocarbons had minor changes compared to aliphatic hydrocarbons, due to the higher extraction behavior of aliphatic contents by $SCCO_2$. Moreover, the contents of oxygen-containing groups increased in Eagle Ford and Mancos samples by an average of 13.46% after $SCCO_2$ treatment, which proved the high adsorption capacity of CO_2 in shales.

4. The impact of $SCCO_2$ treatment pressure on the properties of clay-rich shales has been investigated. Increasing the treatment pressure to 24MPa resulted in reducing the clay and carbonate contents for Eagle Ford sample by 25% and 57% respectively. This behavior led to a significant increase in the contents of aromatic hydrocarbons (32%) and oxygen-containing groups (20%), while a minor increase was reported in the aliphatic hydrocarbons (3%).

5. The changes in the pore structural system were mainly caused by the adsorption-induced expansion by $SCCO_2$ on the shale surface. The histogram profiles of the SEM images revealed a reduction in the macro-pore volume by 23% in Eagle Ford sample after $SCCO_2$ treatment, which resulted in narrowing the pores between the grains. While the macro-pore volume of Mancos samples increased by 13% after the treatment and led to the development of micro-cracks on the shale surface. This behavior can provide the potential for creating new pores in the shale matrix.

6. Evaluating the alterations in the specific surface area and fractal dimensions helped determine the adsorption capacity of shales. The findings reported that the fractal dimensions and the specific surface area had a positive linear correlation. The specific surface area of Eagle Ford shale was reduced by 35.46% after the $SCCO_2$ treatment, which reduced the surface roughness and complexity. On the other hand, the specific surface area was increased by 27.4% in Mancos shale, leading to increasing the surface roughness and complexity.

7. Understanding the behavior of fractal geometry together with the pore structure parameters is beneficial for understanding gas flow in shales. The high surface fractal dimension is favorable for gas adsorption, therefore, the adsorption capacity of clay-rich shale may reduce in the long-term during ESGR and CO_2 storage applications, whereas quartz-rich shale can provide better fluid transportation.

8. The alteration in the shale/water contact angles and surface wettability has been investigated for different types of shales. The results reported that the mineral composition had a direct influence on the wetting behavior after $SCCO_2$ treatment. Clay-rich shales such as Eagle Ford and Wolfcamp displayed a possible turn in wetting behavior to CO_2-wet with extending treatment time and increasing the treatment pressure and temperature, which may reduce the sealing integrity in the long term. Conversely, quartz-rich shales such as Mancos, remained strongly hydrophilic (water-wet) after various $SCCO_2$ treatment conditions, which suggested better sealing integrity and higher CO_2 storage potential.

9. A simplified one-dimensional reactive transport model was constructed using PHREEQC-interactive software, to simulate the CO_2/brine/shale interaction at

geological time scales. Both equilibrium and kinetic models had revealed that the geochemical interactions caused minerals dissolution and precipitation, which confirmed the high reactivity of shales to the injection of CO_2.

10. The main changes in dissolution and precipitation of minerals occurred in the middle phase of CO_2 storage duration (between 10-100 years). The kinetic model indicated that carbonate and clay minerals can be significantly dissolved in the presence of CO_2, and enhance the mineral trapping as an effective sealing mechanism of CO_2. This outcome is confirming the high feasibility of CO_2 sequestration applications in shales.

8.2 Source of Error

In this research, every reasonable effort has been made to reduce the experimental and simulation errors, but some errors were not plausible to avoid (given the conditions of the experiment/simulation). This section briefly identifies the possible source of error and describes the impacts on the results.

1. **Samples preparation**: The bulk sample was crushed and ground into powders, and then samples were sieved into different sizes, which may develop a level of uncertainty to the results. However, the samples were prepared following the common practice to avoid major changes in the composition.

2. **Supercritical CO_2 treatment experiment**: Static reactor system was used for $SCCO_2$ treatment, however, the reactor setup requires adding water to the vessel to sustain its internal temperature during the experiment. This may allow certain portions of $SCCO_2$ to dissolve in the vapor and affect the shale structure. Therefore, the shale samples were placed on the upper shelf ensuring not in direct contact with water.

3. **Analytical analysis:** Due to the shale heterogeneity, the XRD analysis may not accurately detect the small changes in mineralogy, causing a 3-5% variation in results. Therefore, two XRD runs were performed on each sample. To minimize the uncertainty of the SEM analysis, several spots were marked on the sample surface

and the images were captured on these spots before and after the treatment. To reduce the errors during FTIR analysis, sample proportions were maintained as consistently as possible and tested more than three times.

4. **Contact angle measurement**: The sample surface was ground and polished with 1500 silicon carbide grit, and then cleaned with ethanol to remove any possible contamination after grinding. Moreover, the measurements were taken from different spots scattered on the sample surface, and the average value was reported. The standard deviation was calculated to ensure minimum experimental errors.

5. **Simulation Model:** Some limitations of the geochemical model can cause uncertainties should it be implemented on large-scale reservoirs. The model considered ideal mineral phases, pure CO_2 injection and simplified the calculations of the surface area in natural systems. These assumptions are not valid on the reservoir scale, which requires additional investigations through sensitivity analysis.

8.3 Upscaling Challenges of CCS

As stated in the Paris Agreement, CCS could account for one third of the emissions reduction required to meet the global net zero target by 2050. However, the assessment of global CCS prospects is relatively high-level and sets broad boundaries around parameters and projections. The challenges related to technical feasibility, economic viability and environmental impact has been well-addressed in the literature. However, policy regulations and policymakers need to work together with scientists and industrial companies to include strategies for CCS deployment in their energy and climate plans. The longer these regulations are delayed, the less likely that CCS will reach the deployment rates required and, ultimately, that long-term climate goals will be met.

Scientists and researchers have achieved considerable accomplishments in evaluating the potential of carbon deployment, and provided some insights on upscaling the technology. As so, several regions are currently on the mission of scaling up the CCS market to deliver net-zero emissions. In 2020, there were 51 large-scale CCS facilities worldwide at different stages; 19 in operation, 4 under construction, 10 in advanced development and 18 in early development [150]. However, the challenge in scaling up CCS remain a big concern for many countries as many factors are involved that can add uncertainties to the commercial applications of CCS and carbon deployment. Below are some of the technical and non-technical challenges for future CCS upscaling:

8.3.1 Technical challenges

1. The geochemical interactions between brine/rock/CO_2 is well-understood through experimental and small-scale simulation models. However, to ensure successful and effective CO_2 sequestration that can have an optimum positive impact on the environment requires accurate evaluation of many factors including but not limited to: 1) Geophysical Imaging, 2) Reservoir Sealing/ Trapping, 3) CO_2 subsurface hosting, 4) CO_2 Injection, and 5) Regular Monitoring. Also, sensitivity analyses for the involved factors (i.e. pressure, temperature, mineralogy, wettability and pore structure system) are required to accurately estimate CO_2 storage capacity, and ensure the efficiency and safety of subsurface CO_2 containment.

2. Mineralogy and heterogeneity of shales could cause a high uncertainty applying CCS field-scale projects, due to the high complexity of field scaling compared to laboratory set-ups. Therefore, additional subsurface data such as the formation thickness, the physical properties (porosity and permeability), the actual specific area, and the matrix heterogeneity are required for accurate estimation of heterogeneity index and mineral alterations.

3. The evaluation of geophysical properties is also a challenge for upscaling CCS technology. Accurate identification of existing faults and fractures, can provide early detection of potential CO_2 leakage sites. Additionally, the presence of other gases (these gases are injected as cushion gases to reduce the cost of CO_2 injection) such as CH_4, N_2 or H_2 can impact the CO_2 leakage assessment and trapping mechanisms. Therefore, the impacts of cushion gases on formation pressure maintenance and CO_2 leakage deserve further assessment. Further, the wettability

alteration of shales be assessed at the presence of gas mixers, and determine the carbon leakage potential through diffusion process in the phase of brine. This assessment will help to evaluate the integrity of seals and trapping.

4. The mobility of CO_2 during injection also should be accurately evaluated through the assessment of relative permeability hysteresis. This evaluation can help predicting future CO_2 migration pathways. Based on each site, the development of optimal injection strategies (i.e. huff-n-puff, WAG), can reduce uncertainty that comes with history matching.

5. CO_2 adsorption and desorption at in-situ conditions should be further assessed as well, to determine the mechanical stability and dispersion or rocks, and the associated alterations in mechanical properties.

8.3.2 Non-technical challenges

1. According to the Global CCS Institute [150], economic support for carbon price is a pre-requisite to ensure economic deployment of carbon. It was suggested that the minimum carbon price of US$90/tonne for most industrial applications can make upscaling of CCS viable. For difficult-to-decarbonize sectors like steel it’s up to US$120/tonne; and for cement can be up to $200/tonne.

2. The transportation of CO_2 should be enabled as a commercial or regulated activity as part of gas market legislation.

3. Policy regulations can should also ease the funding of CCS projects, and encourage economists and industrial companies to include strategies for CCS deployment in their Energy and Climate Plans.

8.4 Recommendations for future work

The outcomes of this study provide a wide understanding of the impact of CO_2/shale interaction on shale properties and evaluated the implications on CO_2 storage capacity.

However, due to some limitations of this study, the following further studies are recommended in future work:

6. The impact of CO_2 treatment on wetting behavior is an open research area, due to the complexity of the CO_2/brine/shale wettability system. It is recommended to evaluate the alteration in CO_2 wettability (two-phase fluids), and evaluate the impact on other properties such as fluid flow, capillary pressure, and relative permeability.

7. The wettability alteration during CO_2 injection is not well investigated at reservoir conditions. Factors such as heterogeneity, capillary forces, and the maturity of organic matter content could have an impact on the wetting behavior, sealing integrity and CO_2 capillary leakage, which deserves more investigation.

8. The mineralization process needs further studies to understand the long-term mineral trapping mechanism. It is recommended to evaluate the mineral control of shales at a large reservoir scale by performing a fully quantitative analysis. Carbonate minerals, in particular, can precipitate as silicates and increase the storage capacity in the presence of CO_2. Therefore, it is recommended to study the mechanism of minerals carbonation during CO_2 injection.

9. Clay swelling can occur due to the affinity of clays to interact with CO_2 in in-situ conditions. It is recommended to investigate the swelling mechanism in shales to understand the chemical kinetics and CO_2 adsorption behavior and evaluate its impact on the overall storage capacity.

10. The variations in micropores structure after CO_2 treatment needs further investigation for better classification of the alteration in the pore structure system. This can be evaluated through the applications of nuclear magnetic resonance (NMR) and low-pressure CO_2 adsorption techniques.

11. In this thesis, a 1-D reactive transport model was constructed to simulate the CO_2/brine/shale interactions in the long term. It is recommended to perform 2-D and/or 3-D simulation models that can help minimize the level of uncertainty in the geochemical modeling. Further studies are required to fully capture the geochemical

process associated with CO_2 injection at field scale, in terms of evaluating storage potential, trapping mechanism and CO_2 adsorption capacity, which can provide a practical guideline for CO_2 sequestration applications in shales.

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APPENDIX I

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1. **Fatah, A.**; Bennour, Z.; Ben Mahmud, H.; Gholami, R.; Hossain, M.M. A Review on the Influence of CO_2/Shale Interaction on Shale Properties: Implications of CCS in Shales. Energies 2020, 13, 3200 (**2020**).

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APPENDIX II

ATTRIBUTION OF AUTHORSHIP

- **CHAPTER 2: Fatah, A.**; Bennour, Z.; Ben Mahmud, H.; Gholami, R.; Hossain, M.M. A Review on the Influence of CO_2/Shale Interaction on Shale Properties: Implications of CCS in Shales. Energies, 13, 3200 (**2020**).

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	Conception and Design	Acquisition of Data and Method	Data Conditioning and Manipulation	Analysis and Statistical Method	Interpretation and Discussion	Final Approval
A/P Hisham Khaled Ben Mahmud	√				√	√
I acknowledge that these represent my contribution to the above research output. Signature:						

	Conception and Design	Acquisition of Data and Method	Data Conditioning and Manipulation	Analysis and Statistical Method	Interpretation and Discussion	Final Approval
Dr. Ziad Bennour	√				√	√
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Prof. Raoof Gholami	√				√	√
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- **Chapter 3: Fatah, A.**; Ben Mahmud, H.; Bennour, Z.; Hossain, M.M; Gholami, R. Effect of Supercritical CO_2 Treatment on Physical Properties and Functional Groups of Shales. FUEL, 303, 121310 (**2021**).

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- **CHAPTER 7**: **Fatah, A.**; Ben Mahmud, H.; Bennour, Z.; Gholami, R.; Hossain, M.M. Geochemical Modelling of CO_2 Interactions with Shale: Kinetics of Mineral Dissolution and Precipitation on Geological Time Scales. Chemical Geology, 592, 120742 (**2022**).

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APPENDIX III

LIST OF CHEMICAL REACTIONS

Below table provides a comprehensive list of chemical reactions induces by CO_2 injection with various minerals [151]. Throughout this thesis, the author chose to include related reactions in the discussion based on the presented mineralogy of the shale samples (i.e. reactions of Illite, Kaolinite, Calcite, Dolomite and Feldspar).

Comprehensive list of chemical reactions induced by CO_2 injection [151] (S: solid phase, g: gas phase, l: liquid phase)

Reaction	Type and Description/ Primary Mineral
$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^{-} \leftrightarrow 2H^+ + CO_3^{2-}$	CO_2 dissolution in water
$OH^- = H_2O + H^+$	Release of OH^- ions
Calcite ($CaCO_3$) + H^+ = Ca^{++} + HCO_3^-	Calcite dissolution
Dolomite ($CaMg(CO_3)_2$) + $2H^+ = Ca^{++} + Mg^{++} + 2HCO\text{-}_3$	Dolomite dissolution
Illite ($K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$) + $8H^+ = 5H_2O + 0.6K^+ + 0.25Mg^{++} + 2.3Al^{++} + 3.5SiO_2(aq)$	Illite dissolution
K-feldspar ($KAlSi_3O_8$) + $4H^+ = 2H_2O + 0.6K^+ + Al^{++} + 3SiO_2(aq)$	K-feldspar dissolution
$Al_2Si_2O_5(OH)_4$ (Kaolinite) + $6H^+ \leftrightarrow 2Al^{3+} + 2SiO_2$ (Quartz) + $5H_2O$	Kaolinite dissolution
$SiO_2(s) + 2H_2O \rightleftharpoons H_4SiO_4 \rightleftharpoons H^+ + H_3SiO_4^- \rightleftharpoons H^+ + H_2SiO_4^{2-}$	Silicates / Quartz Solubility
$CaAl_2Si_2O_8(s) + CO_2(g) + 2H_2O(l) \rightarrow CaCO_3(s) + Al_2Si_2O_5(OH)_4(s)$	Arnorthite dissolution/ produce Calcite and kaolinite)
$Ca_{0.6}Na_{0.4}Al_{1.6}Si_{2.4}O_8 + 5.4H^+(l) + CO_2(l) \rightarrow 0.6Ca^{2+}(l) + HCO^{3-}(l) + 2.2H_2O(l) + 0.4Na^+(l) + 1.6Al^{3+} + 2.4SiO_2(l)$	Labradorite dissolution
$NaAlSi_3O_8(s) + CO_2(g) + H_2O(l) \rightarrow NaAl(CO_3)(OH)_2(s) + 3SiO_2(s)$	Albite dissolution
Glauconite $+14H^+(aq) \rightarrow 1.5\ K^+(aq) + 2.5Fe^{3+}(aq) + 0.5Fe^{2+}(aq) + Mg^{2+}(aq) + 1.0Al^{3+}(aq) + 7.5SiO_2(aq) + 9H_2O(l)$	Glauconite
annite $+3CO_2 \rightleftharpoons$ 3siderite + K-feldspar	Annite dissolution/ produce Siderite and K-feldspar
Chlorite $+20H^+(aq) \rightarrow 5Fe^{2+}(aq) + 5\ Mg^{2+}(aq) + 4Al(OH)_3(aq) + 6H_4SiO_4(aq)$	Chlorite dissolution/ produce Aluminium hydroxide
$2\ KAl_2(AlSi_3O_{10})(OH)_2$ (muscovite) + $3H_2O(I) + 2H^+\ (aq) \rightarrow 3Al_2Si_2O_5(OH)_4$ (kaolinite) + $2\ K^+\ (aq)$	Muscovite