

Theoretical studies of Methane Hydrate Dissociation in porous media using RetrasoCodeBright simulator

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Abstract

Methane hydrates in reservoir are generally not in chemical equilibrium, there may be several competing hydrate phase transitions like for instance hydrate dissociation due to pressure or temperature changes, hydrate reformation, hydrate dissociation due to contact with under saturated fluids and mineral surfaces. The limited numbers of reservoir simulators, which have incorporated hydrate, are normally simplified by considering only pressure and temperature as criteria for hydrate stability region. If kinetic description is used it is very oversimplified and usually extracted from models derived from experiments in pressure, temperature volume controlled laboratory cells. Reservoir scale simulation of hydrate dynamics are important investigations, which enable engineers to predict the production potential of a methane hydrate reservoir and propose efficient production scenarios. Several research groups have been recently working on this subject but there seems to be significant differences in their approaches and results. In this work a reactive transport reservoir simulator, namely Retraso CodeBright (RCB), has been modified to account for hydrate kinetic phase transitions in the reservoir. For this purpose, hydrate has been added as a pseudo-mineral component and advanced kinetic models of hydrate phase transitions have been developed. The main tools for generating these models have been phase field theory simulations, with thermodynamic properties derived from molecular modelling. The detailed results from these types of simulations provides information on the relative impact of mass transport, heat transport and thermodynamics of the phase transition which enable qualified simplifications for implementation into RCB. The primary step was to study dissociation of methane hydrate under depressurization condition with a certain kinetic rate on a model inspired based on real methane reservoir. Messoyakha methane hydrate reservoir from East Siberia was chosen for constructing model for this theoretical study. Details of the simulator, and numerical algorithms, are discussed in detail and some relevant examples are shown.

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1. Introduction

1.1 Background

Methane gas hydrates are the largest source of natural gas on earth. Methane hydrate is an ice like structure in which water enclathrates small non-polar, and slightly polar, molecules. Unlike ice it can

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Nomenclature

| | |
|--------------|---|
| F | Degree of freedom |
| n | Number of components |
| π | Number of phases |
| ΔG_i | Gibbs free energy change |
| H | Hydrate phase |
| i | Any of the seven phase transition scenarios |
| p | Liquid, gas and adsorbed phases |
| x | Compositions |
| μ | Chemical potential |
| δ | 1 for hydrate formation or reformation, -1 for hydrate dissociation |
| w | Water |

form at temperature above zero degrees Celsius if pressure is high enough. The two dominating structures are named structures I and II. Structure I is more common. Maximum amount of methane that can occur in a structure I methane hydrate is fixed by the clathrate geometry at $\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$ [1]. Methane hydrates are also known as natural gas hydrates. These hydrates are not stable in porous media. The hydrogen bonded structure is not compatible with partial charges on atoms in mineral surfaces, requirements for equilibrium according to Gibbs phase rule is normally not fulfilled and/or levels of free energy for possible phases prevents equilibrium. Its distribution throughout the world and huge quantity of natural gas trapped in hydrates has resulted in a rapidly increasing interest in hydrate energy. The most promising resources of hydrates in terms of exploitation are unconsolidated sand filled structures on top of a free gas zone, which is the case for the Messoyakha field in Russia. 11.6 Billion Standard cubic meters have been produced from this reservoir since 1970 and roughly half is interpreted to result from dissociated hydrate due to pressure reduction. Nankai Through offshore Japan is estimated to contain energy for Japan for more than 100 years [2]. In this paper a different approach according to non-equilibrium nature of hydrate phase transitions in the reservoir will be presented and a new reservoir hydrate simulator will be introduced which is developed on a former reactive transport reservoir simulator namely RetrasoCodeBright (RCB). The module is designed so that it can easily work according to the non-equilibrium thermodynamic package which is being developed in this group. At this stage kinetic models of hydrate formation and dissociation from phase field simulations are used to examine the performance of the module through example cases.

1.2 Theory

Common to all current hydrate exploitation simulators is the limitations in thermodynamic description and oversimplified kinetic models. When a clathrate hydrate comes into contact with an aqueous solution containing its own guest molecules (CH_4 or CO_2), the number of the degrees of freedom available to the new system of three phases (aqueous, gas, hydrate) will be decreased compared to the two-phase system (aqueous, gas) due to the Gibbs phase rule. For the two-phase system comprising two components, water and gas, there will be two degrees of freedom. In a three-phase system of the same components, with hydrate as an additional phase, there will be only one degree of freedom. If both temperature and pressure are specified, as will be the case locally in a reservoir, the system is over-determined and will be unable to reach three-phase equilibrium. In this system, as well as other systems which are over or under determined in terms of Gibbs phase rule, directions of minimum free energy development will determine the progress of the system. By considering only pressure/temperature projection and assuming equilibrium according to this projection is in best case an over simplification but

it is worse than that. A given system may very well be inside hydrate P T stability region but will dissociate if the concentrations in neighbouring phases are under saturated. This means that the hydrate might sublime towards gas if the gas is under saturated with respect to water. Or it can dissociate towards liquid water phase if the water is under saturated with methane. The system will, however, always tend towards the minimum free energy, and when the hydrate is inside its pressure–temperature stability region, this means that its free energy is lower than that of the aqueous solution [3]. So the term under saturated in a non equilibrium system have a reference to the lowest free energy phase. As an example we can consider carbon dioxide dissolved in water at 1 degree Celsius and 150 bars. Extrapolations of Henry's law would estimate solubility in liquid water of 3.3 mole per cent carbon dioxide. The same condition with hydrate present will result in 1.6 per cent of carbon dioxide in water co existing with hydrate [4, 5].

In case of hydrate formation and dissociation in the reservoir the system will be even more complex because hydrate can form from or dissociate towards phases with different free energies, which will produce different phases. Consequently, degree of freedom will decrease further and there will be no equilibrium condition and competing phase transition reactions of hydrate formation, dissociation and reformation among different phases will rule the system. The free energy of a hydrate forming from methane dissolved in water and water versus free energy of hydrate forming from methane gas and liquid water will be different. This can be seen from the statistical mechanical model for hydrate [6] where the chemical potential for water in hydrate depends on guest molecules chemical potentials though the cavity partition functions. In a non equilibrium situation chemical potential for methane is different for different phases. In hydrate created from gas methane the chemical potential of guest molecule in hydrate can be expanded from equilibrium conditions using a Taylor expansion to actual conditions and properties inside a cavity of the hydrate. Similar expansion for a hydrate created from dissolved methane gives another chemical potential for the same type of guest molecule.

The main factor in such a system is therefore the minimum free energy of the system and kinetics of competing "reactions". Methane and water are considered as the only components available in the system. The degree of freedom for such a system is one while it can reduce to -1 if two additional phases of CH₄ and water adsorbed to both solid grains and hydrate are also considered. It is while temperature and pressure are fixed in the reservoir. Potential phase transition scenarios due to hydrate dissociation and reformation in this system can be summarized through:

$$\Delta G_i = \delta \left[x_w^{H,i} (\mu_w^{H,i} - \mu_w^p) + x_{CH_4}^{H,i} (\mu_{CH_4}^{H,i} - \mu_{CH_4}^p) \right] \quad (1)$$

In equation (1), 'H' represents hydrate phase, 'i' represents any of the seven phase transition scenarios, 'p' represents liquid, gas and adsorbed phases, 'x' composition and 'μ' chemical potential. δ is 1 for hydrate formation or reformation and -1 for dissociation. The chemical potential for water in the hydrate of type i can be estimated using a modified version of the statistical-mechanical model [6]. A summary of some scenarios of phase transition involving hydrate in a non-equilibrium situation is summarised in table 1 below.

Table 1. Different phase transition and corresponding driving forces (G=Gas, L=Aqueous, H=Hydrate).

| i | δ | Initial phase(s) | Driving force | Final phase(s) |
|---|----|---------------------|--|----------------|
| 1 | -1 | Hydrate | Outside stability in terms of P and/or T | G, L |
| 2 | -1 | Hydrate | Sublimation (gas under saturated with water) | G, (L) |
| 3 | -1 | Hydrate | Outside water under saturated with methane | L, (G) |
| 4 | +1 | Gas+Liquid water | Hydrate more stable than surrounding fluids | H |
| 5 | +1 | Surface reformation | Non-uniform hydrate rearranges due to mass limitations | H |
| 6 | +1 | Aqueous Phase | Liquid super saturated with methane. | H |
| 7 | +1 | Adsorbed | Water and methane adsorbed on mineral surfaces | H |

The phase transition with index 5 is driven by non-uniform hydrate on the interface between an aqueous phase and a gas phase. The initial hydrate will rapidly grow to a thickness where mass transport through the hydrate film becomes very small (low diffusivity coefficients). In this case the system will

appear in a state of quasi-equilibrium where the gas side of the hydrate can grow from water in gas to a quasi equilibrium on that side. On the other side hydrate can grow from dissolved methane. Parallel to this there will be a rearrangement of hydrates on the surface since the hydrate will be non-uniform. Hydrates initiates at fairly random spots on the interface and thickest hydrate sections will be more stable than thinner ones in terms of lower free energy. With limited available "free" mass the less stable spots will dissociate in favour of growth of the more stable thick regions.

All impossible ($\Delta G > 0$) and unlikely ($|\Delta G| < \varepsilon$) cases locally in a reservoir simulation grid will 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. Taking also into account possibly mass transport limited cases, which would be unlikely to proceed during the average retention time then all the remaining realistic phase transition scenarios will be evaluated. In the case of mass limitations then the different kinetic equations for the possible competing phase transition will be subject to an analyses of free energy minimization under mass constraints. The purpose of this study is to develop a hydrate reservoir simulator which has the possibility to consider the free energy changes of all phase transition scenarios and take into account the effect of the realistic ones on the flow and properties of the porous media through advanced kinetic models.

1.3 Kinetic model

The results from phase field theory simulations [7] 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 been going on in the same group on application of phase field theory in prediction of hydrate formation and dissociation kinetics which is still in progress [3, 7 - 12]. In this study, the simulation results of such studies have been extrapolated and used as a constant rate in the numerical tool.

1.4 Numerical tool : RetrasoCodeBright

Retraso CodeBright(RCB) is used in this study and 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. RCB is a coupling of a reactive transport code Retraso with a multiphase flow and heat code CodeBright. CodeBright contain an implicit algorithm for solution of flow, heat-flow and geo-mechanical model equations. The Retraso extension of CodeBright involves an explicit algorithm for updating the geochemistry. Details of RCB are given elsewhere [13-17]. The results from this model for some important mechanical, hydraulic properties were assembled and illustrated through a graphical window GiD [18]. The kinetic rate used in this study is calculated from extrapolated results of phase field theory simulations by Svandal et al. [8].

1.5 Reactive transport in Retraso

The Retraso part of the code has a built in state of the art geochemical solver and in addition capabilities of treating aqueous complexation (including redox reactions) and adsorption. Different types of nonlinear models are already implemented in the CodeBright part of the code and the structure of the code makes it easy to implement new models derived from theory and/or experiments. The current version of RCB has been extended from ideal gas into handling of CH₄ according to the SRK equation of state. This equation of state is used for density calculations as well as the necessary calculations of fugacity of the CH₄ phase as needed in the calculation of dissolution of CH₄ into the water. The dissolution and precipitation of minerals, with the exception of some carbonates, is slow natural processes and in our example mineral/fluid reactions are described by built-in kinetics based on available experimental data from open literature [12].

2. 2D model's description

The simulation model used in this study was constructed as simplified version of Messoyakha gas field reservoir, all reservoir properties such as temperature, pressure, depth, porosity and permeability were taken from Messoyakha gas hydrate reservoir [2]. The geometry of the 2D domain is 400m x 90m rectangle. For simulation purpose this reservoir was further divided into smaller elements of size 10m x 5m. There are two separate layers in the aquifer, upper layer hydrate layer and it consists of methane hydrate, methane gas and water. Lower layer is gas layer and it consists of methane gas and water. Thickness of hydrate layer is 50m and thickness of gas layer is 40m. Gas production well is located in gas layer, 5m below the hydrate layer as can be seen in figure 1. Pressure of gas production well was kept lower than surrounding pressure in the reservoir.

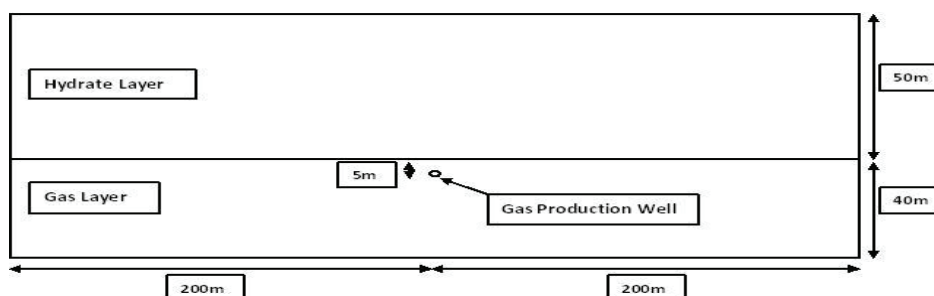


Fig. 1. Geometry of 2D model with CH₄ gas production well

Table 2, 3 and 4 contain data related to chemical species, material properties and initial pressure, temperature ranges for reservoir nodes as well as boundary conditions.

Table 2. Chemical species in different forms

| Species | Hydrate Layer | Gas Layer |
|--------------------|---|---|
| Aqueous | H ₂ O , H ⁺ , OH ⁻ , CO ₃ -2, HCO ₃ -, O ₂ (g) | H ₂ O , H ⁺ , OH ⁻ , CO ₃ -2, HCO ₃ -, O ₂ (g) |
| Hydrate Saturation | CH ₄ Hydrate (0.4) | - |
| Gas | CH ₄ | CH ₄ |

Table 3. Material properties

| Property | Hydrate Layer | Gas Layer |
|---|---------------|-----------|
| Young's Modulus (GPa) | 0.5 | 0.5 |
| Poisson's Ratio | 0.25 | 0.25 |
| Zero stress porosity | 0.35 | 0.35 |
| Zero stress permeability, (mD) | 500 | 500 |
| Van Genuchten's gas entry Pressure, (kPa), (at zero Stress) | 196 | 196 |
| Van Genuchten's exponent, (m) | 0.457 | 0.457 |
| 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 4. Initial and boundary conditions (values vary with depth, so they are in range)

| Parameter | Hydrate Layer | Gas Layer |
|---|---------------|--------------------------|
| Pressure, (MPa) | 7.4-7.9 | 7.9-8.3 |
| Temperature(°C) | 8.94-10.64 | 10.64-12.0 |
| Mean Stress(MPa) | 14.3-16.3 | 16.3-18.07 |
| CH ₄ Production Pressure (MPa) | - | 7.5(initial), 7.2(final) |
| Gas outgoing Pressure (MPa) | 7.4 | 8.3 |

3. Results and discussion

Results for hydrate saturation change, gas flow rate and gas pressure in reservoir were generated using RCB simulator. Pressure and temperature plays big role in hydrate dissociation, for this study we focused on effects of pressure drop. Pressure of gas production well was kept 3 to 6 bar below surrounding reservoir pressure. This led to pressure drop in reservoir; due to this pressure drop hydrate started dissociating according to kinetic rate of hydrate dissociation, which was a function of temperature and pressure. Hydrate dissociation can be observed by change in hydrate saturation as visible in figure 2. It is clearly visible that hydrate saturation was going down, which means hydrate was disappearing because of dissociation reaction. This change in hydrate saturation is directly proportional to kinetic reaction rate of hydrate dissociation. Due to small difference in production well pressure and surrounding pressure, change in hydrate saturation was small. First visible change appeared after 9 months and it grew afterward with time.

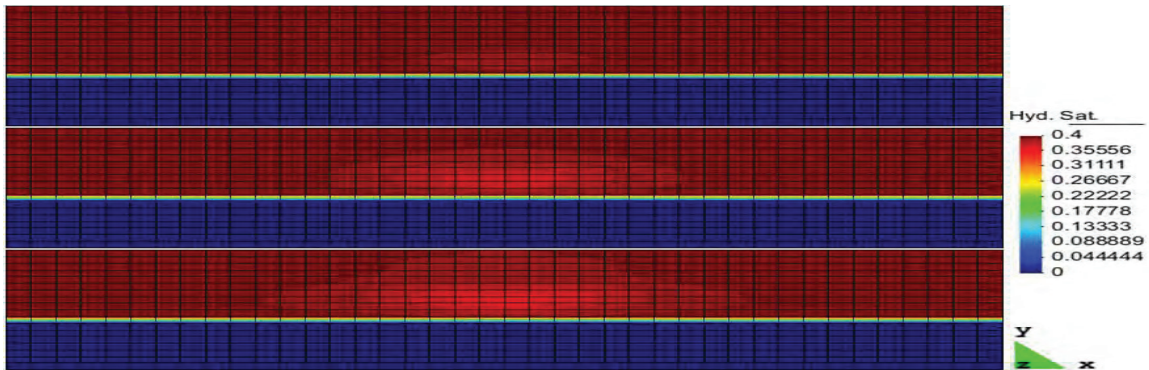


Fig. 2. Hydrate Saturation (%) – after (a) 9 months (b) 20 months (c) 28 months

Gas production was mainly from free gas layer below hydrate layer as visible in figure 3. Hydrate layer also contributed in gas production, but due to slow dissociation rate this contribution was small. Entire reservoir was affected by fluid flow as the production well was situated in the middle of the reservoir. High flow rates of gas are visible around gas production well; figure 3 can also be used to calculate total gas production from the well.

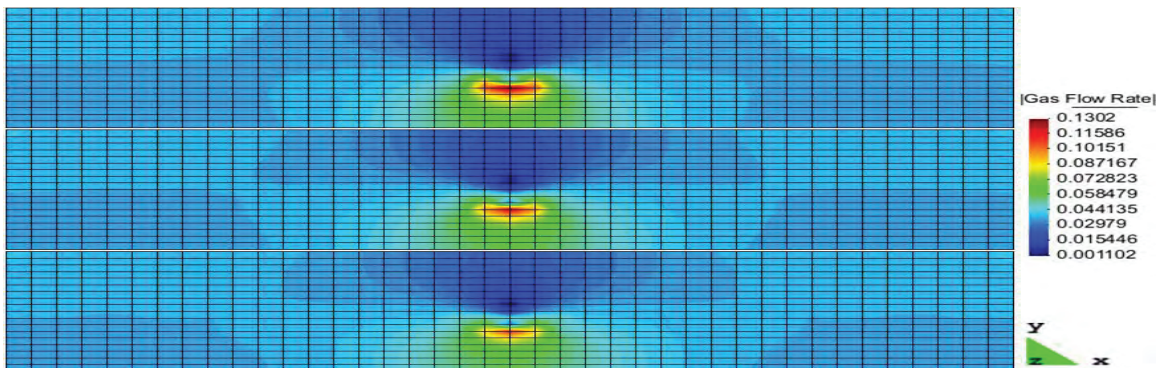


Fig. 3. Gas Flow Rate (M3/Sec) - after (a) 9 months (b) 20 months (c) 28 months

Area above gas production well was affected by pressure drop as can be seen in figure 4. It explains the reason why hydrate dissociation took place mainly in that particular area. Other areas of hydrate layer remained almost unaffected during entire simulation run. Figure 4 approves effectiveness of pressure drop in hydrate dissociation reaction.

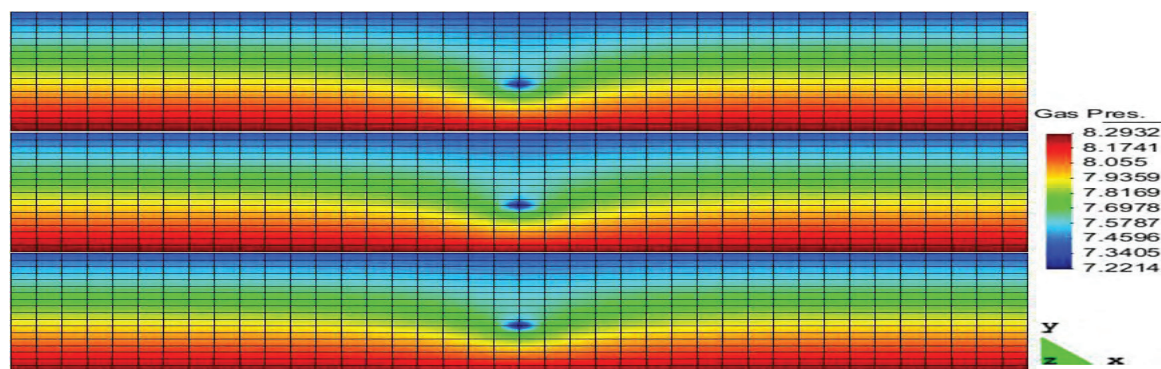


Fig. 4. Gas Pressure (MPa) - after (a) 9 months (b) 20 months (c) 28 months

3.1 Comparison of results with other theoretical studies

Similar theoretical studies of depressurization induced methane hydrate dissociation were also carried out by Grover et al.[19] for Messoyakha field in East Siberia, Moridis et al.[20] for Mount Elbert sites in Alaska, Rutqvist et al. [21] for Mallik and Mount Elbert deposits in Alaska and Alp et al.[22] for hypothetical hydrate reservoirs. Code comparison studies of different hydrate reservoir simulators such as CMG STARS, HydrateResSim, MH-21 HYDRES, STOMP-HYD, and TOUGH+HYDRATE were carried out by Wilder et al.[23] and Gaddipati[24]. RCB simulator estimates similar results compare to some of these codes. In future, we aim to compare RCB with some of these hydrate simulators in more details.

4. Conclusion

In this work we have demonstrated the implementation of CH₄ hydrate in RetrasoCodeBright and used a simple example to illustrate the impact of hydrate dissociation on hydrate saturation, gas pressure and gas production rates. This is the first step in further extensions to include competing phase transition of hydrate growth as well as dissociation toward under saturated phases. These hydrate phase transitions are in non-equilibrium and hydrates formed from different phases will generally have different compositions and different free energies. Different hydrates can be treated as pseudo minerals and then using the same logistics as for mineral dissolution and formation. This makes it easy to implement phase transition kinetics for the different hydrate phase transitions as estimated from theory or measured experimentally. We demonstrate that RCB is capable of handling hydrate formation and dissociation reaction and can be used to study the possibilities of gas production from hydrate reservoirs.

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