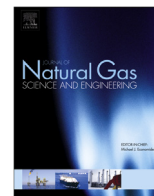




Contents lists available at ScienceDirect

## Journal of Natural Gas Science and Engineering

journal homepage: [www.elsevier.com/locate/jngse](http://www.elsevier.com/locate/jngse)

# Non-equilibrium simulation of hydrate formation and dissociation from CO<sub>2</sub> in the aqueous phase

Khadijeh Qorbani\*, Bjørn Kvamme, Richard Olsen

Department of Physics and Technology, University of Bergen, Allégaten 55, 5007 Bergen, Norway

## ARTICLE INFO

### Article history:

Received 30 January 2016

Received in revised form

20 March 2016

Accepted 29 March 2016

Available online xxx

### Keywords:

Hydrate simulation

Carbon dioxide storage

Reservoir simulation

Non-equilibrium thermodynamics

## ABSTRACT

The RetrasoCodeBright (RCB) hydrate simulator has the ability to calculate the amount of CO<sub>2</sub>-hydrate formed from water and CO<sub>2</sub> as well as dissociation towards CO<sub>2</sub> gas when the gas phase is undersaturated with water (or in the case where the pressure and temperature conditions are outside of the hydrate stability region). By implementing a non-equilibrium thermodynamic module into RCB, we added another route for hydrate-phase transitions towards CO<sub>2</sub> in the aqueous phase as well as in the water phase. We also considered hydrate instability due to the undersaturation of CO<sub>2</sub> in the contacting water phase. As a kinetic model, we used classical nucleation theory, where the phase transitions were treated as non-equilibrium processes under the local constraint of mass and heat fluxes. We verified CO<sub>2</sub>-hydrate formation and dissociation by observing supersaturation and undersaturation with respect to the thermodynamics variables, CO<sub>2</sub> mole-fraction, pressure, and temperature. We determined competing hydrate phase transitions by investigating the Gibbs free-energy differences between hydrate and parent phases (origin of hydrate formers), and we calculated the energy differences from variations in the chemical potentials, which were estimated using non-equilibrium thermodynamics. In this paper, we discussed our implementation, as well as results obtained from simulations utilizing our modifications.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Gas hydrates are crystalline water-based structures with guest hydrocarbon or non-hydrocarbon molecules, where guest molecules are trapped within a crystal structure composed of water molecules (Weatherford Laboratories, 2016). Huge amounts of gas are trapped inside the hydrate structures. 1 m<sup>3</sup> of hydrate dissociating at standard temperature and pressure will result in 164 m<sup>3</sup> of gas (at standard conditions) and 0.8 m<sup>3</sup> of water (Kvenvolden and Howell, 1993).

Methane is the dominant gas component of natural gas hydrates (NGHs) (Weatherford Laboratories, 2016), and methane hydrates exist in places where the pressure and temperature conditions are within the hydrate stability zone (Lerche and Bagirov, 1998). The quantity of the in-place natural gas stored in hydrate-bearing sediments significantly exceeds the conventional fossil-fuel resources (Kvenvolden and Howell, 1993). Thus, NGH reservoirs have become attractive as unconventional sources of fossil fuel.

However, its exploitation is difficult because of the lack of economically feasible production methods (Weatherford Laboratories, 2016). The worldwide distribution of natural gas hydrates is different compared to that of conventional hydrocarbons, and countries such as Japan have large natural gas reserves trapped as methane offshore Japan, while having almost no conventional hydrocarbons. Depressurization, thermal stimulation, and inhibitor injection are the three conventional methods used to exploit methane from hydrate reservoirs (Sloan and Koh, 2007). All of these gas-production mechanisms will result in the dissociation of hydrates and the production of a large amount of water. This may result in an increase of the overburden stress, which can affect the geomechanical stability of hydrate-bearing sands, resulting in subsidence and landslides in hydrate-dissociated regions. Thus, we require a new production method to avoid this problem.

Over the past few decades, the Earth's climate has undergone rapid changes. One reason is believed to be an excess of CO<sub>2</sub> in our atmosphere, emanating from the burning of fossil fuels (Stocker et al, 2014). One possible solution to reversing its effects is to capture CO<sub>2</sub> gas and inject it into CH<sub>4</sub>-hydrate reservoirs for storage in the form of CO<sub>2</sub>-hydrate (Graue et al., 2008).

It was proposed that captured CO<sub>2</sub> could be injected into

\* Corresponding author.

E-mail address: [Khadijeh.Qorbani@ift.uib.no](mailto:Khadijeh.Qorbani@ift.uib.no) (K. Qorbani).

methane-hydrate reservoirs, replacing the methane hydrate with CO<sub>2</sub>-hydrate (as well as mixed CO<sub>2</sub>/CH<sub>4</sub> hydrate) (Graue et al., 2008). This would result in the production of methane (Graue et al., 2008), and is made possible because methane hydrate is less stable than both pure CO<sub>2</sub>-hydrate and mixed CO<sub>2</sub>/CH<sub>4</sub> hydrate (Svandal, 2006). Two mechanisms are involved in this process. The dominant mechanism is the formation of new CO<sub>2</sub>-hydrate from injected CO<sub>2</sub> and water from the pores. The second mechanism, which is slower, is the solid-state exchange of CH<sub>4</sub> with CO<sub>2</sub>, which is dominated by solid-state mass transport (Graue et al., 2008; Ersland et al., 2009; Kvamme et al., 2007, 2014, 2009; Buanes et al., 2006). As a result, the heat of formation of new CO<sub>2</sub>-hydrates will assist with the dissociation of in-situ CH<sub>4</sub>-hydrate. The application of this method also satisfies the stabilization of the hydrate-bearing layers, and the sequestration of CO<sub>2</sub> in the form of hydrate inside CH<sub>4</sub>-hydrate reservoirs maintains the local geomechanical stability of the CH<sub>4</sub> producing zone (Ohgaki et al., 1996).

As a result of the changing climatic conditions, NGHs may start to dissociate, enabling the released CH<sub>4</sub> to find its way to the atmosphere (Chabert et al., 2011). Furthermore, hydrates are continuously undergoing dissociation by contact with water that is undersaturated with methane through fractures and faults. Considering that methane is a much more aggressive greenhouse gas than CO<sub>2</sub> (Bollmann et al., 2010), gas hydrates may potentially have a significant effect on future global warming (Leggett, 1990a, 1990b). Typical values indicate that the effect of methane may be of the order of 25 times worse than that of CO<sub>2</sub> as a greenhouse gas (Bollmann et al., 2010). However, the lifetime of methane in the atmosphere is significantly shorter than that of CO<sub>2</sub> because of its lower molecular weight and density of CH<sub>4</sub> (Solomon et al., 2007; Blasing). For CH<sub>4</sub>, a lifetime of twelve years in the atmosphere has been frequently reported (Anderson et al., 2010). However, when burnt as a fuel, it releases much less CO<sub>2</sub> than many other fossil fuels. Thus, because of the ever-increasing energy demands, these reservoirs may become important sources of energy for future use through the controlled production of methane, which can be used as a fuel.

In the literature, there is limited information about long-term processes that occur if CO<sub>2</sub> is injected into CH<sub>4</sub>-hydrate or if CH<sub>4</sub> is produced from hydrate reservoirs. The use of field-scale experiments is a costly way of obtaining this information. Furthermore, because of the time scales of the processes that are relevant to hydrate dynamics in practice, it would be an intractable task to solve the problem experimentally. However, the use of computer simulations is an inexpensive way of determining the outcomes of possible scenarios. Proper reservoir modelling may be used to shed light on possible scenarios within a limited computational time.

When modelling hydrates in nature, it is important to consider that hydrates are formed from a variety of phases. Liquid water can create hydrates from gas-phase hydrate formers, as well as from hydrate formers in aqueous solution or adsorbed hydrate formers. This gives rise to the formation of various types of hydrates that have different filling fractions, and as a result, different free energies and phase-transition rates. This means that there will be different hydrate phases in nature. Thus, even when they are stable over the pressure and temperature domains, hydrates are generally unable to attain thermodynamic equilibrium because of Gibbs' phase rule. As a result, to obtain a more accurate description of hydrate phase transitions, computer simulations should treat these processes as processes of non-equilibrium competing phase transitions under local constraints of mass and heat transport dynamics. It is also important to include all hydrate phases in such a simulation. In addition, hydrate phase transition rates are much faster than those of conventional mineral precipitation and dissolution rates. This means that there is a requirement for an implicit

geomechanical calculation during the simulation to avoid the time lag of geomechanical analysis in each time-step.

Only few reservoir simulators, including hydrates, are available in academia and industry. STOMP-HYDT-KE (White) is the third version of the STOMP family, and has the ability to simulate ternary hydrates of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> mixtures. Kinetics of hydrate-phase transitions are included using constant rates. TOUGH + HYDRATE (Moridis et al., 2012) is an added module to TOUGH+, enabling the simulation of methane hydrates, while the commercial code, FLAC3D, is used to couple the flow and geomechanical properties. TOUGH + HYDRATE uses both equilibrium and kinetic models for the hydrate-phase transitions, where the kinetic parameters of the hydrate reactions are obtained using the models proposed by Kim et al. (Kim et al., 1987), and of Clarke and Bishnoi (Clarke and Bishnoi, 2001). STARS is a compositional and geomechanical reservoir simulator developed by the Computer Modelling Group (CMG) (Tabatabaie and Pooladi-Darvish, 2012). The kinetics of hydrate-phase transitions are calculated using a combination of the equilibrium-hydrate-decomposition model with the Kim and Bishnoi kinetic equation (Kim et al., 1987). HydrateResSim (HRS) (Moridis et al., 2005) is based on an early version of TOUGH-Fx, and is the only open-source code available to the public through the National Energy Technology Laboratories (NETL) (National Energy Technology Laboratory, 2016). This code is able to simulate the conventional methods of gas production from methane-hydrate reservoirs. It incorporates both the equilibrium and kinetic models of hydrate formation and dissociation. The revised code, Mix3HydrateResSim, which was modified by Gaparati and Anderson (Garapati, 2013), is capable of simulating the production of methane through the injection of CO<sub>2</sub> and N<sub>2</sub> into the hydrate reservoir. To obtain mixed hydrate data, Mix3HydrateResSim uses the cell potential method. It utilizes the equilibrium and kinetic models of hydrate formation and dissociation, and uses the model proposed by Kim et al. (Kim et al., 1987) in kinetic-model calculations. MH21-HYDRES (Research Consortium for Methane Hydrate Resources in Japan, 2016) is a compositional simulator that has been developed by the Research Consortium to simulate the behaviour of methane-hydrate reservoirs. Hydrate dissociation is modelled using the Clarke-Bishnoi equation (Clarke and Bishnoi, 2001; Konno et al., 2008), and hydrate-formation modelling utilizes the model proposed by Malegaonkar et al. (Malegaonkar et al., 1997).

Most of the hydrate simulators mentioned above treat hydrate-phase transitions as an equilibrium process, and those that employ the kinetic approach in their models utilize simple laboratory methods such as the Kim and Bishnoi (Kim et al., 1987) approach. This approach is based on laboratory pressure/volume/temperature (PVT) experiments. As such, it is unknown whether these results can be transferred to dynamically flowing systems in porous media (Vafaei et al., 2014). Furthermore, it is common to utilize a limited thermodynamic description where only temperature and pressure projections are considered. Another widely used simplification is to assume only a single route for the hydrate phase transitions.

In order to understand and characterize the behaviour of hydrates, there is a need to understand all of the coupled dynamic phase transitions that can lead to hydrate formation, as well as processes that can lead to local hydrate dissociation. In addition to the hydrate stability dependence on temperature and pressure, it is necessary to focus on the total thermodynamic dependency of hydrate stability by also including concentrations and densities of all co-existing phases of impact for hydrate stability. This also includes adsorbed phases on mineral surfaces. These mineral surfaces will typically structure water to resulting chemical potentials that are far below the chemical potential of liquid water (Olsen et al., 2015). Different minerals adsorb hydrate guest molecules such as

Download English Version:

<https://daneshyari.com/en/article/5484787>

Download Persian Version:

<https://daneshyari.com/article/5484787>

[Daneshyari.com](https://daneshyari.com)