Energy Conversion and Management 68 (2013) 313–323

Contents lists available at SciVerse ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Simulations of long term methane hydrate dissociation by pressure reduction using an extended RetrasoCodeBright simulator

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ARTICLE INFO

Article history:
Received 14 May 2012
Received in revised form 26 August 2012
Accepted 3 September 2012
Available online 12 October 2012

Keywords:
Methane hydrates
RetrasoCodeBright
Hydrate dissociation
Depressurization
Gas production

ABSTRACT

Methane hydrates in sediments are generally not in thermodynamic equilibrium. This implies that there may be several competing hydrate phase transitions in naturally existing hydrate reservoirs. In addition to dissociation due to instability imposed by changes in temperature and/or pressure which can bring hydrate outside stability also gradients in chemical potential caused by concentration gradients may lead to dissociation or formation of hydrate. Mineral surfaces bring additional thermodynamic phases of impact for hydrate phase transitions. 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. In cases where kinetic description is used it is normally based on oversimplified models, typically models derived from experiments in pressure, temperature volume controlled laboratory cells. In the case of hydrate production through pressure reduction heat transport might dominate the kinetics and simplified heat transport kinetic models are frequently in use for this purpose. In lack of reliable data from full scale hydrate production the reservoir simulators are the only tools which can be used to evaluate efficiency of different production scenarios. Several research groups have been recently working on this subject. The approaches for inclusion of hydrates as a phase, and corresponding production simulation results from different simulators vary. In this work we have applied a fundamentally different approach, in which we have reworked a reactive transport reservoir simulator, namely RetrasoCodeBright into a hydrate simulator. This has been accomplished by adding hydrates as pseudo-mineral components. This opens up for non equilibrium thermodynamic description since kinetic models for different competing hydrate phase transitions can be included through their respective kinetic models. The main theoretical tool for generating these kinetic models has been phase field theory simulations, with thermodynamic properties derived from molecular modeling. The detailed results from these types of simulations provide information on the relative impact of mass transport, heat transport and thermodynamics of the phase transition, which enable qualified simplifications for implementation into RetrasoCodeBright. Details of the simulator, and numerical algorithms, are discussed in detail and some relevant examples are shown. In particular we applied the reservoir simulator to data from Mount Elbert methane hydrate deposits from North Slope, Alaska. Pressure reduction is used as gas production method.

1. Introduction

1.1. Background

Amount of natural gas present in the form of gas hydrates is enormous. According to some estimates natural gas hydrates are the largest source of natural gas on earth. Its distribution throughout the world and huge quantity of natural gas trapped in hydrates has resulted in a rapidly increasing interest in hydrate energy [1]. Natural gas hydrate (NGH) is an ice like structure in which water enclathrates small non-polar, and slightly polar, molecules. The main component of natural gas is methane and most sources have biogenic origin. Hydrates from thermogenic sources are characterized by the addition of significant amounts of ethane and propane. The two dominating structures for NGH are named structure I (sI) and structure II (sII). Among these types sI is the most common in natural gas hydrate occurrences since biogenic sources of methane dominate. Maximum amount of methane that can occur in a sI methane hydrate is fixed by the clathrate geometry at $CH_4{\cdot}XH_2O$ where X is less than 5.75 since complete filling of all cavities is impossible to achieve. NGH is found mainly in offshore outer continental margin sediments and in Polar Regions commonly associated with permafrost [2]. NGH is not stable in porous media as a consequence of Gibbs phase rule. The system of fluid/hydrate/mineral is over determined and several phases compete for the

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http://dx.doi.org/10.1016/j.enconman.2012.09.003

Nomenclature

F	degree of freedom (–)
n	number of components (–)
π	number of phases (–)
ΔG_i	Gibbs free energy change (kJ)
H	hydrate phase (–)
x	compositions (mol)
μ	chemical potential (kJ/mol)
w	water (–)
σ_0	surface tension at temperature in which P_0 has been measured (0.072 Nm^{-1})
S_{rl}	residual saturation (0)
S_{rg}	residual saturation (0)
ω_1^h	mass of solute per mass of liquid (–)
$\sigma_i j'$	effective stress (MPa)
P'	pore pressure (MPa)
V_m	molar volume of a mineral (m^3/mol)
φ_0	reference porosity (–)
λ	shape function for retention curve (0.457 m)
S_l	liquid saturation (–)
S_g	gas saturation (–)
P_e	CH_4 hydrate equilibrium pressure (MPa)
A	constant [1]
P_0	measured P at certain temperature (0.0196 MPa)
k_0	intrinsic permeability corresponding to φ_0 (–)
S_{ls}	maximum saturation for liquid phase [1]
S_{gs}	maximum saturation for gas phase [1]
M_i	molecular weight (g/mol)
σ_{ij}	total stress (MPa)
δ_{ij}	Kronecker symbol ($\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$) (–)

available mass according to progress towards minimum free energy locally. A typical pitfall in analyses of hydrate stability regions is the unconditional use of the pressure, temperature projection of the phase diagram to construction of hydrate stability regions in reservoir, regardless of flow which my dissociate the hydrate in concentration gradients [3].

1.2. Methane production from natural gas hydrate reservoirs: methods and theoretical studies

There are several methods for methane production from natural gas hydrate reservoirs. Depressurization method, in which the pressure is reduced to outside the pressure/temperature stability region for hydrate, is attractive due to the limited associated costs of exploitation. Efficiency varies, depending on a number of different factors like for instance the filling of underlying regions (gas, water, soft clay or shale) and heat transport characteristics of the surroundings. It is currently considered as the most feasible process considering expenses and production rate and has been investigated by many research groups through experiments and simulation studies. Thermal stimulation is another method which has been extensively investigated. Injection of steam or hot water brings the hydrate outside stability region and also supports heat for hydrate dissociation. It is considered to be costly due to huge amount of energy waste to the surroundings. A third method is to use chemicals like for instance thermodynamic hydrate inhibitors, such as methanol or brine, to shift the equilibrium curve and dissociate hydrate. This is a costly option and is hardly considered as a standalone production option. Yet another and more recent novel method is injection of CO_2 into the methane hydrate reservoirs. CO_2-hydrate is more stable than CH_4-hydrate over large regions of temperature and pressure. Mixed CO_2/CH_4 hydrate, in which CH_4 remains trapped in small cavities after conversion, is more stable than either one of the pure hydrates for all pressures and temperatures. Direct conversion of CH_4 hydrate into a mixed CO_2/CH_4 hydrate through CO_2 injection is feasible but a slow solid state conversion. Parallel to this new CO_2-hydrate formation will be formed from the pore water and injected CO_2. The released head from this formation will provide the necessary heat to dissociate in situ methane hydrate. Both mechanisms lead to a win–win situation of combined natural gas production method and CO_2 sequestration [4].

During more than two decades several research teams worldwide have conducted theoretical studies of methane production from hydrate reservoirs through modeling on different scales, including development of hydrate reservoir simulators [5–12]. As a result there are both academic and commercial hydrate simulators available although there are still many uncertainties and questionable approximations in the present generation of simulators. It is beyond the scope of this paper to give a detailed review of these simulators as this is already available through an ongoing code comparison study under the NETL program for methane hydrates [13]. The web-page for this code comparison study is continuously updated and has necessary links to publications on results as well as descriptions of the different simulators. So instead of repeating reviews of these different simulators in this paper we put emphasis on describing an alternative and fundamentally different way of handling the hydrate phases and corresponding phase transition dynamics involved in production modeling.

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. This simulator is developed on the RetrasoCodeBright (RCB) [14] reactive transport reservoir simulator platform. An important advantage of this simulator is that the hydrate can be treated as pseudo minerals. This opens up for a transparent implementation of non-equilibrium thermodynamics as competing phase transitions will enter the mass- and energy-balances in a similar fashion as competing reactions of mineral precipitations and mineral dissolutions. 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 theory simulations are used to examine the performance of the module through example cases as mentioned above.

1.3. Theory

Common to all current hydrate exploitation simulators is the limitations in thermodynamic description and oversimplified kinetic models. Hydrates in a porous media are generally exposed to at least surrounding aqueous phase and mineral surfaces but also sometimes free gas phase. In the simplest case of pure methane as hydrate former there are only two components and three (or four if free gas is present) phases (aqueous, hydrate, adsorbed). This leaves only one degree of freedom according to Gibbs phase rule and equilibrium cannot be established since both pressure and temperature is defined by hydrodynamics and geothermal gradients.

$$F = n - \pi + 2 \tag{1}$$