

CRANFIELD UNIVERSITY

MOHAMMED DAHIRU AMINU

CARBON DIOXIDE STORAGE IN THE UK SOUTHERN NORTH SEA:
EXPERIMENTAL AND NUMERICAL ANALYSIS

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Ph.D. in ENERGY (CARBON CAPTURE AND STORAGE)

DEGREE OF DOCTOR OF PHILOSOPHY

Academic Year: 2015 – 2018

Supervisor: Professor Vasilije Manovic
Associate Supervisor: Professor Athanasios Kolios
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Summary

This thesis contributes to the significant portfolio of research on carbon capture and storage (CCS) in general, and the potential for CO₂ storage with impurities within the UK Southern North Sea (UKSNS) to meet the global greenhouse gas emission reduction targets. First, this thesis extensively reviews the current developments in carbon dioxide storage, highlighting major options for CO₂ sequestration, storage site evaluation criteria, behaviour of CO₂ in the reservoir, methodologies for estimating storage capacity, appraisal of the major storage projects, and a projection of the future outlook for CO₂ storage. The review draws attention to the fact that although a high-quality knowledge base has been developed through CCS research, the main hinderance to CO₂ storage deployment is associated with public acceptability of the technology. Second, this thesis involves laboratory experimental investigation of the effect of impure CO₂ on reservoir grain size distributions and permeability using rock samples from the Bunter saline aquifer. The thesis shows that the presence of impurities in the CO₂ stream can affect the grain size distribution and fluid transmissivity. Third, this thesis uses numerical modelling to evaluate the effect of impure CO₂ on reservoir performance with a case study from the Bunter saline aquifer. The results show that depending on the impurities present in the CO₂ stream, the limits of stability during storage operations in saline aquifer varies, however, the variation does not affect reservoir performance negatively during long-term injection and storage.

Dedication

For my great-uncle, Bappa Tijjani, who, without doubt, is a rare breed of humanity; and for my parents, who sacrificed the joys of their own lives so that my siblings and I could be happy—nothing in my life would have been possible without their strife.

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This work used samples and data from the ULTimateCO₂ (Understanding the Long-Term fate of geologically stored CO₂) project funded from the European Union's Seventh Framework Programme for research, technological development, and demonstration under grant agreement no. 281196. I gratefully acknowledge the support of the British Geological Survey (BGS) in Nottingham, UK, where the experiments were conducted. Dr. Christopher Rochelle and Mr. Keith Bateman of the BGS Hydrothermal and Hydrates Laboratories are specially acknowledged for their assistance throughout the period of the research.

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1 INTRODUCTION

1.1 Background of the study

1.1.1 Global warming and greenhouse gases

Throughout the long history of the earth, it has warmed and cooled repeatedly. Its climate changes when the earth receives more or less sunlight because of sudden shifts in its orbit, as the surface or atmosphere changes, or when energy from the sun fluctuates [1]. But in relatively recent times, through industrialisation, human activity became a major force that influences the earth's climate [1,2].

In 1895, an Irish physicist, John Tyndall, did the first major scientific demonstration to improve the ideas of the Genevan and Savoyan scientist, Horace-Bénédict de Saussure, and the French mathematician, Jean-Baptiste Joseph Fourier, that surface temperature can be influenced by polyatomic gases in the atmosphere [3,4]. Four years later, Tyndall further suggested, that changes in the same gases could affect the surface temperature of the earth. However, in 1896, Swedish scientist, Svante Arrhenius, used hand calculations to show that doubling of the atmospheric CO₂ might increase the surface temperature of the earth by 3 or more °C depending on latitude [4,5]. In his popular science book, *Worlds in the Making*, published in 1907, Arrhenius showed a clear link between climate change and combustion of coal, wherein he noted that “any doubling of the percentage of carbon dioxide in the air would raise the temperature of the earth's surface by 4°C.” [4,6]. After Arrhenius' work, there have been various changes in ideas about global warming, some of which include arguments that it might be beneficial to mankind. The English scientist, Guy Callendar, advocated the theory that anthropogenic global warming was potentially

significant, despite extensive scepticism [4,7]. In the last several decades however, a consensus was reached that global warming portends a significant threat for humanity due to its large, potentially negative effects [4,8].

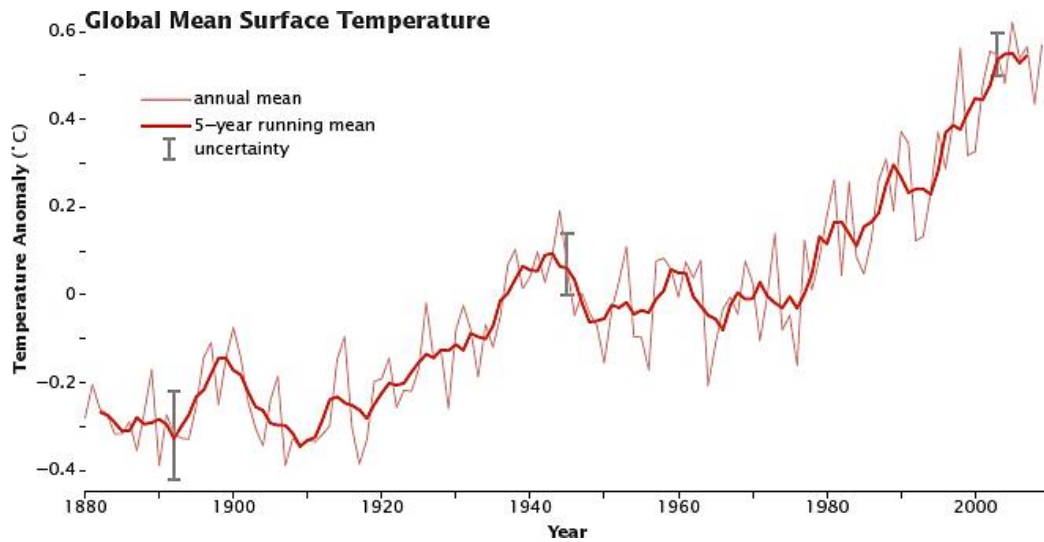


Figure 1-1: Global mean surface temperature at the beginning and end of the 21st century [1].

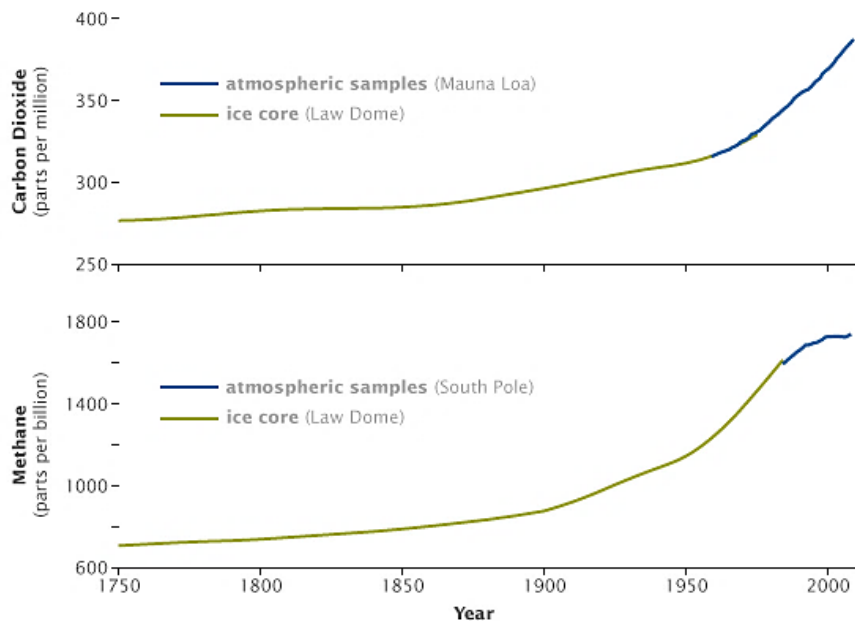


Figure 1-2: Atmospheric CO₂ and CH₄ concentrations [1].

Figure 1-1 shows the global mean surface temperature at the beginning and end of the 21st century, and **Figure 1-2** shows increase in atmospheric CO₂ and CH₄ concentrations taken from specified locations of the earth for period coinciding with the start of the Industrial Revolution in about 1750. Between 1906 and 2017, the global average surface temperature of the earth rose ~ 0.6 to 1.05 °C [1,9], and the rate of temperature increase has almost doubled in the last 50 years [1], nonetheless temperatures are predicted to rise even further in the next several decades unless climate change mitigation strategies are put in place.

There are basically five greenhouse gases, which are CO₂, CH₄, N₂O, O₃ and water vapour. Although, these gases are naturally occurring in the atmosphere, their emissions from human activities have caused significant levels to rise, which impacts global warming. Human activities alone, such as burning of fossil fuels, farming and forestry, cement manufacturing and aerosols [10], have caused an immense rise in the atmospheric

CO₂ levels from 280 parts per million to 400 parts per million in the last one and half century [11], contributing the most effect on net increase in global warming [12]. In addition, of all greenhouse gases, CO₂ gets the most attention because climate change is primarily a problem of CO₂ [13], since its atmospheric lifetime is between 50-200 years [14]. Therefore, this means that it takes at least 50 years before CO₂ becomes part of another chemical reaction or is absorbed by a sink [14].

Figure 1-3 shows annual GHGs emissions by sector, highlighting the most important GHGs as CO₂, CH₄, N₂O and water vapour. It must be noted however, that while all these gases occur naturally in the atmosphere, their emissions from human activities has caused significant levels to rise; which impacts global warming.

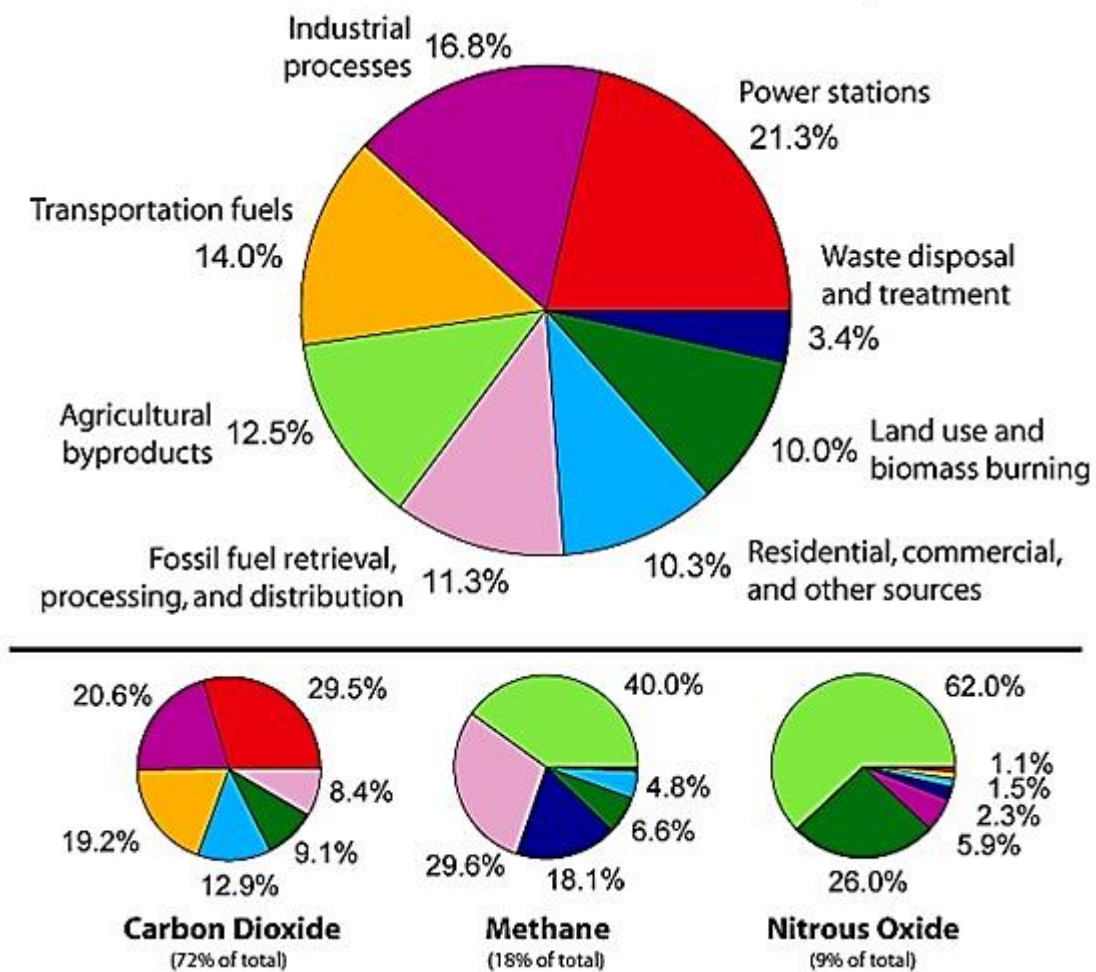


Figure 1-3: Greenhouse gas emissions by sector [15]. Top panel shows the sum over all man-made greenhouse gas, weighted by global warming potential for the next one century. Lower panels show comparable information for each of these primary greenhouse gases, with same colouring as used in the top chart.

1.1.2 Carbon capture and storage technology

To drastically reduce the overall CO₂ emissions by 90% or more, Carbon Capture and Storage (CCS) has been proposed as a global warming mitigation technology [16]. CCS is the process of capturing CO₂ from large point sources such as power plants, carbon-intensive industries (e.g. steel, cement, lime, etc.), and refineries, transporting it to storage

sites via pipelines, ship, road tanker, and thereafter disposing it in geological formations underground [16,17]. Since the world's current energy producing technologies would not be changed dramatically within the next several decades due to growing energy demand relative to technology advancement, CCS is a 'bridge' technology in the transition between fossil fuels and renewable and clean energy technologies [17,18].

The CCS chain consists of three main stages: capture, transport, and storage. In the capture stage, three basic routes are available: (i) pre-combustion; (ii) post-combustion; and (iii) oxyfuel combustion [19]. In the pre-combustion processes, solid, liquid or gaseous fuel is converted into a mixture of hydrogen and CO₂ through processes such as CO₂ gasification and reforming, and in that way carbon separation from the fuel is enabled before it is used for heat/electricity generation. In the post-combustion scenario, CO₂ is captured from the flue gas, i.e. after combustion process, using suitable solvents or sorbents, or other techniques such as gas-selective membranes. In the oxyfuel combustion scenario, oxygen is separated from air before combustion, and fuel is burned in oxygen which is diluted in a recycled flue-gas, producing high-concentrated CO₂ stream ready for purification, compression, transport and storage [16]. After separation and compression, CO₂ is transported by pipelines, ships, or road tanker, to points where it is being stored safely in geological formations underground. These underground formations are basically saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, and basaltic rocks. Other 'niche' applications may include hydrate storage of CO₂ within the subsurface environment and use of CO₂ within enhanced geothermal systems.

After publication of the IPCC special report on CCS in 2005 [16], there have been significant research and developments in all stages of the CCS process, with international developments in the deployment of CCS becoming increasingly massive. In 2015, the

Massachusetts Institute of Technology listed some of the major CCS projects around the world including operational, non-operational, and planned projects [20]. It is important to state, however, that given that CCS is expected to account for the mitigation of approximately 14 to 20% of total anthropogenic CO₂ emissions, by the mid-21st century, the CCS industry may have to be larger by a factor of 2-4 in volume terms than the current global oil industry [21]. This is a very challenging task since it implies that the world has just several decades to make an industry that is larger than one which has taken approximately a century to develop [21].

1.2 Motivation for the research

The dissolution of CO₂ in saline aquifers lowers the pH of formation water which causes geochemical reactions between CO₂-brine-rock. These reactions can affect the physical quality of the reservoir by influencing rock properties such as porosity and permeability. In the presence of impurities which are typically contained in the CO₂ stream, the chemical reactivity of the saline aquifers and the solid phases as well as the physical behaviour of the CO₂ plume [22] can be further affected. Additionally, the impurities could affect the reservoir storage capacity [23] and storage cost [24]. It is therefore critical to understand to what extent impure CO₂ can influence the physicochemical behaviour of the CO₂ phase in the reservoir. Since impure CO₂ alters the reservoir rock properties such as their storativity and transmissivity, it is also important to evaluate the effect of impure CO₂ on injectivity and storage through the analysis of key reservoir performance indices in order to assess to what extent the boundaries in the CO₂ phase diagram could be affected.

1.3 Project description

1.3.1 Aim

The main aim of this research is to evaluate the carbon dioxide storage potential in the UK Southern North Sea (Bunter Sandstone formation) in the presence of impurities in the CO₂ stream, using experimental and numerical methodologies.

1.3.2 Objectives

Based on the stated aim, research objectives are to:

1.3.2.1 Extended literature review

- Critically evaluate the current developments in carbon dioxide storage highlighting major options for CO₂ sequestration, storage site evaluation criteria, behaviour of CO₂ in the reservoir, methodologies for estimating CO₂ storage capacity, appraisal of the world's major CO₂ storage projects, and a projection of the future outlook for CO₂ storage;

1.3.2.2 Experimental

- Carry out CO₂-brine-rock reaction experiments using rock samples of the Bunter Sandstone formation (under near in-situ pressure and elevated temperature conditions) to assess the effect of CO₂ stream impurities on reservoir grain size distributions and permeability as an indication of variation in physical reservoir quality;

1.3.2.3 Numerical modelling

- Conduct modelling to determine the effect of pure and impure CO₂ on the reservoir performance in a sandstone saline aquifer using both laboratory experimental data and realistic field data to construct a simplified model.

1.4 Publications

- Aminu MD, Nabavi SA, Rochelle CA, Manovic V. A review of developments in carbon dioxide storage. *Applied Energy* 2017;208C:1389–419.
- Aminu MD, Nabavi, SA, Manovic, V. CO₂-brine-rock interactions: The effect of impurities on grain size distribution and reservoir permeability. *International Journal of Greenhouse Gas Control* 2018;78C:168–76.

1.5 Thesis structure

Chapter 1 gives a brief introduction on the topic and rationale behind the study. It also gives a brief overview of the aims and objectives of the thesis and how each of it will be addressed.

Chapter 2 elaborates on key concepts of the study. It reviews the current state of development in carbon dioxide storage, highlighting options for CO₂ sequestration, storage site selection criteria, behaviour of CO₂ in the reservoir, the major CO₂ storage projects in the world, and a future outlook for CO₂ storage. It is presented in a paper format titled: “A review of developments in carbon dioxide storage”.

Chapter 3 presents and discusses the general grain morphologic changes as it affects the reservoir rock from Bunter Sandstone formation in a paper format titled: “CO₂-brine-rock

interactions: The effect of impurities on grain size distribution and reservoir permeability”.

Chapter 4 presents the relationship between changes in grain size distribution and permeability and reservoir performance during CO₂ storage with impurities in the Bunter Sandstone formation, in a paper format titled: “A modelling study to evaluate the effect of impure CO₂ on reservoir performance in a sandstone saline aquifer”.

Chapter 5 presents a general discussion and implementation of the work.

Chapter 6 highlights key conclusions from the study and recommendations for future research.

For the chapters written in paper formats, it may involve some extent of repetition of the key concepts presented in previous chapters especially in the introductory sections.

2 A REVIEW OF DEVELOPMENTS IN CARBON DIOXIDE STORAGE

Abstract

Carbon capture and storage (CCS) has been identified as an urgent, strategic and essential approach to reduce anthropogenic CO₂ emissions, and mitigate the severe consequences of climate change. CO₂ storage is the last step in the CCS chain and can be implemented mainly through oceanic and underground geological sequestration, and mineral carbonation. This review paper aims to provide state-of-the-art developments in CO₂ storage. The review initially discusses the potential options for CO₂ storage by highlighting the present status, current challenges and uncertainties associated with further deployment of established approaches (such as storage in saline aquifers and depleted oil and gas reservoirs) and feasibility demonstration of relatively newer storage concepts (such as hydrate storage and CO₂-based enhanced geothermal systems). The second part of the review outlined the critical criteria that are necessary for storage site selection, including geological, geothermal, geohazards, hydrodynamic, basin maturity, and economic, societal and environmental factors. In the third section, the focus was on identification of CO₂ behaviour within the reservoir during and after injection, namely injection-induced seismicity, potential leakage pathways, and long-term containment complexities associated with CO₂-brine-rock interaction. In addition, a detailed review on storage capacity estimation methods based on different geological media and trapping mechanisms was provided. Finally, an overview of major CO₂ storage projects, including their overall outcomes, were outlined. This review indicates that although CO₂ storage is a technically proven strategy, the discussed challenges need to be addressed to accelerate the deployment of the technology. In addition, beside the necessity of techno-

economic aspects, public acceptance of CO₂ storage plays a central role in technology deployment, and the current ethical mechanisms need to be further improved.

Abbreviations

ACTL	Alberta Carbon Trunk Line
API	American Petroleum Institute
ARI	Advanced Resources International
CAS	Chinese Academy of Sciences
CBM	Coal Bed Methane
CCS	Carbon Capture and Storage
CCSU	Carbon Capture Storage and Utilisation
CO2CRC	The Cooperative Research Centre for Greenhouse Gas Technologies
CSLF	The Carbon Sequestration Leadership Forum
DOE	Department of Energy
DoReMi	Derivative of Refractive Microtremor
ECBM	Enhanced Coal Bed Methane recovery
EGS	Enhanced Geothermal System
EOR	Enhanced Oil Recovery
EPRI	Electric Power Research Institute
FEP	Features, Events and Processes
GHG	Greenhouse Gas
HCPV	Hydrocarbon Pore Volume
IDLH	Immediately Dangerous to Life or Health
IMO	International Maritime Organisation
InSAR	Interferometric Synthetic Aperture Radar
IPCC	Intergovernmental Panel on Climate Change
LNG	Liquefied Natural Gas
MIT	Massachusetts Institute of Technology
MoU	Memorandum of Understanding
MRCSP	Midwest Regional Carbon Sequestration Partnership
MVA	Monitoring, Verification and Accounting
NETL	National Energy Technology Laboratory
OBPP	Otway Basin Pilot Project
OGCM	Ocean General Circulation Model
OGIP	Original Gas in Place
OOIP	Original Oil in Place
OSPAR	Oslo Paris
PCOR	Plains CO ₂ Reduction Partnership
PFTs	Perfluorocarbon tracer compounds
PTRC	Petroleum Technology Research Centre
SECARB	Southeast Regional Carbon Sequestration Partnership
SEM	Scanning Electron Microscope
SSEB	Southern States Energy Board
SWP	The Southwest Regional Partnership
TRL	Technology Readiness Level
UKCCSRC	UK Carbon Capture and Storage Research Centre

US-DOE	United States Department of Energy
USGS	United States Geological Survey
VSP	Vertical Seismic Profile
XRD	X-Ray Diffraction

2.1 Introduction

The anthropogenic emissions of CO₂ and other greenhouse gases (GHGs) have been identified as the main contributor to global warming and climate change [25]. The atmospheric concentration of CO₂ has increased from 280 ppm, in the mid-1800s, to nearly 404 ppm in 2016, and caused almost 1 °C increase in mean earth temperature, from pre-industrial levels [26,27]. This temperature rise, only between 1901 and 2010, led to a 20 cm increase in global mean sea level [28]. It is recognised that the mean earth temperature rise from pre-industrial levels should be kept well below 2 °C by 2100 in order to mitigate severe events of climate change [16]. Accordingly, European Union and the G8 have targeted to reduce GHG emissions by at least 80% from the 1990 baseline by 2050 [29–31].

Power plants and energy-intensive industries are considered as the major CO₂ emitters, and are obligated to drastically cut their CO₂ emissions. The high carbon intensity of the power sector (42%) is attributed to the large share of coal-fired plants in the global electricity supply. In addition, the emergence of shale gas in North America has led to higher American exports of coal. Consequently, it caused a considerable reduction in coal price, which in turn led to a higher tendency for coal-based electricity production [32]. Hence, decarbonisation of power and industrial sectors is essential to meet emission reduction targets.

Carbon capture and storage (CCS) is considered as the key strategy for decarbonisation of the power and industrial sectors [33]. It is estimated that CCS alone can contribute almost 20% reduction in emissions by 2050, and the exclusion of CCS can cause up to 70% increase in global cost of achieving emission reduction targets [34]. Permanent sequestration of CO₂ is the

last step in the CCS chain and can be implemented using a variety of strategies, mainly mineral carbonation, oceanic, and underground geological storage including saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, and other geological media. The main characteristics of a feasible CO₂ storage option are net reduction in CO₂ emission, large storage capacity, long-term isolation of CO₂ (at least several hundred years), reasonable cost and energy penalty, and minimised environmental impact [35]. On the other hand, public acceptance/embracing is another key factor that can significantly affect the deployment of the technology [36].

There have been several reviews that discussed different aspects of CO₂ storage [37,38,47–56,39–46]; see **Table 2-1**. However, some aspects have not been covered yet or analysed in detail. Despite CO₂ storage being a technically proven technology, further deployment of the technology is delayed by some uncertainties and challenges associated with estimation of storage capacity, tracking verification and monitoring of CO₂ during and after injection, characterisation of potential injection-induced seismicity, standardisation of storage evaluation criteria, and effective ethic mechanisms. In addition, CO₂ storage is a fast-developing field and recent progress and development need to be reviewed and discussed.

Table 2-1: Summary of review studies on carbon dioxide storage.

Source	Review scope
Bai et al. [37]	Review on well integrity issues for CO ₂ storage and enhanced gas recovery highlighting mechanisms responsible for loss of well integrity, well integrity criteria, determination of well integrity for operational wells, and risk-based approaches for abandoned wells.
Abidoeye et al. [38]	Detailed review on geosequestration of CO ₂ in relation to two-phase flow in porous media highlighting aquifer storage capacity, sealing integrity of caprock, displacement of brine by supercritical CO ₂ , simultaneous flow of free and buoyant phases of CO ₂ , and various trapping mechanisms.
Bachu [39]	Review of CO ₂ storage efficiency in deep saline aquifers highlighting storage efficiency and capacity, factors that affect CO ₂ injection and plume evolution (such as boundary conditions, driving forces and fluid properties, displacement characteristics of CO ₂ -water systems in sedimentary rocks, and aquifer characteristics), storage efficiency coefficients for volumetric estimates of storage capacity, and pressure and time effects on storage efficiency.

- De Silva et al. [40] Review of geochemical aspects of CO₂ sequestration in deep saline aquifers highlighting solubility trapping (effective factors for trapping, and experimental and modelling studies), and mineral trapping (trapping in sandstones, reactions in potassium- and sodium-rich feldspars, and experimental and modelling studies).
- Boot-Handford et al. [41] CCS update highlighting capillary trapping and multiphase flow (pore-scale properties and natural analogues), regional assessment of storage capacity (definition of storage reservoirs and storage complexes, challenges to the concept of large-volume storage, and CO₂-EOR (enhanced oil recovery)).
- Burnside and Naylor [42] Review of CO₂/brine systems, highlighting estimates and measurements of relative permeability and residual saturation (experimental procedures and experimental biases).
- Carroll et al. [43] Review of environmental issues for sub-seabed geological storage of CO₂, highlighting physical data processes (natural CO₂ levels/concentrations and fluxes, shallow seabed geophysics and geology, CO₂ seepage and seabed sediment-water chemistry, reservoir storage chemistry and water-rock reactions).
- Godec et al. [44] Review of the status and global potential for CO₂-ECBM (enhanced coalbed methane) highlighting factors influencing CO₂ storage and enhanced gas recovery in coal seams, CO₂-ECBM storage trials in San Juan Basin, USA, and estimate of global CO₂ storage capacity in coal seams.

- Humez et al. [45] CO₂ intrusion in freshwater aquifers highlighting isotopic (C and O) methods as tracer tools for CO₂ presence, and potential application of ‘non-traditional’ isotopes of dissolved species to CO₂ storage.
- Tang et al. [46] Review of CO₂ sequestration projects and application in China highlighting major geosequestration options.
- Li et al. [47] Review of progress in CCS in the Chinese Academy of Sciences (CAS) highlighting identified major storage options and opportunities in China.
- Song and Zhang [48] Review of caprock sealing mechanisms in geological CO₂ storage highlighting various leakage paths (diffusion, capillarity and faults).
- Liu et al. [49] Review of CO₂-brine-caprock interactions and reactivity experiments with the Eau Claire Formation, Midwest USA region, highlighting observed mineral reactions from laboratory experiments and safety function of caprocks from insights in geochemical modelling work.
- Pires et al. [50] A brief introduction to CO₂ storage options.
- Zahid et al. [51] Review on present and future prospects for CO₂ geological storage highlighting major trapping mechanisms, capacity estimation of storage sites, monitoring techniques, and simulation tools used for storage projects.

- Zhang and Bachu [52] Review of integrity of existing wells highlighting in-situ conditions for geological storage, and determination of carbonation rates relevant to CO₂ storage through laboratory and field studies.
- Shukla et al. [53] Review of studies on CO₂ sequestration and caprock integrity highlighting major sequestration projects in operation, geosequestration systems, and CO₂ migration in reservoir formation rocks (CO₂-brine-rock interaction, and caprock integrity).
- Abu-Khader [54] Review of progress on CO₂ sequestration with a brief introduction to geological storage.
- White et al. [55] Review of CO₂ sequestration in coal with ECBM recovery highlighting monitoring and verification of geologically-sequestered CO₂ (lessons from underground storage of methane, pressure monitoring and methods, leak detection using soil gas measurements, chemical tracers, and reservoir simulators).
- Voormeij and Simandl [56] Technical review on geological, ocean, and mineral CO₂ sequestration, highlighting storage in oil and gas reservoirs, coal seams, deep ocean, salt caverns, and mineral carbonation.
-

2.2 Options for CO₂ sequestration

In the CCS framework, the potential options for CO₂ sequestration are underground geological storage, deep ocean storage, and mineral carbonation [16], in which underground geological storage itself comprises several options including saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, hydrate storage, and CO₂ within enhanced geothermal systems [57–59]. This section provides a comprehensive discussion on each storage strategy, and correspondingly, outlines the possible future studies that can advance the current understanding.

2.2.1 Underground geological CO₂ storage

Underground geological storage has been considered as the most viable sequestration approach. There are several factors that make geological storage the superior sequestration strategy, in comparison with carbonation and oceanic storage, including economic aspects, site accessibility (in the case of ocean and mineral sequestration), and associated concerns regarding the security of stored CO₂ and negative environmental impacts of mineralisation and ocean storage. There are several potential geological storage options **Figure 2-1** that will be comprehensively discussed in this section.

2.2.1.1 Saline aquifers

CO₂ storage in saline aquifers is considered as one of the most feasible technology deployment options [60–63], probably because it provides the largest potential storage volume [59]. In addition, the majority of saline aquifers are currently not suitable for other synergic or conflicting applications [64], particularly in the framework of densely populated countries [65]. However, from an economic aspect, many saline aquifers are currently less desirable as a

storage option due to the absence of necessary infrastructure, such as injection wells, surface equipment and pipelines, and the capital cost associated with developing such infrastructure [66,67].

There has been much research carried out around the world on the potential of CO₂ storage in saline aquifers [68], mostly in conjunction with EOR fields (such as the Boundary Dam- Apache case). These studies involve factors such as site selection criteria, site characterisation and future planning [69], as well as the variation of synergic and/or conflicting uses of the subsurface [65,70].

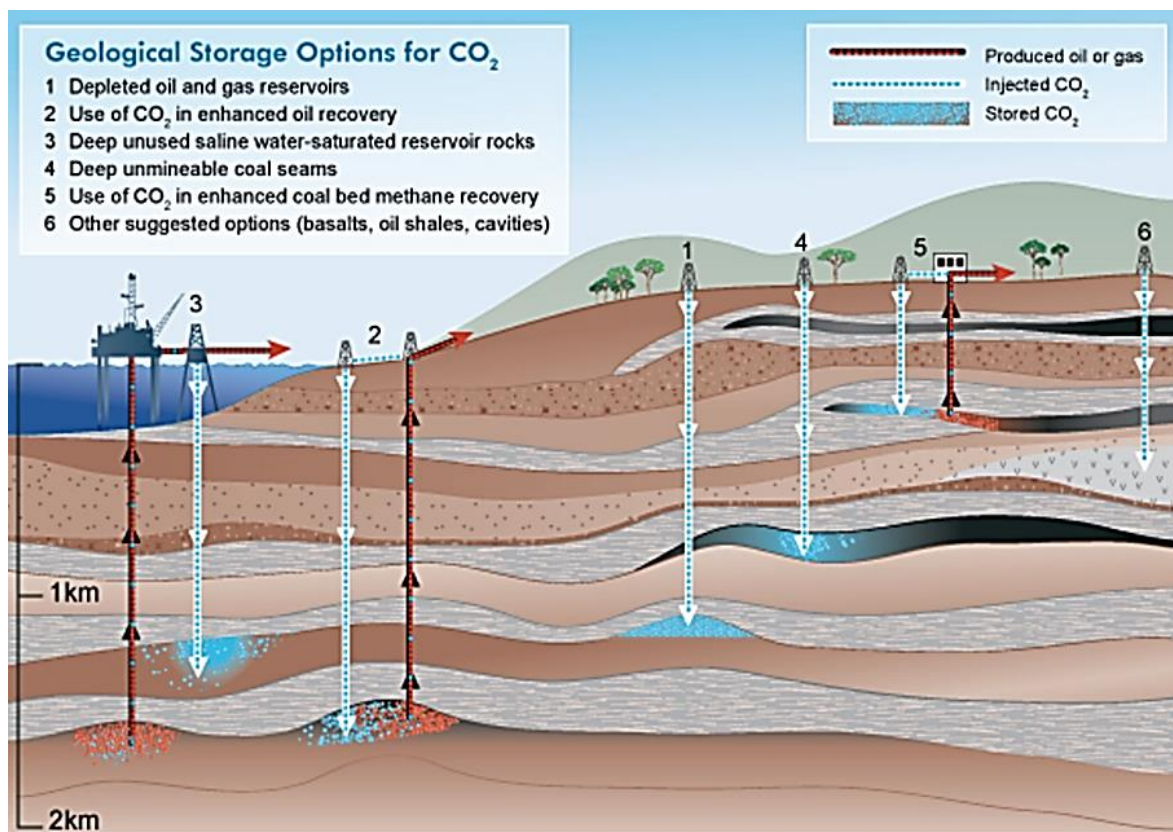


Figure 2-1: Some geological storage options for CO₂ [71].

It is revealed that all deep-seated (>1 km) saline aquifers (perhaps excepting aquifers found between deeply-buried old lava flows) [59] of the world are located within sedimentary basins.

Such basins can host enormous quantities of CO₂ due to their large pore volume and high permeability that minimise the number of necessary injectors, and ease pressure dissipation [53]. Once supercritical CO₂ enters the storage reservoir, it displaces saline pore water and then begins to react with groundwater, gas and rocks in the formation [72,73], which eventually leads to precipitation of new minerals and/or dissolution of pre-existing minerals [74]. Formation and dissolution of minerals can affect the rock porosity and consequently change the capacity of the host reservoir [75].

The density of supercritical CO₂ in saline reservoirs is about 0.6-0.7 g/cm³, which is lower than the density of saline formation water, thus causing CO₂ to rise towards the caprock due to buoyancy force [76,77]. To assure long-term CO₂ storage, the host basin must be considerably large and the caprock must possess a good sealing capacity [78]. Fleury et al. [79] defined a caprock as a low- to very low-permeability formation above the CO₂ storage formation, in which no CO₂ migration should occur. This low-permeability caprock is essential to prevent CO₂ from migrating out of the storage reservoir, and minimising the CO₂ leakage. The presence of unrecognised fracturing or faulting is another critical factor that can result in loss of caprock integrity and CO₂ leakage. However, further research is needed to explore the effect of pervious faults on the caprock integrity [80].



Figure 2-2: The four main CO₂ trapping mechanisms [81].

There are four main trapping mechanisms that can securely store CO₂, namely, structural/stratigraphic, residual, solubility, and mineral trapping, **Figure 2-2** [53,82]. These are: (i) Structural/stratigraphic trapping: Once CO₂ is injected, it can rise up to the top of geological structures and remain below an impermeable top seal [83], where it is stored as a high-density free phase that is unable to enter the pore space of the caprock, except through slow diffusion or through faults, **Figure 2-2a** [84]. This is the most dominant trapping mechanism. (ii) Residual trapping: In this mechanism, the injected CO₂ initially displaces the fluid as it progresses through the porous rock. As CO₂ continues to move, the displaced fluid returns and disconnects and traps the remaining CO₂ within pore spaces, **Figure 2-2b** [82]. It is reported that the phenomenon does not happen within structural and stratigraphic traps, but only where water drainage occurs during CO₂ injection [85]. (iii) Solubility trapping: In this

mechanism, CO₂ dissolves in brine, reducing the volume of free-phase CO₂, **Figure 2-2c**. CO₂ dissolution increases the brine density and can induce a gravitation instability, which accelerates the transfer of injected CO₂ to CO₂-lean brine [86]. (iv) Mineral trapping: In this mechanism, CO₂ is involved in geochemical reactions with saline water and minerals in host rock leading to the precipitation of carbonate phases that effectively lock up the CO₂ in immobile secondary phases for geological timescales, **Figure 2-2d** [87]. This process is slower than solubility trapping and takes place over a longer geologic timescale [88–90].

2.2.1.2 Depleted oil and gas reservoirs

CO₂ storage in depleted oil and gas reservoirs is considered as one of the most effective storage options because of several advantages including: (i) depleted oil and gas reservoirs have been extensively studied before and during the hydrocarbon exploration stage, including the storage capacity, (ii) surface and underground infrastructure, e.g., injection wells and pipelines, already exist and can be utilised for the storage process either without or with only minor modifications [56,68,91–94], and (iii) the injection of gases such as CO₂ as an EOR technique has been widely known and employed within the oil and gas industry and, therefore, such experience can be used for the storage process [66]. In addition, oil and gas reservoirs are valuable hydrocarbon-containing analogues that can be used to demonstrate the effectiveness of caprock or seal over geological periods [95], since if this was not the case, the oil and gas in such reservoirs would have escaped long ago.

Storage in oil and gas reservoirs has many similarities to storage in saline aquifers, since the rock types are similar [96], and brine is present in both cases. On the other hand, oil and gas reservoirs can be potentially considered for EOR, which makes them economically more favourable than saline aquifers [97–99]. Since the global average factor for recovery in typical

oilfields is approximately 40% [100], there is often a substantial amount of oil which is left in the reservoir. This is the main driver for deployment of EOR around the world. However, challenges of the technology deployment remain (mainly the dynamic nature of the downhole environment), although some of these uncertainties could have been considered and addressed during the early stages of a field's exploration and/or production.

Amongst existing options for EOR, including gas, thermal, chemical, or plasma-pulse injection methods, gas injection is the most commonly used technique. In the gas injection technique (typically CO₂, nitrogen and natural gas), miscible gases are introduced into the reservoir to reduce the interfacial tension between oil and water and improve oil displacement, while maintaining reservoir pressure. CO₂ is considered as the most suitable option, since it can reduce the oil viscosity, and also is cheaper compared to liquefied natural gas [101]. Since the advent of CCS technology, more CO₂ for EOR is expected to be available from large point sources [16]. For example, it has been reported that the utilization of CO₂ for EOR has led to additional production of almost 250,000 barrels of oil per day in the United States [102].

The main requirements for deployment of CO₂-EOR projects are [103]: (i) additional characterisation of storage site by gathering key information on caprock integrity and abandoned wells, to determine the risk of leakage; (ii) additional measurements of fugitive and venting emissions from any surface processing facilities; (iii) enhanced monitoring and field surveillance to identify, and/or estimate leakage rates from sites to assess whether reservoir behaviour is as anticipated or not; and (iv) modifications to abandonment processes such as removal/retrofitting of any components of the well, to ensure such components can withstand effects of corrosion.

Nevertheless, in addition to the aforementioned requirements, governments need to consider legal issues and provide legislation that can cover storage site operation. These issues derive from different models of regulation for CO₂-EOR and CO₂ permanent storage, in which the former should be focused on resource recovery, and the latter on waste disposal [104]. For example, where recovery of hydrocarbon is prioritised, the effective decontamination of oil remaining in place after production ceases may cause legal issues. Such situation can be specific to jurisdiction, and may be particularly important where onshore mineral and storage rights are held privately (i.e., United States) [104].

The type and level of impurities in CO₂ streams is one of the important factors that needs to be critically characterised prior to a CO₂-EOR project. The impurities in the CO₂ stream depend on the point source of CO₂ and its corresponding capture technologies [105]. The acceptable impurities and their concentration are determined based on a combination of transport, storage, and economics-related parameters. Typically, the minimum acceptable purity of CO₂ streams is around 90%_{vol} [106]. Higher levels of impurities can shift the boundaries in the CO₂ phase diagram to higher pressures, implying higher operating pressures are needed to maintain the CO₂ in its dense phase. Moreover, it has been reported that non-condensable impurities often lead to a reduction in the CO₂ storage capacity by a degree greater than the molar fraction of the impurities in the CO₂ stream [107].

Corrosion is the main associated concern with impurities. Corrosive impurities (such as CO, NO₂, SO₂, H₂S, Cl) can significantly impact the transport and injection facilities; thus, it is essential to limit the level of impurities on a case-specific basis, and to establish viable mitigation strategies regarding the potential challenges [105]. It should be pointed out that although some impurities are flammable in nature (such as CO, H₂, H₂S, CH₄), the CO₂ stream would not be flammable due to relatively low concentrations of those impurities, and such

safety concerns for flammability are usually not considered in the evaluation of safety procedures. The excessive concentration of O₂ in CO₂ streams is another factor that can affect efficiency of the CO₂-EOR process. The presence of O₂ can trigger microbial activity in the reservoir [105], and can eventually lead to operational issues such as injection blockage, and oil degradation and oil souring [108].

Environmental aspects of EOR are associated with production of large amounts of water which may contain radioactive substances and toxic heavy metals [109]. These substances can contaminate the sources of potable water if a proper waste management and disposal strategy is not adopted. Although regulations already exist, governments must assure that the operators adhere to existing regulations where reinjection of brine (deep into the ground) for recovery is authorised (such as in the United States) [110].

The Weyburn-Midale CO₂ storage project in Canada is one of the examples in which the captured CO₂ is successfully and effectively used for EOR and storage in the Weyburn oilfield. In this project, not only is a considerable amount of additional oil recovered [111], but also the life cycle of the oilfield is extended for 20-25 years [20]. CO₂-EOR studies based on the Weyburn case history have been mainly focused on long-term monitoring [112,113], induced seismicity [114], core assessment of CO₂ impact on the reservoir [115], and interaction of formation waters, oil and minerals [116]. Cantucci et al. [74] developed a geochemical model for CO₂ storage in deep reservoirs using the Weyburn case history, and studied brine/oil geochemical equilibrium. They assessed reservoir evolution during CO₂ injection, and predicted precipitation and dissolution processes over 100 years post injection. They found that CO₂ and carbonate dissolution are the main chemical reactions in the reservoir, and this takes place within the first year of simulation. In addition, evolution of chemical features by time suggested that CO₂ can be safely stored by both mineral and solubility trapping.

Although the CO₂-EOR process has significantly increased oil recoveries, the following strategies can potentially lead to further improvement [117]: (i) increasing the amount of injected CO₂ compared to the typical range – such as conducted in the San Joaquin basin, where a recent numerical model was developed and used to prove that it was possible to recover 67% of the original oil in place (OOIP) by injecting 2.0 HCPV (hydrocarbon pore volume) of CO₂ [118]; (ii) utilising innovative flood design and well management to obtain a higher proportion of residual oil through strategies such as isolation of poorly swept reservoir intervals for CO₂ injection, altering injection and production well patterns, and deploying much closer well spacing [119]; (iii) improving the mobility ratio by increasing the viscosity of water [120]; and (iv) minimising miscibility pressure using miscibility-enhancing agents [121].

2.2.1.3 Unmineable coal seams

Unmineable coal seams provide another option for storing anthropogenic CO₂. The presence of cleats within the coal matrix provide some permeability to the system. In addition, the coal matrix contains a very large number of micro-pores which makes it capable of absorbing significant amounts of gases. The CO₂ trapping mechanism is based on the higher affinity of coal towards gaseous CO₂ than methane. Therefore, the injected CO₂ can replace previously adsorbed methane and be permanently stored, while enhancing methane production [53]. This provides the opportunity of storing large amounts of CO₂ while still improving the profitability and efficiency of commercial operations of coalbed methane (CBM) [122,123]. It should be noted that CO₂ accelerates CBM production, but the total amount of produced methane is not necessarily greater than that without CO₂ injection. IEAGHG [124] outlined the principal technical criteria that are required for successful application of enhanced coal bed methane (ECBM) recovery, including: (i) reservoir homogeneity; (ii) minimal faulting/folding; (iii) optimal depth range; (iv) concentrated coal geometry; and (v) adequate permeability.

The ECBM approach has been tested at two demonstration sites, namely, the Alberta Carbon Trunk Line (ACTL) project in Canada, and the San Juan Basin pilot project, USA, [122]. At the completion of the Alberta project tests, key lessons learned were: (a) continuous injection of CO₂ is possible even in tight reservoirs; (b) despite injectivity declines, injection can still proceed; (c) it is possible to predict significant enhanced CBM production; and (d) injected CO₂ remains within the reservoir while sweep efficiency is increased [125]. For the San Juan Basin pilot project, the key conclusions were: (a) there was an increase in methane recovery over the estimated ultimate primary recovery; (b) given the prevailing gas prices at the time of implementation of the project (without considering any tax credit benefits), the pilot itself was uneconomic, although gas prices in the future may make it appear economically attractive; and (c) the injected CO₂ causes a reduction in coal permeability and correspondingly CO₂ injectivity, which in turn compromises any likely increment in methane recoveries and project economics. Another small-scale study on a CBM field is in the Central Appalachian Basin (Buchanan County, Virginia, USA) where several monitoring, verification and accounting (MVA) techniques are being used in improving the understanding of storage complexities [123,126]. In addition, the potential ECBM implementation and the major differences in production between close wells with the same stratigraphy (but different groundwater/bacterial presence) have been initially investigated (such as those in the Surat basin, Australia [127]). However, further exploration is required to fully characterise and depict those differences.

Although CO₂-EOR is an established approach in the oil industry, utilisation of CO₂ for ECBM is yet to be well understood. However, many of the uncertainties in ECBM recovery can be addressed based on the existing knowledge of the CO₂-EOR process. For example, for recoverable reserves in ECBM production, it may be important to consider existing technologies from the oil industry which can be utilised with slight modification. For the well

integrity in ECBM production, existing well materials can be considered as a benchmark and used after appropriate improvements. Additionally, field management strategies, including risk assessment and monitoring, can be adopted from established processes and applied throughout project lifecycles.

2.2.1.4 Basalt formations

Deep basalt formations, found within large igneous provinces, have been proposed as a potential option for CO₂ storage [128–130]. Basaltic rocks form approximately 8% of the continents and much of the ocean floor. Therefore, there is an enormous potential CO₂ storage capacity in basaltic rocks [131]. The key positive aspects of their potential for CO₂ storage are their high reactivity and abundance of divalent metal ions in such rock which can potentially fix CO₂ for geological timescales [132]. However, basalt flows have highly heterogeneous permeability and porosity (including that of matrix and fractures), and typically consist of a low-permeability centre, with high permeability zones at the upper and lower portions. Thus, the key parts of a basalt sequence for CO₂ storage are the rubbly zones between individual flows.

Injection of free-phase CO₂ into deeply-buried basalts (such as the CarbFix pilot project in Iceland) can displace water in pore spaces and fractures [133]. The reduction in the amount of water can hinder carbonation and hydration of the basalt. Therefore, injection of CO₂ with an optimum amount of water in the same reservoir may be a potential solution. Goldberg et al. [134] studied CO₂ injection in deep sea basalt and reported that it: (i) facilitates formation of stable carbonates in relatively short geologic time, and delays return of CO₂ to the atmosphere; (ii) provides enough depth that allows denser CO₂ liquid to sink; (iii) stops upward migration of acidified basement fluids through an impermeable sediment cover; and (iv) forms stable

hydrate when CO₂ escapes to shallower depths containing water with lower temperatures. It is important to note that sparse and rare CO₂ leakage in a limited amount does not necessarily affect the sea bottom environments.

Due to the potential formation of secondary carbonate mineral and the possibility of long-term CO₂ trapping in basalts, it is important to consider changes in rock volume and to determine whether there is the probability of self-healing of fractures. Such issues were numerically explored by Van Pham et al. [132]. They reported that at 40°C, calcium was significantly consumed by oxide which could possibly be limited to the formation of siderite and ferromagnesium carbonates. However, at higher temperatures, 60-100°C, magnesite formed together with ankerite and siderite. They also found that both carbonation and hydration reactions resulted in an increase in the volume of solids and blockage of available pores, and consequently a reduction in the maximum amount of stored CO₂.

Alongside basalt mineral assemblages, there have been studies aimed at understanding the fundamentals of long-term CO₂ storage through mineral carbonation reactions that involve common magnesium silicates in serpentinites. CO₂ reacts with magnesium silicates in the form of serpentinites, which are both abundant and thermodynamically suitable rocks to form magnesium carbonates [135]. Andreani et al. [136] studied the carbonation process under optimal flow conditions and their study suggested that reduction in porosity and permeability is confined to diffusion-limited zones or reduced flow, although high flow rates result in armoring of mineral surfaces after initial dissolution.

The presence of fractures in the caprock layer of basalt formations has also been a source of uncertainty. There is a possibility for leakage through the fractures, which may imply that basalts appear unlikely to be suitable for CO₂ storage. On the other hand, the migrating CO₂

through the fractures can potentially undergo mineralisation before reaching the surface, and be stored within the formation [137]. Thus, comprehensive exploration is needed to characterise the kinetics of CO₂-basalt interactions.

2.2.1.5 Hydrate storage of CO₂ within the subsurface environment

Subsurface storage of CO₂ as hydrates is also a promising, novel option which aims to use CO₂ hydrate to trap CO₂ molecules in a lattice of water molecules [58]. CO₂ hydrate can rapidly form in the presence of water (that is abundant underground) and the appropriate pressure and temperature conditions [138]. In addition, its fast formation kinetics may potentially allow a degree of self-sealing in the unlikely event of fracture formation in the hydrate cap. Formation of CO₂ hydrates is applicable in both underground geological and oceanic storage. However, since the hydrates are stable only at elevated pressures and temperatures below 10°C [139], its applicability is limited to a few environments, including shallower sediments that are beneath cold waters, and below thick permafrost, where there may not be large sources of CO₂ nearby.

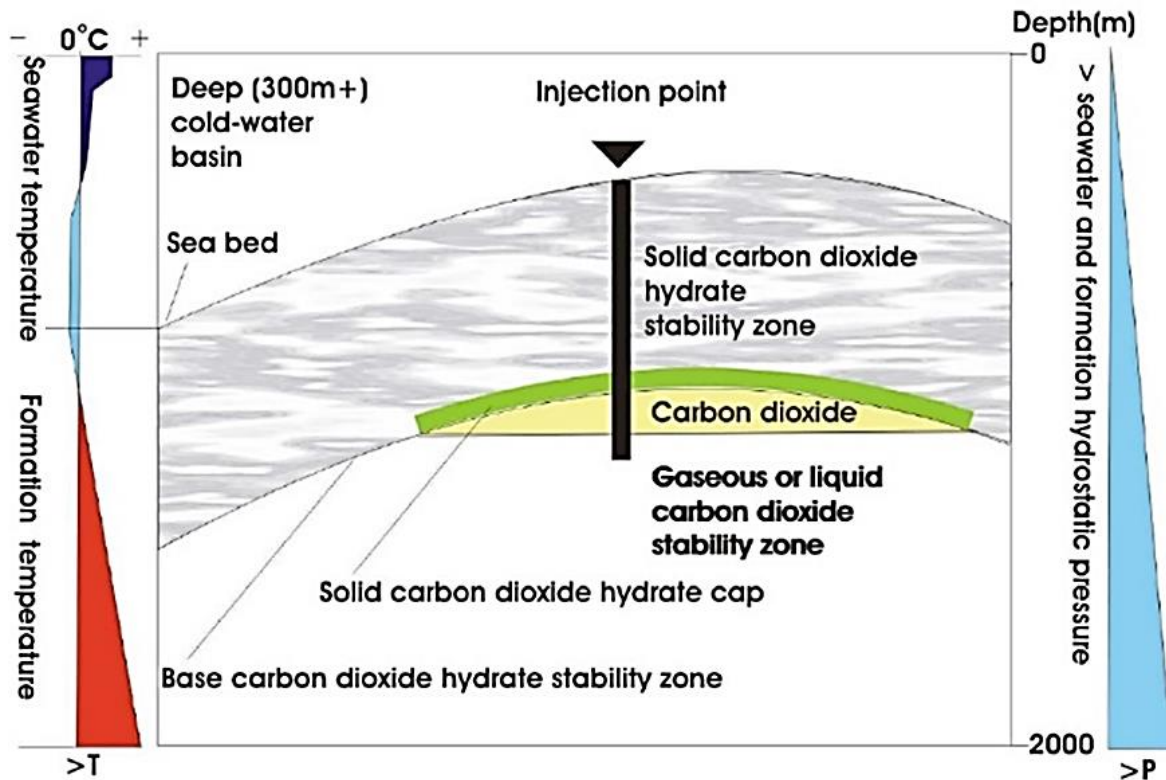


Figure 2-3: Schematic of hydrate storage and associated ‘cap’ of CO₂ hydrate [139].

The CO₂ hydrate storage mechanism is mainly based on the formation of an impermeable CO₂ hydrate cap over a large amount of buoyancy-driven migrating liquid CO₂, **Figure 2-3**. In this method, the liquid CO₂ is injected into deep-water or sub-permafrost sediments, beneath the CO₂ hydrate stability zone. Migration of the rising liquid CO₂ to the cooler hydrate stability zone leads to precipitation of CO₂ hydrates within rock pore spaces and formation of an impermeable layer of CO₂ hydrates, that blocks the upward migration beneath liquid CO₂ [139]. Alternatively, a hydrate storage strategy based on CO₂-EGR (enhanced gas recovery) was proposed by US DOE (Department of Energy). In this approach, the CO₂ is injected into methane hydrate-bearing sediments in order to release the methane from methane hydrates, and subsequently form CO₂ hydrates instead [60]. However, CO₂-EGR is a relatively new concept and its viability has not yet been fully explored. One of the main associated concerns with CO₂-

EGR is the possibility of mixing of the injected CO₂ with existing methane which in turn may degrade the resources [140].

CO₂ hydrate storage is still at a relatively low technology readiness level (TRL), and the majority of the work has been focused on theoretical modelling [141,142] and lab-scale experiments [143–145]. Therefore, there are uncertainties that remain, particularly in respect to CO₂-EGR. Drilling through hydrate-bearing sediments can change local temperature and pressure, and may eventually destabilise the hydrate [146]. The key remaining issues that need to be addressed to advance the assessment of hydrate storage feasibility are the demonstration of hydrate cap formation, and understanding of the CO₂-methane hydrate exchange mechanism and its impact on methane production.

2.2.1.6 CO₂-based enhanced geothermal systems

The thermal properties of dense-phase CO₂, like water, make it capable of transporting significant amounts of heat. However, it also possesses some superior physical properties, such as significantly lower viscosity, higher compressibility and expansivity [147–150]. Therefore, CO₂ can be applied for the extraction of heat from the subsurface, and used for geothermal power production. Owing to its low viscosity, CO₂ can effectively access the rock mass, and can be particularly utilised as a working fluid for enhanced geothermal systems (EGS) [57,150]. One of the drawbacks of using water as the heat transmission fluid in EGS is its inevitable loss during fluid circulation. Since water is considered a valuable commodity, its loss is associated with economic liability. On the other hand, the loss in CO₂-based EGS would offer the possibility of geological storage of CO₂ underground, and can be considered as an ancillary benefit [150].

For an effective and successful storage strategy based on CO₂-EGS, the CO₂-filled rock mass needs to remain separate from the surrounding water-filled rock mass, and the stored CO₂ should be isolated. The key mechanism that can ensure the aforementioned criteria is based on fast CO₂-water-rock reactions that result in precipitation of carbonate minerals at the interface between the CO₂-filled core of the EGS and the surrounding water-filled regions. In terms of geographical aspects, this approach would only be appropriate for countries which have subsurface formations with sufficiently high temperatures at economically-drillable depths. In addition, in densely populated countries, the synergic use of subsurface can be more challenging, and requires a high level of coordination [65].

In general, the technique is currently at a relatively low TRL, and the majority of conducted work has been mainly limited to theoretical modelling [151], and laboratory experiments [152]. The key barrier for further advance of this technology is associated with uncertainty in effectiveness of sealing around the CO₂-filled zone. In addition, the CO₂-rock interaction at elevated temperature is not clearly known, and further studies are required to characterise the effect of CO₂ on dissolution and precipitation, and consequently variation in fracture permeability and EGS operation.

2.2.2 Deep ocean storage

An alternative strategy for sequestration of anthropogenic CO₂ is to deliberately inject the CO₂ into deep ocean water. Oceans cover 70% of the earth's surface with an average depth of 3.8 km [153], and have absorbed almost a third of cumulative anthropogenic CO₂ emission from the atmosphere over the industrial period [154]. Mathematical models have shown that injected CO₂ could remain in the ocean for several hundred years [153]. These cold (ca. 1°C) and deep

(ca. 4-5 km) waters move slowly, and can remain isolated from the atmosphere for millennial timescales.

The main proposed approaches for ocean storage are based on direct dissolution of CO₂ into the seawater. In the first approach, liquid CO₂ is directly discharged to the seafloor and forms rising droplet plumes. Alternatively, liquid CO₂ is injected into a column, where it can react with seawater, at a controlled rate, to form hydrate [153]. There is, however, opposition regarding deep ocean storage of CO₂ due to the potential local acidification of seawater around the CO₂ injection point [155,156], and correspondingly, possible negative impact on benthic organisms. In addition, it is not yet clear whether international regulations will allow ocean storage projects [47]. In 1996, the London Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (also known as the London Convention) prohibited disposal of industrial wastes into the sea [157]. Therefore, if CO₂ is considered as an industrial waste, disposing it beneath the sea is prohibited. However, there has not been agreement whether CO₂ is regarded as industrial waste or not, even though in 2006, there was an amendment to the London Protocol, in which CO₂ is included in the “reverse list” allowing it to be considered for storage below the seabed. In parallel, the Convention for the Protection of the Marine Environment of the North-East Atlantic (also known as the ‘OSPAR Convention’) pointed out that “CO₂ can be only stored in accordance with an authorisation or permit given by the Party’s competent authority” [158]. Thus, the uncertainties associated with the oceanic sequestration and its environmental aspects need to be evaluated and possible mitigation strategies should be specified.

The main key parameters that can be used to evaluate the efficiency of oceanic sequestration are injection depth, residence time (time-scale at which the stored CO₂ returns to atmosphere), and the distribution of CO₂ concentration. Xu et al. [159] studied the potential of storing CO₂

in the North Pacific by developing a regional ocean general circulation model with different parameters of sub-grid mesoscale mixing, and assuming a zero air-sea CO₂ exchange. Their results showed that the storage depth is one of the key parameters for isolating the stored CO₂ and minimising its return to the atmosphere. It was determined that to store CO₂ in the ocean over a few hundred years, an injection depth of over 1000 m is necessary. In addition, it was revealed that after 50 years of continuous CO₂ injection (at different locations and a maximum depth of 5750 m) more than 10% of dissolved CO₂ would return to the atmosphere, which can be considered as a source of leakage. Hill et al. [160] evaluated the storage efficiency by means of mean residence time for impulse injections based on several scenarios, using an ocean circulation model. It was found that the North Atlantic is more efficient for sequestration of CO₂ over timescales of several hundred years and longer, while the Pacific basin is more efficient for shorter timescales. It should be noted that this study was based on relatively small magnitudes and the effect of air-sea CO₂ exchange was neglected; however, for large boundaries, the significance of this effect is unknown and needs to be investigated.

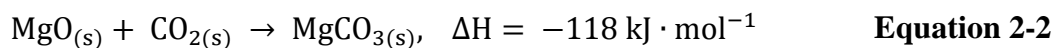
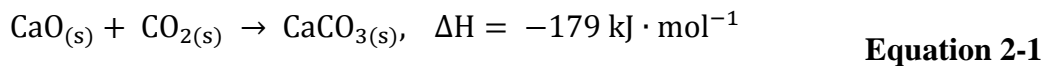
The distribution of CO₂ concentration after injection can be used to assess the sequestration site selection. The ideal site is referred to where the CO₂ is efficiently diluted and has the least negative impact on biota. Masuda et al. [161] studied the local distribution of CO₂ concentration as a function of injection rate and eddy activity distribution, by simulating CO₂ injection into several sites around Japan using an oceanic general circulation model. It was revealed that the maximum concentration of CO₂ can differ by a factor of 10 amongst sites, and this discrepancy is mainly attributed to the local distribution of eddy activity. Further, it was determined that no chronic impact on biota would be caused if injection rates are limited to 20 Mt/a.

According to aforementioned discussions, there are several improvements and uncertainties that need to be considered and addressed in future research in order to enhance the evaluation of oceanic sequestration, including: (i) improving the current numerical model by including an air-sea CO₂ exchange mechanism for better evaluation of storage efficiency; (ii) further investigating the determination and quantification of ocean site selection criteria; and (iii) further quantification and demonstration of the viability of transporting large amounts of CO₂ in the Pacific Ocean.

2.2.3 Mineral carbonation

The concept of CO₂ mineral carbonation (mineralisation) as an alternative CO₂ sequestration strategy was first proposed by Seifritz [135]. In this method, the captured CO₂ is sequestered through the process of mineralisation where CO₂ is reacted with alkaline earth metal oxides or hydroxides, such as calcium- and magnesium-rich minerals to produce stable carbonates,

Equation 2-1 and **Equation 2-2**.



There are two methods of mineral carbonation: in-situ and ex-situ. The in-situ method involves the production of carbonates through the injection of CO₂ into a geologic formation, while the ex-situ method is carried out above ground in an industrial plant using previously mined or local rock [162,163]. In-situ mineral carbonation would typically be considered in basalts or ophiolite rocks which are enriched in magnesium, iron, and calcium silicates [162]. Major advantages for the in-situ mineral carbonation method stem from the fact that no extensive mining is needed as only a few boreholes are required for the process. On the other hand, there

can be major uncertainties such as lack of geological characteristics or unknown caprock or seal potential. In addition, geochemical reactions may act to reduce reactivity, porosity, and permeability, which in turn can cause lining of the initially formed flow paths. Ex-situ mineral carbonation can be done through either direct (gas- and aqueous-based) or indirect processes. In the direct gas-based method, gaseous CO₂ is reacted with minerals to produce carbonates [164,165]. The gas-solid carbonation reaction typically takes place at temperatures below 650°C [135,166,167], and the main limiting factors are the reaction rate and rock storage capacity. In the direct aqueous-based method, CO₂ is reacted with minerals in the presence of an aqueous solution, usually taking place in a single step [164]. Sanna et al. [162], Olajire [168] and Bobicki et al. [164] reported that constraints like mineral dissolution, CO₂ dissolution, and product layer diffusion are the main factors that make direct mineral carbonation less viable for commercial deployment and development.

Matter and Kelemen [169] studied permanent CO₂ storage in geological reservoirs by mineral carbonation using natural analogues. Results from their study showed that the rate of mineralisation is high in host rocks rich in magnesium- and calcium-bearing minerals. Their results also showed that precipitation of carbonate minerals can clog pre-existing voids, although stress induced by rapid precipitation may also lead to fracturing and increased pore volume. The local environment may also be affected through mining, as certain types of calcium- and magnesium-rich mineral deposits may contain asbestiform phases and other health-depleting impurities [16].

Although magnesia (MgO) and lime (CaO) are the most naturally abundant alkali and alkaline earth metal oxides, they do not exist as binary oxides in nature and are usually bonded up as silicate, such as serpentine [41]. Cipolli et al. [170] and Bruni et al. [171] studied CO₂ interactions with serpentine from spring waters in Genova (Italy). After geochemical analysis

of the high-pH waters from serpentinites and reaction path modelling for sequestration in aquifers containing serpentinites, Cipolli et al. [170] confirmed that the progressive reaction of ultramafic rocks with meteoric waters is affected by serpentinisation. This initially led to the formation of MgHCO_3 waters when the system is exposed to CO_2 and subsequently the formation of Na- HCO_3 and Ca-OH type waters upon further interaction with the host rock under highly reducing closed-system conditions. After simulating high-pressure CO_2 injection into deep aquifers by reaction path modelling, their results indicated that serpentinites have good capacity for CO_2 sequestration, mainly because of the formation of carbonate minerals. It should be noted that this process caused a reduction in porosity of the aquifer under closed system conditions. This suggests that such implications need to be carefully evaluated by further field and laboratory tests.

From a survey of spring waters in the Genova province using irreversible water-rock mass transfer, Bruni et al. [171] reported that many neutral Mg- HCO_3 and some high-pH Ca-OH waters were found to be associated with serpentinites. They explored the viability of using serpentinite dissolution and calcite precipitation under open- and closed-system conditions for long-term CO_2 sequestration. From their study, the interaction of these waters, which are of meteoric origin (as indicated by stable isotopes of water and dissolved N_2 and Ar), show a progressive evolution in chemistry of the aqueous phase from immature magnesium-rich, SO_4Cl facies of low salinity to intermediate Mg- HCO_3 facies and to some mature Ca-OH facies. Further, the high-pH Ca-OH water can absorb CO_2 and form calcite deposits, suggesting that the process can be utilised for the sequestration of anthropogenic CO_2 .

On the other hand, the less attractive aspects of mineral carbonation are the potential environmental and human concerns. Mineral carbonation processes have the potential for terrain alteration through large-scale mining operations, and subsequent disposal of the reacted

materials. In addition, certain types of calcium- and magnesium-rich mineral deposits may contain asbestiform phases and other health-depleting impurities [16].

According to the reviewed literature, future studies, that potentially help to evaluate the viability of CO₂ sequestration by mineral carbonation, can be focused on: (i) mineral carbonation with respect to mineral and CO₂ dissolution; (ii) product layer diffusion; (iii) the possibility of less terrain alteration; and (iv) handling mineral impurities in the sequestration process.

2.3 CO₂ storage site evaluation criteria

Before the deployment of storage technology, it is important to identify key storage site evaluation criteria that allow assessing whether the technology is credible, safe, reliable, trustworthy, environmentally benign, and economically viable. This is especially important if the ethics management mechanisms are not established. The identification of key evaluation criteria and recommendations in the site evaluation process should provide clear inputs for costs-risks-investment business decisions [172]. Studies on site-selection and -evaluation criteria for CO₂ storage in geological formations have highlighted that the main criteria to be considered are geological, geothermal, geohazards, hydrodynamic, hydrocarbon potential and basin maturity, and economic, societal, and environmental issues [59,173–178].

2.3.1 Geological factors

The most suitable CO₂ storage strategy has been currently attributed to sedimentary basins, where sedimentary rocks, containing appropriate porosity and permeability, are often located at or near to power stations and energy-intensive industries [179]. This implies the importance of the distance between point sources of CO₂ and storage sites, in order to minimise the cost of

transportation. Thus, for point sources of CO₂ that are not located close to ideal sedimentary formations, the high cost of transportation can be avoided by selecting an alternative storage option.

The key geological parameters for storage site evaluation are aquifer properties such as reservoir volume/porosity/permeability, pressure and temperature, sweep efficiency (which is a function of heterogeneity of formation), caprock permeability, entry and fracture pressures, quantities of reactive minerals, thickness of formation for CO₂ injection, CO₂ solubility in saline water, potential for seismogenic faults, and stress regime. Injectivity is another factor that is used to evaluate both the economic and technical suitability of a storage site, and enhance the security of storage [174,175]. Injectivity itself is a function of several parameters such as vertical and horizontal permeability, rock compressibility, effective thickness, reservoir heterogeneity, reservoir and fracture pressures, and depth of injection [174].

The Bunter Sandstone formation in the UK Southern North Sea is a specific case where detailed CO₂ containment studies were conducted on both reservoir storage capacity and caprock integrity. Heinemann et al. [95] numerically simulated the injection of CO₂ into the formation over a period of 30 years and at a rate of 1 Mt/a of CO₂ for each well. They reported that since there are few producing fields, information about reservoir and caprock is sparse, but can be evaluated through legacy borehole records which were targeting deeper horizons. They found that approximately 3.8-7.8 Gt of CO₂ can be stored in the reservoir, depending on the maximum safe pressure of injection, and the seal is capable of effectively retaining CO₂.

Geological site assessment can be further improved upon using systematic, yet generally accepted approaches that consider and focus on injection capacity and risks of containment. A possible way to achieve these improvements is to adopt experiences from the oil and gas

industry, especially by utilising numerical models that can quantify the roles of dominant CO₂ trapping mechanisms for basins. In addition, there are only a few studies on geophysical and geochemical risk assessments that are prerequisites to induced seismicity and potential leakage and, thus, learn-by-doing methods [65] should also be considered in future studies.

2.3.2 Geothermal gradient

With regard to the critical point of CO₂ (7.38 MPa and 31.1°C, equivalent to a hydrostatic head of 738 m) a slight variation in geothermal gradient by depth can cause CO₂ to enter supercritical conditions. Assuming the pressure distribution within a sedimentary basin is hydrostatic, the associated minimum threshold depth for injecting CO₂ in the supercritical state at a geothermal gradient of 30°C/km and surface temperature of 10°C is around 800 m [180,181], **Figure 2-4**. Nevertheless, hydrodynamic and geothermal conditions are not always constant across all basins, and for the same basin, are not the same from place to place. The limiting factors for geothermal regime in any sedimentary basin may include: (i) basin type, age and tectonism; (ii) basement heat flow, (iii) thermal conductivity and heat production in the sedimentary succession, and (iv) temperature at the top of the sedimentary succession. For ECBM projects, the minimum depth can be <800 m only if CO₂ is adsorbed by coal. A pilot CO₂ storage experiment at depth <800 m is the Ketzin Project [182]. However, this project did not receive positive public acceptance due to concerns on the possibility of leakage [183].

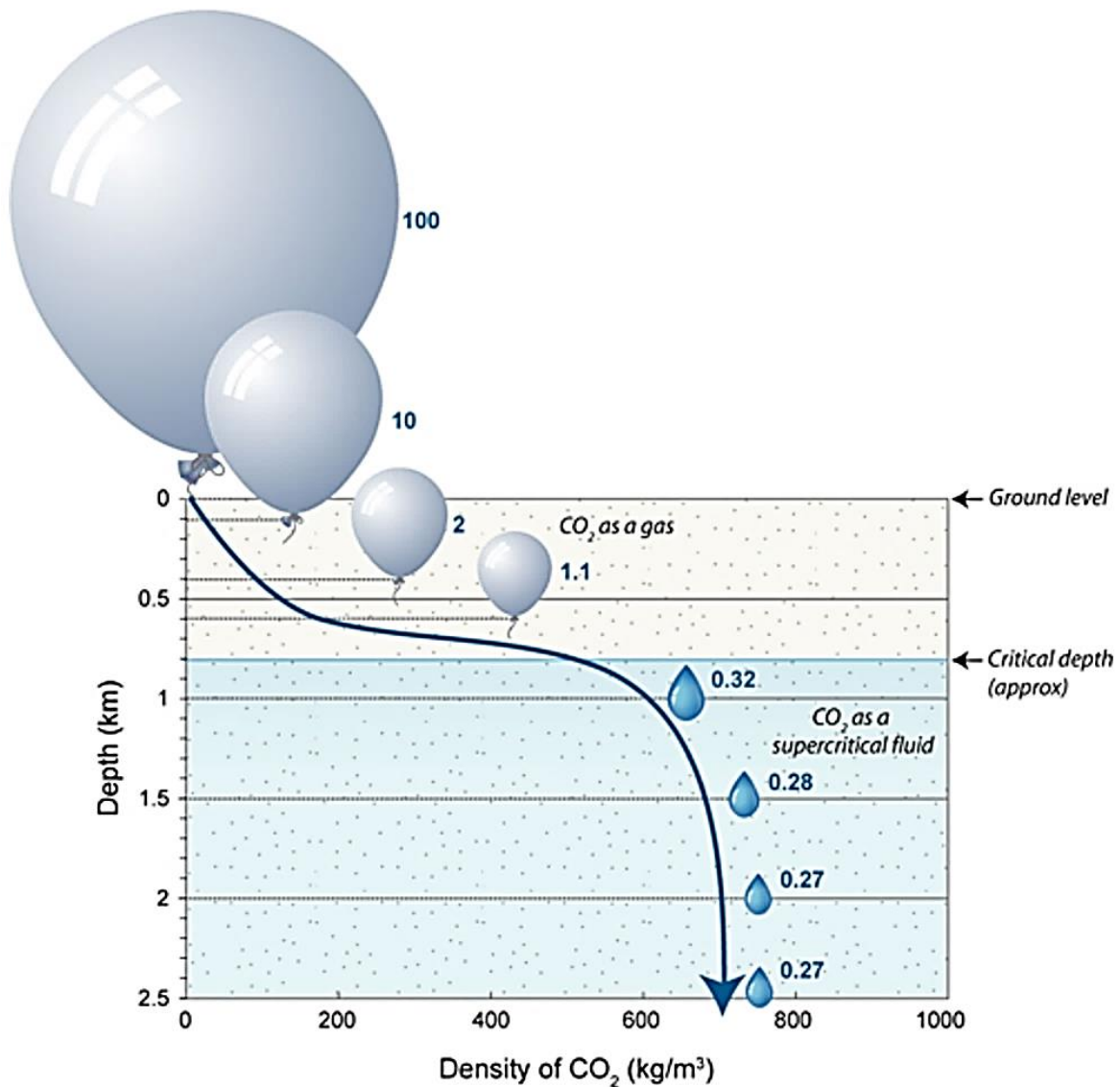


Figure 2-4: Relative volumes of CO₂ stored underground as a function of depth in storage reservoirs [184]. Note: Blue numbers in this figure represent relative volume of CO₂ at each depth.

2.3.3 Geohazards

Geohazards are attributed to the short- and long-term geological and environmental conditions that can potentially cause widespread damage to storage systems, and are necessary to be appraised as part of storage site selection criteria. Accordingly, for effective CO₂ containment

after injection, geologically hazardous areas should be avoided. For storage systems, the geohazards are mainly associated with seismicity, landslides and volcanic activity. In a study on the geo-database of caprock quality and the distributions of deep saline aquifers for geological CO₂ storage in Italy by Buttinelli et al. [80], it was highlighted that shallow and deep seismicity, magmatism, presence of degassing structures and anomalous thermal flux, are some geodynamical domains that can negatively affect storage systems. They identified the primary geological risks that are needed to account for selection of a potential injection structure, namely: (i) seismogenic sources and areas, as identified through geophysical and geological studies; (ii) historical and recent distribution of seismic events; and (iii) natural diffuse degassing structures. This study can be used as a benchmark for identification of local geohazards.

2.3.4 Hydrodynamic factors

The hydrodynamic regime of formation water (including local pressure, salinity, and flow velocity) is very crucial for CO₂ storage, especially when injection is done in depleted oil and gas reservoirs [59], where the movement of CO₂ plume within the reservoir is influenced by hydrodynamic trapping. There is a close relationship between basin type and formation water flows. For example, in intracratonic and foreland basins which have undergone some uplift and erosion, the formation water flow is affected by lateral and vertical erosional rebound. This can make aquifers significantly under-pressured [185], as was seen in the Alberta basin in Canada [186]. Under-pressurised formations are the best for geological confinement and storage of CO₂ as they have a greater ability to cope with increasing pressure during injection operations. The role of faults in hydrodynamic regime and their permeability structure are still to be evaluated as a consequence of sealing processes inside the fault bodies [187].

2.3.5 Hydrocarbon potential and basin maturity

In basins with limited or no known resource potential (such as hydrocarbon reservoirs) [188], there are several reasons that may constrain CO₂ storage, namely because [59]: (i) most of the hydrocarbon resources are still undiscovered, thus there is concern about likelihood of contamination; (ii) being immature with respect to development means there are no depleted oil and gas reservoirs yet; and (iii) limited exploration means the geology and hydrogeology of basins are not understood. Certainly, since occurrence of energy reserves in such basins is not identified, it is not practical to proceed based on CO₂ storage in oil and gas formations (both for EOR and permanent storage). However, since there is still the possibility of having deep saline aquifers in such basins, storage may still be feasible only after evaluating detailed environmental and economic considerations [59]. For basins with relatively recent geological history and known hydrocarbon potentials that are still under exploration and production, contamination of hydrocarbons with CO₂-related impurities are the main source of concern that must be addressed before technology deployment. This also involves the early stages of primary production in CO₂-EOR. For basins which are either under development stage or for which limited exploration data exist, the lack of in-depth subsurface information is a limiting factor for storage site evaluation. Nevertheless, for all cases, 3D geophysical and geochemical modelling can improve the limited knowledge of such basins. On the other hand, CO₂ storage in mature basins is highly applicable for several reasons, including availability of ample data on the geothermal regime, hydrocarbon reserves, and coal beds [59].

The extent of basin development is another important factor that should be considered for site selection, given that many of the factors that make a reservoir suitable for an oil/gas reservoir also make it suitable for CO₂ storage. Strategic planning is also required to ensure that

hydrocarbon extraction operations and CO₂ storage operations do not interfere with each other. For a well-explored basin with hydrocarbon potential, significant information exists on the rocks, reducing geological uncertainty. The presence of oil/gas may also allow for CO₂-EOR/EGR, and this may help reduce the cost of CO₂ storage. However, the presence of potentially thousands of hydrocarbon wells (some possibly several decades old), may increase uncertainties in long-term storage due to a greater potential for borehole-related CO₂ leakage.

2.3.6 Economic, societal and environmental issues

Economic considerations in CO₂ geological storage usually revolve around existing or required infrastructure, and are dependent on ongoing climate change policy. In mature continental basins, the infrastructure such as pipelines, wells, and access roads may already be in place. In immature basins, infrastructure may be either missing or very limited [59]. In offshore basins, a major challenge is that CO₂ injection and storage may be very expensive, due to the necessity for construction of new infrastructure, including long pipeline routes. Therefore, a specific mandatory carbon tax might be considered, such as the one for features, events and processes (FEPs). However, it is important that the development of infrastructure and regulatory models for CO₂ storage should reflect expectations and attract government attention, while not compromising storage security and its impact on the environment. Achieving these key purposes is crucial for storage economics, since meeting technology deployment capable of substantially reducing anthropogenic CO₂ would greatly depend on decades of extensive investments.

Many suitable sedimentary basins for CO₂ storage are in developing countries (e.g., India and Nigeria). In the majority of developing countries, the top priority in development targets is to increase the living standards of their population, which may be rated higher than climate change

and deployment of CCS [59,189]. This can imply that CO₂ storage in geological media may be economically more acceptable in developed countries such as those in North America and Europe [59]. In addition, the distribution of cities and natural resources, such as coal and oil/gas, are some aspects of environmental monitoring and ethics management that can affect the deployment of CO₂ storage. Development of storage projects in heavily-farmed areas can lead to challenges such as land access and right-of-way for facilities, which need to be considered during site characterisation activities. In addition, CO₂ storage can potentially influence the quality of natural resources such as oil and gas, metals and non-metals [174]. Therefore, it is important to consider preliminary regional planning on synergic and conflicting subjects of concern.

A substantial reduction in anthropogenic CO₂ can only be achieved if the majority of countries, including developing countries, participate in the implementation of CO₂ storage technology soon. Thus, it is important for stakeholders in the CCS industry to embark on technology transfer to build national capability. The awareness campaigns need to highlight the global importance of storage deployment for the local public. Furthermore, CO₂ storage should be promoted as an environmentally benign activity, and as a measure to address the environmental problems of communities.

In summary, the associated factors for assessment of storage site selection were discussed. A combination of these factors determines the feasibility of a potential storage site. Although the aforementioned principal factors need to be considered for evaluation of storage sites, there may be additional aspects which are specific to particular storage sites. These additional factors can include (but are not limited to): (i) size and nature of site for potential future expansion; (ii) political aspects, such as the possibility of future regional development plans; and (iii) cultural heritage aspects, such as the existence of Native Title Claims where a person or a group

may claim that they hold rights and interests in a given land or area according to traditional customs and laws.

2.4 CO₂ in the reservoir

The candidate technology for development of CO₂ storage in the subsurface should potentially assure a minimum residence time of 1000 years and a leakage rate of less than 0.1% per year [16]. Therefore, one of the most important aspects of CO₂ storage is to have a clear understanding of the mid- to long-term behaviour of CO₂ in the reservoir. The CO₂ behaviour in the reservoir is a complex process (**Figure 2-5**) which depends on a variety of components within the reservoir system, including geochemistry, mineralogy, fractures, pore fluid dynamics, and variation in geochemical effects such as dissolution and precipitation of minerals [53,190], and can continue for thousands of years, until the stored CO₂ is immobilised as solid carbonate precipitates. There are several factors that influence containment of CO₂ within the reservoir, including CO₂-rock interaction, induced seismicity during the injection, and the potential risk of leakage that will be comprehensively discussed in this section. In addition, accurate estimation of reservoir storage capacity is one of the key prerequisite parameters for evaluating the suitability of a storage site, and will be covered in this section.

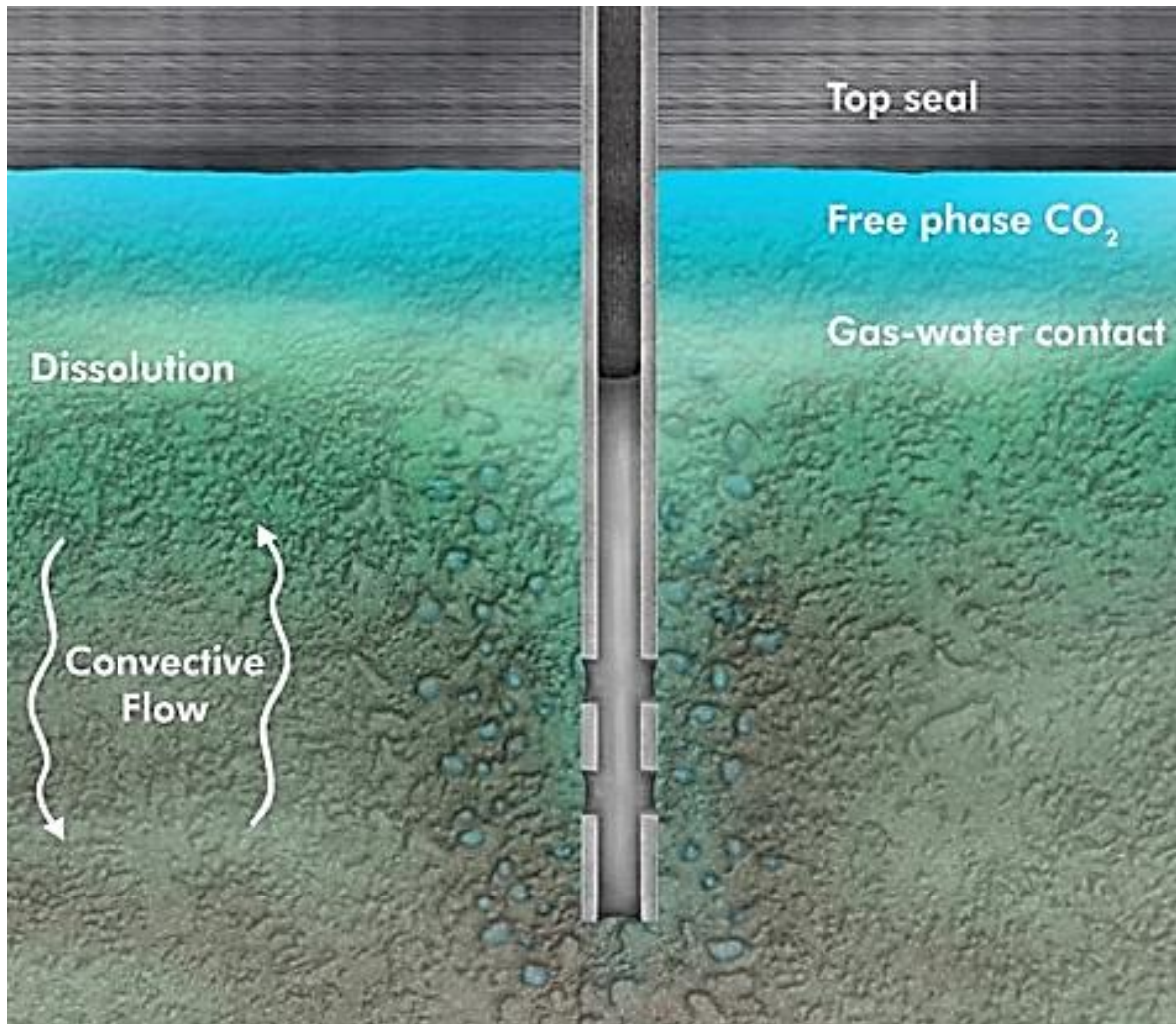


Figure 2-5: Post-injection dispersion of CO₂ in the reservoir [191].

2.4.1 CO₂ natural analogue

CO₂ analogue cases can be used to advance our understanding of the behaviour of CO₂ in reservoirs, and to further improve reservoir management strategies [187,192,193]. Much research has been conducted on different aspects of CO₂ analogues by means of CO₂ storage, including natural accumulations [194], gas migration along fault systems [195], CO₂ leakage [192], seal efficiency [187,196], and storage security in natural reservoirs [197]. In many natural analogues, where the CO₂ is ultimately generated from volcanic and mafic processes,

and sometimes from the mantle [187,196], some seals have been capable of securely trapping CO₂ for up to several million years in sedimentary formations. Whilst the mode of formation of these CO₂ analogues may differ from that in a CO₂ storage project, many of their features are analogous to man-made storage schemes, which implies the feasibility of long-term CO₂ storage [193].

Pearce et al. [194] reported that natural CO₂ accumulations occur in many basins across Europe, suggesting that it is possible to identify the potential CO₂ leaks and to predict the long-term geomechanical and geochemical behaviour of a storage site, **Figure 2-6**. They found that although volcanic activity and seismically active areas allow CO₂-rich fluids to migrate to the surface, stratigraphic traps allow accumulation of CO₂ below limestone, evaporites, and mudstone caprocks. In areas where reactivation of fractures allows migration of CO₂-rich fluids, some degree of limited self-healing may occur through calcite precipitation. In addition, a comparative study between reservoir sandstone and equivalent formations nearby indicated that feldspar dissolution in reservoir sandstones can potentially increase the secondary porosity [194]. Annunziatellis et al. [195] studied gas migration along fault systems and through the vadose zone in the Latera caldera of central Italy, by integrating near-surface gas geochemistry and structural geology surveys, to understand the migration behaviour of CO₂. Their results revealed the pattern of gas migration along high-permeability pathways within faults with discharge occurring typically from spatially restricted gas vents. However, the distribution, size and strength of vents seemed to be controlled by both the evolution and deformation style of the fault, which in turn is associated with rheology of lithological units cut by fault. It implies that the gas migration may be changed drastically along a strike.

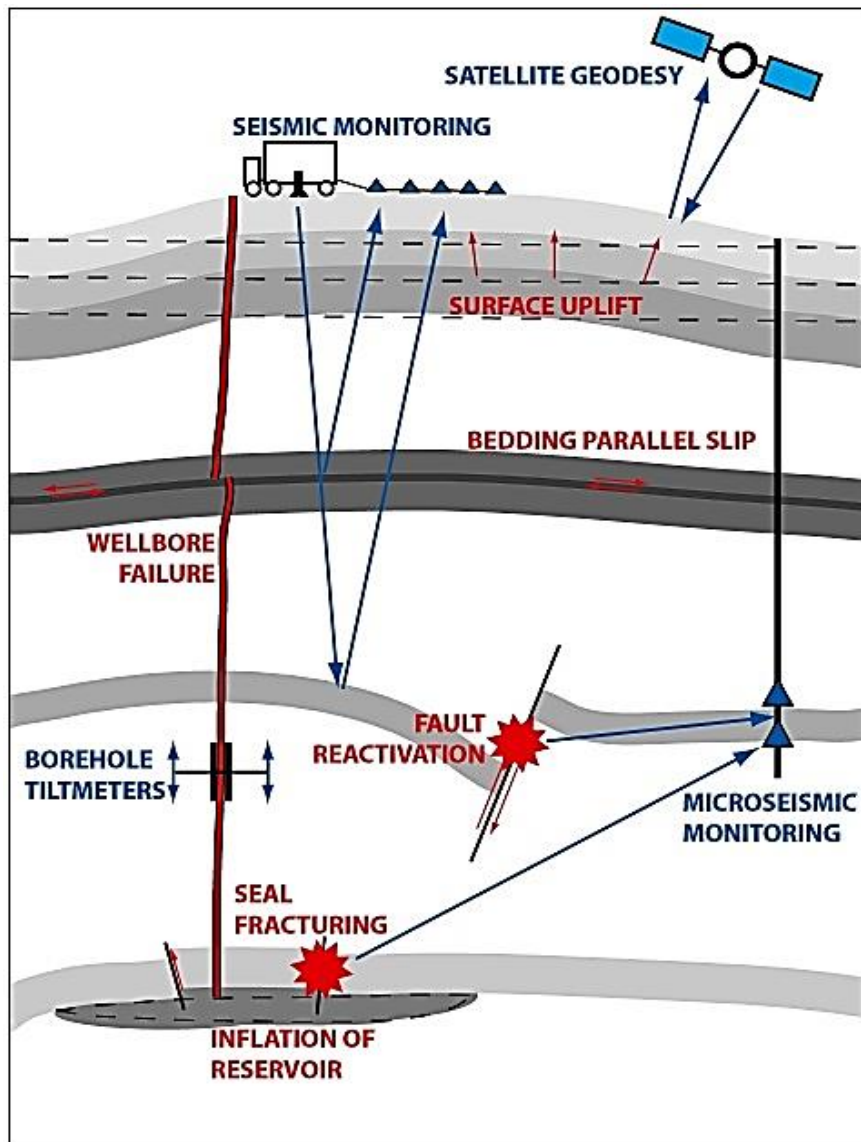


Figure 2-6: Schematic description of geomechanical deformation in CO₂ storage sites (in red text) with potential monitoring options (blue text) [198].

Jeandel et al. [199] reported the lessons learned from natural and industrial analogues for storage of CO₂. Initially, they sampled gases from natural analogues in the Colorado Plateau and the French carbo-gaseous provinces from both leaking and well-confined sites. Furthermore, they performed a tracing study for two years on subsurface natural gas storage. It was pointed out that since in natural analogues, geochemical fingerprints depend on

geological context and containment criteria, these analogues are sufficient tools for the detection of deeply-seated CO₂ toward the surface.

Quattrocchi et al. [192] conducted research on strategic CO₂ natural analogues from slightly anomalous leakage of CO₂, CH₄ and radon along the main activated faults of the strong L'Aquila earthquake (magnitude 6.3, Italy), using soil gas survey and groundwater sampling approaches. Their study also highlighted the implications for risk assessment monitoring tools and public acceptance of CO₂ and CH₄ underground storage. It was revealed that the geochemical measurements from soils can be successfully used for discrimination of activated seismogenic segments. In addition, it was highlighted that the geochemical anomalies are not deleterious to human health. Therefore, there is no associated concern with the CO₂-CH₄ explosion during the recurrence of strong earthquakes (such as L'Aquila), where gases are stored naturally in the subsurface at a depth of 1-2 km. A comprehensive natural CO₂ reservoir dataset, consisting of 76 CO₂ natural analogues around the world, was developed by Miocic et al. [197]. Their analysis highlighted that the key controlling factors for successful retention of CO₂ are thick and multiple caprock, dense CO₂ phase, and a minimum reservoir depth of 1200 m. In addition, although the faults can securely isolate CO₂, it is important to fully characterise the sealing ability of faults during the storage site assessment.

2.4.2 Induced seismicity

Extensive injection experience in oil and gas operations has demonstrated that CO₂ injection procedures must be carefully monitored, otherwise undesirable side effects can be caused. These include both short-term (such as induced seismicity) and long-term geomechanical effects (**Figure 2-7**), that in turn may affect the caprock integrity (as the seal) and, consequently efficiency of storage [200,201]. The CO₂ injection can potentially affect subsurface stress and

lead to changes in in-situ fluid pressure and induced seismicity [202]. Fluid pressures are known to play a key role in seismicity, as pore pressures act against tectonic and gravitational forces. Thus, excessive increase in fluid pressures may cause rock failure, and consequently induced seismicity [203]. Induced seismicity is also associated with hydraulic fracturing when a rock is fractured purposely by injection of water at high pressures to increase permeability of reservoirs such as in enhanced geothermal activities or shale gas production, and the disposal of oilfield waste fluids.

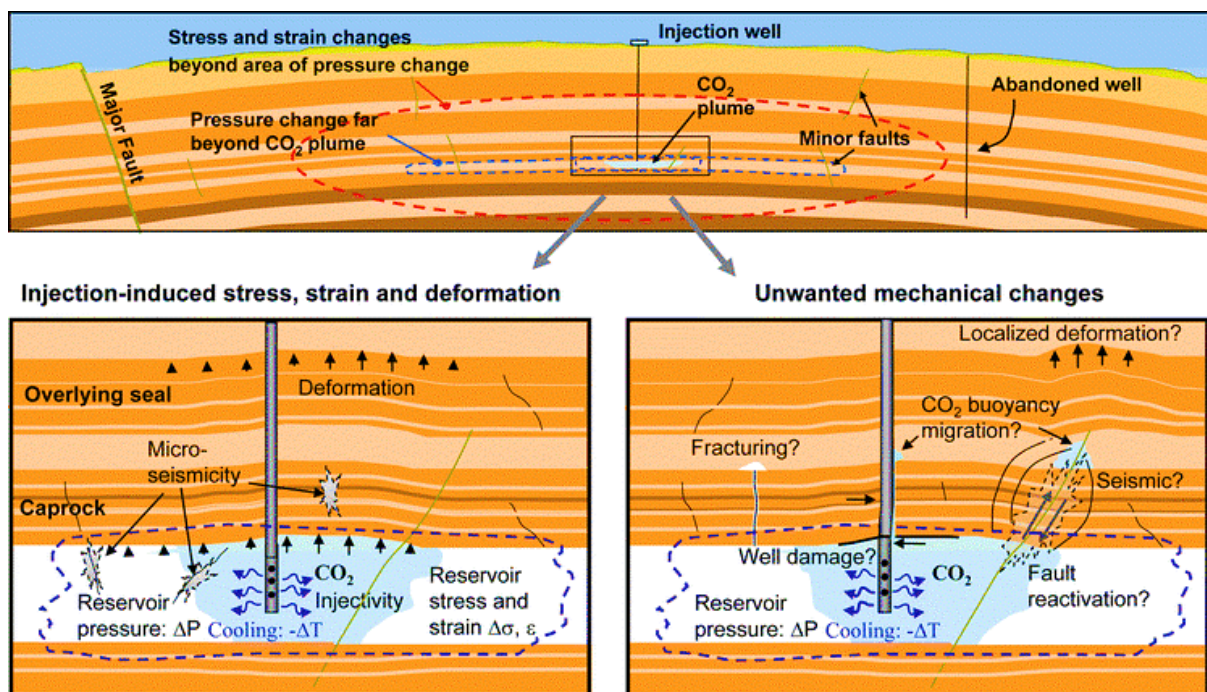


Figure 2-7: Some geomechanical processes and key technical issues with geological carbon storage in sedimentary formations [204].

Nevertheless, there may be some similarities in seismicity induced by CO₂ and by water [205–208]. It is reported that there were similar rates and magnitudes of induced seismicity between the two fluids; however, there is a difference when fluid is injected into low or high pressure. Verdon et al. [207] suggested that since the viscosity and bulk modulus of CO₂ are lower than

water, induced seismicity is less likely to occur. Although from a geomechanical outlook, the key factor that leads to fault reactivation is change in the stress acting on the fault, which is influenced mainly by pore pressure changes caused by injection. Thus, it confirms that the increase in pore pressure across a reservoir is predominantly determined by pore volume occupied by the injected fluid.

The potential risk of induced seismicity caused by CO₂ injection has been outlined above. Accordingly, the following mitigation strategies can be considered [209]: (i) selection of sites with high porosity and permeability, (ii) estimating stress state of potential sites, (iii) selecting sites which are associated with no evidence of faulting, and (iv) selection of sites in regions with low rates of natural seismic activity.

2.4.3 Leakage pathways

In an ideal storage site, CO₂ will be permanently confined to its host formation. However, in the unlikely event of migration and leakage, there are various potential modes in which CO₂ can escape from the storage formation. Leakage pathways for CO₂ can correspond to well leakage, diffusive loss, induced migration by capillary pressure, and escape through faults and fracture networks. However, it should be mentioned that there has been no report that proves noticeable leakage of CO₂ from any known storage sites.

2.4.3.1 Well leakage and abandoned orphaned wells

Leakage of buoyant CO₂ up the wells is possible when the integrity of the well plug or caprock-cement seal is compromised [52,210,211]. Therefore, the presence of high-quality well sealing (and eventual plugging) is a pre-requisite for both hydrocarbon exploration and production, and for CO₂ storage [212]. The American Petroleum Institute (API) standardised a procedure

and cement composition for well plugging in 1952. Accordingly, the wells in the United States are classified in three categories: wells not plugged with cement, wells plugged before 1952, and wells plugged after 1952 [213]. The wells plugged after 1952 are associated with the least potential leakage due to modern technology and strict regulation. However, the possibility of cement degradation should be considered. Slightly acidic CO₂-rich brine can react with alkaline borehole cement, breaking down cement minerals, and forming carbonate minerals and silica. These reactions may be sufficient to block porosity, especially if the volume of secondary solids exceeds that of the original phases. However, if fluid flow were maintained (e.g., through a larger flow feature in a poorly-completed well), there is the possibility for dissolution of the carbonated cement. Factors such as extensive rains, temperature, cement type, rock composition, presence of aggressive impurities such as H₂S and brine concentration control the degree of reaction, and hence degree of degradation [212,213], and consequently alter the lifespan of the cements. This issue can be escalated especially for old abandoned wells.

Connell et al. [214] studied the integrity of wellbore cement in CO₂ storage using core flooding experiments and simulations. Their experimental results showed that the degradation of cement occurs in two stages: the first stage is the precipitation of carbonates from various cement phases, and the second stage is erosion of cement as the calcium carbonate dissolves in formation water. It was revealed that considerable erosion can occur only when the water flow (which is under-saturated in carbonate and calcium ions) across cement dissipates the dissolved calcium carbonate. Thus, even if the bottom of a cement seal reacts initially, the reaction may soon stop if the borehole is well-sealed. On the other hand, if the seal is poor, the continuous fluid flow allows progressive reactions to increase the initial permeability. Thus, assuring the quality of the initial seal is crucial to long-term well-sealing performance. However, this is not usually the case for older infrastructure. Moreover, in some countries, there has been extensive

experience in plugging CO₂-leaking wells, even though it is still important to evaluate and monitor wells depending on case-specific instances [215].

Upon completion of injection and well closure, most abandoned wells are plugged such that CO₂ escape is unlikely. However, abandoned wells are associated with high permeability, and there is a potential risk if the monitoring strategy is not properly deployed. The potential risk is more likely associated with abandoned orphaned wells that are no longer under jurisdiction of the operating company, and the liability is left to the state. In such events and processes, the current regulatory measures may not be adequately sufficient, which may impose a potential risk for security of storage [213,216]. Thus, adopting appropriate regulatory measures for abandoned orphaned wells is necessary and should be considered accordingly.

2.4.3.2 Diffusion

A gradient in CO₂ concentration can cause the CO₂ to migrate through and into the water-saturated pore spaces of rocks by molecular transport [48]. For an intact caprock, the CO₂ transport is limited to a very slow molecular diffusion. Therefore, a very small amount of CO₂ can enter the caprock, which in turn limits the reaction rate of mineralisation in the reservoir, and may potentially alter the porosity and permeability due to induced degradation. On the other hand, for the permeable host rock, the advection of flow is more dominant (at the presence of pressure gradient), meaning larger amounts of CO₂ can pass through, and consequently the impact of long-term reaction and mineral trapping is significant [217,218].

Wang and Peng [219] developed a numerical model to simulate the CO₂-brine interaction in the fracture network, and evaluated the caprock sealing efficiency based on deformation, gas diffusion, advection and sorption of CO₂. It was revealed that the diffusion process results in initial swelling and later shrinking of the shale matrix through sorption of CO₂ and alters the

porosity/permeability of the fracture network. However, in their model geochemical reaction kinetics were not implemented, and should be considered to further improve the accuracy of the simulations. It should be highlighted that although diffusion is an important factor when the potential leakage in CO₂ storage systems is considered, the advection flow induced by temperature and pressure build-up during CO₂ injection can be a source of concern [220], especially for storage systems within fractured fields [192].

2.4.3.3 Capillary leakage

Capillary leakage is another factor by which CO₂ can affect the sealing efficiency of caprock. Capillary leakage occurs when the pressure of accumulated CO₂ within brine-saturated caprock exceeds the capillary entry pressure, P_{c,CO_2} (pressure required for a fluid to enter the caprock pores) [221]. Therefore, capillary entry pressure is the maximum permitted overpressure, and should be considered as a measure for sealing efficiency of the caprock. Capillary entry pressure is a function of brine/CO₂ interfacial tension, γ_{w,CO_2} , wettability of caprock (associated with contact angle, θ , of brine/CO₂/mineral system), and pore size, R_{pore} , within caprock, **Equation 2-3**. Thus, any change in these parameters can alter the capillary pressure and may consequently affect the sealing efficiency.

$$P_{c,CO_2} = \frac{2\gamma_{w,CO_2} \cos \theta}{R_{pore}} \quad \text{Equation 2-3}$$

Caprocks undergo a change of wettability when exposed to CO₂ [222–224]. Li et al. [66], Li et al. [225] and Hildenbrand et al. [226] described the relationship between sealing capacity of caprock and interfacial tension, and reported that the interfacial tension between CO₂ and water is lower than that between oil and water and also much lower than that between methane and

water. It implies that sealing efficiency of any given caprock should be lower with regard to CO₂ than the hydrocarbons.

2.4.3.4 Wettability

Wettability is especially important in CO₂ storage involving a multiphase system which comprises rock, aqueous phase and non-aqueous phase liquids. The affinity of the aqueous phase to cover or not to cover the rock surface is commonly described as hydrophilic and hydrophobic, respectively [227]. The impacts of wettability in CO₂ storage can be both direct and indirect. In the direct impact, wettability can affect injectivity, security of stored CO₂, and structural and residual trapping capacities [227]. Indirectly, mineral and dissolution trapping capacities can be impacted through liquid-mineral and liquid-liquid interface areas [227]. Thus, although wettability is a primary parameter which introduces some significant physicochemical complexities, nonetheless, it needs to be assessed in detail for risk assessment and storage capacity estimations [227].

Chiquet et al. [221] reported that one of the critical factors controlling CO₂ storage efficiency in saline aquifers and hydrocarbon reservoirs is the capillary-sealing potential of the caprock. This potential is a function of the maximum overpressure in the reservoir that the brine saturated caprock can sustain, i.e., of the capillary entry pressure [221]. The capillary sealing potential is controlled by the interfacial tension of CO₂ and brine, the pore size distribution in the caprock, and the water-wettability of caprock minerals [221]. Using experimental evidence obtained from contact angle measurements, Chiquet et al. [221] reported that the water-wettability of quartz and mica is affected when CO₂ is present under pressures typical of reservoir storage conditions. However, the effect is even more pronounced when mica is

present. Moreover, both minerals could represent shaly caprocks and are said to be intensely water-wet in the presence of hydrocarbons [221].

Farokhpour et al. [228] studied the CO₂ wettability of minerals relevant to sealing efficiency of caprocks for storage in saline aquifer. In their study, the changes in wettability were determined by measuring the CO₂ contact angle of mineral substrates such as quartz, feldspar, mica and calcite in brine for pressures up to 400 bar and temperatures of 36 and 66 °C. Their results show that change in the contact angle due to pressure was not significant for CO₂ drop on quartz, feldspar and calcite surfaces. However, there was a significant change in contact angle on mica such that the wettability changed from a strong water-wet to an intermediate water-wet. In addition, at 36 °C, the minimum in contact angle near the critical pressure was observed for quartz, feldspar and calcite while the case of mica may be covered due to a significant decrease in contact angle with increasing pressure. The results from wettability phenomena at the CO₂-brine-mineral interface are important for a better understanding of possible leakage through caprocks and capillary trapping in geologic CO₂ storage [229].

2.4.3.5 Faults and fracture networks

Pre-existing fractures and faults can serve as either fast fluid conduits (that allow flow) or flow barriers [48], and need to be regarded as a potential source of leakage. Seismogenic sources can be used as reference for evaluating the fractures and faults in seismogenic country rocks [80]. It is reported that although the potential for seismic activity is higher in locations with pre-existing faults, the stress rate of rocks can be influenced by confining pressure around the rock, or pore pressure [230]. Excessive injection rate during the injection operation can cause a local pore pressure build-up. Consequently, pre-existing fractures can be reactivated and may cause the formation of small new cracks. In addition, reactions within the caprock and reservoir

system, such as mineral dissolution, may impact the sealing capacity of pre-existing faults and fractures. For example, the reactions can cause the dissolution of fracture-filling carbonate minerals, which in turn can potentially widen CO₂ flow paths, and increase the permeability. Therefore, downhole pressures and CO₂ injection rates should be carefully monitored during, and shortly after, active injection operations. It is also important to measure soil gas and CO₂ flux above and near CO₂ storage sites such as in the case of the Weyburn project [231].

It is worth noting that the anisotropic nature of fault rock permeability may cause a discrepancy in CO₂ migration in different orientations. In a study by Farrell et al. [232] the anisotropic permeability values were measured parallel to fault dips and were found to be up to 10 times greater than the permeability along fault strike. Therefore, it is important to take anisotropic permeability into consideration when CO₂ migration and leakage within faults and fracture networks are determined. In addition, the mechanism of permeability anisotropy by grain-scale deformation within the faulting is not well-quantified and needs to be highlighted.

2.4.4 CO₂-brine-rock interaction

Once CO₂ dissolves in formation water, it forms a weak acidic solution, and this initiates a cascade of geochemical reactions that may ultimately trap the CO₂ as solid carbonate minerals. Initially, CO₂ is trapped as dissolved species (such as CO₂(aq) and HCO₃⁻ ions). Dissolution of silicate minerals rich in Ca or Mg can release these elements into solution and, if the pH is high enough, can lead to the precipitation of secondary carbonate phases, trapping the CO₂ in secondary minerals. The involved reaction processes have many similarities to weathering reactions (though at different pressures and temperatures).

The extent of CO₂-water-rock reactions and proportion of free-phase CO₂ versus dissolved CO₂ versus mineralised CO₂ depend on the amounts of reactive minerals in the storage formation

and their rates of reaction, and will thus vary from site to site. However, also crucial is the extent to which CO₂ can mix with water and rock. In terms of injection operations, this could be enhanced by varying well injection to sweep the CO₂ plume through a large rock volume as much as possible. In terms of natural processes, the descent of plumes of CO₂-rich pore water (denser than CO₂-free pore water) would be aided by high vertical permeability and the absence of laterally-extensive permeability barriers.

CO₂-brine-rock interaction enables both mineral dissolution and generation of secondary minerals. In terms of rates of dissolution/corrosion, carbonate minerals dissolve/corrode faster than feldspar, with quartz being more resistant [233]. Since CO₂-brine-rock interaction affects the pore structure, it is possible that after interaction, permeability of the rock as well as displacement pressure could either increase or decrease, and this will have a consequent impact on CO₂ migration rates.

The dawsonite formation during storage and its potential role in trapping CO₂ in reservoirs has been controversial for more than a decade [234]. While natural occurrences in previously CO₂-charged reservoirs showed a lack of dawsonite, numerical studies revealed the possibility of large-scale storage in these reservoirs. In addition, Hellevang et al. [235] reported that based on thermodynamic calculations, dawsonite can be potentially formed at high CO₂ pressure during the injection, while it is not stable once the pressure decreases upon completion of injection. Although exact conditions for formation of dawsonite (CO₂ pressure, temperature, alkalinity, ionic strength) are highly uncertain, experience from natural occurrences, such as in the sequences of the Songliao and Hailaer basins in China, showed that dawsonite can be formed under CO₂ storage conditions. Despite the available aforementioned evidence on formation of dawsonite during CO₂ storage, its formation mechanism, including nucleation (retention time) and growth rate under storage reservoir conditions are not clearly known, and

should be addressed in future studies. On the other hand, the presence of SO₂ or H₂S as impurities in the CO₂ stream may also liberate and reduce iron from mineral grain coatings [236]. The presence of Fe²⁺ in solution can lead to iron-rich carbonate precipitation and enhance CO₂ mineral trapping. However, the presence of such impurities in the CO₂ stream can raise environmental concerns, and may not be acceptable for CO₂ transport processes [237].

Several studies have investigated CO₂-brine-rock interactions in the context of CO₂ storage, by focusing on flood characteristics and fluid-rock interactions of different formations, including South West Hub of Western Australia [238], Lower Tuscaloosa formation (United States) [239], the Zaosie anticline reservoir, central Poland [240]; and the Weyburn site (Canada) [241]. Saeedi et al. [238] investigated sandstone samples for in-situ multiphase flow characteristics using laboratory measurements. The samples were obtained from the Triassic Lesueur Sandstone (Wonnerup Member) in the South West Hub of Western Australia which is currently being considered for CO₂ storage. The results showed that samples possess favourable characteristics in terms of residual capillary trapping. Although absolute gas permeability of the post-CO₂-flood samples is between 25-60%, this degree of permeability alteration did not significantly affect the petrophysical properties of rock. They proposed that the reduction in permeability can be attributed to formation damage by fines which originated from kaolinite particles occurring within the pore space of rock samples. Soong et al. [239] explored geochemical interactions in a static system for CO₂-brine-rock similar to saline aquifers with samples from the Lower Tuscaloosa formation, Jackson County, Mississippi, United States. After continuous exposure to CO₂ for six months, various analytical techniques were utilised to ascertain permeability values for the sandstone core samples before and after the exposure. Results show that the sandstone permeability decreased due to CO₂ exposure, suggesting that it can have implications for long-term reservoir behaviour. Tarkowski et al.

[240] also performed petrophysical analysis through CO₂-brine-rock interaction experiments using samples from the potential Zaosie anticline reservoir in central Poland. The objective of their study was to determine any induced changes in reservoir rock properties and sealing rocks. In-situ conditions were used to test the samples, and to characterise them by means of specific surface area, porosity, pore size and distribution. It was revealed that both rock matrix and cements were partially dissolved; however, reservoir rock properties did not change significantly, and it had a negligible effect on CO₂ storage.

Cantucci [241] performed geochemical modelling of water-rock interaction to evaluate effects of short- and medium-term disposal of CO₂ in deep geological formations, based on the Weyburn (Canada) site case. Results show that after 100 years of injection, CO₂ can be neutralised by solubility (as CO₂(aq)) and mineral trapping through precipitation of dawsonite. Liu et al. [49] also tested CO₂-brine-caprock interaction to assess the long-term security of stored CO₂ in deep geological reservoirs in the Eau Claire formation (United States). They carried out batch experiments of the caprock in brine at 200 °C and 300 bar to test the extent of fluid-rock reactions. The results showed minor dissolution of anhydrite and K-feldspar, and precipitation (pore-filling and pore-bridging) of clay minerals (smectite and/or illite) and siderite in the vicinity of pyrite.

The CO₂-brine-rock interaction in deep coal seams was numerically and experimentally studied by Wang et al. [242]. Their leachate chemistry analysis showed significant mobilisation of major elements because of dissolution of silicate and carbonate minerals in the coal measure strata. For lithic sandstone (after reaction with CO₂-brine and CO₂-free brine), the amounts of quartz, plagioclase, chlorite and illite increased considerably, whereas the amounts of biotite, kaolinite, illite/smectite decreased. However, calcareous mudstone (reacted with CO₂-brine and CO₂-free brine) showed major alteration of minerals after 12 days of treatment. In addition,

it was revealed that CO₂ was permanently trapped as dolomite and siderite. Although their geochemical simulation can indicate the dissolution and precipitation of mineral to some extent, the results did not agree well with experiments. It was suggested that a better prediction can be achieved by further implementing and improving the effect of fluid flow, geochemical reactions and geomechanics in the model.

2.4.5 CO₂-based impurities

Impurities which are usually present in the CO₂ stream depending on source of captured CO₂, includes O₂, N₂, Ar, NO_x, SO₂, SO₃, H₂O, CO, H₂S, H₂, and CH₄. In CO₂ storage operations, the impact of impurities in CO₂ stream is important to be evaluated for safety and economic transport and storage [105,107,243,244]. Thus, the composition of any CO₂ stream which is transported to a storage site using highly pressurised pipelines is governed by environmental, safety and economic considerations. The National Energy Technology Laboratory (NETL) [245] and the Dynamis project [246] have presented the recommended limits of impurities for CO₂ stream components to serve as a benchmark in studies on CO₂ capture utilisation and storage (CCUS) systems [105]. The impurity limits were proposed after considering several factors, so that it could be used as guidelines for conceptual studies. In any transport and storage applications, the concentration of air-derived non-condensable species such as N₂, O₂ and Ar, is recommended to not exceed 4% [105] while other species may not exceed 5% [247,248] for reasons of impact on the compression and storage systems [105]. Sulphur species which include SO₂ and H₂S pose a risk of corrosion when water is present, and it should be removed to a reasonable degree. Additional concerns on toxicity are also likely to arise especially due to the presence of H₂S [105]. NO_x species, on the other hand, which are likely to be present in the CO₂ stream as by-products of combustion, could equally pose a risk of corrosion due to the

formation of nitric acid [105,249]. The IDLH (Immediately Dangerous to Life or Health) NO₂ limitation is given at 200 ppmv, but for CCS sourced CO₂ streams, 100 ppmv limitation has been proposed [105].

The CO₂ capture process involves three basic processes, i.e. pre-combustion, post-combustion and oxyfuel combustion. In the pre-combustion process, fuel (solid, liquid or gas) is converted into a combination of CO₂ and hydrogen through procedures like CO₂ gasification and reforming; making it possible for carbon to be separated from the fuel prior to being used for heat and/or electricity generation. The post-combustion process involves the capture of CO₂ from flue gas after combustion has occurred; with the aid of appropriate sorbents or solvents or via other procedures such as the use of gas-selective membranes. The oxyfuel combustion, oxygen is separated from the air prior to combustion, and the fuel is burned in oxygen diluted in a recycled flue-gas which produces a gas stream that is highly concentrated in CO₂ and set for purification, compression, transport and storage [16].

Table 2-2 summarises the CO₂-based impurities from different capture technologies. The order of purity from these CO₂ capture technologies are oxyfuel (double flashing) (~ 96%), pre-combustion (~ 98%) and post-combustion (~ 99.6%).

Table 2-2: Summary of CO₂-based impurities from different capture technologies [105].

	Oxyfuel combustion			Pre-combustion	Post-combustion
	Raw/dehumidified	Double flashing	Distillation		
CO ₂ % v/v	74.8-87.0	95.84-96.7	99.3-99.95+	95-99	99.6-99.8
O ₂ % v/v	3.21-6.0	1.05-1.2	0.001-0.4	0	0.015-0.0035
N ₂ % v/v	4.0-16.6	1.6-2.03	Trace-0.2	0.0195-1	0.045-0.29
Ar % v/v	2.3-4.47	0.4-0.61	Trace-0.1	0.0001-0.15	0.0011-0.021
NO _x ppmv	100-709	0-150	3-100	400	20-38.8
SO ₂ ppmv	36-800	0-4500	0.1-50	25	0-67.1
SO ₃ ppmv	20	-	0.1-20	-	N.I.
H ₂ O ppmv	100-1000	0	0-100	0.1-600	100-640
CO ppmv	50-162	-	<2-50	0-2000	1.2-10
H ₂ S/COS ppmv				0.2-34,000	
H ₂ ppmv				20-30,000	
CH ₄ ppmv				0-112	

An elaborate explanation on different capture methods with respect to oxyfuel combustion as provided by Porter et al. [105] is summarised, accordingly. In the raw/dehumidified process, raw fluid gas containing the most abundant impurities (e.g. N₂, O₂, Ar and water) is passed through a water-scrubbing packed tower that allows water and soluble gases (e.g. SO₃ and HCl) to be condensed out. Some amount of CO₂, which comes out of the tower is recycled to the boiler and the rest is compressed to a pressure of 15 bar. Two heat exchangers, for boiler feed-water heating and condensate pre-heating in the boiler steam system, are used in recovering the heat of compression. Furthermore, two more heat exchangers provide cooling using water before and after additional compression to a higher pressure of 30 bar is achieved. This 30 bar CO₂-rich flue gas then proceeds to the next stage where further drying, purification and compression is performed. In the double flashing process, raw CO₂ is initially passed into a thermally regenerated dryer equipped with a dual-bed, after which it is passed through two multi-stream heat exchangers. The heat exchangers have flash separators that allows the separation of liquid high purity CO₂ at low temperature from inert impurities in the gas phase. The CO₂ stream is compressed and cooled for transportation at a pressure of 110 bar. In the distillation process, oxygen is reduced to amounts below 100 ppm to avoid oxidation of hydrocarbons and to limit bacterial activity as a requirement for EOR. Since the presence of N₂ and Ar may increase the minimum miscibility pressure of CO₂ and oil, it is required that species concentration be kept below 1% v/v. The purification of CO₂ is achieved using a distillation column at pressure of 30 bar. To avoid formation of ice (which can potentially block heat exchangers and the distillation column), water is stripped before distillation by adsorption with the aid of molecular sieves.

2.4.6 CO₂ storage capacity estimation

Estimation of the CO₂ storage capacity in potential geological formations is one of the main prerequisites that assures effective and safe implementation of CCS. Several authors have either outlined or deployed various methods for the estimation of storage capacity [39,80,255,256,81,82,85,250–254]. The strategies for estimation of capture capacity can be classified into static and dynamic approaches. The static methods use volumetric and compressibility-based algorithms. On the other hand, the dynamic methods are based on transient numerical or analytical models and are used for prediction of injected CO₂ behaviour within the formation over a desired time period [251,256] and can be used to predict and assess injectivity, wellbore pressure, and tracking of CO₂ saturation within the formations during and after the injection period [257–259].

Quantification of CO₂ storage capacity is mainly correlated with the type of geological formations and their associated trapping mechanisms that act over different timeframes, as well as the boundary conditions (open versus closed) [16,251,252,256]. In this section, the available methodologies for estimation of theoretical, G_t , and effective, G_e , storage capacities for different geological formations will be outlined. It should be noted that theoretical capacity provides a maximum upper limit to the storage estimation, while effective capacity (as a subset of theoretical capacity) presents a more realistic measure by taking into account a range of technical cut-off limits [85].

2.4.6.1 Estimation of CO₂ storage capacity in saline aquifers

Estimation of storage capacity in saline aquifers is very complex due to the different physical and chemical trapping mechanisms, including structural and stratigraphic, solubility, residual, and mineral trapping that simultaneously occur at different rates and timescales [252].

However, to the best of our knowledge, the mineral trapping mechanism has not been taken into account by any storage capacity estimation approach, due to complexity of the process and poorly understood timeframes [251].

2.4.6.1.1 The CSLF method

The Carbon Sequestration Leadership Forum (CSLF) [260] provided individual models for estimation of the storage capacity of saline aquifers based on different trapping mechanisms, namely, structural and stratigraphic, solubility, and residual trappings. The CSLF method for structural and stratigraphic trap is a volumetric approach that assumes complete displacement of native formation water down to the spill point [256], and is calculated using **Equation 2-4**:

$$G_e = G_t C_c = A H \varphi \rho_{CO_2} (1 - S_{wirr}) C_c \quad \text{Equation 2-4}$$

where A , H , φ , ρ_{CO_2} , S_{wirr} are trap area, average thickness, porosity, CO₂ density, and irreducible water saturation, respectively. C_c in Eq. (4) is a capacity coefficient associated with cumulative effects of trap heterogeneity, CO₂ buoyancy, and sweep efficiency. The term $(1 - S_{wirr}) C_c$ is equivalent to storage efficiency factor (E) and is provided by Cantucci et al. [256].

The CSLF method for solubility trapping is a time-dependent (dynamic) approach and needs to be accompanied by numerical simulations at the local- and site-scale for a given period of time [85] and can be calculated by **Equation 2-5** [260]:

$$G_e = G_t C = A H \varphi (\rho_{w_s} X_s^{CO_2} - \rho_{w_0} X_0^{CO_2}) C \quad \text{Equation 2-5}$$

where X^{CO_2} and ρ_w are the CO₂ content (mass fraction) in formation water and density of formation water, respectively, and the subscript 0 and s denote the initial and saturation (at the specified time) state. C is a coefficient that accounts for all factors that affect the spread and dissolution of CO₂ in the entire volume of the aquifer.

The CSLF method for residual trapping is a time-dependent approach and needs to be coupled with numerical simulations. The method is based on irreducible CO₂ saturation in the pore space after completion of the injection step, and is calculated using **Equation 2-6** [256,260]:

$$G_t = \Delta V_{trap} \rho_{CO_2} \varphi S_{CO_2,t} \quad \text{Equation 2-6}$$

where ΔV_{trap} and $S_{CO_2,t}$ are the volume of trap CO₂ and trap CO₂ saturation and can only be specified using numerical simulation at the local- and site-scale and for a given time [260].

2.4.6.1.2 The US-DOE method

The US-DOE (United States Department of Energy) method [251] is a volumetric and compressibility-based approach. It only includes the physical trapping mechanism, namely, structural and stratigraphic trapping, for estimation of effective storage capacity of saline aquifers, and is given by **Equation 2-7**:

$$G_e = A H \rho_{CO_2} \varphi E_{saline} \quad \text{Equation 2-7}$$

where E_{saline} is storage efficiency factor that indicates the fraction of pore volume that will be eventually occupied by injected CO₂. The calculated values of E_{saline} for different cases are provided by Bachu [39,251].

2.4.6.1.3 The pressure-limit method

The pressure-limit approach estimates the effective storage capacity of saline aquifers based on the maximum possible amount of CO₂ that can be injected before reaching a maximum allowed pressure [256]. Zhou et al. [250] proposed a quick assessment method for estimation of saline storage capacity of closed and semi-closed boundary systems at early stages of site selection. This method assumes that the displaced native brine, by cumulative injected CO₂, occupies additional pore volume within the formation which in turn results in pore and brine

compressibility and correspondingly transient (dynamic) pressure build-up, $\Delta p(t)$, that can be readily estimated [250], **Equation 2-8:**

$$G_e(t) = A H \rho_{CO_2} \varphi \Delta p(t) (\beta_p + \beta_w) \quad \text{Equation 2-8}$$

where t is time, and β_p and β_w are pore and native brine compressibility, respectively.

Szulczewski et al. [261] developed a time-dependent estimated approach for both open and closed boundary systems, by taking into account CO₂ displacement to brine, residual and solubility trapping, **Equation 2-9:**

$$G_e(t) = H W \rho_{CO_2} \sqrt{\frac{k Z T}{\mu_w} \frac{P_f - (P_0 - \rho_w g D)}{4 \tilde{P}_{max}}} \quad \text{Equation 2-9}$$

where k , Z , T , g , and μ_w are permeability, compressibility factor, temperature, gravitational acceleration, and brine viscosity, respectively, W and D are width of the well array and depth to aquifer, P_f , P_0 , and \tilde{P}_{max} are fracture, initial, and maximum non-dimensional pressures, respectively. \tilde{P}_{max} is determined based on a numerical second-order finite-volume method.

2.4.6.1.4 The USGS method

United States Geological Survey (USGS) [262,263] developed an estimation method by considering both residual trapping in the open part of the aquifer and buoyant trapping,

Equation 2-10:

$$G_e = \rho_{CO_2} V_b E_b + \sum_{i=1}^3 [\rho_{CO_2} (A H \varphi - V_b) R_w R_{i,se} E_{i,r}] \quad \text{Equation 2-10}$$

where V_b is the buoyant trapping pore volume, R_w is the fraction of available area for storage, E_b and $E_{i,r}$ are buoyant and residual trapping storage efficiency, respectively, and $R_{i,se}$ is residual trapping storage-resources based on residual trapping injectivity classes ($i=1-3$).

2.4.6.2 Estimation of CO₂ storage capacity in depleted oil and gas reservoirs

The estimation of storage capacity in oil and gas reservoirs is the most straightforward and almost the simplest compared to other formations, due to the well-known characteristics of oil and gas reservoirs derived from industry experience [260]. The storage capacity is associated with the reservoir characterisation (such as temperature, effective volume, and pressure), resources (such as original gas in place, OGIP, and original oil in place, OOIP, and recovery factor), and CO₂ properties at the reservoir [256].

2.4.6.2.1 The CSLF method

CSLF [260] developed two approaches for estimation of theoretical storage capacity. The first method is based on OGIP and OOIP, **Equation 2-11** and **Equation 2-12**, respectively, at surface conditions and is associated with the available storage volume that was previously occupied by gas and oil and can be replaced by CO₂.

$$G_t = \rho_{CO_2,r} R_f (1 - F_{IG}) OGIP \left[\frac{P_s Z_r T_r}{P_r Z_s T_s} \right] \quad \text{Equation 2-11}$$

$$G_t = \rho_{CO_2,r} \left[\frac{R_f OOIP}{B_f} - V_{iw} + V_{pw} \right] \quad \text{Equation 2-12}$$

where R_f is the recovery factor, F_{IG} is fraction of injected gas, $\rho_{CO_2,r}$ is CO₂ density at the reservoir, and subscripts s and r stand for reservoir and surface conditions, respectively. V_{iw} and V_{pw} are the volumes of injected and produced water, respectively, and B_f is the formation volume fraction that brings the volume of oil from standard to in-situ conditions.

The second method is based on the geometry (volume) of the reservoir, and is given by

Equation 2-13:

$$G_t = \rho_{CO_2,r} [A H \varphi R_f (1 - S_w) - V_{iw} + V_{pw}] \quad \text{Equation 2-13}$$

where S_w is water saturation.

One of the main assumptions to derive Eq. (11) - (13) is that the evacuated pores during the production of the recoverable hydrocarbons should be filled with the injected CO₂ [264]. However, if the reservoirs are underlain by aquifers, water can invade the pores during the production of hydrocarbons. In this event, the pores occupied with water may not all be available for the injected CO₂, and the storage capacity can decrease. Correspondingly, an effective storage capacity can be calculated using **Equation 2-14** [260]:

$$G_e = C_e G_t \quad \text{Equation 2-14}$$

where C_e is a capacity coefficient that accounts for cumulative effects of CO₂ mobility, CO₂ buoyancy on oil and water, reservoir heterogeneity, water saturation, and aquifer strength.

2.4.6.2.2 The US-DOE method

The US-DOE [251] proposed a volumetric algorithm for the estimation of storage capacity, based on the standard industry approach for calculation of OGIP and OOIP [251,265], given by **Equation 2-15**:

$$G_e = \rho_{CO_2, std} A H \varphi B (1 - S_w) E_{oil/gas} \quad \text{Equation 2-15}$$

where B is the initial oil or (and) gas formation volume factor, and $E_{oil/gas}$ is storage efficiency factor that indicates the fraction of total pores associated with produced oil and gas, that can be occupied by injected CO_2 . $E_{oil/gas}$ can be calculated from local CO_2 -EOR experience, or alternatively from reservoir simulation as standard volume of CO_2 per volume of OOIP [251].

2.4.6.2.3 The Zhao-Liao method

Zhao and Liao [253] proposed a model for estimation of CO_2 storage capacity of highly water-saturated oil fields, by considering two new terms in the CSLF method for CO_2 solubility trapping in oil and water [260], **Equation 2-16**:

$$G_e = \rho_{CO_2, r} A H \varphi S_{CO_2} \quad \text{Equation 2-16}$$

where S_{CO_2} is the sequestration factor and indicates CO_2 solubility in oil and water, CO_2 sweep efficiency, CO_2 displacement, CO_2 recovery factor of oil and water, and can be specified using the local CO_2 -EOR experience, or reservoir simulations (such as the stream tube simulation method).

2.4.6.2.4 The IEAGHG method

IEA Greenhouse Gas R&D program (IEAGHG) provided a model for estimation of storage capacity of gas reservoirs by assuming the reservoir can be refilled with CO_2 until the formation returns to its original reservoir pressure (pre-production pressure), **Equation 2-17** [124].

$$G_e = \rho_{CO_2,r} UPR_{g,std} B E_{gas} \quad \text{Equation 2-17}$$

In Eq. (17) $UPR_{g,std}$ is the ultimately recoverable reserves of gas at standard pressure and temperature.

2.4.6.3 Estimation of CO₂ storage capacity in unmineable coal seams

The estimation of storage capacity in unmineable coal seams involves the displacement of coal bed methane (CBM), and assumes that since the coal has a higher affinity towards gaseous CO₂ than CH₄, the CH₄ in coal will be replaced by injected CO₂ [251,256].

2.4.6.3.1 The CSLF method

In the CSLF method [260], the estimated storage capacity is determined based on the initial gas in place, IGIP and reservoir gas deliverability ($C'R_f$), **Equation 2-18:**

$$G_e = \rho_{CO_2,std} R_f IGIP C' \quad \text{Equation 2-18}$$

where C' is the completion factor.

2.4.6.3.2 The US-DOE method

The US-DOE [251] provided a volumetric algorithm for estimation of storage capacity, **Equation 2-19:**

$$G_e = A H \rho_{CO_2,std} C_{CO_2} E_{coal} \quad \text{Equation 2-19}$$

where C_{CO_2} is the maximum adsorbed volume of CO₂ at standard conditions (Langmuir isotherm volume constant), and E_{coal} is storage capacity factor. E_{coal} is a function of available volume for CO₂ storage and displacement, and indicates the total fraction of bulk coal that accommodates the injected CO₂ [251,256].

2.4.6.3.3 The ZLH method

The Zhao-Liao-He (ZLH) method [254] was developed from a model for estimation of storage capacity of the coal bed in the presence of water. The model is based on the CO₂ adsorption in the coal bed, CO₂ displacement to formation water, and CO₂ solubility in water, **Equation 2-20**:

$$\begin{aligned} G_t = 10^{-7} (A H \rho_{coal,b} g_{cs} R_f C_{ER} \rho_{CO_2,std}) & \quad \text{Equation 2-20} \\ & + [A H \varphi (1 - S_w)(1 - R_w)C_{CO_2,w}] \\ & + [A H \varphi S_w R_w \rho_{CO_2}] \end{aligned}$$

where C_{ER} is the replacement coefficient of CH₄ by CO₂ in the coal bed, R_w is the recovery factor of reservoir water, g_{cs} is coal bed gas content, and $C_{CO_2,w}$ is the CO₂ solubility coefficient in water.

2.4.6.4 Assessment of estimation approaches

The NETL [266] conducted a comprehensive comparative study by applying CSLF [260], US-DOE [251], Zhou et al. [250], Szulczewski et al. [261], and USGS [262] methods on 13 saline formation datasets in the identical conditions. It was reported that the lowest and largest storage capacity estimation methods were presented by Zhou et al. [250] and USGS [262], respectively. Cantucci et al. [256] developed a case study (Italian case study) to assess the estimation approaches by applying CSLF [260], Eq. (4), US-DOE [251], and Zhou et al. [250] methods on a potential reservoir in Po Plain (Northern Italy). In this study, the effect of residual and solubility trapping was rather small, and not considered in the calculations. The largest and lowest storage capacities were obtained by CSLF and Zhou et al. [250] methods, respectively. Although the difference between storage efficiency factor obtained from CSLF and US-DOE

methods was relatively small, there was a considerable discrepancy with the Zhao et al. [250] model. However, as it was pointed out by Goodman et al. [251], the uncertainty in estimation of storage capacity arises from variability and characterisation of aquifers and is much more significant than uncertainty in selection of estimation method. Therefore, estimation and evaluation of specific geologic formation characteristics, rather than utilisation of arbitrary and constant values, is critical and needs to be considered. In addition, although the volumetric approaches are helpful for identification of the prospective CO₂ storage in pre-feasibility studies, further numerical modelling is needed to advance the characterisation, and assess the dynamics of CO₂ storage based on operational and regulatory factors.

On the other hand, it was noticed that no methodology has been developed to account for the mineral trapping mechanism for estimation of CO₂ storage capacity. The significance of mineralisation on overall storage capacity in comparison with other trapping mechanisms is not well-understood. Thus, considering the mineralisation trapping may lead to a more accurate determination of long-term storage capacity.

2.5 Major world CO₂ storage projects

This section provides an overview of current and past major large-scale CO₂ projects worldwide, **Table 2-3**. In most of these projects CO₂ has been stored in saline aquifers or used for EOR.

The most important factor that assures the success of storage projects depends on the security of containment. Accordingly, it is necessary to continually improve site selection and characterisation, technical operation parameters, monitoring and verification tools and quantitative risk assessments. Addressing these factors holistically will form the basis for

appropriate technical regulations and the enactment of positive public perception to enable unhindered deployment of large-scale CO₂ storage operation.

2.5.1 In Salah project

The In Salah storage project (**Figure 2-8**), is located in Algeria, and is jointly operated by a consortium of British Petroleum, Statoil and Sonatrach. This project is a fully operational world-pioneering onshore gas field which receives CO₂ from the In Salah oil field [267]. This formation is a depleted oil and gas reservoir, found at 1800 m [268], 1850 m [269], 1900 m [270,271] in the subsurface (**Figure 2-9**). The project has been operated since 2004 [268,270]. It is estimated that total capacity of the formation is about 17 Mt of CO₂ [20,269], and a total of 4 Mt has already been injected between 2004 and 2011 [272]. During the injection, almost 4000 t of CO₂ per day [53] was injected into the 20-m-thick methane-producing Carboniferous sandstone Krechba formation via three wells [269,270,273]. The injection cost approximately \$6/t of CO₂, and the total cost of storage was estimated around US\$2.7 billion [274–277].

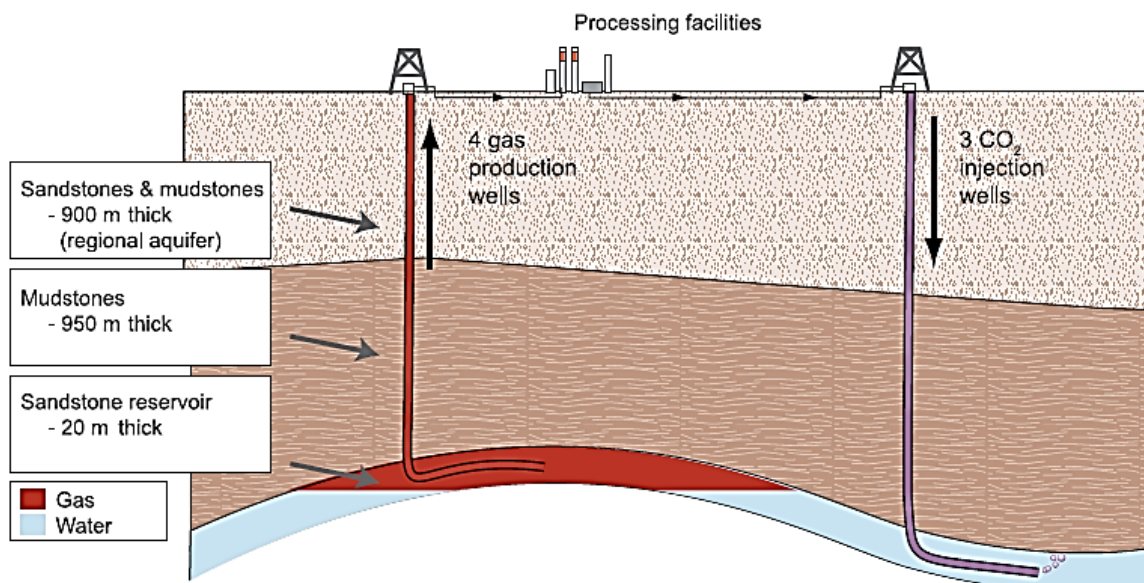


Figure 2-8: CO₂ storage in the Krechba formation, In Salah gas project [16].

The project site has been carefully monitored using satellite InSAR (Interferometric Synthetic Aperture Radar), and time-lapse seismic and micro-seismic data. All collected monitoring data have been used in refining and updating the geological, flow dynamic and geomechanical models of the storage project. The injection was suspended in June 2011 over fears about the integrity of the caprock [268,278]. Although, there was CO₂ migration from reservoir into the overburden, no CO₂ leakage into the atmosphere was envisaged [272]. In addition, Verdon [207] noted that CO₂ injection caused substantial induced seismic activity. Since then, injection strategies for the future have been reviewed, and comprehensive site monitoring strategies outlined through an intensified research and development program. Although the reviewed site monitoring strategies are yet to be fully disclosed in the open literature, the new scheme should include a detailed and improved microseismic monitoring array that provides real-time and intensive geomechanical response surveillance that would allow operators to quickly adjust injection parameters to ensure safe operation of the project [274]. Such monitoring strategies should equally improve understanding of geological and geomechanical characterisation of

reservoir and overburden [267]. Experience from the In Salah project can be relevant in understanding injectivity of CO₂ in other settings around the world where storage is either ongoing or intended in clastic reservoirs with low permeability.

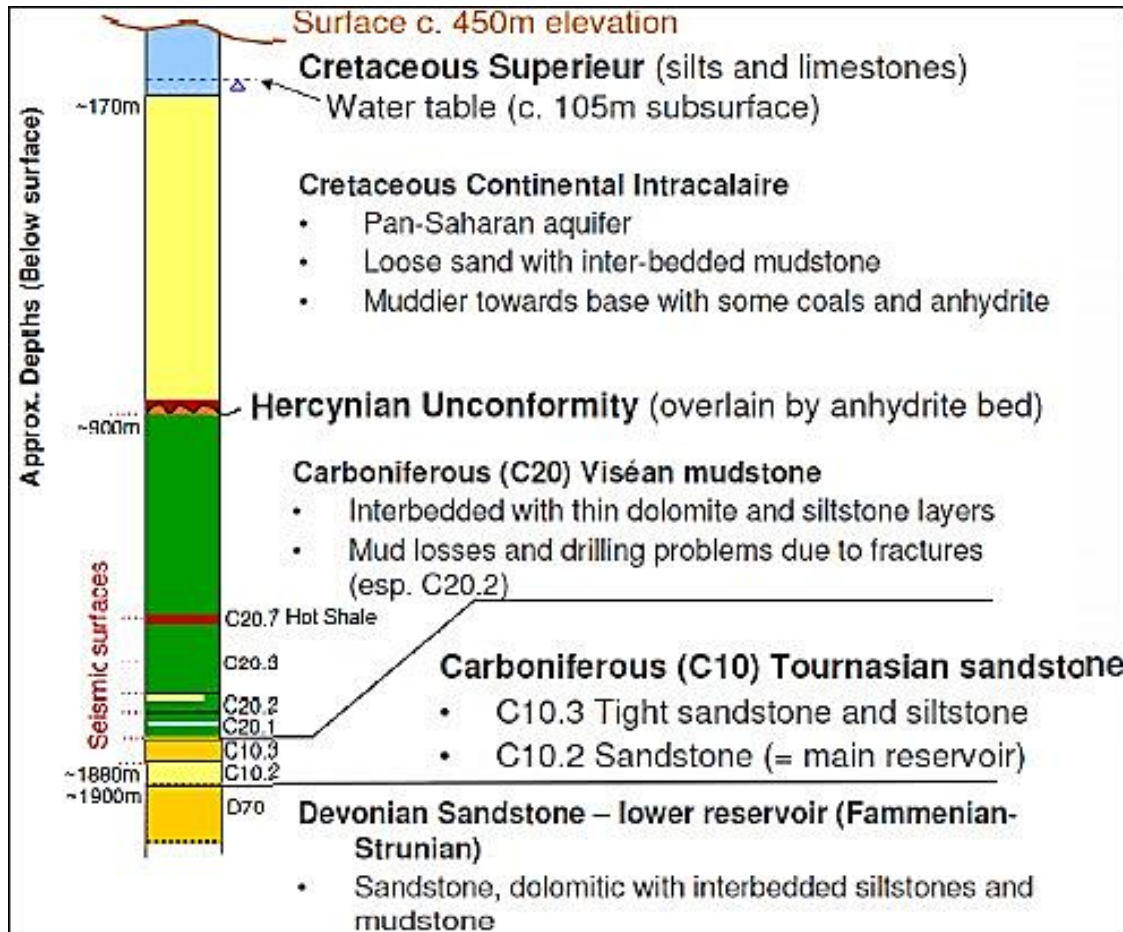


Figure 2-9: Krechba stratigraphic column, In Salah gas project [268].

2.5.2 Ketzin project

The Ketzin storage project is located in Ketzin, Germany, was led by The Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences and Ketzin Partners, started in 2008 and was completed in 2009. The project, which operated for a relatively short period when compared to other projects reviewed here, was sought to store CO₂ in the subsurface so that it

could be monitored to provide information relevant for future policy and environmental regulations. This project was known as the first onshore CO₂ storage project in Europe. A continental Triassic siliciclastic unit called the Stuttgart formation (**Figure 2-10**), which is characterised by sandstones, was used as the CO₂ reservoir [20,279–283]. The source of CO₂ for the project was a hydrogen production and oxyfuel pilot plant (*Schwarze Pumpe*). The CO₂ was transported by a pipeline and stored in a saline sandstone formation aquifer at approximately 630 m in the subsurface. By the end of the project, a total of 67,271 t of CO₂ was successfully stored in the reservoir. Even though CO₂ was stored at a relatively low depth in the Ketzin project reservoir, experience from monitoring of CO₂ flow behaviour in the subsurface did not suggest detectable leakage throughout the period of injection.

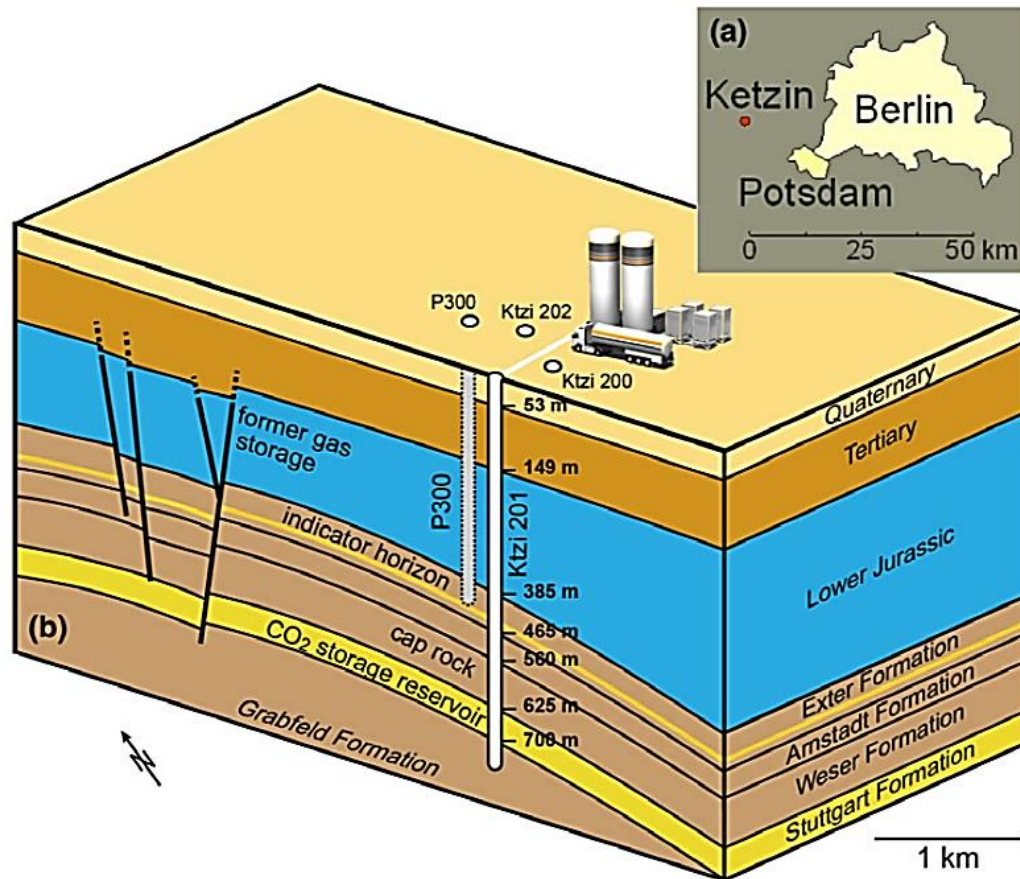


Figure 2-10: (a) Location of the Ketzin CO₂ project; (b) schematic block diagram of the Ketzin CO₂ target reservoir and other structural features [284].

2.5.3 Sleipner project

The Sleipner storage project, located in the mid-central North Sea (**Figure 2-11**), is operated by Statoil. This project is the first commercial-scale CO₂ injection project in the world [285–287]. The project was conceived by the need to evade Norwegian carbon tax, that would be payable if CO₂ had vented [288,289]. Injection began in 1996 and uses a North Sea Norwegian saline aquifer found between 800-1000 m below the sea floor. The storage formation is of the late Cenozoic age and called the Utsira formation [290–293]. The Utsira formation is a 200 to 250 m thick massive sandstone, with 15.5 Mt of injected CO₂ since the project started until

June 2015 [20]. The source of Sleipner's CO₂ is the captured CO₂ through scrubbing from the natural gas processing field located at Sleipner West [288,294,295]. The stored CO₂ is prevented from escaping to the surface by a 200-300 m thick layer of shale called the Nordland shales, which acts as caprock [59,290,296]. Mackenzie et al. [297] reported the occurrence of a 50 m deep confined wedge of sandstone, which is found closer to the lower seal of the Utsira formation, that provides additional capacity for storage in the reservoir.

Although there is no evidence of leakage at the sea bottom, as 3D seismic monitoring has confirmed (**Figure 2-12**), the CO₂ plume has risen through eight thin shale rock layers within the aquifer and reached the caprock in less than three years since the start of injection and storage. However, the shales are very efficient in enhancing mixing and consequently CO₂ dissolution. These will hopefully address major challenges and improve risk management in the lifecycle of CO₂ storage projects in all stages and elements.

Nevertheless, while it is true that extensive experience on storage has been gained from CO₂ storage projects like Sleipner, given the natural heterogeneity of geologic formations that vary from place to place, more far-reaching experience is needed to attain maturity in areas such as site selection, CO₂ flood engineering and reservoir management, workflow integration, monitoring and remediation and regulatory development.

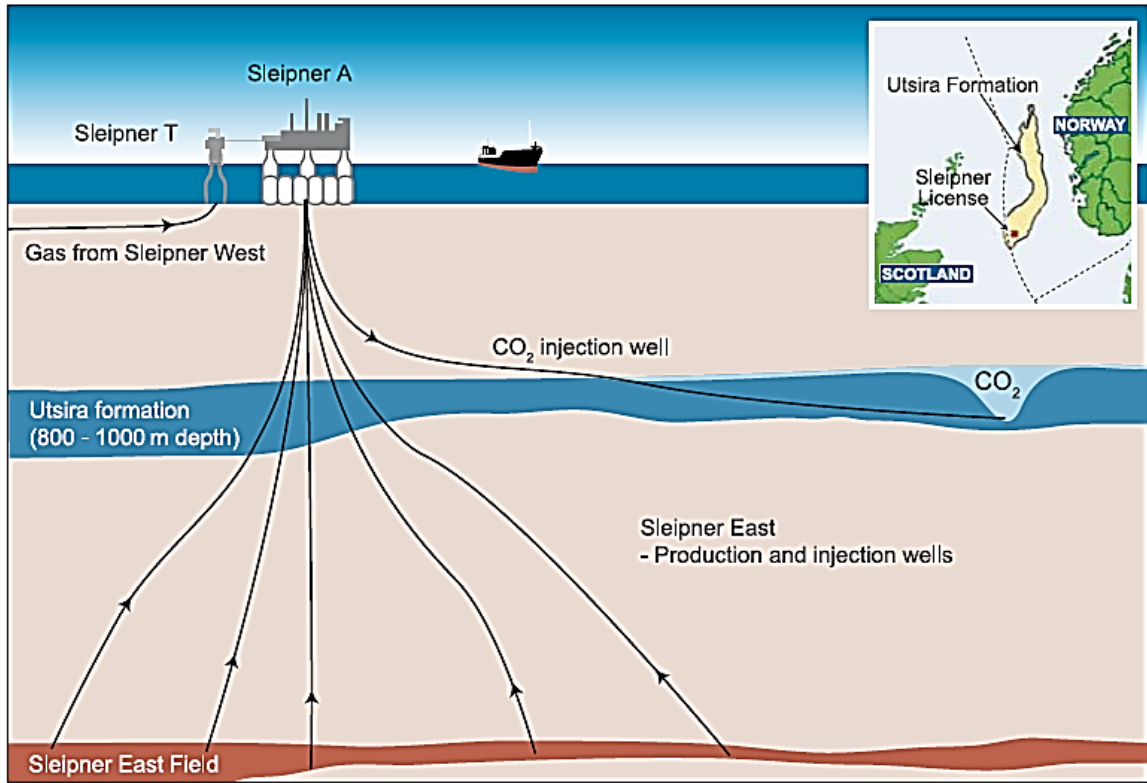


Figure 2-11: A simplified diagram of the Sleipner CO₂ storage project, with an inset depicting the extent of the Utsira formation [16].

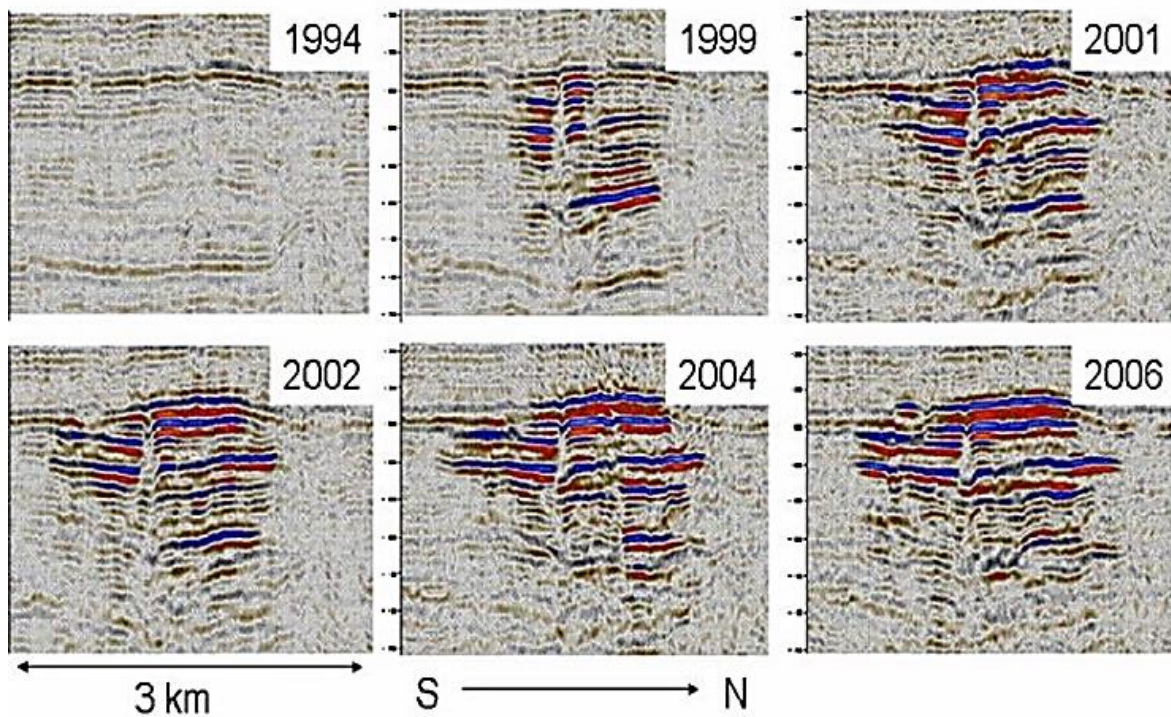


Figure 2-12: Vertical seismic sections of CO₂ plume in the Utsira sandstone, Sleipner gas field, North Sea [298].

2.5.4 Weyburn – Midale project

The Weyburn-Midale storage project, located in south central Saskatchewan (Canada), is operated by Cenovus Energy [299], Apache Canada [300], and collectively managed by Petroleum Technology Research Centre (PTRC) [301,302]. The motivation for the project was to increase oil production (CO₂-EOR) [303] and further research and development in the area [304]. Before the commencement of the Alberta Carbon Trunk Line (ACTL) as the world's largest storage project which was expected to commence injection in 2018 [305], the Weyburn-Midale project, which started in 2000, had been the world's largest storage project [306]. The injection of CO₂ is taking place at rates of about 3000 to 5000 t/d [20] which optimises EOR and increases production [303]. The project is expected to have a lifespan of about 20 to 25

years [53]. It has been estimated that the total amount of CO₂ to be stored in the field by 2025 to 2030 is 20 Mt [59,307]. The operating cost is currently about US\$20/t of CO₂ [20].

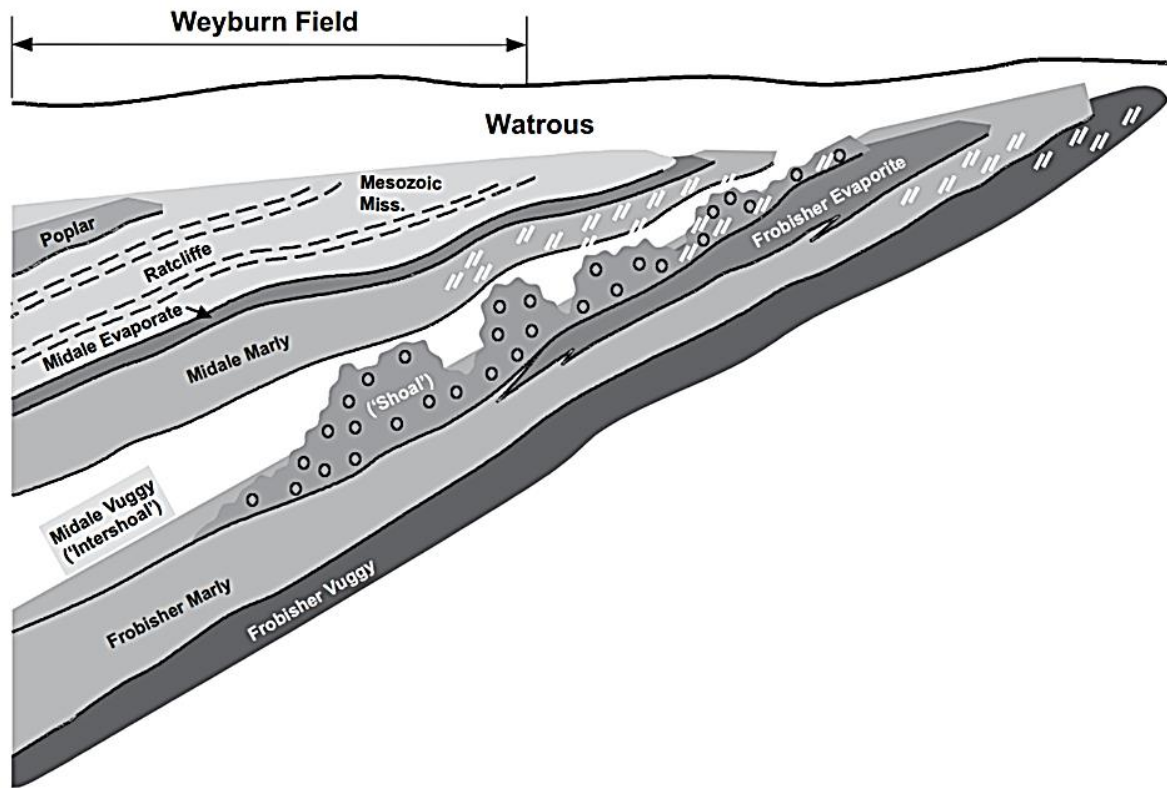


Figure 2-13: Schematic NE-SW cross section through the Weyburn field with underlying geologic formations [308].

There are two different aquifers in the Midale carbonate reservoir (**Figure 2-13**) of the Weyburn project field, namely the vuggy and marly beds [53,241,309,310]. The vuggy beds have suitable reservoir properties in the lower regions, while the upper regions are limestone dominated and characterised by a relatively low permeability but high porosity [53]. The marly beds are a dolostone unit, characterised by low permeability and high porosity. Both aquifer formations are sealed by an anhydrite caprock [307], implying that both vuggy and marly beds can store more fluid or gas than they can transmit. Other information on the geology of the Weyburn area is provided by Wegelin [311] and Rah [312].

In 2011, there was an unsubstantiated claim by a farmer that Weyburn was leaking CO₂ at the surface, from evidence of gas bubbles, dead animals and algal blooms found around a pond in a farm (Kerr farm) near the injection site. This created a controversy in the media but investigations using gas monitoring, CO₂ isotopic analysis and other techniques revealed that there was no leakage of CO₂ from Weyburn [231,313,314].

2.5.5 Snøhvit project

The Snøhvit project, located in offshore Norway, is operated by Statoil ASA and partners [315] which comprise Petoro AS, GDF Suez E&P Norge AS, Total E&P Norge AS, Hess Norge, and Norsk Hydro. Like the Sleipner project, the motivation for CO₂ storage in the Snøhvit project is carbon tax exemption from the Norwegian government [288,316]. Snøhvit started in late 2007, and is the first offshore field where oil is produced without the use of offshore installations. The Snøhvit project sources its CO₂ from an LNG processing project. The CO₂ is captured by a scrubbing approach [317], transported via pipeline from onshore to offshore (**Figure 2-14**), and stored in the saline Tubaen sandstone formation reservoirs at 2600 m deep with a thickness of 45 to 75 m [20]. The total storage capacity of sandstone reservoir formation is estimated around 31 to 40 Mt, and about 0.7 Mt of CO₂ has been safely stored per year.

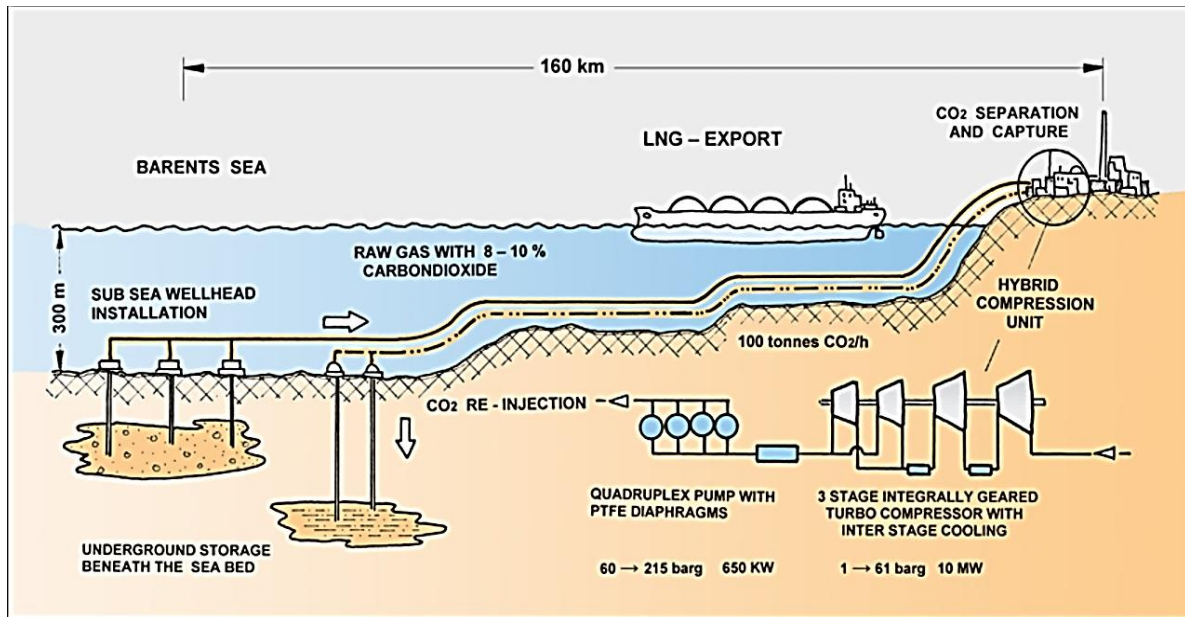


Figure 2-14: Schematic of the Snøhvit storage project showing fluid transport [318].

However, in early 2010 Statoil reported that the storage capacity is lower than that initially expected for Snøhvit, and the possibility of increasing the capacity by drilling new holes or increasing porosity/permeability of the formation by fracturing techniques has been considered. A program has also been set up to monitor and investigate the behaviour of stored CO₂ within the reservoirs of Snøhvit [20]. It is reported that injection of CO₂ ended in April 2011 but injection continued at normal levels in a fall-back reservoir [267].

2.5.6 Alberta Carbon Trunk Line project

The Alberta Carbon Trunk Line (ACTL) project (CO₂-EOR) is in the industrial heartland of Alberta, Canada (**Figure 2-15**), and is operated by Enhance Energy Inc. It is currently the world's largest CCS project, consisting of a 240-km pipeline and infrastructure capable of collecting, compressing, and storing up to 14.6 Mt of CO₂ per year at maximum operational capacity. The CO₂ for the ACTL project is sourced from the North West Sturgeon Refinery and Agrium Fertiliser Plant (Alberta, Canada) [306], and the injection was expected to begin

in 2018 [305]. The total storage capacity is around 2 Gt of CO₂, and the total cost of the project is estimated at US\$1.2 billion [20].



Figure 2-15: Alberta Carbon Trunk Line project location [319].

2.5.7 Otway Basin project

The Otway Basin Pilot Project (OBPP) is located in Australia, and is managed by the Cooperative Research Centre for Greenhouse Gas Technologies (CO₂CRC) [320]. OBPP is considered as the largest geosequestration onshore project, and started in 2008 [53,321,322]. The

CO₂ for the OBPP is sourced from a natural CO₂-rich gas deposit (Buttress gas well) [322], and injected into a 2000 m deep depleted gas reservoir (Waarre formation) (**Figure 2-16**) at a rate of 65445 t/a [323].

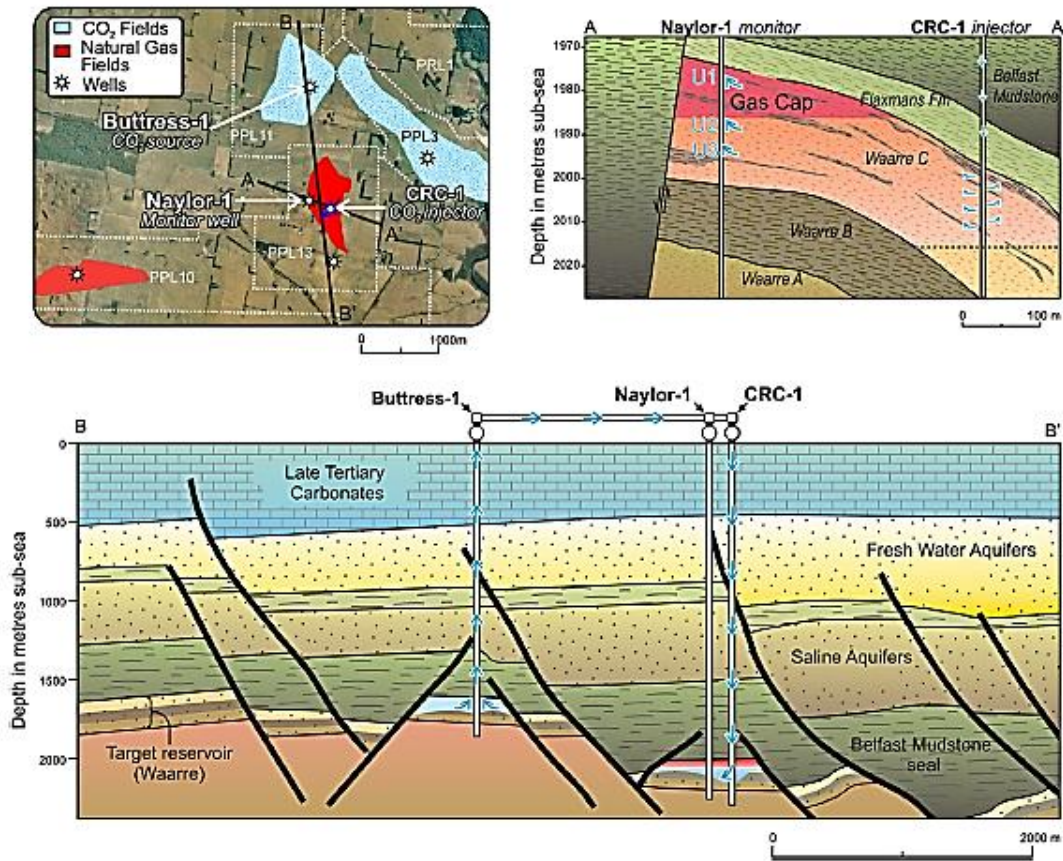


Figure 2-16: (AA') Cross section of the CO₂ injection well (CRC-1) within the Otway project. (BB') The Buttress gas well which is the source for the experiment and the CRC-1 injection well [324]. Note: the dark coloured lines show faults within the subsurface. Faults (if pervious) are cracks in the earth's crust which could be vents for leakage.

Adverse environmental impacts of the OBPP on soils between 2007-2012 were explored by Schacht and Jenkins [325]. Prior and during storage of CO₂ into the Waarre formation, gas concentrations including CO₂, CH₄, N₂, and O₂ were measured for leakage detection. Fixed gas

relationships and isotopic studies showed that CO₂ found in the soil was of biogenic origin, and also there was no deep subsurface source of CO₂. Therefore, the results showed that injected CO₂ has no noticeable impact on the local ecosystem in and around the Otway Project site. Monitoring and investigations are still being carried out within the OBPP, especially to understand geomechanical processes, CO₂ plume migration, caprock integrity and the possibility of fault reactivation [53]. In addition, preliminary probabilistic studies of seismic hazards of the CO₂CRC Otway Project revealed that the potential induced seismicity associated with CO₂ injection and storage is very low [326].

2.5.8 Boundary Dam project

The Boundary Dam storage project is located in Estevan (Saskatchewan, Canada), and is managed by SaskPower. This is the world's first commercial-scale post-combustion capture (lignite firing) and storage project, (**Figure 2-17**), capable of injecting 1 Mt of CO₂ per year, which shows the synergic nature of the CCS value chain. The 90% captured CO₂ is utilised for EOR in the Weyburn field in southern Saskatchewan, which requires only a 66 km pipeline (built by Cenovus Energy), while the remaining CO₂ is used for the Aquistore Project (managed by the PTRC), where CO₂ is stored in a 3.4 km deep brine-sandstone formation.

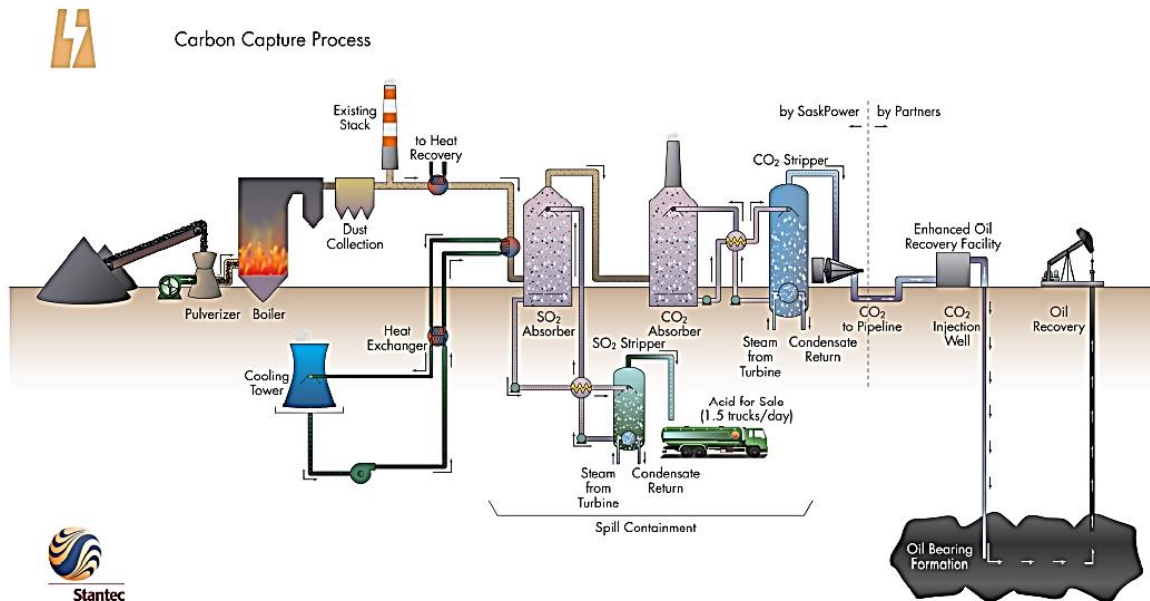


Figure 2-17: The Boundary Dam project process illustration [327].

The deepest units within the Williston Basin, the Winnipeg and Deadwood formations, were chosen as the target zone for CO₂ injection. These two geological formations possess greater storage capacity for CO₂ than any oil reservoir in western Canada. The storage complex suitability was investigated using high-resolution 3D seismic images, and data obtained from injection and observation wells. The obtained data show there are no significant faults in the storage site, and no adverse effect by knolls on the surface of the underlying basement formation. In addition, it was revealed that there is a continuous regional sealing formation in the area [302].

2.5.9 Cranfield project

The Cranfield storage project is located in the Cranfield oilfield in Natchez (Mississippi, USA), and is operated by the Southeast Regional Carbon Sequestration Partnership (SECARB), Department of Energy (DOE), NETL, Southern States Energy Board (SSEB), Texas Bureau of Economic Geology, Denbury Resources, Advanced Resources International (ARI), Electric

Power Research Institute (EPRI), and the University of Alabama (began in 2009). In this project, 1.5 Mt per year of CO₂, sourced from the Jackson Dome (Mississippi), was injected into saline Tuscaloosa sandstone formation occurring down-dip of the Cranfield oilfield [20]. The Tuscaloosa formation is a 15 m thick heterogeneous sandstone of fluvial sedimentology at a depth of 3000 m in the subsurface (**Figure 2-18**), and is widely spread across the region.

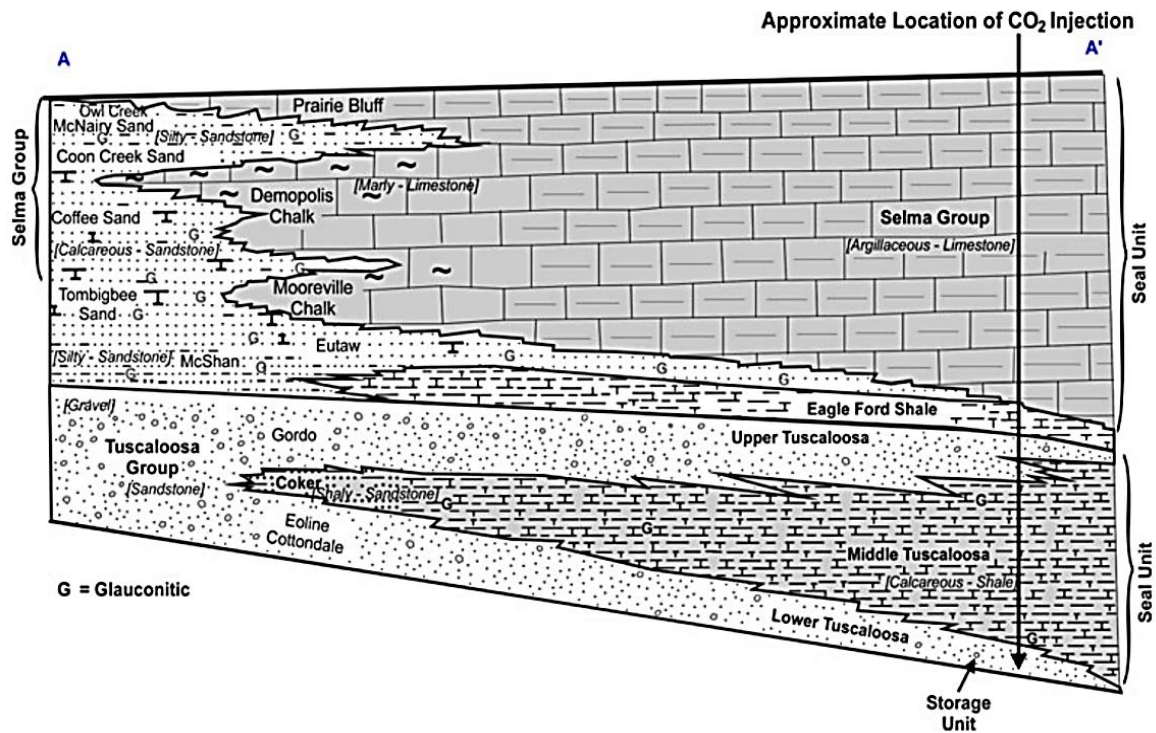


Figure 2-18: Cross section (AA') of lithofacies within the Cranfield project with approximate location of CO₂ injection [328].

The estimated total cost of storage is US\$93 million, and 4.7 Mt of CO₂ was stored until August 2013 [20,329–331]. Anderson et al. [332] investigated CO₂ leakage at the Cranfield project site, between 2009 and 2014, by extensive geochemical monitoring of process-based soil gas ratios, light hydrocarbon concentrations, stable and radioactive isotopes for CO₂ and CH₄, noble gases, and perfluorocarbon concentrations. Their results suggested that although some

gases were detected, their origin cannot be correlated to the subsurface CO₂ reservoirs, and no associated leakage is recorded.

2.5.10 Frio brine pilot project

The Frio Brine Pilot Project (2004-2006) is located in the Texas Gulf Coast (United States), and was operated by DOE and NETL, under the leadership of the Texas Bureau of Economic Geology. CO₂ for the project was sourced from the South Liberty oilfield near Houston [333]. The CO₂ injection in the Frio sandstone formation was conducted in two phases: a 10-day injection in 2004 (1600 t of CO₂ at a depth of 1500 m), and a 5-day injection in 2006 (250 t of CO₂ at a depth of 1600 m) [334].

Prior to implementation of the project, CO₂ storage experience in the United States was limited to hydrocarbon formations [334]. The main objectives of this project were to demonstrate CO₂ injection into brine formation without causing adverse health and environmental effects, to explore subsurface behaviour of injected CO₂, and to develop required experience for the large-scale injection demonstrations in high-permeability, high-volume sandstone [334,335]. On successful completion of the project in 2006, it was suggested that leakage-monitoring above the storage zone should be conducted as an alternative or as a complement to near-surface or surface monitoring [336]. A major success of the project was the ease of on-site analysis using downhole sampling techniques to detect injection tracers and changes in water chemistry, for instantaneous measurements.

2.5.11 Citronelle project

The Citronelle storage project, is located at the Citronelle oilfield in Bucks County (Alabama, United States), and is managed by SECARB, Denbury Resources and Southern Energy. The

project started in 2011, and stored 0.15 Mt of CO₂ within Paluxy formation (thickness of 335 m), in a saline aquifer (southern flank of the Citronelle Dome), at a depth of 3000 to 3400 m. The CO₂ is sourced from the Plant Barry power station in Mobile (Alabama, USA), and transported via a 19 km long pipeline to the storage site [337]. Total storage cost is estimated at US\$111 million [20,338,339].

Although no soil gas baseline survey was reported for the Citronelle Project, Chen and Liu [340] performed geophysical sensing for CO₂ storage using a Derivative of Refractive Microtremor (DoReMi) method to determine changes in geologic formation and migration of CO₂ before and during injection through seismic measurements. The project is currently under post-injection process phase and no evidence of leakage is reported so far [341].

2.5.12 Decatur project

The Decatur storage project (November 2011 - September 2015) is located in Decatur, Illinois Basin (United States), and was operated by Archer Daniels Midland, the Midwest Geological Sequestration Consortium (with Illinois State Geological Survey as leader), Schlumberger Carbon Services, and Richland Community College. The Mount Simon sandstone formation (**Figure 2-19**) was selected as the target formation due to its optimum saline sink and the presence of overlying Eau Claire shale which was expected to provide efficient sealing. The project aimed at assessment of the storage potential of the Mount Simon sandstone formation, and the integrity of the overlying Eau Claire shale as a seal. The total cost of the project was US\$208 million, and CO₂ was sourced from an ethanol production plant in Decatur, and transported via a 1.9 km pipeline. After a year of operation, 317,000 t of CO₂ at the rate of 1100 t/d was injected into the formation using a single injection well. [20,279,342]. It was

revealed that additional storage of 3-4.5 Mt of CO₂ in the same saline aquifer would be feasible in a follow-up project [279].

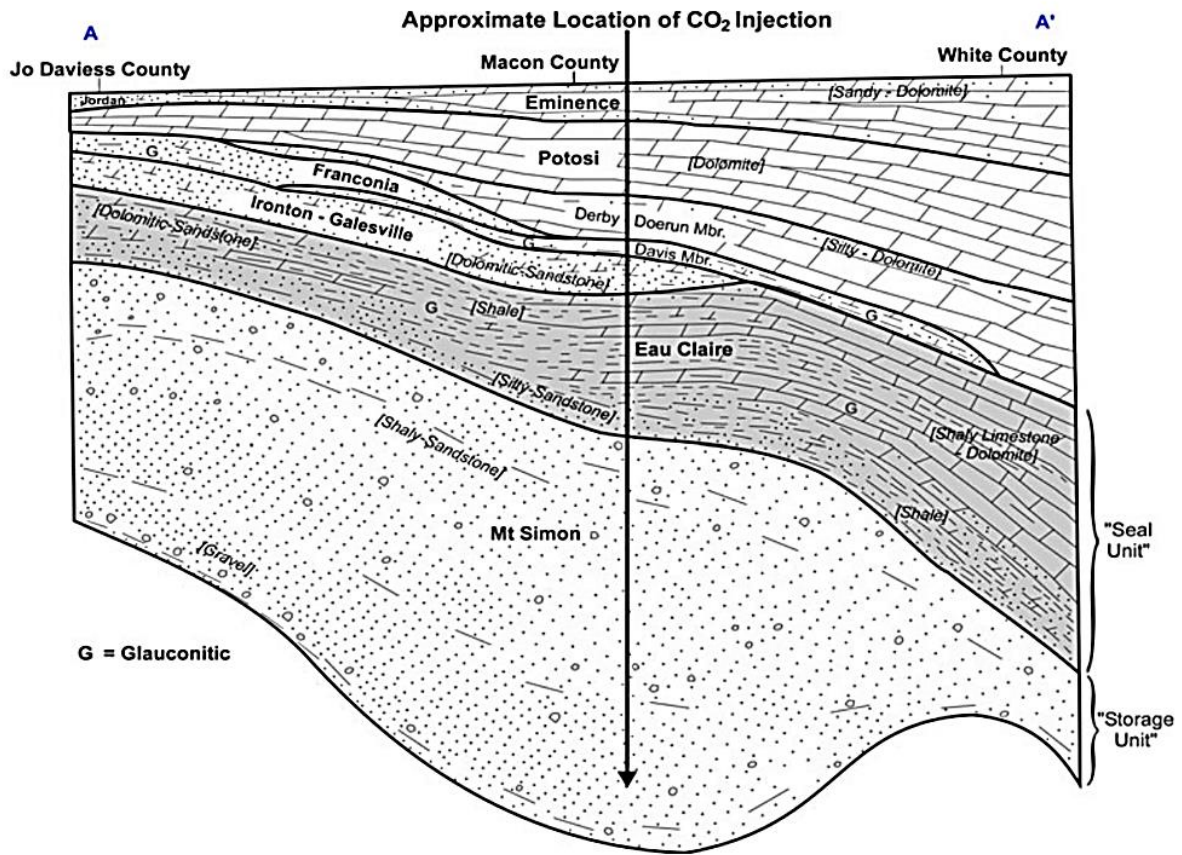


Figure 2-19: Cross section (AA') of lithofacies within the Decatur Project with approximate location of CO₂ injection showing the Mt. Simon formation as storage unit and the overlying Eau Claire formation as seal unit [328].

Streibel et al. [279] performed a comparative study of the Decatur and Ketzin projects, as examples of successful onshore CO₂ storage, by considering project characteristics, monitoring approaches, pressure build-up, and public perception. Both projects aimed to demonstrate CO₂ storage in saline aquifers, but in different fluvial depositional systems, reservoir temperature and pressure conditions, injection rate, and particularly amount of stored CO₂ which was approximately 15 (by volume) times higher in the Decatur project. The results showed that: (i)

the Decatur storage reservoir is thick, but the CO₂ plume is relatively thin, making geophysical detection challenging; (ii) The Ketzin storage reservoir is much thinner, with a thick CO₂ plume, which eases geophysical detection; (iii) geomechanical conditions at Decatur, in combination with the injection rate and pressure, induced microseismic activity, while no such activities were detected at Ketzin; (iv) the induced microseismic activity at Decatur was along pre-existing planes of weakness and could not be detected by geophysical tools; and (v) the project developers recognised the need to monitor the shallow groundwater and soil flux, but they also suggested that subsurface sampling/pressure monitoring and cased-hole logging would be necessary in the case of seal or well failure.

2.5.13 Northern Reef Trend project

The Northern Reef Trend project is located within the Michigan Basin, (Michigan, United States), and is operated by the Midwest Regional Carbon Sequestration Partnership (MRCSP), DTE Energy, Core Energy, and Battelle. The CO₂ is sourced from a natural gas processing plant, transported via a 24-km pipeline, and stored in a depleted carbonate reservoir within the Northern Reef Trend. This formation is characterised by a series of highly compartmentalised reservoirs at about 1800 m in the subsurface where geologic history indicates an ancient coral reef environment. The project started in 2013, and it is planned that in 3 to 5 years of operation about 1 Mt of CO₂ will be injected in the oil field which has undergone waterflooding in recent years and is almost at the end of its productive life. The MRCSP is also tracking and monitoring the behaviour of injected CO₂ to quantify how much CO₂ is retained in the formation after the removal of oil. The total cost of the project is US\$23 million [20,343].

2.5.14 Port Arthur project

The Port Arthur project (January 2013 - September 2015) is located in Port Arthur (Texas, United States), and was operated by Air Products and Chemicals, Denbury Onshore, Bureau of Economic Geology at the University of Texas at Austin, and Valero Energy Corporation. The CO₂ was sourced from the existing steam methane reformers in the Valero Refinery in Port Arthur, and transported via a 19-km pipeline to Denbury's Green pipeline for further transportation over more than 100 km for EOR in the Oyster Bayou and West Hastings oilfields. By May 2013, over 222,000 t of CO₂ was injected into the formation, resulting in an additional recovery of 1.6 to 3.1 million barrels of domestic oil annually. The total cost of the project is US\$431 million [20,344]. To the best of our knowledge, there is no known study on CO₂ monitoring in the Port Arthur project, and it is very likely that a monitoring program will be proposed to confirm that CO₂ is safely stored.

2.5.15 Zama project

The Zama storage project is located near Zama City (Alberta, Canada), and is operated by PCOR (Plains CO₂ Reduction Partnership) and Apache Canada. The project started in 2006 and aims at demonstration of commercial acid gas injection for hydrocarbon recovery, in order to reduce the cost of CO₂ purification. The CO₂ stream contains almost 70% CO₂ and 30% H₂S and is sourced from a gas processing plant [20]. The Zama project is estimated to operate for 18 years and to store 1.3 Mt of CO₂ and 0.5 Mt of H₂S. Since 2006, 80,000 t of H₂S has been stored, which enabled the recovery of more than 35,000 barrels of oil. The storage reservoir of the Zama oilfield, the Keg River formation saline aquifer, is of Middle Devonian, and is at a depth of approximately 1500 m. [20,345].

The co-injection of CO₂ and H₂S (acid gas) into geologic formations for permanent storage is both environmentally and economically beneficial. Bennion and Bachu [346] studied the effect of CO₂ and H₂S at in-situ reservoir conditions on permeability of inter-crystalline sandstone from the Wabamun Lake area (Alberta, Canada). It was revealed that interaction of H₂S-saturated brines-rock is more aggressive than CO₂-saturated brines-rock interaction. Moreover, it is important to note that co-injection of gas mixtures, particularly CO₂-H₂S, has been demonstrated to be safe, and viable for storage to a considerable extent. However, it is also essential to further explore the effect of acid gas injection and its implications on the physical reservoir quality of target formations using both experimental studies for short-term effects and numerical models for long-term prediction.

2.5.16 Ordos project

The Ordos storage project is located in Inner Mongolia (China), and is managed by the Shenhua Group. This project began in 2010 at pilot scale, and will be operated at full scale by 2020. The CO₂ is sourced from a coal liquefaction plant, which is currently emitting 3.6 Mt of CO₂ per year, transported via a 200-km onshore pipeline system, and is injected into a saline aquifer. It is reported that by 2014, up to 150,000 t of CO₂ was stored within the Ordos formation. The total estimated cost of the project is US\$1.46 billion [20,347]. A system for monitoring of ground, above-ground and under-ground was developed [348], and the vertical seismic profile (VSP) was used to track CO₂ migration. The results showed that the injected CO₂ remained within 450 m from the injection well, and no incidence of CO₂ leakage was observed. However, continuous monitoring is suggested to track CO₂ plume movement over a more extended period.

Table 2-3: Major world CO₂ storage projects (large-scale projects either operated previously or currently operating) [20,53].

Name	Location	CO₂ Source	CO₂ Sink	Status	Other important information
In Salah	Tamanrasset, Algeria	Oil and gas	Oil and gas reservoir	2004- 2011	CO ₂ injection stopped for fear about caprock integrity even though storage complex was not compromised.
Ketzin	Brandenburg, Germany	Hydrogen production and oxyfuel plant	Saline aquifer	2008- 2009	First European onshore CO ₂ storage project, motivated by need for information for the future CCS policies in the EU.
Sleipner	Offshore, Norway	Natural gas	Saline aquifer	since 1996	World's first commercial-scale CO ₂ injection project, motivated by the Norwegian carbon tax policy.
Weyburn- Midale	Saskatchewan, Canada	Coal gasification	Oil and gas reservoir	since 2000	World's largest CCS project. In addition to EOR, the project was motivated by need for R&D in the area. In 2011, there were allegations that stored CO ₂ was leaking near injection site, but later investigations did not confirm it.
Snøhvit	Offshore, Norway	LNG processing	Saline aquifer	since 2007	Motivated by the carbon tax in Norway. The first offshore field where oil is produced without the use of offshore installations.

Alberta Carbon Trunk Line	Alberta, Canada	Refinery and fertilizer plant	Oil and gas reservoir	from 2018	When in operation, the world's largest CCS project intended to generate over one billion barrels of oil, with value of ~\$15 billion in royalties.
Otway Basin	Victoria, Australia	Natural CO ₂ - rich gas	Oil and gas reservoir	since 2008	Motivated by the signing of the Kyoto Protocol in 2007, the largest geosequestration onshore project in Australia, aimed at demonstrating transport and geological storage of CO ₂ , testing the regulatory and scientific CO ₂ storage concepts, and evaluating response of public through engaging with stakeholders.
Boundary Dam	Saskatchewan, Canada	Post- combustion lignite-fired plant	Saline aquifer	since 2014	World's first commercial-scale CCS project employing post-combustion capture from lignite-fired plant, motivated by EOR, but also aims to sell CO ₂ , fly ash and sulphuric acid for industrial uses. A major turning point was signing the MoU between SaskPower and UKCCSRC for a 3-year research initiative aimed at improving performance and reducing costs of CCS operations.

Cranfield	Mississippi, USA	Natural source	Oil and gas reservoir	since 2009	First amongst the SECARB commercial-scale projects which reached and exceeded the injection target with > 3 Mt of CO ₂ injected and monitored since the start of the project.
Frio Brine Pilot Project	Texas, USA	Oil processing	Saline aquifer	2004-2006	First demonstration on CO ₂ storage in saline aquifer in the United States.
Citronelle	Alabama, USA	Power station	Saline aquifer	since 2011	Feedstock is provided from the first and largest fully integrated commercial prototype coal-fired source in the USA.
Decatur	Illinois, USA	Ethanol production plant	Saline aquifer	since 2011	Motivated by the need to appraise storage potential of the Mount Simon sandstone formation and the integrity of overlying Eau Claire shale as the seal. Two major milestones reached: establishment of the storage facility; and the public launch of the National Sequestration Education Center.
Northern Reef Trend	Michigan, USA	Natural gas processing	Oil and gas reservoir	since 2013	Uses existing EOR infrastructure to transport CO ₂ 16 km from capture to storage site.

Port Arthur	Texas, USA	Steam methane reformers	Oil and gas reservoir	since 2013	Captured CO ₂ is dried and purified to 97% at the Port Arthur facility, transported 19 km via pipeline to Denbury's Green, and further piped 100 km and used for EOR.
Zama	Alberta, Canada	Gas processing	Oil and gas reservoir	since 2006	Motivated by the need to explore and to demonstrate the effectiveness of injecting mixture of CO ₂ and H ₂ S for EOR, while the costs of CO ₂ separation from H ₂ S are avoided.
Ordos	Ordos, Inner Mongolia, China	Coal liquefaction	Saline aquifer	since 2010 at pilot scale, from 2020 full scale	Managed by China's largest coal mining company. The coal liquefaction plant where CO ₂ is sourced for this project is located on a large deposit of coal tar.

2.6 Conclusions

This work presents a review of state-of-the-art developments in carbon dioxide storage. It discusses critical issues that have been solved as well as challenges that require further attention for CO₂ sequestration, storage site evaluation criteria, behaviour of CO₂ in the reservoir, and methodologies for estimating CO₂ storage capacity. In addition, the major world CO₂ storage projects, including their states of developments were highlighted. Based on our review, it can be concluded that:

(i) Although CO₂ storage, as an emerging technology, is faced with technical challenges which are improving by ongoing research, there are also associated problems with public acceptability of the technology, implying that dispelling of misconceptions on CCS has not yet reached a significant maturity level.

(ii) Although it has been demonstrated that CO₂ can be sequestered by means of mineral carbonation and deep ocean storage, the underground geological storage of CO₂ is still the most viable choice due to economic factors, their wide geographical distribution, and environmental concerns.

(iii) Even though some researchers suggested that CO₂ storage in saline aquifers is preferable (due to relative abundance and availability of huge storage volumes) over oil and gas reservoirs, they often neglect the costs associated with deployment of storage in saline aquifers. Oil and gas reservoirs usually have existing infrastructure that can support storage activities with minor modifications. In addition, they have been comprehensively characterised during exploration and production stages, and could utilise CO₂ for both storage and EOR. Therefore, storage in oil and gas reservoirs can be a better alternative over saline aquifers.

(iv) Since geologic systems are often associated with uncertainties due to their heterogeneity, appropriate site evaluation is crucial for the development of all future storage projects. In addition, continuous monitoring for the existing projects must be undertaken.

(v) CO₂ transportation over long distances from sources to storage sites can incur considerable costs, and is not economically favourable. Therefore, the storage site should be ideally as close as possible to CO₂ sources. In addition, where the point sources of CO₂ are located far from ideal sedimentary formations, the high cost of transportation may be minimised by choosing an alternative storage option. Alternatively, single pipe facilities can be developed for a cluster of CO₂ producers.

(vi) Complex behaviour of injected CO₂ within fluvial depositional structures may potentially lead to undesirable events, such as induced seismicity and leakage, if appropriate reservoir management strategies are not adopted. Thus, detailed geomechanical and geochemical assessments of sites are essential.

(vii) Although monitoring experience from the majority of projects suggested that CO₂ storage can be effectively and securely achieved, issues like induced seismicity can still pose threats to storage projects if such potentials are not well investigated.

Although high-quality knowledge has already been attained covering many aspects of CO₂ storage, the following challenges remain:

(i) Despite the technically proven feasibility of CO₂ storage, low levels of public awareness have greatly affected the pace of technology deployment. Ethical implications of CO₂ storage development need further evaluation, and more effective ethic mechanisms should be adopted to promote public embracing of the technology. Development of scientist-policymaker-public

communication strategies is essential to transfer and highlight the necessity of CO₂ storage to society.

(ii) It is important to establish cost curves involved in the whole sequestration chain such as in the geographical relationship between CO₂ sources and storage sinks. This will play a key role in decision making, especially during large-scale CCS deployment.

(iii) Detailed regional assessments are the key factor to establish how well an emission source would match suitable storage options, and what storage volumes are required. On a case-by-case basis, it is always important to assess risks associated with storage such as CO₂ leakage and induced seismicity, as well as public acceptance of the technology.

(iv) Although legal and regulatory frameworks for facilitating CO₂ storage implementation exist, it is important to make inter-subjective comparisons between frameworks for different countries or regions such as United States-Canada and the European Union, Australia, and Asia.

(v) For further deployment of alternative storage options, such as serpentinite and basaltic formations, it is necessary to enhance our understanding in order to distinguish potential uncertainties and explore the corresponding mitigation strategies. This can include the understanding of CO₂ migration in the presence of potential faults or excessive pressure build-up and the effect of CO₂-rock interaction to facilitate or impede the migration, using both experimental and, particularly, numerical approaches.

(vi) Helping industry in terms of long-term stability or financial instruments is essential to enable timely deployment of large-scale commercial CO₂ storage projects considering that CCS is a short- to medium-term climate change mitigation strategy.

(vii) There are currently limited data defining reservoir system strength variation in relation to reactions of rock minerals by CO₂-enriched brine. Therefore, further research is required to focus on grain-size parameters of the reservoir formations to assess the effect of supercritical CO₂ and how it alters reservoir quality, such as porosity and permeability, and its corresponding effects on CO₂ migration. It is also important to take into consideration the effects of impurities such as NO₂, SO₂ and H₂S in such studies.

(viii) Numerical models capable of describing changes in reservoirs over longer periods of injection and storage could also be utilised to understand long-term effects of CO₂ and impurities on physical reservoir quality. In addition, such numerical models can be potentially coupled with volumetric approaches to further depict the dynamic aspects of storage capacity estimation during and after the injection period.

(ix) Models, with higher performance capacity than existing ones, are required for building and calibrating 3D pre-injection and 4D post-injection reservoir geomechanical simulations to have a better assessment of fault and caprock integrity, especially in deep saline aquifers and depleted oil and gas formations. These models should take into consideration critical pore pressure for fault activation.

(x) There is a necessity in demonstrating stability of borehole seals in the longer term, as their failure will govern CO₂ leakage regardless of the quality of any caprock. It is also required to demonstrate the ability of remediation in the unlikely event of well leakage.

3 CO₂-BRINE-ROCK INTERACTIONS: THE EFFECT OF IMPURITIES ON GRAIN SIZE DISTRIBUTION AND RESERVOIR PERMEABILITY

Abstract

The Bunter Sandstone formation in the UK Southern North Sea has been identified as having the potential to store large volumes of CO₂. Prior to injection, CO₂ is captured with certain amounts of impurities, usually less than 5%_{vol}. The dissolution of these impurities in formation water can cause chemical reactions between CO₂, brine, and rock, which can affect the reservoir quality by altering properties such as permeability. In this study, we explored the effect of CO₂ and impurities (NO₂, SO₂, H₂S) on reservoir permeability by measuring changes in grain size distributions after a prolonged period of 9 months, simulating *in situ* experimental conditions. It was found that the effects of pure CO₂ and CO₂-H₂S are relatively small, i.e., CO₂ increased permeability by 5.5% and CO₂-H₂S decreased it by 5.5%. Also, CO₂-SO₂ slightly decreased permeability by 6.25%, while CO₂-NO₂ showed the most pronounced effect, reducing permeability by 41.6%. The decrease in permeability showed a correlation with decreasing pH of the formation water and this equally correlates with a decrease in geometric mean of the grain diameter. The findings from this study are aimed to be used in future modelling studies on reservoir performance during injection and storage, which also should account for the shifts in boundaries in the CO₂ phase diagram, altering the reservoir properties and affecting the cost of storage.

Abbreviations

BSE Backscatter Electron

ESEM	Environmental Scanning Electron Microscope
GHGs	Greenhouse Gases
PTFE	Polytetrafluoroethylene
QXRD	Quantitative X-ray Diffraction
SDD	Silicon Drift X-ray Detector
S-CO ₂	CO ₂ rock sample
S-CO ₂ -NO ₂	CO ₂ -NO ₂ rock sample
S-CO ₂ -SO ₂	CO ₂ -SO ₂ rock sample
S-CO ₂ -H ₂ S	CO ₂ -H ₂ S rock sample
S-NR	Non-reacted rock sample
UKSNS	UK Southern North Sea
XRD	X-ray Diffraction

3.1 Introduction

Since the start of the industrial revolution, there have been increases in the atmospheric concentration of CO₂ and other greenhouse gases (GHGs) [16], which in turn resulted in a rise of the global average surface temperature, and consequently climate change [1,16]. Between 1906 and 2017, the global average surface temperature rose ~ 0.6-1.05 °C [1,9], and the rate of increase has almost doubled in the last 50 years [1]. The average temperature is certain to rise further unless climate change mitigation strategies are implemented. Carbon capture and storage (CCS) is a key technology aimed at reducing CO₂ emission to the atmosphere. CCS involves capturing CO₂ from large point sources and storing it underground in geologic formations such as saline aquifers, depleted oil and gas reservoirs, unmineable coal seams and basalt formations [16,17].

The storage reservoirs are formed of aggregated rock minerals, and mineralogical properties can change upon variation in reservoir conditions, such as acidity of formation waters, during

injection of CO₂. The changes in mineralogy can often be complex, which could lead to the formation of new minerals and/or obliteration of pre-existing minerals. These changes alter individual grain contacts to either increase or reduce their ability to transmit and store fluids. Thus, one of the greatest variability factors which determines the efficiency of storage is influenced by the host reservoir properties such as porosity, permeability, pressure and temperature of formation and mineralogical composition [349–352].

Several experimental and numerical studies on CO₂ storage in geological media have reported that a significant amount of alteration of rock properties could occur following injection of CO₂ in the reservoir due to the decrease of pH of formation waters [237,287,324,353–357]. Although these alterations are slow under laboratory test conditions, they could be significant and more complex over the storage time frame [49].

More recently, some studies have investigated the influence of CO₂ and associated impurities on the reservoir formation through batch experiments [24,67,243,358–361] and geochemical modelling [22,359,362–364] for both reservoir and caprock core samples obtained from different locations around the world. It was reported that the presence of impurities in the injected CO₂ stream can potentially affect the reservoir storage capacity [23], fluids miscibility in oil and gas reservoirs [365], solubility trapping [237,366], and corrosion of well casings, which can result in environmental concerns in the case of leakage from injection facilities [366], and increased storage cost [24].

It was reported that the dissolution of quartz increased after exposure to CO₂ and SO₂ in high-pressure reactors for 45 days using samples from a potential saline aquifer storage formation in western Canada [67]. Results from the same study highlighted the importance of assessing the rate of quartz dissolution to determine suitable operation conditions for CO₂ injection and

storage. Pearce et al. [358] studied mineralogical controls on porosity and brine chemistry during O₂-SO₂-CO₂ reaction in CO₂ storage reservoirs using samples obtained from a potential reservoir in Queensland, Australia. They reported that there was no change in the mineralogically clean quartzose core samples with originally high porosities after 3 days of exposure to fluids. However, it was noted that the movement of minerals, such as kaolin, in the core samples can potentially reduce the permeability by blocking pore throats.

Although several studies have investigated CO₂-water-rock interactions in reservoir conditions to ascertain mineral reactions and their effects on physical reservoir quality through the alteration of porosity and permeability, the variation of grain size distribution and corresponding impact on permeability upon exposure to impurities contained in CO₂ streams in reservoir conditions are yet to be explored [17]. It is important to note that the reservoir rock permeability is a function of grain size distribution [367,368], and this can be affected by the pH of formation water based on the composition of injected fluids [17,49,53]. Additionally, the majority of work available in the open literature has been based on relatively short-term tests, between 12 days and 6 months [67,239,242,369]. Also, it should be noted that within the previous studies, the effects of impurities on reservoir rock were only considered for exposure periods of 45 days (CO₂-SO₂ test) and 30 days (CO₂-H₂S test), while all other studies considered the effect of only CO₂. Also, due to the inherent heterogeneous assemblages of depositional facies and sub-facies in the reservoir, it is important to address morphological changes through extended experimental tests under more realistic conditions.

Therefore, the aim of this study is to assess the effect of CO₂ and impurities (NO₂, SO₂, and H₂S) on the reservoir grain size parameters and to determine their impacts on physical reservoir quality using permeability variations as indications. Rock samples from the Bunter Sandstone formation (BSF) in the UK Southern North Sea were exposed to CO₂ and impurities for a

prolonged period, and the resulting morphological changes were explored. The results from this study are aimed to be used in future studies for characterisation and modelling of reservoir performance under different compositions of injected fluids.

3.2 Geological background

The BSF in the UK Southern North Sea (UKSNS) has been identified as a target reservoir due to its significant potential to store large amounts of CO₂ (3.8 – 7.8 Gt of CO₂ could be stored using a multi-well injection strategy for a period of 30 years depending on maximum safe pressure increase) [17,95]. **Figure 3-1** shows the distribution of the formation and its onshore stratigraphic equivalent, and a generalised stratigraphy of the offshore UKSNS. The formation has both the required reservoir properties for CO₂ storage and a suitable caprock which acts as a seal to prevent CO₂ leakage [95,370–373]. A study of the BSF top seals has indicated that the presence of the over eight natural gas fields where the formation occurs demonstrates the capability of the formation to effectively seal significant gas volumes over geologic timescales [374]. Although the formation of domal structures within the BSF have subjected the overlying top seals to extensional stresses, but it does not appear to have affected the ability of the faults to seal CO₂ [370,371,373–375]. However, modelling for large-scale CO₂ injection into the formation indicated that more detailed evaluations are required along the reservoir, specifically around the injection point and at regional scale to conclusively determine the structural integrity as well as CO₂ storage capacity [371].

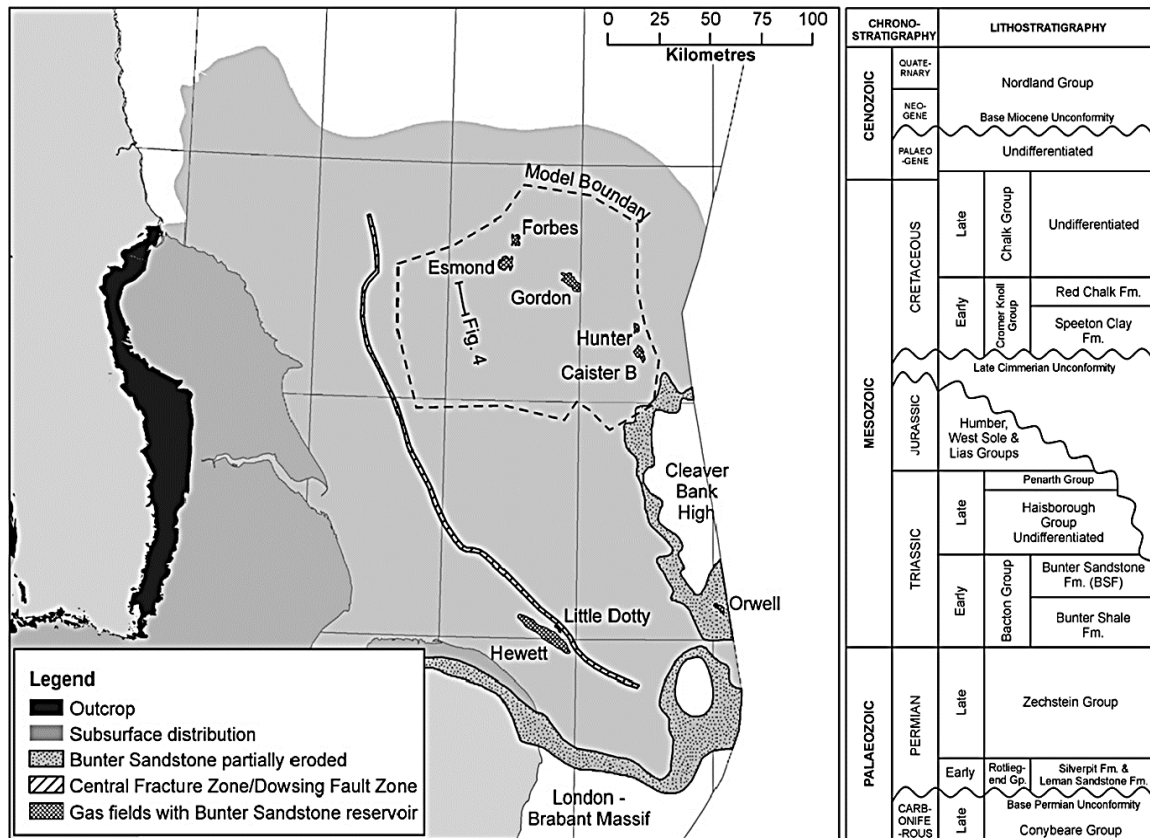


Figure 3-1: Distribution of the Bunter Sandstone formation (offshore) and Sherwood Sandstone Group (onshore) in the UK Southern North Sea (UKSNS) and eastern England [40] and generalised stratigraphy of the offshore UKSNS [39].

The BSF was deposited between 230 and 260 million years ago during the late Permian and Triassic periods. It comprises pebbly sandstones and sandstones intercalated with low amounts of conglomerates, mudstones and siltstones. The BSF reservoir is typically 200 m or more thick, with fair to good porosity and permeability, and it is found at depths between 1000 – 3000 m [371].

There are eight gas fields in the UKSNS where the BSF occurs. The development of salt pillows and domes within the underlying Zechstein Group led to the formation of periclinal folds within

the formation [376] and some of these periclinal are gas-bearing [377] while others are not [371].

Bifani [378] studied the depositional environment of the Gordon, Forbes and Esmond gas fields complex which shows an arid to semi-arid fluvial depositional environment consisting of alluvial fans dissected by braided fluvial channels. Ritchie and Pratsides [377] reported that around the Caister B gas field, sediment is sourced from the west-southwest, and is thought to drain into a playa lake to the north and northeast of the field through a series of low-sinuosity channels, which transect a low-relief alluvial braid plain.

The porosity and permeability for the BSF reservoirs were investigated by Cooke-Yarborough and Smith [379], Ritchie and Pratsides [377] and Bifani [378,380], and typical values for fields are: 21% and 500 mD (Hewett); 21% and 350 mD (Little Dotty); 23-24% and 87 mD (Esmond); 21% and 100 mD (Caister B); 15-25% (Forbes); and 14-21% (Gordon). Ketter [381] reported the occurrence of halite and anhydrite cements within the BSF, with quantities varying within respective fields. The halite cementation which fills rock pores shows that it can be a barrier to permeability below the gas-water contact in the formation of the Caister B field [377], while in the Gordon, Forbes and Esmond fields, a patchy distribution of halite cementation, which obliterates porosity, is prominent within coarser-grained sandstones [378,380].

In areas of the UKSNS where hydrocarbons are not found, highly saline brines fill up open pore spaces of the rock formations. This makes the BSF hydrostatically pressured with variable amounts of brine of variable salinity and density. Brine salinities and brine densities were investigated by Ritchie and Pratsides [377] and Warren and Smalley [382]. Typical values for fields are: 294000 ppm and 1.211 g cm⁻³ (Esmond); 303000 ppm and 1.220 g cm⁻³ (Forbes); 180000 ppm and 1.119 g cm⁻³ (Orwell); and 250000 ppm and 1.174 g cm⁻³ (Caister B). Using

a fluid property mixture simulator (TOUGH2), Pruess [383] calculated *in situ* temperature and pressure for the BSF as 42°C and 9.39 MPa, respectively, at 884 m.

The BSF is structurally compartmentalised [371] and the nature of these compartments in a reservoir is relevant in determining CO₂ storage capacity in saline aquifers. The effective pore volume of each compartment, compartment boundary permeability and compressibility of rock and fluids are key parameters which control the amount of CO₂ which can be injected into a reservoir before pore fluid pressure is reached, which is a limiting factor [371]. Although little published literature exists on the extent of compartmentalisation within the formation, Cooke-Yarborough and Smith [379] reported a pressure communication between the Little Dotty field and the Hewett gas fields even though these fields are approximately 5 km apart [371].

3.3 Experimental procedure

Rock samples from the BSF were used for experiments in this study. The samples were obtained from the UKSNS hydrocarbon industry well 43/12-1 at approximately 1392 m. It should be noted here that although more realistic porosity and permeability values can be measured using core samples, crushed samples were used in this study because of unavailability of core samples from the BSF. Crushed samples were reacted in bespoke titanium pressure vessels, **Figure 3-2**. Each pressure vessel (430 mL) had a gas inlet and a fluid outlet, where the gas inlet was used to supply CO₂ into the vessel through a pair of ISCO 500D syringe pumps (USA) running in ‘constant pressure’ mode [384,385]. Four set of batch experiments were conducted for a period of 9 months. The experiments are designated as CO₂-brine-rock, CO₂-NO₂-brine-rock, CO₂-SO₂-brine-rock, and CO₂-H₂S-brine-rock, considering the impurities added to CO₂ reacting with the brine rock.

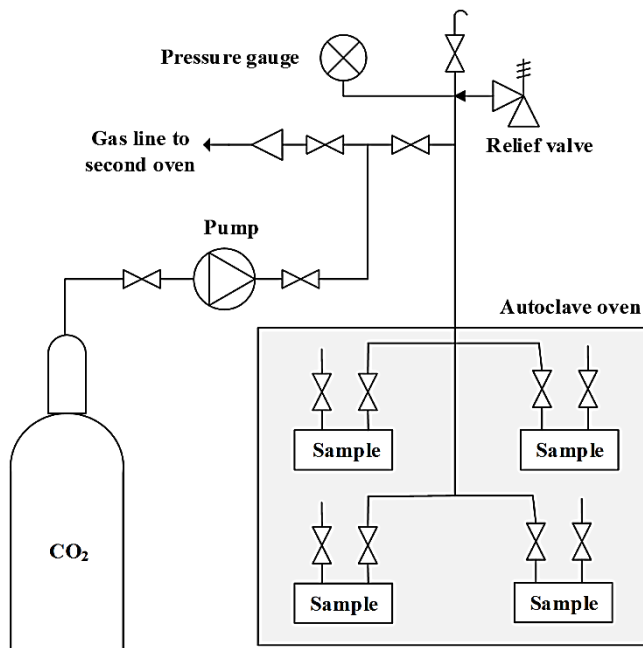


Figure 3-2: Schematic diagram of experimental set-up.

A magnetic stirrer was used to provide sufficient mixing between gases, pore water and samples in the vessel. The PTFE-covered stirrer was placed at the base of each experiment so as to have direct contact with synthetic water and rock sample. The sample was agitated every four hours for two minutes using a stirrer bar. The stirring speed was relatively low in order to avoid degrading the samples. A pressure of 140 bar, which was close to the *in situ* pressure of the origin formation of the samples, was used in the experiments. An elevated temperature of 70 °C, which was higher than the *in situ* temperature, was used to accelerate chemical reactions, i.e., to simulate longer exposure to the CO₂/impurities-containing fluid. The 0.5 M NaCl used in the experiments was prepared with 18 MΩ demineralised water using analytical grade reagents. 300 mL of solutions was added to each vessel with 15 g of crushed rock with size range 125–500 μm. Since a CO₂ concentration of 95%_{vol} and above is typically required for storage applications, CO₂ with 5%_{vol} impurities was used for each test, and the samples with the corresponding content of the impurity in CO₂ are tabulated in **Table 3-1**. The pH of the

fluid was measured at the beginning and at the end of the tests, i.e., after 9 months. For each set of the experiment, 1 mL of the reacted fluid was taken for pH measurements. The procedure consisted of degassing the aqueous fluid straight into a polythene syringe, and immediate pH measurement at room temperature after sampling and degassing, using an Orion VERSA STAR pH meter. It should be noted that since the dissolved CO₂ is degassed to reach equilibrium with the atmosphere, the measured pH is higher than the *in situ* values. However, it has been shown that the degassing effects are considerable only after several hours [386], and it is expected that the discrepancy between measured and *in situ* pH values is negligible in this work.

Table 3-1: Test designation and impurity content (%vol.).

Test	CO ₂	NO ₂	SO ₂	H ₂ S
S-NR	-	-	-	-
S-CO ₂	100	-	-	-
S-CO ₂ -NO ₂	95	5	-	-
S-CO ₂ -SO ₂	95	-	5	-
S-CO ₂ -H ₂ S	95	-	-	5

Upon completion of the tests, samples were collected from the pressure vessel, placed onto a small Buchner funnel, and washed with deionised water to remove saline fluid. The samples were then dried under partial vacuum before further analysis.

3.3.1 Material characterisation

3.3.1.1 X-ray diffraction (XRD) analysis

XRD analysis was conducted using a PANalytical X'Pert Pro series diffractometer equipped with a cobalt-target tube and operated at 45 kV and 40 mA. Samples were scanned from 4.5-85°2 θ at 2.06°2 θ /minute. Diffraction data were initially analysed using PANalytical X'Pert Highscore Plus version 4.1e software. Quantitative mineralogical data were accomplished using a least squares fitting process applying the Rietveld refinement technique [387,388]. For the whole-rock XRD analysis, the samples were ground in a pestle and mortar and then micronised to a fine powder (<10 μ m) using acetone. A 10% portion of corundum standard was added to each sample prior to micronising to detect and quantify crystal and amorphous phases present in the samples. The samples were then back-loaded into standard sample holders for analysis.

3.3.1.2 Fluid sample analysis

The samples were first filtered using a 0.2 μ m Anotop® nylon syringe filter, and then placed into a polystyrene tube. Inductively-coupled-plasma mass spectrometry (ICP-MS) and ion chromatography (IC) techniques were used to analyse the reacted fluid samples with respect to major and trace cations and anions.

3.3.1.3 ESEM analysis

Image acquisition was conducted using a FEI XL30 environmental scanning electron microscope (ESEM) equipped with Oxford Instruments AZTec Energy Dispersive X-ray Spectroscopy software with a 50 mm² Peltier-cooled silicon drift X-ray detector (SDD). Samples were prepared as grain mounts without conductive coatings and under variable

pressure conditions, using water as the SEM chamber atmosphere at pressure of 0.8 Torr. Images were obtained using the backscatter electron (BSE) imaging technique.

3.3.2 Image analysis

The estimation of permeability can be done by: (a) field pumping or injection test; (b) permeameter; or (c) available empirical relationships [389]. In this study, we adopted the latter approach, since it provides an effective method for approximation of variations in grain size and grain sorting after weathering of rock minerals by CO₂-charged brine. In general, the field pumping or injection test can be time consuming and expensive [389]. On the other hand, the laboratory measurements of fluid flows through whole rock cores using a permeameter do not allow for the provision of loose grain samples and a more exposed grain surface area per unit volume for effective analysis. Although the best approach to quantify reservoir-scale permeability is measuring the permeability of intact whole rock cores, it has been shown that empirical correlations can also be used as a valid alternative approach to estimate permeability of reservoir sandstones from unconsolidated rock samples [390]. Namely, Coskun and Wardlaw [390] compared the measured permeability of sandstone rock samples with estimated values from empirical correlations. They reported that the coefficient of determination varied between 0.90-0.94, which indicates the high accuracy of empirical correlations for estimation of the permeability of rock samples.

Mostaghimi et al. [391] and Blunt et al. [392] used image analysis to cover a range of applications such as understanding the behaviour of supercritical CO₂ in aquifers for effective and long-term containment. This revealed that, like other physical properties of porous materials, permeability is a function of a material's complex microstructure. Although many researchers in the past have attempted to relate permeability to other computed parameters such

as specific surface area and porosity [393], there is still no explicit function to accurately correlate permeability, which is crucial to model flow through porous media [391]. Alternatively, the Krumbein and Monk method [368], later adopted by Beard and Weyl [394], is used in this study for more accurate prediction of permeability. In this method, 2D-high-resolution images of rock are obtained from the 3D representations of the samples [395]. This is achieved using the object-based method, which allows measuring grain shape and size [396] as well as statistical analyses of the objects deposited in the 2D images [397–399] as opposed to 3D stack. This method has been commonly used by researchers. For example, Coskun and Wardlaw [390] employed this approach to estimate the rock permeability in a North American oil reservoir using 2D images of rock samples. **Figure 3-3** provides an example of the image analysis process used in this work to estimate the permeability from 2D images of rock samples.

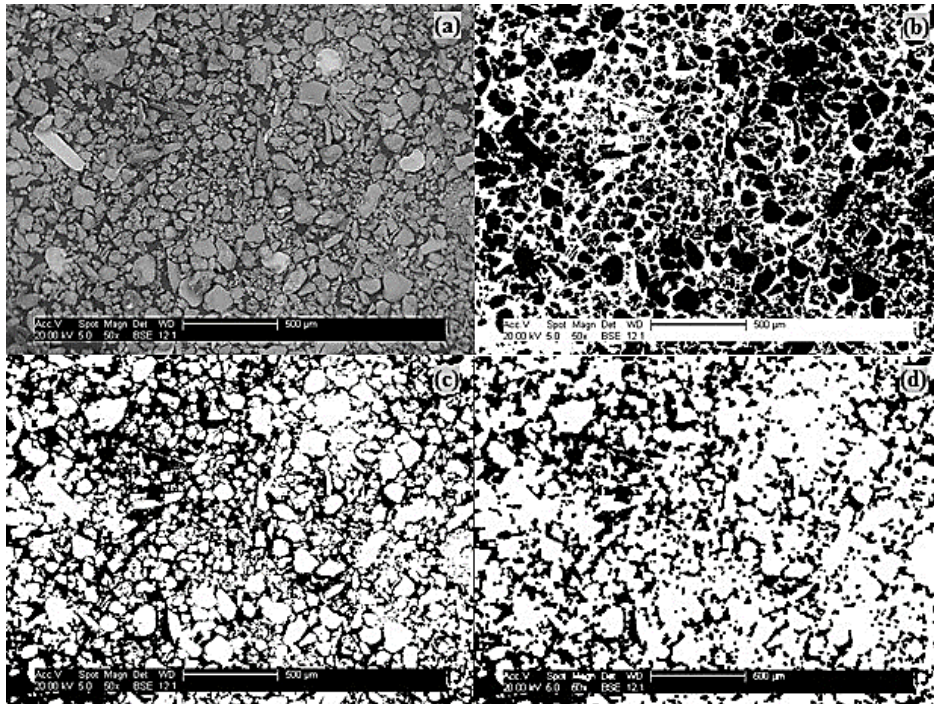


Figure 3-3: Annotated SEM microphotographs under ImageJ software analysis of (a) cleaved surface showing grain morphology, packing and cementation of a post-treatment sample, (b) grain morphology after thresholding of a post-treatment sample, (c) image after further thresholding, and (d) an example of image after thresholding and opening of binaries.

Image processing was conducted using ImageJ software (V. 1.50i). All images are scaled based on the provided scale bars in each photograph, **Figure 3-3**. The image is then sharpened using the ‘Sharpen’ command. Further, the grains were segmented using the ‘Threshold’ command, then smoothed, and the isolated pixels were removed using the ‘Binary (Open)’ command. Finally, the grain size was analysed using the ‘Analyse Particles’ command. For each measurement, a total of 100 grains were sampled and analysed. Each measurement was repeated 4 times and the average quantities were reported in Feret diameter, D (mm), which is defined as the farthest distance in the boundaries of a grain. Further, for each set of

measurements, the Feret diameters of samples were used to calculate the geometric mean, d_g (mm), **Equation 3-1**:

$$d_g = \sqrt[n]{\prod_{i=1}^n D_i} \quad \text{Equation 3-1}$$

Where n is the number of grains ($n = 100$). The calculated d_g is presented in **Figure 3-4**. Grain sorting, σ_D , was then calculated by obtaining the standard deviation of ϕ , where ϕ is defined based on the Krumbein logarithmic transformation, **Equation 3-2** [400]:

$$\phi = -\log_2 D \quad \text{Equation 3-2}$$

The sample permeability, k , was calculated based on a proposed method by Krumbein and Monk [368] and Beard and Weyl [394], **Equation 3-3**:

$$k = 760d_g^2 \exp(-1.31\sigma_D) \quad \text{Equation 3-3}$$

The calculated sample permeabilities are presented in **Figure 3-5**.

3.4 Results and discussion

Previous studies [17,49,401–403] report that the acidification of formation waters, due to the dissolution of CO_2 , leads to brine-rock interaction and triggers dissolution or precipitation of rock minerals and cementation of the rocks which hold the rock grains together. Consequently, it can alter the reservoir rock grain-size characteristics and result in changing the permeability. In addition, the presence of impurities in the CO_2 stream, injected into the reservoir, and their reaction with the formation water can further produce either weak or strong acids which can possibly affect rock permeability.

Quantitative XRD (QXRD) analyses of the samples are presented in **Table 3-2** and the corresponding change observed in the reacted brine (ICP-MS and IC) are presented in **Table 3-3**. The non-reacted sample (S-NR) was characterised as a closely-packed granular sandstone structure which primarily comprised feldspar group minerals (k-feldspar and albite) and mainly quartz as the dominant mineral phases, and clay (mica), iron oxide (hematite), halite, ankerite, and analcime as accessory minerals. Moreover, the inter-grain cementation material is composed of calcite and chlorite.

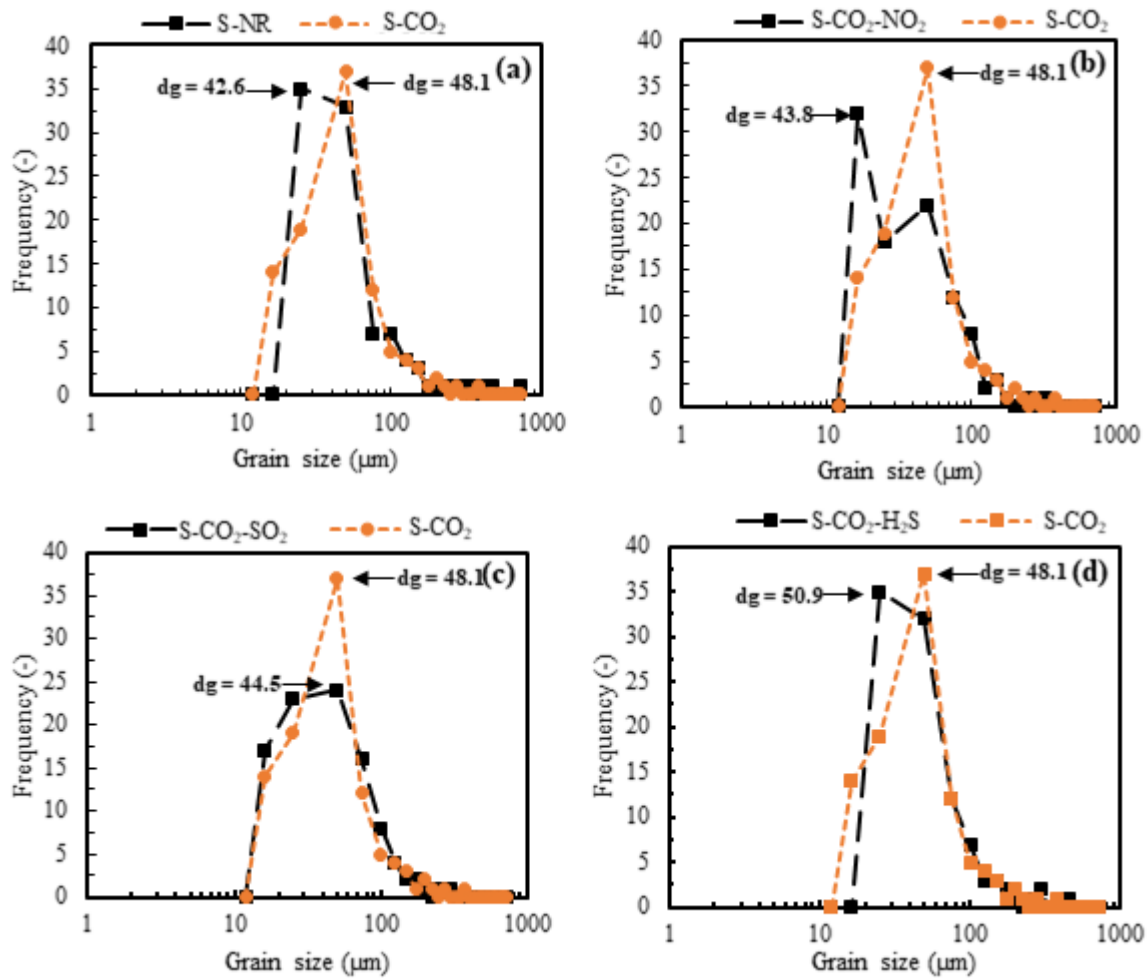


Figure 3-4: Logarithmic plots of changes in grain size distribution and for unreacted and reacted samples with pure and impure CO_2 , showing comparisons between (a) S-NR and S-CO_2 , (b) $\text{S-CO}_2\text{-NO}_2$ and S-CO_2 , (c) $\text{S-CO}_2\text{-SO}_2$ and S-CO_2 , and (d) $\text{S-CO}_2\text{-H}_2\text{S}$ and S-CO_2 . Note: d_g is the geometric mean of the grain diameter.

Table 3-2: QXRD analysis of mineral phases (wt.%) for unreacted and reacted samples.

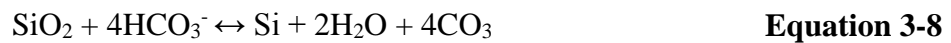
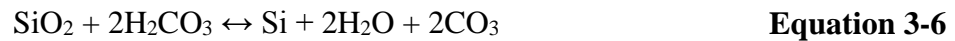
Sample	Albite	Analcime	Ankerite	Calcite	Chlorite	Halite	Hematite	K-feldspar	Mica	Quartz
S-NR	18.1	3.3	17.8	<0.5	0.8	1.1	0.5	7.8	7.9	42.6
S-CO₂	19.5	3.6	10.4	-	1.1	-	0.5	9.2	7.6	48.1
S-CO₂-NO₂	18.7	3.7	15.8	-	1.3	-	0.6	8.8	7.3	43.8
S-CO₂-SO₂	18.5	4.0	15.6	<0.5	1.7	-	0.5	8.5	6.6	44.5
S-CO₂-H₂S	20	3.5	8.9	-	1.1	-	<0.5	9.1	6.3	50.9

Table 3-3: Analyses of reacted brine.

Gas Used	Brine Composition	Ca	Mg	K	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Total S	SiO ₂	Ba	Sr	Mn	Total Fe ²⁺	Fe
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
CO ₂	Initial	<10	<0.60	1.30	0.00	<40	<24	25.0	<0.34	<0.01	17.8	0.02	0.03	<0.005
	Final	247	264	8.10	2036	<40	<24	<16	33.4	1.77	15.1	0.19	0.78	<0.005
CO ₂ -NO ₂	Initial	<10	<0.60	1.30	0.00	<40	<24	25.0	<0.34	<0.01	17.8	0.02	0.03	<0.005
	Final	453	317	13.9	1852	84.1	736	45.0	52.1	1.16	17.2	0.12	41.9	37.6
CO ₂ -SO ₂	Initial	<10	<0.60	1.30	0.00	<40	<24	25.0	<0.34	<0.01	17.8	0.02	0.03	<0.005
	Final	694	368	12.9	2294	834	<24	518	40.3	0.22	18.5	4.95	6.80	6.97
CO ₂ -H ₂ S	Initial	<10	<0.60	3.70	0.00	<40	<24	117	<0.34	0.01	<0.0	<0.01	0.10	0.06
	Final	515	265	2.80	2903	<40	<24	142	24.2	2.12	0.54	3.70	0.18	0.23

After exposure to CO₂ in the S-CO₂ test, the largest changes in weight fractions were shown by quartz, which increased by about 11.4%. Meanwhile the fraction of ankerite decreased substantially by about 41.6%, while halite disappeared completely, which could be related to the initial salinity of the solution, and could also be further influenced by stirring during experiments as was discussed by Weisbrod et al. [404]. A notable observation is that the addition of NO₂ and SO₂ decreased the fraction of quartz. On the other hand, the presence of H₂S in the CO₂ stream increased the fraction of quartz. The increase in quartz fraction is marginal given that H₂S is only slightly soluble in water to produce a weak acid, which immediately dissociates to produce other ions.

Depending on the impurities and pH of the formation water, quartz can react with carbonic acid, hydrogen ion or bicarbonates, which had already formed from the dissolution of CO₂ in water, **Equation 3-4 to Equation 3-8** [401,405].



In addition, the fraction of quartz can be possibly influenced by the reaction of k-feldspar and CO₂ within the formation water, **Equation 3-9** [406].



However, the laboratory tests were relatively short compared to a real storage lifespan, and the quartz and feldspar dissolution may require extended time. Therefore, longer tests are required to further confirm the dissolution/precipitation behaviour of quartz and feldspar.

The effect of the CO₂ stream impurities on the pH of brine over 9 months is given in **Table 3-4**. The variation in permeability of rock samples after exposure to pure and impure CO₂ streams is a function of the impurity type, the pH value of brine, and the stability of rock minerals. Depending on the type of impurity associated with the CO₂ stream, the pH is altered due to the formation of strong or weak acids.

Table 3-4: The effect of CO₂ stream impurities on the pH of brine over time.

pH	CO ₂	CO ₂ -NO ₂	CO ₂ -SO ₂	CO ₂ -H ₂ S
Initial	7.65	7.65	7.65	7.65
Final	5.97	5.23	5.86	6.55

The pH of the brine exposed to the CO₂ stream, for the period of 9 months, was decreased from 7.65 to 5.97. In comparison with dissolution of the pure CO₂ stream in the formation water that forms carbonic acid or bicarbonate [407], dissolution of NO₂ impurity results in the production of a weak acid, HNO₂, and a strong acid, HNO₃, **Equation 3-10** and **Equation 3-11**.



Therefore, the addition of NO₂ led to a reduction in pH from 5.97 to 5.23. The addition of SO₂ led to a reduction in pH of the formation water from 5.97 to 5.86. The effect of SO₂ in the CO₂ stream can be explained according to **Equation 3-12** to **Equation 3-14**:



These reactions cause the formation of weak acids H₂SO₃ and H₂S, and/or strong acid H₂SO₄ in the formation water. The reduction of the pH due to CO₂ and SO₂ mixtures in a sandstone saline aquifer during injectivity and storage has been confirmed by Waldmann et al. [22].

The addition of H₂S led to an increase in pH of the formation water from 5.97 to 6.55, which can be explained according to the following reactions **Equation 3-15** and **Equation 3-16**:



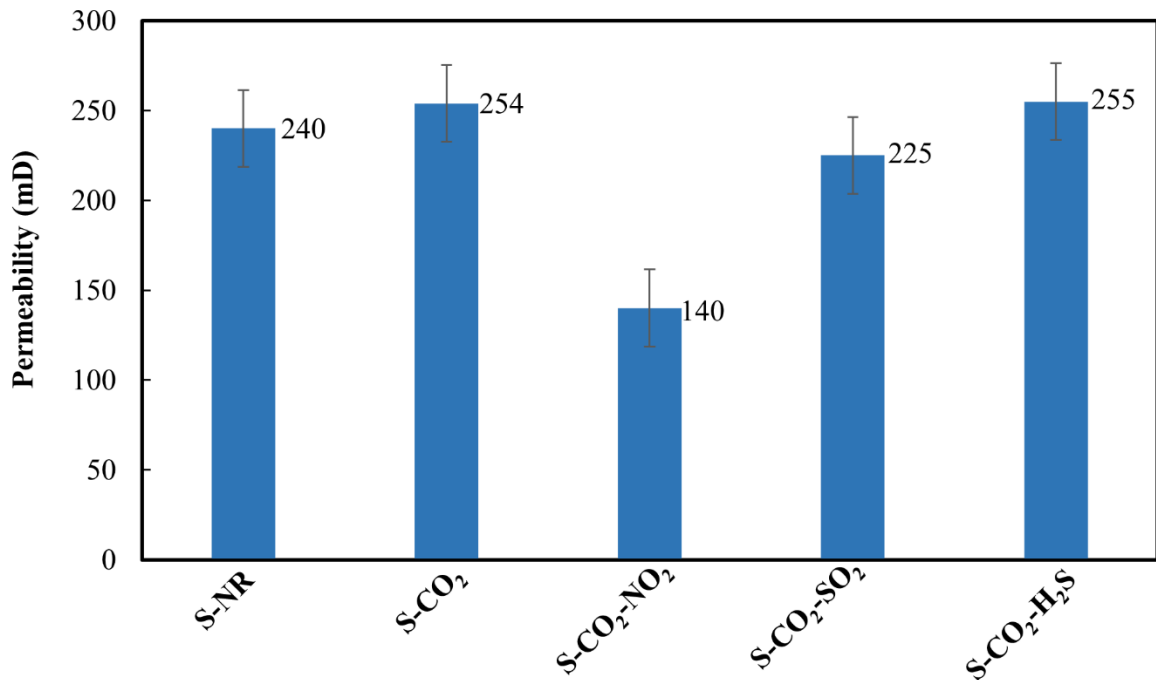
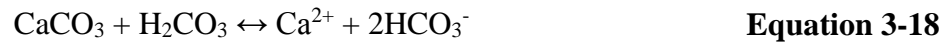


Figure 3-5: Permeability of unreacted samples and samples reacted with pure and impure CO₂.

Figure 3-5 shows the effect of impurities on the permeability of rock samples over 9 months. The permeability of the sample exposed to the CO₂ stream was increased from 240 to 254 mD. When compared with samples exposed to impure CO₂, the introduction of NO₂ and SO₂ decreased permeability to 140 and 225 mD, respectively, while the effect of H₂S was negligible (255 mD). A reduction in the permeability in the presence of SO₂ (1%_{vol.}) is also reported by Waldmann et al. [22]. They found that SO₂ accelerates the dissolution of silica and precipitation of carbonates and sulphates, causing an alteration in the permeability of the samples. Wang et al. [67] also observed that the dissolution of quartz was much faster in the presence of SO₂ (2.5%_{vol.}), when Si is undersaturated in water. In addition, they found that the enhanced dissolution of quartz can cause precipitation of salt, which could also decrease the permeability of reservoir rocks.

As mentioned, the permeability of the rock sample is affected by dissolution/precipitation of both the cementing material and rock minerals such as calcite. The dissolution/precipitation of calcite involves three main simultaneous reactions, **Equation 3-17** to **Equation 3-19** [408]:



It is reported that the dissolution of even small amounts of cementing material (e.g., calcite) can considerably change the rock permeability by affecting the grain size distribution [409–412]. **Figure 3-4** presents the effect of pure and impure CO₂ on the grain size distribution of the rock samples. In comparison with the S-NR sample, exposure to the pure CO₂ stream (S-CO₂ test) resulted in an increase in d_g of the sample from 42.6 to 48.1 μm. The increase in d_g can be associated with the decreased pH of the formation water in the S-CO₂ test. With regard to the S-CO₂-NO₂ and S-CO₂-SO₂ tests, the introduction of NO₂ and SO₂ into the CO₂ stream resulted in a reduction in d_g to 43.8 and 44.5 μm, respectively. However, in the S-CO₂-H₂S test, the addition of H₂S into the CO₂ stream resulted in a slight increase in d_g to 50.9 μm. The decrease in d_g of rock samples exposed to impurities can be attributed to the lower pH of the formation water, compared to that with S-CO₂, which usually results in further dissolution of cementing material and quartz as the dominant mineral. However, it can be noted that switching from S-CO₂-SO₂ to S-CO₂-NO₂, for example, caused only a slight change in d_g but there was a significant change in permeability. This phenomenon can be explained by production of strong acid due to dissolution of CO₂-NO₂ in the formation water, which enhances dissolution of inter-grain cementation, increasing permeability without necessarily causing a pronounced effect on grain size.

Finally, it should be noted that in addition to experiments, numerical simulations should be performed to determine the effects of CO₂ and impurities, especially on storage capacity beyond the injection point, to understand overall injection efficiency. Previous studies [413–415] required reservoir permeability values to solve problems of fluid flow in a variety of realistic settings, and the permeability values from this work can be used as inputs for cells in reservoir models, as well as for better understanding of risk associated with impure CO₂ injection and migration in the reservoir.

3.5 Conclusions

In this work we studied, over a 9-month period, the changes in grain size parameters due to exposure to CO₂ and impurities in simulated reservoir conditions using rock samples of the Bunter Sandstone formation to ascertain implications on physical reservoir quality using permeability variations as an indicator. The most significant changes in permeability were caused by CO₂-NO₂ brine-rock reactions which reduced sandstone permeability by 41.6%. The results in this study revealed that the geometric mean of the grain diameter, and consequently, permeability of the rock samples reduced due to the effect of CO₂ and impurities, which can be correlated with decreasing pH of the formation water. These results also suggest that it is necessary to evaluate the physical reservoir quality of potential storage formations depending on the nature of impurities present in the CO₂ stream. The obtained data can, therefore, reduce the uncertainties about CO₂ storage capacity with impurities in the CO₂ stream and can be used to model the operation and performance of CO₂ storage in saline aquifers.

4 A MODELLING STUDY TO EVALUATE THE EFFECT OF IMPURE CO₂ ON RESERVOIR PERFORMANCE IN A SANDSTONE SALINE AQUIFER

Abstract

Carbon capture and storage (CCS) is expected to play a key role in meeting greenhouse gas emissions reduction targets. In the UK Southern North Sea, the Bunter Sandstone formation has been identified as a potential reservoir which can store very large amounts of CO₂. The formation has fairly good porosity and permeability and is sealed with both effective caprock and base rock, which makes CO₂ storage feasible at industrial scale. However, when CO₂ is captured, it typically contains impurities, which shift the boundaries of the CO₂ phase diagram, implying the operation at higher pressures during the storage stage and affecting the costs. In this study, we modelled the effect of CO₂ and associated impurities (NO₂, SO₂, H₂S) on the reservoir performance of the Bunter Sandstone formation. The injection of CO₂ at constant rate and pressure using a single horizontal well injection strategy was simulated for up to 30 years, as well as an additional 30 years of monitoring. The results show that impurities in the CO₂ stream affect injectivity differently, but this is usually encountered during the early stages of injection and may not necessarily affect cumulative injection after an extended period. It was also found that the porosity of the storage site is the most important factor controlling the limits on injection. The simulations also suggest that injected CO₂ remains secured within the reservoir for 30 years after injection is completed, indicating that no post-injection leakage is anticipated.

Nomenclature

Abbreviations

BSF	Bunter Sandstone formation
CCS	Carbon capture and storage
ETI	Energy Technologies Institute
FPR	Field pressure
GHG	Greenhouse gas
WBHP	Well bottom hole pressure
WGIR	Well gas injection rate
WGIT	Well gas injection total

Notations and Symbols

q	Discharge per unit area (m/s)
k	Permeability (mD)
μ	Fluid viscosity (Pa.s)
∇p	Pressure gradient (Pa/m)
ρ	Density (kg/m ³)
g	Acceleration due to gravity (m/s ²)
v	Velocity (m/s)
\emptyset	Porosity (%)
v_α	Velocity of phase α (m/s)
k_α	Relative permeability of phase α (mD)
μ_α	Fluid viscosity of phase α (Pa.s)
∇p_α	Pressure gradient of phase α (Pa/m)
ρ_α	Density of phase α (kg/m ³)
∇z	Flow in the z direction (m/s)
τ	Tortuosity (-)
S_α	Saturation of phase α (%)
X_i	Mole fraction of component i (-)
D	Diffusivity (m ² /s)
c	Total molar concentration (M)
J_i	Flux of component i per unit area (m ³ /s)
D_i	Diffusion coefficient of component i (m ² /day)
TD	Diffusivity, the analogue of transmissibility for diffusive flow (m ² /s)
y_i	Vapour mole fractions (-)
P_c	Capillary pressure (KPa)
P_n	Pressure of the non-wetting phase (KPa)
P_w	Pressure of the wetting phase (KPa)
ρ_b	Brine density without dissolved CO ₂ (kg/m ³)
M_{CO_2}	Molar weight of CO ₂ (kg/mol)
C	Concentration of dissolved CO ₂ (mol/dm ³)

V_{φ} Molar volume of dissolved CO₂ (dm³/mol)

4.1 Introduction

The global emissions of carbon dioxide into the atmosphere, caused mainly by the burning of fossil fuels such as those from industrial processes (e.g., cement, steel and lime production), power and transportation sector, have caused global warming and climate change [16]. Carbon capture and storage (CCS) has been considered as one of the viable climate change mitigation technologies, and it is expected to help in reducing over 20% of the global greenhouse gas (GHG) emissions by 2050, while its exclusion can cause over 70% increase in the global cost of meeting emission reduction targets [34].

The main options for CO₂ storage in underground geological formations are saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, basalt formations, hydrate storage of CO₂ within the subsurface environment, and CO₂-based enhanced geothermal systems [17]. Among these options, storage in saline aquifers is considered as one of the most feasible choices for technology deployment, since they provide the largest potential storage volume [59] and are unsuitable for other uses.

Depending on the source of the captured CO₂, some impurities (usually <5%_{vol.} [247,248]) are contained in the CO₂ stream. The type and amount of impurities in the CO₂ stream may have a significant effect on the physical quality of the storage reservoir. The presence of impurities can alter the molar volumes and result in shifting the boundaries in the CO₂ phase diagram to higher pressures, which implies higher operating pressures and cost may be required for CO₂ storage [17]. Therefore, the overall storage capacity can be adversely affected [22]. On the other hand, the possible short term effects of impurities on the performance of reservoir may indicate the necessity of a change in the injection strategy [22]. Although, it is crucial to

quantify the long-term effect of impurities on storage sites in real life applications, the experimental approaches are complicated, costly and inadequately slow. Alternatively, numerical simulations can be used to accelerate the evaluation of the impurity effects. Several numerical studies have been conducted to evaluate the long-term reservoir performance when impure CO₂ is injected into geological formations [22,24,67,416], and such studies suggest that the presence of impurities may cause a considerable influence on injection and storage mainly due to chemical reactivity of the host rock with formation water resulting in changes in permeability and porosity. The presence of SO₂, for example, could lead to the formation of strong acids, and lower the pH of formation water, and thereby, increase the dissolution and precipitation of rock minerals. On the other hand, the presence of impurities in the injected CO₂ and the subsequent geochemical reactions with saline water and minerals in the host rock can lead to the precipitation of authigenic or secondary mineral phases which could effectively lock up the stored CO₂ in immobile secondary phases for geologic timescales [87].

Waldmann et al. [22] studied the physicochemical effects of discrete CO₂-SO₂ mixtures on injection and storage in order to assess the impact on overall storage capacity in the Ketzin injection site, Germany. In their study, they considered geological conditions in the Ketzin site, and they assessed the impact of SO₂ on the physicochemical behaviour of the CO₂ phase by geochemical modelling of fluid-rock interactions. Since variations in porosity and permeability of the host rock can negatively influence the CO₂ storage capacity, the results obtained from chemical models on porosity and permeability were integrated into the reservoir simulations to assess likely impacts. Results from their study revealed that the presence of SO₂ causes a significant reduction in porosity compared to pure CO₂ during the period of injection. Their results also suggested that the overall impact of SO₂ (<1%_{vol.}) was low, although the morphology changes due to chemical reactions reduced the space in pores available for storage.

Similarly, Wang et al. [67] studied the impact of SO₂ on CO₂ injectivity in the Basal Cambrian sandstone saline aquifer in Western Canada. In their study, 2.5%_{vol.} SO₂ was used, and for the first time they reported that enhanced quartz dissolution due to the effect of SO₂ apparently caused significant precipitation of NaCl, which could reduce the permeability of reservoir rocks.

In this study, we evaluate the effect of CO₂ and impurities, i.e., NO₂, SO₂ and H₂S, during injection and storage in a sandstone saline aquifer. We evaluate their effect on key reservoir performance indicators, i.e., well bottom hole pressure, CO₂ injection rate, field pressure and cumulative gas injection in the reservoir using a single horizontal well injection strategy for a 30-year period, and an additional 30-year period of monitoring. The Bunter Sandstone formation (BSF) in the UK Southern North Sea was selected as a case study, and a simplified model for reservoir simulation to evaluate the reservoir performance during injection and storage using time and specific observation point indices is developed.

4.2 Numerical model

4.2.1 Modelling procedure, reservoir size and boundary conditions

To develop the model of the BSF for flow simulations, we used simplified box models where the geology and domain of research are characterised as horizontal layers and representative bulk values were assigned for the various reservoir properties using data from our laboratory experimental analysis [417] and from the open literature. The injection and storage of CO₂ into the BSF saline aquifer system was simulated using the ECLIPSE 300 compositional simulator which can model fluid flow as a multiphase and multicomponent system. A similar reservoir simulator (ECLIPSE E100 black oil simulator) was used in previous studies [373,375,418–

420] on CO₂ storage but did not consider the composition of injected fluids and the effect of impurities on reservoir performance.

The simulation process involves several steps which include inputting data to the CO2STORE module of the simulator that conforms with the reservoir properties of the targeted storage formation; the use of lithostatic pressure gradient for model validation with respect to the injection depth; and conducting sensitivity tests with respect to grid dimensions in order to select the grid that provides optimum injection within the targeted reservoir. The rock and fluid properties used for multiphase flow simulations are presented in **Table 4-1**. A grid of 10 x 10 x 3 cells (300 grid cells in total) was used, and the model dimension was discretised into 90 km x 90 km x 3 km. An adaptive mesh refinement for optimising the reservoir performance was not conducted in the simulation as it is known that for a single injector that seeks to store CO₂ over a storage region of large lateral extent such as the BSF, even a less refined mesh provides an accurate representation of the reservoir performance [421–423].

The depth to the crest of the Bunter storage structure was 1171 m [424], and the thickness of the BSF at the storage point is 215 m [424]. Therefore, we use 1171 m as depth of the top face of the grid block, and we adopt 1181 m as injection depth. To validate the model against the lithostatic pressure gradient, 0.165 bar/m was used. This was chosen as the typical value for lithostatic pressure gradient reported by ETI [424] for the Bunter storage development plan and is close to the values used by Noy et. al. [371] and Williams et al. [373]. Additionally, in order not to suffer mechanical failures at any point during injection operations, the simulation was initially run (with the average porosity and average permeability values of the BSF derived by ETI [424]) and injection pressure was limited to 90% of the lithostatic pressure (175 bar) at injection depth (1181 m). The pressure constraints from our simulations were found to be in good agreement with anticipated pressure, and we established that our model runs within safe

injection pressure. Moreover, injection operations are expected to be free from any sanding risks due to geomechanical issues. The analysis of existing wells within the BSF suggest that the reservoir is relatively strong and sand failure events around the near wellbore area [424], which could cause subsequent operational problems, are unlikely.

Saline aquifers are usually very large as they cover hundreds of km² and the BSF is not an exception. Therefore, modelling for CO₂ storage in saline aquifers is usually focused on the area affected by the CO₂ plume distribution [373], which is usually around the injection point and surrounding regions. However, in selecting an appropriate reservoir size for modelling, it is important to note that a fairly considerable aquifer size should be adopted since pressure footprint due to injection can extend much further in the aquifer [371,373,425] to cause unrealistic pressure build-up in the model [373]. Therefore, in this study, the optimum reservoir size was obtained by conducting simulations with various grid sizes and correlating the results with available pressure data [424]. The grid dimension was kept constant while the grid block size was varied in the DX and DY directions by a deduction of 20 m from the previous grid block size in each subsequent simulation. The variation of these grid blocks was then limited to reservoir sizes that were capable of sustaining CO₂ injection for the specified 30-year period. In order to select the optimum reservoir size, we used a method proposed by ETI [424] for the Bunter storage development plan, which suggests that the optimum reservoir size should be selected from a grid in which the injection rate can be maximally sustained.

It is generally agreed that the boundaries of a reservoir can influence the pressure build-up and storage capacity. The most conventional estimate is the assumption that all horizontal and vertical boundaries of the model are closed [421,425]. However, for CO₂ storage applications over injection timescales and subsequent migrations of <100 years, the boundary conditions are found to have a negligible impact on reservoir performance [426]. This is due to the large

areal extent of the Bunter region [426]. Therefore we believe that our results are valid for both sets of open and closed boundary conditions since they are based on reservoir performance evaluation over this timescale [426].

Table 4-1: Rock and fluid properties used for the simulations.

Parameter	Value	Unit	Reference
Grid dimension	10 x 10 x 3	-	-
Grid block size	300 x 300 x 10	m	-
Porosity (lower and upper limits for all model runs)	10, 22	%	Vincent [427]
Permeability (variable depending on impurity present)	254 ^a , 140 ^b , 225 ^c , 255 ^d	mD	Aminu et al. [417]
Depth to top face of grid block	1171	m	ETI [424]
Reference depth	1181	m	-
Model datum depth	1181	m	-
Initial reservoir temperature	37	° C	ETI [424]
Average reservoir pressure	124	bar	ETI [424]
Bottom hole pressure limit	175	bar	-

Volume of impurity in the CO ₂ stream	5	%	-
Diffusion coefficients of components in water	3.0 x 10 ⁻⁴ (H ₂ O ^e), 1.4 x 10 ⁻⁴ (CO ₂), 1.0 x 10 ⁻⁴ (NaCl ^f), 1.21 (NO ₂ ^g), 0.0001 (SO ₂ ^h), 0.0002 (H ₂ S ⁱ)	m ² /day	^e Mills [428]; ^e Holz et al. [429]; ^f Guggenheim [430]; ^g Dekker et al. [431]; ^h Koliadima et al. [432]; ⁱ Haimour and Sandall [433]. Cussler [434]
Diffusion coefficients of components in air	0.232 (H ₂ O), 1.382 (CO ₂)	m ² /day	
Rock density	2300	kg/m ³	ETI [424]
Lithostatic pressure gradient	0.165	bar/m	ETI [424]
Pore compressibility	4.5 x 10 ⁻¹⁵	bar ⁻¹	Zhou et al. [435]; Noy et al. [371]

Fluid injection rate	6×10^6	$\text{Sm}^3\text{CO}_2/\text{day}$	-
Injection period	30	Year	-
Monitoring period	30	Year	-

Note: a, b, c, and d, denote permeability values obtained after exposure to CO₂, CO₂-NO₂, CO₂-SO₂ and CO₂-H₂S, respectively.

4.2.2 Reservoir and fluid properties

The BSF was deposited during the late Permian and Triassic periods. It comprises pebbly sandstones and sandstones intercalated with small amounts of conglomerates, mudstones and siltstones. The reservoir formation is typically 200 m thick and has fair to good porosity and permeability, and occurs at depths of about 1000 to 3000 m [371]. The BSF is also overlain primarily by the Triassic mudstones of the Haisborough Group which act as caprock or seal **Error! Reference source not found.**, and it is underlain by the Permian Bunter Shale and the evaporitic strata of the Zechstein Group [372,436,437].

At the grid block scale of the reservoir, two different porosities, 10 and 22%, were considered for simulations, which agrees well with the lowermost and uppermost intervals of the BSF in the UK Southern North Sea based on selected borehole neutron logs [427]. The permeability values were experimentally determined by Aminu et al. [417] using empirical relationships to account for variations in reservoir grain size distributions from rock samples exposed to CO₂ and impurities for a period of 9 months using simulated reservoir conditions. The permeability in the vertical direction was derived from a generic vertical to horizontal permeability ratio of 1:10 and this agrees well with the work of Heinemann et al. [95]. We assume that the overlying and underlying boundaries of the model are impermeable due to the presence of effective

caprock and base rock. Therefore, we do not anticipate any fluid flow out of the simplified reservoir model compartment.

Very limited relative permeability data exist for CO₂-brine systems from North Sea formations [373,424]. Therefore, uncertainties might exist in understanding the relative permeability of the reservoir. However, we use data made available by ETI [424] for the Bunter storage development plan, which were derived by endpoint inputs from available experimental values. The reservoir was assumed to have an initial temperature of 37 °C and initial average pressure of 124 bar.

With reference to CO₂ and impurities, the main properties of the simulated fluids considered as inputs in the model runs were the percentages of both CO₂ and an associated impurity within the injection stream, and the diffusion coefficients of all components in water and air, which were experimentally determined by different workers as presented in **Table 4-1**. The fluid properties of the injection stream (e.g. viscosity) and properties of the formation water (e.g. pH) are not required inputs in a compositional model run as these are determined by the simulator in each run.

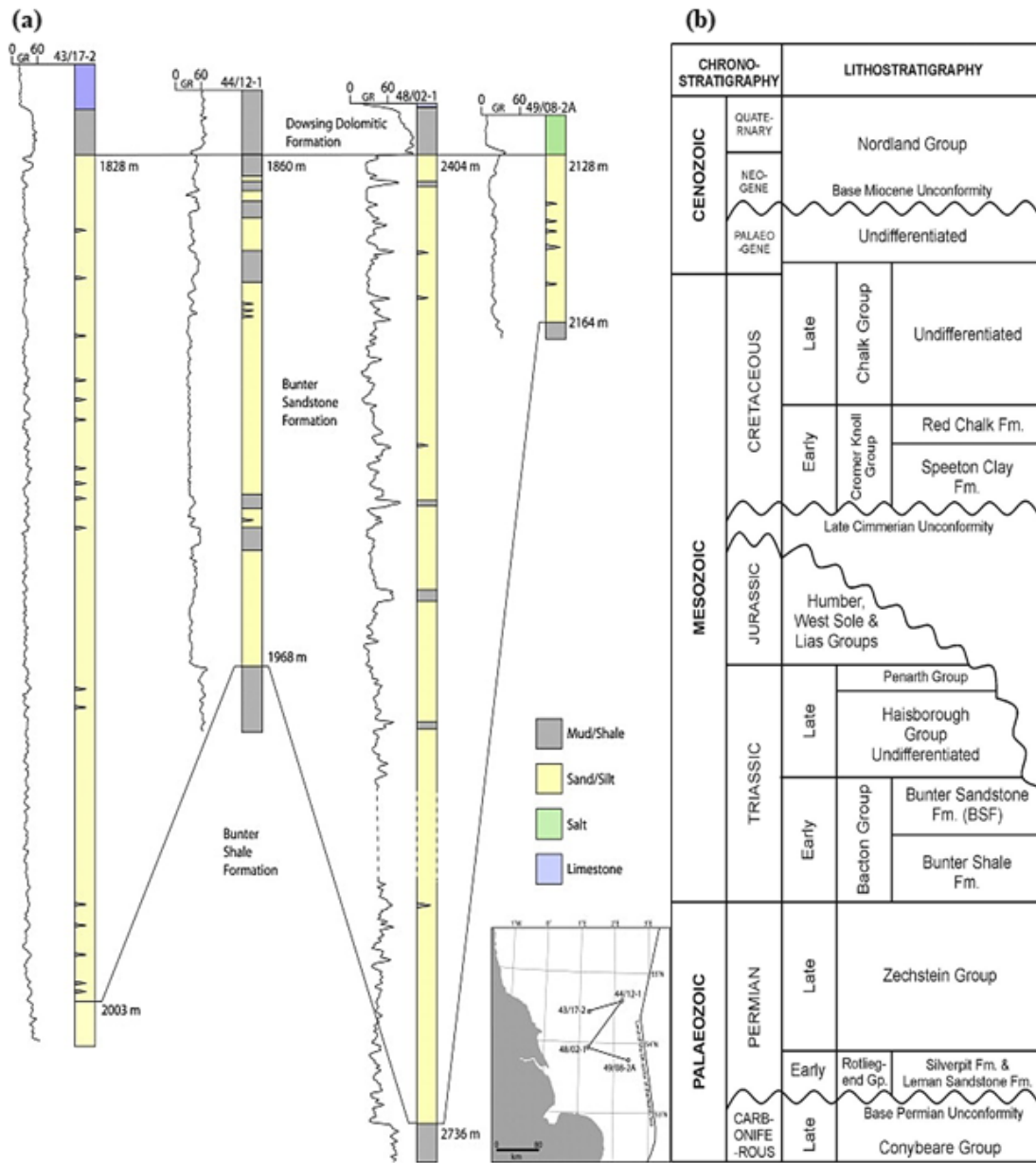


Figure 4-1: (a) Gamma ray logs of the Bunter Sandstone formation [95]; and (b) A generalised stratigraphy of the UK sector of the southern North Sea [370]. Note: Depth to the face of the Bunter vary considerably across different locations.

4.2.3 Governing equations

For the multiphase flow model used in this study, the governing equations for simulation of CO₂ injection for storage into a saline aquifer are like those used for oil, water, and CO₂ flows through porous reservoirs. Darcy's law incorporates mass and energy conservation equations, as reviewed by Jiang [438], and was used for the simulations **Equation 4-1**.

$$q = - \frac{k}{\mu} (\nabla p - \rho g) \quad \text{Equation 4-1}$$

Using **Equation 4-1**, it is possible to calculate velocity through the porous medium:

$$v = \frac{q}{\phi} = - \frac{k}{\mu\phi} (\nabla p - \rho g) \quad \text{Equation 4-2}$$

In terms of the positive z-direction as vertically up (opposite to gravity), multiphase extension of Darcy's law can be used for an individual fluid phase α , thus:

$$v_\alpha = \frac{q_\alpha}{\phi} = - \frac{kk_\alpha}{\mu_\alpha\phi} (\nabla p_\alpha - \rho_\alpha g \nabla z) \quad \text{Equation 4-3}$$

For CO₂ storage, the flow is modelled as a multiphase which requires considering CO₂, brine, rock, and multicomponents such as the CO₂ and water system. Thus, the number of components and phases can differ depending on application. In **Equation 4-4**, the conservation of mass is expressed by the balance of four components that represent all possible mechanisms of mass transfer, which are: temporal rate of change of mass at fixed point, which can also be referred to as the local derivative or fixed term; convective mass transport; diffusive mass transport; and sink or source term for mass.

$$\frac{\partial}{\partial t} \left[\phi \sum_{\alpha} (\rho_{\alpha} S_{\alpha} X_i^{\alpha}) \right] + \sum_{\alpha} \nabla (\rho_{\alpha} X_i^{\alpha} q_{\alpha}) - \sum_{\alpha} \nabla (\phi S_{\alpha} \tau_{\alpha} D_{\alpha} \rho_{\alpha} \nabla X_i^{\alpha}) = S_i \quad \text{Equation 4-4}$$

The gas phase diffusion coefficient for each component is also accounted for in a compositional run. These are used to define diffusive flows in terms of vapour mole fractions. The normal diffusion coefficients are defined by the following condition, **Equation 4-5** (Reid et al. [439]):

$$J_i = -cD_i \frac{\partial y_i}{\partial d} \quad \text{Equation 4-5}$$

These diffusion coefficients are used in the compositional model run to obtain gas inter-block diffusive flows, which take the form, **Equation 4-6**:

$$F_{ig}^{diff} = T_D D_{ig} (S_g b_g^m) \Delta y_i \quad \text{Equation 4-6}$$

For CO₂ storage reservoir simulations, the capillary forces are significant both in residual and structural/stratigraphic trapping. In the seal or caprock, the threshold of the capillary force can be high enough to keep the non-wetting phase, which can be CO₂ fluid or gas phase, from entering small pore throats in the seal. The capillary force also keeps bubbles of the CO₂ phase in an immobile state in small pore spaces of the reservoir during CO₂ migration. Thus, the capillary pressure, which is the pressure difference between the non-wetting phase and wetting phase in porous medium, is given as, **Equation 4-7**:

$$P_c = P_n - P_w \quad \text{Equation 4-7}$$

The compositional model run uses a modified Peng-Robinson equation of state [440] which is able to correctly compute the density, viscosity and compressibility of CO₂ as a function of temperature and pressure, as well as the mutual solubility of CO₂ and brine.

For the density of brine and CO₂, the determination of amount of CO₂ that will be dissolved in brine is important for the estimation of storage capacity and in understanding the interactions

between CO₂-brine-rock because of low pH or acidity of CO₂-saturated brine [441]. Since the dissolution of CO₂ in brine influences the solution density, the influence of dissolved CO₂ on brine is expressed thus, **Equation 4-8**:

$$\rho = \rho_b + M_{CO_2}C - C\rho_bV_\phi \quad \text{Equation 4-8}$$

4.2.4 Model study design

In this study, we designed a reservoir simulation case to evaluate the limits of stability of various chemical phases in the CO₂ stream with respect to operational uncertainties. This will allow us to account for the likely uncertainties that could arise in the deployment of CO₂ storage in the BSF with different impurities in the gas stream using surface flow rate as the well control mode. In practice, a CO₂ injection project could operate with multiple injection wells, e.g., the In Salah project [269,270,273], or single injection well, e.g., the Sleipner project [16]. However, the number of injection wells that can be deployed for any storage project may vary depending on several factors such as the reservoir heterogeneity [421], the amount of CO₂ which can be injected into a single well without causing adverse overpressure [442], the trade-off between cost of adding a well [421] and/or the amount of CO₂ that could be taken by any single well.

Previous studies on CO₂ storage in the BSF [95,371,373,421] suggests that the motivation for using multiple injection wells for storage is largely driven by the amount of CO₂ that could be taken by each well per year. Typically, industry practice has suggested that volumes ranging from 1-2 MtCO₂/year [421,443] could be stored in geologic formations beneath the North Sea, and this can be achieved with 20 injection wells [421], or even 12 injection wells [371,421]. Moreover, ETI [424] deployed 4 injection wells to store approximately 7 MtCO₂/year over a

period of 40 years. A constant injection rate as well as a constant injection pressure for the entire period of injection were assumed. In practice, the CO₂ injection rate could vary to maximise injectivity. However, it must be noted that the limits of stability in the CO₂ phase diagram regarding the operational uncertainties occur during the well pressure build-up prior to stability. Thus, the variation of injection rate after peak pressure is attained could only lead to a reoccurrence of the shifts in the boundaries of the CO₂ phase diagram as it was in the case of the preceding injection rate. We also assume that 6×10^6 Sm³CO₂/day is made available from an industrial site and transported for injection at the storage site. Thus, 6×10^6 Sm³/CO₂/day is set as injection rate, but the volume of CO₂ injected is initially dependent on the well control modes, although the injection will normally be affected by the pressure build-up in the reservoir. Since the allowable bottom hole pressure for injection was set to 90% lithostatic pressure at depth, the constant injection pressure used during the storage period ensures that this limit is not exceeded.

While our modelling did not consider the likely effect of impurity on any change in reservoir porosity, so that initial porosity values from experimental data can be assigned in each impurity case as we did for changes in reservoir permeability obtained from laboratory experimental analysis [417], we do not claim that impurities could not have affected the porosity of the BSF, and hence its reservoir performance. However, our assumption for adopting the upper and lower limits of the BSF porosity as reported by Vincent [427] in these simulations was informed by the analysis of mineral phases of rock samples after exposure to CO₂ and impurities, as reported in our previous study [417]. From the results in that study, we can infer that there could be a significant reduction in porosity due to dissolution of clay minerals such as mica [444,445] and an increase in porosity due to the dissolution of quartz [446], feldspar and albite [447].

4.3 Results and discussion

After injection, CO₂ plume is expected to migrate to the top of a reservoir due to buoyancy and it gradually spreads out laterally. The force of buoyancy causes the less dense gas to rise over denser saline water. The pattern of plume migration thus, occurs both laterally and vertically and is expected to behave in this way due to the absence of any geological barriers to flow. The presence of impermeable seals atop and beneath the storage formation is expected to keep the plume spreading across the radial distance of the reservoir.

The well bottom hole pressure (WBHP) build-up in the reservoir was monitored at two periods which correspond to the first day of injection and the time it takes to reach the peak pressure, for each simulation case respectively. These observations will enable the determination of any potential effect of impurities on pressure perturbations and stability during injection. The WBHP build-up for the storage sites with 10% and 22% initial porosity for pure and impure CO₂ storage is shown in **Figure 4-2**. For all storage sites, we observe a continuous increase in pressure until a maximum of 175 bar was reached, which then remains constant throughout the period of injection. However, for different simulation cases, the time to reach the maximum WBHP varies.

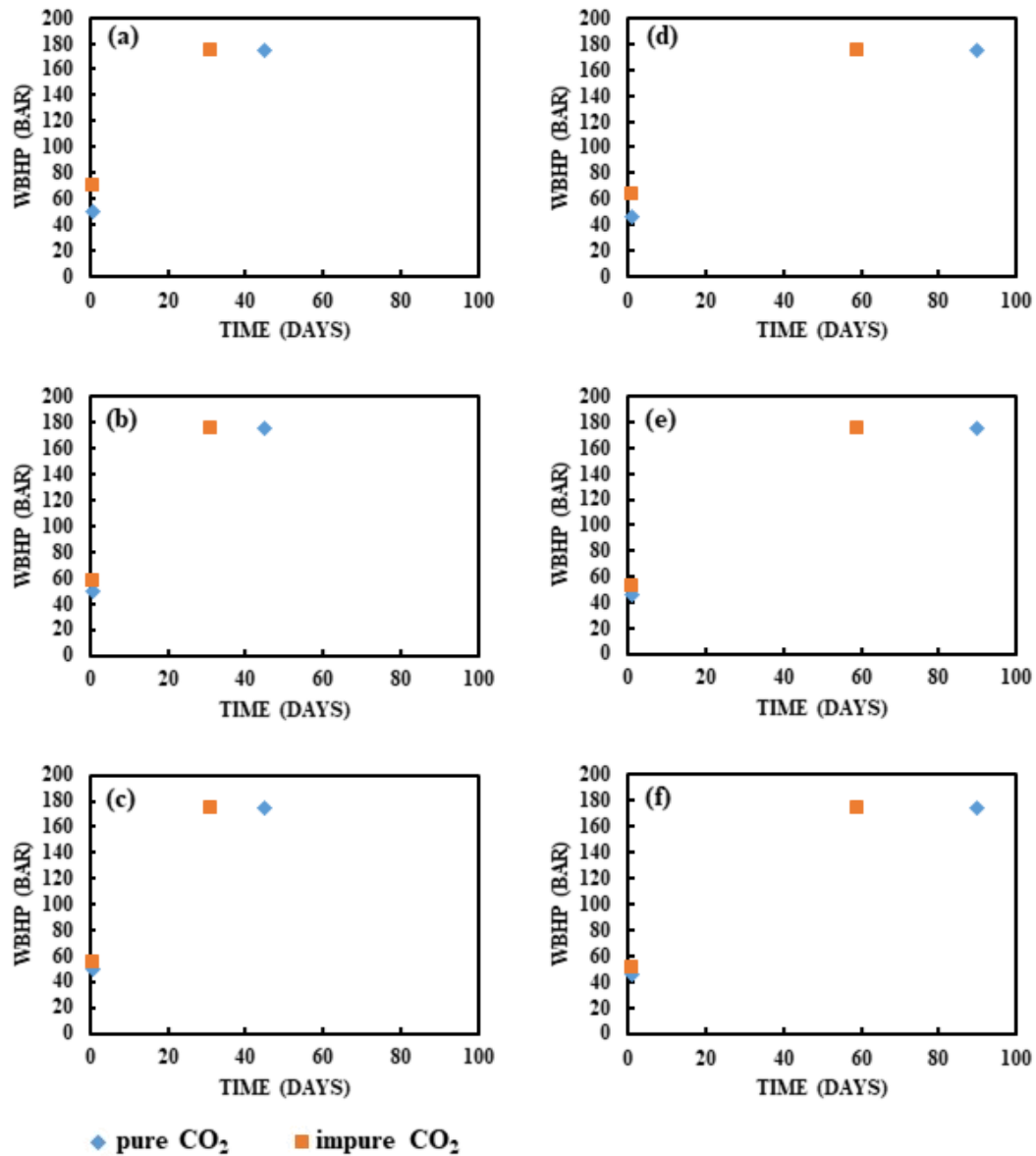


Figure 4-2: Well bottom hole pressure (WBHP) build-up for pure and impure CO₂ storage for sites with 10% initial porosity ((a) CO₂-NO₂, (b) CO₂-SO₂, (c) CO₂-H₂S), and 22% initial porosity ((d) CO₂-NO₂, (e) CO₂-SO₂, (f) CO₂-H₂S).

The WBHP of pure CO₂ injection into the storage site with 10% initial porosity reached its maximum pressure after 45 days of injection. In comparison to injection with impurities, the

injection of CO₂-NO₂ resulted in the maximum pressure being attained within a relatively shorter period. Likewise, after the injection of CO₂-SO₂ and CO₂-H₂S, the time it took to attain maximum pressure in each case was the same as it was in the case of CO₂-NO₂.

For pure CO₂ injection into the storage site with 22% initial porosity, the WBHP reached its peak after 90 days of injection. In comparison to injection with impurities, the introduction of CO₂-NO₂, CO₂-SO₂ and CO₂-H₂S in each case, showed that maximum pressure was attained relatively faster than in the pure CO₂ case. The WBHP rise suggests that it is consistent with reservoir porosity. These suggest that for storage sites with lower porosity, the maximum pressure is attained relatively faster than for sites with a higher porosity.

The corresponding well gas injection rate (WGIR) at three observation points is shown in **Figure 4-3**. The observation points were considered against the WBHP. These points correspond to the first day of injection (observation point index 1), the peak WBHP (observation point index 2) and the last day of injection (observation point 3). For all storage sites, we observe an initial injection rate of $6 \times 10^6 \text{ Sm}^3\text{CO}_2/\text{day}$ at observation point 1 and this rate remains constant until the WBHP attains stability when injection rate begins to decrease with time until the well is shut.

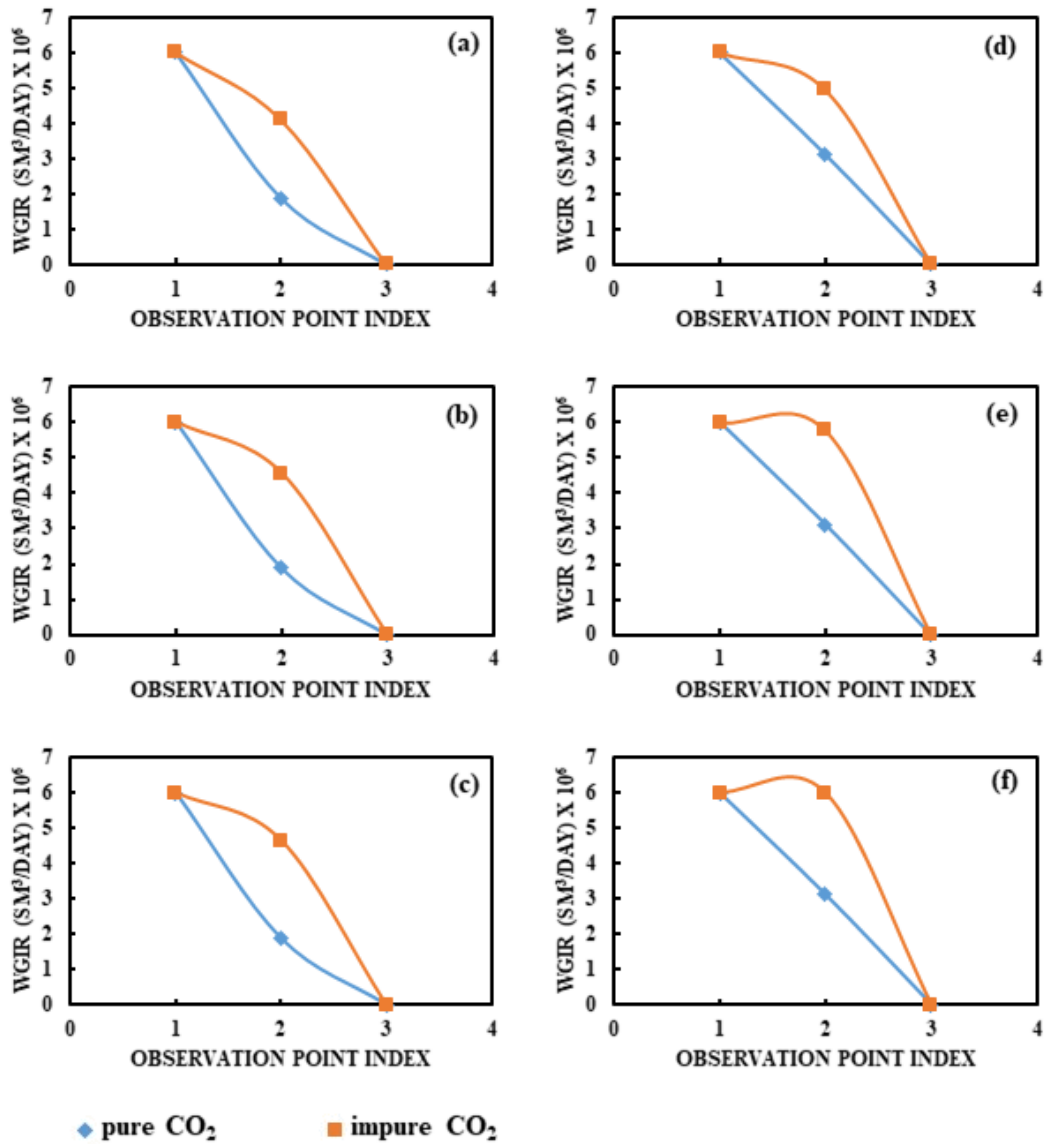


Figure 4-3: Well gas injection rate (WGIR) for pure and impure CO₂ storage for sites with 10% initial porosity ((a) CO₂-NO₂, (b) CO₂-SO₂, (c) CO₂-H₂S), and 22% initial porosity ((d) CO₂-NO₂, (e) CO₂-SO₂, (f) CO₂-H₂S).

The injection rate of pure CO₂ at the storage site with 10% initial porosity was $1.87 \times 10^6 \text{ Sm}^3$ at observation point 2. Since we do not consider a new injection rate at any time after the peak WBHP was attained, for all storage sites, we do not expect to have a significant volume of CO₂

to be injected when the well is shut. Therefore, the introduction of impurity, in each case, caused a significantly higher injection rate to be attained. For all the impurity cases, the injection volume at this observation point were similar.

On the other hand, when pure CO₂ was injected in storage site with 22% initial porosity, an injection rate of $3.1 \times 10^6 \text{ Sm}^3$ was encountered at observation point 2. The injection of CO₂-NO₂ caused a considerably higher injection rate to be encountered at the same observation point. Furthermore, the introduction of CO₂-SO₂ and CO₂-H₂S impurities, in each case respectively, resulted in an even more considerable injection rate in comparison with the pure CO₂ case. It should be noted however, that these large degrees of difference in the injection rates at observation point 2, for all storage sites, may not necessarily be a strong factor that could cause a considerably less injection volume in the long term.

The results from WGIR seem to show a correlation with the initial reservoir porosity and permeability, although the effect of porosity appear to be more overwhelming. We observed that a more porous injection site lead to higher injectivity being attained. However, this scenario is specific to observation point 2, for all cases.

Figure 4-4 shows the field pressure (FPR) at three observation points for sites with 10% and 22% initial porosity. The FPR was observed with respect to WBHP on the first day of injection (observation point index 1), peak WBHP (observation point index 2), and at the end of injection period (observation point index 3). For all cases simulated, we observe an increasing field pressure from an initial pressure of approximately 124 bar, and this increases gradually, without stabilising at observation point 2 until a peak pressure of 274 bar is attained. The peak FPR attainment time varies for each simulation case, and such pressure is always reached before the end of injection when the well is shut. The variation in FPR for various storage sites is a result

of differences in the change in hydrostatic pressure which is a function of the bulk properties of the reservoir.

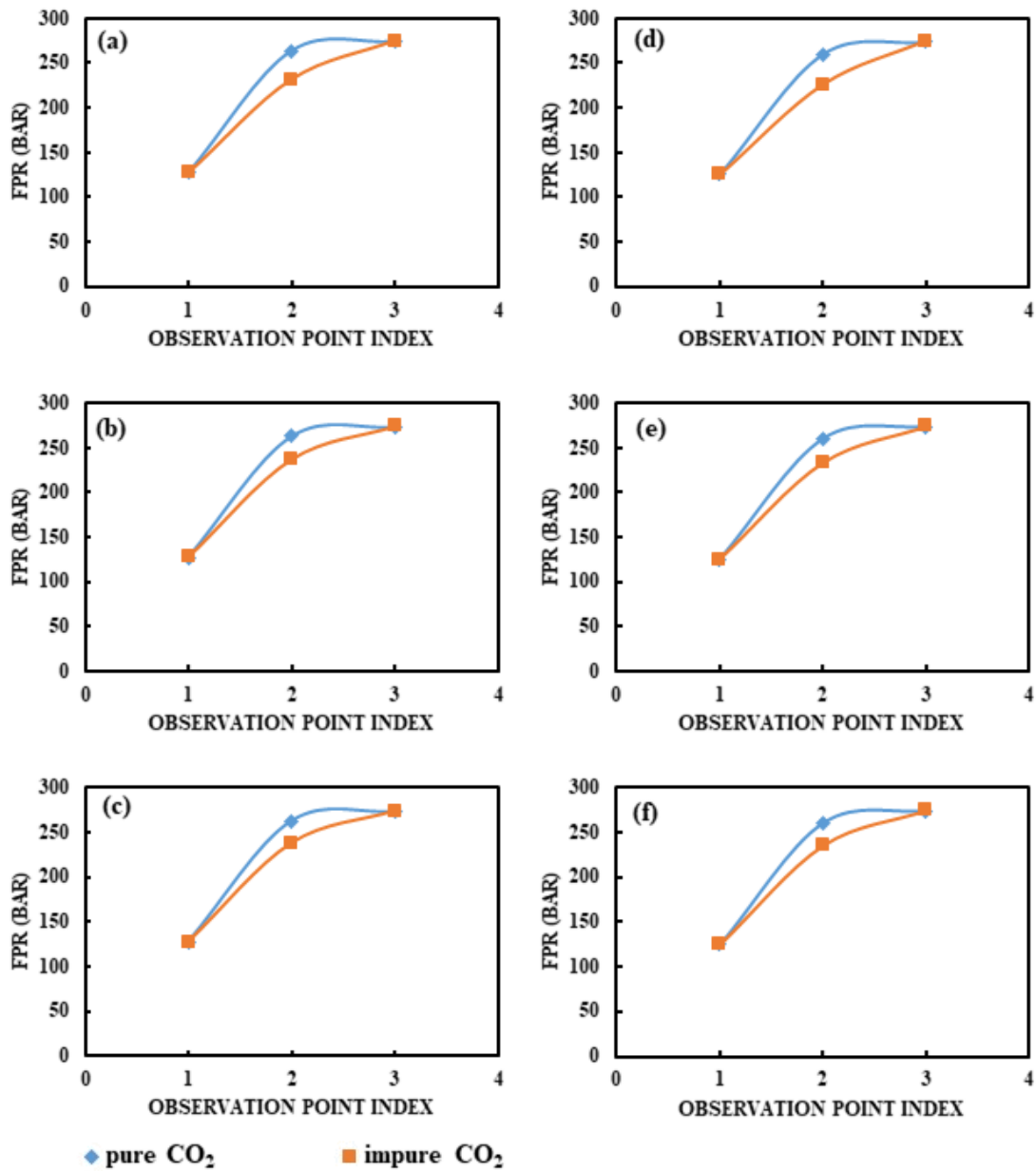


Figure 4-4: Field pressure (FPR) for pure and impure CO₂ storage for sites with 10% initial porosity ((a) CO₂-NO₂, (b) CO₂-SO₂, (c) CO₂-H₂S), and 22% initial porosity ((d) CO₂-NO₂, (e) CO₂-SO₂, (f) CO₂-H₂S).

The FPR for pure CO₂ injection at the storage site with 10% initial porosity was 263 bar at observation point 2 and 273 bar at observation point 3. When CO₂-NO₂ was injected, there was a reasonable decrease in FPR at observation point 2 and nearly same pressure was maintained as in the pure CO₂ case at observation point 3. The injection of both CO₂-SO₂ and CO₂-H₂S also lead to an appreciable change in the FPR by a considerable decrease in comparison with the pure CO₂ case at observation points 2, respectively. However, as it is expected, for all impurity cases, there has not been significant difference in the FPR as in the pure CO₂ case, for all impurity cases respectively. Additionally, there was no significant discrepancy in FPR at the time the well was shut and after the monitoring period. This suggests that the field pressure in the reservoir remains the same all through the monitoring period and it also implies that reservoir containment is dependable.

In storage site with 22% initial porosity, the FPRs encountered for pure CO₂ were 259 bar and 273 bar, at observation points 2 and 3, respectively. The injection of CO₂-NO₂ caused the FPR to decrease somewhat reasonably at observation point 2, while there was an almost similar FPR at observation point 3, as with the case for pure CO₂ injection. Additionally, the injection of CO₂-SO₂ caused a considerable decrease in FPR at observation point 2, while similar FPR was encountered in observation point 3, relative to the pure CO₂ injection case. Lastly, the injection of CO₂-H₂S also showed a large decrease in FPR at observation point 2, relative to the pure CO₂ case.

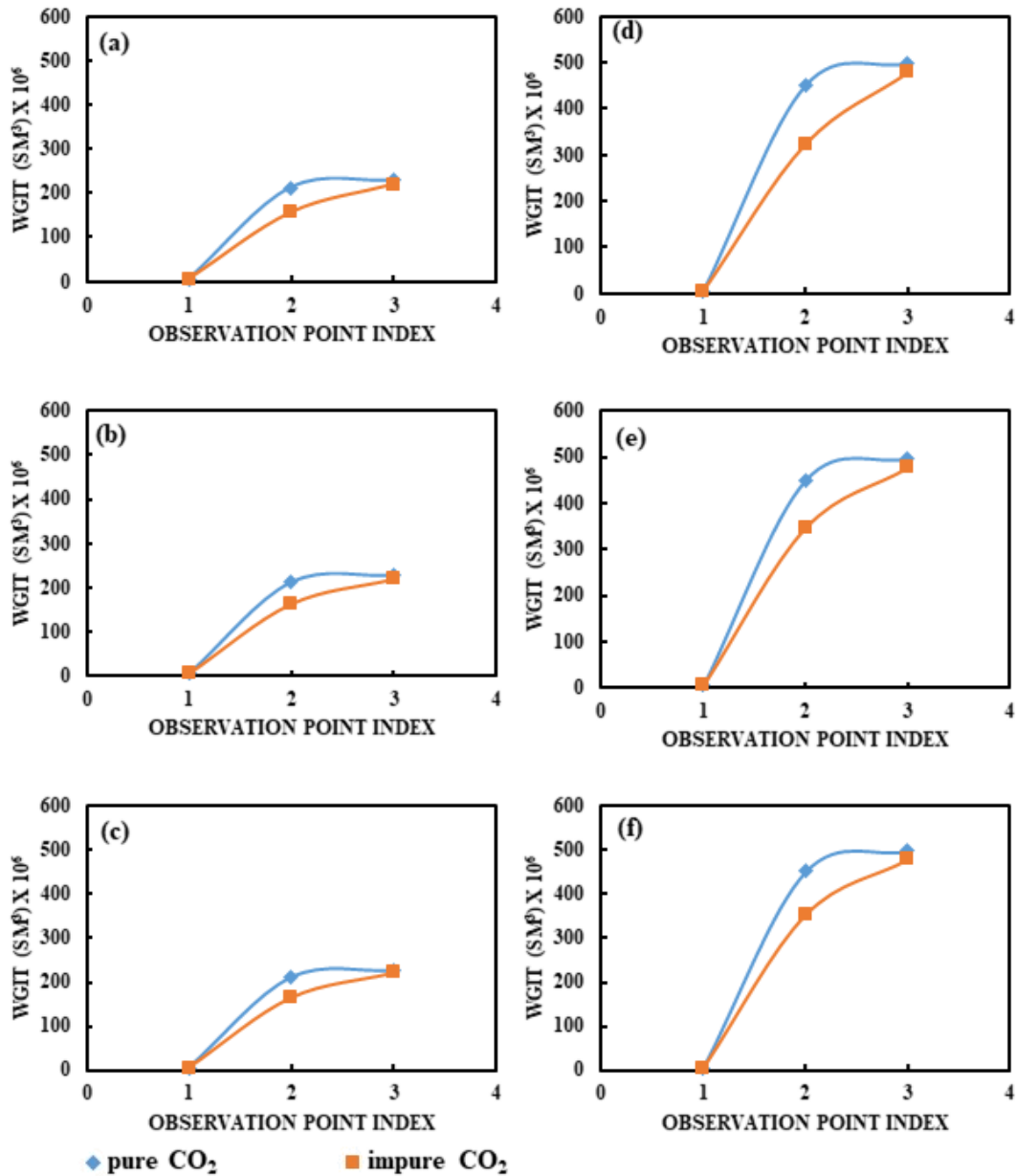


Figure 4-5: Well gas injection total (WGIT) for pure and impure CO₂ storage for sites with 10% initial porosity ((a) CO₂-NO₂, (b) CO₂-SO₂, (c) CO₂-H₂S), and 22% initial porosity ((d) CO₂-NO₂, (e) CO₂-SO₂, (f) CO₂-H₂S).

The well gas injection total (WGIT) for sites with 10% and 22% initial porosity is presented in **Figure 4-5**. This is also the same as the cumulative injection. The observation points were considered against the WBHP on the first day of injection (observation point index 1), the peak

WBHP (observation point 2) and at the end of injection period (observation point 3). For all cases simulated, we observed an increasing CO₂ injection until the well is shut. Besides the effect of impure CO₂ which is manifest at the observation point 2, the initial porosity of the storage site controls, to a larger extent, the cumulative injection.

Based on the findings from these simulations, it can be said that although fluid properties such as brine composition, diffusion of various components in both water and air, changes in viscosity, and interfacial tension could all affect the reservoir performance to a certain degree. However, the main cause of differences in the pressures and volumes (besides the properties of the storage formation) between pure and impure CO₂ injection is controlled by the volume of impurity within the CO₂ stream. Additionally, we observed that for all impurity cases simulated, the difference between target and actual injection rates is minimal and this can be due to the spatial variance in reservoir properties such as porosity and permeability and the implicit use of constant values for these properties in the model. Thus, the influence of non-linearity and heterogeneity as obtained in realistic settings is not considered in the model. This minimal difference between target and actual injection rates for the simplified models has been observed in a previous study on the BSF [426]. Moreover, it is important to state that for all injection cases simulated in this study, we monitored the cumulative CO₂ injected at the end of injection period and after the post-injection monitoring, without any noticeable discrepancy. Nonetheless, the use of simplified models will continue to be helpful in the evaluation of opportunities for CO₂ storage deployment in the UK offshore reservoir systems as a viable step toward the decarbonisation of the global economy [426]. The BSF, due to its large areal extent is in conformity with the use of simplified models to predict both regional and local reservoir behaviour in response to different injection scenarios.

4.4 Conclusions

The presence of impurities in the CO₂ stream can significantly affect the physical quality of the storage reservoir and it may also alter the molar volumes and shift the operational boundaries in the CO₂ phase diagram; affecting the limits of stability during injection operations. The main aim of this study is to evaluate the effect of CO₂ and impurities on reservoir performance during injection and storage in a sandstone saline aquifer. These included the evaluation of key performance indicators such as bottom hole pressure, well gas injection rate, field pressure and cumulative injection for each impurity case. The results suggest that the effect of impurities influence the reservoir performance but mostly at the early injection stages, and it does not affect the targeted injection rate. The results from this study show that the porosity of storage sites, controls, to a greater degree, the cumulative injection. Additionally, it was observed that the effect of impurities does not affect the security of stored CO₂ as neither the injected volume nor field pressure were found to decrease 30 years after injection has ceased. We expect that the conclusions from this study can be extended to other saline aquifers with similar depositional- and post-depositional history. However, since the BSF is suited for simplified modelling, we recommend the further application of simplified models for the prediction of reservoir behaviour with other impurity types that have not been previously studied, be evaluated. The analysis of these uncertainties will increase confidence in the evaluation of CO₂ storage potential in saline aquifers.

5 GENERAL DISCUSSION AND IMPLEMENTATION OF THE WORK

Carbon capture and storage (CCS) is widely accepted as an essential technology for reducing significant quantities of anthropogenic CO₂ emissions from the industrial and energy sectors. The effective implementation of CCS technology would substantially help to mitigate climate change due to the effects of these emissions [16]. Currently, there are sets of technologies that are being developed to enhance the capture, transport, storage and utilisation of CO₂. These technologies will typically advance in a sequence of scaled-up steps, which are basically: (i) bench and laboratory scale, (ii) pilot-scale, (iii) demonstration scale, and finally, (iv) commercial scale [448,449].

In the United Kingdom, a significant reduction of emissions is possible if CCS is applied to industrial plants. In 2013, CO₂ accounted for 84.4% of total emissions of greenhouse gas in the UK; with the “energy supply, water and waste” sector emitting the largest amount, representing 29.5% of total emissions [450]. The major potential for long-term storage of CO₂ in the UK are in offshore oil and gas fields; and offshore saline water-bearing aquifers. While the storage of CO₂ in offshore depleted oil and gas reservoirs is viable as such reservoirs guarantee low leakage risk and adequate storage capacity, there are a few concerns that ought to be addressed to encourage commercial scale storage. Most of these concerns are related to site specific issues and they may include: (i) field availability, (ii) suitability of timing for abandonment and storage, (iii) possibility of reusing the infrastructure such as wells and facilities, and (iv) well integrity [451], etc.

On the other hand, generally, saline aquifers are still the most viable amongst all storage options, particularly because of their widespread geographic distribution and they also offer the potential for large scale CO₂ containment [17]. However, there are still many issues that need to be addressed to resolve several generic, regional, and site-specific concerns. In the UK Southern North Sea, the Triassic Bunter Sandstone formation is a priority target saline aquifer which is proposed as having an enormous potential for commercial scale CO₂ storage [371,373,424], although key challenges still remain before technology can be deployed. In this study, we aim to evaluate the potential for CO₂ storage in the UK Southern North Sea in the presence of impurities in the CO₂ stream. To achieve this aim, we proposed a set of objectives which included a bench study, laboratory experiments and numerical analysis.

In the bench study, we critically evaluated the current developments in carbon dioxide storage [17]. We discussed critical issues that have been solved and the challenges that require further research especially on CO₂ sequestration options, storage site evaluation criteria, behaviour of CO₂ in the reservoir, the methodologies for storage capacity estimation, and the current state of development for major world storage projects. Additionally, we noted that although a high-quality knowledge base is already established, paramount amongst the challenges hindering CO₂ storage is its public acceptability. It is important that while research is ongoing to address current and emerging technical challenges, ample mechanisms should be put in place to advocate for CCS practice in general so that public misunderstandings and negative perceptions can be dispelled. A more detailed discussion on the future outlook for CO₂ storage has been presented in the literature review section of this thesis.

Studies from the literature [233,240,242] suggest that laboratory experimental studies can be used to evaluate changes in reservoir physical quality due to CO₂-brine-rock interactions. These changes can be complex as it may involve the precipitation of new rock minerals and/or the

dissolution of pre-existing minerals, which can affect the ability of the reservoir to store and transmit fluids. It was also reported that the presence of impurities in the CO₂ stream can potentially affect the storage capacity of the reservoir [23], and although several studies have investigated CO₂-brine-rock interactions in laboratory test conditions to ascertain varying levels of mineral reactions through alterations of reservoir rock porosity and permeability, the variation of grain size distribution and corresponding effect on permeability has not been explored [17]. Additionally, we found that the majority of work in the open literature has been based on relatively short term experimental tests, lasting between 12 days and 6 months [67,239,242,369]. Moreover, within the previous studies, we found that the effect of impurities on the reservoir rock were only considered for exposure periods of 45 days for CO₂-SO₂ test, and 30 days for CO₂-H₂S test, while other studies considered the effect of CO₂ only. Therefore, we believe that due to the inherent yet distinctive heterogenous assemblages of the depositional facies and sub-facies of the Bunter reservoir, it is critical to address morphological changes through extended experimental tests under more realistic conditions. Thus, in our study, we used reservoir rock samples from the Bunter Sandstone formation to assess the effect of CO₂ and impurities (NO₂, SO₂ and H₂S) on its physical reservoir quality by accelerated temperature and high pressure hydrothermal and multiphase fluid-rock reactions for a prolonged period of 9 months.

Several experimental steps were taken in the process of this investigation: (i) x-ray diffraction analysis to quantify the mineralogical data of the rock samples, (ii) fluid analysis to analyse reacted fluid samples, (iii) environmental scanning electron microscope analysis to obtain image of rock samples using backscatter electron imaging technique, (iv) image processing analysis using the ImageJ software for measuring the grain diameter of rock samples. The main conclusion from these investigations is that the decrease in permeability of the Bunter

Sandstone formation showed a correlation with decreasing pH of formation water and this equally correlates with decreasing geometric mean of the grain diameter.

In terms of the influence of source water properties and natural solution pH, it was not possible to use a fluid matching the reservoir rock sample during laboratory experimental studies, due to the unavailability of analytical data for water chemistry [386]. For that reason, 0.5 M NaCl fluid was used, and this compares favourably with previous studies on CO₂ geochemical interactions, although with a different rock sample (Utsira formation) as case study [452]. In managing the pH during the experiments, each time a reacted fluid was taken for measurement, the aqueous fluid is degassed and put into a polythene syringe, after which the pH values were taken at room temperature. Since the dissolved CO₂ is degassed to reach equilibrium with the atmosphere, the measured pH will be higher than natural solution values [417]. Nevertheless, it has been shown that the degassing effects are significant only after several hours [386,417], which makes the discrepancy between the measured and natural solution pH negligible in this study. While this study is site-specific, it is expected that the findings from this work will be of wider scientific application especially on saline aquifers that share a similar geologic history with the Bunter Sandstone formation. It is also worthy of note that the results presented in the laboratory experimental section of this study only provides a clue as to the behaviour of CO₂ and impurities under relatively short-term reactivity conditions that is not typical of storage timescales. Hence, the results from the numerical modelling section, which evaluates the effect of impurities in storage conditions in which diffusion, adsorption and other reaction properties are expected to be dynamic, are more representative of the CO₂ storage conditions. Furthermore, based on the findings from our laboratory experimental studies, the CO₂-brine-rock reactions which alters the permeability of the rock samples can be said to occur in a number of stages: in the formation water; within the rock (i.e. by dissolution of dominant

minerals), within the cementing material (e.g. calcite) and to some degree, at the pore scale, causing dissolution of inter-grain cementation, without a significant effect on grain size.

It should be highlighted that the main novelty of this investigation is the quantification of the variation in physical reservoir quality (using changes in permeability as main indicator) of the Bunter Sandstone formation due to the effect of impurities; and this has not been reported in the open literature.

Several numerical modelling methods [95,370,371,373,421,426] have been used to evaluate CO₂ storage potential in the Bunter saline aquifer. These studies include novel techniques for the assessment of storage capacity [95], pressure constraints on storage capacity [370], the viability of large-scale CO₂ injection [371], CO₂ storage within the Bunter Sandstone closed structures [373], the impact of energy systems demands on pressure limited CO₂ storage [426] and the impact of time-varying CO₂ injection rate on large-scale storage [421]. While these studies highlight the relevance of addressing challenges to technology deployment to give more confidence on the CO₂ storage potential of the reservoir, the effect of impurities is yet to be evaluated. The type and amount of CO₂-associated impurities may significantly affect the reservoir physical quality by altering molar volumes and shifting the operational limits in the CO₂ phase diagram. Thus, these effects could lead to higher operation costs and pressures [17] and it may also affect the reservoir storage capacity [22]. Conversely, if the effect of such impurities are not very well pronounced with respect to reservoir performance, there could be a need to simply reconsider the strategy for injection [22]. Therefore, in this research, we evaluated the effect of impurities (NO₂, SO₂, H₂S) in the CO₂ stream during injection and storage in the saline aquifer of the Bunter Sandstone formation. We used time and observation point indices to show the effect of such impurities judging from key reservoir performance indicators. In the study, a single horizontal well injection strategy was used and simulations for

CO₂ injection were conducted over a 30-year period and an additional 30-year post-injection monitoring.

The steps taken in the process of the numerical investigation include: (i) input of data to the CO2STORE module of ECLIPSE E300 compositional simulator, corresponding with the reservoir properties of the targeted storage formation, (ii) model validation using data from the lithostatic pressure gradient with respect to injection depth, (iii) sensitivity tests for reservoir performance with respect to grid dimensions to ascertain optimum injection grid. The main conclusions from the numerical investigation is that impurities affect injectivity differently, and the difference is usually noticeable during the early injection period; without having significant effect on the cumulative injection after an extended period. Though the effect of impurities in the CO₂ stream can be fairly significant, the porosity of storage sites is found to be the most critical factor controlling injection limits. In addition, based on the results from this study, it can be safely concluded that the differences in pressure and volumes during injection, is controlled, to a greater extent, by the volume of impurity found in the injection stream. However, it should also be noted that other fluid properties (e.g. composition of brine, diffusion of different fluids in air and water, viscosity changes, interfacial tension, etc.) could affect the performance of the reservoir, but to a lesser degree.

Furthermore, it should also be emphasised that the central novelty of the numerical investigation is the evaluation of impurity effects during injection and storage in saline aquifer using a compositional modelling approach; taking a case study from the Bunter Sandstone formation; which has not been previously reported in the open literature.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This thesis can be broadly divided into three main parts: (i) extended literature review, (ii) laboratory experimental, and (iii) numerical analysis.

The first part covers a critical review of the literature on carbon dioxide storage. These include options for CO₂ sequestration, storage site evaluation criteria, behaviour of CO₂ in the reservoir, the major CO₂ storage projects in the world, and a future outlook for CO₂ storage. The chapter discusses the critical issues that have been solved and the challenges that require further attention within the discipline of CO₂ storage in general. The recommendations for further research based on the literature review are presented in detail in Chapter 2 and are not repeated in the present chapter. The reader is thus, referred to the literature review section of this thesis.

The second part is a laboratory experimental study that explored the effect of impure CO₂ on grain size distribution and reservoir permeability. The study adopted a method known as CO₂-brine-rock interaction for the evaluation of changes in physical reservoir quality using variation of permeability as indicator. The novel contributions include: (i) the laboratory experimental evaluation of the effect of impure CO₂, containing NO₂, SO₂ and H₂S as impurities on the physical reservoir quality of the Bunter Sandstone formation; (ii) the use of variation in grain size distribution to account for changes in reservoir permeability due to the effect of impurities; (iii) in the previous studies, the effect of impurities on the reservoir rock were only considered for exposure periods of 45 days (CO₂-SO₂ test) and 30 days (CO₂-H₂S test), while all other studies considered the effect of only CO₂ [67,239,242,369]. Thus, in this study, we performed

extended experimental tests under more realistic conditions with different impurities. The study showed that the most significant changes in permeability were caused by CO₂-NO₂ brine-rock reactions which reduced sandstone permeability by 41.6%. The results in this study revealed that the geometric mean of the grain diameter, and consequently, permeability of the rock samples reduced due to the effect of CO₂ and impurities, which can be correlated with decreasing pH of the formation water. These results also suggest that it is necessary to evaluate the physical reservoir quality of potential storage formations depending on the nature of impurities present in the CO₂ stream. The obtained data can, therefore, reduce the uncertainties about CO₂ storage capacity with impurities in the CO₂ stream and can be used to model the operation and performance of CO₂ storage in saline aquifers.

The third part of the thesis is an evaluation of the effect of impure CO₂ on reservoir performance in a sandstone saline aquifer. The study was conducted using a multiphase flow model and the geology and domain of investigation were defined as horizontal layers with representative bulk values derived from laboratory experimental data [417] and the open literature. The novel contributions of the work include: (i) an evaluation of reservoir behaviour during injection and storage of impure CO₂ using the Bunter Sandstone formation as a case study; (ii) the use of time and observation point indices to account for the effect of various chemical phases with respect to reservoir performance in saline aquifer; (iii) the effect of impure CO₂ on reservoir performance in a sandstone saline aquifer has not been previously presented in the open literature. Hence, we performed simulations for pure and impure CO₂ injection at constant rate and pressure using a single horizontal well injection strategy for a period of 30 years and an additional 30-year monitoring. The main conclusion from this study show that impurities affect injectivity in a different way in comparison to pure CO₂. However, the effect is encountered at the early stages of injection and this does not affect the cumulative

injection volume after a prolonged period. The results also suggest that although impure CO₂ affects injectivity, the porosity of storage sites is key factor that should be considered in maximising injection. Additionally, the injected CO₂ remained safely secured 30 years post-injection; suggesting that containment is effective. Based on the results from this study, it is suggested that simplified models be further applied to evaluate reservoir performance with other impurity types that were not previously studied. We anticipate that the results presented in this study can be extended to other saline aquifers that may have a similar geologic history with the Bunter Sandstone formation. Therefore, our findings should be a source of further assurance on the practicality of technology deployment in the UK Southern North Sea.

6.2 Recommendations

The following recommendations are made for further investigation and implementation of the work developed in this thesis:

(i) The critical review of literature conducted in this thesis suggest that although a high-quality knowledge base has been established on CO₂ storage in general, there are still challenges that need further attention. These challenges have been highlighted in detail in **Section 2.6**. However, of all the identified challenges, it seems that the major hindrance to CO₂ storage deployment lies in public acceptability of the technology. Therefore, it is important for future research to focus greatly on changing the public opinion toward CCS in general. These can be achieved probably through the implementation of better communicative practices such as by enhancing social and technologically mediated information flows through which informed opinion circulates.

(ii) Although this study investigated the effect of impurities on grain size distribution and reservoir permeability, it did not consider, in detail, the effect of same impurities on the

reservoir porosity. It is important for future studies to incorporate porosity evaluation during CO₂-brine-rock interaction studies in the presence of impurities. It will also be interesting if such approach is explored for CO₂-associated impurity types that were not considered in this study.

(iii) The rise of pore fluid pressures may constrain the storage capacity of the reservoir affecting the expected physical containment. The effect of pore fluid pressure rise should be investigated with regards to CO₂ storage capacity estimation for all geologic formations; and this should be considered for impure CO₂ cases in the case that a significant effect on reservoir performance is caused by the effect of any given impurity.

(iv) Before CO₂ storage is undertaken in any geologic formation, a detailed site characterisation is required. Thus, site characterisation studies should always consider the effect of impurities on CO₂ storage reservoirs.

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