

Theoretical studies of CO₂ hydrates formation and dissociation in cold aquifers using RetrasoCodeBright simulator

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Abstract: - Hydrates of CO₂ and water can form during aquifer storage if the reservoir has regions where conditions of pressure and temperature are inside the hydrate forming conditions. A very common assumption is that formed hydrate will be stable and will block the flow in all directions in regions where hydrate is formed, and as a consequence hydrate could seal incomplete sealing of clay or shale. In some limits this could be practically true but in general hydrates formed in sediment cannot be thermodynamically stable. Even if the hydrate is inside stability region of pressure and temperature, the hydrate may be unstable with respect to the different component concentrations (and corresponding chemical potentials) in the different phases.

In this work we present a first order Taylor expansion for thermodynamic properties outside of equilibrium and apply classical nucleation theory to estimate kinetic rates for hydrate formation kinetics and similar rates in cases of under saturation. Results are applied in model studies of hydrate formation and dissociation in a model reservoir.

We compare between two kinetic approaches: the first one is based on the effect of super saturation (or under saturation) in the classical nucleation theory of hydrate growth or dissociation. The second one is based on the model of Kim and Bishnoi.

Unlike other reservoir simulators we apply a reactive transport reservoir simulator, RetrasoCodeBright (RCB), which considers hydrate phase transitions as “pseudo reactions”. CO₂ hydrate is added to the simulator as a pseudo-mineral component and the reservoir simulator was improved to implement non-equilibrium thermodynamic calculations.

Key-Words: - Gas hydrate, RCB, CO₂ storage, Phase transitions dynamics

1 Introduction

Gas hydrates are ice like colorless solid crystalline consisting of water and small gas molecules (referred to as guests molecules). Guests molecules are trapped within a cage-like lattice of ice crystals (called hosts). Hydrate formation is promoted under suitable conditions of low temperature and high pressure. These conditions are found offshore in shallow depth below the ocean floor and onshore beneath the permafrost regions.

According to some estimates methane gas potential of in situ hydrate resources is around 20 million billion cubic meters [1]. This estimated amount of hydrocarbon resources trapped in hydrates exceeds the total energy content of all known conventional fossil fuel resources [2].

Hydrates are also widely spread worldwide and countries which have little or no conventional hydrocarbons have rich hydrate reservoirs. Examples are Japan and India. Gas hydrates are therefore an interesting future resource for natural

gas. Four different categories of methods for gas recovery from hydrate have been extensively studied: (1) Depressurization, which involves shifting of the hydrate stability condition by lowering of the pressure to a pressure below the equilibrium pressure. Heat for dissociation will be supported from surrounding due to the imposed temperature gradient due to pressure reduction. (2) Thermal stimulation method, in which heat is introduced into the reservoir and changing the surrounding temperature to outside the hydrate stability region. This method is considered to be expensive because of the huge amount of energy waste to the surroundings which calls for careful planning and engineering to reduce heat losses. (3) Use of inhibitors such as methanol or glycol 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 [3] and (4) Injection of CO₂ into the methane hydrate

reservoirs; this concept consists replacing the CH_4 molecule by CO_2 molecule. This method has several benefits over other 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_4 hydrate 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 CO_2 accumulation 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 natural gas. The exchange process consist of two mechanisms in which the fastest one is creation of new CO_2 hydrate 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 [4, 6].

Significant portions of the international scientific community within climate research, claims that the main cause of global warming is the rise of atmospheric concentration of CO_2 [7]. For example, the atmospheric concentration of CO_2 has increased from 280 parts per million by volume (ppmv) in 1894 to 358 (ppmv) in 1994 [8]. The concept of Carbon dioxide Capture and Storage (CCS) is considered one of the promising technologies used to reduce CO_2 emissions to the atmosphere [9], of which this work only focus on specific issues related to the storage part.

An attractive option is the underground sequestration in aquifers. Worldwide this option have capacity for storing huge quantities of CO_2 , although the different factors (sealing, capillary trapping, mineralization etc.) that determine the sealing integrity varies significantly. The natural CO_2 at Pisgah in central Mississippi, USA is an example of long time scale retaining of CO_2 . This field is older than one million year [10].

Some full scale sequestration projects are currently running throughout the world. Sleipner West in the North Sea was the world's first offshore CCS plant and has been in operation since October 1996. Snøhvit in the Barents Sea is another example. In this project 0.7 million tons of carbon dioxide is separated from the natural gas and injected in a saline aquifer below the hydrocarbons reservoir in zones at depth of 2600 m. The Weyburn-Midale

CO_2 Project in Canada which was, as per 2008, considered as the largest CO_2 capture and storage project is a third project. Unlike the two previously mentioned projects this project uses the CO_2 for enhanced oil recovery. The In Salah project in Algeria [11] is a fully onshore operational gas field. The CO_2 is extracted from the natural gas and injected into a geological formation at depth of 1800 m. There are also some other projects which is planned to start in the near future in different countries.

Some storage reservoirs will have zones in which the temperature and pressure are inside hydrate formation condition for CO_2 hydrate. Examples are offshore northern parts of Norway and the Barents Sea. Upper regions of Snøhvit also have regions of hydrate formation conditions.

During the last two decades there have been numerous speculations in the role of hydrate formation and whether hydrate could actually repair incomplete sealing (clay, shale). This is a complex question since hydrate stability is a function of not only temperature and pressure but also concentrations of all components in all phases, including also the adsorbed phase on mineral surfaces. There is incompatibility between partial charges of water molecules in the regular hydrate structure and partial charges on atoms in the mineral surfaces and hydrate cannot attach to the surfaces of the minerals which imply that CO_2 hydrate will not entirely block the pores. Nevertheless, permeability will be substantially reduced in hydrate filled sediments and might assist the vertical sealing but will also modify pathways of horizontal migration and spreading of CO_2 .

There have been many attempts to study hydrates reservoirs using different types of theoretical methods and simulations, including extended versions of classical reservoir simulators for oil and gas or hydrogeological codes. Many international research groups have been working in this area and a number of academic and commercial reservoir simulators for this purpose are available already. A review of past studies dealing with different theoretical approaches of modeling and simulation of methane production from hydrate shows that hydrate formation and dissociation are mostly treated as an equilibrium reaction.

Ahmadi et al. [12] used depressurization method to study hydrate dissociation in a confined reservoir by developing a 1D reservoir model. They considered equilibrium conditions, within the pressure and temperature projection of the equilibrium, at the dissociation front and neglected water flow in the

reservoir and also neglecting the Joule – Thomson effect.

Liu et al. [13] 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 [14] have presented a detailed theoretical description of the open source reservoir hydrate simulator HydrateResSim developed previously by Lawrence Berkley National Laboratory (LBNL). They have also applied it to a system of three components (methane, water and hydrates) and four phases (aqueous, gas, hydrate and ice). Local thermal equilibrium is considered in the code. It considers both equilibrium and kinetic approaches, using Kim and Bishnoi [15] as the kinetic model of hydrate dissociation. They concluded that equilibrium approach over predicts the hydrate dissociation compared to kinetic approach.

EOSHYD2 proposed by Moridis [16] is designed to model hydrate behavior in both sediments and laboratory conditions. It includes both equilibrium and kinetic models for hydrate formation and dissociation. He used just the equilibrium approach because of a lack of enough suitable data necessary for the parameters of the kinetic model, while mentioning that slower processes such that depressurization follow kinetic dissociation. Later on using the same module, Kowalski and Moridis [17] 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 vapor), the aqueous phase, the solid ice phase and the solid hydrate phase. They considered that the system always exists on equilibrium, with the occurrence of the various phases and phase transitions determined by the availability and relative distribution of heat and of two components [17]. This statement about equilibrium approach is somewhat confusing and cannot describe a realistic hydrate reservoir, since it

could happen only in a unique temperature, pressure, and composition.

In this paper we compare between two kinetic approaches and the corresponding situations of competing phase transitions. The first approach is based on the model of Kim and Bishnoi [15], the second is based on the effect of super saturation in the flux according to the classical nucleation theory and based on Kvamme et al. [18]. RetrasoCodeBright (RCB) reservoir hydrate simulator is used [19]. This simulator is a reactive transport simulator and as such it has the logistics for treating competing reactions of mineral formation as well as mineral dissolution. Hydrates can therefore be implemented into the structure as pseudo minerals, with appropriate kinetic models for the different possible "reactions" of hydrate formation and dissociation. One way to estimate kinetic rates for the different "reactions" involving hydrate is through fundamental modeling using phase field theory (PFT) approach [20]. Non-equilibrium thermodynamic properties for the PFT simulations in situations of super-saturations (leading to hydrate formation) and sub-saturations (leading to hydrate dissociation) are based on a first order Taylor-expansion from equilibrium state as discussed by Kvamme et al. [21]. This represents an alternative to the more commonly applied Kim & Bishnoi equation [15]. The results of the Taylor expansion can still be fitted into a similar equation. But one of the advantages is that hydrate and fluid phase free energies are locally updated according to degree of super and under saturations for different possible hydrate phase transitions. The number of different possible routes to hydrate formation which is presently included is limited but part of the goals of this paper is to illustrate a general scheme for inclusion of non-equilibrium thermodynamics and a corresponding route to kinetics of phase transitions. Even though classical nucleation theory is used to illustrate the connection from free energy differences over to kinetics there are almost as numerically simple theories which are more rigorous in terms of accounting for phase transition interfaces (thickness, interface free energy) in a better fashion, see for instance Kvamme et al. [18]. There is ongoing work on interface properties within the same group and this information will be transferred into the code at later stages parallel to implementation of MDIT theory [18] as replacement of classical nucleation theory. The performance of the simulator is demonstrated through example cases.

2 Theoretical Background

Hydrates in nature are generally not in equilibrium, and unable to reach through thermodynamic equilibrium due to the number of active phases (including mineral/fluid/hydrate interactions). The degree of super saturation or under saturation gives thermodynamic conditions for growth or dissociation of hydrate.

Fluid thermodynamic outside of equilibrium is continuous and requires no extra mathematical treatment. But hydrate models are derived from statistical mechanics based on an equilibrium state and as such require mathematical methods for extrapolation outside equilibrium. This will be discussed more detailed in section 2.1.

2.1 Hydrate thermodynamic

The local filling of hydrates in sediment pores vary substantially dependent on pressure, temperature and local fluid flow.

Estimation of local time dependent co-existence between different phases in a reservoir containing hydrates is of crucial importance for evaluation of hydrate production scenarios as well as for natural dynamics when evaluating leaking from natural gas hydrate, or evaluating sediment stability over time. Two independent thermodynamic variables are always given. Local pressure and temperature are in a static situation defined by gravity and geothermal gradient and will be affected by flow but still locally defined as combinations of static limits and flow induced changes. 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 know as 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 distribute 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. As indicated above, pressure and temperature is already given locally in a reservoir so if the Gibbs phase rule number differ from two then equilibrium is not possible. For the two phase system comprising two components, water and one gas component, if the temperature and pressure are defined in a local point of the reservoir at a given time the system reach equilibrium when the degree of freedom of system is two. The gas component

could be any hydrate forming component but quite randomly CH_4 is used in the discussion below.

If we consider a system consisting of three phases (aqueous, gas and hydrate) and if in additional the system is inside the hydrate stability zone. As a consequence, the degrees of freedom will decrease to 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.

Inside hydrate stability region, under suitable conditions of temperature and pressure, hydrate is then for water, the phase of lowest chemical potential. Since the system is over determined we can consider which processes that might lead to hydrate dissociation.

The different independent thermodynamic variables, which in addition to P and T, are the concentration of water and CH_4 in all co existing phases. If the hydrate is brought in contact with pure water then the hydrate will dissociate due to an under saturation of methane in water compared to the hydrate and the thermodynamic driving force is the chemical potential of methane in water (close to infinite dilution) minus the chemical potential of methane in hydrate. If the hydrate is now exposed towards a CH_4 gas (or liquid) phase then at least 3 scenarios may occur:

1) The chemical potential of CH_4 is lower in the gas and water chemical potential is lower in the gas which implies that the gas is under saturated with water on the basis of hydrate as reference state and the hydrate will dissociate both due to CH_4 and water driving forces.

2) The chemical potential of CH_4 is lower in the gas and water chemical potential is higher in the gas. This situation is more complex and might eventually first lead to hydrate formation until the gas is saturated with water based on hydrate water as reference and would then dissociate due to lower CH_4 chemical potential in gas. But there might also be other scenarios since for two components corresponding number of thermodynamic driving forces the overall progress would be determined by sign of free energy change, and gradients of free energy, in all possible directions of possible scenarios.

3) The chemical potential of CH_4 is higher in the gas and water chemical potential is higher in the gas. For this situation hydrate is the lowest free energy state. One could argue that addition of a second component, like for instance CO_2 , to the gas could

fulfil Gibbs phase rule and as such open up for an equilibrium situation. The problem, however, is that the dynamic nature would not create one uniform hydrate phase. The most stable hydrate would fill CO₂ in most of the large cavities while CH₄ occupies small cavities until some point where lack of CO₂ in the final end results in CH₄ hydrate. There will as such be a continuous spectre of hydrate phase from the CO₂ rich hydrate all the way to pure CH₄ hydrate. And it is not given that rearrangement into a uniform hydrate is fast or even possible. Depending on the local situation and analogies to the different scenarios of surroundings discussed above the CO₂ rich hydrate might even be the lowest free energy state.

What these examples illustrate is that hydrates in reservoirs are not in equilibrium and not likely to be uniform in terms of compositions and corresponding free energies. However, this presents one of the problems of current hydrate reservoir simulators. The current simulators merely check equilibrium in terms of pressure and temperature projections and disregard the thermodynamic requirements for equilibrium also along axes of concentrations in phases. In a porous medium, the situation described above becomes even more complex. A distinct new adsorbed phase is added by a solid surface. This plays an important role because hydrates are unstable towards solid mineral surfaces. This is because hydrate water hydrogen bonding structures are incompatible with partial charges of surfaces of atoms in the minerals [22].

Practically in a local point in a reservoir the temperature and pressure are given. When a clathrate hydrate comes into contact with an aqueous solution containing its own guest molecule, the number of the degree of freedom will decrease to one, this system is thermodynamically over-determined. There will be more than one process which competes. Each process has now a unique reference free energy as reference for the non-equilibrium thermodynamics.

Hydrates in reservoirs are also uniquely different from PVT experiments conducted for equilibrium and/or kinetic studies of bulk systems. Those experiments are normally closed and the volumes are very large compared to small pore volumes containing fluids and hydrate. Hydrates in reservoirs are never closed systems. At some boundary – even kilometres away – there will be some fracture, fault or other types of deficiencies that brings the hydrate section in contact with under saturated phases

(water and/or gas) that induce hydrate dissociation. Hydrate filled reservoirs will therefore never even be close to 100% filling of pore volumes with hydrate and permeability will exist even if it might be extremely small. In summary hydrate filled reservoir sections are open systems even if they have no gas cap below or any contact with massive water filled sections. So in view of the above, and the fact that even only hydrate and two adsorbed phases (one controlled by mineral and one controlled by hydrate) can never reach equilibrium, hydrates in reservoirs are never able to reach true thermodynamic equilibrium.

The changes in the free energy for a hydrate formation/dissociation are calculated according to equation (1)

$$\Delta G^{PhaseTransition} = \delta \cdot \left[\begin{array}{l} x_w^H (\mu_w^H - \mu_w^p)_+ \\ x_{CH_4}^H (\mu_{CH_4}^H - \mu_{CH_4}^p)_+ \\ x_{CO_2}^H (\mu_{CO_2}^H - \mu_{CO_2}^p) \end{array} \right] \quad (1)$$

In this equation, H represents hydrate phase, p represents either liquid, gas and adsorbed phases depending on where the components building the hydrate comes from, x composition and μ chemical potential and δ is equal to 1 in case of formation and -1 in case of dissociation.

For a given hydrate to grow unconditionally Gibbs free energy change according to (1) must be negative and all gradients in free energy change (temperature, pressure, concentrations) must be negative.

In case of super-saturation (non-equilibrium), the chemical potential for H₂O, CH₄ and CO₂ in the hydrate can be calculated according to equation (2)

$$\begin{aligned} \mu_i^H(T, P, \bar{x}_i^H) &= \mu_i^{H,eq}(T^{eq}, P^{eq}, \bar{x}_i^{eq}) + \\ &\left(\frac{\delta \mu_i^H}{\delta P} \right)_{(T^{eq}, \bar{x}_i^{eq})} \cdot (P - P^{eq}) + \\ &\left(\frac{\delta \mu_i^H}{\delta T} \right)_{(P^{eq}, \bar{x}_i^{eq})} \cdot (T - T^{eq}) + \\ &\sum_{i=m,c,w} \left(\frac{\delta \mu_i^H}{\delta x_i} \right)_{(T^{eq}, P^{eq}, \bar{x}_i^{eq})} \cdot (\bar{x}_i^H - \bar{x}_i^{eq}) \end{aligned} \quad (2)$$

Superscript eq is abbreviation for equilibrium point in all independent thermodynamic variables. In this equation $\mu_{CO_2}^{H,eq} = \mu_{CO_2}^{Fluid}$ and $\mu_{CH_4}^{eq} = \mu_{CH_4}^{Fluid}$ are at equilibrium conditions. Subscript i is component index and 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

$$\left(\frac{\delta \mu_i}{\delta P} \right) = \bar{V}_i \quad (3)$$

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

The chemical potential of a guest molecule in the hydrate is given by:

$$\mu_k^H = \Delta g_{kj}^{inc} + RT \ln(h_{kj}) \quad (4)$$

Where, Δg_{kj}^{inc} is the Gibbs free energy of inclusion of the guest molecule k in cavity j . The canonical partition functions can be expressed as:

$$h_{kj} = \exp(\beta(\mu_{kj} - \Delta g_{kj}^{inc})) \quad (5)$$

Here 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 I (SI) contains 3 large cavities and 1 small cavity per 23 water molecules, $v_l = 3/23$

and $v_s = 1/23$. The chemical potential for water in hydrate can be estimated using a modified version of the statistical-mechanical model:

$$\mu_w^H(T, P, \bar{x}^H) = \mu_w^{H,0}(T, P) - \sum_j v_j \ln(1 + \sum_k h_{kj}) \quad (6)$$

Where superscript $H, 0$ denote empty clathrate [23], v_j is the fraction of cavity of type j per water molecules and h_{kj} is the canonical partition function for guest molecule of type k in cavity type j .

The filling fractions are given by:

$$\theta_{kj} = \frac{h_{kj}}{1 + \sum_k h_{kj}} \quad (7)$$

Where θ_{kj} is the filling fraction of guest molecule k in cavity type j and x_{kj} is the mole fraction of guest molecule k in the hydrate type j and will be calculated according to the equation (8)

$$x_{kj} = \frac{\sum_i v_i \theta_{kj}^i}{1 + \sum_i \sum_k v_i \theta_{kj}^i} \quad (8)$$

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

The derivative of the above equation with respect to the mole fraction:

$$\frac{\delta \mu_w^H}{\delta x_r} = -RT \sum_j v_j \left[\frac{\frac{\sum_k \frac{\delta h_{kj}}{\delta x_r}}{\left(1 + \sum_k h_{kj}\right)}}{\left(1 + \sum_k h_{kj}\right)} \right] \quad (9)$$

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

Equation (10) gives the relationship between molar enthalpy and the chemical potentials. Chemical potentials are directly estimated outside equilibrium,

$$\frac{\delta \left[\frac{\mu_k}{RT} \right]_{P, \bar{N}}}{\delta T} = - \frac{\bar{H}_k}{RT^2} \quad (10)$$

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.

2.2 Kinetic Model

Since the principle purpose of this paper has been to illustrate the impact of non-equilibrium thermodynamic, we use a simple model for kinetics based in classical nucleation theory to illustrate impact of under saturation or super saturation discussed in section 2.1. For comparison we adopt the Kim Bishnoi model [15] which frequently used in other hydrate codes but with rate constants derived from Phase Field Theory [24, 25].

The equation (11) is used to describe CO₂ hydrate equilibrium conditions in the simulation. This is based on the model developed by Kvamme and Tanaka [23] where SRK equation of state is used to calculate the fugacity of liquid phase.

$$\begin{aligned}
 P^{eq} = & 9.968156693851430 \times 10^{-7} \times T^6 \\
 & - 1.721355993747740 \times 10^{-3} \times T^5 \\
 & + 1.237931459591990 \times T^4 \\
 & - 4.745780290305340 \times 10^2 \times T^3 \\
 & + 1.022898518566810 \times 10^5 \times T^2 \\
 & - 1.175309918126070 \times 10^7 \times T \\
 & + 5.624214942384240 \times 10^8
 \end{aligned}
 \quad (11)$$

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

The first kinetic approach is based on the results from the effect of super saturation in the flux according to the classical nucleation theory and based on Kvamme et al. [18]. At this stage the free energy perturbation from equilibrium due to pressure gradient is considered. Figure 1 shows this effect on the flux. For each temperature, the technique of polynomial fitting has been used to calculate the flux with respect to varying pressure.

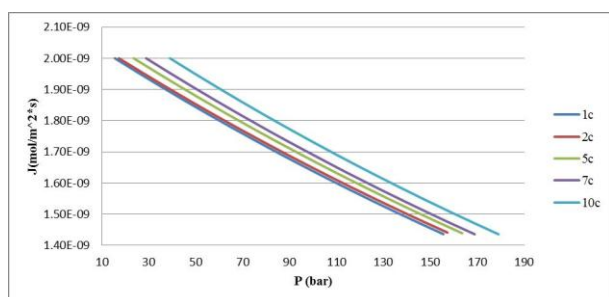


Figure 1 Flux due to the perturbation of free energy from the equilibrium at constant temperature and composition

For the temperatures between the selected points, we used the numerical method known as linear interpolation function on segments.

The validity of classical theory is not discussed here. For solid/fluid it might be off by orders of magnitude for nucleation and therefore other theories like MDIT [26] or phase field theory (PFT) might be more appropriate. So the use of classical theory in this context is merely for the purpose of qualitative indications of the impact of different thermodynamic variables giving rise to super saturations or under saturation. This follows from the main purpose of this paper which is to bring more focus on the fact that hydrates in nature are in a non-equilibrium situation and the analysis of phase transitions have to be based on that.

Note that MDIT theory reduces to classical nucleation theory if the interface thickness is set to zero.

A very common model is the model due to Kim and Bishnoi [15].

$$-\frac{dn_H}{dt} = k_d A_s (f_e - f) \quad (12)$$

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 temperature $T(^{\circ}C)$ at equilibrium and in the gas phase.

The kinetic rate used in this study is calculated from extrapolated results of phase field theory simulation [24, 25].

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.

3 Numerical tool

In regions where hydrate can form, the volume of water can increase by 10%. In addition, CO_2 can be supplied by dissolution of carbonates in regions of low pH or even in regions of high pH since due to the transport and precipitation of ions, CO_2 can be extracted from water and hydrate. 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 geo-mechanical 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) [20, 21]. This implies that the hydrate phase transitions involving CO_2 will automatically be coupled to geochemical reactions via the logistics of the reactive transport simulator.

In the work presented here, code RCB (RetrasoCodeBright) has been chosen as the software platform. RCB is the result of

coupling of Retraso (REactive TRAnsport of SOLutes) which was designed for solving two dimensional reactive transport problems [27] and CodeBright (COupled DEformation of BRIne Gas and Heat Transport) which permits the modelling of deformation, mechanical processes in implicit solution of multiphase mass and heat transport [28]. Retraso involves an explicit algorithm for updating the geochemistry as shown in figure 3 [27, 29], while CodeBright is containing an implicit algorithm of material flow, heat-flow and geo-mechanical model equations [29, 30].

RCB is extended with hydrate phase transitions as "pseudo reactions". RCB is capable of realistic modelling of the reaction rates for mineral dissolution and precipitation, at least to the level of available experimental kinetic data. Generally, hydrates in sediments are not in thermodynamic equilibrium. Different mineral surfaces have different distribution of partial charges on surface atoms. This implies that their structuring impact on surrounding adsorbed molecules is unique for each mineral. It also implies that the molecules which are adsorbed will be a separate phase because density, structure and composition are different from surrounding phases [31]. This also implies that the chemical potentials of adsorbed molecules [22] are different from that of surrounding phase(s) if the system is not in equilibrium. Similarly a hydrate phase will be separated from "bulk" liquid water by an interface [32, 33, 34], which is also unique in structure, density and composition. The partial charges on water molecules in the hydrate lattice gives distributions that are not compatible with partial charges on mineral surfaces. From fundamental thermodynamics the minimum number of phases for systems of hydrate in sediments are therefore 3. The hydrate phase plus two adsorbed interfaces, one controlled by mineral and another one controlled by hydrate. When local T and P are locally given in sediment through geothermal gradients (and other factors) and hydrostatics (or hydrodynamics) the system is over determined according to Gibbs phase rule. Possible consequences of corresponding free energy gradients in this non-equilibrium system

is a complex function of free energy mineralization under constraints of mass and heat transport. Phase Field Theory with implicit hydrodynamics is a possible theoretical toolbox that could shed light on how such a non-equilibrium system might develop [22]. As an example hydrate of carbon dioxide growing in cold zones during aquifer storage can never "glue" to the wall of the minerals and will be separated by two adsorbed phases (mineral controlled adsorbed layer and hydrate controlled layer). In addition to these minimum number of three phases (which makes the system over determined by one degree of freedom) there will practically always the fluid phase inside the pores in these open systems of hydrate in sediments. Even fractures, faults and inhomogeneity far from the hydrate will have impact on the flow through the hydrate filled sediments. There could vents leaking dissociated gas from hydrate as well as feed of gas through fracture systems leading to the hydrate layers. Even in permafrost regions hydrate saturations are significantly below 100%. 4 to 5 phases (2 adsorbed phases plus water, fluid and hydrate) are the most common situation so according to Gibbs phase rule hydrates in natural porous media are over determined by 2 – 3 degrees of freedoms. Practically this implies that all phases need to be described by thermodynamics that stretched beyond classical equilibrium calculations. For this purpose non-equilibrium thermodynamics of hydrate is employed to determine the kinetic rates of different competing scenarios in each node and each time step according to the temperature and pressure. Hydrate formation and dissociation can be observed through porosity changes in the specific areas of the reservoir. Hydrate formation is indicated by porosity reduction and hydrate dissociation is indicated by porosity increase.

In contrast to some oil and gas simulators the simulator have 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. 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. The Newton-Raphson method iterations are used to solve the non-linear algebraic systems of governing partial differential equations [29].

In one step the CodeBright calculates mass flow, heat transport and geo-mechanical deformation. All these properties are transferred to Retraso. Porosity is updated according to mineral erosion/precipitation or hydrate formation/dissociation, and permeability is updated according to a commonly used correlation [35] and all detailed results from the individual flux and phase properties are transferred back to CodeBright for the next time step.

The schematic illustration of the coupling of the two modules is given in the figure 2.

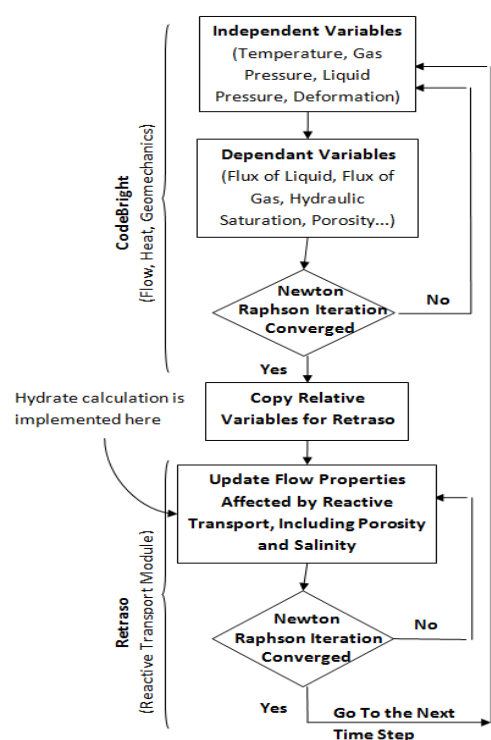


Figure 2 RCB solves the integrated equations sequentially in one time step

3.1 Constitutive equations, equilibrium restrictions and the independent variables

The governing equations such as stress equilibrium equations, mass balance equations and internal energy balance equation of the medium as a whole are included. The variables and corresponding equations are tabulated in table1.

Table 1 equations and independent variables

Equation	Variable Name
Equilibrium of stresses	Displacements
Balance of liquid	Liquid pressure
Balance of gas mass	Gas pressure
Balance of internal energy	Temperature
Balance of solid mass	Porosity

Table 2 includes the constitutive laws and equilibrium restrictions incorporated in the general formulation and the corresponding independent variables that are computed using each of the laws.

Table 2 Constitutive equations and equilibrium restrictions

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
Retention curve	Liquid phase degree of saturation
Mechanical constitutive model	Stress tensor
Phase density	Liquid density
Equilibrium restrictions	Variable name
Henry's law	Air dissolved mass fraction
Psychometric law	Vapor mass fraction
Gas Law	Gas density

The details about the governing equations can be found elsewhere [27, 28, and 36].

3.2 Calculation of permeability and porosity in RCB

Reactive transport properties can also affect the thermo hydraulic problem. RCB can model the effect of formation or dissociation of the hydrate and precipitation or dissolution of minerals on porosity and permeability. The change in porosity is calculated from the change in the concentrations of the minerals /hydrates Δc_m through:

$$\Delta\phi = -\sum_i \bar{V}_{m,j} \Delta c_{m,i} \quad (13)$$

Here $\bar{V}_{m,j}$ is the partial molar volume of the mineral/hydrate.

Intrinsic permeability and relative permeability of liquid/gas are calculated based on porosity. For calculation of intrinsic permeability, Kozeny's model is used [37, 38]

$$k = k_0 \frac{\phi^3}{(1-\phi)^2} \frac{(1-\phi_0)^2}{\phi_0} \quad (14)$$

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

$$q_\alpha = \frac{-kk_{r\alpha}}{\mu_\alpha} (\nabla P_\alpha - \rho_\alpha g) \quad (15)$$

Where k is the tensor of intrinsic permeability, $k_{r\alpha}$ is the relative permeability of the phase, μ_α is the dynamic viscosity of the phase α and g is a vector of gravity forces.

Liquid phase relative permeability and gas phase relative permeability are given as

$$k_{rl} = A(S_{el})^\lambda \quad (16)$$

$$k_{rg} = A(S_{eg})^\lambda \quad (17)$$

S_{el} and S_{eg} are respectively effective saturation for liquid and gas. These are calculated by using the Van Genuchten model [39]

$$S_l = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = \left[1 + \left(\frac{P_g - P_l}{P} \right)^{1-\lambda} \right]^{-\lambda} \quad (18)$$

$$S_{eg} = \frac{S_g - S_{rg}}{S_{gs} - S_{rg}} \quad (19)$$

$$\sigma = 0.03059 \cdot \exp\left(\frac{252.93}{273.15 + T}\right) + 0.04055 \cdot \omega_i^h \quad (20)$$

$$P = P_0 \frac{\sigma}{\sigma_0} \quad (21)$$

$$\omega_i^h = \frac{\sum_i c_{ai} M_i}{1 + \sum_i c_{ai} M_i} \quad (22)$$

Where, P_0 is measured at certain temperature, σ_0 is surface tension at temperature in which P_0 was measured, λ is the shape function for retention curve, S_{rl} is residual saturation, S_{ls} is maximum saturation for liquid phase, S_{rg} is residual saturation, S_{gs} is maximum saturation for gas phase, ω_i^h is mass of solute per mass of liquid and M_i is the molecular weight.

3.3 Effective stress calculation in RCB

RCB is a reservoir simulator with an implicit coupling between reactive flow and the geo-mechanical analysis

To study geo-mechanics of the system, effective stress calculation has been implemented into RCB according to Terzaghi's Principle [40]. According to this principle, effective stress controls the mechanical failure of rock and is defined as:

$$\sigma'_{ij} = \sigma_{ij} - P\delta_{ij} \quad (23)$$

Where σ'_{ij} is effective stress, σ_{ij} is total stress, P is pore pressure and δ_{ij} is the Krönecker symbol ($\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$).

According to this definition, a tensile fracture will happen if the minimal effective stress is negative and its absolute value is greater than tensile strength of the formation [41]. In other words, the conditions of fracturing are based on a comparison between the effective stress according to the Terzaghi's principle and the tensile strength.

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

$$\nabla \cdot \sigma' + b = 0 \quad (24)$$

Where, σ' the effective stress tensor and b is the vector of body forces. In comparison with the stress terms, we can adopt the assumption that the inertial terms can be neglected since both velocities and accelerations are small [42].

3.4 Modification in RCB

In comparison of the original version of RCB, the current version has been extended from ideal gas into handling of CO₂ according to the SRK equation of state [43].

The nonlinear partial differential equations of the system are solved numerically. 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 [43, 44].

To account for non-equilibrium thermodynamics of the hydrate some modifications of the code have been made in this study. The kinetic rate used is calculated according to the classical theory based on Kvamme et al. [18] for equilibrium thermodynamics and the theory of non-equilibrium thermodynamics described earlier in the theory section for the super-saturated or under-saturated situations. 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 though the changes in the porosity (in terms of available volume fraction at disposal for fluids) in specific areas of the porous media.

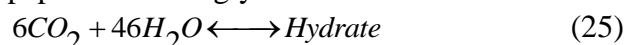
For Kim and Bishnoi model [15], the kinetic rate used in this study is calculated from extrapolated results of phase field theory simulations [24]

The free energy change of the reaction (25) outside equilibrium is given by equation with appropriate chemical potentials outside equilibrium as discussed in more details in section 2.1

The corresponding enthalpy changes are given by the fundamental thermodynamic relationship

(10), where different terms of equation (1) have trivial results from gas phase (SRK equation of state) as well as from gas phase. For hydrate phase the contribution to equation (10) is evaluated by numerical differentiation

Filling fractions will of course vary but the main purpose here is to illustrate other aspects so slight differences due to lower than full filling is not critical for the purpose of this paper. Accordingly we use:



4 Model description

So far there are no real field data for hydrate formation during aquifer storage of CO₂. Snøhvit offshore Norway do have hydrate formation regions within the upper hundreds of meters if a CO₂ plume reaches that far up. But detailed data on the Snøhvit structure are confidential and not available for use in this project. For this reason we will use a model system to illustrate the impact of non-equilibrium thermodynamics and impact of competing phase transitions.

The geometry of the 2D domain is 1000m x 300m rectangle. There are 2 aquifers, 1 cap rock and 1 fracture zones. The fracture has a zigzag path throughout the cap rock from 500 m to 680 m along the x-axis and from 270 m down to 320 m along the y-axis. The fracture is treated as a thin reservoir section with extreme permeability. CO₂ is injected 10 m above the reservoir bottom in the right corner at constant pressure of 4 MPa as shown in the figure 3

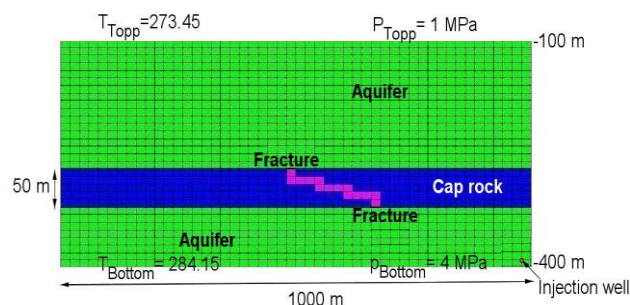


Figure 3 schematic diagram of the simulated 2D reservoir

The reservoir temperature gradient is 3.6 °C / 100 m and pressure gradient is 1 MPa/100m. 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 320m. Tables 3 to 5 present the information regarding available species in different phases, initial and boundary conditions and material properties.

Table 3 Chemical species in different formations

Species	Aquifer	Cap rock	Fracture
Aqueous	H ₂ O, HCO ₃ ⁻ , OH ⁻ , H ⁺ , CO ₂ (aq), CO ₃ ²⁻ , O ₂ , SiO ₂ (aq), H ₂ SiO ₄ ²⁻ , HSiO ₃ ⁻	H ₂ O, HCO ₃ ⁻ , OH ⁻ , H ⁺ , CO ₂ (aq), CO ₃ ²⁻ , O ₂ , SiO ₂ (aq), H ₂ SiO ₄ ²⁻ , HSiO ₃ ⁻	H ₂ O, HCO ₃ ⁻ , OH ⁻ , H ⁺ , CO ₂ (aq), CO ₃ ²⁻ , O ₂ , SiO ₂ (aq), H ₂ SiO ₄ ²⁻ , HSiO ₃ ⁻
Gas	CO ₂ (g)	CO ₂ (g)	CO ₂ (g)
Rock Mineral	Quartz	Quartz	Quartz

Table 4 Initial and boundary conditions

Parameter	Top	Bottom
Pressure, (MPa)	1.0	4.0
Temperature, (°C)	273.35	284.15
Initial mean stress (MPa)	2.33	8.76
CO ₂ injection pressure (MPa)	-	4.0

5 Results and discussion

In lack of available field data on hydrate related to CO₂ storage we have applied a model system to illustrate this reservoir simulator, with non-equilibrium thermodynamics. The difference between the RCB hydrate simulator and other simulators which include hydrate as a phase is the use of a reactive transport simulator platform, which opens up for non-equilibrium thermodynamics and logistics of handling

competing routes for hydrate formation and dissociation. At this stage only implementation of hydrate formation from water and free hydrate former phase and corresponding reverse hydrate dissociation into water and liquid water is completed. Work is in progress on implementation of other hydrate “reactions” like hydrate formation from aqueous solution and hydrate dissociation towards under saturated phases (under saturated gas). Nucleation and growth towards solid mineral surfaces are other examples of phase transitions that will be implemented. The simulator is under continuous development and other hydrate phase transitions will successively be implemented in the future.

In all the following figures the script A refers to the simulation using the classical nucleation theory, which is a limit of the MDIT theory when the interface thickness is reduced to zero [18]. Figures with script B refers to the simulation using Kim and Bishnoi approach [15].

The change in porosity is one of the more direct indications of hydrate phase transitions. As shown in figures 9A and B, the reduction of porosity indicates hydrate formation and the increase of porosity indicates hydrate dissociation.

Table 5 Material properties

Property	Aquifer	Cap rock	fracture
Young's Modulus (GPa)	0.5	0.5	0.5
Poisson's Ratio	0.25	0.25	0.25
Zero stress porosity	0.3	0.03	0.4
Permeability, (m ²)	10 ⁻¹³	10 ⁻¹⁷	10 ⁻¹⁰
Van Genuchten's exponent	0.457	0.457	0.457
Van Genuchten's gas entry pressure (at zero stress (kPa))	196	196	196

CO ₂ Hydrate reaction enthalpy (J/mole)	51858	51858	51858
CO ₂ Hydrate kinetic formation rate constant (mol/Pa m ² s)	1.441×10 ⁻¹²		
CO ₂ Hydrate kinetic dissociation rate constant (mol/Pa m ² s)	-1.441×10 ⁻¹⁶		

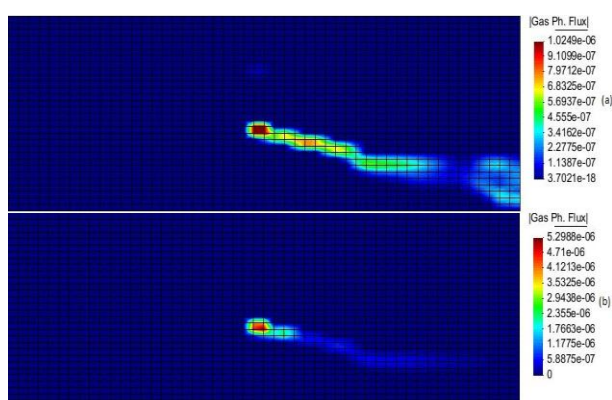


Figure 4A Graphical representation of Gas phase flux (m/s) (a) after 468 days (b) after 641 days

In figures 4(A, B) (a), 5(A, B) (a), gas and liquid flux patterns are plotted after the hydrate formation. Figures 5(A, B) (b), 6(A, B) (b) illustrate gas and liquid flux patterns after the dissociation of small quantities of hydrate.

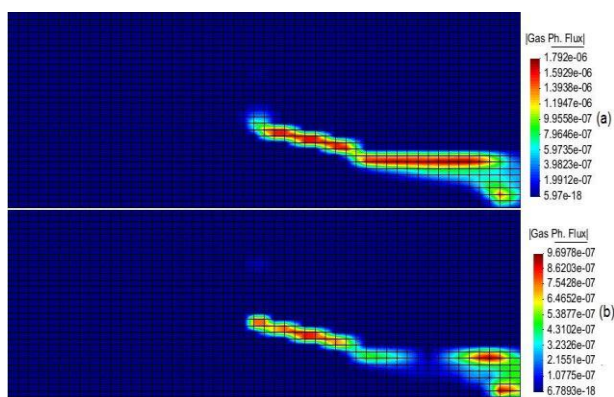


Figure 4B Graphical representation of Gas phase flux (m/s) (a) after 417 days (b) after 458 days

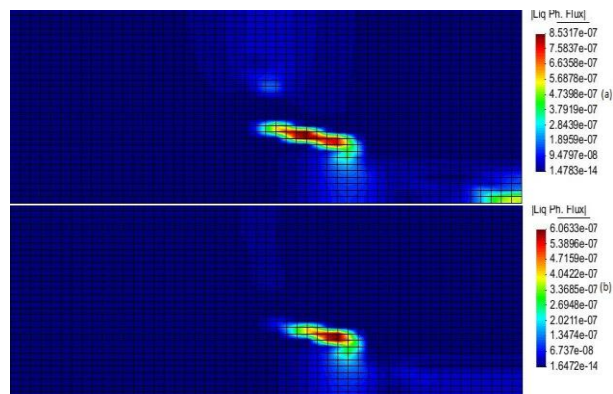


Figure 5A Graphical representation of Gas phase flux (m/s) (a) after 417 days (b) after 458 days

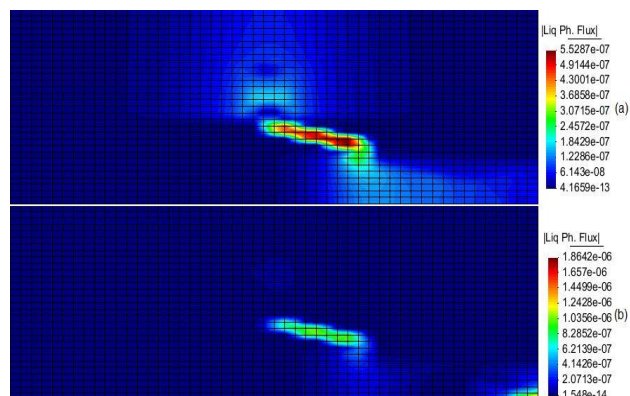


Figure 5B Graphical representation of liquid phase flux, (a) after 417 days (b) after 458 days

The injected CO₂ rises towards forming a plume below the cap rock. Large amounts of CO₂ fill the high permeable zone and are transported to the upper aquifer and create a new plume of gas. Figures 6 (A, B) also show the replacement of the liquid with gas through liquid saturation reduction in the lower aquifer. Figures 7 and 8 illustrate gas and liquid pressures during the CO₂ storage.

The largest flux is observed in the injection zone, as shown in figures 4 and 5; the flow is also increasing in the fracture zone. As a consequence, gas saturation and density increase, porosity and driving pressure gradient change over the length of the fracture.

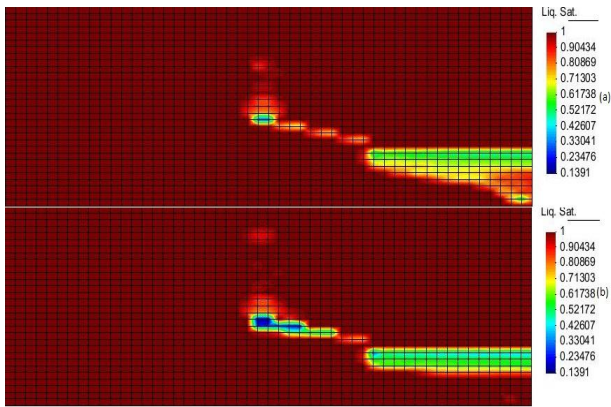


Figure 6A Graphical representation of liquid saturation (a) after 468 days (b) after 641 days

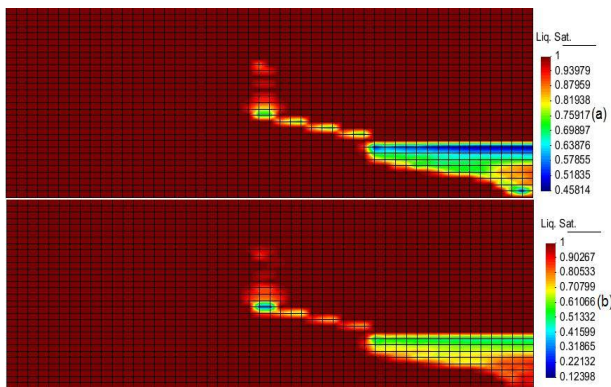


Figure 6B Graphical representation of liquid saturation (a) after 417 days (b) after 458 days

The porosity changes are plotted in figure 9. By porosity in this context we use the interpretation of volume fraction available to fluids i.e. formation of hydrate will be considered as increase in solid volume fraction and corresponding reduction of volume available for fluids. Figure 9A is a graphical representation of porosity changes in the case of the simulation using the classical nucleation theory approach. Figures 9A (a) and 9B (a) illustrate the change in porosity at the same time. The changes in degree of porosity illustrated by figure 9A (a) is little compared to changes at the same time (397 days) illustrated by the figure 9B (a).

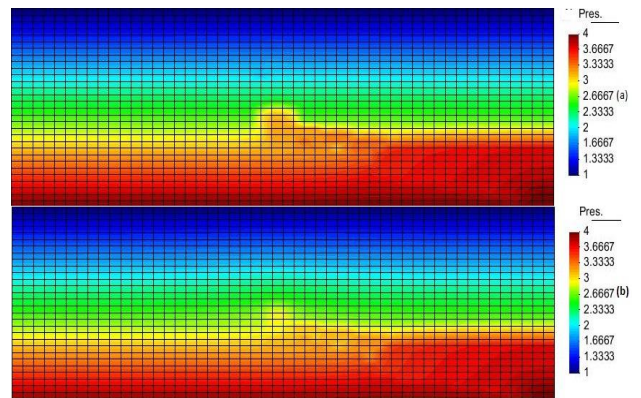


Figure 7A Graphical representation of gas pressure (MPa) (a) after 468 days (b) after 641 days

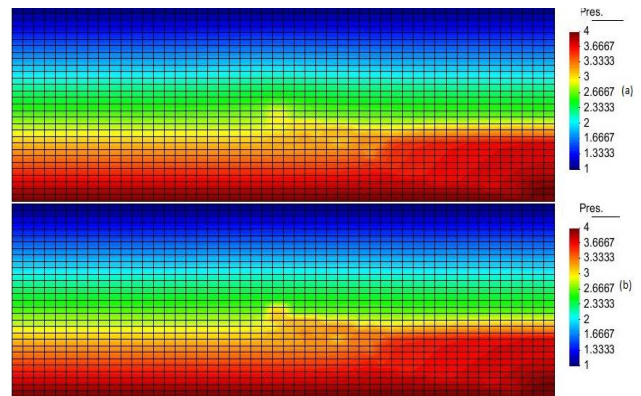


Figure 7B Graphical representation of gas pressure (MPa) (a) after 417 days (b) after 458 days

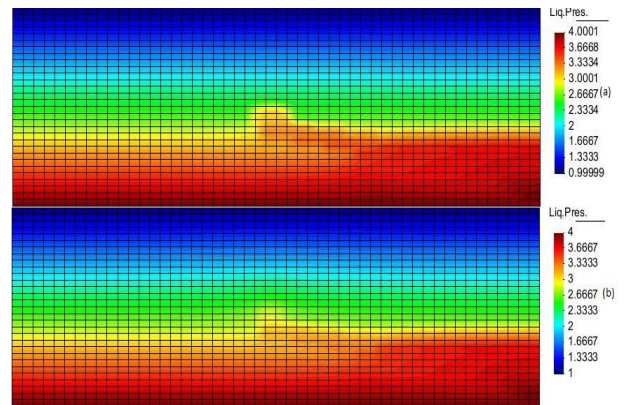


Figure 8A Graphical representation of liquid pressure (a) after 468 days (b) after 641 days

Using Kim and Bishnoi approach [15], we obtain the results for porosity change plotted in figure 9B. The changes in porosity are significant after 397 days and continue until the porosity, in the section above the fracture, is substantially reduced after 417 days.

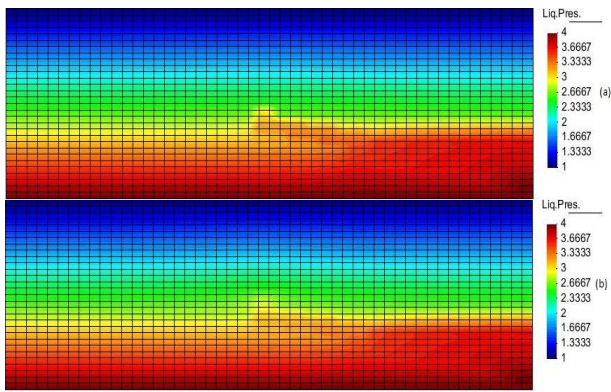


Figure 8B Graphical representation of liquid pressure (a) after 417 days (b) after 458 days

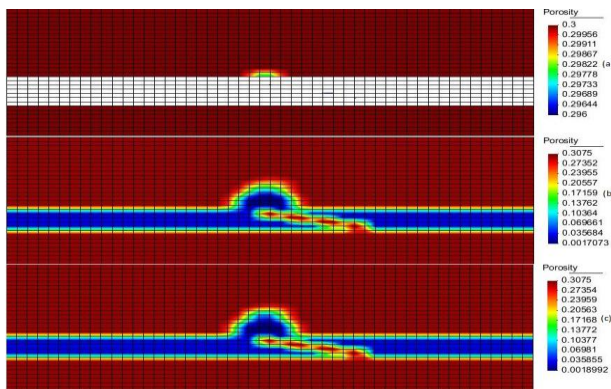


Figure 9A Graphical presentation of porosity (a) after 397 days, (b) after 468 days (c) after 641 days. White area in figure 10 A (a) refers to porosity 0.03 in cap rock

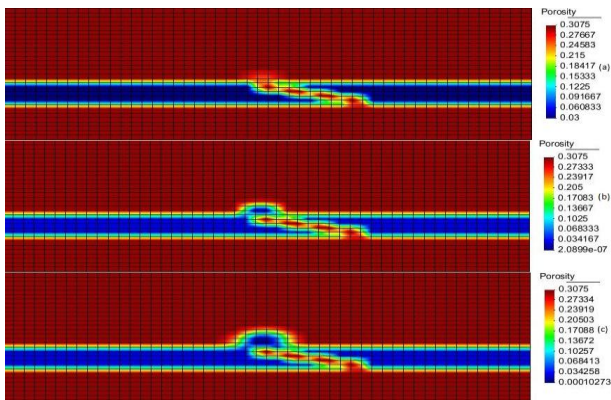


Figure 9B Graphical presentation of porosity (a) after 397 days, (b) after 417 days (c) after 458 days

The degree of porosity increased from $1.70 \cdot 10^{-3}$ at day 468 to $1.89 \cdot 10^{-3}$ at day 641 in case A (see figures 9A(b) and 9A (c)) and from $2.08 \cdot 10^{-7}$ at day 416 to $1.02 \cdot 10^{-4}$ at day 458 in case B (see figures 9B(b) and 9B (c)) due to dissociation of small quantities of hydrate.

The contour of the net deposited hydrate is completely different in the two presented cases. The

reason is different gas expansion pattern in these two cases (see Figures 9A (b-c) and 9B (b-c)).

The fast kinetics of hydrate formation in the case of Kim and Bishnoi approach [15] rapidly reduces the porosity substantially and eventually leads to very low permeability and close to fluid flow blocking of fluid fluxes, which explains the reduction of the hydrate expansion zone in this case in comparison to the similar zone obtained with kinetic model based on classic nucleation theory.

In the current version of RCB simulator, the correlations between saturations, porosity and permeability are applied by equations (13) and (14). The hydrate formation and growth is indicated by reduction of porosity according to equation (13) which results in corresponding reduction in estimated permeability according to equation (14). As a consequence, as shown in figures 4A (b), 4B (b), 5A (b) and 5B (b), fluid flux reduction is observed in zones where hydrate is growing. It is important to emphasize that these equations may not be for hydrate in a quantitative sense, for the qualitative example use of these equations can at least provide indications though.

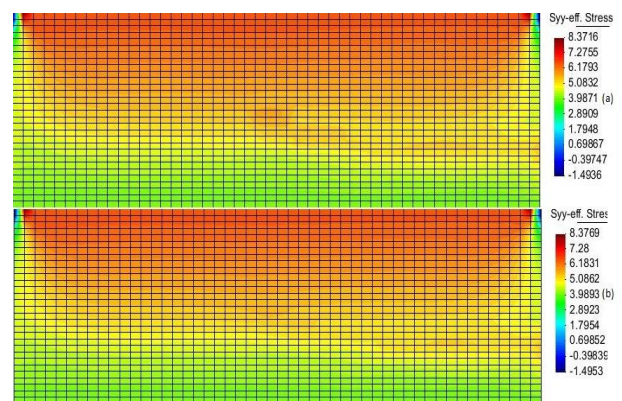


Figure 10A Graphical representation of effective stress in y direction S_{yy} (MPa) (a) after 468 days (b) after 641 days

For the particular system in this study it is expected that hydrate dissociation towards under saturated water will increase the dissociation rate for some elements of the simulation grid. For the limits that hydrate dissociation is faster than the surrounding diffusivity transport of CO_2 that bring CO_2 away from the dissociating front hydrate may reform on the interface between CO_2 and water or from CO_2

enriched solution. The maximum concentration of CO_2 in liquid water that is not affected by hydrate is higher than the concentration of water in vicinity of hydrate [6, 18]. Theoretically this implies that surrounding groundwater may dissociate hydrate, as well as being a source for creation of hydrate depending on local flow. These phase transition will be implemented using theoretical results from Phase Field theory [34, 37, 45 and 51].

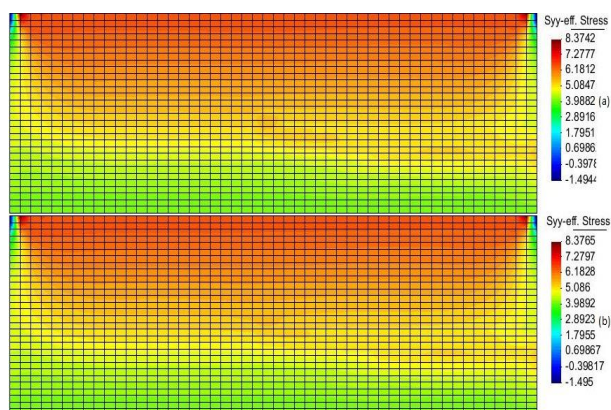


Figure 10B Graphical representation of effective stress in yy direction S_{yy} (MPa) (a) after 417 days (b) after 458 days

To predict if there is any possibility of reservoir failure due to hydrate formation and dissociation, it's necessary to study the stresses in reservoir.

The strength of hydrate bearing sediment is higher than the strength of sediment not containing hydrates and it's directly related to the amount of hydrate in the pore space [52].

As observed in figures 5, 6, 10 and 11, fluid movement, distribution of pressure and hydrate formation, have a direct impact on effective stresses.

The estimated principle effective stress in yy direction is plotted in figures 10A and 10B. 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 11 are in the lower rock zone, in the aquifer, in the zone of the fracture, and in the zone where the hydrate forms or dissociates. 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 (for instance

carbonate reactions) and longer time scales (for instance quartz dissolution).

The main development is observed in the gas plume zone towards the zone where the hydrate will form (or dissociate) with vertical effective stress below 7.0 MPa. The area of compaction arches in the corners of the lower aquifer with values below 6.0 MPa. The increase of the effective stress observed in the hydrate zone above the upper fracture will influence the local permeability of the escaping gas due to the pore compaction. This may practically as shown in figures 9A and 9B reduce the permeability to very low levels and the CO_2 plume below may take more time to dissolve in the surrounding water and sink which explains the decrease in water saturation as shown in figure 7.

In RCB, there is no time shift between flow analysis and geo-mechanical impact. The geo-mechanical analysis does not involve any trigonometric functions and the effective stress in each element can be directly compared to the tensile strength of the material. According to the figures 11A and 11B, minimum effective stress is estimated to be -1.495 MPa for this model system.

Applying the criteria used by Rohmer et.al. [41], it is possible to make a comparison between tensile strength of sand stone reported in literature [53] and the minimum effective stress in this simulation. This comparison suggests that the observed change in effective stress might be well within safe limits for any mechanical failure in the reservoir.

6 Conclusion

Hydrates in reservoirs are not able to reach equilibrium due to Gibbs phase rule and other factors, including the fact that these hydrate filled systems are open systems in a thermodynamic sense. A very common approximation in several existing hydrate simulators is the assumption of local equilibrium using the pressure and temperature projection only and thus disregarding composition dependencies of equilibrium. The reason for this particular simplification can be the particular choice of platform used for development of the hydrate simulator. In this work we have applied a reactive transport simulator, RetrasoCodeBright (RCB), as a basis for easier inclusion of competing phase transitions in a general non-equilibrium situation. At this stage only a limited number of all possible hydrate phase transitions are implemented but this is an ongoing effort.

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

A simplified kinetic model is derived on the base of the effect of super saturation (or under saturation) in the classical nucleation theory of hydrate growth or dissociation. For comparison, the Kim Bishnoi model [15] is adopted which frequently used in other hydrate codes but with rate constants derived from Phase Field Theory. A simple model simulation for CO₂ injection into an aquifer system connected by one fractured cap rock layer is then presented to demonstrate the model performance.

When using Kim and Bishnoi approach [15], the reduction in available pore volume (porosity) decreased rapidly to a very low level and close to 100% filling of pore volumes was observed (figure 9B(b)). The resulting permeability was so low that it practically implied a blocking of fluid fluxes. This also explains an observed reduction in expansion of the hydrate zone in the hydrate regions. This behaviour is not observed for the same simulation case when using the approach based on the effect of super saturation (or under saturation) in the classical nucleation theory of hydrate growth and dissociation. We should also keep in mind that the results so far are based on only a limited spectrum of all the possible routes to hydrate formation and dissociation. Work is in progress on extending the code to a more complete set of non-equilibrium possibilities for hydrate phase transitions.

Since hydrates in sediments are generally not in thermodynamic equilibrium, hydrate filled reservoirs will never be close to 100% filling of pores volumes which makes the method based on the results from the effect of super saturation in the flux according to the classical nucleation theory more realistic.

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