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Numerical Predictions of Experimentally Observed Methane Hydrate Dissociation and Reformation in Sandstone

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S *Supporting Information*

ABSTRACT: Numerical tools are essential for the prediction and evaluation of conventional hydrocarbon reservoir performance. Gas hydrates represent a vast natural resource with a significant energy potential. The numerical codes/tools describing processes involved during the dissociation (induced by several methods) for gas production from hydrates are powerful, but they need validation by comparison to empirical data to instill confidence in their predictions. In this study, we successfully reproduce experimental data of hydrate dissociation using the TOUGH+HYDRATE (T+H) code. Methane (CH_4) hydrate growth and dissociation in partially water- and gas-saturated Bentheim sandstone were spatially resolved using Magnetic Resonance Imaging (MRI), which allows the in situ monitoring of saturation and phase transitions. All the CH_4 that had been initially converted to gas hydrate was recovered during depressurization. The physical system was reproduced numerically, using both a simplified 2D model and a 3D grid involving complex Voronoi elements. We modeled dissociation using both the equilibrium and the kinetic reaction options in T+H, and we used a range of kinetic parameters for sensitivity analysis and curve fitting. We successfully reproduced the experimental results, which confirmed the empirical data that demonstrated that heat transport was the limiting factor during dissociation. Dissociation was more sensitive to kinetic parameters than anticipated, which indicates that kinetic limitations may be important in short-term core studies and a necessity in such simulations. This is the first time T+H has been used to predict empirical nonmonotonic dissociation behavior, where hydrate dissociation and reformation occurred as parallel events.

■ INTRODUCTION

Gas hydrate is a solid state of special gases (capable of forming hydrates) and water, in which hydrogen bonding and van der Waals interaction forces provide stability to the crystal structure. Of the various hydrate-forming gases in natural hydrates, methane (CH_4) is overwhelmingly the most common. The CH_4-hydrate stability is governed by pressure and temperature, and its hydration reaction is commonly described by

$$CH_4 + N_H H_2O = CH_4{\cdot}N_H H_2O + \text{heat}$$

where the hydration number N_H is estimated to be 5.99 ± 0.07.[1]

Vast resources are associated with gas hydrates,[2] and depressurization is often considered one of the more promising approaches for hydrate dissociation.[3] Dissociation requires less energy relative to thermal methods but is limited by the endothermic reaction and therefore relies on heat transfer from the surroundings.

Numerical modeling is a valuable tool for conventional oil and gas production. Space and time are discretized into a finite number of subdivisions, where coupled equations describe the physical and chemical conditions of each subdomain. A range of simulation tools are available for hydrate simulation.[4] Several case studies have been performed due to limited field data,[5−10] while others use field specific parameters for evaluation.[11−19] Code verification has been performed through comparison with available production data and open-hole pressure-response tests.[20,11,21,22] A series of studies have also aimed at code-validation through comparison with experimental data.[23−31] This study compares experimental dissociation data with numerical data in order to determine the robustness and advantages of numerical modeling.

T+H[32] is a multicomponent, multiphase fluid and heat flow simulator that describes hydrate formation and dissociation through coupled equations of mass and heat balance. These processes are predicted by an equilibrium and kinetic model. Phase transitions in the equilibrium model are governed by temperature and pressure, where the different phase combinations are described in Figure 1.[7] The kinetic model is described by an Arrhenius-type equation, where kinetic parameters are considered in addition to temperature and pressure. In a study involving several gas hydrate configurations and long-term production, the equilibrium and the kinetic models exhibited a similar dissociation response.[33] In short-term processes (such as laboratory studies of dissociation in core samples that lasted a few hours), the kinetic and the equilibrium models exhibited significantly different behavior, which converged as time advanced. Thus, Kowalsky and Moridis (2007)[33] recommended the use of the kinetic model in short-term processes.

The kinetic model is based on the work of Bishnoi and co-workers[34,35] but was modified to account for geometry

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