

Effects of CO₂-Brine-Rock Interactions on CO₂ Injectivity – Implications for CCS

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Preface

This thesis has been submitted to the Department of Geosciences at University of Oslo in accordance with the requirements for the degree of Philosophiae Doctor (PhD). The study herein was completed as part of the SUCCESS project. SUBsurface CO₂ storage – Critical Elements and Superior Strategy (*www.fme-success.no*) is a consortium with partners from industry and science, hosted by Christian Michelsen Research, and is an Environment-friendly Energy Research (FME)-center assigned by the Research Council of Norway (RCN). In particular, this Ph.D. thesis has contributed to injectivity assessment within KMB-INJECT, a fully integrated part of SUCCESS consortium.

This thesis uses Manuscript Document Format and is organized in two parts. In the first part, relevant scientific background, parameters affecting injectivity, the utilized thermodynamic framework and the physics of salt precipitation are given a thorough review. The second part consists of published articles. The result of this work has contributed to scientific knowledge in the terms of six manuscripts (hereinafter referred to as "Paper") of which I am the first author of five and a co-author of one. A self-contained summary of the most important findings of these papers is given in Chapter 4. The papers and proceedings themselves are attached at the end of the thesis in chronological order.

Rohaldin Miri, Oslo, July 2015

Abstract

Carbon capture and storage (CCS) in geological reservoirs – especially saline aquifers – is a key midterm solution to mitigate climate changes caused by increasing anthropogenic CO₂. In order to ensure that a CCS project reach the required level of success, three essential elements need to be guaranteed; storage capacity, injectivity and containment. Among these elements, relatively less research has been conducted relevant to the injectivity, thus there are several technical uncertainties in this regard that should be understood and quantified in order to ensure long-term storage of CO₂. This thesis is therefore centered at improving such knowledge and understanding by addressing some of the vague research areas in regard to CO₂ injectivity including: CO₂/H₂O mutual solubilities, salt precipitation and depositional heterogeneities.

First part of this study is devoted to thermodynamic modeling of fluid mixtures relevant for CO₂ storage with particular focus on effect of methane (CH₄) and sulphur dioxide (SO₂) impurities. To do this, a molecular based framework, Statistical Association Fluid Theory (SAFT) is chosen and the molecular parameters required by the model were adjusted against the available experimental data. The developed model is effectively used to predict phase partitioning, the aqueous phase density and water drop-out in contact with solid surface, which we believe to be especially well-suited to the assessment of injectivity of a proposed CO₂ storage reservoir.

In the next part of this thesis, the processes of drying-out and salting-out were explored in more detail. This work encompasses the fabrication of the two sets of glass microchips, as well as series of experimental characterisation that has given us a valuable insight into the mechanism of salt precipitation. In particular, we have identified two mechanisms which together dramatically intensify the precipitation rate and amount of salt precipitated. From this insight, the reported discrepancies in the literature regarding the salt precipitation could be successfully explained and a new prototype for modeling of the process could be provided. We have also studied, but to a lesser extend, the effect of prepositional heterogeneities on the plume migration and pressure response at the injection well. We came to the conclusion that extreme well and aquifer pressures are unlikely for the setting studied in this thesis.

Rohaldin Miri, Oslo, July 2015

Acknowledgments

First and foremost, I offer my sincerest gratitude to my supervisors, Professor Per Aagaard, Dr. Helge Hellevang, and Magnus Wangen for the continuous support, patience, motivation, and immense knowledge. Their complementary qualities, both professionally and personally, have been crucial for me as a PhD student and I owe them great thanks. *Helge* – Your dedication and enthusiasm for scientific research has inspired me so much. I will miss those hot discussions which we had every day on my office whiteboard.

I am highly indebted to Professor Bjorn Kvamme and Professor Tatiana Kuznetsova, who have introduced me for the first time to the beautiful world of surface chemistry and molecular dynamic simulation.

Completing this work would have been all the more difficult were it not for the support and friendship provided by the other members of the Department of Geoscience at UiO. I have enjoyed our numerous conversations, both subject related and non-subject related. Working with so many skilled and cheerful people has made my PhD period much easier. I record my sincere thanks to *Anja, Beyene, Irfan, Karoline, Marcel, Anne, Charlotte* and *Asger* for their gracious attitude and boundless help during my study. *Salah, Mohammad, Mohsen, Amir, Noora* and *Hossein* thanks for all Persian gatherings we have had together. And man with a bag of solutions, *Gudmund*. I know you have suffered a lot reading my "blah, blah, blah" manuscripts. Thanks a lot!

I must express my thankfulness in depth to Fatemeh, my wife, who beyond my understanding, has kept up with me through these last intensive months. I was continually amazed by your patience as you experienced all of the ups and downs of my research. I also express my gratitude to my dear *Family* and for their endurance, support and encouragement without which it would have been impossible for me to complete this work in its present form.

In conclusion, I would like to express my gratitude towards Department of Geoscience at UiO, the Norwegian Research Council and the SUCCESS center for financial support of this Ph.D. fellowship and hosting me. This study was partly funded by the RCN and industry partners through the project 190002/S60 Subsurface storage of CO₂ - Injection well management during the operational phase (Inject). The work has also been partly funded by the University of Oslo and the SUCCESS Centre for CO₂ storage under grant 193825/S60 from the RCN.

Rohaldin Miri, Oslo, July 2015

List of Papers

This thesis consists of an introduction and the following articles:

Paper A: *Examination of CO_2 – SO_2 solubility in water by SAFT1– implications for CO_2 transport and storage*

R. Miri, H. Hellevang and P. Aagaard

Published, J. Phys. Chem. B, 2014, 118 (34), pp 1021410223

Paper B: *Phase relations in the Longyearbyen CO_2 Lab reservoir – forecasts for CO_2 injection and migration*

R. Miri, H. Hellevag, A. Braathen and P. Aagaard

Published, Norwegian Journal of Geology, Vol 94, pp. 217232. Oslo 2014. ISSN 029-196X

Paper C: *On the water content of dense phase CO_2 – SO_2 system – implications for CO_2 transportation and injection*

R. Miri, Bjørn Kvamme, Tatiana Kuznetsova, H. Hellevag and P. Aagaard

Unsubmitted manuscript

Paper D: *Salt precipitation during CO_2 storage - a review*

R. Miri and H. Hellevag

Submitted to International Journal of Greenhouse Gas Control

Paper E: *New insights on the physics of salt precipitation during injection of CO_2 into saline aquifers*

R.Miri, R. V. Noort, P. Aagaard and H. Hellevag

Published, International Journal of Greenhouse Gas Control

Paper F: *Modelling CO_2 migration in aquifers; considering 3D seismic property data and the effect of site-typical depositional heterogeneities*

A. Sundal, R.Miri, T. Ravn, and P. Aagaard

Published, International Journal of Greenhouse Gas Control 39 (2015) 349365

Invited Talks:

1. **Miri, R.**; Hellevang, H.; Aagaard, P., Pore-Scale Simulation of Water Films Connectivity during CO₂ Injection into Saline Aquifers. CLIMIT, 2014
2. **Miri, R.**; Hellevang, H.; Aagaard, P., Modeling the Water Content of Carbon Dioxide with CH₄ and SO₂ Impurities Using Statistical Association Fluid Theory. GHGT 2014
3. **Miri, R.**; Hellevang, H., Developments in SAFT EOS for Carbon Capture and Storage (CSS), Fourth EAGE CO₂ Geological Storage Workshop. 2014.
4. Sundal, A.; Hellevang, H.; **Miri, R.**; Aagaard, P., (2014, April). On Layer Specific CO₂ Plume Distributions and Variability in Mineralization Potential. In Fourth EAGE CO₂ Geological Storage Workshop
5. Sundal, A., **Miri, R.**, Petter Nystuen, J., Dypvik, H., & Aagaard, P. (2013, April). Modeling CO₂ distribution in a heterogeneous sandstone reservoir: the Johansen Formation, northern North Sea. In EGU General Assembly Conference Abstracts (Vol. 15, p. 13770).
6. Sundal, A.; Nystuen, J. P.; Dypvik, H.; **Miri, R.**; Aagaard, P., Effects of Geological Heterogeneity on CO₂ Distribution and Migration-A Case Study from the Johansen Formation, Norway. Energy Procedia 2013, 37, 5046-5054.

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Part I
Introduction

Chapter 2

Introduction

Research has shown that, due to human activities, the level of atmospheric carbon dioxide has increased significantly since the beginning of the Industrial Revolution. The following chapter gives a brief introduction to the consequences of this effect on the earth climate which may serve as a general motivation for this study. In addition, the motivations and the research objectives of this study are described and thesis outline is given.

1.1 Background

The United Nations Intergovernmental Panel on Climate Change (IPCC) in numerous studies has assessed the increasing of earth temperature due to the anthropogenic emissions of Greenhouse Gas (GHG) (Pachauri et al., 2014; Stocker et al., 2013). GHGs such as water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4) and ozone (O_3) absorb the radiated heat from the Earth toward space through the natural greenhouse gas effect, thus keeping the planet from freezing. However, human activities, such as the burning of fossil fuels are increasing the level of GHGs, leading to what is known as global warming. Land-surface temperature analyses have shown that the rise in average world land temperature is approximately $1.5\text{ }^\circ\text{C}$ in the past 250 years, and about $0.9\text{ }^\circ\text{C}$ in the past 50 years (Rohde et al., 2013). Recent temperature records reveal that 2015 has so far been the warmest year in more than a century, owing to the ever-growing amounts of greenhouse gases in the atmosphere (Hansen et al., 2015). Global warming may result in intense environmental concerns such as increasing sea level, loss of fragile ecosystems, increased intensity of meteorological phenomena, and increased flooding and droughts (Pachauri et al., 2014). Nowadays, these series of environmental concerns are recognized as climate change and it is well accepted that to avoid this, GHG emissions has to be reduced significantly over 21st century.

CO_2 is identified as the main anthropogenic GHG, accounting for 80 percent of the human contribution to the greenhouse effect (Hartmann et al.,

2013). Since the industrial revolution, the atmospheric CO₂ concentration has continuously increased to ~ 397 ppmv (at a rate of about 1 ppmv per year) and under a business-as-usual energy scenario, it is expected that throughout the coming centuries, this value may reach ~ 750 ppmv (Houghton et al., 2001; Tans, 2015; Wigley et al., 1996; Yang et al., 2010).

IPCC Working Group I has proposed a set of pathways to stabilize the atmospheric CO₂ concentration at 450, 550 and 750 ppmv over the next hundred years (Wigley et al., 1996). Out of the several mitigation options carbon capture and storage (CCS) in geological reservoirs is recognized as the best solution with respect to mitigation potential (Bruant et al., 2002; Bruckner et al., 2014). Nevertheless, there are other mitigation options, such as ocean storage, mineral carbonation and replacing fossil fuels with renewable energy, that have gained less attention owing to environmental implications or intense energy requirements (Zeidouni, 2011). Recent investigations by the International Energy Agency have shown that CCS can contribute to 14 % of the reduction in global greenhouse gas emissions required by 2050 in order to limit global warming to 2 °C (IEA, 2013).

Large-scale CCS projects could be planned and demonstrated via several CO₂ geological storage possibilities (Metz et al., 2005), including:

- Deep saline aquifers (~ 2,000 - 20,000 GtCO₂¹)
- Depleted oil and gas reservoirs (~ 675 - 1,200 GtCO₂)
- Enhanced oil/gas recovery (~ 160 - 370 GtC)
- Un-mineable coal seams (~ 146 - 228 GtC)

Generally, we are interested in determining the suitability of these geological options for CO₂ storage. In order to be suitable for storing CO₂, each of these settings are required: to have sufficient pore volume to store the significant amounts of CO₂ (storage capacity), to have sufficiently high permeability to allow fluid flow of the CO₂ (injectivity), and to have a sealing structural layer to prevent possible CO₂ leakage to the surface (containment). In this research, the focus is specifically on injectivity. However, a big portion of study is also reverent to storage capacity estimation and leakage risk assessment.

1.2 Motivation and objectives

A combination of technical, economic and political considerations defines the ideal CO₂ injection scenario, *i.e.*, to store the amount of planned CO₂ (based on storage capacity estimations) with the maximum possible injection rate in the shortest possible operational time (20-30 years), and with the minimum number of drilling wells (Gaus et al., 2008; Miri and Hellevang, 2015; Miri et al., 2015; Yang et al., 2010). Carbon dioxide, however, is a reactive fluid, and its physical and chemical interactions with the host rock induced by pres-

¹ 1 GtCO₂ = 10⁹ metric tons of CO₂ = 10¹² kg of CO₂ = 0.27 GtC

sure (because of dissolution), temperature (cooling and Joule-Thompson effects) and saturation variations (geochemical reactions) make the assessment of injectivity complicated and different from petroleum industry experience of non-reactive fluid injection (André et al., 2014; Muller et al., 2009; Ott et al., 2015; Peysson et al., 2014a; Pruess and Müller, 2009; Zeidouni et al., 2009). Despite the importance of these interactions, little success has been achieved on the quantification of the expected impact on the formation injectivity and near-well pressure build-up (Bachu, 2015; Gaus et al., 2008). In addition, extend and basic mechanisms which these interactions through it affect the injectivity is not well understood yet and is place of discussion. Therefore, the present-day uncertainty regarding injectivity alteration caused by fluid-rock interactions is very high (Gaus et al., 2008; Miri et al., 2015).

The overall aim for this thesis has been to improve the prediction of reservoir injectivity with a particular focus on complex phenomena involved in the near wellbore region. This dissertation has embraced multidisciplinary methods and the work involves numbers of carefully selected experimental and theoretical studies in order to reduce uncertainties associated with assessment of injectivity of a proposed CO₂ storage reservoir. This PhD study addresses following three main research topics:

- **Thermodynamic modeling:** The first component of this thesis is devoted to thermodynamic modeling of fluid mixtures relevant for CO₂ storage with particular focus on effect of methane (CH₄) and sulphur dioxide (SO₂) impurities (Paper A and B). Some of the main addressed research questions in this part are: How mutual solubility between CO₂ and water and the aqueous phase density changes with respect to the impurities? and how this, in turn, will impact the injectivity? In what way and how will SO₂ affect the overall chemistry of the CO₂-rock system? How and to what degree will the efficiency of the transportation and CO₂ injectivity be altered? (Paper C)
In addition to the case specific applications and objectives given above, other more general goals have been implicitly considered for the first part, such as, (1) having a reliable and robust thermodynamic package for later integration with in-house fluid-flow solvers or commercial packages, to assess the injectivity (2) to estimate the effect of impurities on the water content of CO₂ for later application to formation dry-out and salt precipitation.
- **Drying-out and salting-out:** The primary purpose of this paper is to provide the reader with a comprehensive review for understanding the state-of-the-art knowledge on salt precipitation in the context of CO₂ storage in saline aquifers. Other goal for this review study is to specify how serious salt precipitation is for CO₂ storage and whether its importance has been overlooked (Paper D). The most important question to investigate in this part is whether trapped water films in

porous media have enough continuity and conductivity to transport fresh brine to an evaporating front, and therefore whether these can cause increased rates and quantities of salt precipitation (Paper E).

- **Reservoir Heterogeneities:** This component of thesis aims to examine the effect of depositional heterogeneities and physical boundaries of the reservoir (*i.e.*, closed or open) on the pressure response at the injection well (Paper F).

1.3 Outline

This thesis is organized in two parts. First part is referred to as *Introduction* where the purpose of the text is to provide supporting information for understanding and motivation for the papers, to link the papers together and to put the work into a broader context. This part is organized as follows: In chapter 1, we provide the necessary preliminaries and background. Technical considerations in relation to CCS technology are given a short review in Chapter 2, succeeded by a discussion on the parameters affecting injectivity and the physics of salt precipitation. In chapter 3, the utilized thermodynamic framework are given a thorough review. This material is not new, but at present it is scattered around in many works, meaning that a new researcher in this area will have to read several articles, often with small, but significant differences in formulas and notation. Chapter 4 summarizes main results from our papers. The last chapter of this part, chapter 5 contains conclusion and suggestions for further work.

The second part consists of published articles. The result of this work has contributed to scientific knowledge in the terms of six manuscripts (hereinafter referred to as "Paper") of which I am the first author of five and a co-author of one. The content of the papers will not be explicitly repeated in part 1, but a self-contained summary of all papers is given in Chapter 4. The appendix contains the proceedings and an example of the implemented thermodynamic model input file.

Chapter 2

Scientific Background

In this PhD thesis we assess factors influencing the CO₂ injectivity of a proposed CO₂ storage reservoir. In this chapter, the supporting information for understanding of the papers is provided, including an overview of the parameters affecting injectivity and the physics of salt precipitation. First we will give a quick introduction to the principles of a CCS project.

2.1 Trapping mechanisms

Sequestration of CO₂ in deep saline aquifers can be achieved through number of trapping mechanisms, which are active at different time and length scales. How these mechanisms will develop largely depends on the physical and chemical characteristics of the rocks and fluids. The following four mechanisms are commonly distinguished for trapping CO₂ underground after injection (Bachu and Adams, 2003; Benson and Orr, 2008; Hellevang, 2015):

2.1.1 Structural trapping

Under normal thermodynamic conditions relevant to CCS in saline aquifers, the injected CO₂ is usually at supercritical state and its corresponding density is 30-40 % less than that of the ambient groundwater or brine (Kaldi and Gibson-Poole, 2008; Miri and Hellevang, 2015). Therefore, due to buoyancy, the CO₂ plum tends to rise to the top of the formation and accumulate beneath a low permeability seal. Seals or caprocks can be defined as physical (typically a low permeability shale) and/or hydrodynamic barriers that will confine the CO₂ to the reservoir. Typically, seals will be formed by water saturated fine-grained sediments like mudstones, shales or fine-grained chalks in contact with the host fluids (water, oil, gas) from below (Halland et al., 2011). To form an efficient seal, the rocks must have a small pore throat radius leading to a higher capillary entry pressure, thus compensating the buoyancy effect.

Molecular diffusion is another way for CO₂ to migrate into the caprock. However, the effective penetration length of CO₂ via this process is very limited in time scales of less than thousands of years. The extensive experience from oil and gas production has proven the seepage of oil and gas reservoirs. The seepage has attributed to the fractures or faults that might open up or reactivate under certain conditions such as pressure build-up induced by the injection process. Therefore, to minimize the risk of leakage to the surface or shallower subsurface levels, the mechanical integrity of the seal should be guaranteed. The geochemical interaction of CO₂ with the caprock might also affect its integrity. However, the picture is uncertain in this case and research is in progress. Structural trapping accounts for 80 % of early-time trapping during geological storage of CO₂, but its contributions decrease over time (Li, 2013; Sundal et al., 2015).

Structural trapping is mostly represented by traps formed by folded or fractured rocks, where the natural storage structure keeps the CO₂ plume from migrating. If instead the plume is trapped due to a change in rock type, in which a layer is discontinuous preventing migration, it is referred to as a stratigraphic trap. Examples of various types of traps are shown in Fig 2.1. If we have a reservoir like the one depicted in the Fig 2.1a, the CO₂ plume will only migrate until it reaches the highest point, and there remain trapped. In this kind of reservoir structural trapping is the most dominant trapping mechanism, and will remain so for thousands of years given that no fractures or faults are created or reactivated, causing escape. There is also the option of having an open system, which relies more on the other trapping mechanisms. There is still a caprock preventing direct vertical migration, but the plume is allowed to flow laterally, and to some extent vertically, though the relation between the two depends on the slope of the reservoir. In all cases the CO₂ is trapped as a free phase, typically supercritical. (Hellevang, 2015).

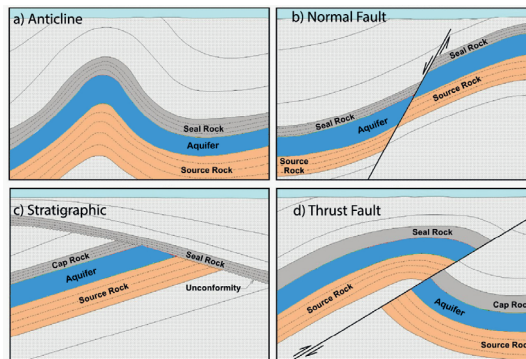


Figure 2.1: Schematic showing various options for structural trapping of CO₂ in underground geological formations (Geologyin, 2015)

2.1.2 Residual trapping

Residual trapping refers as pore scale immobilization of CO₂ by capillary forces. During injection of CO₂, the saturation of gas (non-wetting phase) in the reservoir increases as the gas phase migrates upwards due to buoyancy forces. In other words, at the leading edge of the moving front a drainage process occurs and gas phase displaces formation water out of the porous media (Miri and Hellevang, 2015; Ott et al., 2015; Zeidouni et al., 2009). Generally, the reservoir fluid (typically saline water) is the wetting phase, so there will always be thin films of water coating the inside of the pores and irregular corners (Miri et al., 2015). Because of this, capillary forces are dominant at the trailing edge of CO₂ plume, and the water phase will flow back along the edges into the pore space via an imbibition process (Kim et al., 2012; Pruess and Müller, 2009). When the water flows back, thin brine films swell snapping off the connection between the CO₂ blobs in the neighboring pores (Chatzis and Dullien, 1983; Dong and Chatzis, 2010). Therefore, the CO₂ is disconnected and trapped in the center of the pores as an immobilized phase. This is because the threshold pressure never will become large enough to create the needed capillary pressure for the bubble to move through the brine (Dong and Chatzis, 2010; Pentland et al., 2010). Thus, a trail of residual CO₂ is left behind the upwardly migrating plume and trapped as immobile CO₂ bubbles surrounded by water (Juanes et al., 2006). This trapping mechanism is illustrated in Fig 2.2.

Since this trapping occurs as a result of the overall migration of the CO₂ plume, the efficiency of the trapping will depend on the flow within the reservoir, the pore size distribution and the initial CO₂ saturation (Li, 2013). Capillary trapping mechanism makes an important contribution to overall CO₂ trapping in terms of the amount, duration and safety of storage. The estimations has shown that capillary trapping provides the most significant contribution to overall CO₂ trapping (approximately 40 % of injected CO₂) in the first 100 years after injection, and may control the extent of solubility and mineral trapping at the later stages (Sundal et al., 2013a).

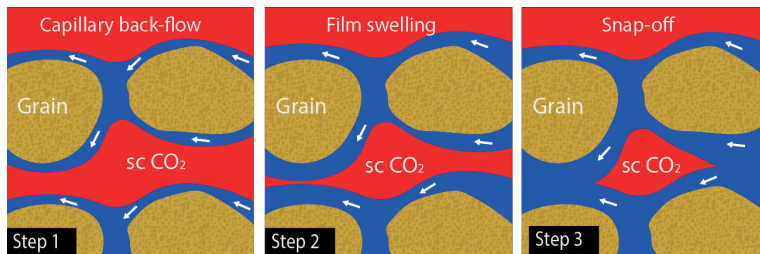


Figure 2.2: Schematic showing pore scale mechanism of capillary trapping due to brine films swelling and snapping off the connection between the CO₂ blobs in the neighboring pores

Thus, this process occurs much faster than bulk dissolution and chemical reaction and is considered to be main sequestration mechanism for sloping aquifers (Doughty, 2007). However, capillary trapping mechanisms are poorly understood and quantification of the residual trapping efficiency over time remains a challenging task mainly due to lack of well-characterized and well-controlled experimental data.

From a modeling point of view, residual trapping requires models that capture capillary pressure and relative permeability hysteresis, *i.e.*, irreversibility of flow processes in porous media would result in different saturation distribution for each of the drainage and/or imbibition processes. In order to correctly know the capillary pressure and relative permeability, we must know the history of saturation changes (Juanes et al., 2006). The van Genuchten model is one of several ways of relating relative permeabilities to CO₂ and brine saturations (Van Genuchten, 1980). The model is empirical and requires experimental data to find model parameters. The trapped-gas saturation (S_{gr}) that remains at the end of the imbibition process and shape of the relative permeability are key features of hysteresis phenomena that require special consideration during parametrization of van Genuchten model (Hellevang, 2015).

2.1.3 Solubility trapping

Solubility trapping accounts for the amount of CO₂ dissolved in the formation brine through both physical and chemical processes. This mechanism provides the most significant contribution to overall CO₂ trapping on the time scale of decades after injection, and may be a driver to mineral trapping at later stages (Sundal et al., 2013a). The rate of dissolution depends on factors such as the contact area between the CO₂ plume and the unsaturated brine, and diffusion of dissolved CO₂ away from the interface (Hellevang, 2015). Therefore, solubility trapping will be most efficient in sloping aquifers where the CO₂/water interface is large or in heterogeneous reservoirs where the CO₂ plume spreads over larger volumes of the reservoir, providing more surface area for dissolution (Hellevang, 2015; Sundal, 2015a).

The total amount of molecular CO₂ that dissolves in water is a function of pressure, temperature, and brine salinity (Spycher and Pruess, 2005; Spycher et al., 2003). At supercritical condition, CO₂ has a considerable solubility in formation water. Higher temperature and salinity as well as lower pressure will give less dissolution of CO₂ (Miri et al., 2014a; Spycher and Pruess, 2005). Dissolution of CO₂ in the brine is due to three mechanisms:

- *Diffusion of CO₂ within the brine*; the difference between the chemical potential of CO₂ molecules across the interface between phases would result in diffusion of CO₂ within the brine allowing more CO₂ from the gas phase to be dissolved in the brine (Liebscher et al., 2013).

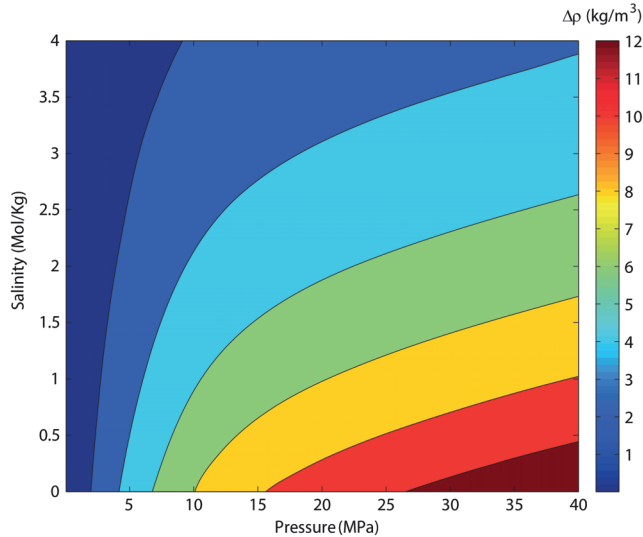


Figure 2.3: Density difference of water and water saturated CO_2 at 37°C for different pressures and salt modalities. The density difference decreases with increasing molality as CO_2 solubility decreases (Miri et al., 2014a).

- *Convective mixing effect*; within thermodynamic conditions relevant to CO_2 storage, the density of the CO_2 saturated water is approximately 1-1.5 % higher than the density of pure water and difference (e.g., see Fig 2.3) is decreasing with increasing salinity (De Silva and Ranjith, 2012; Miri et al., 2014a). This density difference would result in a density instability (Rayleigh-Taylor instability) in an isotropic media and consequently plumes of CO_2 saturated water will migrate downwards. This can accelerate the mixing process as instabilities act like eddy currents and enhance the diffusion process (Ghesmat et al., 2011; Hassanzadeh et al., 2007). As these narrow plumes of CO_2 enriched water plunge downwards, new unenriched fluid is allowed to flow upwards and meet the transition layer, thus allowing for further dissolution (Han et al., 2010). Through this process significant quantities of CO_2 are trapped and it will then migrate with the brine.

This trapping mechanism starts with injection and occurs all along the surface of the plume. This happens in the near well area, but perhaps more significantly further away from the injection well. This is called the *convective mixing effect* or *density-driven mixing* and is regarded as the dominant mechanism for CO_2 dissolution, as it is orders of magnitude faster than the others and it enhances the overall dissolution of CO_2 (e.g., see Fig. 2.4). It is however argued that in layered sedimentary reservoirs with high degree of heterogeneity, there is a very limited possibility for density-driven mixing in large scales (Bjørlykke,

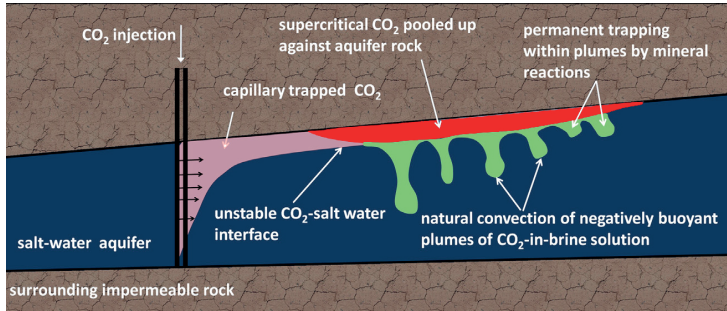
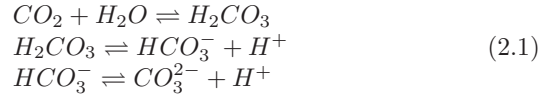


Figure 2.4: Schematic illustration of residual and dissolution trapping mechanisms. Dissolution occurs through the contact area between the CO₂ plume and the formation brine (modified after [Riaz and Cinar, 2014](#)).

1993; [Frykman and Wessel-Berg, 2014](#)).

- *Chemical dissolution*; In addition to the physical solubility (*i.e.*, the equilibrium between gaseous CO₂ molecules and CO₂ in the aqueous solutions), CO₂ in formation brine will form a weak carbonic acid which dissociates in two steps to form bicarbonate and carbonate:



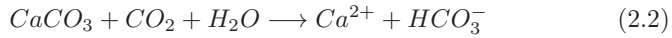
where the equal sign (\rightleftharpoons) denotes equilibrium. This process consumes CO₂, and will in turn lead to dissolution of minerals that originally were stable and to formation of carbonate minerals. This is referred to as mineral trapping or CO₂ carbonatisation and will be briefly described in the next section.

2.1.4 Mineral trapping

During injection, some CO₂ dissolves in the formation brines, whereupon the pH decreases typically from near neutral to 3 or even lower depending on the CO₂ pressures encountered during CO₂ storage ([Benson and Cole, 2008](#); [Hellevang, 2015](#)). The increased acidity of the formation water will alter the geochemical environment of the reservoir and lead to dissolution of some primary minerals and precipitation of secondary mineral assemblages. These reactions may change the formation porosity and permeability ([Hellevang, 2015](#); [Hellevang et al., 2013](#); [Pham et al., 2011](#)).

However, the time scale for mineral trapping is of the order of hundreds to thousands of years, making this one of the slowest of the sequestration mechanisms ([Giammar et al., 2005](#)). The amount of CO₂ that will be stored in the form of carbonate minerals varies with rock type, gas pressure, temperature,

porosity and mineral composition (Kharaka et al., 2006; Oelkers and Cole, 2008). In carbonate reservoirs, these processes will be faster than in siliciclastic reservoir rocks (André et al., 2010). Assuming we have a carbonate reservoir that is predominantly calcite, we have the following reaction:



Dissolution of the reservoir rock will in turn change the porosity and permeability of the rock, which will affect the flow of the CO_2 in the rock, and this may in the long run cause compaction of the rock. In addition we may have formation of larger cavities. This occurs because we will have smaller pressure variations in the reservoir. When two saturated fluids with different partial pressures of CO_2 mix, the resultant fluid will be undersaturated, and chalk will dissolve, forming larger caves in the reservoir rock, often referred to as wormholes (Bemer and Lombard, 2010; Egermann et al., 2006; Lombard et al., 2010). However, carbonates will also reach saturation soon and the reactions stops. Therefore, the wormhole formation is not likely to occur in the CO_2 storage settings as it requires an open system with large flow. Overall, some reactions may be beneficial to storage, but others may result in formation of preferential flow pathways, which in turn can compromise the safety of long-term CO_2 sequestration (Yang et al., 2010).

Mineralization is the most permanent trapping mechanism and it depends primarily on the amount of carbonate minerals present in the reservoir rock and fluid. However, in sandstone reservoirs formation of minerals will typically be less important during the injection phase, as this is a fairly slow process that starts after several years and only becomes truly significant after ~ 1000 years (André et al., 2011; Pham et al., 2011). In carbonate reservoirs we may see mineralization at an earlier stage in time given a large enough partial pressure of CO_2 . This is due to the fact that carbonate minerals are more reactive and will be affected by the CO_2 to a greater extent (André et al., 2010; Xu et al., 2001).

However, this is still less important as an initial trapping mechanism during the injection phase. The reprecipitation of minerals in a carbonate reservoir would under perfect conditions with completely pure chalk, occur almost immediately. However, there are almost always some impurities that will cause these reactions to be much slower. Both dissolution and precipitation are in addition dependent on temperature, pressure, pH and fluid composition, which will vary from reservoir to reservoir.

2.2 Storage potential

Storage capacity (*i.e.*, accommodation capacity) and injectivity (*i.e.*, sustainable flow capacity) are two deterministic criteria which largely characterize the storage potential for candidate geological sites (Cinar et al., 2007;

Yang et al., 2010). The storage capacity of a candidate reservoir, however, is an ambiguous term and recent research suggest using *CO₂ storage resource* and/or *CO₂ storage reserve* instead (Bachu, 2015). The CO₂ storage resource refers to the total amount of CO₂ that theoretically can be stored into a reservoir. The CO₂ storage reserve, however, represents the amount of CO₂ that can be commercially stored into a reservoir within a known time, using existing technology and under current economic conditions, operating methods and governmental regulations. Simply, the storage reserve is an achievable or accessible fraction of the CO₂ storage resource. Therefore, the storage reserve could be increased with time utilizing artificial means or engineering methods (*e.g.*, increasing number of injection wells, drilling water producing wells). However, the storage resource is a time and space independent estimation as the entire aquifer is considered (Bachu, 2015). Estimating the CO₂ storage reserve is a complex process that involves integrating geological and engineering data. USDOE (2007) provides a relatively simple equation for the calculation of CO₂ storage capacity in saline aquifers as:

$$M_{CO_2} = A \cdot h_g \cdot \phi_{tot} \cdot \rho \cdot SE \quad (2.3)$$

Where M_{CO_2} , A , h_g , ϕ_{tot} , ρ are, respectively, mass of CO₂, aquifer area, gross thickness of saline formations, average total porosity and density of CO₂ at reservoir condition. SE represents the CO₂ storage efficiency, which is described in the next section.

2.2.1 Storage efficiency

The *storage efficiency* or *storage factor*, SE , is a measure of the completeness of storage of CO₂ into a reservoir. In other words, storage efficiency refers to the degree of filling of a reservoir. The coefficient is defined as the ratio of the quantity of the stored CO₂ to either the total pore volume (*i.e.*, resource) or the accessible pore volume (*i.e.*, reserve) of the reservoir under similar conditions. The former definition is referred to as regional-scale storage efficiency and can be used in connection with Eq.(2.3) to estimate the static or volumetric storage resources of a given reservoir (USDOE, 2007).

$$SE^{regional} = \frac{V_{CO_2, injected}}{V_{\phi} = A \cdot h_g \cdot \phi_{tot} = CO_2 \text{ Resource}} \quad (2.4)$$

The later definition is referred to as the local-scale storage efficiency and can be used to in connection with Eq.(2.3) to estimate the dynamic storage reserve of a given reservoir.

$$SE^{local} = \frac{V_{CO_2, injected}}{CO_2 \text{ Reserve}} \quad (2.5)$$

In storage of CO₂ in saline aquifers, the storage efficiency is determined by three factors:

- the geological properties of the reservoir, such as porosity, permeability, net to gross, thickness and area (called geological factor, E_{geol})
- the completeness of displacement of water by CO₂ (called the displacement factor, E_d)
- the degree of conformance of the entire aquifer (called the conformance factor, E_V)

In this case the storage efficiency is expressed as the product of the geological, displacement and conformance factors (Bachu, 2015; Birkholzer and Zhou, 2009).

$$SE = E_{geol} \times E_V \times E_d \quad (2.6)$$

The conformance factor or macroscopic displacement efficiency, E_V , depends to a great extent on the non-uniformity of the reservoir and the ratio of the viscosity of the water to that of CO₂. The more heterogeneous the structure and physical properties of the bed and the greater the viscosity ratio, the lower the value of the conformance factor (*e.g.*, Bachu, 2015; Sundal, 2015a; Sundal et al., 2013a). The displacement factor or microscopic displacement efficiency, E_d , describes the fraction of water displaced from the pores by the injected CO₂, in those pores which are contacted by the CO₂. In a simpler language, E_d is a measure of the average effective CO₂ saturation which for the most ideal scenario and on the scale of pore is $1 - S_{w_{irr}}$ (Bachu, 2015; Birkholzer and Zhou, 2009). Here $S_{w_{irr}}$ is irreducible water saturation. However, because of poor displacement efficiency, local and regional heterogeneity, CO₂ buoyancy and processes like imbibition, the residual CO₂ saturation is far from ideal condition and could vary such as $0.045 \leq S_{CO_2,irr} \leq 0.415$. For a more detailed description of parameters determining storage efficiency the reader is referred to Bachu (2015).

It is important to note that the storage efficiency is a distinct characteristic of reservoirs. It is not possible to obtain a universal value for it. However, to give a clue of typical values, published values in the literature vary in a wide range from $\leq 1\%$ to $\geq 10\%$ (Bachu, 2015). Nevertheless, the values are small in comparison with other gas injection processes in the oil industry, showing poor displacement efficiency overall. The storage efficiency is primarily used to estimate the storage resource or reserve of a given reservoir. However, there are other implications as for example, to compare storage potential of two different reservoirs or to monitor the storage performance with time. The attention, therefore, must be given to use values which are obtained in a similar time reference as storage efficiency is a time dependent parameter in relation to injectivity.

2.2.2 Injectivity

Having a high storage capacity alone is not enough for a reservoir to be considered as a suitable storage site. There are two other requirements; high, sustainable injectivity and safe containment. The *reservoir injectivity* measures the ability of a reservoir to accept CO₂ at maximum possible flow rate before loosing its mechanical integrity (keep average reservoir pressure less than critical pressure). The *well injectivity* (or well capacity), on the other hand, measures the ability of a single injection well to accept CO₂ into a formation without reactivating existing faults or creating new fractures (Birkholzer et al., 2015; Schembre-McCabe et al., 2007). To ensure this, the injection pressure (*i.e.*, the well flowing pressure) must not exceed 90% of fracturing pressure considering all others regulatory factors with regard to the injection such as maximum pump pressure (EPA, 2008; Mathias et al., 2009b). Well injectivity is mathematically quantified by an index represented as the ratio of the injection flow rate divided by the pressure increase (Dake, 1983). A simple model used by reservoir engineers to estimate the injectivity index of a homogeneous and isotropic reservoir under steady-start condition is expressed as:

$$II = \frac{Q}{(P_{bh} - \bar{P})} = \frac{\rho_r}{\rho_s} \frac{2\pi kh}{\left(\ln \frac{r_e}{r_w} + S\right) \mu_{CO_2}} \quad (2.7)$$

where Q is the injection flow rate in [m³/s], ρ_r is the density of the gas under reservoir conditions in [kg/m³], ρ_s is the density of the gas under standard conditions in [kg/m³], k is the permeability of the reservoir in [m²], h is the thickness of the reservoir in [m], r_w is the radius of the well in [m], r_e is radius of the influence in [m], μ_{CO_2} is the viscosity of CO₂ at the well bottom in [Pa.s], S is the skin factor, P_{bh} is the well flowing bottomhole pressure in [Pa], \bar{P} is the average reservoir pressure in [Pa].

As the volume of CO₂ builds up, the pressure required to place CO₂ into the formation gradually increases, and the injectivity decreases. Eq. (2.7) shows that the well injectivity index and the storage capacity are linked through Q , which sometimes referred to simply as the well capacity. Since injectivity is time dependent, the amount of CO₂ that can be stored is often pressure limited. Therefore, well injectivity and reservoir injectivity determine the time frame for achieving a desirable or a planned storage capacity. In other words, both of the injection wells and reservoirs have a limited ability to accept CO₂ within a given time frame owing to the constrains such as fracture pressure of the cap-rock and formation.

In practice, the well injectivity index is used by operators to monitor the performance of an injection well (since it is constant for a given completion) by time and do work-over and recovery techniques (*i.e.*, well stimulation) if needed. In addition, the injectivity index is a coupling parameter connecting

well-bore flowing pressure to the reservoir pressure of adjacent grid block in simulation of CO₂ storage (Peaceman et al., 1983). Therefore, for matching the production or pressure history of a well, the common method is adjusting the injectivity index. The reservoir injectivity, however, has broader implications, such as estimating the local-scale storage efficiency and/or to comparing two or several reservoirs for screening purposes.

Considering Eq. (2.7), the naive reservoir engineering approach for injectivity is to go for reservoirs with a high permeability-thickness ($k \times h$) product (Halland et al., 2011; Hosa et al., 2011). A common practice for direct measurement of the well injectivity is, however, a pilot injectivity test which due to the near well heterogeneities only gives limited information about the full field reservoir performance. It is well accepted that results of a single well injectivity test may differ from the overall reservoir injectivity (Bachu, 2015; Wang et al., 2013).

In addition to the technical issues (*e.g.*, type of test fluid; water, brine or CO₂), the operation related to single well injectivity is economically expensive and usually challenging from the environmental point of view and . Under such a condition numerical simulations can be considered as a powerful alternative. A more accurate assessment of the reservoir injectivity, however, requires detailed reservoir simulations and, if possible, an injectivity test (Miri and Hellevang, 2015; Miri et al., 2015). The basic formulation of the compositional simulation method is described in the section 2.4.

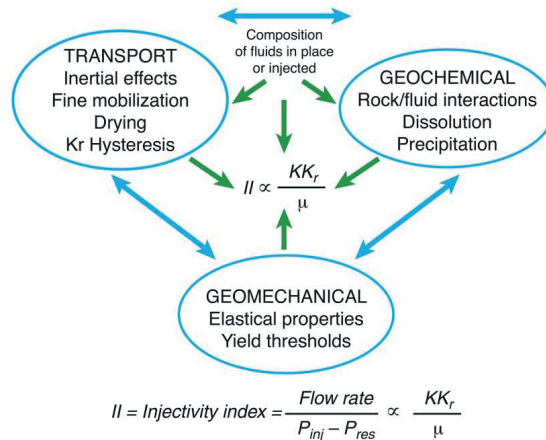


Figure 2.5: Parameters affecting the injectivity of a CO₂ storage project (Lombard et al., 2010)

2.3 Parameter affecting CO₂ injectivity

Formation injectivity is controlled by several factors including absolute and relative permeabilities, formation thickness, well completion, fluid properties and geochemical and petrophysical characteristics (Cinar et al., 2007; Kaldi and Gibson-Poole, 2008; Sundal et al., 2013a). Several processes may change the injectivity in a reservoir as a consequence of CO₂ injection. A massive injection CO₂ can potentially alter environment of the well-bore, thus inducing thermal, hydraulic, mechanical and chemical effects, thereby modifying the injectivity as defined in Eq. (2.7). Lombard et al. (2010) has summarized these parameters into three classes as shown in Fig 2.5. Accurate determination of these parameters and their interplay is essential for a proper modeling of the CO₂ injectivity. These parameters are described in more detail in the following sections.

2.3.1 Physical effects

Injectivity depends strongly on the rock and fluid properties of the storage site. Among various rock properties, the absolute and relative permeabilities are of significant importance for injectivity modeling; because they directly govern the fluid mobility and phase distribution in porous media. Employing an approximate solution for predicting pressure build-up, McMillan et al. (2008) found that uncertainty associated with relative permeabilities can lead to a four-fold variation in injectivity. Mathias et al. (2011) performed a more detailed study and quantified the uncertainty due to relative permeability data for both open and closed aquifers. They found that uncertainty for open and low permeability closed aquifers is as high as 57 %. On the other hand, it is revealed that the uncertainty associated with relative permeabilities is much lower for high permeability closed aquifers, and aquifer compressibility is the governing parameter.

The partitioning of water and CO₂ between phases, the CO₂ and water compressibility and fluid viscosities are the most influential fluid properties that control the pressure build-up. The uncertainty associated with ignoring the effect of compressibility increases dramatically at late injection times when gravity forces dominate. In addition, the mutual solubility between CO₂ and water and the aqueous phase density changes with respect to the impurities. For example, by increasing the hydrocarbon in the injection stream (even in small amount), solubility of the CO₂ in the aqueous phase and consequently the density of the mixture will reduce (Miri and Hellevang, 2014). Therefore, CH₄ would result in a favorable density difference and faster plume migration. Conversely, inclusion of SO₂ to the CO₂ stream the mass density of SO₂-CO₂ mixtures and the total solubility of CO₂ in water increases exponentially with respect to SO₂.

2.3.2 Geological effects

Geological factors such as reservoir heterogeneities, size and physical boundaries are determining factor with respect to plume migration and pressure dissipation. [Lucier et al. \(2006\)](#) performed a coupled fluid flow and geomechanical analysis of the Rose Run Sandstone, and found that injectivity would be quite limited as a result of limited thickness. However, for extensive reservoir units such as the Utsira Sand, there exist a large volume for pressure dissipation thus pressure build-up is minimal, and the injectivity is very high. The Tubaen Formation at Snøhvit, on the other hand, is segregated into a number of individual fluid/pressure compartments—due to steep faults with sealing characteristics—resulting in rapid pressure build-up ([Hellevang, 2015](#)).

It has been shown that variability due to the effect of geological heterogeneity is almost in the same order of magnitude as physical parameters ([Sundal et al., 2013a](#)). The location of the injection well relative to facies settings shows that the fluid distribution varies despite comparable properties (*i.e.*, porosity, permeability, Net/Gross, formation thickness), mainly due to number and extent of cemented layers delimiting gravity driven flow, causing separation and lateral spreading of the plume ([Sundal et al., 2014, 2013a](#)). Although, the depositions heterogeneities can potentially limit the vertical communication of reservoir thus inducing further pressure build-up, the general impact is seen negligible for the setting studied in this thesis ([Sundal et al., 2013b](#)). .

2.3.3 Chemical effects

CO₂ interactions with the formation water and host minerals may also lead to injectivity issues, with indications both from field (*e.g.*, [Baumann et al., 2014](#)), simulations and laboratory experiments of salt formation and reduced permeabilities ([Miri and Hellevang, 2015](#); [Miri et al., 2015](#)). Mineral dissolution can lead to porosity and permeability rise, thus increasing injectivity. Carbonate dissolution is fast and might be important even in the short time scales whereas most siliciclastic mineral components are slow reacting. Halite mineral precipitation is also fast and is induced by brine vaporization in case of dry CO₂ injection and might severely impact the injectivity ([Grude et al., 2014](#); [Muller et al., 2009](#); [Ott et al., 2015](#); [Peysson et al., 2014b](#)). When injecting large volumes of dry supercritical CO₂ into a saline aquifer, formation water eventually evaporates and the molar fraction of the water in the CO₂ stream increases *i.e.* drying-out. In the meantime, as vaporization progresses, the concentration of dissolved salt in the brine builds up. When the salt concentration exceeds its solubility limit under the thermodynamic state of a given reservoir, the excess salt will precipitate out of the aqueous phase (salting-out) and alter the porosity and permeability of the formation ([Cinar and Riaz, 2014](#); [Hurter et al., 2007](#); [Kleinitz et al., 2001](#); [Pruess](#)

and Muller, 2009).

The present-day reservoir scale models of this phenomenon include processes such as evaporation of water into CO₂ and capillary backflow of water into the dried zone, and have the salt formation up-scaled to grid-size. However, salt precipitation via these mechanisms has been suggested to only fill a fraction of the pore network and to not significantly affect the overall permeability. In a recent lab-on-chip study, self-enhancing of salt growth and water film salt transport has introduced as underlying mechanism of salt accumulation in the near-well area (Miri and Hellevang, 2015). This mechanism is active even at extreme CO₂ flow rates and therefore salt formation could be more severe than previously concluded based only on core flooding experiments and numerical simulations. The paper raises a serious need for reconsideration of the currently implemented physics in the simulation tools and also for properly designed laboratory experiments, to ensure that the reservoir volume outside the drainage area, which over time contributes the bulk of precipitated salt, is also included.

2.4 Pressure build-up modeling

Modeling of the pressure build-up has different purposes and implications depending on time-frame of a CCS project. Prior to start of a project, the main purpose of the injectivity modeling is to assess the suitability of a proposed CO₂ storage site. Following the start of injection, however, it is important to guarantee that the total amount of the planned CO₂ can be injected under the planned circumstances. The aim of the injectivity modeling in such circumstances is to check if/how and to the what extent the interactions between CO₂, brine and rock will alter the near wellbore environment. A wide range of commercial numerical tools are available which are capable of simulating CO₂ injection in geological formations. Nevertheless, they all follow the same theoretical background with minor differences in the implementation techniques. The numerical models, as including depositional and structural heterogeneities, provides a better prediction of pressure distribution which can be used to quantify the reservoir injectivity as well as the risk associated with CO₂ storage. In this study the Schlumberger software Eclipse 300 (Schlumberger, 2012) was used for fluid flow simulations performed in Sundal et al. (2015) and Sundal et al. (2014). Here we consider compositional flow that involves two components, the $w = \text{H}_2\text{O}$ and $c = \text{CO}_2$ with phases $l = \text{liquid H}_2\text{O}$ and $g = \text{supercritical CO}_2$. The governing equations for mass conservation of each component is given as:

$$\frac{\partial}{\partial t} \varphi (s_l \rho_l X_w^l + s_g \rho_g X_w^g) + \nabla \cdot \mathbf{F}_w = Q_w \quad (2.8)$$

and

$$\frac{\partial}{\partial t} \varphi (s_l \rho_l X_c^l + s_g \rho_g X_c^g) + \nabla \cdot \mathbf{F}_c = Q_c \quad (2.9)$$

where φ is the porosity, s is the volume fraction, Q is the source/sink term in [mol/m³/s] and X is the mole fraction. Fluxes F are given as:

$$\mathbf{F}_w = \mathbf{q}_l \rho_l X_w^l + \mathbf{q}_g \rho_g X_w^g - \varphi s_l \rho_l D_l \nabla X_w^l - \varphi s_g \rho_g D_g \nabla X_w^g \quad (2.10)$$

and

$$\mathbf{F}_c = \mathbf{q}_l \rho_l X_c^l + \mathbf{q}_g \rho_g X_c^g - \varphi s_l \rho_l D_l \nabla X_c^l - \varphi s_g \rho_g D_g \nabla X_c^g \quad (2.11)$$

where D is the diffusion/dispersion coefficient and q is the Darcy velocity in [m/s] as given by:

$$\mathbf{q}_l = -\frac{kk_l}{\mu_l} \nabla (P_l - W_l \rho_l g z) \quad (2.12)$$

and

$$\mathbf{q}_g = -\frac{kk_g}{\mu_g} \nabla (P_g - W_g \rho_g g z) \quad (2.13)$$

where P is the pressure in [Pa], μ is the viscosity in [Pa s], W is formula weight in [kg/mol], g is the acceleration of gravity in [m/s²] and z is the elevation in [m]. We can simplify these equations by summing Eqs. (2.8) and (2.9) and reformulate in terms of the total component mole fraction for CO₂, Z_c , to obtain a pressure equation which is used in the FLASH method.

$$\frac{\partial}{\partial t} \varphi ((s_l \rho_l + s_g \rho_g) Z_c) + \nabla \cdot \mathbf{F}_c = Q_c \quad (2.14)$$

This equation can be solved utilizing a numerical discretization approach, such as finite difference or volume, to obtain pressure and the mole fraction of each component across the phases.

The simulated pressure response gives valuable information in regard to the reservoir injectivity and also pressure build-up in the geological formations. Nevertheless, determining the pressure build-up using reservoir simulators that take into account the full physics can be very time-consuming

Table 2.1: Comparison between the available analytical models based on the included physics

Publications	BC [†]	Kr [‡]	Cp [§]	Gravity	Solubility
(Nordbotten et al., 2005)	Closed	Yes	No	Yes	No
(McMillan et al., 2008)	Closed	Yes	No	No	Yes
(Mathias et al., 2009a)	Open	No	Yes	Yes	No
(Ehlig-Economides and Economides, 2010)	Closed	Yes	Yes	No	Yes
(Mathias et al., 2011)	Closed	No	Yes	Yes	No
(Azizi et al., 2013)	Closed/Open	Yes	Yes	No	Yes
(Mijic et al., 2014)	Closed/Open	Yes	Yes	No	Yes

[†] K_r = relative permeability.

[‡] BC = boundary conditions.

[§] Cp = phase compressibility.

and it also demands a lot of input data (Paper F). Therefore, there has been a lot of research around developing simple and viable analytical models which can quickly and efficiently determine the pressure build-up during injection of CO₂ into reservoir. The analytical models can provide a primary estimation of the injectivity index which can be used for fast screening and ranking of aquifers with respect to suitability for CO₂ injection. Table 2.1 list some of the available analytical where compared with respect to the included physics. It is obvious that the physics described in the previous sections have only partly been covered by the analytical models (Paper D). Furthermore, the existence of several discrepancies between the experimental results and the numerical models in regard to salt precipitation indicate that further research on the mathematical modelling is the most demanding task today (Paper E).

Chapter 3

Thermodynamic Models Description

The modeling of thermo-physical fluid properties is a very important task when estimating CO₂ transportation efficiency, storage capacity, geochemistry of fluid-rock system and even operational concerns like injectivity. The associated computations accounts for a significant and sometimes even for the largest part of the required computing time for the modeling of the corresponding process. Therefore, when designing a fluid property library, beside the accuracy and applicability, careful attention must be given to the numerical efficiency of the implementation.

To have a accurate and reliable fluid model for further applications in this study, a modular based fluid library is implemented using techniques of the object-oriented programming. The primary focus is to establish a tool for the engineering and the operational needs regarding phase equilibrium modeling in the CCS projects. The implementation is started with the SAFT1 EoS and other classes such as the cubic (*i.e.*, the Van der Waals type EoS's) and the PC-SAFT class and the CPA class were added later (see Fig. 3.1). The implementation is also coupled with a three phase flash scheme and this library can be easily integrated in a separate flow solver. An example of the library input file is given in the Appendix B.

In this chapter, we have reviewed the most applied EoS in this study, the SAFT1-RPM. This material is not new, but at present it is scattered around in many works, meaning that a new researcher in this area will have to read several articles, often with small, but significant differences in formulas and notation.

3.1 Background

Carbon Capture and Storage (CSS) projects deal with various combinations of polar, associating and electrolyte mixtures in different stages from capture to injection. Optimizations of involving processes require accurate thermodynamic properties of pure compounds and mixtures over a wide range of

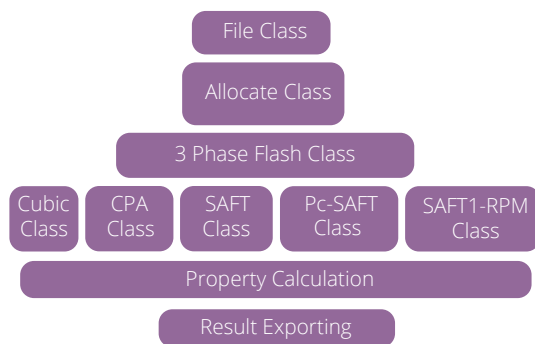


Figure 3.1: Schematic showing structure of the implemented fluid library

temperature and pressure. Due to highly non-ideal intermolecular interactions such as association (hydrogen bonding), polarity, and chain forming, the investigation of phase equilibria of such fluids is one of the challenging engineering tasks of the last decades. Classical EoS's of the Van der Waals type (Peng-Robinson or Soave-Redlich-Kwong) are common choices for phase equilibria modeling of simple fluids (non-polar fluids) for wide pressure and temperature ranges. But for polar and associating molecules (complex fluids) predictability of these models is poor (in particular at high-pressure) especially when van der Waals one fluid mixing rules are used. The most important forces considered in classical cubic EoS's include van der Waals attractions along with weak electrostatic forces due to dipoles, quadrupoles, etc. Thus, strong hydrogen bonding forces cannot be well captured by the attractive term of such cubic EoS. Activity coefficient models which treat the non-ideality as a chemical reaction are suitable alternative for polar compounds; however they are valid only at low pressures.

In the recent years, molecular approaches such as Statistical Associating Fluid Theory (SAFT) (Chapman et al., 1989; Huang and Radosz, 1990) have gained increasing popularity among the researchers for modeling of complex fluids. The SAFT framework has been developed by (Chapman et al., 1989) based on the molecular principles and by incorporating Wertheims thermodynamic perturbation theory of the first order (TPT1). The main contribution in this model is developing a reference term which unlike van der Waals equations can capture chain length (molecular shape) and molecular association. The framework is benefiting from two inherent flexibilities. One is flexibility in adding a new term in order to capture a particular physical effects, such as polarity, ion-interactions, etc. and the other one is flexibility in assigning different reference fluids like Lennard-Jones (LJ), square-well (SW) etc.

The SAFT type EoS has been applied extensively in the literature to hydrocarbons mixtures (Adidharma and Radosz, 1998; Lovell et al., 2007; Zhao et al., 2006), ionic liquids (Andreu and Vega, 2008; Kroon et al., 2006;

Paduszynski and Domaska, 2012), polymers (Adidharma and Radosz, 1998; Gross and Sadowski, 2001, 2002) and solubility of gas and even solid components like salt or sugar in liquids (Ji et al., 2007; Ji and Zhu, 2012; Tan et al., 2006). Adidharma and Radosz (1998) introduced SAFT1 which has promising ability in representation of pure component properties over a wide density range – due to correction applied to the dispersion term. The model incorporates square-well (SW) fluid potentials and formulated as to be applied for both homo and heterosegmented molecules.

Lafitte et al. (2006) and Lafitte et al. (2007) used Mie potentials (which for exponents 12 and 6 also included LennardJones potential) in the SAFT-VR framework (statistical associating fluid theory with variable range) to improve the calculation of repulsion interaction between the segments. The resulted model (SAFT-VR Mie EOS) is applied to n-alkane series and showed a significant improvement on the description of the compressed liquid phase, vapor-liquid equilibria and also estimation of thermo-physical properties. In order to get a full review on different type of SAFT versions and recent improvement in each field we refer the reader to Müller and Gubbins (2001). In current study, SAFT1, because of its accuracy, predictive capabilities and suitability for both vapour and liquid phases, is utilized to model the solubility and density of CO₂ in water with respect to SO₂ and CH₄ impurities. Therefore, our intention in this work is (1) to provide a reliable molecular model for H₂O–CO₂–Impurity mixture using the SAFT1-RPM (Restricted Primitive Model) EoS, and (2) to check the capability of this variation of SAFT compare with other versions with respect to number of adjustable parameter. This model has previously been applied successfully to hydrocarbon mixtures and associating fluids.

3.2 The SAFT1-RPM Equation of State

The SAFT1-RPM EoS is a heterosegmented version of the original SAFT equation proposed by Tan et al. (2005) based on the squarewell (SW) potential. This version of the SAFT is extensively described elsewhere (Tan et al., 2005), therefore we emphasize only on the main features of the model here. Since all other thermodynamic properties can be estimated through Helmholtz free energy, SAFT-type EoS's are usually formulated in term of Helmholtz energy. Taking into the account the fact that most of the fluids are “real”, a reliable EoS is one that more precisely estimates the deviation of Helmholtz energy of the system from ideal state (*i.e.*, molecules with zero size and without interaction) due to different types of non-idealities. Hence, the residual molar Helmholtz energy at constant temperature and density is defined as:

$$a_{(T,\rho,n)}^{res} = a_{(T,\rho,n)} - a_{(T,\rho,n)}^{ideal} \quad (3.15)$$

Helmholtz energy of a system is fundamentally calculated based on the potential energy of interacting molecules (*i.e.*, pair-potential). Within the

SAFT framework, the residual Helmholtz energy (*i.e.*, Helmholtz energy divided by RT) is composed of two parts:

$$a^{res} = \underbrace{a^{hs} + a^{dis}}_{reference} + \underbrace{a^{chain} + a^{assoc}}_{perturbation} \quad (3.16)$$

The reference term, in principle, could be any fluid with known residual Helmholtz energy and radial distribution function. Then, the existing radial distribution function of the reference fluid can be used to calculate the perturbation terms which are incremental Helmholtz energy due to chain formation (a^{chain}) or association (a^{assoc}). The simplest inter-molecular potential which has characteristics of a reference fluid is hard-sphere (HS) potential which is used in the earlier version of SAFT (Chapman et al., 1989; Huang and Radosz, 1990). Helmholtz energy of HS fluid (a^{hs}) – which takes into the account the repulsive forces between the molecules – has been determined empirically by Carnahan and Starling (1969). In order to make the SAFT framework more predictive there has been lots of research to improve the reference term via assigning different reference fluids like LennardJones (LJ), square-well (SW) etc. The SAFT1 uses a square-well (SW) potential as a reference fluid. The SW fluid defines by a steep repulsion at short distances and a short-ranged attraction at intermediate distances through three parameters: radial distance between two segments (r), the well depth (u) and the reduced range of the potential well (λ). The potential energy for two interacting spherical SW segments with contact distance (σ) is given by:

$$\varphi(r) = \begin{cases} \infty & r < \sigma \\ -u & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \quad (3.17)$$

This potential energy (reference term in Eq. 3.16) is composed of two parts (1) the hard-sphere potential and (2) the perturbation given by the well depth (u) to capture short range attraction between molecules. Adidharma and Radosz (1998) incorporated Barker Henderson's perturbation scheme to account for incremental Helmholtz energy due to dispersion (a^{dis}), *i.e.*, the second part in Eq. (3.16). According to SAFT1, molecules are chains composed of (m) spherical segments of equal size bonded tangentially together and interacting via a square-well (SW) intermolecular potential. Therefore,

$$\tilde{a}^{reference} = \tilde{a}^{SW} = \sum_i X_i m_i \left[\tilde{a}_0^{hs} + \tilde{a}_1^{disp} + \tilde{a}_2^{disp} + \tilde{a}^t \right] \quad (3.18)$$

X_i is the mole fraction of chain i , \tilde{a}_0^{hs} is the dimensionless hard-sphere Helmholtz energy per segment, \tilde{a}_1^{disp} and \tilde{a}_2^{disp} are the first and second perturbation terms based on the Barker Henderson's perturbation scheme and \tilde{a}^t is a correction term which account for truncation error of second order

perturbation theory. The incremental residual Helmholtz energy due to the chain formation can be estimated using the SW radial distribution function $g_{\alpha\beta}^{SW}$ as:

$$\tilde{a}^{chain} = - \sum_i X_i (m_i - 1) [\ln g_i^{-SW}(\sigma_{\alpha\beta}) - \ln g_{0,i}^{-SW}(\sigma_{\alpha\beta})] \quad (3.19)$$

Where $\sigma_{\alpha\beta}$ is the distance between canters of segment α and β at contact and g_i^{-SW} is defined as:

$$\ln g_i^{-SW}(\sigma_{\alpha\beta}) = \sum_{\beta \geq \alpha} B_{\alpha\beta, i} \ln g_{\alpha\beta}^{SW}(\sigma_{\alpha\beta}) \quad (3.20)$$

Where $B_{\alpha\beta, i}$ is the bond fraction of type $\alpha\beta$ in molecule of component i . In case of homo-segment chains this value is equal to unity. The $g_{0,i}^{-SW}$ is g_i^{-SW} evaluated at zero density.

$$g_{0,i}^{-SW}(\sigma_{\alpha\beta}) = 1 + u_{\alpha\beta}/T \quad (3.21)$$

The association term is calculated by [Adidharma and Radosz \(2001\)](#) for square well fluids as:

$$\tilde{a}^{assoc} = \sum_i X_i \sum_{\alpha} \left[\sum_{A_i \in \Gamma_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{n(\Gamma_i)}{2} \right] \quad (3.22)$$

Where $n(\Gamma_i)$ is the number of association sites on molecule i and X^{A_i} is the mole fraction of molecules i not bonded at site A_i given by:

$$X^{A_i} = \left(1 + \rho_n \sum_j \left[X_j \sum_{B_j \in \Gamma_j} (X^{B_j} \Delta^{A_i B_j}) \right] \right)^{-1} \quad (3.23)$$

Where ρ_n is the number density and $\Delta^{A_i B_j}$ is the association strength between site A_i at molecule i and site B_j at molecule j , given as:

$$\Delta^{A_i B_j} = e^{\beta \alpha(\rho) u_{ij}} g^{hs}(\sigma_{ij}) (\sigma_{ij}^3 k^{A_i B_j}) (\exp(\varepsilon^{A_i B_j} / k_B T) - 1) \quad (3.24)$$

For detail explanation of these equations we refer the reader to the original paper [Adidharma and Radosz \(2001\)](#).

3.3 Ionic effects

To account for ionic effects on the Helmholtz free energy of the mixtures containing single salts, [Tan et al. \(2005\)](#) suggested coupling of Restricted Primitive Model (RPM) (considering ions in a medium with a uniform di-

electric constant) with SAFT1. He used a hybrid approach in coupling that has both the individual-ion and salt parameters. In this approach the aqueous electrolyte is treated as a binary solution containing water and salt, and the salt treated as a molecule composed of two different segments corresponding to the cation and anion. The ion parameters has been adjusted to vapor pressure and density of H₂O–NaCl by Tan et al. (2005) for a wide range of pressure and temperatures.

$$\tilde{a}^{ion} = -\frac{3X^2 + 6X + 2 - 2(1 - X)^{3/2}}{12\pi\rho_m N_A v d^3} \quad (3.25)$$

where X is the dimensionless quantity defined by

$$X = d \cdot \sqrt{\frac{4\pi}{\varepsilon_w kT} \sum_j q_j^2 \rho_{n,j}} \quad (3.26)$$

where $\rho_{n,j}$ is the number density of ion j , q_j is the charge of ion j ($= z_j e$), z_j is the valence of the ion j , e is the charge of an electron ($= 4.803 \times 10^{-10}$ esu), and the summation is over all ions in the mixture. Also ε_w is the dielectric constant of water.

3.4 VLE calculation

Having calculated the residual Helmholtz energy using SAFT1, all other necessary functions to calculate the phase equilibria and thermodynamic properties can easily be derived. For example, in order to evaluate vapor-liquid equilibria (VLE), equality of fugacity of all components in both phases is required. For a multicomponent system, the equilibrium state between the liquid (l) and vapour (v) phase, is described by the following equation:

$$f_i^v = f_i^l \quad \Rightarrow \quad \hat{\phi}_i^v y_i = \hat{\phi}_i^l x_i \quad (3.27)$$

Where f_i is fugacity of component (i) and $\hat{\phi}$ is fugacity coefficient and x_i and y_i are mole fraction of component (i) in the liquid phase and gas phase, respectively. It is worth mentioning that any chemical reactions and kinetics associated with mutual solubility of water in vapour phase and gases in liquid phase are not our concern here. Moreover it is assumed that the association term can capture the polarity contribution of the molecules. The fugacity can be estimated based on derivatives of residual Helmholtz energy respect to composition as:

$$\ln \hat{\phi}_i = \tilde{a}^{res} + \left(\frac{\partial \tilde{a}^{res}}{\partial x_i} \right)_{T,\rho,x_j \neq i} - \sum_{j=1} \left[x_j \left(\frac{\partial \tilde{a}^{res}}{\partial x_j} \right)_{T,\rho,x_k \neq j} \right] + Z - 1 - \ln Z \quad (3.28)$$

where Z is compressibility factor and calculated with

$$Z = 1 + \rho \left(\frac{\partial \tilde{a}^{res}}{\partial \rho} \right)_{T,x} \quad (3.29)$$

Since the compressibility factor is function of density, iteration over density is required. However, convergence requires little iteration and in general SAFT is computationally quite cheap.

3.4.1 Pure compounds model parameters

In order to evaluate the phase state (*i.e.*, number of phases and corresponding composition) and thermodynamic properties of chemical species, SAFT1 approach requires number of intermolecular parameters to be pre-specified. The model requires four parameters for each compound, namely: (m), the segment number, (v_{oo}), the volume of the SW sphere, (λ), the reduced range of the potential well and (ϵ), the interaction energy of the segment (Adidharma and Radosz, 1998, 2001). For associative molecules, two additional parameters are needed, the association volume ($k^{A_i B_j}$) and the well depth of the association site-site potential ($\epsilon^{A_i B_j}$). For charged molecules, effective diameter d should also be adjusted to the experimental data.

Some of these parameters can be estimated from first principles calculations. For instance, Leonhard et al. (2007) and Singh et al. (2007) have incorporated quantum mechanics principles – ab-initio and density functional theory – to obtain the molecular parameters for PCP-SAFT. However, the most common method is fitting the experimentally obtained saturated liquid densities and vapour pressures against the model. In our studies, the experimental data were taken from the National Institute of Standards and Technology (NIST) online database (www.nist.gov). A trust region Levenberg-Marquardt algorithm is incorporated in order to fit the experimental data to the theory. The average relative deviations (ARDs) is calculated as:

$$ARD = \frac{1}{NP} \sum_{N=1}^{NP} \left(\left| 1 - \frac{P_N^{cal}}{P_N^{exp}} \text{ or } \frac{\rho_N^{cal}}{\rho_N^{exp}} \right| \right) \times 100 \quad (3.30)$$

3.4.2 Mixing rules

The SAFT1 approach performs the phase equilibria calculation through number of cross interaction parameters for binary subsystems which account for the interactions between unlike segments in the mixture. For example, longitudinal distance segment α and β ; ($\sigma_{\alpha\beta}$) and reduced range of the potential well for the α - β interaction ($\lambda_{\alpha\beta}$) are calculated by Lorentz arithmetic mean.

$$\sigma_{\alpha\beta} = \frac{\sigma_\alpha + \sigma_\beta}{2}, \lambda_{\alpha\beta} = \frac{\lambda_\alpha + \lambda_\beta}{2} \quad (3.31)$$

However, for well depth of square-well potential ($u_{\alpha\beta}$), geometric mean alongside a deviation parameter ($k_{\alpha\beta}$) (binary interaction parameter) is suggested:

$$u_{\alpha\beta} = u_{\beta\alpha} = \sqrt{u_{\alpha}u_{\beta}}(1 - k_{\alpha\beta}) \quad (3.32)$$

The binary interaction parameter has been found to be temperature dependent (Ji et al., 2005; Tan et al., 2013) and usually determined through comparison against experimental data at different pressures and temperatures. Mixing rules for the association volume ($k^{A_i B_j}$) and the well depth of the association site-site potential ($\epsilon^{A_i B_j}$) parameters are needed between different associating molecules, in order to calculate the value of the association strength in Eq. (3.24).

$$\sigma_{ij}^3 k^{A_i B_j} = \left[\frac{(\sigma_i^3 k^{A_i B_j})^{1/3} + (\sigma_j^3 k^{A_i B_j})^{1/3}}{2} \right] \quad (3.33)$$

$$\epsilon^{A_i B_j} = \sqrt{\epsilon^{A_i B_i} \epsilon^{A_j B_j}} \quad (3.34)$$

Moreover, the effective (hydrated) diameter in Eq. (3.25) should be extended to the mixture using:

$$d = \sum_i \sum_j x'_j x'_i d_{ij} \quad (3.35)$$

where x'_i is the mole fraction of salt i on a solvent-free basis and the summation is over all salts. And

$$d_{ij} = d_{ji} = \frac{d_i + d_j}{2} (1 - l_{ij}) \quad (3.36)$$

where l_{ij} is an adjustable parameter corresponding to the interaction between two salts i and j .

3.4.3 Association sites and monomer fraction

In this thesis we have incorporated four components (CH₄, SO₂, CO₂, and H₂O) and consequently three segments in the modelling algorithm. The association term of SAFT1-RPM depends on the choice of the association scheme *i.e.*, number and type of association sites for the associating compound.

For associating subsystems in this study, estimation of fractions of non-bonded molecules is not analytically possible; therefore we have implemented a generalized procedure recently proposed by Tan et al. (2006) to evaluate the association term. It is worth to mention that the polar and quadrupoles interactions of water, carbon dioxide and sulphur dioxide are considered by the association (hydrogen-bonding-type) interaction.

Methane is modeled as a non-associating, single segment molecule. The model for water molecules in this study is based on the four-site single segment model used by [Tan et al. \(2006\)](#), in which two associating site of type (H) and type (O) represent the proton-donor sites and electron loan pairs, respectively. Two sites of the same type (*i.e.*, OO or HH) do not associate. It is worth to mention that, cross association between unlike sites (*i.e.*, OH) represent the hydrogen bonding.

CO₂ is modelled as linear molecule with two hard-sphere segments which are bonded tangentially together ([Ji et al., 2005](#)). The large quadrupoles moment of CO₂ allows this molecule to associate with itself or other molecule in the mixture. There are four electron loan pairs in the CO₂ molecule which can contribute to hydrogen bonding, however, our examination on CO₂ with different numbers of association sites showed that three association schemes will gives best fit to experimental vapour pressure and density. Therefore we accept two associating site of type (O) and one site of type(C) for CO₂ molecule. Again, sites of the same type (*i.e.*, O-O and C-C) do not associate with each other.

SO₂ is a symmetrical non-linear molecule with a large dipole moment (1.6 Debye) and high polarity. There are four electron loan pairs in the oxygen atoms of the molecule and one extra loan pair in the sulphur atom. These electron loan pairs are allowed to provide association site for proton-donor sites (hydrogen atoms) and therefore contribute to hydrogen bonding. In case of SO₂ four association site of type (S) and one site of type (O) are considered. The complete set of molecular parameters for different components is listed in Table 3.2 and 3.3. We refer the reader to the original papers for a detailed calculation of phase equilibria of subsystems.

Table 3.2: SAFT1 fitted parameters for H₂O, CO₂, CH₄ and SO₂

Molecule	m	$v^{00}(cc/mol)$	$u/k(K)$	λ	$\epsilon/k(K)$	κ
H ₂ O (Tan et al., 2005)	1.0000	9.48370	313.8758	1.5423	1527.72	0.05848
CO ₂ (Ji et al., 2005)	1.2126	11.5845	230.4929	1.5390	581.432	0.006336
SO ₂ (Miri et al., 2014b)	2.0283	9.52574	219.4379	1.6061	200.720	0.318000
CH ₄ (Miri et al., 2014a)	1.0000	15.0390	105.4800	1.7827	-	-

Table 3.3: SAFT1 fitted parameters for Na^+ and Cl^- at 298.15 K (25 °C)

Ion	m	$v_{25}(\text{cc/mol})$	$u_{25}/k(K)$	λ	$d_{25}(A)$
Na^+ (Tan et al., 2005)	1.0000	1.2797	3349.798	1.7	4.9373
Cl^- (Tan et al., 2005)	1.0000	0.7797	413.9908	1.8	4.9373

Chapter 4

Summary of Papers

Here we will give a short summary of each of the papers and proceedings that are a part of this thesis. This work includes six articles, of which I am the first author of five and a co-author of one. The papers and proceedings are attached at the end of the thesis in chronological order. With the exception of Papers E and F, where I am co-author, I have written and performed most of the work in all papers, with input from discussions with my supervisors. In the paper F, I have contributed to the compositional flow simulations as well as estimating the thermodynamic properties using the EoS developed and tested in Papers A and B.

The papers contribute to the main objectives described in the introduction, including:

4.1 Thermodynamic modeling (Papers A, B and C)

Paper A: *Examination of CO₂-SO₂ solubility in water by SAFT1 implications for CO₂ transport and storage*

Motivation and objectives:

In this paper the capability of the SAFT1 EoS to describe phase behavior of ternary CO₂-SO₂-H₂O mixtures over an extended temperature and pressure range is studied. Due to the highly corrosive nature of SO₂, experimental data on solubility and density of aqueous ternary CO₂-SO₂-H₂O mixtures are not available in the literature. This knowledge, however, is required with respect to a CCS process; because the presence of SO₂ in the CO₂ stream, either as an impurity or with co-sequestration purposes, might affect very much the transportation efficiency, geo-chemistry of fluid-rock systems and even operational concerns like injectivity.

Method and procedure:

The SAFT1 EoS is chosen to achieve the goals of this paper owing to: (1) high non-ideal interactions of the molecules in CO₂-SO₂-H₂O system; and

(2) promising predictive capabilities. The experimental data for the SO_2 and associated binary subsystems were collected and used in the regression process. The molecular parameters of SO_2 were obtained assuming it as an associating molecule composed of four association sites of type (S) and one site of type (O). In addition, self-association is disregarded. The model parameters for water and CO_2 were accepted from [Tan et al. \(2004\)](#). For the cross association parameters, the normal mixing rules were used and no temperature dependent binary interaction coefficient is applied.

Key findings:

The results show that:

- the total solubility of SO_2+CO_2 in water varies exponentially with respect to SO_2 concentrations *i.e.*, at low concentrations of SO_2 , total changes in solubility of the CO_2 in water is negligible;
- inclusion of SO_2 to the CO_2 stream may shift the PT diagram to the higher pressure-temperature region. For example having 5-10 % SO_2 in the injected stream could change the critical pressure and temperature by approximately 0.7-2 MPa and 10-30 °C, respectively;
- the mass density of $\text{SO}_2\text{-CO}_2$ mixtures has an increasing upward trend throughout the whole range pressures up to 30 Mpa;
- the total solubility of CO_2 in water varies exponentially with respect to SO_2 concentrations. This implies that, if the concentration of SO_2 impurity is approximately less than 5 %, which is the case in many CCS applications, then the variation of CO_2 solubility in water is negligible;

Paper B: *Phase relations in the Longyearbyen CO_2 lab reservoir forecasts for CO_2 injection and migration*

Motivation and objectives:

This paper deals with modeling of fluid mixture properties relevant to the Longyearbyen CO_2 Lab pilot project (LYBCO2). The challenging issue, which forms the novelty and the importance of this paper, is presence of the light hydrocarbons (mainly CH_4) in the reservoir and/or cap rocks, as seen by gas flow into exploration wells ([Larsen, 2013](#)). Previous research activities have modeled and explained the phase equilibrium and fluid properties for mixtures containing CO_2 , H_2O and NaCl using various EoS's. However, what has not been investigated is the effect of CH_4 on the ternary and quaternary systems associated with the CO_2 . Although, this paper is of particular interest for the LYBCO2 project, it has broader implications including enhanced gas recovery, hydrate formation and co-sequestration.

Method and procedure:

Heterosegmented SAFT EoS (SAFT1-RPM, [Ji et al. \(2005\)](#)) is chosen for this study because of its promising predictive capabilities and previous suc-

cess in modeling of electrolyte solutions. Binary interaction parameters of the subsystems ($\text{CO}_2\text{-CH}_4$, $\text{CH}_4\text{-H}_2\text{O}$, and $\text{CH}_4\text{-NaCl}$) were tuned against available experimental data, using previously adjusted parameters for pure components and $\text{CO}_2\text{-H}_2\text{O}$ subsystems. A total of eighteen data set were collected from literature and utilized in this stage. Solubility of CH_4 and CO_2 and subsequent mixture densities were predicted at 298 K and pressure up to 100 bar.

Key findings:

The results show that:

- the solubility of the CO_2+CH_4 in the water is less than the solubility of the CO_2 alone;
- by increasing the hydrocarbon in the injection stream (even in small amount) and also salt concentration, solubility of the CO_2 in the aqueous phase and consequently the density of the mixture will be reduced (Miri and Hellevang, 2014);
- CH_4 would result in a favorable density difference and faster plume migration;
- the probability of three phase state (two liquid and one vapor phase) near the bubble line is very high demanding consideration of three phase relative permeability curves;

Paper C: *On the water content of dense phase $\text{CO}_2\text{-SO}_2$ system implications for CO_2 transportation and injection*

Motivation and objectives:

The main objective of this paper is to explore the effect of SO_2 impurity on the water drop-out in the CO_2 transportation and injection pipelines. The water drop-out – which acts as an electrolyte – is a sufficient condition for CO_2 pipeline corrosion. The laboratory experiments at IFE (Dugstad et al., 2013) has confirmed high rate of corrosion in presence of a small percentage of SO_2 even when water drop-out is not expected *i.e.*, if the CO_2 phase is under-saturated with respect to water. One hypothesis was the possible negative effect of SO_2 on the solvent ability of CO_2 . This paper therefore aimed to provide a methodology to assess this hypothesis and explain the unexpected water-out in the presence of SO_2 .

Method and procedure:

Water content of SO_2+CO_2 mixture and its subsequent corrosive behaviour is assessed using two different approaches: free energy calculation of water molecules (1) in the bulk phase using Statistical Association Fluid Theory (SAFT); and (2) in contact with pipeline surface using molecular dynamic simulation plus a modified SAFT equation of state. Both approaches were also coupled with an aqueous speciation model to estimate the pH varia-

tion of the condensed water. For the first approach, the developed model in Paper A is used. In the second approach, chemical potential of the adsorbed TIP4P (a rigid planar four-site interaction potential for water) water molecules were taken from open literature and the cross dispersive parameter of SAFT1-EoS is subsequently returned to keep the consistency of the calculations.

Key findings:

The results show that:

- with the inclusion of SO₂ in the CO₂ stream, the solubility of water in the dense phase increases with increasing pressure, temperature and SO₂ concentration, thus rejecting the primary hypothesis posed in the objectives;
- the water content has an exponential growth behaviour with respect to SO₂ concentration implying insignificant impact compared to the pure CO₂ phase water content (*i.e.*, for SO₂ concentration less than 0.2 mole %);
- the equilibrium between solid surface and dense CO₂ fluid depends on the affinity of the surface which is quantified in this work by using free energy of adsorbed water. The water content calculated taking into account effect of pipe surface, is much lower than calculations based on free energy of water in the bulk phase. For CO₂ in dense phase and a SO₂ concentration less than 20 mole %, for pressure up to 600 bar, the water solubility limit is less than 1000 ppmv;
- inclusion of SO₂ in CO₂ stream has also very little effect on the water solubility limit calculated based on free energy of adsorbed water;
- with inclusion of SO₂, even in small concentrations, aqueous phase pH drops dramatically from 3.1 to 2.0 in an oxygen free environment or 1.0 in a less conservative oxidation scenario. These results along with the new estimated water solubility limit might be explanations of findings from the experimental studies and field observations in regard to high rate of corrosion in the CO₂ transportation pipelines;

4.2 Drying-out and salting-out (Papers D and E)

Paper D: *Salt Precipitation during CO₂ Storage - a Review*

Motivation and objectives:

The primary purpose of this paper is to provide the reader with a comprehensive background for understanding the state-of-the-art knowledge on salt precipitation in the context of CO₂ storage in saline aquifers. This work initially started to update personal knowledge on topic of formation dry-out but it turned out later that there exists number of inconsistencies and contradictions in the literature which were interesting from a more funda-

mental point of view. Therefore, we find it useful to summarize findings in previous studies and specify how salt precipitation affects CO₂ storage efficiency.

Method and procedure:

We have used a conceptual approach to review the literature, meaning that some well-focused research questions were formulated first and then the relevant studies were selected and synthesized using explicit and rigorous criteria.

Key findings:

The results show that:

- the precipitation of salt is undoubtedly a real threat for actual field scale injection of dry CO₂ in saline aquifers and its destructive impact on rock properties has been clearly demonstrated through numerous experimental and numerical studies accomplished on micro to field scale;
- the precipitated salt will distribute in two possible forms; local (homogeneous) and non-local, among them non-local is the most detractive;
- the present day uncertainty regarding injectivity alteration caused by salt precipitation is very high and the only available quantitative studies in this regard are also inconsistent;
- under certain thermo-physical conditions belonging to the capillary drying regime, salt might massively precipitate (*i.e.*, local precipitation) during the course of CO₂ injection. However, a clear measure of necessary conditions is not provided so far. This is mainly because conducted studies are largely qualitative and case specific, thus; drawing a general conclusion is challenging. In fact, it is widely accepted that there is a critical velocity above which local salt accumulation occurs, but a proper formulation is not given;
- there are several weaknesses in relation to laboratory tests, including (1) the lack of measurements of effective permeability, (2) improper design of the experiments in accordance with actual reservoir conditions (*e.g.*, ignoring the significant role of water films and the use of closed boundaries preventing inflow of brine), (3) incomplete coverage of pressure, temperature and salinity relevant to long term CO₂ injection, (4) lack of complying with a standard procedure so that results of tests which are carried out in different situations, are not comparable;
- much of the literature agrees that the extent of salt precipitation at higher salinity is significantly higher. Then again, a critical salinity limit is not defined at this point, but there are some notions that such a limit will depend also on a critical flow rate;
- the existence of several discrepancies between the experimental results and the numerical calculations indicate that the state-of-the-art knowl-

edge regarding modeling of salt precipitation is not commensurate with the complexity of the issue. Although more is being learned about the fundamental mechanisms and the clogging behaviour of the phenomenon, further research on the mathematical modeling is the most demanding task today. Performing dimensional analysis to find a relationship between the dependent variable and independent variables of the phenomenon could help to reduce the reported inconsistencies. Future efforts in implementing salt capillary pressure and development with the aid of pore scale modeling are expected to help progress in this area;

- an assessment of the different criteria for the application of the various mitigation options needs to be extensively undertaken. Nevertheless, fresh water treatment appears to be a viable mitigation option, which, if carefully controlled, could prove to be an effective method to move the risk from the area near the well to somewhere deeper within the aquifer reservoir;

Paper E: *New insights on the physics of salt precipitation during injection of CO₂ into saline aquifers*

Motivation and objectives:

This paper uses two sets of lab-on-chip experiments to address the knowledge gaps identified in the previous review paper. More specifically, we have raised the hypothesis of capillary water films continuity in this contribution *i.e.*, water films in porous media have enough continuity and conductivity to transport fresh brine to the evaporating front, and therefore these water films can increase the rate and the amount of salt precipitation. The experiments were carefully designed in accordance to this hypothesis hoping to provide supporting evidences.

Method and procedure:

Two glass micro-chips were fabricated using laser ablation technique: (1) a two dimensional network which employed a lattice of square grains ($\sim 500 \mu\text{m} \times 500 \mu\text{m}$) connected through throats with polygonal cross section of widths $250 \mu\text{m}$. (2) a single, one dimensional channel ($\sim 2 \text{ mm} \times 100 \mu\text{m}$) which is connected to a two dimensional network similar to the first pattern. The micro-chips were saturated with NaCl solution and replaced afterwards with dry CO₂ under different rates of injection. Pore-scale salt precipitation was visualized under bright field imaging using advanced polarized light microscopy. In addition, to better understand the flux balances in the salt formation process, water evaporation through salt precipitation was also studied inside glass capillary tubes.

Key findings:

Using lab-on-a-chip experiments, we have demonstrated the existence of continuous brine films, and we have identified an important, self-enhancing mechanism which together dramatically intensify the precipitation rate and amount of salt precipitated. Moreover, the results reported in this paper suggest that salt precipitation is a time evolving (dynamic) process which has several elements.

- First, salt has a hydrophilic nature which gives massive capillarity to the salt aggregates to imbibe water.
- Second, salt grows as porous aggregates in the gas phase enhancing the distribution of brine, and increasing the surface area for evaporation, and therefore increasing the evaporation rate.
- Third, evaporation induces nucleation and precipitation which induces further capillary transport *i.e.*, salt aggregates imbibe more water to compensate the increased evaporation.

The net outcome of these elements is a massive salt accumulation in the CO₂ pathways, through a mechanism which is self-enhancing. An important insight is the viable dynamic stability and strong conductivity of the water films owing to the pressure gradient imposed by capillary imbibition. It has been shown that experimental and numerical works which neglect this effect impose improper boundary conditions to their models and thus underestimate the amount of precipitation. Therefore, effect of water films must be taken into account in the assessment of the salt precipitation, permeability and injectivity in porous media. In addition It is shown that the new identified mechanisms can explain many of knowledge gaps described in Paper D and offer a rationale for conducting future research.

4.3 Effect of heterogeneities (Paper F + proceedings)

Paper F: *Modeling CO₂ migration in aquifers; considering 3D seismic property data and the effect of site-typical depositional heterogeneities*

Motivation and objectives:

This paper along with two other proceedings aims to provide a generalised methodology for integrating 3D seismic data and geo-conceptual models in constructing and populating property grids for fluid flow simulations. Additionally, analyzing the effect of depositional heterogeneities and physical boundaries of the reservoir (*i.e.*, closed or open) on the pressure response at the injection well, is the other objective which is partly covered in this PhD thesis. In these paper I have contributed to the compositional flow simulations as well as estimating the thermodynamic properties using the EoS developed and tested in Papers A and B.

Method and procedure:

The study area is the Johansen Fm. a deep, saline aquifer offshore the Norwegian west-coast and a proposed candidate for long term CO₂ storage. Relevant scenarios were constructed by combining reservoir property models generated from seismic (effective porosity from acoustic impedance) with a conceptual, geological understanding. A regional model was constructed for evaluating different injection sites, populated with properties estimated from new seismic data and a revised geological model (Sundal, 2015b). A suite of smaller scenario models were constructed and run for 150 years, in order to investigate the effect of site-typical geological heterogeneities such as discrete layers of low-permeability mudstone, tight calcite cemented layers and directional permeability anisotropy on migration paths and trapping potentials for CO₂. Four sets of relative permeability curves were assigned according to facies. The simulations were performed using the CO2STORE option in Eclipse 300 multi-component (Schlumberger, 2012). Two phases were considered; a CO₂ rich phase and a H₂O rich phase. No flow-boundaries are assumed east and west of the injection site, since the corresponding facies are interpreted as relatively tight marine clays, and there are bounding faults. The MULTPV keyword of Eclipse 300 was used to apply open or closed boundary conditions and simulate natural aquifer outflow towards the North in all models.

Key findings:

- Base model fluid distribution estimates were 20 % mobile CO₂, 29 % CO₂ dissolved in formation water and 51 % residually trapped CO₂ after 1000 years. Adjustments of the injection locations facilitated more migration and enhanced the CO₂ immobilisation potential.
- The immobilised fraction of CO₂ after 150 years varied in the range of 40–65 % between model scenarios, and up-dip migration distances deviated by up to 3 km. The application of a horizontal injection scheme increased the combined residual and dissolved fractions to 83 %.
- Plume shape and layer distributions are important parameters in risk evaluations, and variability due to the effect of geological heterogeneity is in the same order of magnitude as physical sensitivity parameters.
- The simulations illustrate that averaging of the reservoir properties within each sand body might yield oversimplified plume geometries (*i.e.*, funnel shaped - due to unhindered upwards flow towards sealing unit).
- During injection, based on observations of saturation and pressure distribution between the two points, one would be able to resolve to some degree the nature of calcite layers (if present) as well as the overall porosity and permeability distribution.
- Simulations of CO₂ injection and migration predicted limited lateral reaches of fluid migration, low pressure build-up (for both open and

closed scenarios) and high potentials for residual and dissolution trapping (Sundal et al., 2014, 2013a).

- Within the investigated deltaic sandstone, the location of the injection well relative to facies settings shows that the fluid distribution varies despite comparable properties (*i.e.*, porosity, permeability, Net/Gross, formation thickness), mainly due to number and extent of cemented layers delimiting gravity driven flow, causing separation and lateral spreading of the plume.
- With highly permeable sands in between, the presence of flow baffles is an advantage with respect to sweep and volume utilization. The plume geometry is also important with regards to estimating the volume potential and relative effect of the various trapping mechanisms for CO₂ (*i.e.*, stratigraphic-, dissolution-, residual- and mineral trapping).
- Although, the depositions heterogeneities can potentially limit the vertical communication of reservoir thus inducing further pressure build-up, the general impact is seen negligible for the setting studied here. Nevertheless, this requires further investigation and forms the topic of our future research (Sundal et al., 2013b).

Chapter 5

Concluding Remarks

The overall aim for this thesis has been to improve the prediction of reservoir injectivity. Although it is easy to develop a methodology to evaluate pressure build-up and injectivity of a proposed CO₂ storage reservoir using simple analytical/numerical tools, it is a harder task to quantify the associated uncertainties arising from overlooking the complex phenomena involved in the near wellbore region. In this thesis, we looked at three prioritized research topics which we believed deserved the most attention.

The first topic we investigated was thermodynamic modeling of fluid mixtures relevant for CO₂ storage with particular focus on effect of methane (CH₄) and sulphur dioxide (SO₂) impurities. The results from this study is shown that reservoir fluid properties (such as density, viscosity and compressibility) and formation dry-out are largely determined by mutual solubilities of CO₂ and H₂O. In addition, with thermodynamic package developed in this part we found that we could predict which and how impurities that favored mutual solubilities. We found that the total solubility of water in a SO₂+CO₂ mixture varies exponentially with respect to SO₂ concentrations; *i.e.*, at low concentrations of SO₂, total changes in solubility of the water in CO₂ are negligible. In case of CH₄, a similar exponential behaviour is observed, but in the opposite direction, *i.e.*, with increasing CH₄ concentration the water content decreases exponentially. Thus, ignoring or inaccurate consideration of mutual solubilities will pose significant uncertainty to the results of injectivity modeling. The modern SAFT type EoS's were found accurate, reliable and promising for thermodynamic modeling relevant to CO₂ storage; Nevertheless, it is computationally cheaper to choose cubic EoS's when modeling simple fluids.

The potential implication of developed EoS in this thesis is extended further to model water drop-out in presence of SO₂ impurity in a CO₂ transportation pipeline. It turned out that taking into account the effect of the pipe surface on the chemical potential of adsorbed water and thereby on the phase partitioning, another concentration limit for water to drop out from gas can be obtained that could successfully explain the experimental

observations on water drop-out.

The second research topic we addressed in this thesis was formation drying-out and subsequent salt formation. We reviewed the current literature and found that the precipitation of salt is undoubtedly a threat for actual field scale injection of dry CO₂ in saline aquifers and limiting the phenomenon to occur only on high salinities is found to be an obvious mistake. In addition to the review, we studied further the mechanism of salt precipitation using lab-on-chip experiments and distinguished two interrelated and so far unreported phenomena – self-enhancing of salt growth and water film salt transport – which together dramatically intensify the precipitation rate and amount of salt precipitated. We used the developed themes of the pore-scale experiments to construct a conceptual framework which classifies the drying into three regimes, namely the diffusive, capillary and evaporative. As a general conclusion for this part, we believe that carefully designed laboratory experiments and/or multiphysics numerical simulations are essential to be considered as a part of the methodology to evaluate injectivity of a proposed CO₂ storage site. A numerical tool which be able to resolve the physics described in this thesis is still not available and is part of our recommendation for future work. However, we have provided the required modifications for the core flooding experiments to be applicable for the injectivity assessments.

We also partly studied the effect of prepositional heterogeneities on the plume migration and pressure response at the injection well. We found that with highly permeable sands in between, the presence of flow baffles is an advantage with respect to sweep and volume utilization. In addition, based on observations of saturation and pressure distribution, it turned out that, one would be able to resolve to some degree the nature of calcite layers (if present) as well as the overall porosity and permeability distribution. Lastly, although the depositions heterogeneities can potentially limit the vertical communication of reservoir, for the setting studied here we did not observe extreme well pressures. Nevertheless, this requires further investigation and forms the topic of our future research.

5.1 Outlook

A great number of ideas appeared in the course of this PhD thesis, that despite interest, I did not have the time to investigate any further. Here I list several points relating to this work that remain elusive and deserves further consideration:

- **Thermodynamic modeling:** Is it possible to develop an EoS using SAFT framework capturing the effect of pH variations on the solubility of CO₂ in water? We have partly covered this in Paper C through a decoupled scheme, but it is more interesting to express the pH changes

in the form of a residual Helmholtz energy equation. In addition, it is interesting to test the capability of SAFT1 EoS in combination with molecular dynamic simulation to estimate some unexplored fluid properties such as viscosity and surface tension.

- **Drying-out and salting-out:** An important finding of Papers D & E is the viable dynamic stability and strong conductivity of the water films owing to the pressure gradient imposed by capillary imbibition. It has been shown that experimental and numerical works which neglect this effect impose improper boundary conditions to their models and thus underestimate the amount of precipitation. The mechanism for the evaporation induced water transport, however, remains elusive and requires special consideration. Capillary tube experiments along with pore scale models such as Lattice Boltzmann method might be the possible approaches to unfold this issue.

Although more is being learned about the fundamental mechanisms and the clogging behaviour of the phenomenon, however, the degree of uncertainty associated with clogging models is very high as number of inconsistencies is reported in this regard. Therefore, further research on the mathematical modeling is the most demanding task today. Performing dimensional analysis to find a relationship between the dependent variable and independent variables of the phenomenon could help to reduce the reported inconsistencies. Future efforts in implementing salt capillary pressure and development with the aid of pore scale modeling are expected to help progress in this area.

Reservoir heterogeneities: The effect of depositions heterogeneities on the pressure build-up is partly covered in this thesis. However, it is interesting to test this effect under different settings and quantify the consequence such that the results can be used in assessment of injectivity. This work was already started by [Ashraf \(2014\)](#), but can it be automated in a methodological way?

References

- Adidharma, H. and Radosz, M. (1998). Prototype of an engineering equation of state for heterosegmented polymers. *Industrial & engineering chemistry research*, 37(11):4453–4462.
- Adidharma, H. and Radosz, M. (2001). Saft1 for associating fluids: Alkanols. *The Journal of Physical Chemistry B*, 105(40):9822–9827.
- André, L., Azaroual, M., and Menjoz, A. (2010). Numerical simulations of the thermal impact of supercritical CO₂ injection on chemical reactivity in a carbonate saline reservoir. *Transport in porous media*, 82(1):247–274.
- André, L., Azaroual, M., Peysson, Y., and Bazin, B. (2011). Impact of porous medium desiccation during anhydrous CO₂ injection in deep saline aquifers: up scaling from experimental results at laboratory scale to near-well region. *Energy Procedia*, 4:4442–4449.
- André, L., Peysson, Y., and Azaroual, M. (2014). Well injectivity during CO₂ storage operations in deep saline aquifers part 2: Numerical simulations of drying, salt deposit mechanisms and role of capillary forces. *International Journal of Greenhouse Gas Control*, 22(0):301–312.
- Andreu, J. S. and Vega, L. F. (2008). Modeling the solubility behavior of CO₂, H₂, and X_e in [C n-mim][Tf2N] ionic liquids. *The Journal of Physical Chemistry B*, 112(48):15398–15406.
- Ashraf, M. (2014). Geological storage of CO₂ : Heterogeneity impact on the behavior of pressure. *International Journal of Greenhouse Gas Control*, 28:356–368.
- Azizi, E., Cinar, Y., et al. (2013). Approximate analytical solutions for CO₂ injectivity into saline formations. *SPE Reservoir Evaluation & Engineering*, 16(02):123–133.
- Bachu, S. (2015). Review of CO₂ storage efficiency in deep saline aquifers. *International Journal of Greenhouse Gas Control*.
- Bachu, S. and Adams, J. (2003). Sequestration of CO₂ in geological media in response to climate change: capacity of deep saline aquifers to sequester CO₂ in solution. *Energy Conversion and management*, 44(20):3151–3175.
- Baumann, G., Hennings, J., and De Lucia, M. (2014). Monitoring of saturation changes and salt precipitation during CO₂ injection using pulsed neutron-gamma logging at the ketzin pilot site. *International Journal of Greenhouse Gas Control*, 28:134–146.
- Bemer, E. and Lombard, J. (2010). From injectivity to integrity studies of CO₂ geological storage-chemical alteration effects on carbonates petrophysical and geomechanical properties. *Oil & Gas Science and Technology—Revue de l’Institut Français du Pétrole*, 65(3):445–459.
- Benson, S. M. and Cole, D. R. (2008). CO₂ sequestration in deep sedimentary formations. *Elements*, 4(5):325–331.

- Benson, S. M. and Orr, F. M. (2008). Carbon dioxide capture and storage. *MRS bulletin*, 33(04):303–305.
- Birkholzer, J. T., Oldenburg, C. M., and Zhou, Q. (2015). CO₂ migration and pressure evolution in deep saline aquifers. *International Journal of Greenhouse Gas Control*.
- Birkholzer, J. T. and Zhou, Q. (2009). Basin-scale hydrogeologic impacts of CO₂ storage: Capacity and regulatory implications. *International Journal of Greenhouse Gas Control*, 3(6):745–756.
- Bjørlykke, K. (1993). Fluid flow in sedimentary basins. *Sedimentary Geology*, 86(1):137–158.
- Bruant, R., Guswa, A., Celia, M., and Peters, C. (2002). Safe storage of CO₂ in deep saline aquifers. *Environmental Science & Technology DC-*, 36(11):240A–245A.
- Bruckner, T., Bashmakov, I., Mulugetta, Y., Chum, H., de la Vega Navarro, A., J. Edmonds, A. F., Fungtammasan, B., Garg, A., Hertwich, E., Honnery, D., Infield, D., Kainuma, M., Khennas, S., Kim, S., Nimir, H., Riahi, K., Strachan, N., Wiser, R., and Zhang, X. (2014). *Climate change 2014: mitigation of climate change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Carnahan, N. F. and Starling, K. E. (1969). Equation of state for nonattracting rigid spheres. *The Journal of Chemical Physics*, 51(2):635–636.
- Chapman, W. G., Gubbins, K. E., Jackson, G., and Radosz, M. (1989). Saft: Equation-of-state solution model for associating fluids. *Fluid Phase Equilibria*, 52:31–38.
- Chatzis, I. and Dullien, F. (1983). Dynamic immiscible displacement mechanisms in pore doublets: theory versus experiment. *Journal of Colloid and Interface Science*, 91(1):199–222.
- Cinar, Y. and Riaz, A. (2014). Carbon dioxide sequestration in saline formations: Part 2 review of multiphase flow modeling. *Journal of Petroleum Science and Engineering*, 124:381–398.
- Cinar, Y., Riaz, A., Tchelepi, H. A., et al. (2007). Experimental study of CO₂ injection into saline formations. In *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers.
- Dake, L. P. (1983). *Fundamentals of reservoir engineering*. Elsevier.
- De Silva, P. and Ranjith, P. (2012). A study of methodologies for CO₂ storage capacity estimation of saline aquifers. *Fuel*, 93:13–27.
- Dong, M. and Chatzis, I. (2010). Effect of capillary pressure on wetting film imbibition ahead of main liquid–gas displacement front in porous media. *Petroleum Science and Technology*, 28(9):955–968.

- Doughty, C. (2007). Modeling geologic storage of carbon dioxide: comparison of non-hysteretic and hysteretic characteristic curves. *Energy Conversion and Management*, 48(6):1768–1781.
- Dugstad, A., Halseid, M., and Morland, B. (2013). Effect of SO₂ and NO₂ on corrosion and solid formation in dense phase CO₂ pipelines. *Energy Procedia*, 37(0):2877–2887.
- Egermann, P., Lombard, J., and Bretonnier, P. (2006). A fast and accurate method to measure threshold capillary pressure of caprocks under representative conditions. *SCA2006 A*, 46.
- Ehlig-Economides, C. and Economides, M. J. (2010). Sequestering carbon dioxide in a closed underground volume. *Journal of Petroleum Science and Engineering*, 70(1):123–130.
- EPA (2008). Federal requirements under the underground injection control (uic) program for carbon dioxide (CO₂) geological sequestration (gs) wells; proposed rule. fed. reg. 70 (july 144), 4349243541.
- Frykman, P. and Wessel-Berg, D. (2014). Dissolution trapping-convection enhancement limited by geology. *Energy Procedia*, 63:5467–5478.
- Gaus, I., Audigane, P., Andre, L., Lions, J., Jacquemet, N., Durst, P., Czernichowski-Lauriol, I., and Azaroual, M. (2008). Geochemical and solute transport modelling for CO₂ storage, what to expect from it? *International Journal of Greenhouse Gas Control*, 2(4):605–625.
- Geologyin (2015). Hydrocarbon traps. [Online; accessed 1-July-2015].
- Ghesmat, K., Hassanzadeh, H., and Abedi, J. (2011). The impact of geochemistry on convective mixing in a gravitationally unstable diffusive boundary layer in porous media: CO₂ storage in saline aquifers. *Journal of Fluid Mechanics*, 673:480–512.
- Giammar, D. E., Bruant, R. G., and Peters, C. A. (2005). Forsterite dissolution and magnesite precipitation at conditions relevant for deep saline aquifer storage and sequestration of carbon dioxide. *Chemical Geology*, 217(3):257–276.
- Gross, J. and Sadowski, G. (2001). Perturbed-chain saft: An equation of state based on a perturbation theory for chain molecules. *Industrial & engineering chemistry research*, 40(4):1244–1260.
- Gross, J. and Sadowski, G. (2002). Modeling polymer systems using the perturbed-chain statistical associating fluid theory equation of state. *Industrial & engineering chemistry research*, 41(5):1084–1093.
- Grude, S., Landr, M., and Dvorkin, J. (2014). Pressure effects caused by CO₂ injection in the tubaen fm., the snohvit field. *International Journal of Greenhouse Gas Control*, 27:178–187.

- Halland, E., Gjeldvik, I., Johansen, W., Magnus, C., Meling, I., Pedersen, S., Riis, F., Solbakk, T., and Tappel, I. (2011). CO₂ storage atlas: Norwegian north sea. *Norwegian Petroleum Directorate, PO Box*, 600.
- Han, W. S., McPherson, B. J., Lichtner, P. C., and Wang, F. P. (2010). Evaluation of trapping mechanisms in geologic CO₂ sequestration: Case study of sacroc northern platform, a 35-year CO₂ injection site. *American Journal of Science*, 310(4):282–324.
- Hansen, J., Sato, M., Ruedy, R., Schmidt, G. A., and Lo, K. (2015). Global temperature in 2014 and 2015.
- Hartmann, D., KleinTank, A., Rusticucci, M., Alexander, L., Bronnimann, S., Charabi, Y., Dentener, F., Dlugokencky, E., Easterling, D., Kaplan, A., Soden, B., Thorne, P., Wild, M., and Zhai, P. (2013). *Observations: Atmosphere and Surface*, book section 2, page 159254. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Hassanzadeh, H., Pooladi-Darvish, M., and Keith, D. W. (2007). Scaling behavior of convective mixing, with application to geological storage of CO₂. *AIChE journal*, 53(5):1121–1131.
- Hellevang, H. (2015). Carbon capture and storage (ccs). In *Petroleum Geoscience*, pages 591–602. Springer.
- Hellevang, H., Pham, V. T., and Aagaard, P. (2013). Kinetic modelling of CO₂–water–rock interactions. *International Journal of Greenhouse Gas Control*, 15:3–15.
- Hosa, A., Esentia, M., Stewart, J., and Haszeldine, S. (2011). Injection of CO₂ into saline formations: benchmarking worldwide projects. *Chemical Engineering Research and Design*, 89(9):1855–1864.
- Houghton, J., Ding, Y., Griggs, D., Noguer, M., van der Linden, P., Dai, X., Maskell, K., and Johnson, C. (2001). Climate change 2001: The scientific basis. contribution of working group I to the third assessment report of the intergovernmental panel on climate change.
- Huang, S. H. and Radosz, M. (1990). Equation of state for small, large, poly-disperse, and associating molecules. *Industrial & Engineering Chemistry Research*, 29(11):2284–2294.
- Hurter, S., Berge, J. G., and Labregere, D. (2007). Simulations for CO₂ injection projects with compositional simulator.
- IEA (2013). International Energy Agency. Technology Roadmap - Carbon Capture and Storage. <http://www.iea.org/publications/freepublications/publication/name,39359,en.html>.
- Ji, P., Feng, W., Tan, T., and Zheng, D. (2007). Modeling of water activity, oxygen solubility and density of sugar and sugar alcohol solutions. *Food chemistry*, 104(2):551–558.

- Ji, X., Tan, S. P., Adidharma, H., and Radosz, M. (2005). Saft1-rpm approximation extended to phase equilibria and densities of CO₂-H₂O and CO₂-H₂O-nacl systems. *Industrial & engineering chemistry research*, 44(22):8419–8427.
- Ji, X. and Zhu, C. (2012). Predicting possible effects of H₂S impurity on CO₂ transportation and geological storage. *Environmental science & technology*, 47(1):55–62.
- Juanes, R., Spiteri, E., Orr, F., and Blunt, M. (2006). Impact of relative permeability hysteresis on geological CO₂ storage. *Water Resources Research*, 42(12).
- Kaldi, J. and Gibson-Poole, C. (2008). Storage capacity estimation, site selection and characterisation for CO₂ storage projects. *Report No: RPT08-1001, CO2CRC, Canberra, ACT, AU*.
- Kharaka, Y., Cole, D., Hovorka, S., Gunter, W., Knauss, K., and Freifeld, B. (2006). Gas-water-rock interactions in frio formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology*, 34(7):577–580.
- Kim, K.-Y., Han, W. S., Oh, J., Kim, T., and Kim, J.-C. (2012). Characteristics of salt-precipitation and the associated pressure build-up during CO₂ storage in saline aquifers. *Transport in porous media*, 92(2):397–418.
- Kleinitz, W., Koehler, M., and Dietzsch, G. (2001). The precipitation of salt in gas producing wells. *paper SPE*, 68953:21–22.
- Kroon, M. C., Karakatsani, E. K., Economou, I. G., Witkamp, G.-J., and Peters, C. J. (2006). Modeling of the carbon dioxide solubility in imidazolium-based ionic liquids with the tPC-PSAFT equation of state. *The Journal of Physical Chemistry B*, 110(18):9262–9269.
- Lafitte, T., Bessieres, D., Piñeiro, M. M., and Daridon, J.-L. (2006). Simultaneous estimation of phase behavior and second-derivative properties using the statistical associating fluid theory with variable range approach. *The Journal of chemical physics*, 124(2):024509.
- Lafitte, T., Piñeiro, M. M., Daridon, J.-L., and Bessièrès, D. (2007). A comprehensive description of chemical association effects on second derivative properties of alcohols through a saft-vr approach. *The Journal of Physical Chemistry B*, 111(13):3447–3461.
- Larsen, L. (2013). Analyses of dh4 upper zone injection and falloff data, september 5 october 15, 2013. Report.
- Leonhard, K., Van Nhu, N., and Lucas, K. (2007). Making equation of state models predictive: Part 2: An improved pcp-saft equation of state. *Fluid phase equilibria*, 258(1):41–50.
- Li, X. (2013). *Experimental investigation of carbon dioxide trapping due to capillary retention in deep saline aquifers*. PhD thesis, The Pennsylvania State University.

- Liebscher, A., Möller, F., Bannach, A., Köhler, S., Wiebach, J., Schmidt-Hattenberger, C., Weiner, M., Pretschner, C., Ebert, K., and Zemke, J. (2013). Injection operation and operational pressure–temperature monitoring at the CO₂ storage pilot site ketzin, germanydesign, results, recommendations. *International Journal of Greenhouse Gas Control*, 15:163–173.
- Llovel, F., Florusse, L. J., Peters, C. J., and Vega, L. F. (2007). Vaporliquid and critical behavior of binary systems of hydrogen chloride and n-alkanes: experimental data and soft-saft modeling. *The Journal of Physical Chemistry B*, 111(34):10180–10188.
- Lombard, J., Azaroual, M., Pironon, J., Broseta, D., Egermann, P., Munier, G., and Mouronval, G. (2010). CO₂ injectivity in geological storages: an overview of program and results of the géocarbone-injectivity project. *Oil & Gas Science and Technology–Revue de l’Institut Français du Pétrole*, 65(4):533–539.
- Lucier, A., Zoback, M., Gupta, N., and Ramakrishnan, T. (2006). Geomechanical aspects of CO₂ sequestration in a deep saline reservoir in the ohio river valley region. *Environmental Geosciences*, 13(2):85–103.
- Mathias, S. A., de Miguel, G. J. G. M., Thatcher, K. E., and Zimmerman, R. W. (2011). Pressure buildup during CO₂ injection into a closed brine aquifer. *Transport in porous media*, 89(3):383–397.
- Mathias, S. A., Hardisty, P. E., Trudell, M. R., and Zimmerman, R. W. (2009a). Approximate solutions for pressure buildup during CO₂ injection in brine aquifers. *Transport in Porous Media*, 79(2):265–284.
- Mathias, S. A., Hardisty, P. E., Trudell, M. R., and Zimmerman, R. W. (2009b). Screening and selection of sites for CO₂ sequestration based on pressure buildup. *International Journal of Greenhouse gas control*, 3(5):577–585.
- McMillan, B., Kumar, N., Bryant, S. L., et al. (2008). Time-dependent injectivity during CO₂ storage in aquifers. In *SPE Symposium on Improved Oil Recovery*. Society of Petroleum Engineers.
- Metz, B., Davidson, O., De Coninck, H., Loos, M., and Meyer, L. (2005). Ipcc, 2005: Ipcc special report on carbon dioxide capture and storage. prepared by working group iii of the intergovernmental panel on climate change. *Cambridge, United Kingdom and New York, NY, USA*, 442 pp.
- Mijic, A., LaForce, T. C., and Muggeridge, A. H. (2014). CO₂ injectivity in saline aquifers: The impact of non-darcy flow, phase miscibility, and gas compressibility. *Water Resources Research*, 50(5):4163–4185.
- Miri, R., Aagaard, P., and Hellevang, H. (2014a). Examination of CO₂–SO₂ solubility in water by saft1. implications for CO₂ transport and storage. *The Journal of Physical Chemistry B*, 118(34):10214–10223.

- Miri, R. and Hellevang, H. (2014). Developments in soft eos for carbon capture and storage (css). In *Fourth EAGE CO₂ Geological Storage Workshop*.
- Miri, R. and Hellevang, H. (2015). Salt formation during CO₂ storage - a review. *International Journal of Greenhouse Gas Control*, Manuscript submitted for publication.
- Miri, R., Hellevang, H., Braathen, A., and Aagaard, P. (2014b). Phase relations in the longyearbyen CO₂ lab reservoir-forecasts for CO₂ injection and migration. *Norwegian Journal of Geology*, 94(2-3):217–232.
- Miri, R., Noort, R. v., Aagaard, P., and Hellevang, H. (2015). New insights on the physics of salt precipitation during injection of CO₂ into saline aquifers. *International Journal of Greenhouse Gas Control*, Manuscript submitted for publication.
- Müller, E. A. and Gubbins, K. E. (2001). Molecular-based equations of state for associating fluids: A review of soft and related approaches. *Industrial & engineering chemistry research*, 40(10):2193–2211.
- Muller, N., Qi, R., Mackie, E., Pruess, K., and Blunt, M. J. (2009). CO₂ injection impairment due to halite precipitation. *Energy procedia*, 1(1):3507–3514.
- Nordbotten, J. M., Celia, M. A., and Bachu, S. (2005). Injection and storage of CO₂ in deep saline aquifers: Analytical solution for CO₂ plume evolution during injection. *Transport in Porous media*, 58(3):339–360.
- Oelkers, E. H. and Cole, D. R. (2008). Carbon dioxide sequestration a solution to a global problem. *Elements*, 4(5):305–310.
- Ott, H., Roels, S., and De Kloe, K. (2015). Salt precipitation due to supercritical gas injection: I. capillary-driven flow in unimodal sandstone. *International Journal of Greenhouse Gas Control*.
- Pachauri, R. K., Allen, M., Barros, V., Broome, J., Cramer, W., Christ, R., Church, J., Clarke, L., Dahe, Q., Dasgupta, P., et al. (2014). Climate change 2014: Synthesis report. contribution of working groups I, II and III to the fifth assessment report of the intergovernmental panel on climate change.
- Paduszynski, K. and Domaska, U. (2012). Thermodynamic modeling of ionic liquid systems: Development and detailed overview of novel methodology based on the pc-soft. *The Journal of Physical Chemistry B*, 116(16):5002–5018.
- Peaceman, D. W. et al. (1983). Interpretation of well-block pressures in numerical reservoir simulation with nonsquare grid blocks and anisotropic permeability. *Society of Petroleum Engineers Journal*, 23(03):531–543.
- Pentland, C. H., Itsekiri, E., Al-Mansoori, S., Iglauer, S., Bijeljic, B., Blunt, M. J., et al. (2010). Measurement of nonwetting-phase trapping in sand-packs. *Spe Journal*, 15(02):274–281.

- Peysson, Y., Andre, L., and Azaroual, M. (2014a). Well injectivity during CO₂ storage operations in deep saline aquifers part 1: Experimental investigation of drying effects, salt precipitation and capillary forces. *international journal of Greenhouse Gas Control*, 22:291–300.
- Peysson, Y., Andre, L., and Azaroual, M. (2014b). Well injectivity during CO₂ storage operations in deep saline aquifers part 1: Experimental investigation of drying effects, salt precipitation and capillary forces. *international journal of Greenhouse Gas Control*, 22:291–300.
- Pham, V., Lu, P., Aagaard, P., Zhu, C., and Hellevang, H. (2011). On the potential of CO₂–water–rock interactions for CO₂ storage using a modified kinetic model. *International Journal of Greenhouse Gas Control*, 5(4):1002–1015.
- Pruess, K. and Müller, N. (2009). Formation dry-out from CO₂ injection into saline aquifers: 1. effects of solids precipitation and their mitigation. *Water Resources Research*, 45(3).
- Pruess, K. and Muller, N. (2009). Formation dry-out from CO₂ injection into saline aquifers: 1. effects of solids precipitation and their mitigation. *Water Resources Research*, 45(3).
- Riaz, A. and Cinar, Y. (2014). Carbon dioxide sequestration in saline formations: Part ireview of the modeling of solubility trapping. *Journal of Petroleum Science and Engineering*, 124:367–380.
- Rohde, R., Muller, R., Jacobsen, R., Muller, E., Perlmutter, S., Rosenfeld, A., Wurtele, J., Groom, D., and Wickham, C. (2013). A new estimate of the average earth surface land temperature spanning 1753 to 2011. *Geoinfor Geostat Overview 1:1*, doi:10.4172/2327-4581.1000101.
- Schembre-McCabe, J. M., Kamath, J., Gurton, R. M., et al. (2007). Mechanistic studies of CO₂ sequestration. In *International Petroleum Technology Conference*. International Petroleum Technology Conference.
- Schlumberger (2012). Eclipse 300 compositional. <http://gts.sourceforge.net/>.
- Singh, M., Leonhard, K., and Lucas, K. (2007). Making equation of state models predictive: Part 1: Quantum chemical computation of molecular properties. *Fluid phase equilibria*, 258(1):16–28.
- Spycher, N. and Pruess, K. (2005). CO₂–H₂O mixtures in the geological sequestration of CO₂. ii. *Partitioning in chloride brines at*, pages 12–100.
- Spycher, N., Pruess, K., and Ennis-King, J. (2003). CO₂–H₂O mixtures in the geological sequestration of CO₂. I. assessment and calculation of mutual solubilities from 12 to 100 °C and up to 600 bar. *Geochimica et Cosmochimica Acta*, 67(16):3015–3031.

- Stocker, T., Qin, D., Plattner, G., Tignor, M., Allen, S., Boschung, J., Nauels, A., Xia, Y., Bex, B., and Midgley, B. (2013). IPCC, 2013: climate change 2013: the physical science basis. contribution of working group i to the fifth assessment report of the intergovernmental panel on climate change.
- Sundal, A. (2015a). *Geological reservoir characterization for sub-surface CO₂ storage*. PhD thesis, University of Oslo.
- Sundal, A. (2015b). *Geological reservoir characterization for subsurface CO₂ storage: Methodologies for evaluation of reservoir quality and effects of depositional heterogeneities*. PhD thesis, University of Oslo.
- Sundal, A., Hellevang, H., Miri, R., Dypvik, H., Nystuen, J. P., and Aagaard, P. (2014). Variations in mineralization potential for CO₂ related to sedimentary facies and burial depth—a comparative study from the north sea. *Energy Procedia*, 63:5063–5070.
- Sundal, A., Miri, R., Petter Nystuen, J., Dypvik, H., and Aagaard, P. (2013a). Modeling CO₂ distribution in a heterogeneous sandstone reservoir: the johansen formation, northern north sea. volume 15, page 13770.
- Sundal, A., Miri, R., Ravn, T., and Aagaard, P. (2015). Modelling CO₂ migration in aquifers; considering 3d seismic property data and the effect of site-typical depositional heterogeneities. *International Journal of Greenhouse Gas Control*, 39:349–365.
- Sundal, A., Nystuen, J. P., Dypvik, H., Miri, R., and Aagaard, P. (2013b). Effects of geological heterogeneity on CO₂ distribution and migration—a case study from the johansen formation, norway. *Energy Procedia*, 37:5046–5054.
- Tan, S. P., Adidharma, H., and Radosz, M. (2004). Generalized procedure for estimating the fractions of nonbonded associating molecules and their derivatives in thermodynamic perturbation theory. *Industrial & engineering chemistry research*, 43(1):203–208.
- Tan, S. P., Adidharma, H., and Radosz, M. (2005). Statistical associating fluid theory coupled with restricted primitive model to represent aqueous strong electrolytes. *Industrial & engineering chemistry research*, 44(12):4442–4452.
- Tan, S. P., Ji, X., Adidharma, H., and Radosz, M. (2006). Statistical associating fluid theory coupled with restrictive primitive model extended to bivalent ions. saft2: 1. single salt+water solutions. *The Journal of Physical Chemistry B*, 110(33):16694–16699.
- Tan, S. P., Yao, Y., and Piri, M. (2013). Modeling the solubility of SO₂+CO₂ mixtures in brine at elevated pressures and temperatures. *Industrial & Engineering Chemistry Research*, 52(31):10864–10872.
- Tans, P. (2015). NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling scripps institution of oceanography (scrippsco2.ucsd.edu/).

- USDOE (2007). Carbon sequestration atlas of united states and canada.
- Van Genuchten, M. T. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil science society of America journal*, 44(5):892–898.
- Wang, Y., Zhang, K., and Wu, N. (2013). Numerical investigation of the storage efficiency factor for CO₂ geological sequestration in saline formations. *Energy Procedia*, 37:5267–5274.
- Wigley, T. M., Richels, R., and Edmonds, J. A. (1996). Economic and environmental choices in the stabilization of atmospheric CO₂ concentrations.
- Xu, T., Apps, J. A., and Pruess, K. (2001). Analysis of mineral trapping for CO₂ disposal in deep aquifers. *Lawrence Berkeley National Laboratory*.
- Yang, F., Bai, B., Tang, D., Shari, D.-N., and David, W. (2010). Characteristics of CO₂ sequestration in saline aquifers. *Petroleum Science*, 7(1):83–92.
- Zeidouni, M. (2011). *Analytical and Inverse Models for Leakage Characterization of CO₂ Storage*. PhD thesis, Ph. D. Dissertation, University of Calgary, Calgary, Canada.
- Zeidouni, M., Pooladi-Darvish, M., and Keith, D. (2009). Analytical solution to evaluate salt precipitation during CO₂ injection in saline aquifers. *International Journal of Greenhouse Gas Control*, 3(5):600–611.
- Zhao, H., Morgado, P., Gil-Villegas, A., and McCabe, C. (2006). Predicting the phase behavior of nitrogen + n-alkanes for enhanced oil recovery from the soft-vr approach: Examining the effect of the quadrupole moment. *The Journal of Physical Chemistry B*, 110(47):24083–24092.

