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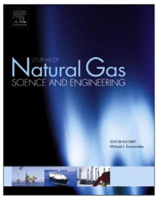

Non-equilibrium simulation of CH_4 production from gas hydrate reservoirs through the depressurization method

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ABSTRACT

Natural gas hydrates (NGHs) in nature are formed from water and hydrate formers from various phases (i.e., aqueous, gas, and adsorbed phases). As a result, owing to Gibbs' phase rule and the combined first and second laws of thermodynamics, CH_4 hydrates cannot reach thermodynamic equilibrium in real reservoir conditions. Thus, there is a competition between hydrate formers, where the most stable hydrates form first. The non-equilibrium nature of hydrates indicates a need for proper kinetic models to describe the various routes that can lead to hydrate formation. Dissociation of hydrates in sediments can also occur as a function of undersaturation of any of the thermodynamic variables. In addition to temperature and pressure being outside the stability region for hydrates, the concentration of water and hydrate formers in co-existing phases can lead to hydrate instability. CH_4 hydrate dissociation towards CH_4 gas and water has previously been implemented using the RetrasoCodeBright (RCB) hydrate simulator. In the present work, we implement an additional route for hydrate phase transitions that enables hydrate dissociation and reformation towards water and aqueous CH_4 and by considering undersaturation or supersaturation with respect to pressure, temperature, and CH_4 mole fraction. CH_4 hydrate dissociation in contact with water undersaturated with methane is considered, as well. An in-house non-equilibrium thermodynamic package has been written and is inserted into RCB to calculate Gibbs free energies. The driving forces for hydrate phase transitions are calculated from differences in the free energies of hydrates and hydrate formers. Competing phase transitions are handled by Gibbs free energy minimizations. Nucleation theory is used to calculate the impact of heat and mass transport and of non-equilibrium thermodynamics on kinetic rates of hydrate phase transitions. Our modifications are used to simulate CH_4 production, covering time spans of 290 days using the depressurization method on a simplified hypothetical model. A complete description of our methodology is presented together with a discussion of our simulation results.

1. Introduction

Natural gas hydrates(NGHs) are widespread around the world, especially in marine shelf sediments (Paull and Dillon, 2001) but also in on-shore polar regions beneath the permafrost (Weatherford Laboratories, 2016). Natural gas components within gas hydrates are typically dominated by methane that is formed as a result of biogenic degradation of biological material in the upper few hundred meters of sediment rather than by thermogenic degradation of fossils, which would result in heavier gas components like C2 and C3 (Weatherford Laboratories, 2016). Gas hydrates are composed of water molecules hydrogen-bonded into cage structures containing hydrocarbon or non-hydrocarbon guest molecules (Weatherford Laboratories, 2016).

Hydrates occur in places where the pressure and temperature conditions are within the hydrate stability region (Lerche and Bagirov, 1998). However, this stability could be affected by changing environmental conditions. A decrease in the pressure, as a result of a reduction in sea level or an increase in ocean temperature, may disturb hydrate stability, causing hydrates to dissociate. Moreover, hydrates could also dissociate when coming into contact with water which is undersaturated with respect to methane through various faults and fractures. Some illustrative mapping has been performed by the national program GANS in Norway (Haflidason et al., 2009). There are also examples of methane bubbling through the water column as a result of hydrate

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dissociation in the groundwater and seawater around Svalbard (Veloso et al., 2015).

Due to the increasing demand for energy worldwide, gas hydrate reservoirs have become attractive as potential sources of unconventional fossil energy for the future. Enormous amounts of gas are caged inside hydrate structures. It has been estimated that the amount of fuel-gas reserves in NGHs are higher than conventional explored fossil fuels explored up to the present (Kvenvolden, 1993). Moreover, released CH_4 from NGHs dissociated by natural processes that result in hydrate instability could very likely find its way into the atmosphere. Even though the life-time of CH_4 is shorter in the atmosphere, CH_4 is a far more aggressive greenhouse gas than CO_2.

CH_4 is the dominant component in NGH reservoirs, and its production from NGHs includes conventional methods such as pressure reduction, thermal stimulation, and inhibitor injection (Sloan and Koh, 2007). There also exist some newly developed methods such as CO_2 gas exchange through sequestration of CO_2 into NGH-filled sediments (Graue et al., 2008), use of fluorine gas, and microwave technology (Singh and Arora, 2015).

One limitation of the methods mentioned above except for CO_2 gas exchange is the production of substantial amounts of water from dissociated NGHs following production of CH_4 gas. This may cause uncontrolled increases of overburden pressure in hydrate-bearing layers which can affect the geomechanical stability of underground structures, subsequently resulting in subsidence and landslides in surrounding areas.

Injection of CO_2 into NGH reservoirs leads to the formation of more stable CO_2-dominated hydrates. Exchange processes can occur by two mechanisms. The dominant mechanism is direct CO_2 hydrate formation from free water and injected CO_2. The heat of formation of this hydrate contributes to the dissociation of in-situ CH_4 hydrate and the release of CH_4 gas. The second mechanism, which is very slow in comparison with the first, is a solid-state exchange of CH_4 with injected CO_2 inside the lattice structure. The second mechanism results in formation of mixed hydrates of CH_4 and CO_2 as well as the release of CH_4 from the large cavities of the hydrate structure. Since this mechanism depends on solid-state diffusivity, it becomes dominant when the saturation of free water in the NGH pores approaches zero. An advantage of CO_2 injection into in-situ CH_4-hydrate-filled sediment is that the reduction in pore-filled volumes by dissociation of CH_4 hydrate is compensated by formation of new CO_2-dominated hydrate.

As of today, only one field is producing natural gas from hydrates – the Messoyakha field (Makogon, 1997). However, data monitoring from this field is too limited to reveal possible gradual changes that may eventually lead to later instability. It is also a permafrost reservoir; thus, the ice and frozen structures above also delay possible geomechanical failure of nearby geological structures. Gaining knowledge of NGHs through real field analysis is expensive and difficult since many changes involve gradients over geological time scales. Conducting laboratory-scale experiments would not be representative enough of real conditions present since most reservoirs are in a stationary state that has developed over geological time scales. However, computer simulations may help to extend our knowledge of possible scenarios that might occur in a reservoir during production of gas from NGHs.

Lack of reliable field data makes it difficult to predict production potential and safety of CH_4 production from NGHs. Computer simulations can be used as a tool to investigate CH_4 production in different scenarios.

There are only a few available simulators which are specialized in simulating hydrate production. The basis of today's hydrate simulators are two-fold: on the one hand, we have oil and gas simulators (e.g., STARS (Thermal & Advanced Processes Reservoir Simulator, 2016)), and on the other hand we have hydrogeological simulators (e.g., RCB (Saaltink et al., 2005) and TOUGH (Moridis et al., 2012)). A recent review of the literature on this topic revealed that most hydrate simulators within academia and industry treat hydrate phase transitions as an equilibrium process, and those employing the kinetic approach frequently utilize models derived from simple laboratory data (for instance, those published by Kim and Bishnoi (Kim et al., 1987) in their models) (Vafaei et al., 2014). Furthermore, it is typical to utilize a limited thermodynamic description where only temperature and pressure projections of the total hydrate stability dependency (which also involves concentrations in all co-existing phases) are considered. Another widely used simplification is to assume only a single route for hydrate phase transitions. As discussed above, NGH reservoirs in nature are the results of formation from hydrate formers arising from various phases. Fig. 1 shows different routes of phase transitions involving hydrates.

In a non-equilibrium system, hydrate formers in gas phases, dissolved water, or adsorbed onto mineral surfaces have different chemical potentials. From the statistical mechanical models frequently applied in calculations of chemical potentials of water in hydrates, it is straightforward to demonstrate that variations in chemical potentials for hydrate formers result in variations of the filling of hydrate formers in hydrate cavities. According to thermodynamic definitions, the resulting differences in hydrate densities and compositions results in individual hydrate phases since free energies of these various hydrate phases are different. Because pressures and temperatures are known in real reservoir conditions, the presence of different phases in the system implies that equilibrium could not be established under Gibbs' phase rule and the combination of the first and the second laws of thermodynamics. Thus, realistic modeling of hydrate reservoirs should be done from a non-equilibrium thermodynamic perspective. Having a kinetic model that can relate thermodynamic variables, as well as heat and mass transfer, to phase transitions provides a much more realistic simulation of reservoir conditions during CH_4 production from NGHs.

Proper modeling of NGHs requires consideration and evaluation of all possible phase transitions that include hydrates. In contrast to

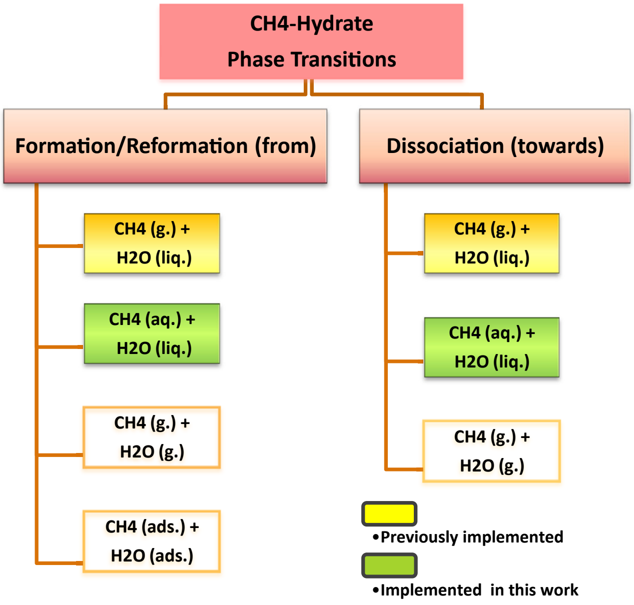

Fig. 1. Different routes of hydrate phase transitions in nature.

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