Modeling Hydrate Phase Transitions in Porous Media Using a Reactive Transport Simulator

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Dissertation for the degree of philosophiae doctor (PhD)
at the University of Bergen, Norway

2014

Dedication

I would like to dedicate this thesis to my late father Latief Jemai (my first teacher), to my mother Zina Mrabet and to my wife Raedaa Touma.

Acknowledgements

I am indebted to several people at the Department of Physics and Technology, University of Bergen, for their contribution to the work presented in this thesis.

First of all I am deeply indebted to my supervisor Professor Bjørn Kvamme for his guidance and advice. I would like to express my deep gratitude for his great interest and support. He has always been ready to give advice whenever needed and in great depth; without his assistance and help this work will never be completed. I am thankful to him for introducing me to the field of natural gas hydrates.

I am also deeply indebted to my co-supervisor Professor Tatiana Kuznetsova, who helped me with her great knowledge in computer programming to solve problems related to the simulation code errors.

Special words of thank to Mohammad Taghi Vafaei and Ashok Chejara for their contribution to the development of the RCB code. Their valuable suggestions and advises was very useful and helpful for me during the performance of this work.

My special regards and thanks to Saleh Rayyen, Ahmed Issa, Rachid Maad, Kassim Adan, Mohammed Madi, Somaya Madi, Ali Saied, and Abdelraouf Alfsili for advising me during the writing of this thesis.

I also wish to thank my colleagues and friends Mohammad Qasim, Khuram Baig, Bjørnar Jensen, Sara and Neda at the department of physics and technology for providing me a friendly environment. I am also thankful to all my colleagues at Os gymnas for their encouragements; special thanks go to Kåre Perry Solibakke, Tore Moberg, Knut Døsen Lunde and Rune Rosland for their support.

I am forever deeply indebted to my family in Tunisia. I would like to express my sincere gratitude to them for their support and encouragement. I extend my thanks to my brothers and sisters and their families and with deep love to them. Finally, I want to thank my wife Raedaa and children Tesnim, Isra, Boshra and Mohammed for their great patience and never-ending support.

List of Publications

Reviewed publications in scientific journals

Vafaei, M.T., Kvamme, B., Chejara, A., Jemai, K., "Non-equilibrium modeling of hydrate dynamics in reservoir", *Energy & Fuels*, **2012**, *26* (6), pp 3564–3576 (**Paper 2**)

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 5**)

Jemai, K., Kvamme, B., Vafaei, M.T "Theoretical studies of CO_2 hydrates formation and dissociation in cold aquifers using RetrasoCodeBright simulator", Submitted to *WSEAS Transactions on Heat And Mass Transfer* (**Paper 6**)

Vafaei, M.T., Kvamme, B., Chejara, A., Jemai, K., "Simulation of Hydrate Dynamics in Reservoirs".2014, SPE Journal (**Paper 1**)

Vafaei, M. T., Kvamme, B, Chejara A., Jemai, K. "A new reservoir simulator for studying hydrate dynamics in reservoir". 2014, International Journal of Greenhouse Gas Control, 23: p. 12-21. (**Paper 7**)

Chejara, A., Kvamme, B., Vafaei, M. T., Jemai, K., "Simulations of long term methane hydrate dissociation by pressure reduction using an extended Retraso CodeBright simulator ", Energy Conversion and Management, 2013. 68: p. 313-323. (**Paper 8**)

Chejara, A., Kvamme, B., Vafaei, M. T., Jemai, K., "Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator", Energy Procedia, 2012, 18: p. 1533-1540. (**Paper 9**)

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(**Paper 3**)

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 (**Paper 4**)

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

Publications in conference proceedings without review system

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 03, 2011 to April 08, 2011.

Kvamme, B., Vafaei, M.T., Chejara, A., Jemai, K., "Reservoir scale simulation of hydrate dynamics", European Geosciences, Union General Assembly 2011, Vienna, Austria, April 03, 2011 to April 08, 2011.

International presentations

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 CO2 sequestration", CECAM-HQ-EPFL, Lausanne, Switzerland, June 22, 2011 to June 24, 2011

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 03, 2011 to April 08, 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

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, 2011 to November 17, 2011.

Jemai, K., Kvamme, B., Chejara, A., Vafaei, M.T., "Simulation of geomechanical effects of CO2 injection in fractured reservoir", European Geosciences Union General Assembly 2011, Vienna, Austria, April 03, 2011 to April 08, 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, 8 pages

Kvamme, B., Jemai, K., Chejara, A., Vafaei., M.T., "Simulation of geomechanical effects of CO2 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, 6 pages

Vafaei, M. T., Kvamme, B., Chejara, A., Jemai, K., "Simulation of Hydrate Dynamics in Reservoirs", Presented at the International Petroleum Technology Conference, Bangkok, Thailand, November 15–17, 2011,13 pages

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Chapter 1: Introduction

This chapter introduces some basics related to gas hydrate and its occurrence in nature with focus on the aspects that are relevant to this PhD work. A brief overview of important historical milestones in hydrate knowledge development is presented in section 1.1. The structures and some properties of hydrates are presented in section 1.2. A brief overview of hydrate and climate issues is given in subsection 1.3.1. The effect of hydrates dissociation on the geomechanical stability of gas hydrate deposits is discussed in subsection 1.3.2. The availability of hydrates and its potential energy resource is presented in subsection 1.3.3.

1.1 Hydrate knowledge development

Hydrate knowledge development can be divided into three periods. The first period started when Joseph Priestly (1733 - 1804) produced gas hydrate in laboratory by bubbling SO_2 through water at 0^0C and atmospheric pressure [1]. He was then followed by Sir Davy Humphrey who obtained the crystals of aqueous chlorine in laboratory and called it Cl_2Hydrates. Gas hydrates were also documented by Sir Humphrey, his experiments with chlorine was done at temperatures above the water freezing point, by this way he is considered to be the first to discover ‘warm ice’ [2]. Faraday (1823) confirmed the existence of this crystalline solid and suggested that its composition was almost 1 part of chlorine and 10 parts of water [3]. The studies of hydrates did not gain serious attention prior until 1934.

The second period started in 1934, often called the industrial hydrate period, when Hamershmidt noticed during the inspection of gas pipelines, the existence of ice solid plugs in the winter time [4]. The laboratory studies showed that plugs consisted of hydrate of the transported gas. This discovery caused more interest in investigation of the conditions of formation of gas hydrate and how to find an effective means of preventing hydrate plugs from forming in pipelines. During this period, most of the researches in gas hydrate considered it as a problem for oil and gas industry. Many researchers like Hamershmidt (1939), Deaton and Frost (1946) and Woolfolk (1952) investigated the effect of inhibitors in hydrate to prevent blocking of pipelines due to hydrate plugs [2]. In the early of 1950s von Stackelberg studied the structure of hydrates by using X-ray diffraction which helped Van der walls and Platteeuw (1959) to develop the statistical thermodynamic model of the hydrate.

The third period started in the 1960s and is related to the discovery of gas hydrate in nature. The existence of natural gas hydrate was proven after drilling Markhinskaya well in Yakutia in 1963. A section of rock was revealed at 0°C temperature at 1450 m depth. Comparing the conditions of that section of rock, Makogon confirmed in 1966 the existence of natural gas hydrate when he succeeded to form it in porous media and in real cores samples. Thereafter in 1970 a group of geologists founded the first gas hydrate deposit in the Massayokhah field in the permafrost regions [1, 2] .The Massayokhah field estimated to have one third of all gas reserves in the word. It was also recognized in the 1970s that gas hydrates occur naturally both in polar continental regions and in deep water sediments of oceanic regions at outer continental margins [5].

1.2 Hydrate structure and property

Gas clathrates (commonly called hydrate) are crystalline water based on solids which looks macroscopically like ice (figure 1). Clathrates occur (clathrate is derived from Greek *klathron* which means closure) when water forms a lattice which can host smaller molecules typically a gas or liquid.

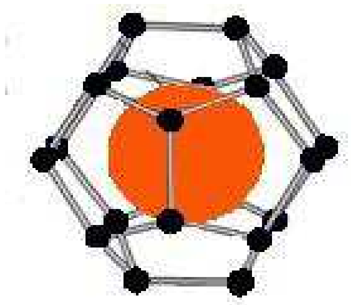
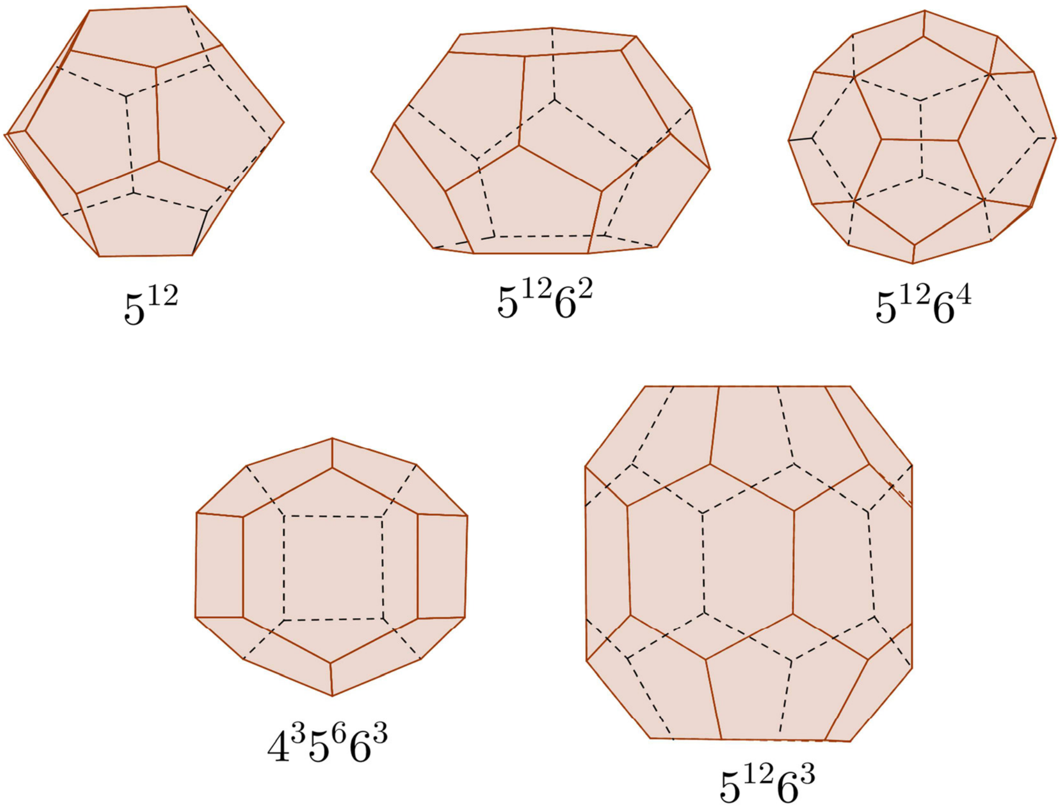


Figure 1 the gas (large ball) is enclosed in a cage formed by water molecules

Gas hydrates are not chemical compounds because there is no chemical bonding between the host water and the enclosed guest molecules whose molecular diameter is less than the diameter of the cavity. Many gases can be guest molecules such as methane, ethane, propane, Carbon dioxide and hydrogen sulfide depending on the diameters of the guest molecule and cavity, figure 2 shows the five most common cavities.



5^{12} $5^{12}6^{2}$ $5^{12}6^{4}$

$4^{3}5^{6}6^{3}$ $5^{12}6^{3}$

Figure 2 Geometry of cavities

5^{12}: means that there are 12 structures that have 5 sides.

$5^{12}6^{2}$: means that there are 12 structures that have 5 sides and 2 structures that have 6 sides.

$5^{12}6^{4}$: means that there are 12 structures that have 5 sides and 4 structures that have 6 sides.

$5^{12}6^{8}$: means that there are 12 structures that have 5 sides and 8 structures that have 6 sides.

$4^{3}5^{6}6^{3}$: means that there are 3 structures that have 4 sides, 6 structures that have 5 sides and 3 structures that have 6 sides.

Natural gas hydrates crystallize mostly in two cubic structures (sI, sII) and one hexagonal structure (sH) [2]. sI consists of $2 \times 5^{12} + 6 \times 5^{12}6^{2}$. sI stabilizes by guest molecules having diameter between 4.2 Å and 6.0 Å. The cage 5^{12} can host methane, carbon dioxide, ethane and hydrogen sulfide and $5^{12}6^{2}$ can host all 5^{12} members plus Ethane.

sII consists of $16 \times 5^{12} + 8 \times 5^{12}6^{4}$. sII stabilizes by guest molecules having diameter less than 4.2 Å and diameters between 6 and 7 Å. The cage 5^{12} can host all the sI members plus

$\mathrm{Ar}, \mathrm{Kr}, \mathrm{N_2}, \mathrm{O_2}$ at normal pressures and $\mathrm{He}, \mathrm{H_2}, \mathrm{N_2}$ at high pressure. The cage $5^{12}6^4$ can host all 5^{12} members plus C_2, C_3, C_4 families.

sH consists of $3 \times 5^{12} + 2 \times 4^3 5^6 6^3 + 1 \times 5^{12}6^8$. sH stabilizes with larger guest molecules like iso-pentane (7Å < diameter < 9Å) when it accompanied by smaller molecules such as nitrogen, methane or hydrogen sulfide

Table 1 Characteristics of different structures of gas hydrates [2]

Hydrate crystal structure	Structure I (**sI**)	Structure II (**sII**)	Structure H (**sH**)
Cavity	5^{12} $5^{12}6^2$	5^{12} $5^{12}6^4$	5^{12} $4^35^66^3$ $5^{12}6^8$
Radius Å	3.91 4.33	3.902 4.608	3.91 4.96 5.71
Number of cavity/Unit cell	2 6	16 8	3 2 1
Description	Small Large	Small Large	Small Medium Large
Number of water molecules/unit cell	46	136	34

The guest molecule stabilizes the hydrogen bonded cage by repulsion; this causes the stabilization of hydrate molecule. The larger size is more stable due to the absence of columbic effect. The addition of a second guest molecule contributes to the stabilization of hydrate of large molecules.

Hydrates have many similarities to ice because they contain almost 85% of water. The hydrogen bonds are only 1% longer than those in ice. The O-O-O angles differ from those in ice by 3.7^0 in structure (sI) and by 3.0^0 in structure (sII).

Some important differences from ice are as follows:

Thermal conductivity: Is much lower than ice. The water molecules are restricted from translation and rotation. The trapped guest molecules vibrate anharmonically. The anharmonicity provides a mechanism for scattering the incoming thermal energy as phonons.

Thermal expansion: is significantly higher than ice. The hydrogen bonds are weaker due to collision of the guest molecules with the cage wall

Dielectric constant: is significantly lower than water because of lower density of hydrogen bounded H_2O and the reorientation of H_2O molecules are slower.

Yield strength: The guest molecules provide support to hydrates molecules so hydrates are more resistant to crush than ice.

1.3 Natural gas hydrates in nature

While industrial problems related to processing and transport of hydrocarbons was a substantial motivation for hydrate research for several decades, the focus has shifted much more over to different aspects of hydrates in nature in the last three decades. As is discussed in more detail elsewhere in this thesis and the enclosed journal papers, hydrates in nature are not able to reach thermodynamic equilibrium. They will rather adjust to different degrees of stationary situations depending on sealing structures (shale, clay), flow, influx of hydrocarbons, leakage pathways etc. Leakage pathways that support methane to the oceans gives additional fluxes to the carbon cycle in the oceans and potentially through to the air. Direct fluxes of methane from dissociating hydrates in regions of permafrost give rise to an additional increase in greenhouse gases in the air.

Hydrates that dissociate will give rise to compaction and may lead to possible geomechanical instabilities. Dissociation can be caused by increased temperatures or by contact with under-saturated water. This can happen during direct contact with the ocean, or through fracture systems connecting the hydrate to under-saturated water.

1.3.1 Climate issue

Hydrates in porous media are generally exposed to at least surrounding aqueous phase and mineral surfaces but also sometimes free gas phase. Hydrate saturation varies substantially, depending on local fluid flows, fracture/fault systems which brings hydrate in contact with groundwater that leads to local hydrate dissociation.

Hydrate reservoirs are then in a situation depending on fluid flow and they cannot be able to reach thermodynamic equilibrium (see chapter 5 about non equilibrium). Many geologists now admit that catastrophic climate warming have occurred several times in the past as a result of hydrate dissociation. As a consequence of these climate changes many species disappeared. For almost 55.5 million years, the $\delta^{13}\mathrm{C}$ in the ocean and in land decreased by $2.5 - 5\%_0$ on a time scale less than 10000 years, the decrease of $\delta^{13}\mathrm{C}$ is an indication of methane release [6]. The most recent event occurred when hydrate released

$\sim 2500\ \mathrm{Gt}\ (10^{15}\mathrm{g})$ of carbon at the PETM (Paleocene/Eocene thermal maximum; ~ 55.5 Ma). Moreover, sudden deep-ocean warming (the mechanism for the PETM release [7]) may be stochastic and difficult to predict throughout Earth's history [8]. Climate change was global, fast (1 000 to 10 000 years to appear) and correlated with high extinction of benthic foraminifera and extraordinary diversification of terrestrial mammals.

Methane is less abundant in the atmosphere than $\mathrm{CO_2}$but its greenhouse effect is 20–30 times more powerful [9]. The release of the methane directly from the hydrate reservoir within a relative short time could increase the methane concentration in the atmosphere by a factor of 1000 times over pre – anthropogenic values. The methane hydrate reservoir has the potential to warm earth's climate to PETM conditions within just few years and some studies suggest according to the stocktaking of hydrate that a global $3^0\mathrm{C}$ warming could release up to 940 GTC which could lead to an additional $0.5^0\mathrm{C}$ to global warming [10]. Fortunately, most of the hydrate reservoirs seem insulated from the climate of the Earth's surface, so that any melting response will take place on time scales of millennia or longer [6].

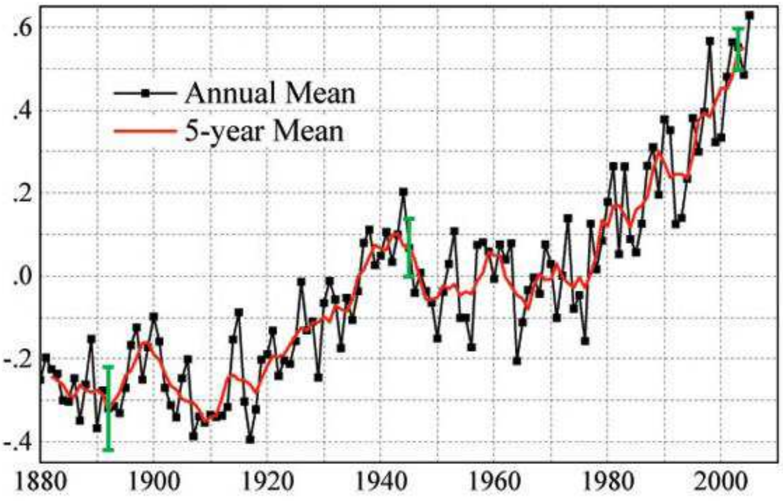


Figure 3 Increase in the average temperature of the earth (source Nasa)[1]

Significant number of researchers within the scientific international community claims that the main cause of global warming is the rise of the concentration of $\mathrm{CO_2}$ in the atmosphere.

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[1] http://www.nasa.gov/centers/goddard/news/topstory/2008/earth_temp.html

One of the techniques used to reduce the accumulation of CO_2 in the atmosphere is the concept of capture and storage of CO_2 (CCS).

There are several ways to sequester CO_2 in geological media: geologic disposal into coal seams, depleted oil/gas reservoirs, salt caverns, and deep oceans.

It is preferable to store CO_2 into deep-sea sediments because CO_2 stored in terrestrial sites is buoyant. The water pressure and dilution by oceanic water prevent direct emission of CO_2 into the air. Some relevant reservoirs are located in regions with temperature and pressure suitable for hydrate formation (Snøhvit: offshore Norway reservoir is cold enough in the upper hundreds of meters below seafloor for CO_2 hydrate to form).

Several studies ([11];[12];[13]) suggest that injection of CO_2 should be below the hydrate stability zone in deep-water sediments or in sub permafrost sediments. At deep sea sediments the CO_2 can reside in its liquid phase and can be denser than the overlying pore fluid causing the injected CO_2 to be gravitationally stable. Additionally, hydrate may start to form when the CO_2 reach the hydrate stability zone. This will lead to cementation of sediments by newly formed hydrate phase which will serve as a second cap in the system [13]. This cementation will facilitate underground geological CO_2 sequestration [14].

A promising new technology used to reduce the carbon content in the atmosphere is the subsurface CO_2 storage through clathrate hydrate formation. CO_2 hydrate is more stable than CH_4 hydrate for substantial regions of pressure and temperature. And a mixed hydrate in which CO_2 dominates filling of the large cavities and CH_4 dominates filling of the small cavities is more stable than CH_4 hydrate over all regions of pressure and temperature. Injection of CO_2 as a liquid converts methane hydrate into carbon-dioxide dominated hydrate while at the same time releasing the trapped natural gas [15].

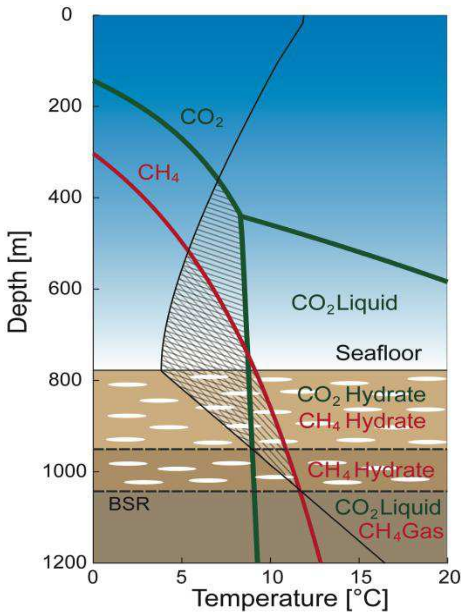

Figure 4 Seafloor CH_4-hydrate (red) and CO_2-hydrate (green) stability zone; within the overlapping shaded area both phases exist; at pressures equivalent to 800-1000 m water depth spontaneous exchange of CO_2 for CH_4 takes place [16]

1.3.2 Geo-hazards

Global warming can affect the stability of gas hydrate deposits, which can cause serious geo hazards in the near future [10].

Geomechanical instability can be caused by local changes in temperature, but also can be triggered by many years of hydrate dissociation towards under-saturated seawater or groundwater. Seawater which is under-saturated can penetrate horizontally into the porous media and cause hydrate dissociation which over the years can lead to instability of unconsolidated sediments. But it can also penetrate vertically downwards through sediments by diffusions and capillary driven transport in water wetting sediments. More massive contact between seawater and hydrate through systems of fractures and faults gives rise to fluxes of releasing methane which can be quite massive and appear as bubbling columns.

Gas hydrates may contribute to a serious geo-hazard in the future because of the unfavorable effects of climate change on the stability of gas hydrate deposits both in permafrost and ocean sediments.

The structure of ice sheets due to regional warming may also lead to the destabilization of gas hydrates. As ice sheets shrink, the weight removed allows the coastal region and the adjacent continental slope to rise through isostasy. This suppression of hydrostatic pressure could destabilize gas hydrates and leads to slope failure [10]. Many examples of the connection between submarine failure and dissociation of gas hydrate are discussed in open publications. Surficial slides and slumps on the continental slope and rise of West Africa; slumps and collapse features on the U.S; Atlantic continental slope; large submarine slides on the Norwegian continental margin [17] are some few examples.

The stability of the sea floor where there is an active search for conventional hydrocarbon deposits is of crucial importance. The possibility of hydrate dissociation in oceanic sediments due to heat transfer during oil production can cause to sediment failure and collapse of platforms [18].

The permeability of the sediment to gases and liquids decreases when gas hydrates form. The most part of the sediment, where the hydrate is stable, will be occupied by the gas hydrate. This leads to continuous sedimentation as well as more burial of gas hydrate. Deeper burial of gas hydrate will lead to an increase of the temperature in the lower part of the hydrate zone, the hydrate will not be longer stable. The gas start to release, leading to a zone of weakness (low shear strength) where failure could be triggered by gravitational loading or seismic disturbances, and submarine landslides result [19, 20].

Hydrate stability zone depends on temperature and pressure. This zone is sensitive to changes in both temperature and sea level. Changes in climate and sea level lead to instability of hydrate turning it into gas.

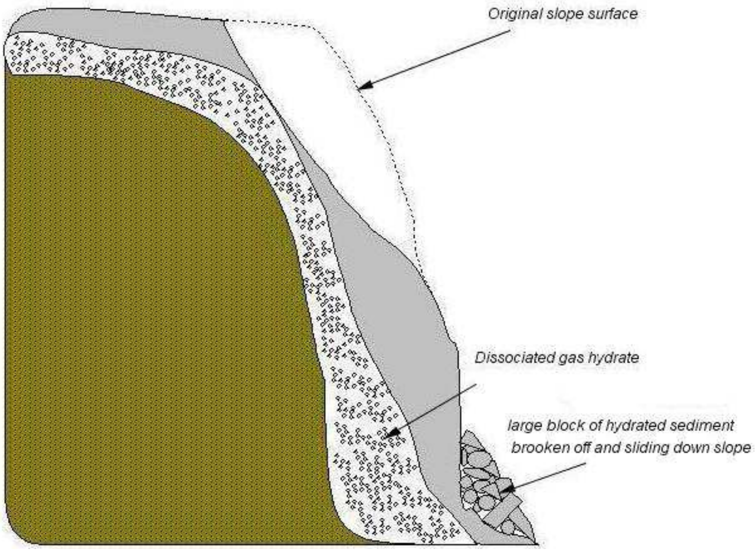

Figure 5 Diagram showing the effects of dissociation of gas hydrate and the resulting subsea slope failure

This process may weaken sediments and trigger landslides, from which methane might escape into the oceans and atmosphere. A significant quantity of methane released into the atmosphere can lead to important implications for Earth's climate [21].

The methane released from the hydrate reservoir into the water column and eventually into the atmosphere could contribute to further climate change. The global warming can lead to lowering of sea level which will reduce the pressure on the sediment causing gas hydrate to become unstable and turn to gas. This mechanism can trigger submarine landslides (figure 6).

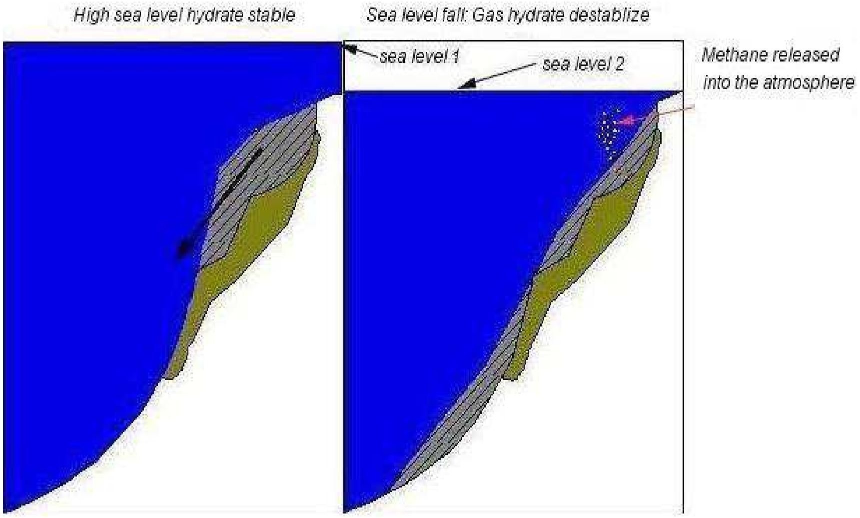

Figure 6 The sea level change can affect gas hydrate stability and can launch submarine landslides

There exists many examples of connection between submarine failure and dissociation of gas hydrate [17]. The most known example of submarine landslides in which gas hydrates are implicated, the Storegga slide situated on the passive Norwegian margin, is known as one of the world's biggest underwater slides and has been proposed as a significant source of past methane release into the atmosphere [22, 23]. Storegga slide refers to the enormous retrogressive and multi-phase slide dated at$\sim 8.2\ \mathrm{ka}$ and has a known volume of 3000 km^3[24].

Instability also due to contact with under-saturated water which dissociates hydrate, like hydrate zones facing seawater influx that dissociates hydrate as mentioned above.

In the case of offshore hydrate's deficiencies in sealing above the hydrate layers in the form of fractures and faults will lead to contact between hydrate and groundwater. The result is dissociating hydrate and methane seepage to the ocean above. Since methane is a more aggressive greenhouse gas than $\mathrm{CO_2}$, the global methane fluxes from hydrates and free methane are global environmental concern. In the long run these leakage situations may lead to dement instabilities and in the worst case cause landslides. In some permafrost regions the ice above is the only trap for the gas hydrate. Decreasing permafrost ice is therefore a global concern.

1.3.3 Gas hydrate as energy resource

Gas hydrates occur generally in two regions, permafrost and deep oceanic, at subsurface depth ranging from about $130\ \mathrm{m}$ to $2000\ \mathrm{m}$ and below the seafloor at depth ranging from about $100\ \mathrm{m}$ to $1100\ \mathrm{m}$ respectevily [25].

The worldwide amount of hydrate is estimated to be $(1-5)\cdot 10^{15}\mathrm{m}^3$ [26]. Kvenvolden et al. [27] estimated that over 99% of natural gas hydrates has methane as a guest molecule. A few hydrate deposits contain heavier hydrocarbons, $\mathrm{CO_2}$,and $\mathrm{H_2S}$ [26]. A 15% production of this amount will provide 200 years of energy for the whole world at the current level of energy consumption [28].

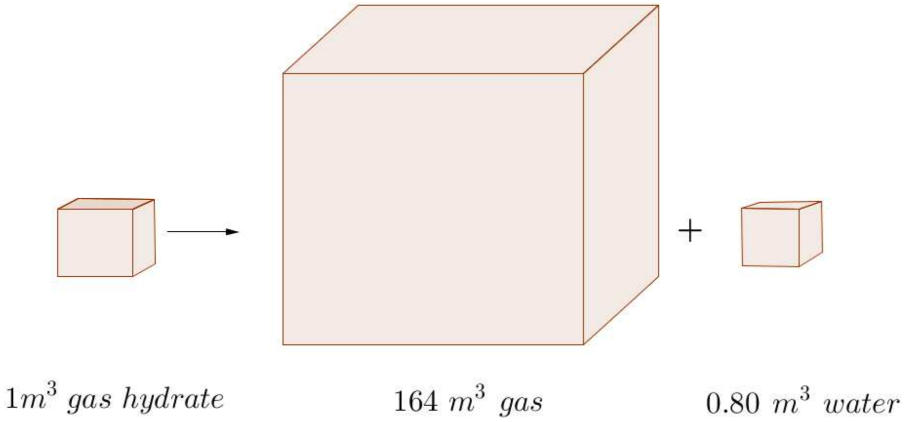

Figure 7 Proportional volumetric relationship between hydrate, water and gas: One m3 of gas hydrate yields 164 m^3 *of gas and 0.8 m*^{3} *of water at standard temperature and pressure (Modified from [29]).*

$1m^3$ of fully saturated methane hydrate contains about $164\ m^3$of methane at standard pressure and temperature and $0.80\ m^3$ of water [2, 30]. Gas hydrate may present an important potential future source of hydrocarbon fuel, but the recovery of gas from hydrate deposits seems to be difficult and costly ; even menacing the global climate. To date, only one field (Messoyakha gas field) was exploited commercially by recovering the gas from the field through depressurization.

A promising new technology has been developed by Bjørn Kvamme and Arne Graue at the University of Bergen. This technology consists of injecting CO_2into hydrate and extracting CH_4 by direct exchange [15][2],[3]

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[2] http://www.vg.no/nyheter/innenriks/artikkel.php?artid=184534

[3] http://www.netl.doe.gov/research/oil-and-gas/methane-hydrates/co2_ch4exchange

Chapter 2: Characteristics of Gas hydrates in reservoirs

Natural gas that supports hydrate growth is either from biogenic decomposition of organic material in the upper depth levels, or from deeper sources through thermogenic decomposition. A brief overview of the source of hydrates is given in section 2.1. The natural gas hydrate deposits vary substantially but from a production perspective, the most important resources can be classified in some few classes as described in section 2.2. Some characteristics of hydrates in reservoirs, also from a production perspective are summarized in section 2.3. Important aspects related to production from different classes of hydrate deposits listed in section 2.2 is described in section 2.4. A brief review of reported hydrate production studies from open literature is given in section 2.5.

2.1 Source of hydrates

Methane which is the main gas component in *in situ* hydrates is generated by two processes either biological processes of organical material in the upper few hundred of meters (biogenic natural gas) or by thermal cracking of organic material in deep sediments (thermogenic natural gas).

Most of the natural gas hydrate is attributed to biogenic methane. Biogenic gases are often formed at temperatures that are within the stability zone for hydrate in terms of temperature and pressure. Thermogenic gases are produced at temperatures outside the hydrate stability zone at high temperatures. This gas migrates (usually through faults or channels) to connect with groundwater at conditions of temperature and pressure within hydrate stability zone. Thermogenic gas is formed deep in the Earth at temperature ranged from $50-2000^0$ C. In this process large molecules in deposits of organic materials known as kerogen (as precursor to oil) are cracked to a smaller molecules. During this process high concentrations of hydrocarbons such as methane, ethane and propane are formed.

It is possible to distinguish if hydrate is coming from biogenic or thermogenic gases by looking at the ratio of ^{13}C / ^{12}C and /or the mole fraction of propane:

$$\delta^{13}C=\left[\frac{\left(\left[{}^{13}C\right]/\left[{}^{12}C\right]\right)_{\text{Sample}}}{\left(\left[{}^{13}C\right]/\left[{}^{12}C\right]\right)_{\text{Standard}}}-1\right]\times10^{3}$$

The ratio $\delta^{13}C$ in biogenic gas $(-60\%_0$ to $-85\%_0)$ is less than the ratio $\delta^{13}C$ in thermogenic gas $(-25\%_0$ to $-55\%_0)$ [2]. For biogenic gases, the mole fraction of propane is almost 0% however a high molar fraction of propane (1% to 20%) is indicative of thermogenic gas.

2.2 Classification of hydrate deposits

Hydrate can exist in two types of deposits: permafrost deposits and ocean deposits. These deposits can be divided into 4 main classes [31, 32]. Classes 1, 2 and 3 are characterized by high intrinsic permeability while class 4 deposits are characterized by low intrinsic permeability.

Class 1 comprises two zones: a well-defined gas hydrate bearing layer and an underlying two- phase fluid zone that contains free gas and liquid water. This class deposit is at the base of the gas hydrate stability zone (GHSZ).

Class 2 is composed of two zones: a hydrate bearing layer and an underlying layer with water mobile zone with no free gas (e.g., aquifer). This class of deposits is at the base of, or within, the GHSZ when gas charged is limited [33].

Class 3 consists of a single zone hydrate layer with absence of underlying zone with mobile fluids.

Class 4 is characterized with low hydrate saturation (less than 10%) and low intrinsic permeability. This class of deposits is associated with fine-grained marine sediments in which gas hydrate occurs primarily at the base of CHSZ [34]. Class 4 is generally related to oceanic accumulations.

Each class includes subclasses named C, F, M and R [35, 36]. These sub-classes are described as confined or unconfined deposits.

Type C is hydrate deposits with relatively unconsolidated coarser-grained sediments. This type of reservoirs has a high intrinsic permeability. Type C is generally characterized with high hydrate saturation (more than 50%). This type of reservoirs occurs in permafrost but in a smaller proportion of marine settings and is the most favorable type of potential energy production.

Type F is characterized by unconsolidated, fine-grained, low permeability sediments. Type F accumulations may be possible as a potential energy production. This type of sediments has low mechanical strength and may have profound implications for natural environmental change over long time-frames [34, 36].

Type M occurs on the sea-floor and/or in very shallow sediments in association with cold seeps. This type is not hosted in sediments. The amount of methane is small in them and would tend to exclude commercial activity [35].

Type R refers to unique instances where gas hydrate occurs within rocks. The Messoyakha field is an example of fields of type R.

It should be noted that this classification of hydrate deposits should be considered as guides rather than strict rules [37].

2.3 Characteristics of hydrates in reservoirs and the difference from hydrates produced in laboratory and hydrates as plugs in pipelines.

From a thermodynamic point of view the combination of mass conservations and conditions of equilibrium defines minimum criteria of possibility to reach equilibrium, most often known as a Gibbs phase rule.

Gibbs Phase rule is simply the conservation of mass under the constraints of equilibrium. Mathematically this phase rule ends up to be the number of components that can be distributed among the phases minus the number of phases plus two, which is then the number of thermodynamic independent variables that must be defined if equilibrium can be established. If the temperature and pressure are defined in a local point of the reservoir at a given time the system reaches equilibrium when the degree of freedom of the system is two. If we consider a system consisting of three phases (aqueous, gas and hydrate) and if in addition the system is inside the hydrate stability zone, the degrees of freedom will be one and the system is thermodynamically over-determined. The system will tend towards minimum free energy for the whole system under the constraints of the total mass and distribution of this into all the possible phases and a system in a reservoir cannot reach equilibrium. Practically there will always also be fluid phase(s) in the system due to the facts that hydrates in nature are open systems. No hydrate reservoir reaches infinite in any direction. There is an absolute bottom line at which hydrate is in contact with fluids and/or clay at a temperature for given depth where hydrate cannot be stable. In the horizontal directions, the hydrate reservoir may enter fracture systems that bring the hydrate in contact with groundwater that dissociates hydrate and/or other boundaries where fracture systems bring fresh hydrocarbon feed into the hydrate zones. In summary, this implies that all hydrate reservoirs are open systems. Natural hydrate resources are not even close to 100% in hydrate saturation. It should also be noted that Gibbs phase rule is a minimum criteria for equilibrium and that the number of phases that can co-exist also depends on free energy level of the different phases since the masses in the system will distribute in a way so as to minimize total free energy. If some of the theoretical phases cannot exist, these are excluded and a new analysis is conducted. In addition, if one or more phases are consumed a new Gibbs free analysis have to be conducted along with a subsequent analysis of free energy levels of the remaining phases.

The hydrates formed in PVT-cell are close to 100% in hydrate saturation since this system is closed (limited impact of solid walls and symmetric stirring). Hydrates produced in the PVT-cell have a large degree of uncertainties in solid phase homogeneity but equilibrium constants are more “predictable”.

Hydrate plugs in pipelines are the result of abnormal flow. When water falls out from a gas stream, it can be adsorbed on the walls of the pipe itself. The water will wet the surface and the adsorbed water acts like heterogeneous nucleation site. Hydrate form at the walls of the pipe. The pipe wall has the lowest temperature and encourages deposits. The hydrate will grow further and narrows the flow channel. The deposit becomes irregular and the pressure drop increases.

2.4 Gas production from different classes deposits

The main known methods of gas production from hydrate are depressurization, thermal stimulation and use of inhibitors. The depressurization involves shifting of hydrate stability condition by lowering to a pressure below the equilibrium pressure. Heat for dissociation will be supported from the surroundings due to the imposed temperature gradient and due to pressure reduction. Thermal stimulation consists of introducing heat in the hydrate bearing sediments in order to increase the surrounding temperature above the stability temperature of the hydrate which causes gas release. This method is considered expensive because of the huge amount of energy waste to the surroundings which calls for careful planning and engineering to reduce heat losses.

Inhibitors such as methanol or glycol are used to decrease the hydrate stability conditions. Although this method is technically feasible, the large use of chemicals like methanol is costly from economic and environmental point of view [25].

A new promising method consists of injecting CO_2 into the methane hydrate reservoirs; with this concept CH_4 molecule is replaced by CO_2 molecule. The main replacement is CH_4 in large cavities, in which CO_2 has substantial benefits in terms of stabilization over CH_4. CO_2 can enter the small cavity of structure I (sI). This method has several benefits compared with the previously mentioned methods: (a) the heat of formation of CO_2 is larger than the heat of dissociation of CH_4 hydrate. (b) CO_2 hydrate is more stable than CH_4hydrate over substantial regions of pressure and temperature and mixed hydrate in which CH_4 occupies portions of large cavities is more stable than CH_4 hydrate over all regions of pressure and temperature. (c) During the production, the exchange of CO_2 with CH_4 will maintain mechanical stability of the hydrate bearing formations. (d) A substantial reduction of the accumulation of CO_2 in the atmosphere is required in order to avoid a situation of irreversible global heating. The process of sequestration of CO_2 as clathrate hydrates is environmental friendly; CO_2 will be removed from the atmosphere while simultaneously releasing methane gas. The exchange process consists of two mechanisms in which the fastest one is the creation of new CO_2 hydrates from free water between hydrate and minerals and associated dissociation of the *in situ* CH_4 hydrate due to heat release from CO_2 hydrate formation. The second mechanism is a slower solid-state exchange [38-40].

The depressurization method is often used for gas production from Class 1. The existence of a free gas zone provides a significant economic advantage because it guarantees the gas production even where hydrate contribution is small [32].

In case of Class 2 deposits, the depressurization method appears theoretically more effective than in Class 1 because the disturbance of pressure is stronger and is usually detected by a large area of the interface water-hydrate [31]. In addition, the water located in the underlying layer faciliates the endothermic dissociation reaction due to its heat capacity. Although of favorable depressurization conditions, the gas production is disserved by low relative permeability conditions which hinder the maintenance of gas phase in a previously water saturated zone. The gas production is accompanied by water production which represent 98 % of the total mass produced. The production of such volume of water can have serious complications related to the environmentally sensitive area, in addition to economic considerations in relation with the pumping of large volumes of water [41].

The depressurization technique seems to be not favorable for Class 3 hydrate deposits because this class of hydrate accumulations has a high hydrate concentration which reduces the effective permeability of reservoir fluids. Additionally, if the intrinsic permeability of the medium is low, the flow through the hydrate becomes difficult. Contrary to Class 1 and 2 deposits, Class 3 hydrates are characterized with a lack of permeable zones which are in direct contact with the hydrate layer. A combination of thermal stimulation and depressurization production methods might be more productive in Class 3 deposits [42].

Moridis and Sloan [43] evaluated the gas production potential of Class 4 deposits subject to depressurization-induced dissociation over a 10-year production period by using numerical simulation study. They concluded that gas production is very limited, never exceeding a few thousand cubic meters of gas during the 10-year production period. Their results indicate very low gas production volumes accompanied with huge amount of water production. Their overall conclusion is that such hydrate deposits are not promising targets for gas production.

2.5 Theoretical modeling of hydrate production and hydrate dynamics in porous media based on open publications

Simulators play an important role in estimating the potential production of natural gas from gas hydrate reservoirs. Nowadays, the simulation is the main method used to decide about gas production's scenarios from gas hydrate bearing sediments. The Simulator of gas hydrates differs from a classical simulator of reservoir of oil and gas by the governing equations of flow of fluids in porous media. These equations must be coupled to the kinetic and thermodynamic equations governing the attitude of hydrates [37].

A Limited review of the past studies of hydrate exploration with the approach of modeling and simulation is presented below. As there are commercial interests behind some of the simulators there are lack of details as well as fairly few studies reported in open publications.

In the earlier studies, hydrate dissociation was treated in terms of boundary displacement by using the classical Steffan's problem for melting and by assuming the dissociation process to be isothermal. Holder [44] built a 3D model for studying hydrate dissociation effect on gas production due to depressurization. Several assumptions were made to simplify the calculations. They considered the dissociation to happen only at the interface between hydrate and gas phase and only conduction was considered to find temperature distribution in the gas phase. Burshears et al. [45] developed a two-phase model consisted of water and methane. They considered radial flow and equilibrium conditions in the gas hydrate interface. Yousif [46] developed a one dimensional model to simulate isothermal depressurization of hydrate in Berea sandstone samples. The model considered three phases of water, gas and hydrate and used kinetics model of Kim and Bishnoi [47] for dissociation of hydrate. Swinkels and Drenth [48] used a 3D thermal reservoir simulator. They represented the reservoir fluid by a gaseous, a hydrate and an aqueous phase. The hydrate phase is assumed immobile over the full saturation range. Measurements of the relative permeability of gas and water in the presence of hydrates were not available. Their system consisted of three components including two hydrocarbons and a water component. The heat was considered as an extra component for all phases internally in the simulator. Nazridoust and Ahmadi [49] developed the hydrate simulator FLUENT to study hydrate dissociation in an axisymmetric model of the core. This core was developed and solved for multiphase flows during the hydrate dissociation. The core model contained three separate phases: methane hydrate, methane gas, and liquid water. They used kinetics rate of dissociation proposed by Kim and Bishnoi [47] and they used Corey's model for relative permeability variation.

Moridis [50] has proposed a new module for TOUGH2 (a descendent of the TOUGH family (Transport Of Groundwater and Heat)) simulator named EOSHYDR2. This simulator is designed to model hydrate behavior in both sediments and laboratory conditions. It includes both equilibrium and kinetic models for hydrate formation and dissociation. It uses hydrate reaction model of Kim and Bishnoi [47] for kinetic studies. He has used just equilibrium approach due to lack of enough suitable data necessary for the parameters of the kinetic model while he mentioned that slower processes such as depressurization follow kinetic dissociation.

Some simulators from TOUGH+ family (TOUGH-Fx/HYDRATE, TOUGH+HYDRATE, HydrateResSim, MH-21 HYDRES, STOMP-HYD) and CMG STARS (Computer Modeling Groups Steam, Thermal and Advanced Process Reservoir Simulator) are designed for handling the reactions of methane hydrates. CMG STARS is an oil reservoir simulator adapted to handle hydrate reservoirs and is modified (with TOUGH+HYDRATE, HydrateResSim, STOMP-HYD) to handle both $\mathrm{CO_2}$ and $\mathrm{CH_4}$ reactions.

TOUGH+HYDRATE was developed at LBNL (Lawrence Barkley National Laboratory), is a descendent of TOUGH family and was the first reservoir simulator designed to study hydrate reservoirs. TOUGH+HYDRATE can contain up to four components (hydrate, water, methane and inhibitors) and four phases (hydrate, water, ice and gas). This simulator couples mass and energy balances in order to model the non-isothermal dissociation of hydrates [51].

CMG- STARS, which is originally designed to study oil reservoirs, handles reservoir as an oil phase. This phase, when the thermodynamic conditions are favorable, can dissociate into methane and water. This simulator uses the kinetic model based on the model of Kim and Bishnoi [47]. The hydrate phase is represented as a solid due to the high viscosity given to it [37]. The National Institute of Advanced Industrial Science and Technology, Japan Oil Engineering Co., Ltd. developed MH-21 Hydrate Reservoir Simulator (also known MH21 HYDRES). It has been designated to investigate the key factors for the success of depressurization – induced method for gas production. With the simulation results, it has been concluded that the gas productivity was affected by the initial effective permeability and hydrate-bearing sediments should have an effective permeability greater than the actual threshold value [52]. STOMP-HYD is a reservoir simulator developed at the Petroleum Engineering Department at the University of Alaska. This simulator was used to reproduce numerically and demonstrate the feasibility of producing natural gas and sequestering $\mathrm{CO_2}$ using the direct exchange technology in geologic media [53].

Most of these developed gas hydrate reservoir simulators consider the solid phases to be rigid and no deformation is assumed in most of them.

To represent multicomponent flow, geological heterogeneities on different scales, there is a need for up to millions of grid blocks. However, due to the complexity of phase changes and subsurface flow, most of the simulators are limited to systems of up to several thousand grid blocks [54].

As mentioned above, it is clear that in most of the reservoir simulators the hydrate phase transition process are treated as an equilibrium reaction and in fewer cases as kinetics based on the kinetic model of Kim and Bishnoi [47]. The use of this model for fitting laboratory experiments from PVT cell and then using these data for a reservoir situation might be more questionable since it has never been proven that these data are transformable to real situation of hydrate phase transition in nature.

Most of hydrate simulators use the classical method of calculation of absolute and relative permeability. The absolute permeability of porous media is calculated as a function of hydrate saturation and relative permeability functions are calculated based on a combined equation of Genuchten capillary pressure function and Mualem porosity distribution function [55].

The use of more recent techniques for prediction of permeability such as those proposed by Sugita et al. and Hirabayashi et al. [56, 57] are more appropriate . The advantage of this method is the possibility to combine the experimental CT scan images with models of fluid transport and fracture rocks such as Navier-Stokes equation or Lattice Boltzman method. This method allows the interfacial tensions between fluid and hydration as well as fluid and other minerals to be considered. It is also possible to account for the geometry of the system more accurately than classical methods of permeability calculation.

Chapter 3: Motivation for PhD study reported in this thesis

Present levels of evaluation of hydrate dynamics in porous media and corresponding models range from very empirical concepts and models to the more recent development of hydrate reservoir simulators. They are all very oversimplified and assumption of local equilibrium in pressure and temperature projections is a very common approximation. None of the simulators mentioned in this chapter, as well as in other chapters of this thesis and enclosed papers includes a proper description of phase transition since the thermodynamic variable dependency also includes all concentrations in all phases in co-existence with the hydrate. This also includes adsorbed phases on mineral surfaces and hydrate surfaces.

One aspect of this study is to develop an approach according to the non-equilibrium nature of hydrate phase transitions

Another aspect that motivated this study was the lack of geomechanical description in the simulators, which is obviously important in natural gas hydrate systems as illustrated in subsection 1.3.2 above.

A very brief review of some previous studies which contain these limitations of equilibrium in pressure and temperature is given in section 3.1 below.

Development of stresses during dynamic flow is implicitly linked to flow of mass and energy. Explicit couplings to external geomechanical codes may be inaccurate for many of the rapid phase transitions related to hydrate in porous media. Section 3.2 below discusses this aspect briefly.

3.1 Non equilibrium

A limited review of some studies dealing with the modeling of hydrate exploration shows that the hydrate formation and dissociation is commonly treated as an equilibrium reaction governed by the pressure – temperature projection of the fluid/water/hydrate equilibrium curve.

Ahmadi et al. [58] developed a 1D reservoir model to study hydrate dissociation by using the depressurization method. The equilibrium conditions are used at the dissociation front and neglected water flow in the reservoir and also neglecting the Joule – Thomson effect.

Huong et al. [59] presented 2D model to cylindrical model study. They studied the effect of the hydrate zone on the gas production from the gas layer and the importance of the intrinsic kinetics of hydrate decomposition with respect to equilibrium assumptions. They concluded that the kinetic equation was affected only when it was considered 5 orders of magnitude lower than the values found by Kim and Bishnoi [47] in a PVT cell.

Liu et al. [60] used also a 1D model to study depressurization of hydrate in porous media. They separated the hydrates and gas zones by a moving front where conductive and convective heat transfer in gas and hydrate zones were considered. They considered equilibrium (in terms of pressure and temperature equilibrium curve) at the front and concluded that the assumption of stationary water phase results in overproduction of dissociation front location and underproduction of gas production in the well.

Gamwo and Liu [61] have presented a detailed theoretical description of the open source reservoir hydrate simulator HydrateResSim. Local thermal equilibrium is considered in the code. It considers both equilibrium and kinetic approaches, using Kim and Bishnoi [47] as the kinetic model of hydrate dissociation. They concluded that equilibrium approach over predicts the hydrate dissociation compared to kinetic approach.

EOSHYDR2, a model proposed by Moridis, which can simulate hydrate behavior in both sediment and laboratory conditions, includes both equilibrium and kinetic models for hydrate formation and dissociation. Because of scarcity of suitable data for the parameters of the kinetic model, Moridis employed the equilibrium approach [50].

Later on, using the same module, Kowalski and Moridis [62] made a comparison study between kinetic and equilibrium approach and concluded that the kinetic approach is important on short time and core scale system while equilibrium approach can be used for large scale simulations. In their equilibrium model, they considered the system composed of heat and two mass components (CH_4 and H_2O) that are distributed among four possible phases; the gas phase (composed of CH_4 and H_2O), the aqueous phase, the solid ice phase and the solid hydrate phase. They considered that the system always exists in equilibrium, with the occurrence of the various phases and phase transitions determined by the availability and relative distribution of heat and of two components [62]. This statement about the equilibrium approach is somewhat confusing and cannot describe a realistic hydrate reservoir, since it could happen only in a unique temperature, pressure, and composition. Depending on temperature, the water phase will exist as ice or liquid water except at the triple point where both can exist. Outside the triple point, there is only one degree of freedom according to Gibbs phase rule when there is free gas containing the hydrate former. Temperature is given by the local geothermal gradient and surface temperature (or sea floor temperature in the case of marine hydrates) so there is only one pressure in the reservoir for which equilibrium between all these three phases can exist. But even that is not correct since all phases are affected by minerals and corresponding adsorbed phase on the mineral surfaces. Strictly speaking the degrees of freedom is therefore zero. Therefore, even if all gas were consumed it would still not be possible to reach equilibrium. Consequently, the masses in the system will be distributed to minimize the free energy according to 1st and 2nd laws of thermodynamics.

A few studies used a kinetic approach based on the kinetic model of Kim and Bishnoi developed according to laboratory experiments [47]. Employing of fitted data from PVT cell to make this kinetic model and then using it in reservoir conditions might be unreliable. A different approach according to the non-equilibrium nature of hydrate phase transitions should therefore be developed.

3.2 Geomechanical stability

Some productions methods such as depressurization, thermal methods and injection of inhibitors are being considered to extract CH_4 from hydrate bearing sediments (HBS). As a consequence, the hydrate will dissociate and may pose a significant hazard with potentially adverse consequences for stability of the sediments [63].

Solid hydrates consist, for some hydrate deposits, a strong cementing agent. These deposits involve unconsolidated sediments characterized by limited shear strength. The dissociation of solid hydrates can affect the structural stability of HBS. In such deposits, it is the hydrate that supplies mechanical strength of the medium, and hydrate dissociation for gas production dramatically changes the geomechanical status of the system. The geomechanical status of the system is generally controlled by the properties of the specifics of the flows, phases in the pores and the solid system. The changes in the pressures can affect the stress fields as a result of permeability and porosity which may imply failures and evolution of fractures; these processes can affect the flow behavior of the system. [64].

Some reservoirs which are suitable for storage of $\mathrm{CO_2}$ are located in regions of low sea floor temperature which facilitate the formation of $\mathrm{CO_2}$ hydrate (Snøhvit located in the offshore of Norway is cold enough in the upper section). These hydrates may practically reduce the permeability and as such provide some extra sealing capacity. The hydrate formation may lead to cementation of sediments by newly formed solid phase. The new formed phase will impart mechanical strength of the medium and makes the sediment more stable.

Chapter 4: Project goals and choice of scientific methods

Hydrate phase transition dynamics are coupled on many scales – from the nano scale aspects of phase transitions and interactions with porous media surfaces up to hydrodynamic coupling on scales from molecular diffusions all the way up to turbulent flow – The fact that hydrates are unable to reach full thermodynamic equilibrium adds further challenges.

The primary goal of this project has been to develop a hydrate simulator that can incorporate non-equilibrium thermodynamic analysis. Based on literature survey of existing hydrate simulators (see section 2.5 for a review); none of the existing platforms were found feasible for different reasons mainly because analysis of stability and non-stability in most of the codes are based only on pressure and temperature variables as criteria for hydrate stability. Other limitations in the codes are found in the kinetic descriptions. A brief review of theoretical studies of hydrate in porous media are given in section 4.1

In a general situation of non-equilibrium hydrates formed from different phase results in different hydrate fillings and corresponding differences in free energies of the different hydrates. In this sense, it seemed reasonable to use a platform in which it would be possible to incorporate different hydrates as “pseudo minerals”. The project is limited to hydrates of CO_2 and CH_4.

In a general non-equilibrium situation, the kinetic expressions for all possible hydrate formations and dissociations are formulated as competing pseudo reactions with specific kinetic rates. Specifically this involves hydrate formation on water/ CO_2/CH_4 interface, from water solution and from CO_2/CH_4 adsorbed on mineral surfaces, as well as all different possible hydrate dissociation possibilities. The basic idea is that direction of free energy minimum, under constraints of mass and heat transport will control the progress of phase transitions in non-equilibrium systems.

Another goal has been to enable geomechanical analysis related to systems of rapid hydrate phase transitions. Examples are natural gas production from hydrates and vent systems and massive gas release from dissociating hydrates. A third goal has been to develop a simulator that should be able to estimate slow changes caused by natural changes. This implies that the model needs to handle molecular diffusion as the lowest level of transport and for the rapid changes. The geomechanical analysis should be an implicit evaluation so as to avoid possible uncertainties due to time shifts in the geomechanical analysis.

The three goals defined above limits the possible scientific methods to a reservoir simulator which can incorporate the physics of the system (non-equilibrium and geomechanics) in a best possible fashion.

More details on the goals of the project related to the non-equilibrium phase transitions and how these are handled is given in section 4.2. A secondary goal of the project has been to incorporate geomechanical analysis and some objectives and goals related to that aspect are discussed in section 4.3

4.1 Development of a new hydrate reservoir flow simulator as scientific method for model studies of hydrates in sediments.

Different types of theoretical methods and simulation approaches have been applied to study hydrates in reservoirs. For modeling production of hydrocarbons from hydrate, which is one of the primary focus areas of this thesis, there are no alternatives than reservoir simulation. There are, however, different ways of including the hydrate phase in the flow model. Hydrate phase transition kinetics are by physical nature Nano-scale processes across thin interfaces, typically in the range of 1 to 2 nm. These phase transitions are dynamically coupled to phenomena ranging from pore-scale phenomena and impact of solid surfaces all the way upwards to Darcy flow and length scales of meters and kilometers. Different types of studies can be applied to explore smaller scale phenomena. But there is no way around a numerical tool that can couple all relevant dynamic processes from Nano-scale to reservoir scale in a way so as to retain the physics as fundamental as possible given realistic restraints of computational times. Available academic and commercial hydrate reservoir simulators in academia have typically been extended from different versions of classical reservoir simulators for oil and gas, or from hydrogeological codes. The available data on hydrate reservoirs are scarce and most often limited to interpretations of seismic and/or resistivity measurement.

Laboratory experiments can never reproduce a real hydrate reservoir, which during geological time scale have entered a situation of stationary balance between fluid phases and hydrate as a function of all factors that determines the local flow fluxes and mass exchange between phases. In summary, neither data from real hydrates in nature nor hydrates from laboratory experiments can provide the level of confident reference data needed in development and verification of mathematical models in reservoir simulators.

In view of the above, it is quite obvious that stronger emphasis has to be put on advanced theoretical modeling of the different parts of the coupled dynamics which are critical for the use of the reservoir simulator. With reference to the work in this thesis, the main focus is hydrate formation dynamics during CO_2 storage in reservoirs with cold sections, and production of gas using pressure reduction.

To handle the non-equilibrium approach, there is a need for a reactive transport simulator which can handle competing processes of formation and dissociation of hydrates as well as the coupling between reactive flow and the geo-mechanical analysis. The simulator should have a flow description ranging from diffusion to advection and dispersion and as such is able to handle flow in all regions of the reservoir, including the low permeability regimes of hydrate filled regions.

4.2 The choice of a compositional reactive transport reservoir simulator; focus areas for application.

The global warming issue is a big challenge facing significant parts of scientists within climate research. The rise of CO_2 concentration in the atmosphere is considered the main cause of global warming. In order to avoid a situation of irreversible global warming, the reduction of CO_2 in the atmosphere is required.

One of the most promising technologies used for reducing emissions of CO_2 to the atmosphere is the concept of CCS (CO_2 Capture and Storage) (Metz et al. 2005), of which the first part of this work only focus on specific issues related to the storage part.

Several options for CO_2 storage have been proposed. Among all these options the geological disposal of CO_2 within porous rocks underground is the most attractive and is already in industrial use.

Another approach occurs at cooler temperatures with relatively high pressure beneath permafrost regions or in sediments of deep oceans. For example, the Snøhvit (offshore Norway) reservoir is cold enough in the upper hundreds of meters below seafloor which allows CO_2 hydrate formation. Hydrate formation will have impacts on local porosity, permeability and geomechanics. Hydrates in sediments are generally not in thermodynamic equilibrium. This implies that there may be several competing hydrate phase transitions in the reservoir. Mineral surfaces bring additional thermodynamic phases of impact for hydrate phase transitions.

Although relevant reservoirs for storage of CO_2 are located in regions which facilitate formation of CO_2 hydrate (offshore Norway), open data are still scarce. In addition, at the current stage, a large-scale commercial hydrate production is impossible. At the same time our knowledge about geomechanical behavior of hydrate bearing sediments during decomposition and their effects are very limited [63]. The mathematical models and numerical simulators are essential tools in predicting the dynamic properties of hydrates in reservoirs. To handle the non-equilibrium approach, there is a need for a reactive transport simulator which can handle competing processes of formation and dissociation of hydrates. According to these conditions, it is desirable to develop a reservoir simulator with an implicit coupling between reactive flow and the geomechanical analysis. This is feasible since hydrate might be considered as a pseudo mineral and the kinetics of different "reactions" involving hydrate can be modelled according to results from more fundamental theories like phase field theory (PFT) [65, 66]. This implies that the hydrate phase transitions will automatically be coupled to geochemical reactions via the logistics of the reactive transport simulator.

4.3 Extended RetrasoCodeBright as chosen platform

A brief overview of previous studies on hydrates in porous media and available reservoir simulators in academia, industry and research institutions like for instance National laboratories in the USA was given in section 2.5. Although the review presented in section 2.5 is too short to give any detailed overview of the inherent limitations of the existing platforms, none of these was considered as appropriate for further developments in this project, for different reasons. There are simply too many questionable approximations in the description of hydrate dynamics to give the necessary confidence in simulation of natural gas hydrate production scenarios, hydrate-sealing effects during CO_2storage in cold reservoirs and the long-term development of hydrate reservoirs during geological time scales.

The main goal of the project is to develop a new state of the art hydrate simulator which is able to model non-equilibrium thermodynamics of competing hydrate formation processes and competing hydrate dissociation processes to address:

- Hydrate production through pressure reduction and/or thermal stimulation
- Incorporate additional hydrate phase transitions that affect the dynamics during the methods above, like dissociation towards under-saturated phases and mineral surfaces
- Prepare for inclusion of production of hydrates by injection of CO_2 and CO_2 with additives
- Implicit geomechanical evaluation
- Development of hydrate filled structures during long time scales for future evaluation of possible geo hazards
- Natural leakages of methane from hydrates
- The role of hydrate formation during CO_2 storage in sediments containing cold zones

The first part of this PhD project is focused on theoretical studies of CO_2 hydrates formation in cold aquifers. Two kinetic approaches are used: the first one is based on the effect of super saturation (or under saturation) as applied in the framework of classical nucleation theory of hydrate growth or dissociation [67]. This theory is numerically simple and can be applied directly with the free energy changes related to the individual phase transitions which are possible. The super saturation must at least be negative enough to overcome the barrier of pushing aside the surrounding fluids. This barrier is proportional to interface free energy. Another approach, which is applied indirectly, kinetic information from hydrate formation and dissociation from phase field theory (PFT) simulations [15] are extracted and fitted to simple models suitable for reservoir simulation.

Non-equilibrium thermodynamic properties for the PFT simulations in situations of super-saturations (leading to hydrate formation) and under-saturations (leading to hydrate dissociation) are based on a first order Taylor-expansion of hydrate from equilibrium state as discussed by Kvamme et al. [67]. The performance of the simulator is demonstrated through example cases.

Implications of hydrate formation on geomechanical properties of the models reservoir are other aspects addressed in this work. The effects of hydrate formation on the geomechanics of the reservoir are illustrated through analysis of the effective stress.

According to some studies the worldwide amount of gas trapped in natural gas hydrates is estimated to more than twice all known conventional fossil fuels [27]. The second part of this PhD project has focused on theoretical study of gas production from hydrate bearing sediments. An alternative way of treating hydrates in reservoir simulations which makes use of well-known logistics from reactive transport simulators. Kinetic rates for different hydrate dissociation "reactions" are derived from Phase Field Theory simulations and similar for different hydrate formation "reactions". Pressure reduction is used as gas production method. The effects of hydrate formation on the structure of the reservoir are illustrated through analysis of the effective stress developments but lack of realistic tensile strengths does not enable any conclusions on the geomechanical implications of hydrate formation and dissociation for the specific examples.

Chapter 5: Theoretical background

It is not the intention of this work to go into very many details on the kinetics of phase transitions but a brief description of some basics is useful as a background for the more advanced models that is being applied to provide kinetic models for the different possible phase transitions involved in hydrate dissociation and formation.

To account for non-equilibrium thermodynamics of the hydrate the results from phase field theory simulations [68] have been modified to be used in the kinetic model. Phase field simulations are based on the minimization of Gibbs' free energy on the constraint of heat and mass transport. Extensive research has gone on in the same group on application of phase field theory in the prediction of hydrate formation and dissociation kinetics which is still in progress [67, 69-73]. In this study, the simulation results of such studies have been extrapolated and used as the constant rate of the kinetic model in the numerical tool.

A corresponding kinetic rate based on mathematical description of super and under saturation is also used. This kinetic rate is calculated according to the classical theory [67]. The results are then implemented into the RCB code by means of a numerical method known as linear interpolation function on segments. The hydrate formation and dissociation can be observed in all flow related properties as well as the changes in the porosity (in terms of available volume fraction at disposal for fluids) in specific areas of the porous media

5.1 Brief fundamentals on kinetics of hydrate formation and dissociation

The process of hydrate formation can be divided into three steps: Nucleation, growth and induction. The nucleation is normally very fast: it takes only few nano-seconds [67] and it occurs when the driving force in terms of free energy difference exceeds the penalty for giving space for the new phase, as discussed below. The growth step can also be fast in terms of the thermodynamic contribution but is often constrained by limited mass transport. As it will be discussed below, nucleation and growth are physically well-defined processes but on the scales which makes them difficult to follow dynamically by experiments. Induction time is another term that occasionally occurs in the open literature. This can be interpreted as the onset of massive growth, and as such is not physically well defined. Detection resolution of induction time is therefore subject to detection principles, whether it is through the detection of pressure changes, optical devices, sound or other types of detection principles.

Within the main focus of this thesis, it is sufficient to describe the important stages above in terms of a simple theory, the classical nucleation theory.

A cluster is an ensemble of a number of molecules. In terms of hydrate precursors it will contain water and hydrate formers like for instance CH_4 or CO_2. If the cluster is considered to be spherical, there are two competing processes occur. The first is related to the phase transition itself and the second is where the solute molecules become part of the surface of the growing crystal and requires energy (pushing term). The associated free energy change ΔG can be formulated as:

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta g_v$$

ΔG_s, is the surface free energy, ΔG_v is the volume free energy. The first of these is the work needed to push away the surrounding old phases ("parent" phases) and represents a penalty and barrier towards the phase transition. The second term is the free energy gain of the phase transition itself. These two processes are shown in figure 8 below:

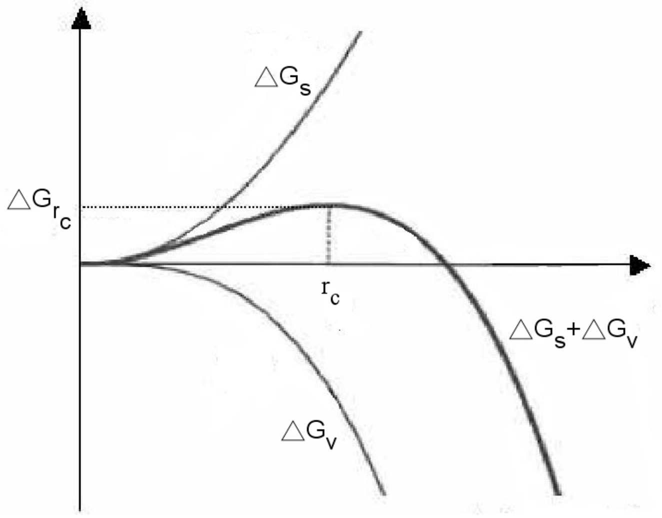

Figure 8 variation of free energy as function of cluster size (modified from [2])

The pushing term is dominating at the small cluster sizes. The process is normally characterized by physical elements of random when the size is below a certain critical size r_c and the cluster is instable. The degree of randomness varies depending on apparent phase(s) are related to randomness elements of molecular motions and associated energy fluxes in different directions. Once the cluster reaches the critical size r_c the free energy will decrease steadily due to the domination of the phase transition term. r_c is given by the following equation:

$$\frac{\partial(\Delta G)}{\partial r} = 4\pi r_c^2 g_v + \sigma \cdot 8\pi r_c = 0$$

$$r_c = \frac{-2\sigma}{g_v}$$

The critical size allows us to calculate the flux of growth from classical nucleation theory:

$$J^* = J_0 e^{-\beta W^*}$$

Where J_0 is the kinetic mass transfer term, $\beta = 1/RT$, and W^* is the critical work involved in the creation of the first stable particle (at r_c) and can be found by:

$$W^* = \int_0^{r_c} \partial w \cdot dr = \Delta G(r = r_c)$$

Even particles larger than critical size can decay again if there is a lack of access to mass and more stable particles (lower free energy) close to the particle can benefit of consuming mass from less stable particles.

Modeling of hydrate kinetics has often been empirical fitting to some functions of super-saturation conditions (growth) or under-saturation conditions (dissociation). Other methods model the mass transport constants according to the sum of some kinetic stages believed to limit the mass transport, and the thermodynamic driving forces are often modeled as difference of real state fugacity and equilibrium state fugacity [47].

The main methods, as mentioned above, applied for dissociation of *in situ* natural gas hydrates are injection of inhibitors, depressurization and thermal stimulation. The process of dissociation is endothermic. Heat must be provided in order to break hydrogen bonds between water molecules. During thermal stimulation for production from natural gas hydrates, this heat is provided directly and the dynamics of the heat dissipation become part of a more complex model. During depressurization, heat will be extracted from the surroundings and this transport can in many cases be rate limiting for the kinetics.

5.2 Thermodynamics

This section gives a brief overview of the thermodynamic calculations involved in hydrate phase transitions, including calculations of thermodynamic properties outside of equilibrium (subsection 5.2.5). Details are kept at a minimum level since the enclosed papers provide a more detailed overview of the methods and models applied to the different systems studied.

5.2.1 Free energy

The second law of thermodynamics states that any isolated system will tend towards maximum entropy. The changes in internal energy of phase i are given in combination of 1st and 2nd law of thermodynamics:

$$dU^i \leq T^i dS^i - pdV^i + \sum_{i=1}^{n} \mu_i^i dN_i^i \tag{5.1}$$

Where, S is the entropy μ is the chemical potential and N is the number of moles of components. For reversible changes, the equation becomes equality.

By subtracting $d(T^iS^i)$ and adding $d(P^iV^i)$ on both sides we obtain Gibbs free energy:

$$dG^i \leq -S^i dT^i + V^i dp^i + \sum_{i=1}^{n} \mu_i dN_i^i \tag{5.2}$$

V^idP^i is the shaft work and the addition of $d(P^iV^i)$ into the equation (5.1) eliminates the internal work of pushing fluids in a flowing system. The subtraction of $d(T^iS^i)$ was made to change natural variable from S to T. Also, note that the T is the temperature acting from the surrounds, which is seen by the incorporation of second law into the first law. The last term in right hand side is the chemical work related to extracting or inserting particles. At constant temperature and pressure (5.1) and (5.2) give:

$$dG^i \leq \sum_{i=1}^{n} \mu_i dN_i^i \tag{5.3}$$

When hydrate is homogeneously being forming or dissociating from/to liquid water solution, the heat transport is very rapid, typically 2 to 3 orders of magnitude faster than mass transport. Heat transport is therefore not kinetically rate limited and phase transitions might be studied by isothermal approximation, like in the studies of [15, 68] which allows reversible and irreversible processes related to phase transitions progress until achieving a minimum free energy in the system. This implies:

$$\begin{aligned} dG^{total} &= 0 \\ dG^{total} &= dG^{total}_{min} \end{aligned} \tag{5.4}$$

This means that the system will progress towards total minimum free energy under constraints of temperatures, pressures and mass distribution over all possible phases. Total free energy is the extensive free energy as sum of extensive free energies of all the phases in the system. If the system can reach equilibrium then the limits of the equation (5.4) implies that the chemical potential of each component is the same in all the coexisting phases, as well as uniform temperatures and pressures across the entire system.

As mentioned in previous chapter, hydrate in nature is generally not in equilibrium. From a thermodynamic point of view, the combination of mass conservations and conditions of equilibrium defines minimum criteria of possibility to reach equilibrium, most often known as Gibbs phase rule. Gibbs phase rule is simply the conservation of mass under the constraints of equilibrium.

$$F = N - \pi + 2 \tag{5.5}$$

In equation (5.5) F is the degree of freedom, N is the number of components that actively participate in phase transition and π is the number of theoretical phases. Locally in a reservoir, temperature and pressure are given and according to Gibbs phase rule the degree of freedom is equal to two while with a system consisting of three phases (aqueous, gas and hydrate), there will be only one degree of freedom and the system is over-determined and the three-phase system will be unable to reach equilibrium. The combination of 1st and 2nd law of thermodynamics will dictate the system to tend towards the minimum free energy for the whole system under the constraints of the total mass and distribution of this into all the possible phases.

Equation (5.5) is a minimum condition for equilibrium in the sense that some theoretically possible phases may not be possible due to levels of free energy because of the combined first and second law (free energy) since distribution onto fewer phases might provide the lowest free energy for the distribution of the total mass. In that case, a new analysis according to equation (5.5) is needed in order to evaluate whether the system can reach equilibrium or not. This has to be repeated until the number of actual possible phases from the point of mass balance and equilibrium as well as free energy levels is fulfilled.

5.2.2 Hydrate Thermodynamic

The chemical potential for water in hydrate can be estimated using a modified version of the statistical-mechanical model:

$$\mu_w^H(T,P,\vec{x}^H) = \mu_w^{H,0}(T,P) - \sum_j v_j ln(1+\sum_k h_{kj}) \tag{5.6}$$

Where superscript $H,0$ denote empty clathrate [69], v_j is the fraction of cavity of type j per water molecules and h_{kj} is the canonical partition function of guest molecule of type k in cavity type j and $\mu_w^{H,0}$ is the chemical potential for water in an empty hydrate structure. The canonical partition functions can be expressed as:

$$h_{kj} = exp(\beta(\mu_{kj} - \Delta g_{kj}^{inc})) \tag{5.7}$$

In equation (5.7) μ_{kj} is the chemical potential of guest molecule k in cavity j in hydrate. The second term in the exponent is the free energy change of inclusion of the component k in cavity type j, which is independent of the specific hydrate type.

Hydrate structure 1 (s1) contains three large cavities and one small cavity per 23 water molecules, $v_l = 3/23$ and $v_S = 1/23$.

The filling fractions are given by:

$$\theta_{kj} = \frac{h_{kj}}{1 + \sum_{k} h_{kj}} \tag{5.8}$$

Where θ_{kj} is the filling fraction of guest molecule k in cavity type j. x_{kj}, is the mole fraction of guest molecule k in the hydrate type j and will be calculated according to the equation (5.9)

$$x_{kj} = \frac{\sum_{i} v_i \theta_{kj}^{i}}{1 + \sum_{i} \sum_{k} v_i \theta_{kj}^{i}} \tag{5.9}$$

Here v_i is the number of type i cavities per water molecule.

The changes in the free energy for a hydrate formation is calculated according to equation (5.10)

$$\Delta G = \left[x_w^H (\mu_w^H - \mu_w^p) + x_{CH4}^H (\mu_{CH4}^H - \mu_{CH4}^p) + x_{CO_2}^H (\mu_{CO_2}^H - \mu_{CO_2}^p) \right] \tag{5.10}$$

In this equation, H represents hydrate phase, p represents either liquid, gas and adsorbed phases depending on where the components building the hydrate come from, x composition and μ chemical potential.

For a given hydrate to grow unconditionally Gibbs free energy change according to (5.11) must be negative and all gradients in free energy change (temperature, pressure, concentrations) must be negative.

5.2.3 Fluid thermodynamics

The free energy of the fluid phase is given as:

$$G_i^{Fluid} = \sum_{i=1}^{3} x_i \mu_i^{Fluid} \tag{5.11}$$

Where μ_i^{Fluid} is the chemical potential of the fluid phase of the ith component.

The water chemical potential with some approximation of fugacity and activity coefficients is given as:

$$\mu_w^{Fluid} = \mu_w^{ideal\,gas}(T,P) + RTln(y_w) \tag{5.12}$$

Where y_w is the mole fraction of water in the fluid phase which is given by Raoul's law:

$$y_w = \frac{x_w \gamma_w (T,P,\bar{x}) P_w^{Sat}(T)}{\phi_w (T,P,\bar{y}) P} \tag{5.13}$$

Where ϕ and γ are respectively fugacity and activity coefficient, x_w is the mole fraction of water in the aqueous phase. The mole fraction of water is close to unity. The chemical potential for the mixed fluid states are expressed as:

$$\mu_i^{Fluid} = \mu_i^{ideal\,gas\,pure} + RTln(y_i) + RTln\phi_i(T,P,\bar{y}) \tag{5.14}$$

Where i is either CO_2 and CH_4 and the fugacity coefficients of component i in the mixture are calculated using the classical SRK equation of state (EOS).

5.2.4 Aqueous thermodynamics

The free energy of the fluid phase is given as:

$$G_i^{aqueous} = \sum_{i=1}^{3} x_i \mu_i^{aqueous} \tag{5.15}$$

Where $\mu_i^{aqueous}$ is the chemical potential of the fluid phase of the ith component. $\mu_i^{aqueous}$ is derived from excess thermodynamics and have the following form

$$\mu_i^{aqueous} = \mu_i^{\infty} + RTln(x_i \gamma_i) + v_i^{\infty}(P - P_0) \tag{5.16}$$

μ_i^{∞} is the chemical potential in water of component i at infinite dilution, R is the universal gas constant, γ_i is the activity coefficient in the aqueous of component I in the asymmetric convention and v_i^{∞} is the partial polar volume at infinite dilution of component i. μ_i^{∞} are found by assuming equilibrium between fluid and aqueous phases $\mu_i^{aqueous} = \mu_i^{fluid}$ at low pressure and solubility. The chemical potential of water is described as:

$$\mu_w = \mu_w^{pure\,liquid} + RTln(x_w \gamma_w) + v_w(P - P_0) \tag{5.17}$$

v_w is the molar volume of water and $\mu_w^{pure\,liquid}$ is the pure chemical potential of water. The description for calculating the activity coefficient γ_w is given by Svandal et al.[70]

5.2.5 Non equilibrium thermodynamics and driving forces for phase transitions

Equation (5.18) below represents hydrates dissociation free energy differences.

$$\Delta G = -\left[x_w^H(\mu_w^H - \mu_w^p) + x_{CH4}^H(\mu_{CH4}^H - \mu_{CH4}^p) + x_{CO_2}^H(\mu_{CO_2}^H - \mu_{CO_2}^p) \right] \tag{5.18}$$

Driving forces for hydrate dissociation are conditioned when pressure and temperature are outside the hydrate stability zone, or situations where water is under-saturated with methane or sublimation when gas is under-saturated with water. Hydrate dissociates into gas and liquid water in the first case. In the second case, the final phase is water and in the third case, (sublimation) final phase will be gas.

A non-equilibrium logistic system inside a reservoir simulator analyses the system locally (every element at every time step). All impossible ($\Delta G > 0$) and unlikely ($|\Delta G| < \varepsilon$) cases must be disregarded. ε is a value that discriminates phase transitions with far too low driving force compared to the limited average retention time in the element as well as the nucleation barrier given by the interface free energy between the new and old phase. This also includes possibly mass transport limited cases, in which the phase transition is unlikely to proceed during the average retention time due to slow mass transport. In the case of mass limitations then the different kinetic equations for the possible competing phase transition will be subject to an analysis of free energy minimization under mass constraints.

In case of super-saturation (non-equilibrium), the chemical potential for H_2O, CH_4 and CO_2 in the hydrate can be calculated according to equation (5.19)

$$\begin{aligned} \mu_i^H(T,\ P,\ \overrightarrow{x_i^H}) &= \mu_i^{H,eq}(T, P, \overrightarrow{x_i^{eq}}) + \left(\frac{\delta\mu_i^H}{\delta P}\right)_{(T^{eq},\overrightarrow{x_{eq}})} \cdot (P - P^{eq}) \\ &+ \left(\frac{\delta\mu_i^H}{\delta T}\right)_{(P^{eq},\overrightarrow{x_i^{eq}})} \cdot (T - T^{eq}) + \sum_i^{i=m,c,w} \left(\frac{\delta\mu_i^H}{\delta x_i}\right)_{(T^{eq},P^{eq},\overrightarrow{x_{j\neq i}^{eq}})} \cdot (\overrightarrow{x_i^H} - \overrightarrow{x_i^{eq}}) \end{aligned} \tag{5.19}$$

In this equation $\mu_{CO_2}^{H,eq} = \mu_{CO_2}^{Fluid}$ and $\mu_{CH_4}^{eq} = \mu_{CH_4}^{Fluid}$. The superscript *eq* denotes the equilibrium state, and ***i*** can be water, Carbon dioxide or methane for the systems in focus here. But of course the equations are general for other hydrate formers and water as well and not limited to two hydrate formers.

The chemical potential gradients with respect to pressure can be given by

$$\left(\frac{\delta\mu_i}{\delta P}\right)=\overline{V}_i \tag{5.20}$$

Where $\overline{V}_i$ denotes the partial molar volume of each component.

The derivative of the equation (5.6) with the respect to the mole fraction:

$$\frac{\delta\mu_w^H}{\delta x_r}=-RT\sum_j v_j\left[\frac{\sum\limits_k \frac{\delta h_{kj}}{\delta x_r}}{\left(1+\sum\limits_k h_{kj}\right)}\right] \tag{5.21}$$

Here r can be methane, carbon dioxide, or water.

Equation (5.22) gives the relationship between molar enthalpy and the chemical potentials. Chemical potentials are directly estimated outside equilibrium,

$$\frac{\delta\left[\frac{\mu_k}{RT}\right]_{P,\vec{N}}}{\partial T}=-\frac{\overline{H}_k}{RT^2} \tag{5.22}$$

for any component *k* in a given phase. The line above *H* indicates partial molar enthalpy. To obtain the enthalpy information for the convective terms of the energy balances in the reservoir simulator, it suffices to sum the contributions to each enthalpy of all components in each phase.

Chapter 6: RCB simulator

The RetrasoCodeBright (RCB) is the result of the coupling of two codes: CodeBright and Retraso. This code was designed to model problems consisting of coupled thermal, hydraulic, geochemical and geomechanical processes. CodeBright contains an implicit algorithm for integrating material flow, heat-flow and geomechanical model equations [71, 72]. Retraso involves an explicit algorithm for updating the geochemistry as shown in figure 9 [73, 74].

The original RCB code was written as a hydrogeological code based on low-pressure gas phase (ideal gas). The first set of extension was made by incorporating an equation of state for describing $\mathrm{CO_2}$ and $\mathrm{CO_2}$ mixed with impurities as relevant for studies of $\mathrm{CO_2}$ storage in aquifers [75]. The equations of state included are by choice either Peng-Robinson [76] or Soave-Redlich-Kwong [77] . At this stage, we make no arguments about on the accuracy of these two equations for $\mathrm{CO_2}$. There are indeed better equations of state available for pure $\mathrm{CO_2}$, like for instance the Span-Wagner equation [78]. At this stage, and for current generation of hydrate reservoir simulators, there are other uncertainties which are substantially higher. The extension of RCB for handling of hydrate as a phase is accomplished by defining every hydrate phase as a pseudo mineral. There are two advantages of that. First, it makes use of the logistics inside RCB for handling competing reactions based on lowest free energy pathways in every grid block of the system. Secondly, it has an interface for easy implementation of reaction kinetic models and corresponding parameters for all the "pseudo reactions". These two features allow for implementation of "reaction models" for competing growth and dissociation routes depending on availability of surrounding mass and degree of super and under saturations for different competing "reactions" locally.

The mathematical equations for the system are highly non-linear and solved numerically. The numerical approach can be viewed as divided into two parts: spatial and temporal discretization. Finite element method is used for the spatial discretization while finite differences are used for the temporal discretization. Newton-Raphson method iterations are used to solve the nonlinear algebraic systems of governing partial differential equations [73].

In one time step the CodeBright part solves for mass flow, heat transport and geomechanical deformation. All these properties are then transferred to Retraso. Porosity is updated according to mineral dissolution/precipitation and/or hydrate formation/dissociation, and permeability is updated according to a commonly used correlation [79] and all detailed results from the individual flux and phase properties are transferred back to CodeBright for the next time step as mentioned above.

The schematic illustration of the coupling of the two modules is given in the figure 9. The results from this simulator are illustrated through a graphical window GiD[4].

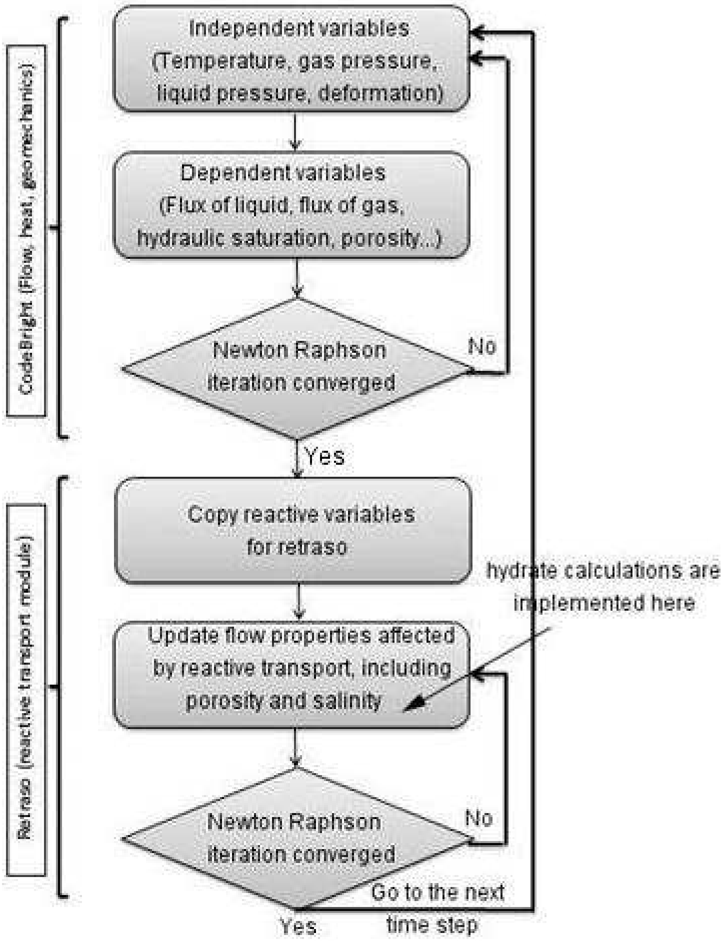

Figure 9 RCB solves the integrated equations sequentially in one time step

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[4] CIMNE, International Centre for Numerical Methods in Engineering, gid@cimne.upc.edu , Barcelona, Spain. “GiD – The personal pre- and post-processor”, See also: http://gid.cimne.upc.es/

6.1 Governing equations

With reference to the master flow sheet illustrated in figure 9 the governing equations involved in the two sections of the code, the CodeBright part in the first loop and the Retraso part in the second loop.

6.1.1 Mass balance of solid

$$\frac{\partial}{\partial t}(\theta_s(1-\phi))+\nabla\cdot(j_s)=0 \tag{6.1}$$

Here θ_s is the mass of solid per unit volume of a solid, j_s is the flux of solid and ϕ is porosity. From this equation, an expression for porosity variation is obtained as:

$$\frac{D_s\phi}{Dt}=\frac{1}{\theta_s}\left((1-\phi)\frac{D_s\theta_s}{Dt}\right)+(1-\phi)\nabla\cdot\frac{du}{dt} \tag{6.2}$$

Here, u is a solid displacement. The material derivative with respect to the solid has been used and its definition is:

$$\frac{D_s}{Dt}(\bullet)=\frac{\partial}{\partial t}+\frac{du}{dt}\cdot\nabla(\bullet)$$

6.1.2 Mass balance of water

$$\frac{\partial}{\partial t}(\theta_l^w S_l\phi+\theta_g^w S_g\phi)+\nabla\cdot(j_l^w+j_g^w)=f^w \tag{6.3}$$

Where, θ_l^w and θ_g^w are respectively mass of water in liquid and gas phase, S_l , S_g are degree of saturation of liquid and gaseous phases i.e., fraction of pore volume occupied by each phase, f^w is the external supply of water.

6.1.3 Mass balance of gas

$$\phi\frac{D_s(\theta_l^a S_l+\theta_g^a S_g)}{Dt}+(\theta_l^a S_l+\theta_g^a S_g)\frac{D_s\phi}{Dt}+((\theta_l^a S_l+\theta_g^a S_g)\phi)\nabla\cdot\frac{du}{dt}+\nabla\cdot(j_l^a+j_g^a)=f^a \tag{6.4}$$

Where, θ_l^a and θ_g^a are mass of gas component (CH_4, CO_2 ...) per unit volume in liquid and gas phase respectively.

6.1.4 Momentum balance of the medium

The momentum balance reduces to the equilibrium of stresses if the inertial terms are neglected:

$$\nabla \cdot \sigma + b = 0 \tag{6.5}$$

Where, σ is stress tensor and b is the vector of body force.

6.1.5 Internal energy balance of the medium:

The equation for internal energy balance for the porous medium is established taking into account the internal energy in each phase (E_s, E_l, E_g):

$$\frac{\partial}{\partial t}(E_s \rho_s (1-\phi) + E_l \rho_l S_l \phi + E_g \rho_g S_g \phi) + \nabla \cdot (i_c + j_{Es} + j_{El} + j_{Eg}) = f^Q \tag{6.6}$$

Where, i_c is energy flux due to conduction through the porous medium, the other fluxes (j_{Es}, j_{El}, j_{Eg}) are advective fluxes of energy caused by mass motions and f^Q is an internal/external energy supply.

6.1.6 Constitutive equations and equilibrium laws:

The set of necessary constitutive and equilibrium laws as mentioned in the Table 2 associates the above balances.

Table 2 constitutive equations

Constitutive Equation	**Variable Name**
Darcy's Law	Liquid and gas advective flux
Fick's law	Vapor and gas non- advective flux
Fourier's law	Conductive heat flux
Mechanical constitutive model	Stress tensor
Phase density	Liquid density
Retention curve	Liquid phase degree of saturation
Gas Law	Gas density

Generalized Darcy's law is used to compute the advective flux, q, of the α phase ($\alpha = l$ for liquid, $\alpha = g$ for gas) and g is a vector of gravity forces. It is expressed as:

$$q_\alpha = \frac{-kk_{r\alpha}}{\mu_\alpha}\left(\nabla P_\alpha - \rho_\alpha g\right) \tag{6.7}$$

Where k is the tensor of intrinsic permeability, $k_{r\alpha}$ is the relative permeability of the phase α, μ_α is the dynamic viscosity of the phase α.

Van Genuchten's retention curve [80] expressing saturation as a function of liquid or gas pressure:

$$S_l = \left[1 + \left(\frac{P_g - P_l}{P_0}\right)^{\frac{1}{1-\lambda}}\right]^{-\lambda} \tag{6.8}$$

Where, $S_g = 1 - S_l$. P_0 and λ are scale pressure and shape parameters. The relative permeability $k_{r\alpha}$ depends on saturation (S_l) which in its turn depends on P_l and P_g.

For calculation of intrinsic permeability, Kozeny's model is used:

$$k = k_o \cdot \frac{\varphi^3}{(1-\varphi)^2} \cdot \frac{(1-\varphi_o)^2}{\varphi_o{}^3} \tag{6.9}$$

In this equation φ_o is reference porosity and k_0 is intrinsic permeability for matrix with reference porosity.

6.1.7 Chemical Reactions:

Equilibrium Solid-liquid interactions can be described by the law of the Mass Action:

$$X_m \lambda_m K_m = \prod_{i=1}^{N_c} c_i^{v_m^p} \gamma_i^{v_m^p} \tag{6.10}$$

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

For the kinetic solid-liquid interactions, the code uses a general formulation which includes several types of experimental functions:

$$r_m = \sigma_m \zeta_m \exp\left(\frac{E_{a,m}}{RT}\right) \sum_{k=1}^{N_k} k_{mk} \prod_{i=1}^{Ns} a_i^{P_{mki}} \left(\Omega_m^{\theta_{mk}} - 1\right)^{\eta_{mk}} \tag{6.11}$$

Where,

$$\Omega_m = \frac{1}{K_m} \prod_{i=1}^{Nc} a_{i,actual}^{v_{mi}}$$

And

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

r_m is the mineral dissolution rate (moles of mineral per volume of rock and unit time), k_{mk} is the experimental rate constant, Ω_m is the ratio between the ion activity product for the real concentrations and the corresponding equilibrium constant. The parameters θ and η must be determined by fitting to experimental data. $E_{a,m}$ is the apparent activation energy of the overall reaction process, k_0 is a constant. σ_m is the reactive surface. The term $a_i^{P_{mki}}$ accounts for the catalytic effect of some species (particularly of H+). Factor ζ_m takes on values of +1 or -1 depending on whether Ω_m is larger or smaller than 1 (precipitation or dissolution) respectively at equilibrium $\Omega_m = 1$ and therefore $r_m = 0$. The kinetic equation for hydrate is according to two approaches: The first one is based on the results from the effect of super saturation on free energy change for the relevant phase transition. The kinetic impact on the flux is so far estimated according to the classical nucleation theory. An alternative model which is equally simple is MDIT theory [67]. Note that MDIT theory reduces to classical nucleation theory when the interface thickness goes to zero, or is set to zero. The second approach is based on the model of Kim and Bishnoi [47] but the rate constant is fitted based on results from phase field theory simulations.

6.1.8 The aqueous complexiation reactions

These reactions are considered almost instantaneous and can be considered as equilibrium reactions:

$$LogK_a = S_a Logc_a + S_a Log\gamma_a(c_a) \tag{6.12}$$

Where K_a is the equilibrium constant vector, which depends on T and P. S_a is the stoichiometric coefficient matrix for aqueous complexiation reactions (including redox reactions). c_a is the molar concentration vector of aqueous species and γ_a is the vector of thermodynamic activity coefficients.

6.1.9 Gas liquid interactions

For reactions involving aqueous and gaseous phases, the mass action law states that:

$$p_f \gamma_f K_f = \prod_{i=1}^{N_c} c_i^{v_\beta} \gamma_i^{v_\beta} \tag{6.13}$$

where p_f is the partial pressure of the f-th species in the gas phase, γ_f is its activity coefficient, c_i and γ_i are the concentration and activity coefficient of the i-th dissolved primary species, respectively, v_β is the stoichiometric coefficient of the i-th species in the ex-solution reaction of fluid f, and K_f is the equilibrium constant of the reaction.

6.2 Modification in RCB

In comparison of the original version of RCB, the current version has been extended from ideal gas into handling of CO_2 according to the Soave –Redlich- Kwong (SRK) equation of state [81]. This equation of state is used in density calculations as well as the necessary calculations of fugacities of the CO_2 phase as needed in the calculation of dissolution of CO_2 into the groundwater [81, 82].

The equation of state (EOS) and solubility calculations of CH_4 was added in the code. The Soave-Redlich-Kwong (SRK) equation was updated by adding EOS parameters such as critical temperature, critical pressure and acentric factor.

To account for solubility calculations of CH_4, Henry's constant for CH_4 was added. The energy balance of the gas is modified from ideal gas according to equation (6.14) using SRK equation of state to calculate fugacity coefficient and derivatives.

$$H = H^{id.gas} - RT^2 \frac{d(\ln\phi)}{dT} \tag{6.14}$$

The nonlinear partial differential equations of the system are solved numerically [73]. The Newton-Raphson method adopted to find an iterative scheme has been modified to improve the convergence of the numerical solution while increasing the range of working pressure in the system [81].

The equation (6.15) is used to describe CO_2hydrate equilibrium conditions in the simulation. This is based on the model developed by Kvamme and Tanaka [69] where the SRK equation of state is used to calculate the fugacity of the liquid phase.

$$\begin{aligned} P^{eq} = {} & 9.968156693851430\times10^{-7}\times T^6 - 1.721355993747740\times10^{-3}\times T^5 \\ & + 1.237931459591990\times T^4 - 4.745780290305340\times10^2\times T^3 \\ & + 1.022898518566810\times10^5\times T^2 - 1.175309918126070\times10^7\times T \\ & + 5.624214942384240\times10^8 \end{aligned} \tag{6.15}$$

In this equation P^{eq} is calculated in MPa and T in Kelvin.

For CH_4 hydrate, the relationship (6.16) between temperature and pressure proposed by Sloan [2] was used:

$$\begin{aligned} Ln(P^{eq}) = {} & -1.94138504464560\times10^5 + 3.31018213397926\times10^3\times T \\ & -2.25540264493806\times10^1\times T^2 + 7.67559117787059\times10^{-2}\times T^3 \\ & -1.30465829788791\times10^{-4}\times T^4 + 8.86065316687571\times10^{-8}\times T^5 \end{aligned} \tag{6.16}$$

To account for non-equilibrium thermodynamics of the hydrate, some modifications of the code have been made in this thesis. Two kinetics rates are implemented. The first one is the rate calculated according to the classical nucleation theory [67] and the theory of non-equilibrium thermodynamics described earlier in the section 5.2.5. The results are then implemented in the RCB code by means of a numerical method known as a linear interpolation function on segments.

For comparison, the Kim Bishnoi model [47] is also implemented which frequently used in other hydrate codes but with rate constants derived from Phase Field theory:

$$-\frac{dn_H}{dt} = k_d A_s \left(f_e - f \right) \tag{6.17}$$

Here A_S is the surface area (m^2) for the reaction, k_d is the rate constant, f_e and f are respectively the values of the fugacity (Pa) for the pressure at a temperature $T^0(C)$ at equilibrium and in the gas phase.

The kinetic rate used in this study is calculated from extrapolated results of phase field theory simulation [83, 84].

Basically it is hard to see the relevance to a reservoir situation since this equation was derived using experimental data from a PVT cell (limited impact of solid walls and symmetric stirring). For comparison, however, we also examine this model for the model systems we study in the project reported here.

The hydrate formation and dissociation can be observed in all flow related properties as well as though the changes in the porosity (in terms of the available volume fraction of disposal of fluids) in specific areas of the porous media.

This code had been mostly used for isothermal conditions at 25^{0}C. Since the hydrate dissociation and formation are sensitive to temperature variations, the temperature gradient in the reservoir was included and considered in all the simulations.

To study geomechanics of the system, effective stress calculation has been implemented into RCB according to Terzaghi's Principle [85].

Concerning the implementation of hydrate into RCB, different hydrate phases are implemented as “pseudo minerals” so as to benefit from the logistics of RCB through easy implementation of kinetic models and parameters. Every route to hydrate formation (from hydrate forming fluid and water, from dissolved hydrate forming fluid and so on) results in unique hydrates in terms of cavity fillings and free energies. Each route is treated as a mineral reaction and similar for dissociation routes. If dissociation is slower than diffusivity into surrounding water, the hydrate dissociation “reaction” is hydrate to water and hydrate former dissolves in water. If a separate fluid phase is formed then the reaction is to water and fluid phase. In a non-equilibrium case these routes implies different thermodynamic properties for hydrate formers and water.

6.3 Demonstration examples

In this section, two 2D hydro-chemical-mechanical models are presented. The first one presents a model where the temperature is sufficiently low and hydrate will form due to $\mathrm{CO_2}$ injection. For this purpose, hydrate has been used as a pseudo mineral component. The results from the effect of super saturation in the flux according to the classical nucleation theory [67] are used in the kinetic model. The main focus in this example is on hydrate formation effects on porosity in different regions, as well as its influence on the flow pattern and the implication on geomechanical properties of the reservoir.

In the second example, the CH_4 hydrate was implemented in RCB and the impact of hydrate dissociation on porosity, gas pressure as well on its influence on flow pattern. Implications of hydrate dissolution on geomechanical properties of the model reservoir are other aspects addressed in this study of this model. For this purpose, hydrates have been added as a pseudo-mineral and an advanced kinetic model of hydrate phase transitions have been developed. The main tools for generating kinetics models have been phase field theory simulations, with thermodynamic properties derived from molecular modeling.

6.3.1 Simulation of CO_2 hydrates formation due to injection of CO_2 in porous media

The geometry of the 2D domain is $1000\mathrm{m} \times 300\mathrm{m}$ rectangle. There are two aquifers, one cap rock and one fracture zones. The fracture has the dimensions of $20m \times 40m$. Six $\mathrm{CO_2}$ injectors are situated respectively 10m, 30m and 50m above the reservoir bottom on the left and right corners at constant pressure of 4 MPa as shown in the figure 10.

The reservoir temperature gradient is $3.6\,°\mathrm{C}/100\mathrm{m}$ and the pressure gradient is $1\,\mathrm{MPa}/100\mathrm{m}$. The model is discretized into 1500 elements with dimensions of 10m by 20m. The cap rock is located at the depth of 270m down to 310m. Tables 3 to 5 present the information regarding available species in different phases, initial and boundary conditions and material properties.

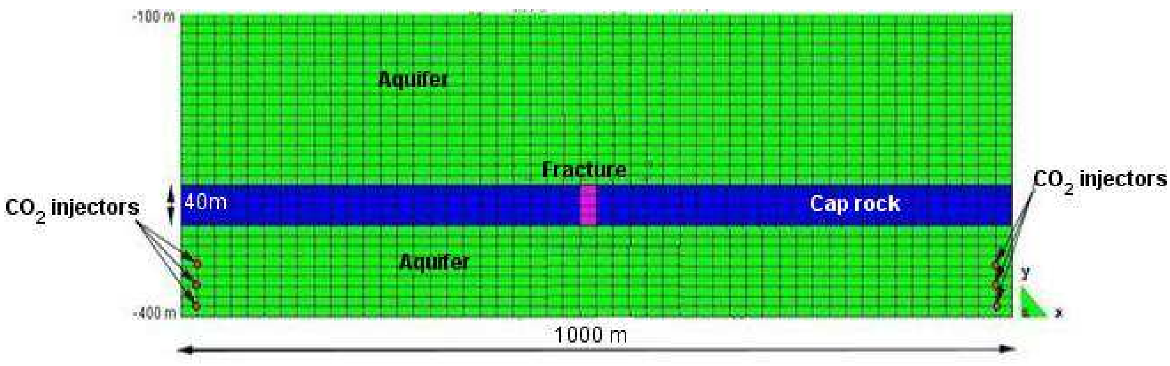

Figure 10 schematic diagram of the simulated 2D reservoir

Table 3 material properties

Property	Aquifers	Cap rock	Fracture
Young's modulus, E [GPa]	0.5	0.5	0.5
Poisson's ratio	0.2 5	0.2 5	0.2 5
Porosity	0.3	0.03	0.5
Zero stress porosity, Φ_0	0.3	0.03	0. 4
Zero stress permeability, k_0 [m^2]	1.0^{-13}	1.0^{-17}	1.0^{-10}
Irreducible gas and liquid saturation, S_{rg}	0	0	0
Van Genuchten's gas-entry pressure, P_0 [MPa], (at zero stress)	0.0196	0.196	0.196
Van Genuchten's exponent [m]	0.457	0.457	0.457
Longitude dispersion factor (*m)*	11	11	11
Molecular diffusion (*m*)	10^{-10}	10^{-10}	10^{-10}

Table 4 Initial and boundary conditions

Parameter	Bottom Boundary	Top Boundary
Pressure, (MPa)	4	1
Mean Stress, (MPa)	8.76	2.33
CO2 initial injection pressure, (MPa)	4.0 (at the injection point)	-

Table 5 Chemical species in different formations

Species	Aquifer	Cap rock	Fracture
Aqueous	H_2O , HCO_3^- , OH^- , H^+, $CO_2(aq)$, CO_3^{2-},$O_{2,}$ $SiO_{2(aq)}$, $H_2SiO_4^{2-}$, $HSiO_3^-$	H_2O , HCO_3^- , OH^- , H^+, $CO_2(aq)$, CO_3^{2-},$O_{2,}$ $SiO_{2(aq)}$, $H_2SiO_4^{2-}$, $HSiO_3^{--}$	H_2O , HCO_3^- , OH^- , H^+, $CO_2(aq)$, CO_3^{2-} ,$O_{2,}$ $SiO_{2(aq)}$, $H_2SiO_4^{2-}$, $HSiO_3^-$
Gas	CO_2 (g)	CO_2 (g)	CO_2 (g)

The simulations results of the different time steps are presented in the following. Liquid and gas fluxes, liquid and gas pressure, porosity and effective stress are the parameters of interest. Each figure shows the results at two time steps: results when the hydrate starts to form at day 360 and after the hydrate formation at day 407. Figures 11 and 12 show the gas and liquid phase fluxes respectively. These figures clearly show that because of the fractures, flow will reach the upper aquifer in a relatively short time. As soon as CO_2 reaches the top aquifer, it will start forming hydrate due to suitable temperature and pressure conditions as shown in figure 17. Figures 13 and 14 show gas and liquid pressures after 360 and 407 days. Pressure increase can be observed below cap rock which is parallel to gas flux pattern in figure 11. Gas phase flow is limited due to cap rock low permeability.

Figures 15 and 16 show respectively the effective stress in xx direction and yy in the reservoir. Positive direction for x is towards right and positive direction for y is upwards. In the absence of any realistic tensile strengths to compare with, these figures merely illustrate the capability and feasibility of the code. The effective stress is readily available from the implicit algorithm at every time step in every grid point. This is a unique feature compared to other reservoir simulation codes dealing with aquifer storage of CO_2 in reservoirs with processes on many different scales, ranging from below seconds (hydrate formation) to minutes, hours, days and longer time scales (for instance quartz dissolution).

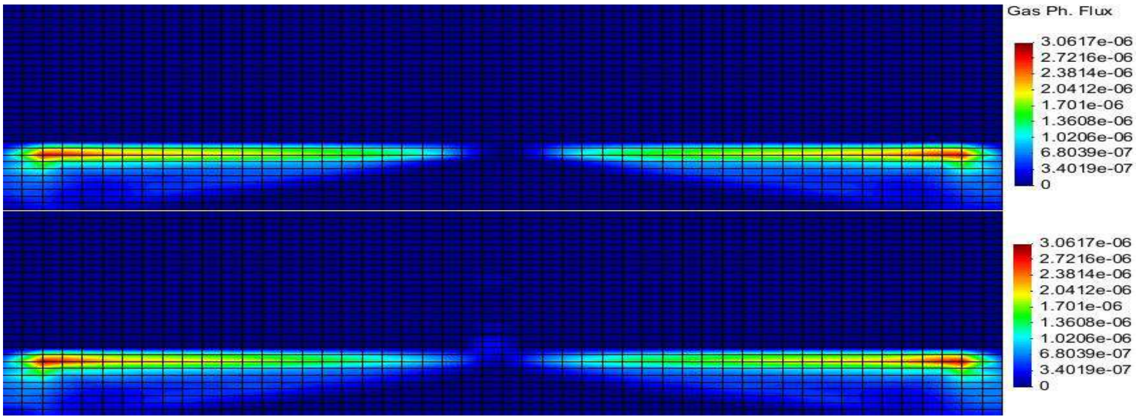

Figure 11 Gas flux (a) after 360 days (b) after 407 days

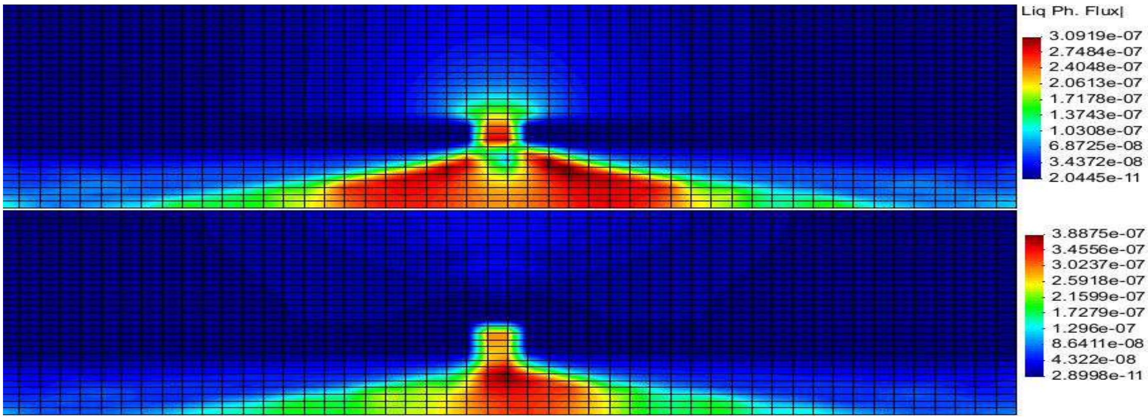

Figure 12 Liquid flux (a) after 360 days (b) after 407 days

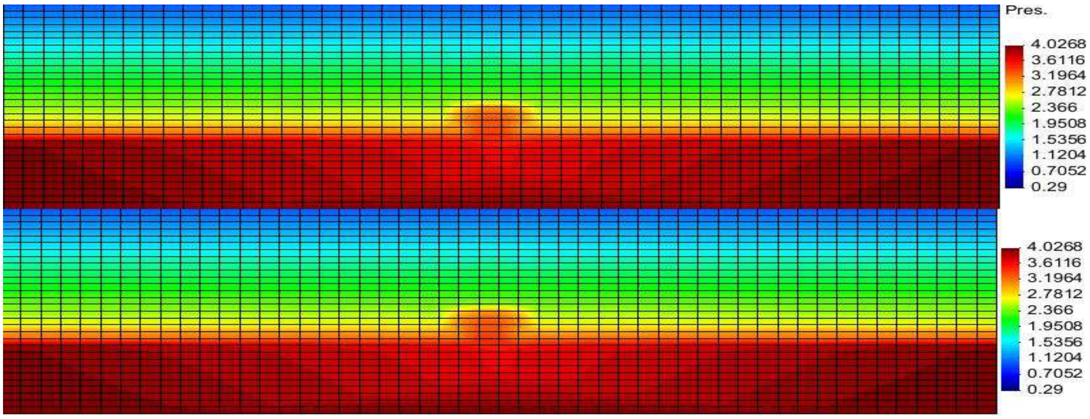

Figure 13 Gas pressure (a) after 360 days (b) after 407 days

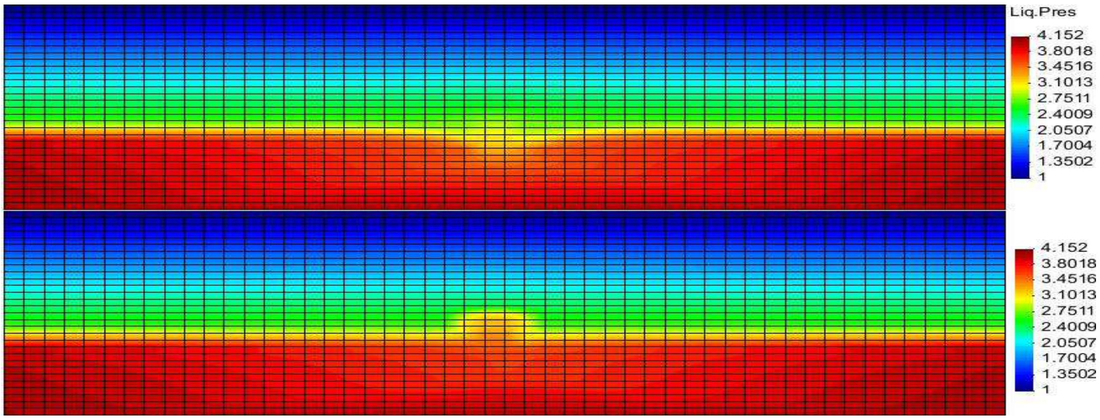

Figure 14 Liquid pressures (a) after 360 days (b) after 407 days

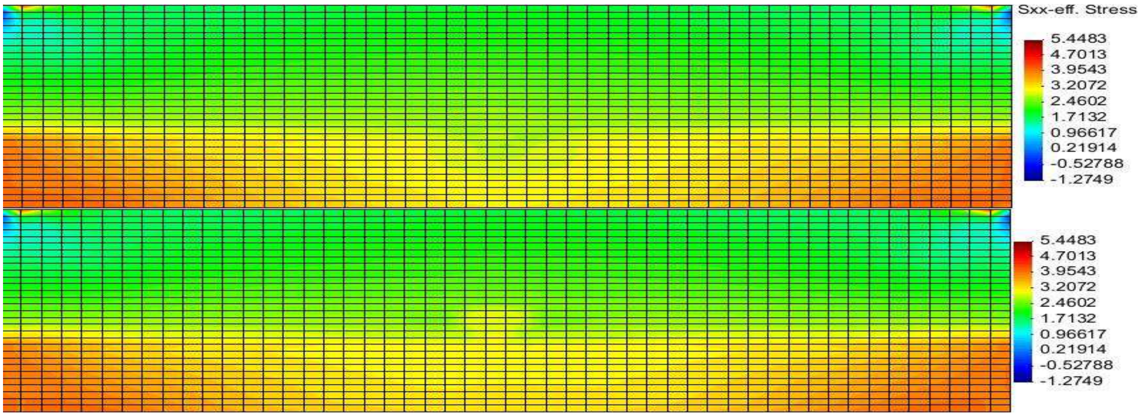

Figure 15 Effective stresses in xx direction Sxx (MPa) (a) after 360 days and (b) after 407 days

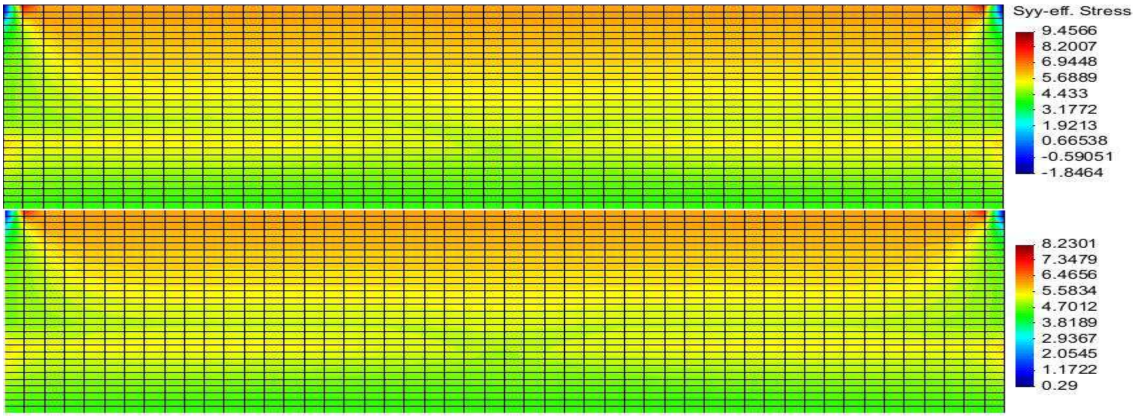

Figure 16 Effective stresses in yy direction Syy (MPa) (a) after 360 days and (b) after 407 days

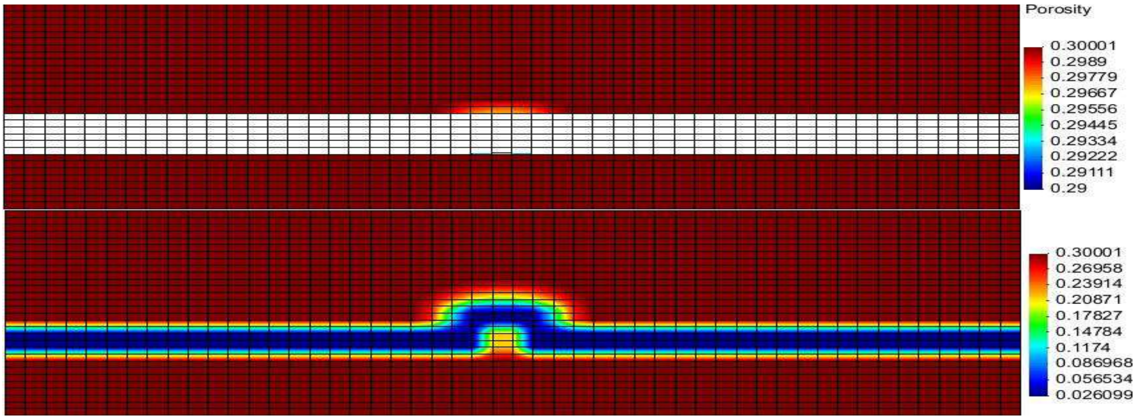

Figure 17 Porosity (a) after 360 days (start of hydrate formation) and (b) after 407 days. White area refers to the porosity of 0.03 in cap rock

6.3.2 Simulation of methane hydrate dissociation in porous media

The geometry of the 2D model is $400\ m \times 90\ m$ rectangle. The reservoir is divided into two layers, the upper layer is hydrate layer and the lower layer is gas layer. Gas production wells are located 15 m above the gas layer at respectively right and left sides of the hydrate layer and as can be seen in figure 18. The pressure of gas production well was kept lower than the surrounding pressure in the reservoir. Tables 6, 7 and 8 present the information regarding available species in different phases, initial and boundary conditions and material properties.

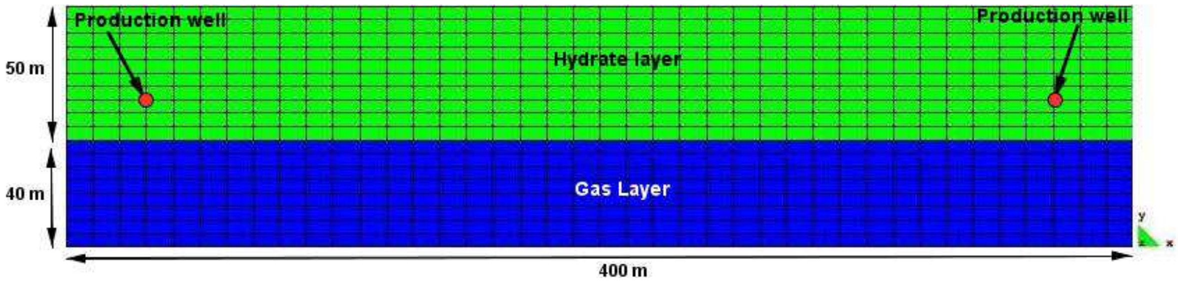

Figure 18 Geometry of 2D model with 2 CH_4 gas production wells

The change in porosity is one of the more direct indications of hydrate phase transitions. As shown in figure 25, the reduction of porosity indicates hydrate formation and the increase of porosity indicates hydrate dissociation. In figures 21, 22, gas and liquid flux patterns are plotted after the hydrate dissociation. Simulation results for different time steps are presented in this section. Liquid and gas phase fluxes, liquid and gas pressures, porosity and effective stress are the parameters of interest in this study. Each figure shows the results at two time steps: Results after 1 year at the top and results after 100 years at the bottom.

Table 6 material properties

Property	Gas Layer	Hydrate Layer
Young's modulus, E [GPa]	0.5	0.5
Poisson's ratio	0.2 5	0.2 5
Porosity	0.3	0.03
Zero stress porosity, Φ_0	0.35	0. 35
Zero stress permeability, (mD)	5x10^2	5x10^2
Irreducible gas and liquid saturation, S_{rg}	0	0
Van Genuchten's gas-entry pressure, P_0 [MPa], (at zero stress)	0.0 196	0.0196
Van Genuchten's exponent [m]	0.457	0.457
Longitude dispersion factor (*m)*	11	11
Molecular diffusion (*m*)	10^{-10}	10^{-10}
Thermal conductivity of dry medium (W/m K)	4.64	4.64
Thermal conductivity of saturated medium (W/m K)	2.64	2.64

Table 7 Initial and boundary conditions

Parameter	Gas layer	Hydrate layer
Pressure, (MPa)	7.9 - 8.3	7.4 – 7.9
Mean Stress, (MPa)	10.64-12.0	8.94 - 10.64
CH_4 production pressure, (MPa)	-	7.4
Gas outgoing pressure (MPa)	8.3	7.4

Table 8 Chemical species in different formations

Species	Gas layer	Hydrate Layer
Aqueous	H2O , H^+, OH- , CO_3^{-2}, $HCO_3^{,}$ O2(g)	H2O , H+ , OH^- , CO_3^{2-},, HCO_3^-, O_2(g)
Gas	CH_4 (g)	-
Rock Mineral	Quartz	Quartz

Due to pressure drop hydrate started dissociating according to the kinetic rate of hydrate dissociation, which was a function of temperature and pressure. Hydrate dissociation can be observed by the change in porosity as visible in figure 25. This change in porosity is directly proportional to the kinetic reaction rate of hydrate dissociation.

The estimated principle effective stress in yy direction is plotted in figures 23 and 24. Positive direction for y is upwards. Effective stress is needed in studies of reservoir stability, compaction or deformation of reservoir. The most noticeable changes in the vertical effective stress (S_{yy}) direction as illustrated in figure 24 (b) are in the hydrate zone where the hydrate dissociates. Reduction in effective stress in both directions indicates that compaction in hydrate layer happened during hydrate dissociation. The reduction of effective stress S_{xx} and S_{yy} were around 1MPa.

Strength of hydrate-filled sediments reported by Ebinuma et al. [86] suggests that this changes in effective stress might be well within safe limits for any mechanical failure in the reservoir.

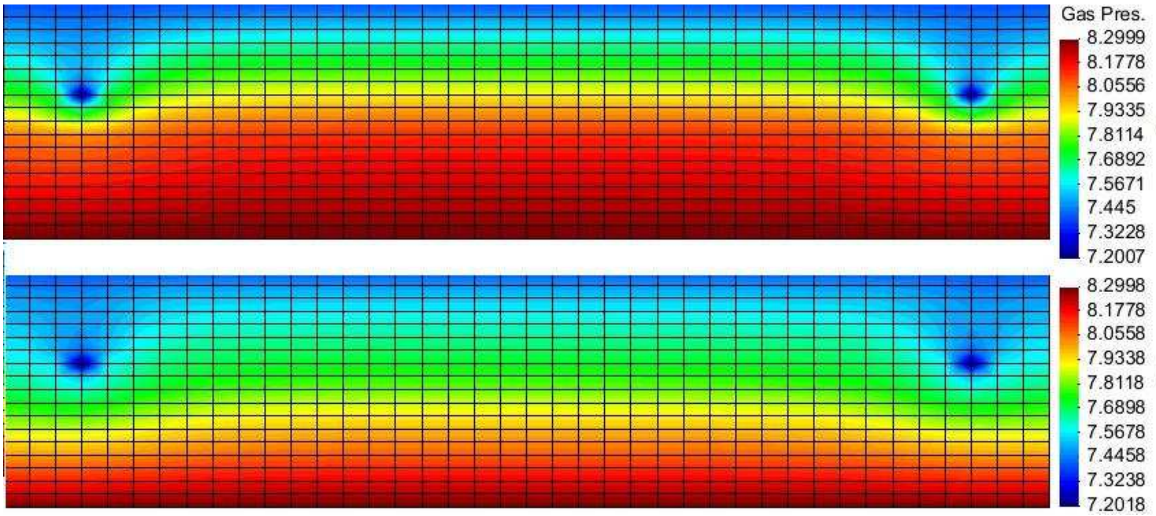

Figure 19 Gas pressure (a) after 1 year (b) after 100 years of production

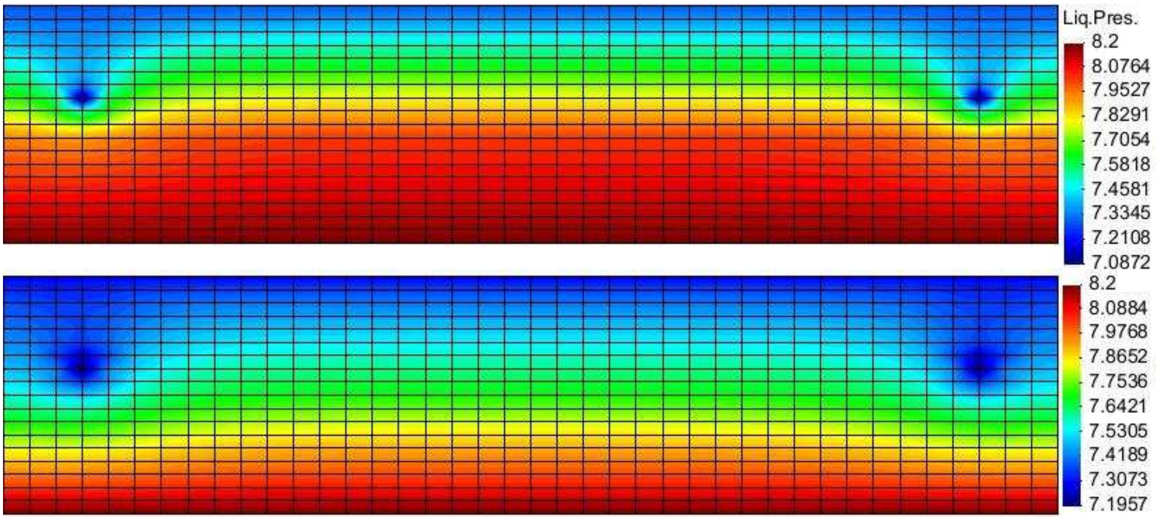

Figure 20 Liquid pressure (a) after 1 year (b) after 100 years of production

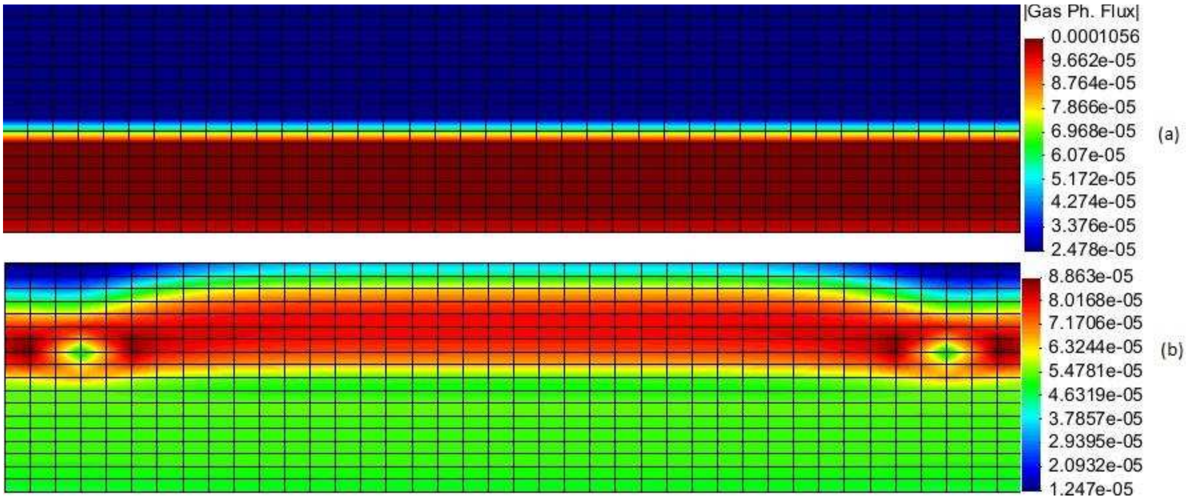

Figure 21 Gas flux (a) after 1 year (b) after 100 years

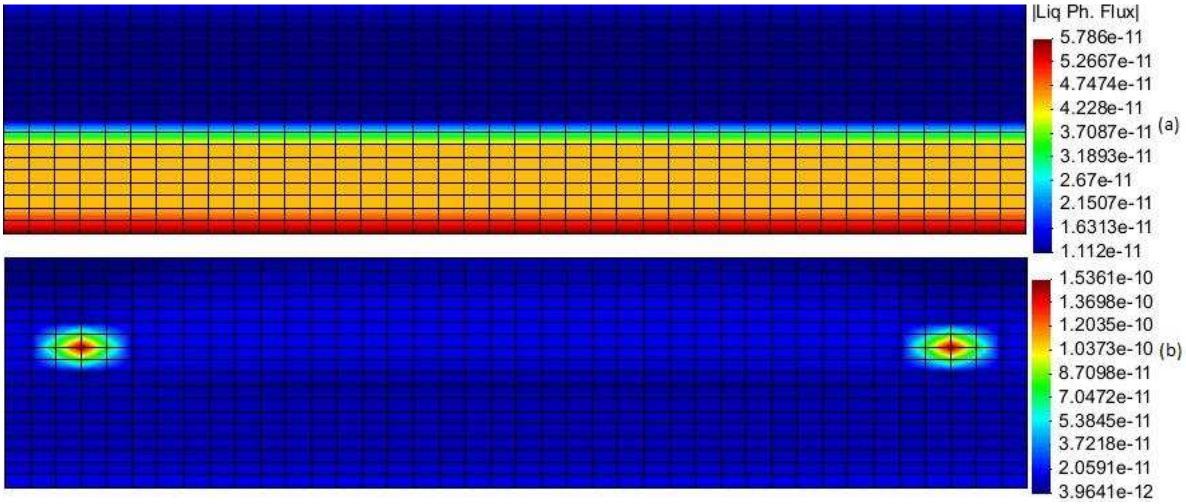

Figure 22 Liquid flux (a) after 1 year (b) after 100 years

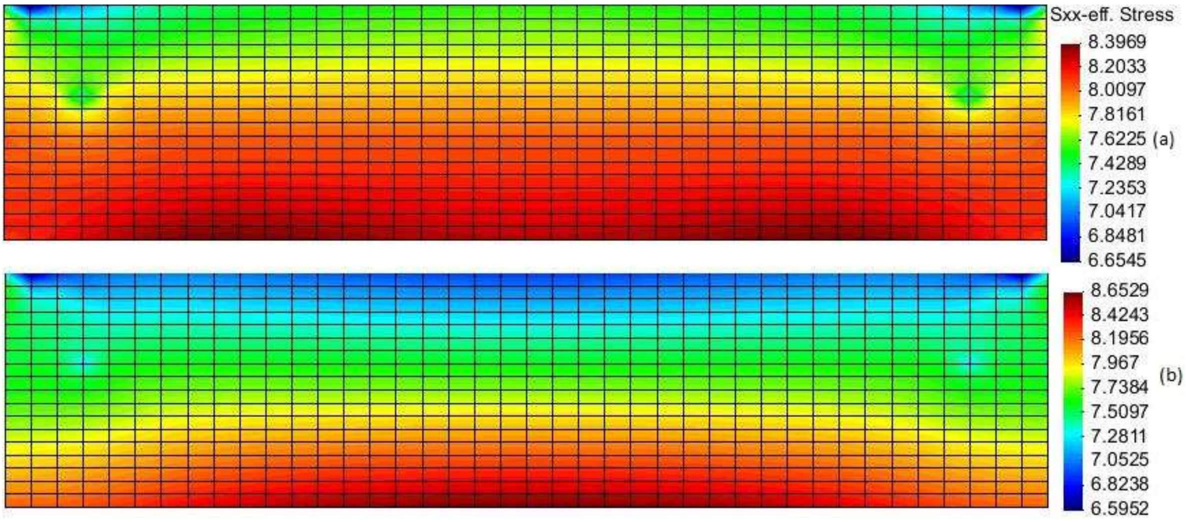

Figure 23 Effective stress in xx direction S_{xx} (MPa) (a) 1 year and (b) after 100 years

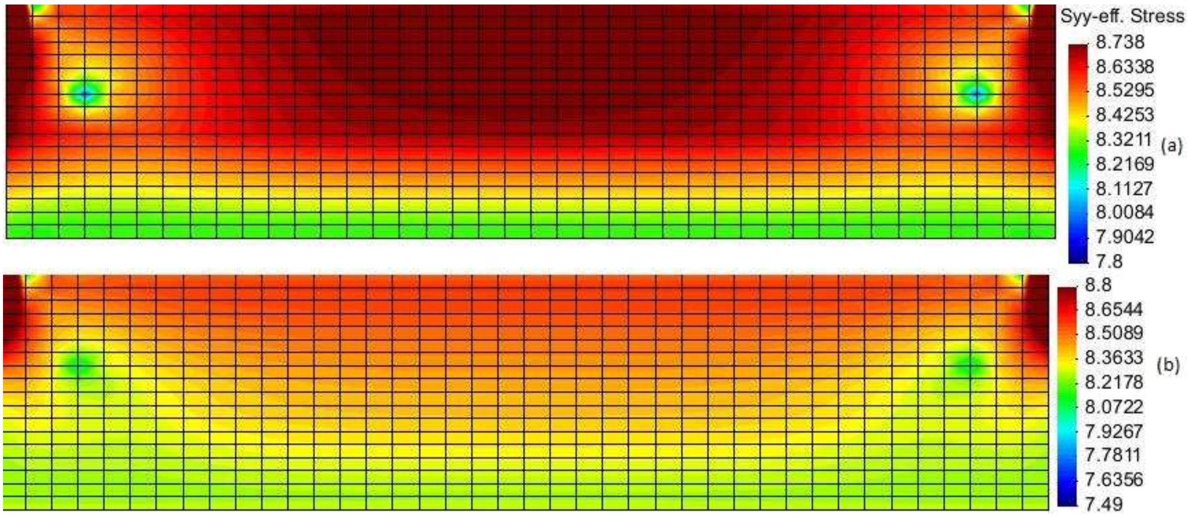

Figure 24 Effective stresses in yy direction S_{yy} (MPa) (a) 1year and (b) after 100 years

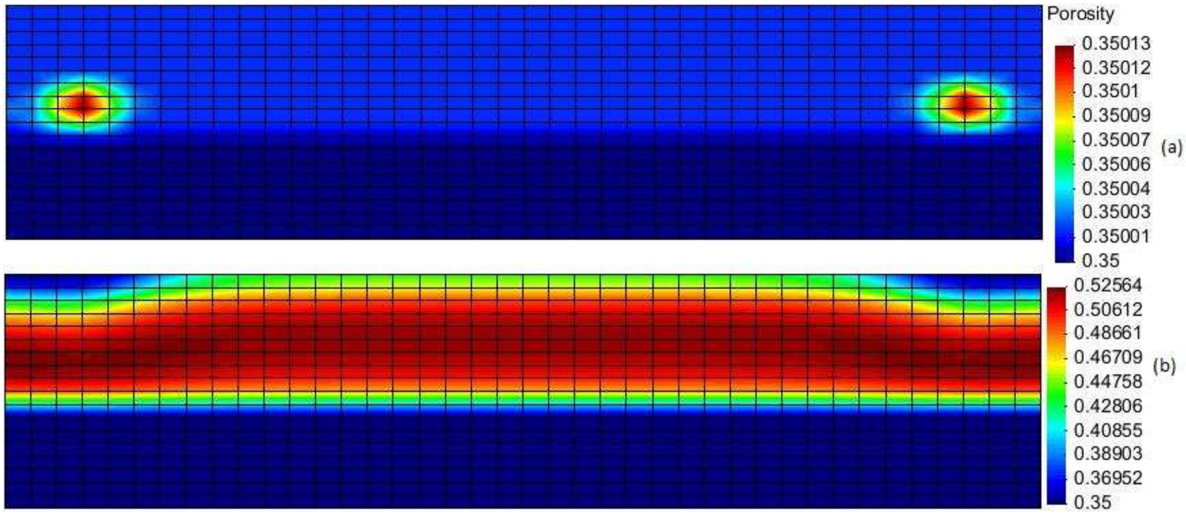

Figure 25 Porosity after (a) 1 year and (b) after 100 years

Chapter 7: Summary of papers

7.1 Simulation of Hydrate Dynamics in Reservoirs (paper 1)

During CO_2 storage in cold aquifers, CO_2 hydrate can form if suitable conditions of pressure and temperature exist there. Gas hydrates in reservoirs are generally not in thermodynamic equilibrium and there may be several competing phase transitions involving hydrate. A kinetic approach was used for hydrate reactions. The main tools for generating the kinetic models for hydrate phase transitions have been phase field theory simulations, with thermodynamic properties derived from molecular modeling [83].

In this paper a simple model based on one zone of aquifer which has a hydrate stability zone. The hydrate formation is confirmed by the results of porosity changes in some parts of the aquifer.

This paper is an extension of a conference paper given in 7.3

7.2 Non-equilibrium modeling of hydrate dynamics in reservoir (paper 2)

This work was an extension of study carried out earlier in 7.1. In this paper the non-equilibrium nature of hydrate in porous media is investigated.

Hydrate formation, dissociation and reformation towards coexisting phases, makes equilibrium impossible according to Gibbs phase rule, even if one of the fluid phases is totally consumed. The presence of mineral surfaces gives rise to adsorption sites that can contribute to hydrate nucleation even though the water molecules in first few layers are hydrate inhibited.

Keeping this statement in mind, we present a study of CO_2 storage through a simulation example. A reservoir consisting of three layers: two aquifers and one cap rock which contains a fracture. The upper aquifer zone of the reservoir had zone of CO_2 hydrate stability, where hydrate formation was studied. All possible phase transitions involving hydrate are formulated and corresponding kinetic models are derived based on phase field theory simulations.

7.3 CO_2 hydrate dynamics during CO_2 storage in saline aquifer (paper 3)

This paper was the first published paper after we reworked the reactive transport RCB into a hydrate simulator. In this work, CO_2storage with possibility of hydrate formation was studied. The implementation of CO_2 hydrate was demonstrated by using a model with two aquifer zones and cap rock in which a fracture was introduced was used. The zone of hydrate stability existed above the cap rock. CO_2 was injected from the right corner of lower aquifer. The hydrate formation was indicated by the reduction of porosity in the area above the fracture (A part of hydrate stability zone). This work was the first step for further improvements of RCB as reservoir simulator.

7.4 Simulation of geomechanical effects of CO_2 injection in cold aquifers with possibility of hydrate formation (paper 4)

In this paper a reactive transport, RetrasoCodeBright (RCB) has been modified to account for hydrate phase transition in the reservoir. The phase transitions are handled as pseudo reactions to ensure the logistics of competing phase transitions in a non-equilibrium system. A model with two fractures in the cap rock was used. The effects of hydrate formation and dissociation on geomechanics of the reservoir were studied in the same time step in which transport calculations are done. Effective stress calculations has been implemented into RCB according to Terzaghi's Principle [85] to enable analysis of geomechanical stability within same time-steps as mass- and heat- flow. Hydrate formation involves close to 10% expansion of water. CO_2storage with the possibilities of hydrate formation in reservoir was studied under realistic conditions and geomechanical impacts of hydrate formation were analyzed. It was concluded that the reservoir might be within safe limits of tensile failure for the model systems considered.

7.5 Simulation of CO_2 hydrates formation in cold aquifers: non-equilibrium approach (paper 5)

In this paper, the RCB simulator was improved to implement the non-equilibrium thermodynamic calculations. The non-equilibrium thermodynamic properties are estimated by first order Taylor expansions from equilibrium state. The results from the effect of super saturation in the flux according to the classical nucleation theory are used in the kinetic model [67].

A reactive transport reservoir simulator, RetrasoCodeBright (RCB) was applied, in which hydrate is treated as a pseudo mineral. A 2D hydro-chemical model was used in order to study the geological storage of CO_2 in reservoirs that are cold enough to facilitate CO_2 hydrate formation. The effects of hydrate formation on liquid and gas fluxes, heat flux, liquid and gas pressures and liquid saturations are the parameters of interest. The effects of hydrate dynamics on geomechanics of the reservoir are illustrated through analysis of the effective stress developments. Lack of realistic tensile strengths from real formations and/or experiments on synthetically generated systems does not provide basis for drawing rigorous conclusions on the geomechanical implications of hydrate formation and dissociation for the specific example examined. Different properties of hydrate formed from different phases were illustrated and discussed.

7.6 Theoretical studies of CO_2 hydrates formation and dissociation in cold aquifers using RetrasoCodeBright simulator (paper 6)

In this paper, two kinetic approaches have been compared: the first one is based on the effect of super saturation (or under saturation) in the classical nucleation theory of hydrate growth or dissociation [67]. The second one is based on the model of Kim and Bishnoi [47]. Results are applied in model studies of hydrate formation and dissociation in a model reservoir.

The modifications implemented into a reservoir simulator for reactive multiphase flow RetrasoCodeBright (RCB) are presented. These modifications include a non-equilibrium thermodynamic approach for gas hydrate formation and dissociation and its feedbacks on porosity, permeability and heat flow. The effects of hydrate formation on the geomechanics of the reservoir are illustrated through analysis of the effective stress.

7.7 A new reservoir simulator for studying hydrate dynamics in reservoir (paper 7)

In this paper, the use of a reactive transport reservoir simulator (RCB) as a new platform for dynamic modelling of hydrates in porous media has been proposed. Each hydrate phase transition (formation and dissociation) is modelled as a pseudo reaction, with corresponding changes in free energies as the driving forces for the phase transition itself and dynamically coupled to transport of mass and heat. The main purpose of this paper is to describe the simulator in detail with integration algorithms as well as approaches for modelling non-equilibrium thermodynamics and kinetics. More specifically a multi-scale approach, with Phase Field Theory as the core, is used for estimating kinetic rates of different possible phase transitions.

7.8 Simulations of long term methane hydrate dissociation by pressure reduction using an extended RetrasoCodeBright simulator (paper 8)

In this paper, a reactive transport reservoir simulator RetrasoCodeBright (RCB) has been reworked into a hydrate simulator. The main purpose of this work was to compare the simulation results of hydrate deposits from Mt. Elbert site, Alaska with results from the code comparison study of Anderson, B.J., et al [87].

Hydrate has been added as pseudo-mineral components. This opens up for non-equilibrium thermodynamic description since kinetic models for different competing hydrate phase transitions can be included through their respective kinetic models.

The RCB code is capable to handle different hydrates as different formation situations as well as different dissociations situations. RCB is also capable of couple between reactive flow and geomechanical analysis.

A model resembling to deposit site at Mt. Elbert site, Alaska was built to illustrate the reservoir simulator. A detailed code comparison was given in this paper.

In order to study the implication of hydrate dissociation on geomechanical properties of the reservoir, the results for changes in stresses with time were included.

7.9 Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator (paper 9)

This paper was the first attempt to study gas production from *in situ* hydrate deposits using RCB. For the simulation model, it has been used an example from real deposits of CH_4 hydrates located at Messoyakha gas field [1]. Some studies confirmed that some of the gas produced from this reservoir is contributed by dissociation of hydrate from hydrate layer [88].

The production from this reservoir was performed by using a simple reaction of dissociation and then results were compared with the results of the hydrate simulator TOUGH+HYDRATE [51].

Chapter 8: Conclusions

A new simulator for hydrates in porous media has been developed through the work documented in this thesis and the enclosed publications. Two major aspects are uniquely different with the hydrate simulator developed through this work compared to other academic and commercial simulators. The simulator is a general non-equilibrium simulator which is able to handle competing hydrate phase transitions of formation and dissociation, and evaluate net hydrate balance in every node and every time step. A second important difference is the use of a reactive transport simulator as platform. Each hydrate phase transition is treated as a pseudo reaction and a free energy analysis determines which "hydrate reactions" are possible.

The reactive transport simulator which was used as a basis, RetrasoCodeBright code (RCB), contains an implicit algorithm of material flow, heat-flow and geomechanical model equations and it involves an explicit algorithm for updating the geochemistry. RCB is designed to model problems consisting of coupled thermal, hydraulic, geochemical and geomechanical processes.

RCB extended with different hydrate phase transitions as "pseudo reactions" makes use of the same logistics as competing mineral reactions in hydrogeological problems. Porosity (as defined through available pore volume fraction for fluids) is updated according to mineral dissolution/precipitation and/or hydrate formation/dissociation "reactions". So far permeability is updated according to a commonly used correlation, which is a temporary simplification. Strategies for more rigorous modelling of permeability and relative permeability are outlined in 9.5. The reactive transport module in this simulator along with the hydrate definition in the system as a pseudo-mineral gives the opportunity to study the dynamics of hydrate in the reservoir by considering all possible phase transition scenarios and by coupling the code with a non-equilibrium thermodynamic module (minimization of free energy).

In this work RCB was applied to modelling of CO_2 storage in cold aquifer, combined with a free energy analysis for determining which hydrate phase transitions that are possible. During hydrate formation, vertical permeability is drastically reduced and horizontal spreading of CO_2 is reduced in the hydrate formation zone, which is an undesirable effect.

The simulator has also been applied to studies of hydrate production using pressure reduction. The lack of real hydrate production data is a limitation for objective evaluation of the simulator. In this work, the performance of the code has therefore only been compared to published results from other simulators. The exception is simulation of hydrate production from Messayokha (Siberia, Russia) which was not considered as real production data due to very limited monitoring on this production. After comparing our results with results of other reservoir simulators it has been demonstrated that the RCB code is competent of generating all important results necessary for detailed analysis of a gas production scenario.

Several kinetic model approaches for hydrate phase transitions are implemented, tested and compared using this code. These are kinetic rates for different hydrate dissociation "reactions" which are derived from phase field theory simulations and similar for different hydrate formation "reactions", kinetic model for hydrate formation and dissociation according to the classical nucleation theory. The corresponding thermodynamic properties of hydrates outside equilibrium in these models are based on first order Taylor expansion from equilibrium pressure, temperature and concentrations. Results are also compared to the kinetic model of Kim and Bishnoi which is frequently used in other hydrate reservoir simulators, although the model was developed based on laboratory experiments without presence of porous medium (pressure, volume, temperature cell).

Hydrates in reservoirs contribute to the geological stability of hydrate bearing sediments. The dissociation of clathrate hydrate could lead to geological instability of reservoirs, and in worst case trigger fractures and landslides.

Hydrate formation during CO_2 storage in cold aquifers involves a 10% expansion of water. Depending on where it forms and the local geology hydrate formation can have geomechanical effects on the stability of the reservoir. This aspect needs to be investigated prior to any project of CO_2 storage in aquifers. The boundaries of hydrate stability are likely to experience more dynamics in hydrate phase transitions. Upcoming hydrate meeting groundwater under hydrate forming conditions will lead to hydrate. But if the groundwater above gets diluted by flow (even diffusion) below co-existence limit of CO_2 in liquid water (quasi-equilibrium) hydrate will dissociate. Inner loop of RCB solves simultaneously for mass-transport, heat flow and development of stress. Avoiding a time shift in evaluation of geomechanics through explicit couplings to geomechanical analysis tool is clearly an advantage. Terzaghi's model for effective stress has been implemented and provides online evaluation of geomechanical consequences.

Chapter 9: Future work

9.1 Combination of heating and pressure reduction methods for producing gas hydrate

Pressure reduction is the only production method tested so far with this extended RCB code. Combination of pressure reduction and heating may be necessary for some hydrate deposits to reduce blocking due to reformation of hydrate in cold zones induced by the pressure drawdown. This can happen in different places in the reservoir. Pressure reduction gradient close to the production well is one of them, but even close to gas/hydrate boundary in reservoirs with hydrate on top of a gas filled section of the reservoir.

There are several ways to thermally stimulate the reservoir. Injection of steam or hot water would be fairly straightforward to include in RCB. Depending on the completion of the reservoir heating can also be supplied by electrical cables embedded in the producing pipelines to avoid close to the well refreezing. This option requires a slight modification of the code to include local heat sources in the energy balance. These types of extensions will also open up for other types of local heating devices implemented into the reservoir.

In situ combustion of fraction of the released gas has also been proposed by some groups. In its present form reactions involve solid (hydrate) and liquid water as primary constituents for either formation of hydrate or dissociation of hydrate. Gas that is involved in the hydrate “reactions” as released or consumed due to the reaction kinetics is transferred to the gas flux balance as corresponding local source or sink terms. Reactions that entirely involve gas (combustion) are not yet implemented but are definitely within reach by following the same logistics for reaction as in the liquid flux balance equations.

9.2 Exchange of methane hydrate to CO_2 hydrate through injection of CO_2

CO_2 Hydrate is more stable than CH_4 hydrate at the same pressure and temperature conditions over significant ranges. Mixed hydrate, in which CH_4 dominates occupation of small cavities and CO_2 dominates occupation of large cavities of structure I is more stable than CH_4 hydrate over all regions. It is therefore possible to inject CO_2 into hydrate and extract CH_4 by direct exchange. Injection of CO_2 as a liquid converts methane hydrate into carbon-dioxide dominated hydrate while at the same time releasing the trapped natural gas [15] and then combine CO_2 storage with production of methane.

We studied until now CH_4 and CO_2 reactions into RCB separately. Exchange reactions can be added in RCB in future and work is in progress on this as funded by new projects.

The kinetic rates for this exchange follow two primary mechanisms. The dominating mechanism involves the creation of new CO_2 hydrate from injected CO_2. The released heat will then contribute to the dissociation of in situ CH_4 hydrate. A second mechanism is direct solid state conversion of CH_4 hydrate over to mixed hydrate. Both are thermodynamically favorable but the kinetic rate of the latter is very slow and proportional to a solid state diffusivity. Since there is always a minimum amount of free water available in the pores, the first mechanism will dominate even in the Alaska reservoirs for which hydrate saturations may be close to 80%. Both mechanisms can be included easily in terms of the thermodynamics. As for the kinetic rates fundamental studies (Molecular dynamics Simulations [39] and Phase Field Theory [15, 40, 65, 89]) have been conducted and the results show a very clear and distinguished change in kinetics from the first over to the second mechanism proportional to reduced amount of free water available for new hydrate formation. These kinetic rate data can be included in simplified forms into RCB along with a lowest free liquid limit for which mechanism one is significant. This is facilitated by couplings to dynamically update of local saturations as functions of hydrate phase transition kinetics.

9.3 Hydrodynamics description of fractures and wells

Fractures are introduced as high porosity and high permeability channels in cap rocks. This method with assumed fractures directions can slow calculation significantly because it can reproduce partially the effect of fluid breaking through the fractures. The passage of fluids are modeled by filtration mechanism because they are formed by regular grid blocks which means that fluids penetrate through faults or fractures by pushing fully or partially.

Since the breaking through fracture happens quickly, it can be described more properly by the inclusion of a hydrodynamic description of flow through the fracture. Therefore it is suggested to extend the code to include a hydrodynamic fracture description. This can be facilitated by the use of Navier-Stokes for realistic geometrical models of the fractures. Fluxes from different flow regimes (Diffusivity and up to Darcy flow) entering the fracture provide the boundary/entering velocities for Navier-Stokes, together with end boundary conditions for the fracture.

Similar descriptions of wells are also feasible and likely numerically more stable due to simpler and relatively smaller regions of boundary conditions connection reservoir flow and Navier-Stokes inside the well.

9.4 Extension of the code to more complete set of non-equilibrium possibilities for hydrate phase transitions.

One of the main goals of this work has been to illustrate the impact of non-equilibrium thermodynamics. For this purpose two models of kinetics were used: The first one is based on the effect of super saturation or under saturation in the flux according to the classical nucleation theory of hydrate growth or dissociation [67]. The second model is based on the model of Kim and Bishnoi [47]. A comparison between these two kinetic approaches has been made. Kim-Bishnoi model is empirical and generally not transferable from the PVT experiments from which it was derived. For the first approach we have considered only the free energy perturbation from equilibrium due to pressure gradient.

This work is still in progress in two directions. One direction is to complete the code with all possible competing hydrate phases' transitions so as to enable a more complete free energy analysis in each local volume grid of the model. Implementation of models for *In situ* conversion of CH_4 hydrate through injection of CO_2 is still in progress and other relevant phase transitions will follow, including also different additions to the CO_2 (chemicals or gases like for instance N_2).

Another direction related to non-equilibrium phase transitions are modeling of super-saturations in all directions of free variables, including concentrations. Work is in progress also in this area. Presently free energy changes due to super saturations in concentrations are calculated by separate thermodynamic codes and imported into RCB as tables for interpolations but correlations to simple mathematical expression is another option for efficient use in RCB. It is also important in this context that all thermodynamic properties related to competing phase transitions are consistent in the sense that water in all phases is based on residual thermodynamics (ideal gas as reference state). Gas, fluid CO_2 and CH_4 are naturally based on ideal gas since equation of state is used for calculating these properties. This common level of free energy for all phases open up for several possible algorithms to minimize free energy in each volume and as such achieves a realistic evaluation on local phase distribution in each local volume of the reservoir.

Numerically algorithms for free energy minimization are an important challenge for the future.

9.5 Relative permeability correlations

The present version of RCB is capable to calculate changes in absolute and relative permeability in every time step. The permeability calculations in the current code are based on porosity changes due to mineral dissolution or precipitation and hydrate formation or dissociation. In the present version of RCB, the thin channels present between solid mineral surface and gas hydrate surfaces are ignored. Fluid permeability calculations should be reworked with respect to these thin fluid channels.

One possible approach is to combine CT scanned image of porous media and select most likely pore structures based upon stress analysis. This gives room for hydrodynamic modeling using Boltzmann flow or Navier-Stokes. Realistic pore fillings of hydrate can be included although interfacial tensions between hydrate and surrounding fluids needs to be estimated from molecular modelling or other approaches. This approach is feasible but might need simplified kinetic models for hydrate phase transitions.

An alternative approach might be to use Phase Field Theory with implicit hydrodynamics and heat transport [89-91]

9.6 Development of new and more accurate models for heat transport

Heat transport dynamics is a critical issue in hydrate production using pressure reduction. Reducing the pressure to outside equilibrium makes the hydrate unstable in terms of free energy but the heat needed for the dissociation must be extracted from the surroundings if heat is not added through some form for thermal stimulation. This can lead to freeze down of the formation and in worst case stop the production for time periods. Heat transport through systems that undergoes phase transitions are very complex problems.

One possible strategy for fundamental development of new simplified models is to use advanced theoretical tools like Phase Field Theory (PFT) [89-91]. One extension to PFT, which is needed for this purpose, is to implement the possibility for setting a pressure gradient over the simulation cell. Another option is to enable point sinks in pressures at local grid volumes. Both of these options are realistic and short term extension of the PFT model [89-91]. It is however, recommended that the heat transport model is separated into conduction and convection instead of the current simplified approximation of an “efficient” heat conductivity.

A second motivation for implementation of more rigorous heat transport models is to be able to more accurately estimate time and location where refreezing to hydrate can happen so that measures can be taken even during development of the production strategies.

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