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A new reservoir simulator for studying hydrate dynamics in reservoir

M.T. Vafaei, B. Kvamme*, A. Chejara, K. Jemai

Department of Physics and Technology, University of Bergen, Allegaten 55, N-5007 Bergen, Norway

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ABSTRACT

Natural gas hydrates in sediments are generally, not in thermodynamic equilibrium, due to Gibbs phase rule. This is when the impacts of solid mineral surfaces and corresponding adsorbed phases are taken into account. As a consequence, the distribution of water and hydrate formers over possible phases, including hydrate is governed by minimum free energy according to the combined first and second laws of thermodynamics. In this work, we propose the use of a reactive transport reservoir simulator as a new platform for dynamic modelling of hydrates in porous media. Each hydrate phase transition (formation and dissociation) is modelled as a pseudo reaction, with corresponding changes in free energies as the driving forces for the phase transition itself and dynamically coupled to transport of mass and heat. This simulator is different from any of the current platforms developed by industry and academia. The main purpose of this paper is therefore to describe the simulator, integration algorithms as well as approaches for modelling non-equilibrium thermodynamics and kinetics. More specifically, a multi-scale approach, with phase field theory as the core, is used for estimating kinetic rates of different possible phase transitions. Kinetic results from these advanced theories for the different hydrate phase transitions are simplified and implemented into the reservoir simulator (RetrasoCodeBright) in a similar fashion as for reaction kinetic models for mineral/fluid reactions. Another advantage of this specific platform is that it contains implicit geo mechanics. Representative examples are used to illustrate the simulator.

1. Introduction

Natural gas hydrate in reservoir is continuously attracting the attention of more researchers around the world. The reason is its importance in different fields of interest, ranging from a potential energy resource to environmental issues. Hydrate can occur in sediments below the oceanic floor or in the permafrost wherever the thermodynamic conditions are suitable and water and guest molecules are available. Investigations show that there are huge resources of natural gas hydrate in the earth which, due to the high volumetric concentration of methane gas per hydrate volume, is considered as a substantial energy resource. Besides, methane combustion releases less CO_2 per unit energy compared to both coal and oil which means a cleaner fuel from environmental point of view. On the contrary, methane can be over twenty times more aggressive than CO_2 in trapping the heat in the atmosphere and in case of leakage from sediments it can affect marine life and the climate substantially. As will be discussed in Section 2 below, hydrates in porous media can never reach true equilibrium simply because there are too many phases to distribute the masses over. But there are also consequences of first and second laws of thermodynamics leading to non-uniform hydrates which formally means different hydrate phases. The objective of this study has therefore been to present a new and alternative simulator for studies of hydrate dynamics in porous media, which incorporates free energy analysis and kinetic models based on the state-of-the-art theory. Capabilities for analysis of geomechanics stability have been another objective and one of the reasons for the development to be based on the RetrasoCodeBright reactive transport platform (Saaltink et al., 2004). This section is organized with a brief overview of the most important hydrate production methods in Section 1.1, followed by a brief summary of existing academic and industrial tools applied for studies of hydrate dynamics in porous media in Section 1.2.

1.1. Hydrate production

There are several scenarios for methane production from natural gas hydrate reservoirs. One such method is depressurization in which hydrate stability is disturbed by pressure reduction according to the water–gas–hydrate equilibrium curve, resulting in hydrate dissociation and release of methane. It is currently considered as a feasible process with respect to expenses and production rate and has been investigated by many research groups through simulation studies. Thermal stimulation is another method which is

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* Corresponding author. Tel.: +47 55580000/55583310; fax: +47 55583380.
E-mail address: Bjorn.Kvamme@ift.uib.no (B. Kvamme).

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based on moving out from stability region by temperature increase. It is considered to be costly due to the huge amount of energy waste. The third method is to use inhibitors such as methanol or brine to shift the equilibrium curve and dissociate hydrate. The final method is injection of CO_2 into the methane hydrate reservoirs. CO_2-hydrate is more stable than CH_4-hydrate. Therefore CO_2-hydrate formation will provide the necessary heat to dissociate methane hydrate. This can be considered both as a natural gas production method and a CO_2 sequestration process (Graue et al., 2008). In this method, the two primary mechanisms for CO_2 to convert in situ CH_4 hydrate are: (1) solid state conversions and (2) new CO_2 hydrate being formed from free liquid water in the pores. Both of these mechanisms have been proven theoretically as well as experimentally (Kvamme et al., 2007, 2013b). Mechanism 1 can hardly be viewed as one of the three “classical” mechanisms mentioned above since the enthalpy change is limited and it is dominated by entropy changes. It is, therefore considered as an independent method.

1.2. Hydrate simulation research

Modelling hydrate production from sediments is fairly new compared to simulations of oil and gas production. In addition, the hydrate phase and its dynamic interactions with other phases are far more complex than conventional oil and gas systems. On top of this, there are practically no reference data of real production to test the simulator since data from the only producing field, Messayokha (Sloan and Koh, 2007) is not detailed enough and its quality may be questionable. The few hydrate reservoir simulators, which are available, are typically not described well enough in open literature to provide sufficient basis for review. There is an on-going code comparison study run by NETL with a brief description on their web pages. A few publications (Anderson et al., 2011a, 2011b; Hunter et al., 2011; Wilson et al., 2011) related to the study are also published. But the different parameters applied by the different simulators for running the test examples in the study are generally not given. There is, as a result, limited value in giving a detailed review of the simulators here. For many simulators it is not even clear how the impact of hydrate formation and dissociation on flow properties are handled. Interested readers are therefore advised to study the NETL code comparison study and eventually send requests towards the different code developers for more details.

The main purpose of this manuscript is to describe an alternative strategy which allows for non-equilibrium modelling and a convenient platform for that. Since this work is directed towards development of a 3D reservoir simulator, it is not our intention to discuss published work on more limited studies, in fewer dimensions and/or very limited model systems. Some examples can be found in the reference lists (Holder and Angert, 1982; Burshears et al., 1986; Yousif et al., 1991; Xu and Ruppel, 1999; Swinkels and Drenth, 2000; Davie and Buffett, 2001; Goel et al., 2001; Hong et al., 2003; Hong and Pooladi-Darvish, 2005; Ahmadi et al., 2004; Nazridoust and Ahmadi, 2007; Liu et al., 2008; Sun and Mohanty, 2006; Uddin et al., 2008; Phirani and Mohanty, 2010; Gamwo and Liu, 2010; Kvamme et al., 2011; Jemai et al., 2014).

From the NETL code comparison study and the few open publications available on results from different simulators it is clear that the hydrate dissociation process in the reservoir is mostly treated as an equilibrium reaction and in fewer cases as kinetics. The majority of kinetic approaches are based on the kinetic model of Kim and Bishnoi (Kim et al., 1987). This is a fairly simple kinetic model in which the molar kinetic rate of hydrate formation is proportional to the difference fugacity of guest at actual condition and at equilibrium. The model has been parameterized by fitting experimental data from kinetic experiments using a laboratory scale PVT cell. The simplicity of the model, as well as the experimental set-up raises questions on transferability to hydrate kinetics in porous media. Pressure reduction as a production method will be highly affected by heat transport limitations and in some simulators kinetic limitations due to heat transport are used to describe associated phase transition kinetics. As will be discussed in more detail in Section 2 below, hydrates in nature are unable to reach thermodynamic equilibrium. An important distinction in this work is that we apply a reactive transport simulator that opens up for describing all competing phase transitions as pseudo solid/fluid reactions of dissociation and formation in its advanced form. Another distinction is that we apply advanced theoretical concepts on multiple scales (quantum mechanics, molecular modelling and statistical mechanics) to develop kinetic models for the different phase transitions.

Based on this approach a new reservoir hydrate simulator which is developed on a former reactive transport reservoir simulator namely RetrasoCodeBright (RCB) will be introduced (Saaltink et al., 2004). The module is designed so that it can easily work according to the non-equilibrium thermodynamic package which is being developed in this group. The choice of this particular package as platform among other reactive transport simulators is the implicit geo mechanical analysis which avoids time step differences involved in explicit couplings to geo mechanical software.

2. Theory

To the best of our knowledge, the hydrate reservoir simulator presented in this paper is the first non-equilibrium simulator that incorporates a free energy analysis and kinetic models of competing phase transitions based on the state-of-the-art theoretical modelling (Kvamme et al., 2012, 2013a and references therein). For this reason, and unlike all other hydrate reservoir simulator platforms, it is based on a reactive transport simulator. Note that this work is progressing and not all possible routes to hydrate formation and dissociation as discussed in Section 1.2 are implemented yet. The most important routes should be implemented by middle of 2014. At this stage we are therefore not able to compare and evaluate the relative impact of the different possible contributions. There is not even a general answer to this since the relative impact will vary with different stages of production – from the initial stimulation towards stationary production and to the final stages of decay of production. Another important distinction from other platforms, as mentioned above, is the use of advanced theoretical concepts for studies of different mechanisms and corresponding rates for kinetics of hydrate formation and dissociation. Details of these theoretical concepts are not given here but some references to published papers on representative results are given in Section 2.2.

2.1. Non-equilibrium thermodynamics

In addition to water and hydrate former phase(s) both mineral surfaces and hydrate surfaces have structural impact on surrounding phases and give rise to adsorbed phases that affects hydrate formation and dissociation. Partial charges on the mineral surfaces are incompatible with partial charges on hydrate surface (Kvamme et al., 2009, 2012; Svandal et al., 2006a, 2006b; Kvamme and Kuznetsova, 2010; Van Cuong et al., 2012a, 2012b). This implies that hydrate never can attach mineral surfaces. On the contrary, mineral surfaces can also adsorb hydrate formers and give rise to favourable heterogeneous hydrate nucleation close to mineral surfaces. Distribution of available mass under equilibrium constraint gives the number of variables which must be specified for a system to be able to reach equilibrium. This degree of freedom boils down to the number of components that participate in the phase transitions minus number of phases plus two (Gibbs phase