Reactive transport modelling of hydrate phase transition dynamics in porous media

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Scientific environment

This PhD study has been performed at Department of Physics and Technology, Faculty of Mathematics and Natural Sciences, University of Bergen. The principle supervisor has been Professor Bjørn Kvamme with Professor Tatiana Kuznetsova as Co-supervisor.

Acknowledgements

Dedicated to my beloved family and my love

Fereshteh

Preface

The work presented in this dissertation has been carried out at Department of Physics and Technology, University of Bergen in the period of 2009 to 2014 and is submitted in partial fulfilment of the requirements for the degree of Philosophiae Doctor.

This article-based dissertation consists of two main parts. First part is an introduction to the field of reservoir hydrate and the progresses and challenges on the way of simulation studies and development of sophisticated simulators. Motivation behind this research study and the methodology is explained in this section. The summary of the results published in journal papers and conclusion are presented followed by suggestion for future works. The second part includes the publications mainly in peer-reviewed journals and as a result of the research activities in this period. Eight papers are included in this part among which six papers are published in peer-reviewed journals, one is published in proceedings of a conference with review system and one is submitted for publication.

The appendices include two articles and two abstracts with my contribution as a co-author.

Abstract

Gas hydrate is believed to be so abundant in nature that some estimates suggest it contains more than two times equivalent energy of the whole fossil fuels on Earth. Besides, reservoir hydrates have other important aspects such as environmental impacts and CO_2 storage potentials. These characteristics make it an important topic of research within academia and industry.

Taking into account the impacts of solid mineral surfaces and corresponding adsorbed phases during hydrate processes in reservoirs reveal that these systems cannot reach equilibrium as explained by Gibbs phase rule. Therefore, water and hydrate formers will distribute among possible phases, including hydrate, under the minimum free energy criteria according to the combined first and second laws of thermodynamics.

Complexities of hydrate behaviour in the reservoir require a coupling between different mechanisms ranging from nano-scale to macro scale. For this reason, in this study a reactive transport reservoir simulator named RetrasoCodeBright (RCB) has been used to develop a new hydrate simulator, which is capable of incorporating the kinetics of hydrate phase transitions due to temperature, pressure and concentration super-saturation and under-saturation. Kinetics of hydrate phase transitions is incorporated in the model through two different methods. The first one is a multi-scale approach in which, phase field theory as the core element has been used for estimating kinetic rates of different possible phase transitions. The results from these advanced theories are simplified and implemented into RCB for different hydrate phase transitions.

Second approach has been based on the use of non-equilibrium thermodynamics. In this method, the change in free energy of the system due to phase transition from one hydrate phase to any other phase is calculated to identify the impossible phase transition scenarios as well as the unlikely ones and prioritize the likely scenarios according to minimization of Gibbs free energy.

Another important aspect of the platform used in this study is the implicit geomechanical module, which allows analysis of stress changes in the reservoir structure as a result of hydrate processes.

The new simulation tool and the explained features are presented in this study and different applications of this simulator are illustrated through example cases and comparisons published in the attached papers. It gives the possibility to study methane production processes from hydrate reservoirs as well as CO_2 storage potentials. The approach used in this study is a step forward towards a more realistic description of reservoir hydrates processes in simulation studies.

List of publications

1. Reviewed publications in scientific journals

Vafaei, M. T., Kvamme, B., Chejara, A., & Jemai, K. (2014). Simulation of Hydrate Dynamics in Reservoirs. SPE Journal, 19(2), 215-226.

Vafaei, M. T., Kvamme, B., Chejara, A., & Jemai, K. (2012). Nonequilibrium Modeling of Hydrate Dynamics in Reservoir. Energy & Fuels, 26(6), 3564-3576.

Vafaei, M. T., Kvamme, B., Chejara, A., & Jemai, K. (2014). A new reservoir simulator for studying hydrate dynamics in reservoir. International Journal of Greenhouse Gas Control, 23, 12-21.

Chejara, A., Kvamme, B., Vafaei, M. T., & Jemai, K. (2012). Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator. Energy Procedia, 18, 1533-1540.

Chejara, A., Kvamme, B., Vafaei, M. T., & Jemai, K. (2013). Simulations of long term methane hydrate dissociation by pressure reduction using an extended RetrasoCodeBright simulator. Energy Conversion and Management, 68, 313-323.

Jemai, K., Vafaei, M.T., Kvamme, B., Chejara, A. Simulation of CO_2 hydrates formation in cold aquifers: non-equilibrium approach. Submitted to the Journal of Porous Media.

Jemai, K., Kvamme, B., Vafaei, M.T. (2014). Theoretical studies of CO_2 hydrates formation and dissociation in cold aquifers using RetrasoCodeBright simulator. WSEAS Transactions on Heat and Mass Transfer, 9, 150-168.

2. Reviewed publications in conference proceedings

Kvamme, B., Vafaei, M.T., Chejara, A., Jemai, K., "Simulation of Hydrate dynamics in reservoirs", Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.

Vafaei, M. T., Kvamme, B., Chejara, A., Jemai, K., "Simulation of Hydrate Dynamics in Reservoirs", Proceedings of the International Petroleum Technology Conference, Bangkok, Thailand, February 7-9, 2012. DOI: 10.2523/14609-MS.

Kvamme, B., Jemai, K., Chejara, A., Vafaei, M.T., "Simulation of geomechanical effects of CO_2 injection in cold aquifers with possibility of hydrate formation", Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.

3. Publications in conference proceedings without review system

Kvamme, B., Vafaei, M.T., Chejara, A., Jemai, K., "Reservoir scale simulation of hydrate dynamics", European Geosciences, Union General Assembly 2011, Vienna, Austria, April 3-8, 2011.

Jemai, K., Kvamme, B., Chejara, A., Vafaei, M.T., "Simulation of geomechanical effects of CO_2 injection in fractured reservoir", European Geosciences, Union General Assembly 2011, Vienna, Austria, April 3-8, 2011.

4. International presentations

Kvamme, B., Vafaei, M.T., Chejara, A., Jemai, K., "Reservoir scale simulation of hydrate dynamics", Presented at the European Geosciences Union General Assembly 2011, Vienna, Austria, April 3-8, 2011.

Vafaei, M.T., Kvamme, B., Chejara, A., Jemai, K., "Simulation of hydrate dynamics in reservoirs", For presentation at the International Petroleum Technology Conference, Bangkok, Thailand, November 15-17, 2011.

Kvamme, B., Vafaei, M.T., Chejara, A., Jemai, K., "Simulation of Hydrate dynamics in reservoirs", Presented at the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.

Jemai, K., Kvamme, B., Chejara, A., Vafaei, M.T., "Simulation of geomechanical effects of CO_2 injection in fractured reservoir", European Geosciences Union General Assembly 2011, Vienna, Austria, April 3-8, 2011.

Kvamme, B., Jemai, K., Chejara, A., Vafaei., M.T., "Simulation of geomechanical effects of CO_2 injection in cold aquifers with possibility of hydrate formation", Presented at the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.

Kvamme, B., Kuznetsova, T, Quasim, M., Vafaei., M.T., Chejara, A., Jemai, K., Baig, K., Jensen, B., Cuong, P., Kivela, P.-K., Bauman, J., "Multiscale modeling of CO_2 storage in cold reservoirs", invited presentation at CECAM workshop "Microscopic-Scale View of CO_2 sequestration", CECAM-HQ-EPFL, Lausanne, Switzerland, June 22-24, 2011.

Chejara, A., Kvamme, B.,Vafaei, M. T., Jemai, K., "Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator", Oral Presentation at TerraGreen12 : Clean Energy Solutions for Sustainable Environment conference, Beirut, Lebanon, February 16-18, 2012.

Chejara, A., Kvamme, B., Vafaei, M. T., Jemai, K., "Simulation of underground CO_2 storage", Oral presentation at Climit PhD Seminar, Oslo, Norway, November 28-29, 2011.

Kvamme, B., Jemai, K., Vafaei, M. T., Qorbani Nashaqi, K., "Non-Equilibrium Phase Transitions of Hydrate Dynamics in Reservoirs Using a Reactive Transport Simulator", Presented at the 8th International Conference on Gas Hydrates (ICGH 2014), Beijing, China, Jul. 28-Aug. 1, 2014.

Kvamme, B., Qorbani Nashaqi, K., Jemai, K., Vafaei, M. T. "Towards a New Non-Equilibrium Hydrate Reservoir Simulator", Presented at the 8th International Conference on Gas Hydrates (ICGH 2014), Beijing, China, Jul. 28-Aug. 1, 2014.

Kvamme, B., Qorbani Nashaqi, K., Jemai, K., Vafaei, M. T. "New Simulator for Non-Equilibrium Modeling of Hydrate Reservoirs", AGU Fall Meeting, San Francisco, USA, Dec. 15-19, 2014.

Publications included in this thesis

Paper 1.

Vafaei, M. T., Kvamme, B., Chejara, A., & Jemai, K. (2014). Simulation of Hydrate Dynamics in Reservoirs. SPE Journal, 19(2), 215-226.

Paper 2.

Vafaei, M. T., Kvamme, B., Chejara, A., & Jemai, K. (2012). Nonequilibrium Modeling of Hydrate Dynamics in Reservoir. Energy & Fuels, 26(6), 3564-3576.

Paper 3.

Vafaei, M. T., Kvamme, B., Chejara, A., & Jemai, K. (2014). A new reservoir simulator for studying hydrate dynamics in reservoir. International Journal of Greenhouse Gas Control, 23, 12-21.

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Paper 6.

Kvamme, B., Jemai, K., Chejara, A., Vafaei, M.T. (2011). Simulation of geomechanical effects of CO_2 injection in cold aquifers with possibility of hydrate formation. Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), July 17-21, Edinburgh, Scotland, United Kingdom.

Paper 7.

Jemai, K., Vafaei, M.T., Kvamme, B., Chejara, A. Simulation of CO_2 hydrates formation in cold aquifers: non-equilibrium approach. Submitted to the Journal of Porous Media

Paper 8.

Jemai, K., Kvamme, B., Vafaei, M. T. Theoretical studies of CO_2 hydrates formation and dissociation in cold aquifers using RetrasoCodeBright simulator. WSEAS Transactions on Heat and Mass Transfer, 9, 150-168.

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Part 1 – Introduction

1. Introduction

The current study has been an effort towards better understanding of hydrates behaviour in reservoirs. Due to the complexities of hydrate phase transition mechanisms during production studies, through processes like depressurization or studies of CO_2 storage in the form of CO_2 hydrate, many efforts have been made to discover different aspects of hydrates in porous media. One of the important classes of methods in this regard has been development of different numerical tools for predicting the response of hydrate systems to natural and human caused disturbances. These start from limited size models based on hydrodynamics aimed at addressing specific phenomena. The main effort, however, have been directed towards the development of hydrate reservoir simulators. There has been a valuable progress in that direction while there are still uncertainties and knowledge gaps (Moridis *et al.*, 2013). The existing academic and industrial simulators have been typically based on either hydrogeological simulators or oil and gas simulators, which have been reworked into hydrate simulators using varying approximations for handling the solid hydrate phase.

The study reported in this thesis represents a contribution in the development of a new hydrate simulator. Unlike existing hydrate reservoir simulators, this simulator is based on an existing reactive transport simulator, which was originally developed for hydrogeological studies of reactive processes in nature. One of the important differences between this simulator compared to other hydrate simulators is its capability to study dynamics of hydrate in reservoir more accurately by incorporating non-equilibrium aspects and competing phase transitions in an efficient fashion. Using the logistics of the competitive reaction module in this simulator opened up for implementation of different competing hydrate phase transition scenarios. This is accomplished by considering competing hydrate phase transitions as competing pseudo reactions. All possible hydrate phase transitions in a given local section of a reservoir can therefore be incorporated as non-equilibrium processes in which Gibbs free energy analysis distinguishes the possible scenarios as well as the most feasible ones.

The thesis starts with the motivation behind this study followed by some information about the background of hydrates in nature and the state of the knowledge within the topic. An overview of the recent developments and the status of the research on reservoir hydrate simulation will be provided. This is followed by definition of this project and arguments for corresponding choices of scientific methods. A detailed description and explanation of the simulator developed in this project is given prior to summary of the published papers as a result of this study. Finally the conclusions from the projects and suggestions for future works are given. The written publications during this study are presented in Part 2 followed by appendices.

2. Motivation

The potential capacity of Methane hydrate as future source of energy has been investigated with increasing intensity during at least the last three decades. During a similar time span there has been promising developments in geological storage of Carbon dioxide as efforts towards reducing emissions of Carbon Dioxide to the atmosphere. These efforts also include storing Carbon Dioxide as hydrate and the impact of hydrate formation during aquifer storage of Carbon Dioxide in reservoirs with cold regions. Yet another interesting option is the storage of Carbon Dioxide in natural gas hydrate reservoirs. This latter option represents a win-win situation since released natural gas may compensate even more than the storage costs since the conversion is self-driven by thermodynamics. On the CO_2 side, the cost of injection is the only cost. All of the above are motivating factors for developing a new reservoir simulator, which gives the possibility of studying the dynamics of Methane and Carbon Dioxide hydrate formation, dissociation and reformation in reservoirs and other sediments (pilot studies and experiments). Because of the complexity of the hydrate behaviour in the reservoir, simplification of the problems during hydrate studies is inevitable. Thermodynamics of hydrate in the reservoir is one of these complex features. As will be discussed further in the coming chapters, hydrate processes in the reservoir are in many cases, of non-equilibrium nature, which requires a lot of resources and efforts to deal with, specifically in the modelling and simulation approaches of hydrate research. Equilibrium assumptions have been widely used to set aside these complexities and allow for further progress in the study of reservoir hydrates. Full impact of these simplifications is not yet known.

In the current study, however, it is chosen not to use equilibrium approach. The reason is that hydrates in nature cannot be in full equilibrium and that some competing phase transitions will be important while others may not. It is important to understand on solid scientific grounds, what approximations are acceptable and what approximations are not. For this purpose, a reactive transport reservoir simulator has been used in this study as the simulation platform. This gives the opportunity to study

hydrate reactions in the reservoir in more detail specially in general non-equilibrium situations.

3. Background

In this chapter a brief history of hydrate discovery will be presented followed by describing different hydrate structures and characteristics. The importance of hydrates in the reservoir will be explained from several points of view including energy resource potentials, environmental risks and CO_2 storage capacities. At the end, classification of hydrate reservoirs and different methods for producing methane from gas hydrate reservoirs will be discussed.

3.1 History

The history of hydrate goes back to 1810 when it was first discovered by Sir Humphrey Davy[1] and continued to be studied by different scientists in laboratory scale as a scientific curiosity (Sloan & Koh, 2008). Hydrocarbon hydrates were not discovered until late 1800 when methane, ethane and propane hydrates were found by Villard[2] in 1888 followed by discovery of several more hydrocarbon hydrates by de Forcrand[3] in 1902 (ibid). But the modern research era on gas hydrates started by recognizing hydrates as the cause of blockage in the gas transmission lines during 1930's. It was the beginning of extensive research efforts on several aspects of hydrates, mainly with the goal of prevention. These studies ranged from determining hydrate composition and the effect of different hydrate inhibitors on the formation process up to initial correlations for predicting hydrate phase equilibrium. Hydrate crystal structures I and II were discovered in late 1940s and early 1950s and hydrate structure H was recognized later in 1980s. These achievements continued with introduction of statistical thermodynamic models for predicting gas hydrate macro-scale properties such as pressure and temperature using micro-scale properties like

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[1] For complete article refer to: Davy, H., 1811: On some of the combinations of oxymuriatic acid gas and oxygen and on the chemical relations of the properties. *Phil. Trans. Roy. Soc.(London),* **101,** 30-55.

[2] For complete article refer to: Villard, P., 1888: Sur quelques nouveaux hydrates de gaz. *Compt. rend,* **106,** 1602.

[3] For complete article refer to: De Forcrand, R., 1902: Sur la composition des hydrates de gaz. Ibid.**135,** 959.

intermolecular potentials. Van Der Waals and Platteeuw (1959) are considered as founders of the method still being used.

A new period in hydrate research started to shape by discovery of natural gas hydrates. The Markhinskaya well drilled in 1963 in Siberia has been the first experience of natural gas production from hydrates and the initiation of the hypothesis regarding the existence of gas hydrate accumulations in colds layers (Makogon, 2010). The first major hydrate deposit in permafrost was found in 1969 in Soviet Union in the gas hydrate field of Massoyakha. It was estimated that the hydrate layer in this reservoir contained at least one third of the whole amount of gas in the field. The depth of the hydrate layer was estimated to reach 900 meters in Massoyakha. Further signs of hydrate reservoirs were found afterwards in different parts of the world such as Alaska, Canada, Gulf of Mexico, Japan etc. Some estimates of world hydrate reserves show a very high and at the same time uncertain amount of 10^{16} m^3 of gas, which can be a sufficient supply of energy for several hundred years (ibid). By discovery of in situ hydrate, different research attempts started in different parts of the world ranging from evaluating different hydrate properties needed for geological research and recovery up to estimation of the feasibility and the amount of recoverable gas from permafrost. These researches still continue and in its most recent developments have now stepped into a new stage of pilot test production on North Slope of Alaska in USA and off the Coast of Honshu Island in Japan.

3.2 Hydrate Structure

Clathrates are a group of substances in which a specific type of molecule creates cages with crystalline structure and encapsulates another type of molecule. Whenever the water creates this crystalline structure, the clathrate is called hydrates (Bollmann *et al.*, 2010). Gas hydrates consist of lattices of crystal structures made by water molecules similar to ice in which 'gas' molecules (guest) are trapped. Ultimately, gas hydrates form a crystalline compound. Since gas hydrate consists of about 85% water, most of its mechanical properties are similar to ice. Hydrogen bounds in hydrate structure create cages in which guest molecules will be trapped and

depending on their sizes and varieties will form different hydrate structures. Most of the 130 compounds which form clathrate hydrate with water molecules produce three hydrate structures of sI, sII, and sH as described below:

- Hydrate Structure sI: Each unit cell of sI hydrate is composed of two small cavities and six large cavities. Each small cavity is formed by twenty water molecules and has twelve pentagonal faces denoted 5^{12}. Each large cavity is formed by twenty four water molecules and has twelve pentagonal and two hexagonal faces denoted $5^{12} 6^2$.

- Hydrate structure sII: Each unit cell of sII hydrate is composed of sixteen small cavities and eight large cavities. Small cavities are similar to small cavities in sI hydrate. Each large cavity is formed by twenty eight water molecules and has twelve pentagonal and four hexagonal faces denoted $5^{12} 6^4$.

- Hydrate structure sH: This structure consists of three different cavity types. Small cavities with twelve pentagonal faces are similar to the small cavities in structure I and II. Medium cavities with three square and three hexagonal faces plus six pentagonal faces are denoted by $4^3 5^6 6^3$. And large cavities with twelve pentagonal and eight hexagonal faces are denoted by $5^{12} 6^8$. Each medium cavity is formed by twenty water molecules and each large cavity is formed by thirty six water molecules. Each unit cell in this structure has three small cavities, two medium cavities and one large cavity. Schematic of different cavity types and summary of hydrate crystal structures are presented in Figure 1 and Table 1 respectively.

Hydrate structures are determined according to the characteristics of the available guest molecules and thermodynamic conditions. The ratio between the guest molecule diameter and the cavity diameter can serve as an indication of the possible hydrate structure. A value between 0.76 and 1.0 is usually necessary to allow the guest molecule to be trapped into the cages. Of course the chemical structure of the guest molecule is also important in the hydration process.
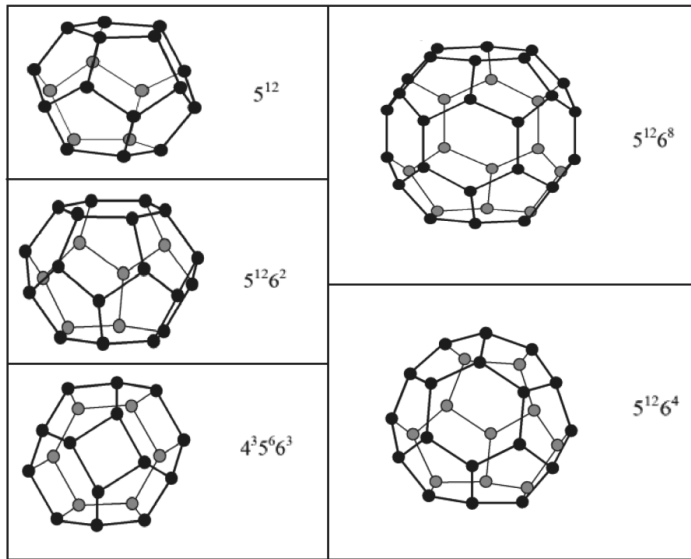
Figure 1 Hydrate cavity structures (Adapted from Ostrovskii & Kadyshevich, 2009)

Table 1 Summary of hydrate crystal structures (Sloan, 2003)

Hydrate crystal structure	I		II		H		
Cavity size	Small	Large	Small	Large	Small	Medium	Large
Cavity description	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$	5^{12}	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Example of guest molecules	Methane, ethane, carbon dioxide		Propane, iso-butane		Methane + neohexane, methane + cycloheptane		

Reservoir hydrate has several important aspects, which makes it a distinctive research area within energy and environmental fields. These include the potentials of hydrate as a future energy source, its environmental risks and CO_2 storage potentials, which will be described briefly.

3.3 Hydrate as an energy source

Abundance of gas hydrates in nature was first claimed by Russian scientists during late 1970s. Gas hydrates occur both in permafrost regions of the arctic as well as deep

water sediments in most of the continental margins worldwide (Collett *et al.*, 2009). Figure 2 shows the median of gas in place in hydrate-bearing sands in different parts of the world. Gas hydrates have been found both in shallow sediment cores of the depths of 10 to 30 m from seafloor such as in the Gulf of Mexico, the Black Sea, the Caspian Sea, the Sea of Japan, the North and South Atlantic Ocean, etc. as well as greater depths such as along the Cascadia margin of the United States and Canada; in the Middle America Trench; offshore Peru, India, China, and South Korea; and on both the eastern and western margins of Japan (ibid).

Onshore and near shore gas hydrates can only exist in close association with permafrost and as such it is expected that gas hydrate exists on the continental shelf of the Arctic Ocean at the depths of 120m (ibid). Onshore and permafrost Gas hydrates have been reported in Canada, Alaska, northern Russia, west Siberian basin, North American Arctic and etc. Core studies of two gas-hydrate research wells provide evidence of gas hydrate existence on the North Slope of Alaska. Studies of gas hydrates in permafrost regions show that gas hydrates may exist at subsurface depths of 130 to 2000m (ibid). However, the abundance of gas hydrates in sediments of marine continental margins is much more than permafrost regions. It is estimated that the former covers 99% of gas hydrates with a saturation of 20% to 80% while the latter contains only 1% (Collett et al., 2009).

Methane forming hydrates in the reservoirs has two main origins. It has originated either from biological activities in sediments referred to as biogenic origin or geological processes which occur deep within the earth and is referred to as thermogenic origin. Biogenic hydrates are produced as a result of bacterial activities happening under the seabed from tens of meters to hundreds of meters in sediments. Thermogenic methane on the other hand is produced in depths of more than 1000m where high temperature and pressure conditions apply.

While most of the oceanic hydrates have a biogenic origin, some exceptions such as Siberian gas field and Golf of Mexico are examples of hydrate systems with

thermogenic dominance (McIver 1981 and Collett et al. 2009 as cited by Ruppel, 2011).
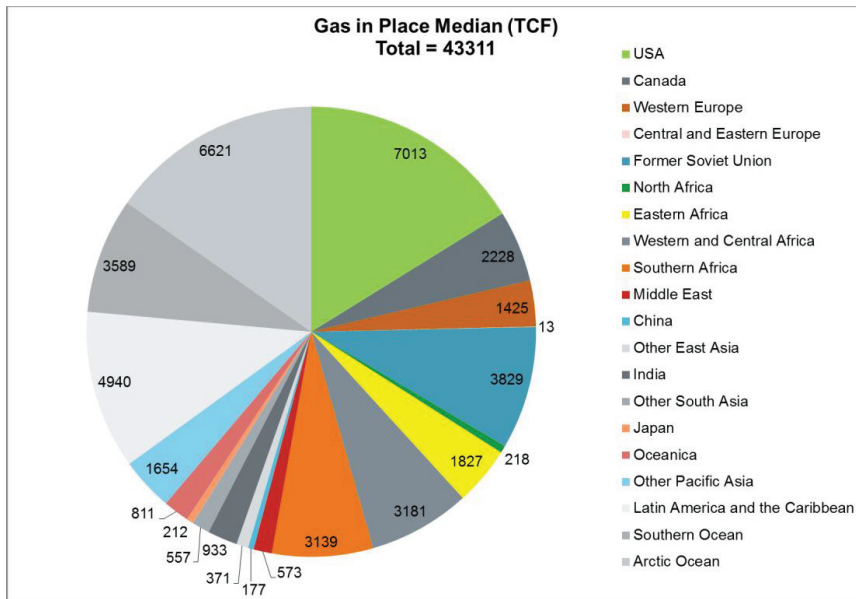
Figure 2 Gas in place from hydrate-bearing sands (Adapted from Archer, 2007).

Hydrate occurs according to the temperature and pressure conditions of the region. As the depth increases in permafrost regions, temperature increases nearly with a constant rate depending on the geothermal gradient of the layer in that region. It is while the pressure increases due to the load of upper layers. This provides a limited depth range, which is suitable for hydrate formation according to the hydrate stability curve. Similar phenomenon happens in the oceanic sediments with a slight difference. The hydrothermal gradient in the oceanic water is negative which results in temperature decrease down to the sea floor. After that, the temperature starts increasing according to geothermal gradient quite similar to what happens in the permafrost. Figure 3 shows this phenomenon for two example cases.
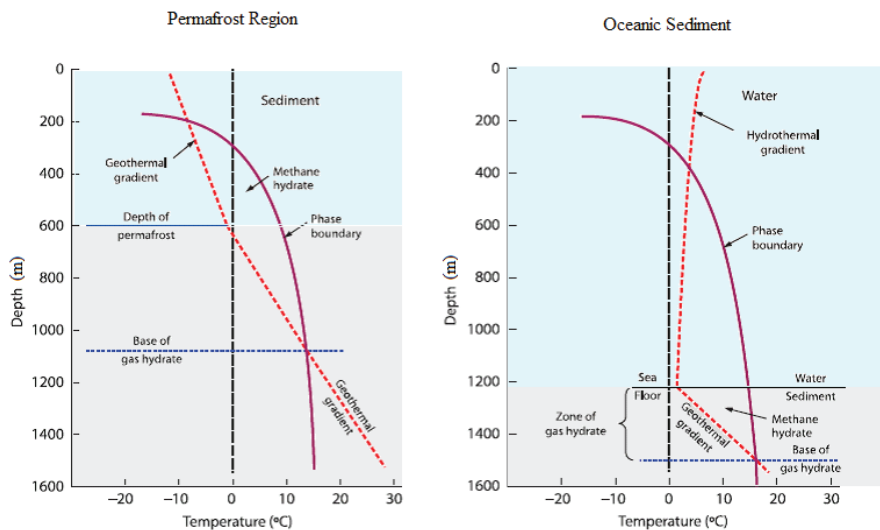
Figure 3 Examples of hydrate stability region (Adapted from Johnson, 2011).

A third parameter, which is less discussed in the literature, is concentration of hydrate formers in the media. Beside suitable temperature and pressure conditions, concentration of hydrate formers should also be sufficient to allow hydrate formation. In analysis of hydrate systems it is usually assumed that hydrate formers are available in abundance and concentration requirement is assumed to be satisfied.

However, in reality many hydrate regions such as those in Gulf of Mexico have sections in between that do not contain hydrate although pressure and temperature conditions are feasible for hydrate (Espen Sletten Andersen, STATOIL, during GANS project meeting in Bergen, Norway, October 1, 2010). One reason might be that these regions are subject to fluxes of under-saturated water, which passes through no hydrate sections, because of for instance fractures. Figure 4 illustrates an isobaric phase diagram of CO_2 and water at 6.2 Mpa and reflects the role of concentration in hydrate systems.
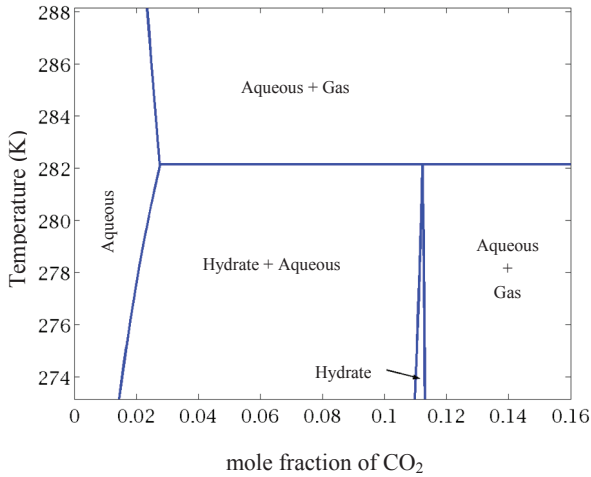
Figure 4 CO₂-water isobaric phase diagram at 6.2 Mpa. (Adapted from Svandal et al., 2006a)

Each cubic meter of gas hydrate releases between 150 to 180 m^3 of natural gas at earth surface conditions (1 atm, 20 ºC). The estimates of the amount of gas stored in the hydrate reservoirs in the world ranges from 2.8×10^5 to 8×10^8 m^3 at standard conditions which is a considerably high value even in its minimum edge (Collett et al., 2009). Of course these studies do not provide estimates of the producible amount of gas from these reserves. Figure 5 presents a comparison between the estimated amount of gas from gas hydrate reservoirs and some other fuel resources.

There have been more than forty locations in the world where gas hydrates have been recovered but only a few of them are studied in detail through deep drilling operations (ibid). Some examples of such studies, which have contributed considerably in development of gas hydrate production field, are the Mallik 2002, the Mallik 2006–2008, and the Mount Elbert projects in northern Canada and Alaska.
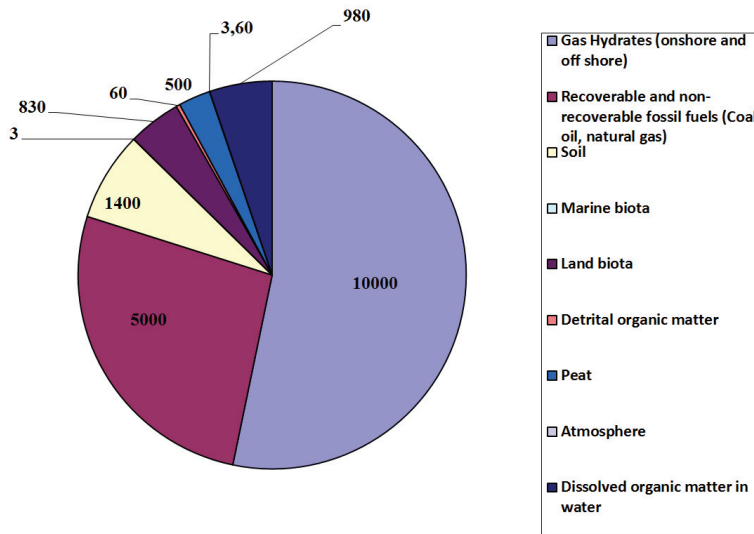
Figure 5 Comparison between different organic carbon sources. Numbers are in units of 10^{15} g of carbon. (Collett et al., 2009)

The Mallik 2002 production studies were conducted to investigate the possibility of gas production from gas hydrate reservoirs using depressurization and thermal stimulation techniques. These are two important techniques in gas production from hydrate reservoirs, which will be explained in the coming sections in more details. According to Collett et al. (2009) its purpose was not to evaluate the commercial recovery as a conventional industry-style production. There were two major expectations from this project:

a) To study the effect of pressure and temperature changes on the gas hydrate in reservoir.

b) To provide data for calibrating reservoir hydrate simulators to give the possibility of long-term simulations.

The results of this project showed the technical possibility of gas production from gas hydrates for the first time. It was concluded that depressurization technique might be more effective than previously expected. Although depressurization produces more

gas than just heating the formation however, using both heating and depressurization would produce the greatest amount of gas (Collett et al., 2009).

Data from the Mallik 2002 operation were used according to the primary plan to calibrate several reservoir simulators in modelling depressurization and thermal stimulation processes. However it did not succeed to generate all the necessary data for this purpose. Therefore, the 2006-2008 Mallik Gas Hydrate Production Research Program was conducted to generate the data lacking from Mallik 2002 as well as responding the need of a longer term production test for evaluating the technical feasibility of long term production of gas from gas hydrates. This project was conducted first in 2006-2007 based on the results of the Mallik 2002 project, with the mentioned goals but was a very short test production operation, which generated only 12.5 hours of successful test data. In this test at least 830 m^3 of gas was produced. However it verified that the depressurization method was effective even for such a short duration. The second attempt was made in the period of 2007-2008 field operations, which lasted for six days. During this test a continuous gas flow of 2000 to 4000 m^3/day was produced summing to a total production of approximately 13,000 m^3 gas and less than 100 m^3 water. The main conclusion from the 2006-2008 Mallik production tests was the possibility of sustained production from hydrates by depressurization alone (ibid).

The Alaska Mount Elbert project is another important scientific effort for improving the knowledge about gas hydrate reservoirs. United States Department of Energy (DOE) has conducted some field studies on exploration and production technology in Alaska North Slope since 2001 with the goal of finding potentials for gas hydrate resources as well as standard gas and large unconventional oil resources (Kvenvolden, 1993). These efforts continued in 2002 in a combined project between DOE and British Petroleum to define fourteen drilling prospects in the Milne Point area. The Mount Elbert well was drilled, cored and tested in early 2007 (DOE, 2012). This project included two types of tests. First type was arranged to study the petro-physical properties of the reservoir. The second type was arranged with the goal of providing further understanding of gas-hydrate response to small-scale pressure

transits (DOE, 2012). It was concluded that it is necessary to have a mobile water phase for starting depressurization process in case the gas hydrate reservoir does not have connection with underlying free gas or water reservoirs (ibid).

3.4 Hydrate environmental risks and importance

As discussed earlier, gas hydrates in reservoir are stable under a certain temperature and pressure conditions. If these conditions are disturbed, hydrates can dissociate towards water and gas resulting in serious consequences. Two of the important effects of uncontrolled hydrate dissociation are geological hazards such as submarine slumps and slides and the probable contribution of methane hydrates on climate change (Kvenvolden, 1999).

3.4.1 Geologic hazards:

Many landslides have been caused by changes in temperature over geological time-scales. However, combinations with changes in underground flow of fluid due to new fractures and/or changes in fracture systems connected to hydrate regions may have caused hydrate dissociations, which are significant enough to cause geomechanical collapse and corresponding geological structure changes.

Gas hydrates in porous media act as a meta-stable cementation agent in the sediment resulting in reduced permeability towards gas and liquid flow (Kvenvolden, 1994). While gas hydrates extend within hydrate stability zone and towards the base line, the lower area below the base of gas hydrate becomes under-consolidated and possibly over-pressured due to gas release from upper zone (ibid). It is important to remember that methane can be up to six times more compact in its hydrate form than its gaseous phase depending on the depth (hydrostatic pressure) and temperature. Figure 6 shows the expansion factor for methane and water due to hydrate dissociation in different pressure and temperature conditions (IEA Greenhouse Gas R&D Programme (IEA GHG), 2008). This results in a zone with low shear strength susceptible to structural failures in the form of landslides.
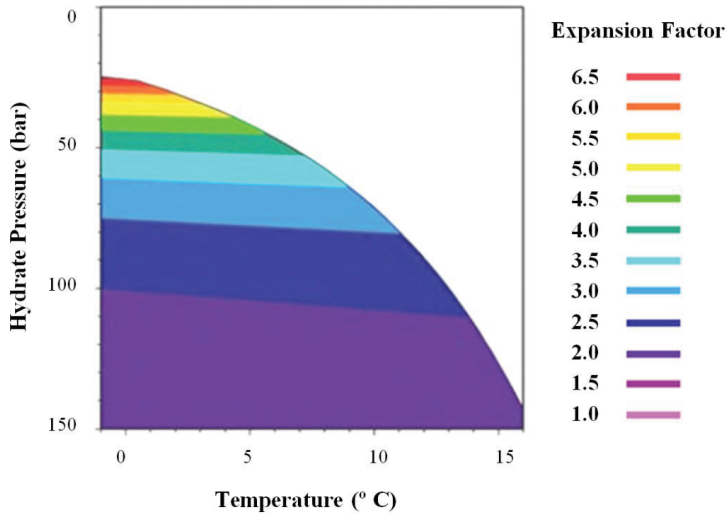
Figure 6 Expansion factor due to hydrate dissociation at different temperature and pressure conditions. The calculation considers the total volume of dissociated water and methane at T, P per unit volume of initial hydrate (Adapted from IEA Greenhouse Gas R&D Programme (IEA GHG), 2008).

On the other hand, hydrate formation in unconsolidated sediments prevents normal compaction process. Uncontrolled disturbances to the hydrate stability conditions in the form of pressure reduction or temperature increase can result in similar geological failures due to hydrate dissociation. In this case, in addition to the previous mechanism, the role of hydrate as a cementing agent will disappear and methane gas will be released to the water column. Several examples of such phenomenon have been identified in different reservoirs across the world such as South West Africa, United States, Norwegian continental shelf, British Columbia, continental margin of Alaskan Beaufort Sea and Caspian Sea (Kvenvolden, 1994). Such disturbances in hydrate stability conditions can be caused by local manipulations such as drilling activities or widespread phenomena such as global warming. Figure 7 illustrates failure in the sediment due to the hydrate dissociation as a result of sea level changes. Methane escapes to the water column in the form of gas plume. If the size and volume of the sliding sediment is very large, it has the potential to generate tsunamis

as it will cause immense perturbation in the seabed and the water column above it (IEA Greenhouse Gas R&D Programme (IEA GHG), 2008).
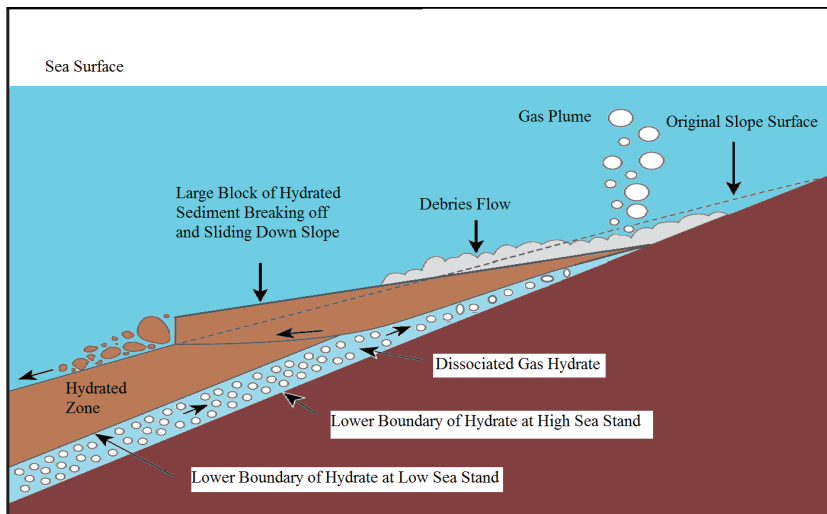
Figure 7 Hydrate dissociation due to sea level changes results in sediment failure and methane release in the form of gas plume (Adapted from Kvenvolden, 1999).

Submarine geo-hazard has been considered as the most important aspect of hydrate with immediate possible effect on human welfare (Kvenvolden, 1999). Although, recent developments and plans towards commercial exploitation of methane hydrates by countries like Japan - for example refer to Kyodo (2013) and Demetriou (2014) - may influence this image.

3.4.2 Climate Change:

It is believed that methane hydrates play an important role in climate change in the past and future according to different researchers and scientists (Sloan, 1998, Henriet & Mienert, 1998, Kennett *et al.*, 2003, Maslin *et al.*, 2004, as cited by IEA Greenhouse Gas R&D Programme (IEA GHG), 2008). During interglacial and glacial climate, which is characterized by global warming and cooling, hydrate sediments have been affected by surface temperature and pressure changes (Kvenvolden, 1993).

One of the scenarios is that during the global warming, ocean level increased as a result of melting glaciers and ice caps. This resulted in further stabilization of marine gas hydrate deposits. However, onshore gas hydrates and polar deposits were destabilized due to increased atmospheric and submarine bottom surface temperatures resulting in methane release, which might have reached the atmosphere (ibid). On the other hand, during a cooling cycle, due to lower sea levels, the pressure on the deep sea water sediments was reduced resulting in destabilization of hydrates and release of methane. These theories and their consequences on the past climate change are speculative and concrete evidence of such processes is needed to support them (Bollmann et al., 2010, Kvenvolden, 1999). "The Clathrate Gun Hypothesis" by Kennett et al. (2003) proposes that stability of methane hydrate reserves during human cultural evolution and its 7000 year recorded history, has resulted in neglecting or under-estimating the role of methane hydrates in climate change over longer periods of geological developments. Modern human has experienced the stable atmospheric conditions with high sea level characteristics, which are ideal for stabilization of hydrate reservoirs. They suggest that it is possible that older generations had experienced dramatic climate changes due to massive methane release to ocean and atmosphere (Kennett et al., 2003). However, the role of methane hydrates in climate change and its extension is still a matter of debate. Some studies have challenged the Clathrate Gun Hypothesis (Maslin et al., 2004, Bock *et al.*, 2010, Ruppel, 2011) and correlate the fluctuations in the atmospheric methane concentrations in different periods to other methane sources such as wetlands (Bock et al., 2010).

The importance of methane in climate changes is mainly because of its greenhouse effect. Methane is a potent greenhouse gas. Each molecule of methane is around 20 times more aggressive than a CO_2 molecule (Bollmann et al., 2010). Although its lifetime in atmosphere is shorter than CO_2, over a period of 100 years each molecule of methane has 25 times the direct global warming potential of a CO_2 molecule (Solomon, 2007, as cited by EPA, 2010). Considering the huge amount of methane stored in the form of hydrates within oceanic sediments and arctic regions and their

sensitivity towards temperature and pressure conditions, it is clear that better understanding of this phenomenon is of great importance. Figure 8 illustrates changes in greenhouse gas concentration for last 2000 years where human's contribution in its recent increase can be deduced. A big part of today's methane emission into atmosphere comes from wetlands, ruminants, fossil fuel production, and rice cultivation (IPCC, 2001 as cited by Ruppel, 2011).
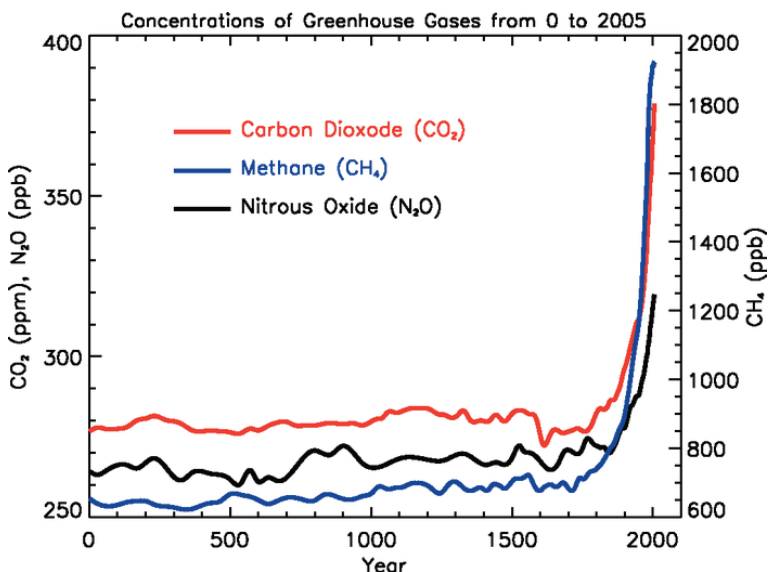
Figure 8 Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years (Forster et al., 2007).

Methane hydrate reservoirs on earth are so vast that even if a small fraction of it dissociates and reaches the atmosphere, has the potential for causing a catastrophic climate change within a few years (Archer, 2007). However, most of the hydrates are located in a depth which is quite safe from surface climate changes at least for a time period of the order of millennia or even longer (ibid). Furthermore, there are several factors which influence the migration of dissociated methane hydrates to atmosphere especially in deeper marine sediments. In these regions, the released methane should travel a long way to reach the sea floor. More than 90% of it can be consumed by anaerobic methane oxidation and then by aerobic microbes within the water column

Table 2 Summary of the mechanisms that result in methane release to atmosphere (Archer, 2007, Ruppel, 2011)

Releases	Estimated % of total hydrate deposits	Potential Release	Impacts	Examples
Deep water hydrate deposits in the ocean	95.5	Any release would take millennia	Effects would be most pronounced on geological timescales	
Deep water marine hydrates at the feather edge of Gas Hydrate Stability Zone (GHSZ)	3.5	On-going today, but time scale for acceleration is probably decades	Released to water column, could reach atmosphere as CH_4	West Spitsbergen continental margin, Canadian Beaufort Sea slope
Subsea permafrost on the circum-arctic shelves	<0.25	On-going today, but time scale for acceleration is probably decades	Released to water column, could reach atmosphere as CH_4	East Siberian Arctic shelf
Thick (> 300 m) continuous permafrost onshore	<1	Any release would take millennia		Mackenzie Delta
Seafloor gas hydrate mounds	Trace	Any release would take centuries	Released to water column, small potential impact on atmospheric CH_4	Gulf of Mexico
Landslides		5 Gton from Storegga	Some release as hydrate which can reach the atmosphere, but also bubbles which dissolve in the water column	Storrega slide

(Ruppel, 2011). Of course this may result in increased acidity of the water column and release of CO_2 into atmosphere after a residence time ranging from less than fifty years to several hundred years (ibid).

Even though global warming may not destabilize deep oceanic hydrates in short term, there are hydrate deposits in shallow sediments, which are currently releasing methane to atmosphere. Some examples are Arctic coastline of Siberia and the hydrate-controlled methane seepage off Svalbard (Shakhova *et al.*, 2010, Berndt *et al.*, 2014, Archer, 2007). A summary of the mechanisms resulting in methane release from hydrates to atmosphere and their impacts is presented in Table 2.

3.5 Potentials of hydrate for CO_2 storage

One of the important aspects of hydrates again from environmental point of view is the possibility of CO_2 storage. Geological storage of CO_2 is known as one of the most feasible solutions to the continuously increasing danger of greenhouse gas effects and global warming. While producing less CO_2 seems very difficult in short term due to world's increasing demand for energy including fossil energies, CO_2 storage has been found to be a short to medium term solution for reducing the CO_2 emissions to atmosphere to an acceptable level (Zatsepina & Pooladi-Darvish, 2012).

One of the important parameters in geological CO_2 storage is to ensure that there is a low probability for leakage for long-term periods. While geochemical reactions resulting in formation of solid minerals can ensure long term storage of carbon dioxide, the time scale for such reactions is of the order of centuries to millennia which makes them impractical (ibid).

Different methods are developed or proposed for geological storage of CO_2 with specific advantages and disadvantages. One of these methods is storage of CO_2 at permafrost regions or sediments where high pressure and low-enough temperature conditions results in stability of CO_2 hydrate and trapping CO_2 for geologically long periods (Rochelle *et al.*, 2009). The process of hydrate formation is quite fast

compared to geochemical reactions and makes it a very attractive solution for sequestering CO_2.

Hydrates characteristics can also be advantageous during storage of CO_2 in deep (>800 m) formations where temperature might be too high for hydrate formation. If such storage sites lay below a cold-water column or permafrost, then in case of CO_2 seepage from faults or fractures, the hydrate suitable region above the storage zone will act as a backup trapping mechanism (Rochelle et al., 2009). Figure 9 is an illustration of geological storage of CO_2 in its hydrate form.
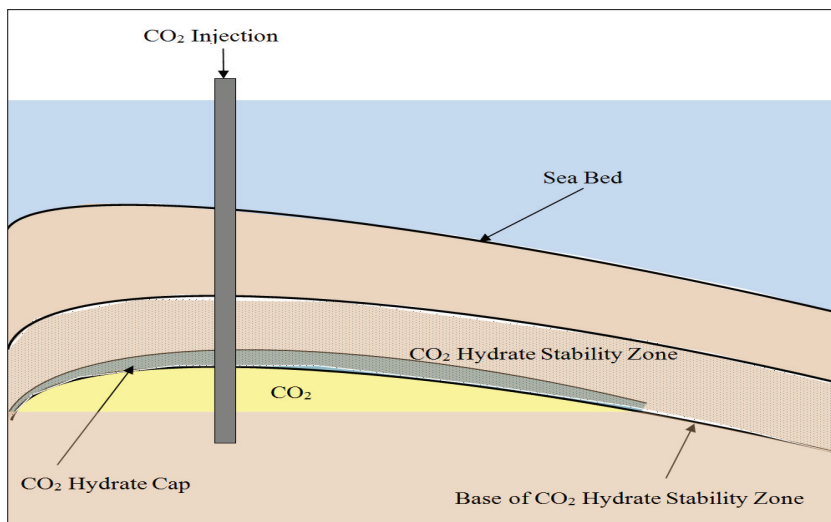
Figure 9 Geological storage of CO_2 as CO_2 hydrate (adapted from Rochelle et al., 2009).

 One step forward would be storage of CO_2 in methane hydrate reservoirs resulting in exchange between methane and CO_2 (Kvamme *et al.*, 2007, Ersland *et al.*, 2009). CO_2 hydrate is more stable than methane hydrate. Therefore, injection of carbon dioxide into hydrate reservoirs will result in natural in situ conversion of methane hydrate to CO_2 hydrate which is both beneficial in preserving geomechanical stability of the structure and producing methane gas as an energy resource (Kvamme et al., 2007).

3.6 Classification of hydrate reservoirs

Hydrate deposits are classified into four classes out of which three are mainly of interest for production studies. This classification considers initial conditions of the reservoir and simple geological features (Moridis & Collett, 2003, Moridis et al., 2013).

- Class 1 hydrate deposits consist of a hydrate bearing layer at the top and a two-phase fluid layer of liquid water and mobile gas at the bottom. In this category, bottom of hydrate bearing layer is usually extended to the bottom of hydrate stability zone. It makes this group a favourable choice for production purpose. Since the hydrate layer is very close to the equilibrium conditions, a slight change can result in its destabilization.

- Class 2 hydrate deposits also consist of two layers. Hydrate bearing layer is located at the top and a mobile water zone at the bottom.

- Class 3 hydrate deposits consist of only one hydrate-bearing layer without any mobile fluid at the bottom. Deposits of class 2 and 3 can be well within hydrate stability zone.

- Class 4 hydrate deposits are characterized as disperse, oceanic accumulations with a low hydrate saturation of less than ten per cent (Moridis et al., 2013).

3.7 Methods for production of natural gas from hydrates

There are essentially four methods for hydrate production, which have been extensively studied by experiments, and some also through pilot plant studies. Three methods have been discussed more in open literature (Moridis et al., 2013, Vafaei *et al.*, 2012 and references in these papers). These are mainly based on hydrate dissociation by disturbing thermodynamic stability conditions of hydrates and producing methane and water. The first method is depressurization of hydrate to a level below hydrate equilibrium pressure. Second method is thermal stimulation. In

this method hydrate is heated to a temperature above the equilibrium condition, resulting in dissociation and release of methane. The third method for gas production from hydrate deposits is use of chemicals, which will change the chemical potential of liquid water. In this technique, inhibitors such as salts or alcohols are used to move the hydrate deposit outside its stable conditions by shifting hydrate equilibrium curve. Figure 10 shows the three method of production from hydrate reservoirs schematically.
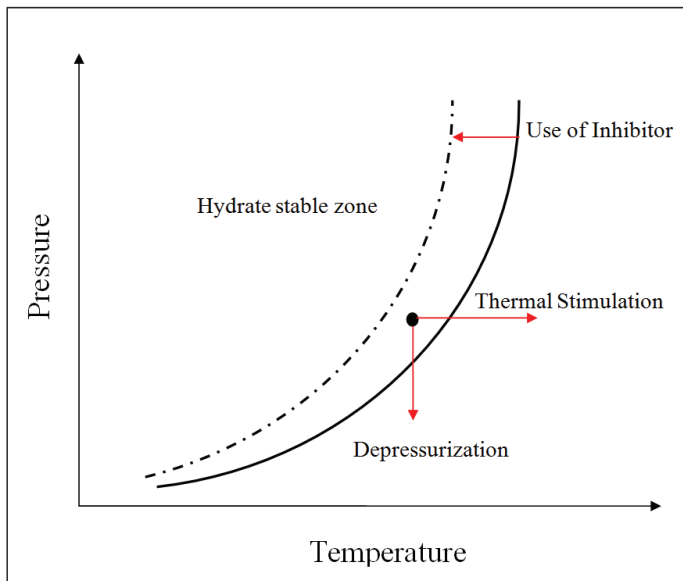
Figure 10 Methods of gas production from hydrate deposits. Solid line indicates original hydrate equilibrium curve while dashed line represents hydrate equilibrium curve after use of inhibitors. Solid circle represents thermodynamic conditions of the hydrate sediment.

Depressurization is considered as the most suitable method of production from different classes of hydrate deposits as it is a simple and effective method from technical and economic perspective (Moridis et al., 2013).

The fourth method, which is less discussed in the literature, is exchanging methane with another hydrate former such as CO_2 through a thermodynamically favourable reaction (Graue *et al.*, 2008, Moridis et al., 2013, White & McGrail, 2008, Collett *et al.*, 2014). In case of CO_2 as the hydrate former the process has the advantage of CO_2

storage in addition to methane production. Also, there would be less concern regarding geological hazards due to hydrate dissociation as explained earlier because a new hydrate phase would replace the older one.

CO_2-hydrate is more stable than CH_4-hydrate over a wide range of pressure and temperature conditions. CO_2 and CH_4 will both form hydrate structure I where, there are 3 large cavities for each small one. In large cavities 24 water molecules surround the guest molecule while in small cavities there are 20 water molecules for this purpose. The method of methane production through injection of CO_2 consists of two main mechanisms:

a) Solid state conversion

b) CO_2 hydrate formation from free liquid water available in the pores

However, the first mechanism is quite slow compared to the second mechanism (Kvamme *et al.*, 2006a, Kvamme et al., 2007, Kvamme *et al.*, 2009a, Kvamme *et al.*, 2006b, Buanes *et al.*, 2006, Buanes *et al.*, 2009). Formation of CO_2 hydrate provides necessary heat for dissociation of methane hydrate and release of methane.

Hydrate does not attach directly to mineral surfaces because of incompatibility with hydrogen bonding and partial charges of atoms in the mineral surfaces. Any hydrates in porous media will therefore be surrounded by fluids that separate them from the mineral surfaces. These spaces makes it possible for released methane to find its way through the porous media to the production well and similarly for the injected CO_2 to propagate through the hydrate sediment (Kvamme et al., 2007).

Within these four categories there are several different methods to achieve the desired effect. Heat can, for instance, be supplied by injecting steam or hot water but can also be supplied by microwaves, heating cables along production pipelines and even by partially burning the released gas. However it is beyond the scope of this project to discuss all proposed methods in the different categories.

4. State of the art

Hydrates in nature usually exist in extreme conditions, which makes it difficult and expensive to perform direct experiments and observations. Moreover, some of the important aspects of clathrate hydrates such as environmental risks are long-term geological phenomena, which make their understanding and predictions even more challenging. Therefore, simulation tools have been used extensively in different stages of hydrate exploration and exploitation processes ranging from design and operation to control and optimization studies (Sun *et al.*, 2014). These studies have contributed significantly in important technological developments in hydrate research (ibid).

Hydrate production studies are highly dependent on numerical simulators for accurate prediction of complex behaviour of hydrates in reservoir (Moridis et al., 2013). These complexities make it impossible to use analytical approaches directly in these studies with a reasonable cost while numerical approaches can provide valuable information about technical feasibility, sensitivity with respect to different parameters and other aspects of the production process even with lack of extensive laboratory or field data (Moridis et al., 2013). However, the accuracy of the numerical model and its applicability to field is highly dependent on the correct description of the physical processes and the knowledge of the governing parameters and relationships as well as thermo-physical properties of the system (ibid).

A lot of efforts have been put into development of simulation models and simulators and the results of these studies are widely published. Vafaei et al. (2012) presented a literature review on the available simulation studies and specifically those that resulted in development of a comprehensive reservoir hydrate simulator. This review mainly concentrates on the thermodynamic approaches used in these models for treating hydrate reactions in reservoir. In another effort, Sun et al. (2014) presented an extensive literature review covering the important and noticeable studies on simulation of hydrates with the goal of exploration and exploitation. In this review, the background and the assumptions of these models are mentioned and the strengths

and limitations are discussed. According to their categorization, simulation models are divided into two groups: physical and empirical. Physical models including numerical and analytical simulations are based on the physical description of the problem and the governing relations as mentioned earlier. On the other hand, the empirical methods rely on the experimental results and statistical analysis (Sun et al., 2014). They usually require empirical correlations or adequate experimental data to be used in different statistical analysis approaches such as artificial intelligence methods.

The focus in the current study has been on the former group and mainly on the efforts made on developing numerical tools. Numerical simulators are mostly based on description of the physics behind multiphase flow in porous media and require suitable assumptions and simplifications. These models are usually based on the derivation of the conservation equations for mass, energy and momentum in porous media. Different assumptions may be used in the number of considered phases and components. The choice of thermodynamic approach for describing the distribution of components in different phases is also diverse. Two main approaches in describing hydrate interactions with other phases are equilibrium and kinetics. In equilibrium approach, the equilibrium relation between phases governs the distribution of components (water, CH_4 and/or CO_2) between all considered phases (Kowalsky & Moridis, 2007). There are a number of publications with equilibrium assumption as the basis for hydrate dissociation mechanism (see for example: Burshears *et al.*, 1986, Xu & Ruppel, 1999, Xu, 2004, Ahmadi *et al.*, 2004).

Unlike equilibrium assumptions, in kinetic approach rates of hydrate dissociation or formation depend on the kinetics of the corresponding reactions between hydrate formers and hydrate. In this case, hydrate is usually considered both a component and a phase. Details of simulation models with kinetic approach can also be found in literature (see for example: Yousif *et al.*, 1991, Goel *et al.*, 2001, Sun & Mohanty, 2006, Uddin *et al.*, 2008, Nazridoust & Ahmadi, 2007).

Some studies such as Moridis (2003), Hong and Pooladi-Darvish (2005) and Gamwo and Liu (2010) used both approaches as alternatives in their simulators.

The kinetic approach used in many of these numerical simulators is based on the proposed model of Kim and Bishnoi (Kim *et al.*, 1987), which correlates the molar kinetic rate of hydrate phase transition to the surface area and the fugacity difference of hydrate guest molecule at actual and equilibrium conditions of the system. The model has been parameterized based on fitting experimental data obtained from kinetic tests performed by a laboratory scale PVT cell.

Due to the importance of heat transport limitations in the reservoir and its effect on hydrate dissociation, kinetics of heat transport has been used in some studies to describe the rate of hydrate dissociation during production studies (Holder & Angert, 1982).

Further details of different simulation studies can be found in Sun et al. (2014) and Vafaei et al. (2012).

To evaluate the importance of kinetic behaviour of hydrates on simulation results, some studies made a comparison between the results from kinetic approach and equilibrium approach (Kowalsky & Moridis, 2007, Hong & Pooladi-Darvish, 2005). These studies concluded that taking into account the kinetics of hydrate in the reservoir is important only at early production stages or in core scale laboratory experiments. The equilibrium model according to these studies can be used in a wide range of large-scale production simulations. However, it is important to mention that these studies also used the kinetic principles of Kim and Bishnoi model to express hydrate reactions in reservoir.

5. Choice of scientific method

Studies of hydrate phase transitions in the reservoir require implicit couplings on several levels ranging from nano-scale to macro scale. The kinetics of hydrate phase transitions and reactions need to be determined through nano-scale studies such as Molecular Dynamic (MD) simulations (eg. Tse *et al.*, 1983, Forrisdahl, 1996, Moon *et al.*, 2003, Kvamme *et al.*, 2005) or Phase Field Theory (PFT) studies (eg. Kvamme *et al.*, 2004, Svandal *et al.*, 2006b, Tegze *et al.*, 2006). On the next level, the impact of solid surfaces in the porous media on phase transitions and reactions is a pore-scale phenomenon and along with the non-equilibrium effects are in the range of nano to micro scale. Mineral and hydrate surfaces have structural impact on the surrounding phases and affect hydrate formation and dissociation. Incompatibility between partial charges on the mineral surfaces with partial charges on hydrate surface is an example of these impacts (Kvamme *et al.*, 2009b, Kvamme & Kuznetsova, 2010, Kvamme *et al.*, 2012, Van Cuong *et al.*, 2012a, Van Cuong *et al.*, 2012b).

These levels of study need to be coupled in a reservoir simulator with effects of reservoir inhomogeneous flow from diffusion to Darcy flow, which is of a macro scale order. Therefore, development of a reservoir hydrate simulator, which is capable of considering all these effects in its calculations, is of significant importance.

Studying reservoir hydrates through such comprehensive simulation software provides the capability of predicting different time scale behaviour of the dynamics of flow and geomechanical impacts on the reservoir caused by human activities (such as hydrate production) or natural developments (such as changes in temperature or creation of new fracture systems). Hydrates in a reservoir are not capable of reaching equilibrium and natural hydrate deposits are in a modus of stationary flow as controlled by boundary conditions with groundwater and possible up-flow of new hydrocarbons. The sum of all processes that were involved in the changes that led to this locally stationary situation has normally been going on for geological time scales. These are not possible to investigate through laboratory or field tests because of the

long time needed for these studies or their expenses. Using Simulators also gives the possibility for monitoring the performance and making decisions among different available alternatives. Studies of hydrate in reservoir have benefitted a lot from simulations. However, the complexity of hydrate dynamics in the reservoir has pushed many research groups and scientists towards simplifications in studying this phenomenon. An overview of the efforts toward reservoir hydrate simulation as presented earlier reveals the need for two major enhancements in this field as will be described as the motivation and the philosophy behind the choice of the method in this research project.

5.1 Non equilibrium nature of hydrate in the reservoir

To study the thermodynamics of hydrate in the reservoir the following example case will be used. A system consisting of two components in the reservoir is assumed; a gas component (for example CH_4) and water as the aqueous phase. Considering only two available phases of gas and liquid, the degree of freedom for this system based on Gibbs Phase Rule will be 'two' according to equation (1).

$$F = N - P + 2 \qquad (1)$$

In this equation 'F' is the degree of freedom, 'N' is number of components and 'P' is the number of available phases. The two properties that should be determined to identify the system are temperature and pressure, which in case of a reservoir are assigned by nature. If a third phase such as hydrate is added to this system, the degree of freedom would reduce to 'one' meaning that such equilibrium system can only exist on the three-phase equilibrium line. Considering the fact that occurrence of such three phase systems are observed within the hydrate stability region (Xu & Ruppel, 1999, Milkov *et al.*, 2004, Paull & Matsumoto, 2000, Henry *et al.*, 1999) where temperature and pressure are both determined by nature and are not necessarily on the three phase equilibrium line, makes the system over-determined. There are still possibilities for additional phases such as ice and hydrates formed from dissolved phase and/or adsorbed phase. All these hydrate phases have different densities and concentrations

and are therefore considered as new phases. This results in further reduction of degree of freedom. According to these facts such a system tends towards minimization of Gibbs free energy under the constraints of heat and mass transfer. It means that formation, dissociation and reformation of different hydrate phases would be the important characteristic of such systems. The literature review presented earlier shows that many researchers have chosen to avoid these complexities in development of their simulators by assuming equilibrium between different phases of a reservoir hydrate system. There have been also several attempts to employ kinetic data from laboratory scale experiments to take into account the kinetics of hydrate in the reservoir. However these experimental data do not have the theoretical basis to make them qualified for implementation into real reservoir conditions. Apart from that, in its most advanced form, these models would be able to describe a single hydrate formation/dissociation mechanism without taking into account the effect of competing phase transition scenarios such as reformation of hydrate from aqueous or adsorbed phase or its dissociation towards under-saturated aqueous phase.

The purpose of this study has been to develop a new reservoir simulator, which is capable of considering mentioned hydrate phase transition scenarios according to the non-equilibrium characteristics of hydrate in the reservoir. For this purpose, a platform is chosen among the available academic and commercial simulators, which considers mineral reactions through a reactive transport module. The module allows calculation of different type of reactions within and between liquid, gas and solid (mineral) phases as described in more details in the coming sections. This is a step forward in improving the numerical simulation approach by expressing the physics and dynamics of reservoir hydrate systems in a more accurate fashion. It will also help to enhance our judgments regarding the consequences of equilibrium assumption on the quality of the simulation results.

5.2 Implicit geomechanical package

Another important aspect of reservoir studies is geomechanical considerations. A sustainable production or storage process depends on our understanding from the

reservoir's geomechanical responses to pressure, temperature and saturation variations. These variations result in stress changes in the reservoir. In specific cases such as fractured and faulted reservoirs or poorly compacted formations it can be the source of considerable effects (Collett et al., 2009).

There are different methods and coupling levels for solving thermo-hydro-mechanical problems including fully coupled methods and partially coupled methods (ibid). Fully coupled method is based on solving the complete set of equations simultaneously while partially coupled methods are based on coupling between reservoir and geomechanical simulators. The majority of simulators considering hydrate in the reservoir either does not consider geomechanical calculations or use an explicit coupling between their reservoir calculations and an external geomechanical simulator. This results in a delay between the reservoir calculations and the geomechanical consequences, which in case of a hydrate system with fast kinetic reactions can be a matter of concern. In this study the selected platform uses an implicit coupling between the flow calculations and geomechanics, which reduces this lag and provides more realistic results. There is also possibility for further improvements of the geomechanical calculations in the simulator according to the characteristics of hydrate formation and dissociation reactions.

5.3 User friendly interfaces and fast set up capability

This is the third important feature of the selected simulator in this project. One of the demanding tasks in setting up a simulation model is preparing the input files. Due to the complexity of the reservoir system, there is a need for a huge number of input data, which usually should be provided, in a predetermined pattern and through different ASCII files based on the characteristics of the simulator. Completing this stage can take very long time depending on the complexities of the model and the simulator itself. The platform used in this project benefits from a graphical interface for preparing those input files, which gives the possibility of setting up very complex models within a few hours. This is again a big advantage compared to some other comparable simulators. The same feature applies to the output files where the results

are produced. This simulator is compatible with some commercial post processor software for illustrating the results in one, two or three-dimensional axis.

6. Simulation Platform

This section gives a brief description of the code, starting with an overview and main flow sheet in section 6.1. This is followed by a description of the governing equations in section 6.2.

6.1 Overview of the code Retraso CodeBright (RCB)

The code RetrasoCodeBright (RCB) is used in this study as the basis for further modifications. It is designed by coupling two codes: CodeBright and Retraso.

CodeBright stands for "COupled DEformormation of BRIne Gas and Heat Transport". It has been developed for the thermo-hydraulic-mechanical analysis of three-dimensional multiphase saline media (Longuemare *et al.*, 2002) and improved repeatedly since the beginning (Olivella *et al.*, 1994, Olivella *et al.*, 1996). The code has been used in different studies of geotechnical engineering problems ranging from environmental impacts of radioactive waste storage in unsaturated rock to modelling deformations during construction of a rock-fill dam (Olivella *et al.*, 2008).

Retraso stands for "REactive TRAnsport of SOlutes" and is a code for solving two-dimensional reactive transport problems (Liu, 2011). It addresses the relevant process for soil and groundwater contamination problems such as ground water quality and water rock interaction (Saaltink *et al.*, 2004).

The coupled code RCB is capable of modelling complex problems consisting of coupled thermal, hydraulic, mechanical and geochemical processes. The following list shows several features of RCB (Liu, 2011):

- Multiphase multidimensional (1D, 2D, 3D) simulation of liquid and gas flow.
- Simulation of heat transport.
- Mass transport Simulation including advection, dispersion and diffusion for chemical species in the liquid and gas phases.
- Simulation of the chemical reactions including:

- ➢ Aqueous complexation (redox and acid-base reactions)
- ➢ Sorption (including cation exchange) by means of electrostatic or non-electrostatic models
- ➢ Precipitation and dissolution of minerals (both equilibrium and kinetic approach)
- ➢ Gas liquid interaction.

- Considering porosity and permeability changes due to mineral precipitation and dissolution.
- Considering the effects of aqueous solutes on certain flow properties.
- Finite element spatial discretization and Finite difference temporal discretization.
- A user-friendly interface for pre and post processing purposes.

In RCB, flow properties such as Darcy flux, temperature, density, saturation and etc. as well as geomechanics are calculated by CodeBright module and transferred to Retraso module for reactive transport calculations. Flow properties will be updated by reactive transport effects. Both calculations are done in independent Newton-Raphson iteration loops as shown in Figure 11.

RCB originally considers three phases of solid (mineral), liquid (water and dissolved air/gas) and gas (dry air/gas and water vapour) as well as three components of water, dry air/gas and heat based on CodeBright module. However, thanks to Retraso module, it is possible to select from an unlimited list of components within all three phases giving the opportunity to define different hydrate phases and hydrate formers. This will happen in the Retraso internal loop performing a compositional mass balance to account for the effect of reactions on the balance. The outcome will be translated into the three mentioned components for overall calculations. RCB runs a set of compositional mass balances over water, gas and heat and assigns a state variable to each mass balance. State variables include liquid pressure, gas pressure and temperature, which are used in constitutive and equilibrium laws to describe the dependant variables of the mass balance. The summary of these equations and laws are presented in the coming sections while further details can be found elsewhere (Saaltink *et al.*, 2005).
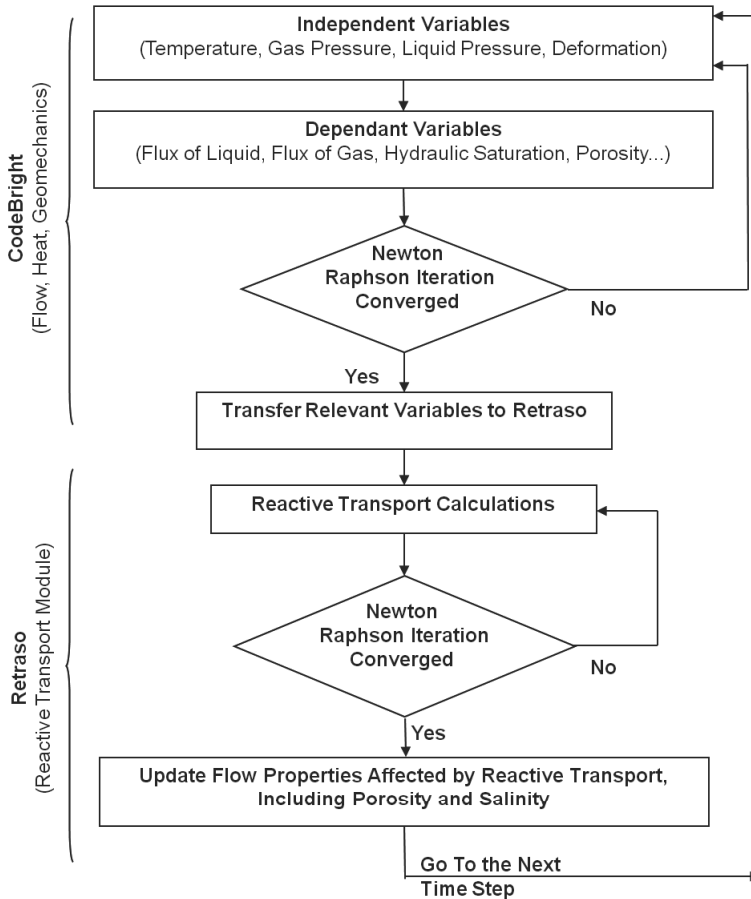
Figure 11 Schematic of coupling between Retraso and CodeBright modules

6.2 Governing equations

The governing equations can be categorized into four main groups of balance equations (section 6.2.1), constitutive equations (section 6.2.2), equilibrium relations (section 6.2.2) and chemical reactions (section 6.2.3).

6.2.1 Balance equations

Mass balances for water and air/gas in RCB are implemented according to the equations (2) and (3).

$$\frac{\partial}{\partial t}\left(x_l^w \rho_l S_l \phi + x_g^w \rho_g S_g \phi\right) + \nabla \cdot \left(J_l^w + J_g^w\right) = f^w \qquad (2)$$

$$\frac{\partial}{\partial t}\left(x_l^a \rho_l S_l \phi + x_g^a \rho_g S_g \phi\right) + \nabla \cdot \left(J_l^a + J_g^a\right) = f^a \qquad (3)$$

In these equations subscripts l, g, w and a, refer to liquid, gas, water and air respectively. x is the mass fraction of a component in a phase, ρ is the density of the corresponding phase, S is the hydraulic saturation, φ is the porosity, j is the total flux including advective, dispersive and diffusive and f is an external source/sink term.

According to these two equations the first two terms for example in equation (2), represent the change of mass of water in the liquid and gas (vapour) phase respectively while the third and the fourth terms represent water transport in liquid and gas phase.

Similarly the internal energy balance is implemented according to equation (4) considering the internal energy of each phase.

$$\frac{\partial}{\partial t}\left(E_s \rho_s \left(1-\phi\right) + E_l \rho_l S_l \phi + E_g \rho_g S_g \phi\right) + \nabla \cdot \left(i_c + j_{Es} + j_{El} + j_{Eg}\right) = f^Q \qquad (4)$$

In this equation E_s, E_l, E_g are internal energies of each phase, i_c is energy flux because of conduction in the porous medium, j_{Es}, j_{El}, j_{Eg} are advective fluxes of energy caused by mass motions and f^Q is the internal/external energy supply.

6.2.2 Constitutive laws and equilibrium restrictions

To evaluate different parameters of the balance formulation it is necessary to use relevant constitutive laws and equilibrium restrictions as described here.

1. Darcy's law

It is used to calculate liquid and gas advective fluxes according to the equation (5).

$$q_i = -\frac{kk_{ri}}{\mu_i}(\nabla p_i - \rho_i g) \qquad (5)$$

In this equation subscript i can be either g (gas) or l (liquid) phases, q represents the corresponding phase flux, k is intrinsic permeability, k_{ri} is relative permeability of the corresponding phase, μ viscosity, p pressure, ρ density and g gravity acceleration.

Intrinsic permeability in this equation is calculated according to Kozeny's model (Saaltink et al., 2005) as following (Kozeny, 1927):

$$k = k_0 \frac{\phi}{(1-\phi)^2} \frac{(1-\phi_0)^2}{\phi_0^3} \qquad (6)$$

Where, Φ is porosity, Φ_0 is reference porosity and k_0 is intrinsic permeability for the reference porosity.

2. Retention curve

The relation between capillary pressure and the degree of saturation is described by water retention curves through several models as presented by equations (7), (8), (9):

$$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = \left(1 + \left(\frac{P_g - P_l}{P}\right)^{\frac{1}{1-\lambda}}\right)^{-\lambda} \qquad (7)$$

Where:

$$P = P_o \frac{\sigma}{\sigma_o}$$

In this equation which is called Van Genuchten model (Saaltink et al., 2005, Van Genuchten, 1980), S_l, S_{rl} and S_{ls} are liquid saturation, residual saturation and maximum saturation respectively. λ is shape function, P_g and P_l are pressures for gas

and liquid phase respectively and P_o is measured pressure at a certain temperature. σ_o is surface tension measured at the same temperature as P_o.

Equations (8) and (9) are called "linear model" and "square law" respectively. In these equations also S_l, S_{rl} and S_{ls} are liquid saturation, residual saturation and maximum saturation respectively and P_g and P_l are pressures for gas and liquid phase. P_o is measured pressure at a certain temperature.

$$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = 1 - \frac{P_g - P_l}{P_o} \qquad (8)$$

$$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = \frac{1}{\sqrt{1 + \frac{P_g - P_l}{P_o}}} \qquad (9)$$

3. Liquid phase relative permeability

Five options are available for this purpose in the simulator. The first one is the most consistent one with Van Genuchten model as in equation (10) (Van Genuchten, 1980):

$$k_{rl} = \sqrt{S_e}\left(1 - \left(1 - S_e^{\frac{1}{\lambda}}\right)^{\lambda}\right)^2 \qquad (10)$$

Parameters of this equation correspond to the same parameters in Van Genuchten model of retention curve.

Apart from the two extreme cases of $k_{rl} = 1$ for completely mobile liquid and $k_{rl} = 0$ for no liquid flow, the generalized power law with and without initial cut off is also included in the calculation methods. Equations (11) and (12) show these two models respectively.

$$k_{rl} = A\left(\frac{S_e - S_{eo}}{1 - S_{eo}}\right)^{\lambda} \qquad (S_e \geq S_{eo}) \qquad (11)$$

$$k_{rl} = AS_e^{\lambda} \quad (12)$$

In these equations A is a constant S_e is effective saturation defined as before and S_{eo} is effective saturation calculated at S_{lo}.

4. Gas phase relative permeability

Relative permeability of the gas phase is calculated by equation (13) as a default. But generalized power law as well as $K_{rg} = 1$ are also included as alternatives in the code.

$$k_{rg} = 1 - k_{rl} \quad (13)$$

5. Diffusive and dispersive fluxes of mass

Fick's law is used for calculation of diffusive and dispersive mass flux. Different models of molecular diffusion coefficient used in the simulator as well as the description of the mechanical dispersion tensor are described in the manual (Van Genuchten, 1980, Saaltink et al., 2005).

6. Dispersive and conductive fluxes of heat

Fourier's law is used to calculated dispersive and conductive fluxes of heat in the simulator. Mechanical dispersion tensor is defined similar to mass dispersion flux but only the contribution of the liquid phase is considered. The conductive heat flux is calculated using two different approaches: 1) considering the dependence on the porosity and temperature; 2) considering the dependence on water content. Both options are described in the manual in detail.

7. Solid, liquid and gas phase properties

Some default values or empirical relations are used to estimate the physical properties of different phases. However, it is possible to assign most of the properties as input data. Density and specific heat of the solid phase is set to a default value internally. These properties for hydrate have been added separately as a modification to the code. Ideal gas law had been used originally to estimate necessary gas phase

properties. This was later improved by replacing the ideal gas law with Soave-Redlich-Kwong (SRK) (Soave, 1972) equation of state (Kvamme & Liu, 2009).

8. Reactive transport effect on porosity

Due to mineral formation/dissolution porosity may change during the calculations of the reactive transport loop. The effect of these changes on the porosity is implemented by equation (14).

$$\Delta \emptyset = - \sum_i V_{m,i} \Delta C_{m,i} \qquad (14)$$

In this equation $\Delta\varphi$ is change in porosity, V_m is the molar volume of minerals and $\Delta C_{m,i}$ is the change in the concentrations of the minerals.

6.2.3 Chemical reactions

RCB has several alternatives to consider chemical reactions within different phases in reservoir. These include chemical equilibrium approach for aqueous complexation within liquid phase, adsorption reactions between solid and liquid phase and interaction between liquid and gas phase. Both equilibrium and kinetic approaches are used as alternatives to describe mineral precipitation and dissolution in reaction with aqueous phase.

Law of mass action is used according to equation (15) to define chemical equilibrium reactions:

$$K = \frac{\prod_i a_i^{m_i}}{\prod_j a_j^{n_j}} \qquad (15)$$

In this equation K is equilibrium constant for a reaction described by equation (16). a_i and a_j are activities of the products and reactants in equation (16) respectively and m_i and n_j are the stoichiometric coefficients for products and reactants.

$$n_1 A_1 + n_2 A_2 + \cdots \leftrightarrow m_1 B_1 + m_1 B_1 + \cdots \qquad (16)$$
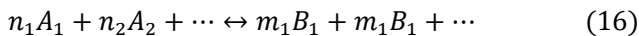
Dependency of equilibrium constant on temperature is implemented by means of equation (17).

$$K = f_1 \times \ln T + f_2 + f_3 T + {f_4}/{T} + {f_5}/{T^2} \qquad (17)$$

In this equation f_1 to f_5 are coefficients obtained by fitting and T is temperature.

Several models are used in the simulator to calculate activity coefficients of water and aqueous components during aqueous complexation reactions (acid-base and redox reactions). These include extended Debye-Hückel formula, Helgeson and Kirkham (1974) and Garrels and Christ (1965).

Electrostatic models and empirical relationships are used in RCB to account for adsorption reactions (see Saaltink et al., 2005).

The equilibrium between gas and aqueous phase is constructed by using Henry's law. Originally ideal gas law was used to calculate gas phase properties such as density. Later, Hellevang and Kvamme (2007) introduced SRK equation of state to improve gas phase calculations as well as dissolved phase fugacity.

The law of mass action is used also to describe mineral dissolution/precipitation reactions with aqueous phase in equilibrium approach.

In kinetic approach, equation (18) is used to consider kinetic rate of mineral reactions.

$$r_m = \sigma_m \zeta_m \exp\left(\frac{E_{a,m}}{RT} \right) \sum_{k=1}^{N_k} k_{mk} \prod_{i=1}^{Ns} acc_i^{P_{mki}} \left(\Omega_m^{\theta_{mk}} - 1 \right)^{\eta_{mk}} \qquad (18)$$

In this equation r_m is the reaction rate (moles of mineral per volume of rock and unit time) and σ_m is reactive surface. ζ_m is a switch, which would be equal to one if Ω_m is larger than one and showing precipitation. If Ω_m is less than one, mineral would dissociate and ζ_m will be equal to minus one. Ω_m is saturation ratio and defined as the ratio between ion activity product and the solubility product. $E_{a,m}$ is the apparent

activation energy of the overall reaction process. R is gas constant and T is temperature. k_{mk} is the experimental rate constant. The term a_{cci}^{Pmki} accounts for the catalytic effect of species such as H+. The parameters θ_{mk} and η_{mk} are determined by fitting to experimental data.

The kinetic approach for hydrate is added as modifications to the code and will be described in the coming chapters.

7. Simulator modifications

RCB has been modified primarily to allow studies of CO_2 storage scenarios in deep saline aquifers. For this purpose, two major modifications have been implemented including the improvement of the numerical algorithm and the introduction of SRK equation of state for thermodynamic calculations of fluid phases (Liu, 2011).

The numerical solution of the non-linear equations derived from temporal and spatial discretization is achieved through an iterative approach by employing Newton-Raphson method. A relaxation factor has been introduced in the method according to the algorithm of (Fujiwara *et al.*, 1993) and a time-step reduction algorithm has been adopted to reduce the computational costs significantly (Liu, 2011).

Implementation of SRK equation of state to replace the ideal gas law has been the second modification in achieving a reservoir simulator for studying CO_2 storage processes in reservoir. SRK equation of state has been used to calculate gas phase properties such as density and compressibility factor as well as determining fugacity coefficient as a parameter in calculating solubility of CO_2 in the underground water (Liu, 2011). The energy balance for gas phase has been also modified to account for real gases by using the implemented equation of state and according to equation (19).

$$\bar{H}_i(P,T,\vec{y}) = \bar{H}_i^{ideal\ gas} - RT^2 \frac{\partial ln\varphi_i}{\partial T} \qquad (19)$$

In this equation, H_i is enthalpy of real gas, $H_i^{ideal\ gas}$ is enthalpy of ideal gas, R is universal gas constant, T is temperature and φ_i is fugacity coefficient.

To extend the simulator for hydrate studies including hydrate phase transition processes during methane hydrate production as well as CO_2 storage in the form of hydrate, several other modifications have been implemented as described in this section.

7.1 Implementation of CH_4 and updateing the corresponding parameters for equation of state and solubility calculations

As stated earlier, RCB has been modified to include CO_2 parameters for SRK equation of state and solubility calculations (Liu & Kvamme, 2007). The current version is modified further to include the critical properties of CH_4 including critical temperature, critical pressure and acentric factor given by Knapp *et al.* (1982) to be used in the SRK EOS (Chejara *et al.*, 2012). To account for the solubility of methane in liquid, Henry's constant has been used as given by Dean (1992).

7.2 Introducing hydrate in RCB as pseudo-minerals

In the current version hydrate is implemented as pseudo-minerals in the geochemical database according to equation (20):

$$G + N_H H_2O \leftrightarrow G.N_H H_2O \qquad (20)$$
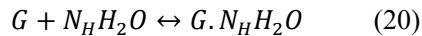
In this equation G is the hydrate former that is CO_2 and CH_4 and N_H is hydration number, which can be modified by user.

The geochemical database keeps track of stoichiometric relations between all possible reactions as well as the corresponding equilibrium constants and serves as an input to RCB. Depending on its application, two versions of the geochemical database had been developed: One including only the equilibrium constant values at 25 ° C and 1 bar for isothermal simulations and the other one with multiple equilibrium constant values in a temperature range of 0 ° C to 300 ° C and along steam table saturation pressure. These databases are the modified versions of the EQ3/6 database in MPATH (Lichtner, 1992).

The geochemical database enables the RCB to establish the sets of primary and secondary species for defining all sorts of reactions (liquid complexation, mineral reactions, gas-liquid reactions…) based on the primary species as described by Saaltink *et al.* (1998). The outcome is significant savings in computational costs.

The implementation of hydrates in the geochemical database has been followed by the modifications in the mineral reaction calculations in the code. While hydrates are considered as minerals in the database, they are treated independently in the code to account for the kinetics of phase transition processes and the subsequent impact on the porosity and permeability. Moreover the energy balance calculations for hydrate are independent of the rest of minerals or solid phase.

7.3 Implementation of hydrate stability curves

The hydrate stability curves have been described by equations (21) - (24) for CO_2 hydrate and CH_4 hydrate and implemented in the code.

$$P = 9.968156693851430 \times 10^{-7} \times T^6 - 1.721355993747740 \times 10^{-3} \times T^5 + 1.237931459591990 \times T^4 - 4.745780290305340 \times 10^2 \times T^3 + 1.022898518566810 \times 10^5 \times T^2 - 1.175309918126070 \times 10^7 \times T + 5.624214942384240 \times 10^8 \qquad (21)$$

This equation is obtained for CO_2 hydrate from model of Kvamme and Tanaka (1995) and pressure and Temperature units are Mpa and Kelvin respectively. This equation has been used for temperatures above 271.1 Kelvin. For temperatures below this the equation of (22) from Phirani and Mohanty (2010) has been used.

$$\ln P = 2.95910923520255 \times 10^{-10} \times T^5 - 3.11697200658458 \times 10^{-7} \times T^4 + 0.000132144540610005 \times T^3 - 0.0284975863532 \times T^2 + 3.21260589574589 \times T - 159.075923757193) \qquad (22)$$

The units in this equation are similar to equation (21).

Equation (23) is used for methane hydrate equilibrium curve and is valid for temperatures above 273.2 Kelvin (Moridis, 2003). Temperature and pressure units are Kelvin and Mpa respectively.

$$\ln P = -1.94138504464560 \times 10^5 + 3.31018213397926 \times 10^3 \times T - $$
$$2.25540264493806 \times 10 \times T^2 + 7.67559117787059 \times 10^{-2} \times T^3 - $$
$$1.30465829788791 \times 10^{-4} \times T^4 + 8.86065316687571 \times 10^{-8} \times T^5 \qquad (23)$$

For temperatures below 273.2 Kelvin equation (24) is used (Moridis, 2003).

$$\ln P = -4.38921173434628 \times 10 + 7.76302133739303 \times 10^{-1} \times T - $$
$$7.27291427030502 \times 10^{-3} \times T^2 + 3.85413985900724 \times 10^{-5} \times T^3 - $$
$$1.03669656828834 \times 10^{-7} \times T^4 + 1.09882180475307 \times 10^{-10} \times T^5 \qquad (24)$$

The units in this equation are similar to equation (23).

7.4 Non-isothermal modelling

Throughout the development of the RCB into a geological CO_2 storage simulator, little attention has been paid to non-isothermal characteristics of the geological reactions in the reservoir. The assumption was to consider the processes under constant temperature conditions of 25°C.

However, by implementation of hydrate in the code the goal has been to include the effect of temperature variations on the equilibrium constants for equilibrium reactions although solution convergence may be affected negatively.

For this purpose every node is defined with an initial temperature condition according to the geothermal gradient to account for temperature variations in the sediments. Non-isothermal geochemical database needs to be used then to get the non-isothermal effects properly.

To overcome the divergence problem especially for complex geometries and have a better control on the input parameters, sensitivity analyses of different variables with respect to temperature variations have been performed. The current version of RCB is able to perform with much higher reliability and robustness in solving complex problems.

7.5 Hydrate saturation

Hydrate saturation has been calculated based on the porosity changes due to hydrate formation and dissociation. This provides the possibility to monitor hydrate phase transition processes and compare the results with other simulators used in scientific arena for hydrate studies. The results have been then exported to the postprocessor for better graphical interpretations.

7.6 Updating the energy balance calculations based on hydrate phase transitions

Another modification implemented in the current version of RCB is the energy balance for Hydrate phase. Since hydrate is implemented as a pseudo-mineral in RCB, it allows for an independent calculation of energy balance. In this version, the energy balance for the solid phase is divided into two separate calculations: the original energy balance for the mineral phase and a new route for hydrate energy balance. At the current state, a constant enthalpy of reaction is used for each hydrate phase transition without considering the effect of temperature change on it. This is due to limited time in this projects and this temporary approximation needs to be changed in upcoming modifications.

7.7 Dynamics of hydrate phase transitions

Two approaches are used to account for dynamics of hydrate phase transitions in modified RCB. The first approach has been the use of kinetic model of Kim et al. (1987) as described in equation (25). This approach was used initially to facilitate the logistics of hydrate implementation in RCB. However, the rate constant in this equation has been derived from extrapolation of the results from phase field theory simulations (Tegze et al., 2006, Baig, 2009).

$$\frac{dn_H}{dt} = k_d A_s (f_e - f) \qquad (25)$$

In this equation n_H is the number of hydrate moles, t is time, k_d is the rate constant, A_s is the reactive surface area, f fugacity and f_e equilibrium fugacity.

However, this has not been the favoured approach as this model has been derived upon experimental data from a PVT cell. Therefore, limited impact of solid walls has been considered and the effect of symmetric stirring cannot be neglected. These characteristics make this model less representative of the real hydrate behaviour in the reservoir.

Second approach has been the use of non-equilibrium thermodynamics. In this method, the change in free energy of the system due to phase transition from one hydrate phase to any other phase can be calculated from equation (26).

$$\Delta G = -\left[x_w^H\left(\mu_w^H - \mu_w^p\right) + x_{CO_2}^H\left(\mu_{CO_2}^H - \mu_{CO_2}^p\right) + x_{CH_4}^H\left(\mu_{CH_4}^H - \mu_{CH_4}^p\right)\right] \qquad (26)$$

In this equation ΔG is the change in Gibbs free energy, x is composition (for water, CO_2 and CH_4), H represents hydrate phase and P represents other phases such as gas and liquid and μ is chemical potential of the components in different phases.

Equation (26) allows identifying the impossible phase transition scenarios ($\Delta G>0$) as well as the unlikely ones ($|\Delta G|<\varepsilon$) and prioritizing the likely scenarios according to minimization of Gibbs free energy. Chemical potential of water and hydrate formers in hydrate phase can be calculated from equation (27).

$$\mu_i^H(T,P,\vec{x}_i^H) = \mu_i^{H,eq}(T,P,\vec{x}_i^{eq}) + \left(\frac{\delta\mu_i^H}{\delta P}\right)_{(T^{eq},\vec{x}_i^{eq})} \times (P - P^{eq}) + \left(\frac{\delta\mu_i^H}{\delta T}\right)_{(P^{eq},\vec{x}_i^{eq})} \times$$

$$(T - T^{eq}) + \sum_i^{i=CH_4,CO_2,water}\left(\frac{\delta\mu_i^H}{\delta x_i}\right)_{\left(T^{eq},\vec{x}_{j\neq i}^{eq}\right)} \times \left(\vec{x}_i^H - \vec{x}_i^{eq}\right) \qquad (27)$$

In this equation μ is chemical potential; i represents water, CO_2 and CH_4, eq and H represent equilibrium conditions and hydrate phase respectively, P is pressure, T is temperature and x is composition. Detailed description and derivation of the equations can be found in (Kvamme et al., 2013a, Kvamme et al., 2014, Kvamme et al., 2013b).

7.8 Sensitivity analyses for convergence improvements

Due to the complexities of the reservoir systems and the number of equations and their non-linearity, it is not always easy to get the solution without divergence problems. Therefore, it is very important to have a control on the input parameters and be aware of the sensitivity of the model and the simulator performance with respect to different parameters. For this reason, a lot of efforts have been made in this study to identify the role of different parameters on the performance of the simulator and improving the solution process.

As a result, several parameters are identified to be influencing the performance of the simulation process significantly including:

- Parameters affecting time-step adjustment.
- Choice of boundary conditions and their corresponding values especially at the injection/production node. These include Injection/production flow rates or pressures.
- Sudden changes in the porosity due to hydrate formation/dissociation, which may affect permeability significantly and cause instabilities.

8. Summary of papers

With reference to the list of publications in the first part of the thesis a selection has been included here and these are briefly summarized in sections 8.1 to 8.8 while the papers are presented in Part 2 of this thesis.

8.1 Simulation of Hydrate Dynamics in Reservoirs

This paper describes the RCB platform and its advantages for becoming a non-equilibrium hydrate simulator. The kinetics of hydrates in the reservoir is elaborated and the system of competing phase transitions between different hydrate phases and the non-equilibrium characteristics of the reservoir hydrates are discussed. An overall picture of the strategy for developing a non-equilibrium hydrate simulator is presented and some preliminary steps in its development and the progress are reported through presentation of simple cases. The model includes inclusion of hydrate components and the integrity of the logistics with the rest of the code. A simple kinetic approach similar to that of Kim et al. (1987) is used to describe hydrate formation and dissociation while the rate constant is modified from phase field theory results. The main purpose of this paper has been to discuss the non-equilibrium concept and the need for such considerations in hydrate studies and it was not meant to describe all details of the future features, which are to be implemented.

8.2 Non-Equilibrium Modeling of Hydrate Dynamics in Reservoir

This paper discusses non-equilibrium characteristics of hydrate in the reservoir in detail and based on the statistical-mechanical model of Kvamme and Tanaka (1995) provides examples of differences in hydrate properties formed from different phases. A literature review over the efforts towards development of hydrate simulators is presented and the distinctions between the current study and the previous works are discussed. In this paper, all possible phase transition scenarios involving hydrate in typical reservoir conditions are formulated and the criteria for selection of the

relevant scenarios by the simulator are discussed. The simplified kinetic model of hydrate phase transition based on the phase field theory simulations is derived and implemented in RCB. A brief description of the simulator along with illustration of its performance is presented through an example case of CO_2 injection into a formation containing hydrate stability regions.

8.3 A New Reservoir Simulator for Studying Hydrate Dynamics in Reservoir

In this paper the modified RCB simulator is used to study a CO_2 injection process into a reservoir with possibility for hydrate formation. The model consists of two horizontal cap rocks and three aquifer layers. Fractures are defined in the cap rock and serve as connections between different aquifer layers. CO_2 is injected from corner bottom of the reservoir and propagates throughout different layers of aquifer and reaches the hydrate stable zone. The porosity changes and the flow patterns illustrate the performance of the simulator and make it possible to study CO_2 storage processes in cold aquifers including hydrate effects.

Since implementation of hydrates in RCB is in the form of pseudo-minerals, it considers hydrate as part of the solid phase. However, the energy balance is treated separately both in internal energy calculations and reaction enthalpy. The paper proposes further implementations as future works in the form of differentiating between heat transport properties of hydrate and the solid phase also as well as inclusion of all possible phase transition scenarios to account for more realistic description of hydrate reactions.

8.4 Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator (CH_4 production from high permeability hydrate deposits)

In this paper the newly developed hydrate simulator based on RCB has been used to demonstrate CH_4 production from a high permeable hydrate deposit. The model

consists of a class 1 hydrate deposit based on the available data (Makogon, 1982) from Messoyakha gas field in Russia. Some studies have claimed that the gas production from Messoyakha gas field has been partly supplied by dissociation of hydrate layers above the free gas zone (Grover *et al.*, 2008). The simulation results have been compared with the results from TOUGH+HYDRATE reservoir simulator as reported by Grover et al. (2008).

8.5 Simulations of long term methane hydrate dissociation by pressure reduction using an extended RetrasoCodeBright simulator (CH_4 production from low permeability hydrate deposits)

This study has been an effort to compare the results from RCB simulator with other hydrate simulators and mainly those participated in the code comparison study of Anderson *et al.* (2011). For this purpose an example case considering a class 3 hydrate deposit from Mt. Elbert in Alaska has been chosen as proposed in the mentioned study. The goal was both to evaluate the performance of RCB simulator against other tools available in scientific community as well as to compare the contribution of kinetic approach with respect to equilibrium assumptions.

The paper discusses the special logic behind development of RCB in differentiating between hydrate formations from different origins (liquid-gas interface, solution, adsorbed phase) and dissociations due to temperature, pressure and concentration under-saturations.

The possibility for geo-mechanical analysis in RCB is another feature highlighted in this paper. Its importance especially during dissociation processes is discussed and the results from the simulations are presented in the form of flow, saturation and stress profiles. The results show an agreement in trends in comparison with the results reported by the code comparison study.

8.6 Simulation of geomechanical effects of CO_2 injection in cold aquifers with possibility of hydrate formation

In this paper the capability of RCB in simulation of geomechanical effects is presented. Due to implicit calculation of geo-mechanics along with flow equations it is possible to study the effects of hydrate phase transitions on geomechanics of the reservoir in the same time step as transport calculations are done.

A reservoir model including two aquifers and a cap rock with two fractures is proposed to study the effect of CO_2 hydrate formation in the top aquifer on the geomechanics of the system. The effective stress model of Terzaghi (1943) is used in RCB to account for geomechanical calculations within the same time-step as mass and heat flow calculations. The results showed that hydrate grows outwards the fractures and results in increased stress out from the fractures and towards the top of the formation.

8.7 Simulation of CO_2 hydrates formation in cold aquifers: non-equilibrium approach

In this paper, non-equilibrium thermodynamics of hydrates in the reservoir is formulated through pressure, temperature and concentration super-saturations and under-saturations. Derivation of Gibbs free energy changes due to deviation from equilibrium as a consequence of any of the super-saturation or under-saturation scenarios is presented. The RCB simulator is modified to account for the effect of non-equilibrium thermodynamics of pressure super-saturation in the calculations. The non-equilibrium thermodynamic properties are estimated by first order Taylor expansion of deviations from equilibrium state.

The consequences of the new modifications on the performance of the simulator are illustrated through an example case of CO_2 storage process in the form of hydrate in a fractured reservoir. The geomechanical effect of the hydrate reactions on the stability of the formation is included in the results by means of effective stress calculations.

8.8 Theoretical studies of CO_2 hydrates formation and dissociation in cold aquifers using RetrasoCodeBright simulator (Comparison between two thermodynamic approaches)

In this paper, a comparison between two kinetic approaches in studying reservoir hydrate dynamics by means of RCB has been made. The first approach is based on the effect of super-saturation and under-saturation in the classical nucleation theory of hydrate growth or dissociation. The second one is based on the model of (Kim et al., 1987).

A CO_2 storage process in a reservoir with suitable thermodynamic conditions for CO_2 Hydrate formation has been chosen for this comparison. The results show a much faster reduction in the available pore volume due to the hydrate formation in the Kim and Bishnoi approach. However, the non-equilibrium approach implemented in RCB based on the classical nucleation theory considers a limited spectrum of all possible phase transition routes, which should be considered during the comparative analysis.

The paper elaborates the implemented modifications in the simulator and the details of the example case. The geomechanical effects are illustrated through effective stress profiles.

9. Conclusion

Despite the considerable advances in reservoir hydrate studies there are still issues and challenges in this field, which require a more comprehensive understanding of different aspects of sediment hydrates. In this study, dynamics of reservoir hydrates during different processes such as CH_4 production from hydrate reservoirs as well as storage of CO_2 in cold aquifers, with possibility of hydrate formation has been discussed. Based on the thermodynamics of hydrate phase transitions in the reservoir and the experimental evidences, it has been argued that hydrate dynamics during reservoir processes are governed by minimum Gibbs free energy of competing phase transition possibilities, which will result in formation, dissociation or reformation of hydrate. The differences in the properties of hydrates formed from different sources (such as liquid-gas interface, adsorbed phase, aqueous phase...) have been calculated and presented in the published papers in this thesis as well as in related publications. Based on these arguments the need for considering these characteristics of hydrates in development of reservoir hydrate simulators has been highlighted.

A new simulator is developed and presented in this thesis to study hydrate processes in porous media. The new simulator has three distinctive characteristics compared to similar tools in research community and industry.

The first characteristic is its capability of analysing hydrate phase transitions through a non-equilibrium approach. It gives the possibility to analyse the competing phase transition scenarios including hydrate formation, dissociation and reformation form different sources/phases and calculate the hydrate balance at each node in the reservoir model and for each time step.

The second characteristic is the use of a reactive transport reservoir simulator RetrasoCodeBright (RCB) as the platform for developing this new hydrate simulator. Thanks to its reactive transport module, different hydrate phases are defined as separate pseudo-components and phase transition processes are treated as pseudo-

reactions. The thermodynamic package then decides which phase transitions should happen.

The thermodynamic package for calculation of hydrate dynamics has evolved in several stages and is continuously under development. The model of Kim et al. (1987) has been used initially combined with phase field theory results for fitting the constants in the rate equations as a preliminary stage before implementing theoretically more sound models. Later, the non-equilibrium package based on deviation from equilibrium due to temperature, pressure and concentration super-saturation and under-saturation has been implemented. A first order Taylor expansion has been used to express this deviation.

Third important characteristic of the developed simulator is the implicit consideration of geomechanics through Terzaghi approach in calculation of effective stress. It is a very important aspect of reservoir hydrate studies both during production and storage processes. While dissociation of hydrate during production processes may result in instabilities in the reservoir structure and consequently turns into landslides or collapses, CO_2 storage in the form of hydrate can also cause geomechanical effects on the reservoir structure because this process involves around 10% expansion in water volume. The geomechanical analysis is included in several papers attached to this thesis.

While the work is still under progress, the performance of the simulator has been evaluated through example cases and model data from the literature. An important effort has been comparison of RCB with other well-known simulators. Comparative results have been achieved which implies that RCB can be used as an established hydrate simulator for hydrate studies in reservoir.

RCB is still under development. As will be described in the next chapter, several implementations and modifications will be done in the future to provide a more accurate description of the thermodynamics of hydrates as well as the geological and transport properties of the reservoir.

10. Future work

As mentioned earlier, development of RCB is under progress and there are several possibilities for enhancement and modifications as will be discussed here.

10.1 Completion of thermodynamic package for hydrate transitions

The thermodynamic package in RCB includes two separate approaches. First one is the kinetic approach based on the model of Kim et al. (1987) with modified constant rate from phase field theory simulations. Second one is the non-equilibrium thermodynamic approach considering deviation from equilibrium due to temperature, pressure and concentration super-saturations or under-saturations. The work needs to be completed in two directions.

1. It is required to include all three variables of temperature, pressure and concentration in the non-equilibrium approach. So far, the effects of concentration and pressure super-saturation are implemented through some preliminary correlations fitted from results of a separate thermodynamic package. These implementations need to be extended with respect to the range of application as well as the accuracy and efficiency of the generated correlations. In addition to that, temperature effect also should be implemented in the future.

2. It is necessary to include the missing hydrate phase transition possibilities in the thermodynamic package. As discussed earlier, hydrate may form from different origins such as: interface between liquid and gas; dissolved phase; gas phase; adsorbed phase etc. At this stage not all of the possible routes are included in RCB and works need to be completed by implementation of the remaining reactions.

10.2 Combination of different production methods during simulation studies

In this work, methane production has been studied through depressurization method only. It is necessary to study the effect of thermal stimulation especially when it is combined with depressurization process.

Hydrate reformation during depressurization methods can cause challenges in the production process especially when it happens around the production well. Use of thermal methods can provide a solution to these problems.

There are several methods for thermal stimulation in the reservoir. Steam and hot water injection are two methods, which can be easily implemented in RCB. However, electrical heating and in situ combustion methods need further modifications, which may be feasible in a longer-term perspective.

10.3 Study of CH_4 exchange during CO_2 injection in methane hydrate reservoirs

An attractive area of hydrate studies is the exchange process of CH_4 with CO_2 in gas hydrate reservoirs. CO_2 hydrate is generally more stable than CH_4 hydrate and can potentially replace methane in the hydrate structure. This is an attractive process as it can result in simultaneous storage of CO_2 and production of CH_4.

The exchange process happens through two different mechanisms. The dominating mechanism is based on formation of CO_2 hydrate as a result of CO_2 contact with free water available in the reservoir. As a consequence of this reaction, necessary heat for dissociation of CH_4 hydrate will be provided and the process will continue.

Next mechanism is solid-state conversion of CH_4-hydrate into a mixed hydrate in presence of CO_2. This mechanism is however, very slow compared to the first mechanism and depends on the solid-state diffusivity. It becomes important only in conditions where free water is not available.

Kinetic rates of these transition processes have been studied through molecular dynamics simulations (Kuznetsova *et al.*, 2012) and phase field theory studies (Kvamme et al., 2004, Kvamme *et al.*, 2011, Kivelä *et al.*, 2012). Therefore, this option is available for implementation through these kinetic rates in a simplified form in RCB and takes into account the effect of exchange mechanisms.

10.4 Improving description of flow through fractures and wells by introducing hydrodynamics

In RCB, wells and fractures are defined as high porosity and permeability regions. In other words, the fluid still needs to push the movable reserves out of the grid blocks under the constraints of relative permeability of the phases and capillary effects (Bogachev & Shelkov, 2010). In reality, fluid breaks through and moves in the fracture very quickly due to the limited capillary forces and this effect can be reproduced only partly by the current method used in RCB while the calculations will slow down significantly.

An alternative could be proper description of the hydrodynamics of the fractures and wells by solving Navier-Stokes equations for certain geometries of fractures. This method is believed to provide accurate prediction of realistic flow through fractures (Al-Yaarubi *et al.*, 2001). It may provide a more stable numerical calculation also since there will be simpler and smaller regions of boundary conditions connecting the reservoir matrix flow to the Navier-Stokes equations inside the wells and fractures.

10.5 Improving relative permeability correlations according to hydrate morphology in porous media

Permeability calculation in RCB is based on the porosity changes as a result of hydrate formation or dissociation. However, hydrate formation in porous media often happens in the middle of the pores depending on the chemical structure of the pores surfaces which creates channels between hydrate surface and solid mineral surface. An accurate permeability model should be able to take into account the effect of these

channels as reservoir fluid can fill these channels and create tiny flow paths. Employing Computerised Tomography (CT) scan images of porous media along with stress analysis can be an approach in definition of the pore structure (Mitsuhori *et al.*, 2010, Okabe & Blunt, 2007, Sugita *et al.*, 2009).

10.6 Improving the energy balance calculations and heat transport models

An immediate modification in RCB would be improving the energy balance calculations. Enthalpy of reaction for hydrate phase transitions in RCB is considered constant and the dependency on temperature is not implemented yet. Use of empirical relations (Kamath, 1984, Kamath & Holder, 1987) or Clausius-Clapeyron equation could be alternatives for this purpose. However, the ultimate goal is to correlate the enthalpy change to free energy of phase transitions according to equation (28):

$$\frac{\partial \left(\frac{\mu_i}{RT} \right)_{P,\vec{N}}}{\partial T} = - \frac{\bar{H}_i}{RT^2} \qquad (28)$$

Where μ is chemical potential, $\bar{H}$ is partial molar enthalpy, R is universal gas constant, T is temperature, i is any component in the given phase, P is pressure and N is the number of moles.

More importantly is the improvement of heat transport models to account for accurate dynamics of hydrate phase transitions during injection or production processes. For example, during depressurization process, hydrate dissociation is an endothermic reaction, which absorbs energy from reservoir. As a consequence, parts of the formation may freeze again and it may affect the production process. Implementation of proper heat transport models to account for these effects especially in presence of several hydrate phase transition scenarios is quite complex and challenging.

Therefore, it is proposed to employ the simplified models generated from advanced Phase Field Theory simulations (Kivelä et al., 2012, Kvamme et al., 2013b, Kvamme

et al., 2013a, Kvamme et al., 2014) and consider conduction and convection mechanisms separately.

10.7 Incorporating the effect of nucleation process on the interface into the thermodynamic package

One of the important mechanisms in determining hydrate formation rate is nucleation process. Different studies have shown that phase interfaces enhance the nucleation mechanism and play and important role in hydration process (Van Cuong et al., 2012a, Van Cuong et al., 2012b). The interfaces between hydrate former and the fluid phase as well as the adsorbed phases on different mineral surfaces are important sites in porous media which can affect hydrate nucleation process. Incorporating these effects into the thermodynamic package of the new RCB code can improve the description of hydrate phase transition scenarios in the reservoir.

References

Ahmadi, G., C. Ji and D. H. Smith, 2004: Numerical solution for natural gas production from methane hydrate dissociation. *Journal of petroleum science and engineering,* **41,** 269-285.

Al-Yaarubi, A. H., C. C. Pain and R. W. Zimmerman, Navier-Stokes Simulations of Fluid Flow in a Rough-Walled Fracture. in Proceedings of the AGU Fall Meeting Abstracts, 2001, p. 0348.

Anderson, B. J., M. Kurihara, M. D. White, G. J. Moridis, S. J. Wilson, M. Pooladi-Darvish, M. Gaddipati, Y. Masuda, T. S. Collett and R. B. Hunter, 2011: Regional long-term production modeling from a single well test, Mount Elbert gas hydrate stratigraphic test well, Alaska North slope. *Marine and petroleum geology,* **28,** 493-501.

Archer, D., 2007: Methane hydrate stability and anthropogenic climate change. *Biogeosciences Discussions,* **4,** 521-544.

Baig, K., 2009: Phase Field Theory Modeling of CH4 and CO2 Fluxes from Exposed Natural Gas Hydrate Reservoirs. *Physics and Technology.* University of Bergen.

Berndt, C., T. Feseker, T. Treude, S. Krastel, V. Liebetrau, H. Niemann, V. J. Bertics, I. Dumke, K. Dünnbier and B. Ferré, 2014: Temporal constraints on hydrate-controlled methane seepage off Svalbard. *Science,* **343,** 284-287.

Bock, M., J. Schmitt, L. Möller, R. Spahni, T. Blunier and H. Fischer, 2010: Hydrogen isotopes preclude marine hydrate CH4 emissions at the onset of Dansgaard-Oeschger events. *Science,* **328,** 1686-1689.

Bogachev, K. Y. and V. Shelkov, A New Approach in Modeling Hydraulic Fractures and Auto Fractures at Injectors in Full-field Models. in Proceedings of the SPE Russian Oil and Gas Conference and Exhibition, Moscow, Russia, 2010.

Bollmann, M., T. Bosch, F. Colijn, R. Ebinghaus, R. Froese, K. Güssow, S. Khalilian, S. Krastel, A. Körtzinger, M. Langenbuch, M. Latif, B. Matthiessen, F. Melzner, A. Oschlies, S. Petersen, A. Proelß, M. Quaas, J. Reichenbach, T. Requate, T. Reusch, P. Rosenstiel, J. O. Schmidt, K. Schrottke, H. Sichelschmidt, U. Siebert, R. Soltwedel, U. Sommer, K. Stattegger, H. Sterr, R. Sturm, T. Treude, A. Vafeidis, C. v. Bernem, J. v. Beusekom, R. Voss, M. Visbeck, M. Wahl, K. Wallmann and F. Weinberger, 2010: World Ocean Review 1 (WOR1). *Living with the oceans: A report on the state of the world's oceans.* maribus.

Buanes, T., B. Kvamme and A. Svandal, 2006: Computer simulation of CO2 hydrate growth. *Journal of crystal growth,* **287,** 491-494.

Buanes, T., B. Kvamme and A. Svandal, 2009: Two approaches for modelling hydrate growth. *Journal of mathematical chemistry,* **46,** 811-819.

Burshears, M., T. O'brien and R. Malone, A multi-phase multi-dimensional variable composition simulation of gas production from a conventional gas reservoir in contact with hydrates. in Proceedings of the SPE Unconventional Gas Technology Symposium, 1986.

Chejara, A., B. Kvamme, M. T. Vafaei and K. Jemai, 2012: Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator. *Energy Procedia,* **18,** 1533-1540.

Collett, T., J.-J. Bahk, R. Baker, R. Boswell, D. Divins, M. Frye, D. Goldberg, J. Husebø, C. Koh and M. Malone, 2014: Methane Hydrates in Nature—Current Knowledge and Challenges.

Collett, T., A. Johnson, C. Knapp and R. Boswell, 2009: Natural Gas Hydrates: A Review. In: T. Collett, A. Johnson, C. Knapp and R. Boswell (eds.), *Natural gas hydrates:*

energy resource potential and associated geologic hazards. American Association of Petroleum Geologists, Tulsa, Oklahoma.

Davy, H., 1811: On some of the combinations of oxymuriatic acid gas and oxygen and on the chemical relations of the properties. *Phil. Trans. Roy. Soc.(London),* **101,** 30-55.

De Forcrand, R., 1902: Sur la composition des hydrates de gaz. *Compt. rend,* **135,** 959.

Dean, J., 1992: *Lange's handbook of chemistry*. McGraw-Hill, New York.

Demetriou, D., 2014: Is 'burning ice' the solution to Japan's energy crisis? The Telegraph.

DOE, 2012: DOE's Methane Hydrate Field Studies. U.S. Department of Energy, Fossil Energy Office of Communications.

EPA, 2010: Methane and Nitrous Oxide Emissions from Natural Sources. U.S. Environmental Protection Agency, Washington, DC, USA.

Ersland, G., J. Husebø, A. Graue and B. Kvamme, 2009: Transport and storage of CO2 in natural gas hydrate reservoirs. *Energy Procedia,* **1,** 3477-3484.

Forrisdahl, O. K., 1996: Methane clathrate hydrates: melting, supercooling and phase separation from molecular dynamics computer simulations. *Molecular Physics,* **89,** 819-834.

Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. W. Fahey, J. Haywood, J. Lean, D. C. Lowe and G. Myhre, 2007: Changes in atmospheric constituents and in radiative forcing. In: S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M.Tignor and H. L. Miller (eds.), *Climate Change 2007: The Physical Science Basis*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Fujiwara, K., T. Nakata, N. Okamoto and K. Muramatsu, 1993: Method for determining relaxation factor for modified Newton-Raphson method. *IEEE transactions on magnetics,* **29,** 1962-1965.

Gamwo, I. K. and Y. Liu, 2010: Mathematical modeling and numerical simulation of methane production in a hydrate reservoir. *Industrial & engineering chemistry research,* **49,** 5231-5245.

Garrels, R. M. and C. L. Christ, 1965: *Solutions, minerals, and equilibrium,* p. 450. Freeman, Cooper, San Francisco.

Goel, N., M. Wiggins and S. Shah, 2001: Analytical modeling of gas recovery from in situ hydrates dissociation. *Journal of Petroleum Science and Engineering,* **29,** 115-127.

Graue, A., B. Kvamme, B. Baldwin, J. Stevens, J. J. Howard, E. Aspenes, G. Ersland, J. Husebo and D. Zornes, 2008: MRI visualization of spontaneous methane production from hydrates in sandstone core plugs when exposed to CO2. *SPE Journal,* **13,** 146-152.

Grover, T., G. J. Moridis and S. A. Holditch, Analysis of Reservoir Performance of Messoyakha Gas Hydrate Reservoir. in Proceedings of the SPE Annual Technical Conference and Exhibition, 2008.

Helgeson, H. C. and D. H. Kirkham, 1974: Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures; II, Debye-Huckel parameters for activity coefficients and relative partial molal properties. *American Journal of Science,* **274,** 1199-1261.

Hellevang, H. and B. Kvamme, 2007: An explicit and efficient algorithm to solve kinetically constrained CO2-water-rock interactions. *WSEAS TRANSACTIONS ON MATHEMATICS,* **6,** 681-687.

Henriet, J.-P. and J. Mienert, 1998: Gas Hydrates: Relevance to world margin stability and climate change. *Geological Society of London Special Publication,* **137,** 338.

Henry, P., M. Thomas and M. B. Clennell, 1999: Formation of natural gas hydrates in marine sediments: 2. Thermodynamic calculations of stability conditions in porous

sediments. *Journal of Geophysical Research: Solid Earth (1978–2012),* **104,** 23005-23022.

Holder, G. D. and P. F. Angert, Simulation of gas production from a reservoir containing both gas hydrates and free natural gas. in Proceedings of the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 1982.

Hong, H. and M. Pooladi-Darvish, 2005: Simulation of depressurization for gas production from gas hydrate reservoirs. *Journal of Canadian Petroleum Technology,* **44,** 39-46.

IEA Greenhouse Gas R&D Programme (IEA GHG), 2008: Assessment of Sub Sea Ecosystem Impacts. In: 2008/8 (ed.).

Johnson, A., Global Resource Potential of Gas Hydrate - A New Calculation. in Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, 2011.

Kamath, V. A., 1984: Study of Heat Transfer Characteristics during Dissociation of Gas Hydrates in Porous Media. Univ. of Pittsburgh, Univ. of Pittsburgh.

Kamath, V. A. and G. D. Holder, 1987: Dissociation heat transfer characteristics of methane hydrates. *AIChE Journal,* **33,** 347-350.

Kennett, J. P., K. G. Cannariato, I. L. Hendy and R. J. Behl, 2003: *Methane hydrates in Quaternary climate change: The clathrate gun hypothesis*. American Geophysical Union.

Kim, H., P. Bishnoi, R. Heidemann and S. Rizvi, 1987: Kinetics of methane hydrate decomposition. *Chemical engineering science,* **42,** 1645-1653.

Kivelä, P.-H., K. Baig and M. Qasim, Phase field theory modeling of methane fluxes from exposed natural gas hydrate reservoirs. in Proceedings of the INTERNATIONAL CONFERENCE OF COMPUTATIONAL METHODS IN SCIENCES AND ENGINEERING 2009:(ICCMSE 2009), 2012, p. 351-363.

Knapp, H., R. Döring, L. Oellrich, U. Plöcker and J. Prausnitz, 1982: *Vapor-liquid equilibria for mixtures of low boiling substances,* p. 970. Dechema Chemistry Data Series, Frankfurt.

Kowalsky, M. B. and G. J. Moridis, 2007: Comparison of kinetic and equilibrium reaction models in simulating gas hydrate behavior in porous media. *Energy Conversion and Management,* **48,** 1850-1863.

Kozeny, J., 1927: Ueber kapillare leitung des wassers im boden. *Sitzungsber. Akad. Wiss. Wien,* **136,** 271-306.

Kuznetsova, T., B. Kvamme and K. Morrissey, An alternative for carbon dioxide emission mitigation: in situ methane hydrate conversion. in Proceedings of the American Institute of Physics Conference Series, 2012, p. 772-775.

Kvamme, B., K. Baig, J. Bauman and P. Kivelä, Thermodynamics and kinetic modeling of CH4/CO2 exchange in hydrates. in Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, 2011.

Kvamme, B., K. Baig, M. Qasim and J. Bauman, 2013a: Thermodynamic and Kinetic Modeling of CH4/CO2 Hydrates Phase transitions. *International Journal of Energy and Environment,* **7,** 1-8.

Kvamme, B., T. Buanes and T. Kuznetsova, 2006a: Kinetics of hydrate growth on the CO2/aqueous solution interface. *WSEAS Transactions on Heat and Mass Transfer,* **1,** 612-617.

Kvamme, B., A. Graue, E. Aspenes, T. Kuznetsova, L. Gránásy, G. Tóth, T. Pusztai and G. Tegze, 2004: Kinetics of solid hydrate formation by carbon dioxide: Phase field theory of hydrate nucleation and magnetic resonance imaging. *Physical chemistry chemical physics,* **6,** 2327-2334.

Kvamme, B., A. Graue, T. Buanes, T. Kuznetsova and G. Ersland, 2007: Storage of CO2 in natural gas hydrate reservoirs and the effect of hydrate as an extra sealing in cold aquifers. *International Journal of Greenhouse gas control,* **1,** 236-246.

Kvamme, B., A. Graue, T. Buanes, T. Kuznetsova and G. Ersland, 2009a: Effects of solid surfaces on hydrate kinetics and stability. *Geological Society, London, Special Publications,* **319,** 131-144.

Kvamme, B., A. Graue, T. Kuznetsova, T. Buanes and G. Ersland, 2006b: Energy from Natural Gas Hydrate Combined With Reservoir Storage of CO2. *WSEAS Trans. Environ. Dev.,* **2,** 699-710.

Kvamme, B. and T. Kuznetsova, 2010: Investigation into stability and interfacial properties of CO2 hydrate–aqueous fluid system. *Mathematical and Computer Modelling,* **51,** 156-159.

Kvamme, B., T. Kuznetsova and K. Aasoldsen, 2005: Molecular dynamics simulations for selection of kinetic hydrate inhibitors. *Journal of Molecular Graphics and Modelling,* **23,** 524-536.

Kvamme, B., T. Kuznetsova and P.-H. Kivelæ, 2012: Adsorption of water and carbon dioxide on hematite and consequences for possible hydrate formation. *Physical Chemistry Chemical Physics,* **14,** 4410-4424.

Kvamme, B., T. Kuznetsova, P.-H. Kivelæ and J. Bauman, 2013b: Can hydrate form in carbon dioxide from dissolved water? *Physical Chemistry Chemical Physics,* **15,** 2063-2074.

Kvamme, B., T. Kuznetsova and D. Uppstad, 2009b: Modelling excess surface energy in dry and wetted calcite systems. *Journal of mathematical chemistry,* **46,** 756-762.

Kvamme, B. and S. Liu, 2009: Reactive transport of CO2 in saline aquifers with implicit geomechanical analysis. *Energy Procedia,* **1,** 3267-3274.

Kvamme, B., M. Qasim, K. Baig, P. H. Kivelä and J. Bauman, 2014: Hydrate phase transition kinetics from Phase Field Theory with implicit hydrodynamics and heat transport. *International Journal of Greenhouse Gas Control,* **29,** 263-278.

Kvamme, B. and H. Tanaka, 1995: Thermodynamic stability of hydrates for ethane, ethylene, and carbon dioxide. *The Journal of Physical Chemistry,* **99,** 7114-7119.

Kvenvolden, K. A., 1993: Gas Hydrates - Geological Perspective and Global Change. *Rev Geophys,* **31,** 173-187.

Kvenvolden, K. A., 1994: Natural Gas Hydrate Occurrence and Issues. *Annals of the New York Academy of Sciences,* **715,** 232-246.

Kvenvolden, K. A., 1999: Potential effects of gas hydrate on human welfare. *Proceedings of the National Academy of Sciences,* **96,** 3420-3426.

Kyodo, 2013: Japan plans viable methane hydrate technology by 2018. The Japan Times.

Lichtner, P. C., 1992: Time- space continuum description of fluid/rock interaction in permeable media. *Water resources research,* **28,** 3135-3155.

Liu, S., 2011: Modelling CO_2 storage in saline aquifers with reactive transport simulator RCB. University of Bergen, Bergen.

Liu, S. and B. Kvamme, Simulating CO2 storage in saline aquifers with improved code RCB. in Proceedings of the Proceedings of the 6th WSEAS international conference on System science and simulation in engineering, 2007, p. 38-62.

Longuemare, P., M. Mainguy, P. Lemonnier, A. Onaisi, C. Gérard and N. Koutsabeloulis, 2002: Geomechanics in reservoir simulation: overview of coupling methods and field case study. *Oil & Gas Science and Technology,* **57,** 471-483.

Makogon, Y. F., Perspectives for the development of gas hydrate deposits. in Proceedings of the Gas hydrates and permafrost: Proceedings of the 4th Canadian Permafrost Conference, 1982, p. 299-304.

Makogon, Y. F., 2010: Natural gas hydrates–A promising source of energy. *Journal of Natural Gas Science and Engineering,* **2,** 49-59.

Maslin, M., M. Owen, S. Day and D. Long, 2004: Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis. *Geology,* **32,** 53-56.

Milkov, A. V., G. R. Dickens, G. E. Claypool, Y.-J. Lee, W. S. Borowski, M. E. Torres, W. Xu, H. Tomaru, A. M. Tréhu and P. Schultheiss, 2004: Co-existence of gas hydrate, free gas, and brine within the regional gas hydrate stability zone at Hydrate Ridge (Oregon margin): evidence from prolonged degassing of a pressurized core. *Earth and Planetary Science Letters,* **222,** 829-843.

Mitsuhori, K., T. Sato, S. Hirabayashi, P. Brumby, Y. Norimatsu, J. Nagao, Y. Jin, Y. Konno, T. Ebinuma and H. Narita, Microscale Numerical Modelling For Permeability Reduction of Solid-Water Phases In Sand Sediment. in Proceedings of the The Twentieth International Offshore and Polar Engineering Conference, 2010.

Moon, C., P. C. Taylor and P. M. Rodger, 2003: Molecular dynamics study of gas hydrate formation. *Journal of the American Chemical Society,* **125,** 4706-4707.

Moridis, G., 2003: Numerical studies of gas production from methane hydrates. *Spe Journal,* **8,** 359-370.

Moridis, G. J. and T. S. Collett, Strategies for gas production from hydrate accumulations under various geologic conditions. in Proceedings of the TOUGH Symposium 2003, Berkeley, California, 2003.

Moridis, G. J., T. S. Collett, R. Boswell, S. Hancock, J. Rutqvist, C. Santamarina, T. Kneafsey, M. T. Reagan, M. Pooladi-Darvish, M. Kowalsky, E. D. Sloan and C. Coh, 2013: Gas Hydrates as a Potential Energy Source: State of Knowledge and Challenges. In: J. W. Lee (ed.), *Advanced Biofuels and Bioproducts.* Springer.

Nazridoust, K. and G. Ahmadi, 2007: Computational modeling of methane hydrate dissociation in a sandstone core. *Chemical engineering science,* **62,** 6155-6177.

Okabe, H. and M. J. Blunt, 2007: Pore space reconstruction of vuggy carbonates using microtomography and multiple- point statistics. *Water Resources Research,* **43**.

Olivella, S., J. Carrera, A. Gens and E. E. Alonso, 1994: Nonisothermal multiphase flow of brine and gas through saline media. *Transport in porous media,* **15,** 271-293.

Olivella, S., A. Gens, J. Carrera and E. Alonso, 1996: Numerical formulation for a simulator (CODE_BRIGHT) for the coupled analysis of saline media. *Engineering Computations: Int J for Computer-Aided Engineering,* **13,** 87-112.

Olivella, S., J. Vaunat, B. Garitte and N. M. Pinyol, Coupled THM problems in geotechnical engineering using CODE_BRIGHT-Gi. in, 2008.

Ostrovskii, V. E. and E. A. Kadyshevich, 2009: Life origination hydrate hypothesis (LOH-hypothesis). *Orig. Life. Evol. Biosp,* **39,** 219-220.

Paull, C. K. and R. Matsumoto, 1. Leg 164 overview. in Proceedings of the Proceedings of the Ocean Drilling Program. Scientific Results, 2000, p. 3-10.

Phirani, J. and K. K. Mohanty, Kinetic Simulation of CO2 Flooding of methane hydrates. in Proceedings of the SPE Annual Technical Conference and Exhibition, 2010.

Rochelle, C., A. Camps, D. Long, A. Milodowski, K. Bateman, D. Gunn, P. Jackson, M. Lovell and J. Rees, 2009: Can CO2 hydrate assist in the underground storage of carbon dioxide? *Geological Society, London, Special Publications,* **319,** 171-183.

Ruppel, C. D., 2011: Methane Hydrates and Contemporary Climate Change. *Nature Education Knowledge,* **3,** 29.

Saaltink, M. W., C. Ayora and J. Carrera, 1998: A mathematical formulation for reactive transport that eliminates mineral concentrations. *Water Resources Research,* **34,** 1649-1656.

Saaltink, M. W., C. Ayora and S. Olivella, 2005: User's guide for RetrasoCodeBright (RCB). Department of Geotechnical Engineering and Geo-Sciences, Technical University of Catalonia (UPC), Barcelona, Spain.

Saaltink, M. W., F. Batlle Pifarré, C. Ayora, J. Carrera and S. Olivella Pastallé, 2004: RETRASO, a code for modeling reactive transport in saturated and unsaturated porous media. *Geologica Acta,* **2,** 235.

Shakhova, N., I. Semiletov, A. Salyuk, V. Yusupov, D. Kosmach and Ö. Gustafsson, 2010: Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science,* **327,** 1246-1250.

Sloan, E. D., 1998: Physical/chemical properties of gas hydrates and application to world margin stability and climate change. *Geological Society of London Special Publication,* **137,** 31-50.

Sloan, E. D., 2003: Fundamental principles and applications of natural gas hydrates. *Nature,* **426,** 353-363.

Sloan, E. D. and C. A. Koh, 2008: *Clathrate Hydrates of Natural Gases*. CRC Press.

Soave, G., 1972: Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science,* **27,** 1197-1203.

Solomon, S., 2007: *Climate change 2007-the physical science basis: Working group I contribution to the fourth assessment report of the IPCC*. Cambridge University Press.

Sugita, T., T. Sato, J. Nagao, Y. Jin and F. Kiyono, Microscale Numerical Simulation for Estimating Permeability of Gas-Water and Solid-Water Phases in Sand Sediment. in Proceedings of the The Nineteenth International Offshore and Polar Engineering Conference, 2009.

Sun, X. and K. K. Mohanty, 2006: Kinetic simulation of methane hydrate formation and dissociation in porous media. *Chemical Engineering Science,* **61,** 3476-3495.

Sun, Y., X. Lü and W. Guo, 2014: A review on simulation models for exploration and exploitation of natural gas hydrate. *Arabian Journal of Geosciences,* **7,** 2199-2214.

Svandal, A., T. Kuznetsova and B. Kvamme, 2006a: Thermodynamic properties and phase transitions in the H2O/CO2/CH4 system. *Phys. Chem. Chem. Phys.,* **8,** 1707-1713.

Svandal, A., B. Kvamme, L. Grànàsy, T. Pusztai, T. Buanes and J. Hove, 2006b: The phase-field theory applied to CO2 and CH4 hydrate. *Journal of Crystal Growth,* **287,** 486-490.

Tegze, G., T. Pusztai, G. Tóth, L. Gránásy, A. Svandal, T. Buanes, T. Kuznetsova and B. Kvamme, 2006: Multiscale approach to CO2 hydrate formation in aqueous solution: Phase field theory and molecular dynamics. Nucleation and growth. *The Journal of Chemical Physics,* **124,** 1-12.

Terzaghi, K., 1943: *Theoretical soil mechanics*. John Wiley and Sons Inc, New York.

Tse, J. S., M. L. Klein and I. R. McDonald, 1983: Molecular dynamics studies of ice Ic and the structure I clathrate hydrate of methane. *The Journal of Physical Chemistry,* **87,** 4198-4203.

Uddin, M., D. Coombe, D. Law and B. Gunter, 2008: Numerical studies of gas hydrate formation and decomposition in a geological reservoir. *Journal of energy resources technology,* **130,** 032501-032514.

Vafaei, M. T., B. Kvamme, A. Chejara and K. Jemai, 2012: Nonequilibrium Modeling of Hydrate Dynamics in Reservoir. *Energy & Fuels,* **26,** 3564-3576.

Van Cuong, P., B. Kvamme, T. Kuznetsova and B. Jensen, 2012a: Adsorption of water and CO2 on calcite and clathrate hydrate: the effect of short-range forces and temperature. *International Journal of Energy and Environment,* **6,** 301-309.

Van Cuong, P., B. Kvamme, T. Kuznetsova and B. Jensen, 2012b: Molecular dynamics study of calcite, hydrate and the temperature effect on CO2 transport and adsorption stability in geological formations. *Molecular Physics,* **110,** 1097-1106.

Van Der Waals, J. H. and J. C. Platteeuw, 1959: Validity of Clapeyron's Equation for Phase Equilibria involving Clathrates. *Nature,* **183,** 462-462.

Van Genuchten, M. T., 1980: A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal,* **44,** 892-898.

Villard, P., 1888: Sur quelques nouveaux hydrates de gaz. *Compt. rend,* **106,** 1602.

White, M. D. and B. P. McGrail, Numerical simulation of methane hydrate production from geologic formations via carbon dioxide injection. in Proceedings of the Offshore Technology Conference, Houston, Texas, USA, 2008.

Xu, W., 2004: Modeling dynamic marine gas hydrate systems. *American Mineralogist,* **89,** 1271-1279.

Xu, W. and C. Ruppel, 1999: Predicting the occurrence, distribution, and evolution of methane gas hydrate in porous marine sediments. *Journal of Geophysical Research: Solid Earth (1978–2012),* **104,** 5081-5095.

Yousif, M., H. Abass, M. Selim and E. Sloan, 1991: Experimental and theoretical investigation of methane-gas-hydrate dissociation in porous media. *SPE reservoir Engineering,* **6,** 69-76.

Zatsepina, O. Y. and M. Pooladi-Darvish, 2012: Storage of CO2 as hydrate in depleted gas reservoirs. *SPE Reservoir Evaluation & Engineering,* **15,** 98-108.