Gas Hydrates in Porous Media: CO$_2$ Storage and CH$_4$ Production

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<tr>
<td>GHs</td>
<td>Gas hydrates</td>
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<tr>
<td>NGHs</td>
<td>Natural gas hydrates</td>
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<td>GHG</td>
<td>Greenhouse gas</td>
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<td>CCS</td>
<td>Carbon capture and storage</td>
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<td>RCB</td>
<td>RetrasoCodeBright</td>
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<tr>
<td>Retraso</td>
<td>REactive TRAnsport of SOLutes</td>
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<tr>
<td>CodeBright</td>
<td>COupled DEformation of BRIne Gas and Heat Transport</td>
</tr>
<tr>
<td>USGS</td>
<td>United States Geological Survey</td>
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<td>NETL</td>
<td>National Energy Technology Laboratory</td>
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<td>CMG</td>
<td>Computer modelling group</td>
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<tr>
<td>BPXA</td>
<td>BP Exploration Alaska, Inc.</td>
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<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
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<td>UNCED</td>
<td>United Nations Conference on Environment and Development</td>
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<tr>
<td>COP</td>
<td>Conference of Parties</td>
</tr>
<tr>
<td>SACS</td>
<td>Saline Aquifer CO$_2$ Storage</td>
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<tr>
<td>LNG</td>
<td>Liquefied natural gas</td>
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<tr>
<td>GSC</td>
<td>Geological Survey of Canada</td>
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<tr>
<td>CCAP</td>
<td>Canada’s Climate Change Action Plan</td>
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<td>IEA</td>
<td>International Energy Agency</td>
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<td>GHSZ</td>
<td>Gas hydrate stability zone</td>
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<tr>
<td>DOE</td>
<td>Department of Energy</td>
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<tr>
<td>EOS</td>
<td>Equation of state</td>
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<tr>
<td>SRK</td>
<td>Soave-Redlich-Kwong</td>
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<td>2D</td>
<td>Two dimensional</td>
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1. Introduction

Gas hydrates (GHs) are well known substances in petroleum industries from long time because of problems related to hydrate formation. The formation of GHs has been responsible for blocking pipelines and process equipments. Petroleum industries spend hundreds of millions of dollars for inhibiting and preventing hydrate formation in pipelines, well and equipment. Numerous research projects have been conducted in this field for overcoming the hazards caused by hydrate formation. This has been the main motivating factor for funding hydrate research in the past.

The main focus in this research work has been on natural gas hydrates (NGHs) and Carbon dioxide (CO$_2$) hydrate. As much as 99% of the world resources of NGHs are of biogenic origin and dominated by methane (CH$_4$). For this reason, the main focus has been on CH$_4$ hydrates. If temperatures are low enough and pressures high enough, CO$_2$ hydrate can form during aquifer storage of CO$_2$. Before going into details about these hydrates and corresponding hydrate phase transition, it is necessary to have basic understanding of GHs. This section is therefore organized with a general brief description of hydrates in section 1.1 followed by a section on hydrate formation and dissociation. Sections 1.3 and 1.4 give some introduction and references to the main systems of focus in this works. A brief review of existing reservoir simulators which have incorporated hydrate is given in section 1.5.

1.1 Gas hydrates

GHs are ice like solid crystalline compounds formed under certain thermodynamic conditions such as low temperature and high pressure. Small gas molecules such as CO$_2$, N$_2$, H$_2$S and CH$_4$ get trapped inside cages formed by hydrogen bonded water molecules. Water is normally denoted as host and gas molecules are called guests in discussions of these crystalline structures. Formations of GHs are not the result of some chemical reactions between guest
and host molecules but are the result of physical encapsulation of the guest molecule by the host. It is mostly due to a water penalty of adjusting structure so as to minimize free energy in the presence of the guest molecules. Guest gas molecules can be polar or non-polar in nature, and it is also not uncommon that more than one type of guest molecules takes part in the formation of GHs. Presently three crystalline structures of GHs have been determined and are well known; Structure I (sI), Structure II (sII) and Structure H (sH) (Sloan and Koh, 2007).

- Structure I is formed with guest molecules having diameter between 4.2 and 6 Å, such as methane, carbon dioxide, ethane and hydrogen sulfide. It is cubical in its crystal structure. One unit cell in it consists of 46 water molecules. It has two small and six large cages in one unit cell. The small cage has the shape of a 12 sided cavity with 12 pentagonal faces in each side and called pentagonal dodecahedron ($5^{12}$). The large cage has the shape of a 14 sided cavity (with 12 pentagonal faces and 2 hexagonal) faces and called tetrakaidecahedron ($5^{12}6^2$).

- Structure II is formed with either by small molecule gases like nitrogen and hydrogen (diameter < 4.2 Å) or by large guest molecules like propane or iso-butane (6Å < diameter < 7Å). It is cubical in its crystal structure. One unit cell is made of 16 small and 8 large cages. Small cage has pentagonal dodecahedron ($5^{12}$) structure. Large cage has 16 sided cavity (with 12 pentagonal faces and 4 hexagonal faces) and called hexakaidecahedron ($5^{12}6^4$).

- Structure H is formed with larger guest molecules like iso-pentane (7Å < diameter < 9Å) when accompanied by smaller molecules such as nitrogen, methane or hydrogen sulfide. Its crystal structure is hexagonal. One unit cell consists of 3 small, 2 medium and 1 large cages. Small cage in this case is also pentagonal dodecahedron ($5^{12}$). Medium cage is called irregular dodecahedron ($4^35^66^3$), it has 12 sided cavity (with 3 square
faces, 6 pentagonal faces and 3 hexagonal faces). Large cage is called icosahedrons \( (5^{12}6^8) \) and it consists of 20 sided cavity (with 12 pentagonal faces and 8 hexagonal faces).

All these three structures of hydrate are consisting of around 85% of water. Many of their mechanical properties are comparable to ice, but some other properties are distinct for example thermal expansion, thermal conductivity and yield strength. This makes the studies related to hydrates very important. More details about these structures and their properties can be found in the book of Sloan and Koh (2007).

1.2 Gas hydrate formation and dissociation

Hydrate formation and dissociation are complex processes involving several competing phases and represent non-equilibrium scenario (Kvamme et al., 2011a, 2011b). Due to fast occurring reactions, some research groups treat hydrate phase transition as equilibrium reactions. But in reality, hydrate systems can rarely achieve equilibrium and for better understanding of the system kinetic approach is more suitable. Gibbs phase rule (Atkins, 2006), which relates the number of components and phases of mixtures to the degree of freedom in a closed system, simply states that hydrate system is in non-equilibrium. In nature, there are normally too many possible co-existing phases for the system to match the two degrees of freedom already imposed by local temperature and pressure.

1.2.1 Hydrate formation

Hydrate formation is a three step process involving hydrate nucleation, growth and induction (quantitative for time for onset of massive growth). Nucleation is normally fast; often it takes only a few nano-seconds (Kvamme, 2002). Second step is the stable growth of hydrate grain. This is also generally fast but very often gets constrained by mass transport limitation. Like for instance on the interface (hydrate former phase/water) formation of hydrate. Once the hydrate film is thick enough serious mass transport limitations though the solid hydrate results in an
induction time which maybe hours (Sloan and Koh, 2007). Induction is the stage in which the growth rate becomes massive (steep change in average growth rate). After this step steady growth of hydrate takes place (Sloan and Koh, 2007).

1.2.2 Hydrate dissociation

Hydrate can exist in favorable thermodynamics, which are regions of low temperature and high pressure conditions. But the stability of hydrates also depends on the concentration of water and hydrate formers in the co-existing phases, including adsorbed phase on mineral surfaces. Although there are several competing reactions between different hydrate phases according to Gibbs phase rule, solid hydrate phase is somewhat stable in low temperature and high pressure conditions. If these conditions change, hydrate start dissociating and produce gas and water (Sloan and Koh, 2007). Some of the gas production methods from NGHs are based on the fact that any disturbance cased in temperature and pressure conditions in GHs can lead to hydrate dissociation.

1.3 Hydrate formation: CO₂ storage

The global warming and increasing energy demand are two big challenges faced by the entire world in the present time. New technologies/methods are being developed to curb the problem of global warming and to increase the energy production from unconventional energy sources. CO₂ is a major greenhouse gas (GHG) responsible for global warming. The process of CO₂ capture, transport to storage site, long term safe storage in deep subsurface geological formations and monitoring of stored CO₂ is called carbon sequestration or carbon capture and storage (CCS). Storage site selection is the first step involving proper investigation of its strength, capacity for CO₂ storage, presence of fractures etc. One potential site for CO₂ storage is saline aquifers. CO₂ can be stored in saline aquifers by injecting it directly into the aquifer. CO₂ will partly dissolve into the groundwater. The rate of dissolution depends on the horizontal and vertical spreading of the CO₂ plume. Over time CO₂ might get trapped by capillary forces inside pores, as well as potentially get trapped through mineralization. If low
temperature and high pressure conditions exist in saline aquifer, there is the possibility of formation of solid CO₂ hydrate if these conditions are inside the hydrate stability regions for CO₂ hydrate. This is the case for the upper regions of several relevant storage reservoirs, including the upper regions of Snøhvit (Heiskanen, 2006), if a CO₂ plume should reach that high.

There are quite a number of possible aquifers for CO₂ storage which contains regions of low enough temperature and high enough pressure to facilitate hydrate formation. This might be positive as a region of very limited vertical permeability and as such some extra sealing capacity. But CO₂ hydrate may also shift regions of horizontal distribution in the same areas so the impacts of CO₂ sealing on one hand and horizontal distribution on the other hand are complex.

Reactive transport reservoir simulator RetrasoCodeBright (RCB) has been developed into a simulator for theoretical studies of CO₂ storage (Liu et al., 2007, 2011). During this PhD project, and other PhD projects in the same research group, this simulator has been extended to account for possible CO₂ hydrate formation and this extension is one of the main deliverables of this project.

1.4 Hydrate dissociation: CH₄ production

A second part of this PhD project have focused on theoretical study of natural gas or CH₄ production from in-situ NGHs or CH₄ hydrates, which are distributed throughout the world both on land in permafrost regions and in offshore deposits. Although the estimates on total amount of gas trapped in NGHs vary, a common number suggest that the trapped energy in natural gas hydrates amounts to twice that of the total oil/gas/coal reserves in the world. This number has been published by Timothy Collett of United States Geological Survey (USGS) few years ago (Collett, 2002, 2004). Earlier estimation is suggest that total amount of gas trapped in NGHs is more than 1.5 × 10^{16} m^3 (Makogon, 1982). Some more recent estimates are even more optimistic, like that from Arthur H Johnson in the National Energy Technology Laboratory (NETL) newsletter (Johnson, 2011).
With time, gradual discovery of huge reserves of NGHs throughout the world led to growing scientific interest in gas hydrates (GHs) for the purpose of gas production from NGHs. Increasing energy demand in the world attracts interest of many researchers and industries to work on unconventional source of energy like NGHs. There are several groups already working on developing new methods for gas production from hydrates. A very common assumption is that hydrates exist in thermodynamic equilibrium in their natural environment in a porous media inside a reservoir. Different approach was followed in this work and it was realized that thermodynamic equilibrium for hydrate phase is not possible. This actually follows from basic thermodynamics and Gibbs phase rule. There are simply too many phases present compared to the number of components that participate in these phase transitions. In a non-equilibrium system different phase transitions will compete under the constraints of first and second laws of thermodynamics (minimum free energy), mass transport and heat transport. This also implies that kinetic description of the different phase transitions are needed. Fundamental modelings of phase transition kinetics are being conducted by other researchers in the same group.

Keeping these two goals in mind, two processes were studied and analyzed: storage of CO$_2$ in cold saline aquifers and production of CH$_4$ from \textit{in-situ} NGHs. Formation and dissociation of hydrates are phase transitions but will throughout this work be treated as quasi reactions. Reactions which have been studied in details in this work are the formation of CO$_2$ hydrate and the dissociation of CH$_4$ hydrate.

1.5 Code comparison

Another goal of this work was to compare RCB with some well known hydrate simulators. The purpose was to check RCB’s performance and efficiency in solving problems involving hydrate phase transition using suitable reservoirs models. Mathematical models and numerical simulators are essential tools for solving hydrate phase transition in reservoirs for both CO$_2$ hydrate and CH$_4$
hydrate related studies. Some of the well known hydrate simulators are TOUGH+ family (TOUGH-Fx/HYDRATE (Moridis et al., 2005a), TOUGH+HYDRATE (Moridis et al., 2008)), HydrateResSim (Moridis et al., 2005b), MH-21 HYDRES (Kurihara et al., 2004), STOMP-HYD (White and Oostrom, 2006), and CMG STARS (CMG STARS user manual, 2004).

Lawrence Berkeley National Laboratory, with support from NETL, developed TOUGH+HYDRATE, the first publicly available model designed exclusively to simulate gas hydrate reservoir behavior and production potential. It is the most recent implementation of the TOUGH-Fx/HYDRATE code (Moridis et al., 2005a). HydrateResSim is a freeware, open-source released by NETL. This open-source version of the code is available for use on NETL website, and NETL provides a limited level of user support for this version of the code. The National Institute of Advanced Industrial Science and Technology, Japan Oil Engineering Co., Ltd. and the University of Tokyo developed MH-21 Hydrate Reservoir Simulator (MH-21 HYDRES). It has been specifically designed to assess production from gas hydrate deposits. The Pacific Northwest National Laboratory and the Petroleum Engineering Department at the University of Alaska, Fairbanks developed gas hydrates simulator STOMP-HYD. Also, those investigating Alaska North Slope gas hydrate resource potential as part of a BP Exploration Alaska, Inc. (BPUA) research project in collaboration with the US Department of Energy have extended work begun at the University of Calgary and the University of Alaska-Fairbanks to apply a commercially available simulator CMG STARS to model production from characterized gas hydrate-bearing reservoirs.

TOUGH+ HYDRATE, HydrateResSim, STOMP-HYD and CMG STARS were designed mainly for handling phase transition of NGHs. These simulators are now also modified such that they can handle both CO₂ hydrate and CH₄ hydrate phase transition. They have been used mostly for gas production studies from NGHs. Recently some CO₂ hydrate related studies were also carried out using these simulators after some upgrading in them. Moridis et al. (2010) developed TOUGH+ HYDRATE to account for CO₂-CH₄ exchange reactions for evaluation

TOUGH+HYDRATE, HydrateResSim, MH-21 HYDRES, STOMP-HYD and CMG STARS were part of code comparison studies carried out by Wilder et al. (2008) and Anderson et al. (2011). These code comparison studies were based on CH₄ hydrate phase transition in reservoir. Wilder et al. (2008) simulated five problems of increasing complexity with all hydrate simulators mentioned above. Hydrate dissociation in 1D and 2D models were carried out and results from all the hydrate simulators were then compared with each other. The output results for the comparison purpose were the produced gas rates, water rates, gas saturation, aqueous saturation and hydrate saturation distribution in reservoir. It was reported that good agreement was observed among all the results produced by all five hydrate simulators for simple 1D and 2D examples.

Anderson et al. (2011) also carried out code comparison study using same five hydrate simulator mentioned in previous paragraph. This study used a 2D model based on Mt. Elbert hydrate deposits. For comparison purpose lag time before significant gas production and gas release/production rates given by all five simulators were used. This study concluded that except for a few exceptions in certain cases, all these codes were in good agreement with each other. Chejara et al. (2012b) compared RCB results with the code comparison study of Anderson et al. (2011). Similarly Chejara et al. (2012a) compared results produced by using RCB code with the results of (Grover et al, 2008a). More details about these comparisons can be found in first two papers included in this thesis.
2. Background

Formation of CO$_2$ hydrates have been an issue in different alternative ways of storing CO$_2$. In ocean storage the depth at which CO$_2$ hydrates can form varies with local sea temperatures and depth and in particular deep ocean storage where CO$_2$ is heavier than water has been argued that hydrate might seal off a CO$_2$ lake on the seafloor. But as discussed several places during this thesis, and the included papers, these system are not equilibrium system. Practically it means that a hydrate seal on the CO$_2$ lake would form and dissociate depending on concentrations of CO$_2$ in the surrounding seawater. Similar situations will occur during aquifer storage in reservoir in which regions of temperature and pressure might facilitate formation of CO$_2$ hydrate. Hydrates in reservoir like either a resource for energy or as a phase transition phenomena during storage of CO$_2$ is the main focus of this thesis and a brief overview of reservoir CO$_2$ storage options are discussed in section 2.1. Section 2.2 gives a short overview on international status on the second focus of this thesis, which is modeling production of methane from methane hydrates.

2.1 CO$_2$ storage

Increase of green house gas CO$_2$ in the atmosphere is by large portions of the scientific community working on climate changes considered to be one of the major factors in global warming. The main reason for targeting CO$_2$ is that among all green house gases, CO$_2$ alone might be responsible for as much as 64% of greenhouse effect (Bryant, 1997). Several energy companies, government agencies, scientist and research laboratories are working toward solutions for reducing emission of CO$_2$ concentrations into the atmosphere. Some of the major efforts in this direction from the international community are evident through many international treaties and commitments proposed by several countries. Many countries pledged their commitment for reducing the total future CO$_2$ emissions. The United Nations Framework Convention on Climate Change (UNFCCC) (UNFCCC Handbook, 2006) is an international
environmental treaty produced at the United Nations Conference on Environment and Development (UNCED), informally known as the Earth Summit, held in Rio de Janeiro in June, 1992. The objective of the treaty is to stabilize greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system (UNFCCC Handbook, 2006). Several other international meetings on the same topic have been arranged, like for instance Conference of Parties (COP) (UNFCCC Handbook, 2006) meetings held every year since 1995.

One of the promising concepts for reducing CO₂ emissions to the atmosphere is called carbon capture and storage. The entire process of removal, or capture, of CO₂ from industrial or utility plant streams, its transport to storage site and its long term storage in such a way that it cannot interact with the climate system is also called CO₂ sequestration (Bachu, 2000). In this work the main focus has been on the final stage of CCS, i.e. safe storage and monitoring of CO₂ in an aquifer storage site.

2.1.1 Methods of geological CO₂ storage

There are several generic modes of geological CO₂ storage (Cooper, 2009). These include storage in:

- Depleted oil and gas reservoirs.
- Association with oil and gas industry enhanced oil recovery (EOR) projects.
- Deep saline formations or aquifers.
- Coal bed formations.

Storage of CO₂ in saline aquifers has been one of the focus areas of this thesis. Saline aquifers are water bearing porous layers of permeable rocks like sandstone or limestone; they are widespread and have high potential for the large scale storage of CO₂ gas. CO₂ get trapped in aquifers through dissolution in water, precipitation as mineral phases, sorption on clay minerals, adsorptions and by
formation of CO₂ hydrate. In this work, dissolution, precipitation of clay minerals and CO₂ hydrate formation possibilities were considered during CO₂ storage. One volume of CO₂ hydrate contains up to 160 volumes of free gas equivalent under standard pressure and temperature conditions. According to some studies saline aquifers have large capacity for CO₂ storage. Gale (2004) estimated that storage capacity of saline aquifers is up to 10,000 Gt. Kvamme et al. (2002, 2007) proposed injection of CO₂ gas into cold saline aquifers containing NGHs. In this concept CO₂ will exchange with CH₄ in the large cavity of structure I and produce a mixed hydrate with up to 75% CO₂. The amount of CH₄ in terms of mole numbers is equivalent to the mole numbers of CH₄ released as energy source.

2.1.2 Current status: ongoing projects on CO₂ storage in saline aquifers

There are several ongoing CCS projects around the world. Among these projects, some are based on the CO₂ storage in saline aquifers. Some of the examples are Saline Aquifer CO₂ Storage (SACS) at Sleipner (Holloway et al., 2004) and Snøhvit (Heiskanen, 2006), Norway; European research project CO₂SINK in Ketzin, Germany (Wuerdemann et al., 2010), CCS project in Salah, Algeria (Mathieson et al., 2010) and The Weyburn CO₂ Project in Saskatchewan, Canada (Preston et al., 2005).

The CO₂ storage at Sleipner, Snøhvit and Salah are industrial projects. SACS was a project undertaken by Statoil. Under SACS project CO₂ injection first started at Sleipner, which is situated in Norwegian margin in North Sea. Sleipner was the first CCS project in the world, started in 1996. The CO₂ produced from natural gas production facility at the Sleipner gas field is captured and stored in sandstone formation called Utsira (Zweigel et al., 2004), which is located more than 800 meter below the seabed. Up to one million ton CO₂ is stored every year. The Snøhvit field is located offshore in the northern Norwegian Sea (the Barents Sea). The CO₂ produced from liquefied natural gas (LNG) facility at Melkøya, is
stored in geological layer of porous sandstone called the Tubâen formation since 2008 (Estublier and Lackner, 2009). Follow-up project of SACS is now known as CO₂STORE (Chadwick et al., 2007); It is a research project with 19 participants from industry and research institutes, partly funded by the European Union. The aim of the CO₂STORE is to identify suitable saline aquifers for future underground CO₂ storage in Norway, Denmark, UK and Germany (Chadwick et al., 2007).

The CO₂SINK project started in April, 2004 and CO₂ injection started in June, 2008. More than fifty thousand tons of CO₂ are injected in the underground (Wuerdemann et al., 2010). In Salah, Algeria, an industrial-scale CCS project has been in operation since 2004. CO₂ is stored as part of a natural gas production process, operated by BP, Sonatrach and Statoil. More than three million tonnes of CO₂ have already been stored in a deep saline formation almost two kilometers below the Earth’s surface (Mathieson et al., 2010). The Weyburn CO₂ Project is the largest CCS project in world; it began in 2000 in Weyburn oilfield, Saskatchewan, Canada. There are actually two separate projects; there is a commercial CO₂ enhanced oil recovery (EOR) project at the Weyburn oil field. The second project is a research project formally known as the International Energy Agency Greenhouse Gas Weyburn-Midale CO₂ Monitoring and Storage Project (Preston et al., 2005). As of June 2010, over 16 million tonnes of CO₂ have been sequestered (Jensen, 2011).

2.1.3 Current status: research on CO₂ storage in saline aquifers with hydrate formation possibility

For an aquifer reservoir to be feasible for CO₂ storage the criteria of sealing integrity in terms of clay and/or shale layers for prevention of leakage though surrounding is still a must. Even though some have claimed that hydrates might seal incompleteness or holes in the sealing if temperature and pressure was in the CO₂ hydrate formation region. As is discussed later in the thesis and the enclosed papers these are non-equilibrium system and at best hydrate formation can slow
down leakage to very low rates and maybe even low enough to be acceptable. If the hydrate dissociation towards the under saturated water above is slow enough then the CO₂ will be dissolved and the heavier water containing CO₂ will sink towards the hydrate layer again. In the best cases of possibilities the water on top of the hydrate might establish a stat of quasi equilibrium between the hydrate and CO₂ saturated water on top. Conventional technologies can be applied to inject CO₂ in suitable storage site, where CO₂ hydrate formation may take place. At present, this concept is based on theoretical considerations and limited laboratory research. Considerable research and development will be required to fully evaluate technology, engineering and environmental practicalities of this concept.

Geological Survey of Canada (GSC) is conducting research to assess the feasibility of geologic sequestration of CO₂ as a solid gas hydrate in reservoirs beneath the Canadian Great Lakes with support from Canada’s Climate Change Action Plan (CCAP, 2005). The GSC research program focuses on advancing the fundamental science of CO₂ hydrate formation and behavior within porous media. It assesses the applicability of conventional oil field methods and engineering technologies for reservoir management, modeling, and subsequent monitoring of the reservoir response to CO₂ injection. One element of this program is an investigation of possible candidate reservoirs for geological sequestration that are located in reasonable proximity to known CO₂ production sources in Canada (Wright et al. 2006).

Shaw (2004) conducted the feasibility study of subterranean disposal of CO₂ as hydrate for the Department of Natural Resources, Pacific Geo-science Centre. APA Petroleum Engineering Inc. was to evaluate technical feasibility on the concept of such a sequestration scheme especially in Alberta where large quantities of GHG are being produced at several major sources related to energy production. In this study, focus should was on depleted gas pools in Alberta, where many pools were identified to be suitable for CO₂ hydrate formation. The other task was to identify technical issues and to design disposal scheme relating to subterranean disposal of CO₂ in hydrate form.
The CO₂ storage in the form of CO₂ hydrate has been considered in several other studies (Takagi et al. 2011; Qanbari et al. 2011; Someya et al. 2006; Koide et al. 1997; Sasaki & Akibavashi 2000; IEA GHG 2000). These studies suggest that injection of CO₂ just below the CO₂ hydrate stability zone in deepwater sediments or sub-permafrost sediments is required in this method. The liquid CO₂ would spread out forming a ‘pool’ capped with an impermeable layer of CO₂ hydrate together with any pre-existing natural low permeability caprock. Some amount of CO₂ may escape through some existing fracture in caprock. When liquid CO₂ rises up and reach to hydrate stability zone in cooler rocks, hydrate formation may start. Significant amount of CO₂ hydrate formation within pore spaces may take place. It will then lead to cementation of sediments by newly formed solid hydrate phase. This cementation by CO₂ hydrate is advantageous for underground CO₂ storage in these terms as suggested by Rochelle et al. (2009):

- It traps CO₂ as a solid hydrate phase.
- It makes relatively poorly consolidated sediment more stable.
- It may help in reducing CO₂ migration through the sediments or, with sufficient hydrate formation, possibly even stopped.

One possibility is that CO₂ hydrate may reduce CO₂ migration through the sediments down to a rate in which possibly dissociated hydrate dissolves into the overlying water.

2.2 Production of natural gas from hydrate filled sediments

NGHs, dominated by CH₄ hydrates, are unconventional sources of energy. Due to the vast amount of CH₄ present in NGHs, it is presently an attractive area for further scientific studies. The challenge at present is to develop advanced technologies for gas production from NGHs which increases the efficiency in terms of volumes produced/day. Several research groups are working in this direction through theoretical work on different scales, experimental work and pilot plants. Despite a rapid increase in general understanding of hydrates in nature every hydrate reservoir is unique because of the natural stationary balance
of a complex non-equilibrium system. The hydrate saturation distribution of each individual reservoir is given by complex connections to fluid flow. Even in the most tightly sealed hydrate reservoirs hydrate saturations are rarely above 50%. Understanding the dynamic nature of each individual hydrate deposit is a necessity for selecting suitable production method and implementation strategy.

2.2.1 Classification of natural gas hydrate deposits

As already mentioned GHs are formed at low temperature and high pressure conditions. Such conditions are found mainly in permafrost regions as well as in some oceanic regions. GHs are stable in a zone called gas hydrate stability zone (GHSZ) in which temperature and pressure condition favors existence of GHs. There are two type of hydrate deposits; permafrost deposits and oceanic deposits. These deposits are further classified into four categories according to well reservoir accumulations; Class 1, Class 2, Class 3 and Class 4 deposits (Moridis and Collett, 2003; Koh et al., 2012; Moridis and Sloan, 2007). Fig.1 illustrates these classifications of hydrate deposits. Class 1, 2 and 3 deposits have high intrinsic permeability, while Class 4 deposits have low intrinsic permeability.

- Class 1 deposits are at the base of the GHSZ. Class 1 accumulations are composed of two layers: the hydrate bearing Layer and an underlying two phase fluid zone containing free or mobile gas and liquid water. There are two kinds of such deposits: the first involves water and hydrate in the hydrate zone (Class 1W, gas-poor system), while the second involves gas and hydrate (Class 1G, water-poor system). In hydrate layer thermodynamically favorable P and T conditions exist, while in the fluid zone, P and T conditions do not favor existence of GHs.

- Class 2 deposits are at the base of, or within, the GHSZ. Class 2 deposits comprise two zones: a hydrate bearing layer overlying and a zone of mobile water below it.
- Class 3 deposits are fully saturated with GHs and are composed of a single zone; the hydrate bearing layer. These deposits are characterized by the absence of an underlying zone of mobile fluids.

- Class 4 deposits comprise low gas hydrate saturations (<10%) and have low intrinsic permeability. Class 4, pertains specifically to oceanic accumulations, and involves disperse deposits that lack confining geologic strata.

![Diagram of hydrate types](image)

**Fig.1 Schematic of types of hydrate (Reconstructed, Moridis and Collett, 2003).**

Each class includes sub-classes, which describe it as confined or unconfined deposits. These sub-classes are named type C, F, M and R. (Boswell et al., 2011) and are described by Koh et al. (2012);

- Type C is hydrate deposits in unconsolidated coarser-grained sediments; it represents much of the permafrost settings and a smaller proportion of the
marine settings. These types of accumulations are most relevant to the potential gas production from hydrates using existing technologies. Some examples of Type C deposits are Nankai Trough, Japan (Fujii et al., 2008) and Mallik, Canada (Boswell et al., 2010).

- Type F is hydrate deposits in unconsolidated, fine-grained and low permeability sediments. This type of accumulations may also be relevant for the gas production from hydrate. Some examples of Type F deposits are offshore Norway (Plaza-Faverola et al., 2010) and Krishna-Godavari Basin offshore East Coast of India (Collett et al., 2008).

- Type M is massive hydrate mounds, associated with cold seeps in very shallow sediments or on the sea floor. These types of accumulations are not sediment hosted. Example of Type M deposits is Gulf of Mexico, Cascadia Margin (Collett et al., 2009).

- Type R is hydrate deposits within rocks. Example of Type R deposits is Messoyahka Field in Siberia (Makogon, 1982).

2.2.2 Methods of gas production from hydrate deposits

Main methods of gas production from hydrate are depressurization, thermal stimulation, use of inhibitors and the CO₂–CH₄ exchange reaction.

- Depressurization, in which the pressure is lowered to below the hydration stability pressure at the constant temperature. Depressurization based production strategies appear well suited for Class 1 and Class 2 deposits due to its simplicity, technical and economic effectiveness. Hydrate response to depressurization based production is relatively fast compare to other methods. The principle is that hydrate is shifted in pressure to a state outside of the pressure, temperature stability region and necessary dissociation energy is transported from the surroundings due to the temperature gradient created by expansion of the surroundings (Makogon, 1997).
• Thermal stimulation, in which temperature is increased above the hydrate stability temperature. Thermal stimulation is slow and ineffective method compared to depressurization, unless immense amounts of heat is injected. Energy requirements are substantial and significant portions of the injected energy is lost in heating of sediments, so it is not economically efficient either. Although thermal stimulation can be effectively used in conjunction with depressurization for localized applications (to destroy secondary hydrate and ice). Similar to tertiary oil recovery the use of controlled burning of in situ hydrocarbon have been proposed as possible production method, although the risks for uncontrolled gas migrations might be a risk (Makogon, 1997).

• Inhibitors addition, in which inhibitors like salts, glycols, and alcohols are added to shift pressure-temperature stability curve for hydrate in such way that hydrate dissociation can be achieved. Inhibitor based production is not considered suitable due to several reasons such as cost of inhibitors, reduced effectiveness because of dilution of the inhibitors by water produced from hydrate dissociation (Makogon, 1997).

• The CO$_2$-CH$_4$ exchange reaction, in which CO$_2$ is injected in CH$_4$ hydrate, which then replaces CH$_4$ from the hydrate and form more stable CO$_2$ hydrate. This method is useful in two ways; CH$_4$ can be produced from NGHs and at the same time GHG CO$_2$ can be stored in geological reservoirs (Kvamme et al., 2004).

In case of Class 3 deposits, permeability of the reservoir is high due to absence of free mobile phase layer; hence depressurization method does not produce results as good as it does in the case of Class 1 and Class 2 deposits. Thermal stimulation and inhibitors based productions are also not effective for Class 3 deposits. Combination of these production methods might be more productive in Class 3 deposits (Moridis et al., 2009).
2.2.3 Current status: ongoing projects on gas production from hydrates

Large scale commercial production from NGHs presents complex problems because each reservoir is absolutely unique. There are several reasons for that; like the non equilibrium nature of hydrates in porous media, geochemistry, porosity trappings etc. A few exceptions do exist where gas is being produced from NGHs. One such example is the Messoyakha gas field (Makogon, 1982), located in the north of the West Siberian Basin, Russia; where gas has already been produced from in-situ NGHs. Gas production from Messoyakha field is mainly from the gas layer underneath gas hydrate layer and conventional gas production led to the depressurization and dissociation of gas from the hydrate layer. So part of the gas production is from the dissociation of NGHs. This has been deduced in different scientific studies on the basis of reported pressure profiles and other sampled data, see for instance Grover et al. (2008b) as one example.

Some pilot scale projects on gas production from NGHs were carried out at Mallik site, Canada in recent times. The Mallik Gas Hydrate Production Research Well, part of the “Methane Hydrate Research and Development (R&D) Program” is located on the northwest side of Richards Islands and is a part of the Mackenzie Delta, entering the Beaufort Sea. The production research well project was developed in the Mallik region after methane hydrate was recovered there by a research project in 1998, led by the Geological Survey of Canada and the former Japan Oil, Gas and Metals National Corporation (JNOC), with participation by USGS, the United States Department of Energy (DOE) as well as other industry partners. The project included working efforts of more than 200 scientists and engineers worldwide. Over a timeline of six years three different wells (two observation wells: Mallik 3L-38 and 4L-38, one production test well: Mallik 5L-38) were successfully drilled at the Mallik research site. In 2002, the first Mallik production test to produce gas from hydrate was carried out. It was the first experiment in the world in which gas was being produced from Class 3
type NGHs and it lasted for 5 days. In total, 470 m³ (surface condition) of gas production was achieved by a thermal-stimulation technique employing hot fluid circulation. After the analysis of experimental data and intensive numerical modeling efforts, the research team concluded that simple reservoir depressurization techniques may be a more efficient gas hydrate production scenario, due to relatively high permeability and an interconnected fluid phase in sand-dominated gas hydrate formations found at Mallik (Yamamoto and Dallimore, 2008).

In 2007, the second Mallik production test was carried out using depressurization techniques and 830 m³ of gas were produced. Although the operation was terminated within 60 hours, total gas production was larger than the first Mallik production test. The test results verified the effectiveness of the depressurization (Yamamoto and Dallimore, 2008).

Another example of pilot scale gas production from methane is ‘The Mt. Elbert Gas Hydrate Stratigraphic Test Well’. It is located on the Alaska North Slope. The well was drilled as part of a larger cooperative agreement between the U.S. DOE and BPXA, in collaboration with USGS and several universities and industry partners, to evaluate whether NGHs from the Alaska North Slope could be viably produced either technically or commercially. The site was selected based on geological and geophysical evaluations that identified the Mt. Elbert site as a fault-bounded gas hydrate trap with two prospective sand-rich reservoirs. Field trial was carried to collect the geologic, petrophysical and engineering data in the Ignik Sikumi #1 gas hydrate test well in April, 2011 (Schoderbek, 2011).

It was a major milestone in a research program based on experimental and numerical modeling studies conducted by ConocoPhillips in partnership with the University of Bergen to demonstrate the potential technical feasibility of the exchange process within porous and permeable sandstone reservoirs (ConocoPhillips, University of Bergen Hydrates Team, 2008). The CO₂-CH₄
exchange reaction method for gas production was tested in the Ignik Sikumi #1 gas hydrate test well. The injection phase of the 2012 production related field trial initiated on February 15 and completed on February 28. During that period nearly \textbf{210,000} standard cubic foot of mixed CO$_2$/N$_2$ gas was injected into the hydrate bearing portion of the Ignik Sikumi #1 hydrate test well. This is an ongoing project and till now amount of production of CH$_4$ is not reported, more results are awaited from this experiment (The Ignik Sikumi Status Report, 2012).

2.2.4 Current status: research on gas production from hydrates

Several researchers are working on theoretical and experimental studies focused on better understanding of NGHs formation/dissociation and gas production from NGHs. Most of these studies are based on gas production from Class 1-3 type hydrate deposits. Some of these studies have also been mentioned by Chejara et al. (2012b). It is important to keep in mind when reading sections below that reservoir modeling of hydrate production is very immature and that most statements are based on the respective author’s conclusions from their own model.

2.2.4.1 Gas production from Class 1 hydrate deposits

Depressurization is often considered the best method for gas production from Class 1 deposits due to its simplicity as well as economical and technical effectiveness. Moridis et al. (2007, 2009) claimed that this is due to a fast response of hydrate to the fast propagating pressure wave. Several research groups studied gas production from Class 1 deposits (Kurihara et al., 2005; Hong and Pooladi-Darvish, 2005; Moridis et al., 2007, 2009; Grover et al., 2008a) from a theoretical point of view. All these studies were based on depressurization induced gas production.

Kurihara et al. (2005) , Moridis and Sloan (2007) suggested that due to strongly endothermic nature of the dissociation reaction, formation of secondary hydrate near production well was one of the possibility which had adverse effects on the
fluid permeability and consequently, on gas production. Thus, the top of the production interval must be located at a sufficient distance from the hydrate layer. Hong and Pooladi-Darvish (2005) applied constant pressure depressurization at a well at the center of a small cylindrical reservoir, and analyzed the sensitivity of the continuously declining production to various properties and operational conditions. Their results indicated that due to endothermic dissociation reaction, temperature in reservoir declined continuously and heat transfer was the dominant mechanism controlling dissociation. Grover et al. (2008a) studied Messoyakha hydrate deposits (Makogon, 1982) and used depressurization technique. Their study concluded that reduction in reservoir pressure during gas production caused gas hydrate to dissociate. Thus, their conclusion was that some part of the gas production was contributed by hydrate dissociation. Chejara et al. (2012a) also studied hydrate dissociation in Class 1 deposits from Messoyakha gas field, and compared results with Grover et al. (2008a). This is discussed in more detail in one of the papers which is part of this thesis.

2.2.4.2 Gas production from Class 2 hydrate deposits

Depressurization is also theoretically found to be the best method for gas production for Class 2 deposits. Moridis and Reagan (2007a) studied Class 2 deposits and used depressurization technique. Due to low permeability of hydrate layer, the top of the production well was kept in mobile water layer. Initially, outer surface of wellbore was heated to cause thermal dissociation of the hydrate and enhance the initial of hydrate dissociation. Due to low permeability of hydrate layer it was found that flow of fluid through the hydrate layer was limited. In order to facilitate dissociation process and increase fluid permeability, hot water was also injected into hydrate layer at a later stage. Production simulations at constant volumetric rates were then carried out from the reservoir. All the gas production came from hydrate dissociation. It was concluded that with lower initial hydrate saturation, gas production is high but this is reversed at later stage when hydrate is depleted. Class 2 deposits gave low gas production initially but this situation improved over time. Moridis and Kowalsky (2006) studied
marine Class 2 deposits and concluded that the production rates were too low to justify considering such accumulations as viable targets.

2.2.4.3 Gas production from Class 3 hydrate deposits

As already mentioned before, depressurization method is not very effective for gas production in the case of Class 3 deposits. Moridis and Reagan (2007b) studied pure thermal stimulation induced gas production and concluded that it had limited potential only. They studied depressurization based production with two different ways i.e. with constant production rate at the well and with constant pressure at the well. Their conclusion was that depressurization with constant production rate was not suitable for Class 3 deposits but depressurization with constant pressure at well was more applicable for deposits with high hydrate saturation.

2.2.4.4 Gas production from Class 4 hydrate deposits

These deposits differ significantly from Class 1-3 deposits in terms of their behavior and gas production potential. Moridis and Sloan (2007) tried to evaluate the gas production potential of disperse, low-saturation ($S_H <0.1$) hydrate accumulations in oceanic sediments through numerical simulation study. They concluded that gas production was very limited from Class 4 deposits. It never exceeded a few thousand cubic meters of gas during the 10-year production period. Their conclusion was that disperse, low-$S_H$ hydrate accumulations in oceanic sediments were not promising targets for gas production.
3. Numerical tool RCB

The code RetrasoCodeBright (RCB) is designed to model complex problems consisting of coupled thermal, hydraulic, geochemical and geomechanical processes. It can be used for simulations of the flow of liquid and/or gas in a multi-phase approach. The code can use one, two and three dimensional finite elements for its spatial discretization. A user friendly interface can be used for pre and post-processing (Saaltink et al., 2005).

3.1 Overview of RCB

RCB is the result of coupling of two codes: CodeBright and Retraso. Fig. 2 illustrates this coupling between these two codes. CodeBright (COupled DEformation of BRIne Gas and Heat Transport) was designed for the thermo-hydraulic-mechanical analysis of three-dimensional multiphase saline media (Olivella et al., 1996). Retraso (REactive TRAnsport of SOlutes) was designed for solving two-dimensional reactive transport problems (Saaltink et al., 1997). Basically, in the coupled code RCB, a CodeBright module calculates the flow properties (Darcy flux of liquid and/or gas, saturation, temperature, density, etc.) and passes it to a Retraso module for the calculation of reactive transport.
Fig. 2 Functioning of RetrasoCodeBright
3.2 Governing equations and processes in the CodeBright part of RCB

RCB applies multi-phase approach for flow process. This helps in dealing with porous media which is composed of solid grains, water and gas as illustrated in Fig. 3. In porous media, hydraulic and thermal aspects are taken into account; simultaneous interaction between these two is considered in an integrated way. Three phases are considered: solid phase (minerals), liquid phase (water and dissolved air/gas) and gas phase (air/gas and water vapors). In total, three components are considered: water, dry air (or gas) and heat.

Fig.3 Schematic of unsaturated porous media

To each of these components, a state variable is associated, for water (liquid pressure $P_i$), for air/gas (gas pressure $P_g$) and for heat (Temperature °C). Mass balance equations for water and air are expressed as a function of state variables
or independent variable and dependent variables. The equation for internal energy balance for the porous medium is established taking into account the internal energy in each phase. Mass balance equations, internal energy balance equation and boundary conditions are given in details elsewhere (Saaltink et al., 2005). A set of constitutive and equilibrium laws are used to express the various parameters or dependent variables of the mass balance equation as functions of the state variables or independent variables. Some examples are Darcy's law that relates liquid and gas advective fluxes to pressure gradients, Fourier's law that relates conductive heat flux to temperature gradient, retention curve that relates saturation to capillary pressure and the psychrometric law that relates vapor mass fraction to temperature and capillary pressure. A full list of all constitutive and equilibrium restrictions can be seen elsewhere (Saaltink et al., 2005). Table 1 presents balance equations, constitutive equations and equilibrium restriction along with corresponding variables.

Table 1. Summary of Equations and Variables in RCB (Olivella et al., 1994)

<table>
<thead>
<tr>
<th>Equation Names</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Balance Equations</strong></td>
<td></td>
</tr>
<tr>
<td>Solid mass balance</td>
<td>$\Phi$ Porosity</td>
</tr>
<tr>
<td>Water mass balance</td>
<td>$P_l$ Liquid Pressure</td>
</tr>
<tr>
<td>Air mass balance</td>
<td>$P_g$ Gas Pressure</td>
</tr>
<tr>
<td>Energy balance</td>
<td>$T$ Temperature</td>
</tr>
<tr>
<td>Momentum balance</td>
<td>$\dot{u}$ Solid velocity</td>
</tr>
</tbody>
</table>
3.3 Governing equations and processes in reactive transport part of RCB

RCB uses the mathematical formulation for reactive transport of Saaltink et al. (1997) with the addition of terms for the transport and chemistry of gaseous species. Detailed information for mass balance and boundary conditions of reactive transport are given elsewhere (Saaltink et al., 2005).

3.3.1 Chemical species

A chemical system is made up of a set of atomic constituents or elements. A chemical species is defined as any chemical entity distinguishable from the rest
due to (1) its elemental composition, and (2) by the phase at which it is present. For instance, CO$_2$ gas is a different species than dissolved CO$_2$. There are two set of species in RCB: primary and secondary species. Primary species are independent of other chemical species. The rest of chemical species other than primary species are called secondary species (aqueous complexes, minerals, gases, and surface complexes). The method for specifying the primary and secondary species is based on that devised by Peter Lichtner for the code MPATH (Lichtner, 1992) and used by Carl Steefel for the code 1DREACT (Steefel, 1993). The code RCB requires the user to specify a set of aqueous primary species (or component species) to determine the number of independent components of the system. The routine database is able to express the secondary species as a function of the set of primary species defined in the chemical system. Secondary species are expressed as lineal combinations of primary species. Unlike conventional geochemical modeling codes, the user can select the secondary species which will be the part of the calculations. This allows performing chemically simplified calculations very useful for multi-component reactive transport problems. The amount of computing time saved is significant compared with the codes assembling a conventional transport and geochemical codes. The run of a geochemical speciation code, such as PHREEQC (Parkhurst and Appelo, 1999) or EQ3NR (Wolery, 1992), for the different expected situations of the problem is recommended in preparing the definition of the chemical input for a reactive transport problem. The user must include among the primary or secondary species the species used in describing the reaction in the masster25 or mastertemp database (geochemical database files).

3.3.2 Chemical reactions

Chemical reactions are divided into different categories: chemical equilibrium reactions, aqueous complexation, adsorption reactions and mineral dissolution/precipitation reaction. Chemical equilibrium is determined based on minimum Gibbs free energy of the system. Adsorption of aqueous species on the surface of solids has been described according to several empirical relationships
and thermodynamic models. The empirical relationships are experimental partition coefficients between the solute in solution and the solute adsorbed. The relationships included in the RCB code are the Freundlich and Langmuir equations, and the ion exchange model. The thermodynamic models are based on surface complexation reactions. The thermodynamic models included in RCB are: the triple layer, diffuse layer, the constant capacitance and the non-electrostatic models. These equations and models are described in details by Saaltink et al. (2005).

3.3.2.1 Solid-liquid interactions (mineral dissolution and precipitation)

There are two approaches for dealing with mineral dissolution and precipitation reaction in RCB: equilibrium and kinetic approaches. Under equilibrium conditions, dissolution-precipitation reactions are described by the Law of Mass Action:

\[
X_m \gamma_m K_m = \prod_{i=1}^{N_c} (c_i^{v_{mi}} \gamma_i^{v_{mi}}) \tag{1}
\]

where \(X_m\) is the molar fraction of the \(m\)-th solid phase, \(\gamma_m\) is its thermodynamic activity coefficient (\(X_m\) and \(\gamma_m\) are taken equal to 1 for pure phases), \(c_i\) and \(\gamma_i\) are the concentration and activity coefficient of the \(i\)-th species, \(v_{mi}\) its stoichiometric coefficient in the dissolution reaction of the \(m\)-th solid phase, and \(K_m\) is the corresponding equilibrium constant.

Since NGHs are not able to attain proper equilibrium, a kinetic approach in RCB has been applied in this study, in which hydrates were treated as pseudo minerals. Kinetics rates of hydrate formation and dissolution in a porous medium is normally faster than corresponding processes for minerals. Geological processes like dissolution and precipitation of many minerals are slow and would rarely reach equilibrium. In RCB, the calculations of kinetic reaction rates for mineral
dissolution and precipitation are based on an equation proposed by Lasaga et al. (1984):

$$r_m = \sigma_m\zeta_m \exp\left(\frac{E_{a,m}}{RT}\right) \sum_{k=1}^{N_k} k_{mk} \prod_{i=1}^{N_i} a_i^{p_{mi}} \left(\Omega_m^{\theta_{mk}} - 1\right)\eta_{mk}$$  \hspace{1cm} (2)$$

Where

$$\Omega_m = \frac{1}{k_m} \prod_{i=1}^{N_i} a_i^{p_{mi}}$$  \hspace{1cm} (3)$$

And

$$k_m = k_0 \exp\left(-\frac{E_{a,m}}{RT}\right)$$  \hspace{1cm} (4)$$

Where $r_m$ is the mineral dissolution rate (moles of mineral per volume of rock and unit time), $k_{mk}$ is the experimental rate constant, $\Omega_m$ is the ratio between the ion activity product for the real concentrations and the corresponding equilibrium constant. The parameters $\theta$ and $\eta$ must be determined by fitting to experimental data; for some reactions they are set equal to 1. $E_{a,m}$ is the apparent activation energy of the overall reaction process, $k_0$ is a constant. Both $k_0$ and $E_{a,m}$ are determined from experiments performed at different temperatures. $\sigma_m$ is the reactive surface. The term $a_i^{p_{mi}}$ accounts for the catalytic effect of some species (particularly of $\text{H}^+$). Factor $\zeta_m$ takes on values of +1 or -1 depending on whether $\Omega_m$ is larger or smaller than 1 (precipitation or dissolution), respectively. At equilibrium $\Omega_m = 1$, and therefore $r_m = 0$.

Different kinetic equations for different GHs were used as an alternative to existing mineral reactions in RCB code. This part will be discussed in details in Chapter 4.

3.3.2.2 Aqueous complexation reactions

The concentration (per unit volume) of dissolved ions in water is high and these ions are in continuous motion. This causes numerous collisions between them, which results in the formation of ion pairs and/or dissolved complexes. These reactions are almost instantaneous and are treated as equilibrium reactions. Eq. 5 below represents aqueous complexation reaction.
\[ \log K_a = S_a \log C_a + S_a \log \gamma_a(C_a) \] (5)

Where, \( K_a \) is the equilibrium constant vector, which depends on temperature and pressure. \( S_a \) is the stoichiometric coefficient matrix for aqueous complexation reactions. \( C_a \) is the molar concentration vector of aqueous species and \( \gamma_a \) is the vector of thermodynamic activity coefficients.

3.3.2.3 Gas-liquid interactions

Gas-liquid interaction reactions are considered as equilibrium reactions in RCB. It is assumed that all gas-liquid reactions are sufficiently fast with respect to flow. For reactions involving aqueous and gaseous phases the mass action law states that:

\[ p_f \gamma_f K_f = \prod_{i=1}^{N_c} (c_i^{v_{fi}} \gamma_i^{v_{fi}}) \] (6)

where \( p_f \) is the partial pressure of the \( f \)-th species in the gas phase, \( \gamma_f \) is its activity coefficient, \( c_i \) and \( \gamma_i \) are the concentration and activity coefficient of the \( i \)-th dissolved primary species, respectively, \( v_{fi} \) is the stoichiometric coefficient of the \( i \)-th species in the exsolution reaction of fluid \( f \), and \( K_f \) is the equilibrium constant of the reaction.

3.4 Porosity and permeability calculations in RCB

Porosity and permeability calculations take place in both CodeBright and Retraso parts of RCB. Porosity and permeability are first calculated in CodeBright part and then are updated in Retraso part. Reactive transport properties can affect the thermo hydraulic problems. RCB can model the effects of dissolution and precipitation of minerals on porosity and permeability.

The change in porosity (\( \Delta \phi \)) is calculated from the change in the concentrations of the minerals (\( \Delta c_{m} \)) through Eq. 7 below:

\[ \Delta \phi = -\sum_i v_{m,i} \Delta c_{m,i} \] (7)
Intrinsic permeability and relative permeability of liquid/gas are calculated based on porosity. For calculation of intrinsic permeability, Kozeny’s model has been used (Bear, 1972):

\[ k = k_o \cdot \frac{\varphi^3}{(1-\varphi)^2} \cdot \frac{(1-\varphi_o)^2}{\varphi_o^3} \]  

(8)

Liquid phase relative permeability is defined as:

\[ k_{rl} = A \cdot (S_e)^\lambda \]  

(9)

Gas phase relative permeability is defined as:

\[ k_{rg} = A \cdot (S_{eg})^\lambda \]  

(10)

Where, \( S_e \) is effective saturation for liquid and \( S_{eg} \) is effective saturation for gas. These are calculated from Van Genuchten model (van Genuchten, 1980):

\[ S_e = \frac{S_t - S_{rl}}{S_{tl} - S_{rl}} = [1 + \left(\frac{P_g - P_l}{P}\right)^{\frac{1}{1-\lambda}}]^{-\lambda} \]  

(11)

\[ S_{eg} = \frac{S_g - S_{rg}}{S_{ge} - S_{rg}} \]  

(12)

\[ P = P_0 \cdot \frac{\sigma}{\sigma_o} \]  

(13)

The surface tension (\( \sigma \)) is calculated according to Eq.14 below (Horvath, 1985):

\[ \sigma = 0.03059 \cdot \exp\left(\frac{252.93}{273.15+T}\right) + 0.04055 \cdot \omega_i^h \]  

(14)

\[ \omega_i^h = \frac{\Sigma_i c_{ai} M_i}{1 + \Sigma_i c_{ai} M_i} \]  

(15)

Where, \( \Lambda \) is a constant. \( P_0 \) Measured \( P \) at certain temperature, \( \sigma_o \) is surface tension at temperature in which \( P_0 \) was measured. \( \lambda \) is shape function for retention curve. \( S_{rl} \) is residual saturation; \( S_{tl} \) is maximum saturation for liquid phase. \( S_{eg} \) is
residual saturation; $S_{gs}$ is maximum saturation for gas phase. $\omega_i^k$ is mass of solute per mass of liquid. $M_i$ is the molecular weight.

3.5 Pre- and post-processors: VisualRetraso and GiD

VisualRetraso (Saaltink et al., 2005) has been used as a pre-processor and GiD (GiD user manual, 2012) has been used as a post-processor along with the code RCB. VisualRetraso and GiD are two interactive graphical user interfaces. VisualRetraso has been used for building simulation models. In VisualRetraso selection of chemical species, definition of the geometry, geochemical data, thermo-hydraulic data and geo-mechanical data were the main inputs. The output files of VisualRetraso have been used as input files in RCB after some modifications. Other input files required in RCB along with these input files are chemical equilibrium and kinetic database files. After the simulations, the output files of RCB have then been visualized using GiD. Fig.4 illustrates the entire process from pre-processor to post-processor.

Fig.4 Flowchart of VisualRetraso-RCB-GiD sequence
4. Modifications in RCB and Simulation Work

The main goal in this work has been to develop the reservoir simulator RCB further into a hydrate simulator, which is capable of handling hydrate formation and dissociation "reactions". At this stage, RCB is being developed such that it can handle simple hydrate formation/dissociation reactions along with some complex mineral reactions in a typical reservoir.

4.1 Addition of new hydrate components

In the input files, RCB requires two types of database files; geochemical and kinetics database files. There are two geochemical database files and are called mastertemp and master25. For isothermal calculations at 25°C temperature and 1 bar pressure, master25 is used. For non-isothermal calculations or in the case of isothermal calculations at temperature other than 25°C, mastertemp is used. Mastertemp is an extension of temperatures from 0 to 300°C and pressure along the steam saturation curve. Both files of database are modified versions of the EQ3/6 database created by Peter Lichtner for the code MPATH (Lichtner, 1992). Geochemical database files contain details related to chemical reactions, primary and secondary components in these reactions, logK entries and the temperatures of each logK entry. The databases are able to express the secondary species (aqueous complexes, minerals, gases, surface complexes) as a function of the set of primary species defined in the chemical system. Kinetics database file contain the data describing the kinetic rate law for dissolution/precipitation of minerals.

CO₂ hydrate and CH₄ hydrate have been added as pseudo-minerals in RCB. All the data files for RCB as well as input files have been updated accordingly. RCB code itself has been modified to accommodate new components as well as their connections with the entire code. CO₂ hydrate and CH₄ hydrate have also been added in both geochemical and kinetic database files. The provision in RCB is such that solid hydrates can only be treated as pseudo-minerals, then only it is possible to add them in database files. The database has been updated
accordingly. Three components of hydrate phase transition; CO₂, CH₄ and H₂O were already present in the database. This made it straightforward to define hydrate “reactions” in terms of already existing primary and secondary components in the database. Newly updated version of RCB has been tested on various examples involving hydrate phase transitions in saline aquifers. The results of these examples from various theoretical simulations are given in papers I-VI.

4.2 Updated equation of state and solubility parameters for CH₄

In RCB, air is the default gas for equation of state (EOS) and solubility calculations. Liu and Kvamme (2007) added CO₂ as an alternate to air for these calculations and used improved code for geological CO₂ storage studies. Chejara et al. (2012a) extended it further by adding EOS and solubility calculations for CH₄. The EOS parameters for CH₄ such as critical temperature Tₛ, critical pressure Pₑ and acentric factor ω given by Knapp et al. (1982) have been used to update Soave-Redlich-Kwong (SRK) EOS (Soave, 1972). For solubility calculations, Henry’s constant for CH₄ has been added in to the code according to Dean (1992).

4.3 Inclusion of temperature variation in calculations

RCB had been used mostly for isothermal conditions at 25°C temperature. In such cases, entire reservoir has to be considered at isothermal conditions. In this work, temperature variation has been considered for some of the simulations. For this purpose initial temperatures have been assigned at each node in reservoir. Initial nodal temperatures have been calculated based on an anticipated value for the geothermal gradient in the reservoir. Hydrates “reactions” are very sensitive to temperature changes as small change in temperature can trigger hydrate formation or dissociation. RCB provides a facility to include temperature change in calculations. The addition of temperature variation in already complex reservoir calculation has been a challenging task. A sensitivity analysis of the
code with respect to temperature sensitivity of the different variables calculated
during the integration in each step made it possible to overcome these challenges
and the current modified version handles temperature variations efficiently and
robust.

4.4 Addition of hydrate saturation

Hydrate saturation calculations in RCB in the present version are based on
already existing calculations related to porosity changes mentioned in Eq. 7. RCB
updates porosity according to solid mineral dissociation or precipitation. GHs are
treated similar to other minerals and hydrate dissociation contributes directly to
increase of available pore volume for fluids, or efficient porosity. Similarly, if
solid hydrate formation takes place in a reservoir, it directly reduces available
pore volume for fluids and as such reduces reservoir porosity. RCB updates
porosity first, and then updates permeability according to porosity changes, as
mentioned, through Eq. 8. One more route into these calculations has been
created by adding hydrate saturation calculations in the code. The output of these
newly added calculations gives updated spatial distribution of hydrate saturation
which then can be viewed using post-processor graphical window GiD (GiD user
manual, 2012). At this stage we have not made any changes to the correlations
between saturations of different phases in the pore and permeability although it is
clear that hydrate behaves quite differently in pores compared to ordinary
minerals.

4.5 Kinetic approach for gas hydrate phase transition

The kinetic reactions for hydrate formation and dissociation for both CO₂ hydrate
and CH₄ hydrate has been added in to the code as a function of temperature and
pressure. These equations are over simplified version of complex phase transition
scenario. The relationship between pressure and temperature has been defined
such that favorable conditions for both formation and dissociation are
incorporated in the absence of advanced non-equilibrium thermodynamics code.
This relationship is presented by Eq.16 for CO$_2$ hydrate and by Eq.17 for CH$_4$ hydrate.

For CO$_2$ hydrate, equilibrium relationship between pressure $P_e$ and temperature $T$ proposed by Phirani and Mohanty (2010) has been used:

$$P_e = 5.624214942384240 \cdot 10^8 - 1.175309918126070 \cdot 10^7 \cdot T +$$
$$1.022898518566810 \cdot 10^5 \cdot T^2 - 4.745780290305340 \cdot 10^2 \cdot T^3 +$$
$$1.237931459591990 \cdot T^4 - 1.721355993747740 \cdot 10^{-3} \cdot T^5 +$$
$$9.968156693851430 \cdot 10^{-7} \cdot T^6$$

(16)

For CH$_4$ hydrate, equilibrium relationship between pressure $P_e$ and temperature $T$ ($T>0$ °C) proposed by Sloan (1998) and Alps et al. (2007) has been used, it is given below:

$$\ln P_e = -1.94138504464560 \cdot 10^5 + 3.31018213397926 \cdot 10^3 \cdot T -$$
$$2.25540264493806 \cdot 10^1 \cdot T^2 + 7.67559117787059 \cdot 10^{-2} \cdot T^3 -$$
$$1.30465829788791 \cdot 10^{-4} \cdot T^4 + 8.86065316687571 \cdot 10^{-8} \cdot T^5$$

(17)

Kinetic rates of formation and dissociation of hydrates has been calculated according to Kim–Bishnoi model (Kim et al., 1987). These are represented by Eq. 18 and Eq. 19.

If ($P_e < P$) then hydrate formation takes place according to Eq. below:

$$R_k = C_f \cdot (P - P_e) \cdot A$$

(18)

If ($P_e > P$) the hydrate dissociation takes place according to Eq. below:

$$R_k = -C_d \cdot (P_e - P) \cdot A$$

(19)

Where, $C_f$ and $C_d$ are formation and dissociation constants respectively. Value $C_f$ and $C_d$ have been taken from the work of Baig (2009). $A$ is initial reactive surface area of the $k^{th}$ mineral (m$^2$ min/ m$^3$ rock).
4.6 Sensitivity analysis of the code

In the newly updated RCB, one of the challenges had been to eliminate the divergence problems. Substantial efforts have been put into investigation of the input parameters, the selection of suitable models and the appropriate boundary conditions. It was found that one of the parameters in one of the input files ‘gen.inp’ had significant influence on convergence / divergence of calculations during simulations. It is called ‘ITIME’ and it performs time adaptation as a function of several convergence criteria provided in the same input file. In short, time increments during time step are adapted by the code according to ITIME. Time adaptation affects overall calculations as these are based on time intervals assigned for each time steps in simulations. A new time increment is predicted from the relative error in variables of the previous time increment. If the relative error is less than defined minimum error value (0.01 in this case) then time increment is reduced according to error deviation. This may cause inconveniences if the user desires the results at precisely fixed times. Values of ITIME from 1 to 10 have been tested on a simple model of saline aquifer to check the sensitivity of the code with respect to this parameter. It has been found that smoother calculations are performed in the code when ITIME value is equal to 6 in most of the cases.

Other important factors which determine convergence of simulations are nature of simulation model, boundary conditions, and initial temperature and injection/production fluid pressure values. Setting up the simulation models as well as defining the boundary conditions requires careful attention and some experience in the sensitive of the code to different variables in order to run smoothly. As mentioned above there were initial problems due to temperature variations, when energy balance and varying temperature was introduced into the calculations. This caused some dramatic changes in reservoir temperatures and led to divergence. Proper selection of input variables and gas injection/production points helped in overcoming these problems.
The sensitivity analysis has been carried out for various cases of gas production from CH₄ hydrate deposits and also for CO₂ storage. As naturally expected it was observed that initial fluid permeability is an important input that can affect output results significantly. Also the spatial hydrate saturation calculations are based on simplified assumptions that basically assume that available volume changes occur on basis of addition or reduction of minerals to pore wall. This may cause permeability changes in entire reservoir more rapid, which in turn can results in divergence of simulation. This problem has been overpowered by using low permeability examples. A proper permeability correlation might help in overcoming these problems. Hydrate is unable to attach to mineral surfaces and unlike minerals they will form geometrically shaped particles in the centre of the pore.
5. Summary of Papers

5.1 CH₄ production from low permeability hydrate deposits (P-I)

In this paper the main goal was to simulate low permeability Class 3 type hydrate deposits from Mt. Elbert site, Alaska and compare the results with the code comparison study of Anderson et al. (2011). An important objective of this paper was to check the capabilities of RCB to handle hydrate phase transition with kinetic approach and compare this with equilibrium approach used by other research groups with well known hydrate simulators. The RCB code has been developed as a new hydrate simulator and it is entirely different in the way it handles hydrate as a pseudo mineral within a reactive transport simulator. The advantage of this is that the code is able to handle different hydrates as arising from different hydrate formation situations (interface, solution, adsorbed), as well as different dissociation situations (pressure, temperature, concentrations). It is not only capable of competing with other well known hydrate simulators but also is a good alternative due to its multi-functional roles. It can handle kinetic and equilibrium hydrate reactions and simultaneously, it can address related geo mechanical analysis of the reservoir through an implicit analysis. Keeping in mind that hydrate production which involves dissociation reduces the pore filled volumes and may lead to significant changes in the stability of the reservoir during the gas production process.

The trend of some of the results, such as continuous increase in gas production rates and value of maximum gas production rate were comparable with the results reported by Anderson et al. (2011) for hydrate simulators TOUGH+HYDRATE (Moridis et al., 2008), HydrateResSim (Moridis et al., 2005b), MH-21 HYDRES (Kurihara et al., 2004), STOMP-HYD (White and Oostrom, 2006), and CMG STARS (CMG STARS user manual, 2004). RCB produced some good results such as ‘lag time’ compared to other hydrate simulators. Lag time is the approximate time before good gas production rates are obtained. Detailed code comparison is given in the paper. A 2D model was built, which resembled actual
hydrate deposit site at Mt. Elbert, Alaska. The selection of hydrate deposit site has been based on the model also considered in the code comparison study of Anderson et al. (2011). This paper also contains results for geo-mechanical effects of hydrate dissociation on the reservoir. Results for changes in stresses and effective stresses (in xx and yy directions) with time are included in the paper.

5.2 CH₄ production from high permeability hydrate deposits (P-II)

This was the first paper on gas production from in situ hydrate deposits using the newly developed hydrate simulator RCB. This paper has demonstrated that implementations of hydrate into RCB with respect to newly added component CH₄ hydrate, and corresponding hydrate reactions have been working properly. Simulation model has been constructed by following an example of Class 1 type hydrate deposits from real life NGHs deposits Messoyakha gas field (Makogon, 1982), Russia. There has been gas production from this reservoir since 1970. Some studies confirmed that portions of the gas originated from dissociating hydrate from hydrate layer that is present above the free gas zone (Grover et al, 2008b). Modeling of production from this reservoir has been conducted using simple hydrate dissociation reaction and results have been then compared with the results obtained by another hydrate simulator TOUGH+HYDRATE (Moridis et al., 2008) in the paper of Grover et al. (2008b).

5.3 CO₂ hydrate dynamics; CO₂ storage in saline aquifer (P-III)

A kinetic approach has been used for hydrate phase transition and kinetic rates obtained from phase field theory simulations (Baig, 2009) have been employed. A simple model based on one zone of saline aquifer was used for this study. This aquifer had both hydrate stability and instability zones. When CO₂ migrated upward (as indicated by results for gas phase flux) and reached hydrate stability zone, hydrate formation took place. Results for porosity changes confirmed
hydrate formation in some parts of the aquifer. This work was an extension of earlier work reported in paper V.

5.4 Non-equilibrium hydrate dynamics during CO₂ storage (P-IV)

The work reported in this paper was an extension of study carried out earlier (paper III). The non-equilibrium nature of hydrate in porous media has been investigated in this paper. Non-equilibrium conditions have been applied to hydrate phase transition (formation and dissociation). One goal of this study has been to move from equilibrium conditions to non-equilibrium conditions in future for all hydrate phase transition reactions. The work reported in this paper is one of the steps forward towards that goal. Non-equilibrium conditions represent a more accurate picture of the complex system that exists in reservoirs, where the number of possible phase makes equilibrium impossible according to Gibbs phase rule.

In case of hydrate formation and dissociation in the reservoir, the entire system is very complex. Hydrate formation or dissociation towards all possible phases with different free energies will produce different product phases. Consequently, degree of freedom will decrease further and there will be no equilibrium condition and competing phase transition reactions of hydrate formation, dissociation and reformation among different phases will rule the system. This paper reports on results for an example of CO₂ storage in a saline aquifer with one fracture in the middle of the sealing layer. The saline aquifer had a zone of CO₂ hydrate stability, where hydrate formation dynamics was studied. On the basis of the statistical mechanical model proposed by Kvamme and Tanaka (1995) differences in properties of hydrates formed from different phases have been illustrated and discussed.
5.5 CO₂ hydrate formation during CO₂ storage in cold aquifer (P-V)

This paper was the first paper published after the extension of RCB in to a hydrate simulator. Previously RCB had been extended to CO₂ storage studies by Liu et al. (2007, 2011). This work carried out similar CO₂ storage studies but with one more possibility taken into the consideration i.e. gas hydrates/hydrate dynamics in reservoir to evaluate the possibility of hydrate formation during CO₂ storage. A simple model was used which had two aquifer zones and one caprock zone separating two aquifers. One fracture in the middle of the caprock was also included in the model. The hydrate stability zone existed above the caprock and the hydrate instability zone existed below the caprock. CO₂ was injected from the bottom right corner of lower aquifer. When CO₂ escaped through the fracture, hydrate formation took place in the vicinity above the fracture. This was confirmed by the results for porosity reduction in the area above fracture, which indicated formation of solid hydrate phase in that area. It was a demonstration of RCB’s capabilities to handle hydrate phase transition reactions and the first step for further improvements of RCB as a hydrate simulator.

5.6 Geo-mechanical effects of CO₂ injection and hydrate formation (P-VI)

In this paper, a model almost similar to that used in paper V was considered, but the model had two fractures in the caprock. Due to implicit calculation of geo-mechanics along with flow equations, it is possible to study the effects of hydrate formation and dissociation on geo-mechanics of the reservoir in the same time step in which transport calculations are done. The CO₂ storage with the possibilities of hydrate formation in reservoir was studied and geo-mechanical impacts of hydrate formation were analyzed. It was concluded that reservoir might be in safe limits from tensile failure.
6. Conclusion

The papers included in this thesis have demonstrated that reservoir simulator RCB is capable of handling hydrate phase transitions as pseudo reactions. The simulator has significant potential for further improvement as a hydrate simulator since non-equilibrium thermodynamics is easily handled in it. And to our knowledge it is the only hydrate simulator which has implicit geo mechanical analysis. The application area of RCB has been significantly increased in this work. Published results in the papers I-VI provide a new insight of RCB as a hydrate simulator. Some main conclusions of this PhD work are:

- Hydrates in porous media are generally in non-equilibrium state. Equilibrium in such systems cannot be achieved due to over defined parameters such as fixed temperature and pressure conditions. According to Gibbs phase rule, degrees of freedom of such cases are low so kinetic approach is the best way to understand such systems.

- With the addition of new hydrate components as pseudo minerals “CO₂ hydrate” and “CH₄ hydrate” RCB now can be used for CO₂ storage studies with the possibility of hydrate formation and also for simulations of CH₄ production from NGHs deposits.

- Kinetic models for CO₂ hydrate and CH₄ hydrate phase transitions has also been incorporated in the code and opens up future implementations of all significant competing phase transitions locally in a reservoir.

- It has been demonstrated that if a CO₂ plume during aquifer storage enters CO₂ hydrate formation region in terms of temperature and pressure then hydrate formation takes place. This affects vertical and horizontal flow and distribution of CO₂. It also affects the mechanical properties in the reservoir. Even Snøhvit storage has regions of hydrate forming conditions and it is likely that a number of other potential storage sites offshore the northern parts of Norway will have. The models developed in this project
might assist in CO₂ storage studies in future, especially for the cases where
the storage site involves regions of hydrate formation.

❖ Productions of CH₄ from real hydrate deposits have been investigated.
Results from CH₄ production simulations demonstrated reasonable results,
even with simple constant kinetic rates of "reactions". The complexity of
the problems and successful numerical solutions shows that RCB can be
used further in such studies.

❖ Comparison of RCB with other well known simulators has given
comparative results and on the basis of this RCB can be considered as an
established hydrate simulator.

❖ Simulations with complex models and more realistic operating conditions
are now possible due to some sensitivity studies carried out in this work,
and subsequent modifications in algorithms and routines for setting up and
initiating the simulations.

❖ Although RCB has been upgraded into a hydrate simulator there is still
much further work to do. One important task is the completion of non-
equilibrium thermodynamics in the hydrate phase transition calculations.
Equilibrium situation practically do not exist in a reservoir situation but if
it did, or if special technical interactions created situation of equilibrium,
then a minimization of free energy would be the route to compositions of
co-existing phase. Otherwise, which is the more general case, kinetic
description of all possible situations of formations and dissociation would
result in a net change in every grid point at every time step.
7. Suggestions for Future Works

7.1 Addition of CO₂ hydrate-CH₄ hydrate exchange reaction in RCB

As a hydrate simulator RCB can simulate more than one hydrate phase transition reactions simultaneously since it is based on a reactive transport simulator basis. Until now, CO₂ hydrate and CH₄ hydrate reactions in RCB were studied separately. It is possible to analyze complex exchange reactions involving CO₂ hydrate, CH₄ hydrate and mix CO₂-CH₄ hydrate. In this way, it will be possible to combine two processes: CO₂ storage and CH₄ production from same reservoir. It is already proven by some experimental studies that CO₂ hydrate is more stable than CH₄ hydrate at same temperature-pressure conditions for substantial region of temperature and pressure and that CO₂ can replace CH₄ from solid hydrate phase (Kvamme et al., 2007). Exchange reactions which result in conversion of CH₄ hydrate into mix-CH₄-CO₂ hydrate or predominately/entirely CO₂ hydrate can be added in RCB in future. Experimental data and results from Ignik Sikumi #1 gas hydrate test well (Schoderbek, 2011) can be used for such studies involving CH₄ hydrate - CO₂ hydrate exchange reactions.

7.2 Inclusion of non-equilibrium thermodynamic code in RCB

At the present moment, RCB lacks proper thermodynamics for all competing hydrate phase transitions in non equilibrium situations. In the absence of these, simple and constant kinetic rates were used for some selected hydrate phase transition “reactions”. New non-equilibrium thermodynamic code should be developed and added in to the RCB code in future. It will enable RCB to estimate net kinetic reaction rates and favorable conditions for formation and dissociation of hydrates based on minimum Gibbs free energy criteria. Local effects of formations and dissociation reactions due to different surroundings may have significant effect on simulated production rates. It is suggested that some of the results published in Chejara et al. (2012a, 2012b) and Vafaei et al. (2012a, 2012b)
should be compared with the results obtained by modified RCB in future after the integration of new non-equilibrium thermodynamic code.

7.3 Gas production by combination of production methods

The CH$_4$ production from hydrate deposits is a vast area of research. It is open for new ideas and variations in model parameters, production well design, combination of production methods, inclusion of more than one phases of hydrate etc. Only depressurization induced gas production method was studied and results were reported in paper I and II. It is also possible to combine depressurization with thermal stimulation for better results in some cases i.e. gas production from Class 2 hydrate deposits. For this purpose, suitable design of production well is necessary. To include thermal stimulation, consideration of injection of hot water or vapor through well at different stages of gas production is needed. For near future, it is suggested that more work related to CH$_4$ production from all categories of hydrate deposits should be carried out with suitable models based on real hydrate deposits data given in open sources.

One challenge faced in this study, was the selection of proper reservoir model and suitable input parameters for stable numerical solution. If similar difficulties occur in future, it is suggested that new study should start with simple model first. This simple model then can subsequently be upgraded into more realistic and complex model which resembles actual hydrate deposits better.

7.4 Detailed code comparison

The newly developed RCB hydrate simulator should be compared with other well known hydrate simulators to evaluate its effectiveness and accuracy in dealing with hydrate phase transition “reactions”. Chejara et al.(2012b) compared RCB results, obtained from depressurization induced gas production study on NGHs, with Anderson et al. (2011). Similar comparisons should be carried out in future after inclusion of non-equilibrium thermodynamic code in RCB. It is an easy code to implement new extensions and also easy to use. Participation in the
existing code comparison study (Anderson et al., 2011) could also be a way to go forward in this direction, although the parameters which have been used by each code may not be known and as such a comparison is more limited in value.

7.5 Permeability correlations

Presently permeability calculations in RCB are based on porosity changes as mentioned in Eq. 7 and Eq. 8. There is scope for further improvement in permeability calculations by defining flow channels in pores with respect to solid hydrate phase in the cavity of pores. When gas hydrate is formed inside the porous media, there are very thin channels present between solid mineral surface and gas hydrate surface. These channels are filled by fluids and can act as flow channels. In current version of RCB such thin flow channels are ignored, so fluid permeability calculations are not perfect. Detailed study of fluid permeability in porous media is required and presence of thin fluid flow channels should be considered for calculations.

7.6 Fracture description by hydrodynamics

Pre-processor VisualRetraso (Saaltink et al., 2005) has been used for building simulation models for RCB. In some of the examples, fractures have also been introduced in the impermeable caprock layer of reservoir. These have been defined as high porosity and high permeability channels in caprock and have been named as fractures. This is one of the ways to define fractures. But this approach has some unphysical approximations causing some distortions of model properties. The existing practice of defining fractures by building high permeability channels along with assumed fracture directions can partially reproduce the effect of fast fluid or gas breaking through the fractures, but it slows calculations significantly. And since the channels are formed from regular model grid blocks, the passage of liquid or gas inevitably gets modeled by filtration mechanism. According to filtration mechanism, liquid or gas penetrate through a fracture by pushing fully or partially. In reality, the breaking through
fracture happens quickly and can be described more properly by hydraulics than the filtration mechanics (Bogachev and Shelkov, 2010). So, for future it is suggested that hydraulics approach for fracture definition in reservoir models should also be taken into consideration.
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