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Numerical analysis of experimental studies of methane hydrate formation in a sandy porous medium

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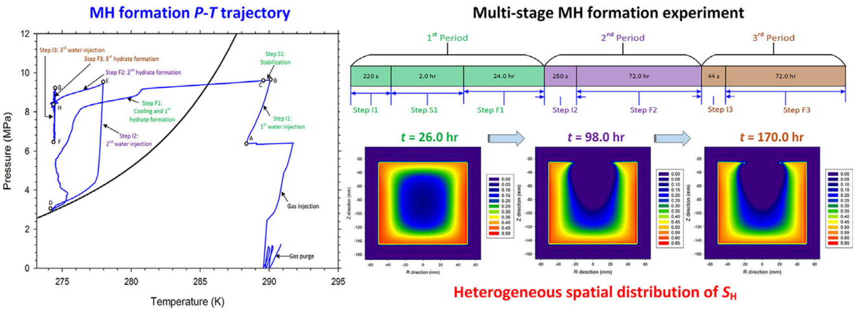
HIGHLIGHTS

- MH formation via excess-water method was numerically analyzed using T + H v1.5.
- MH formation is determined as a kinetic reaction with dominant thermal processes controlling MH formation.
- Flow, thermal, and kinetic rate parameters are optimized using a history-matching technique.
- The spatial distributions of various phases at the end of the MH formation are strongly heterogeneous.

GRAPHICAL ABSTRACT



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ABSTRACT

We analyse numerically an earlier experimental study that involved the formation of methane hydrates by the excess water method in a small reactor filled with a sandy porous medium, and seek to address questions about the type of the hydration reaction and the phase heterogeneity in the resulting hydrate-bearing sand. Using a fine discretization describing the reactor assembly, the experimental process is faithfully replicated numerically. The multi-stage process of hydrate formation is subdivided in 7 steps. The experimental data from the continuously-monitored pressure and temperature during each step are used for comparison against the numerical predictions, the identification of the dominant processes and the determination of the associated parameters through a history-matching process that minimizes deviations between observations and simulation results. The results of this first-ever study on this subject demonstrate unequivocally that the hydration reaction is a kinetic (as opposed to an equilibrium) process, and that the spatial distributions of the various phases (aqueous, gas and hydrate) at the end of the formation process are strongly heterogeneous. This has serious implications in simulation studies of hydrate dissociation that assume uniform initial phase saturation distributions. The history-matching process indicates that (a) the system behaviour is sensitive to some flow parameters (porosity and irreducible water saturation) only during the first water injection, (b) it is insensitive to the sand intrinsic permeability during all steps of the study, and (c) thermal processes dominate after the first water injection, yielding estimates of the thermal properties of the sand and of time-variable key parameters of the kinetic reaction.

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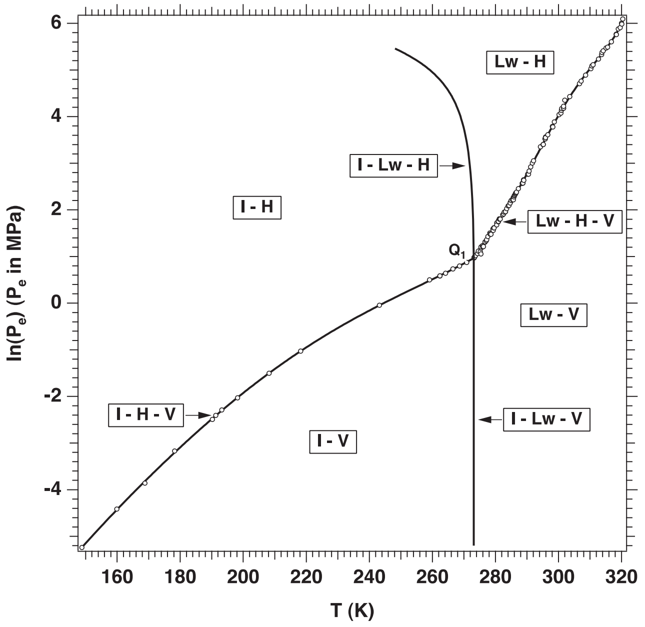

Fig. 1. Pressure-temperature equilibrium relationship in the phase diagram of the $CH_4 + H_2O$ + MH system in T + H showing all possible thermodynamic states [93].

1. Introduction

1.1. Background

Gas hydrates are solid crystalline compounds that consist of water and gas molecules. The water molecules form cage-like crystal lattices (through hydrogen bonds), which encage guest gas molecules that are stabilised by the van der Waal's forces. The typical size of guest gas molecules that can fill the hydrate cages varies between 3.8 and 6.95 Å [1,2]. Common gases in naturally occurring hydrates include hydrocarbon molecules (e.g. CH_4, C_2H_6, C_3H_8), as well as other gases, mainly H_2S, N_2 and CO_2, etc. Depending on the hydrate cavity number, structure and guest molecule size, there are three primary gas hydrate structures: namely, the cubic structure I (sI), the cubic structure II (sII) and the hexagonal structure H (sH) [3]. In general, gas hydrates are stable at suitably low temperatures *T* and high pressures *P*. They are non-flowing crystalline ice-like solids that can store effectively large amounts of gases. For example, 1 volume of methane hydrate (MH) can store 160–180 volumes of CH_4 gas under *STP* [4].

CH_4 is by far (in overwhelming abundance, actually) the most common hydrate-forming gas of naturally occurring hydrates. Pure CH_4 under suitable conditions forms sI type of hydrate as described by the following hydration reaction:

$$CH_4 + N_H H_2O = CH_4{\cdot}N_H H_2O + Q_H \qquad (1)$$

where N_H is the hydration number and typically varies between 5.75 and 6.2 for MH and Q_H is the associated enthalpy (measured to be 54.44 kJ/mol [5]) of the hydrate formation/dissociation reaction. The equilibrium pressure-temperature relationship of the $CH_4 + H_2O$ system is shown in the phase diagram of Fig. 1 [6]. The four main dissociation methods are: (i) depressurization, in which the pressure (*P*) is lowered below the hydrate equilibrium pressure (P_{eq}) at the prevailing temperature (*T*), (ii) thermal stimulation, in which temperature (*T*) is raised above the hydrate equilibrium temperature (T_{eq}) at the prevailing *P*, (iii) the use of chemical inhibitors (salts or alcohols), which shifts the hydrate P_{eq}–T_{eq} equilibrium [2] and (iv) the use of CO_2 (and possibly other gases, such as N_2) to exchange CH_4 in hydrates [7]. It is also possible (and often advisable) to use combinations of the aforementioned production methods [8].

1.2. Hydrates as an energy source

The preponderance of CH_4 in natural gas hydrates and the early realization [5] that these occur in vast amounts raised the issue of exploiting them as an energy source. Thus, there has been a considerable effort to estimate the amount of hydrocarbon gas hydrates resource on a global scale as the necessary first step in their exploitation. The estimates of the total amount of recoverable CH_4 from MH have varied tremendously over the years, ranging from 10^6 trillion cubic meter (TCM) [9] to 10^4 TCM [10–15] to 10^3 TCM [16,17]. These estimates are almost invariably the results of various models that are based on different evaluation criteria, and the uncertainty on the subject is substantial because the number of true physical surveys is very limited and

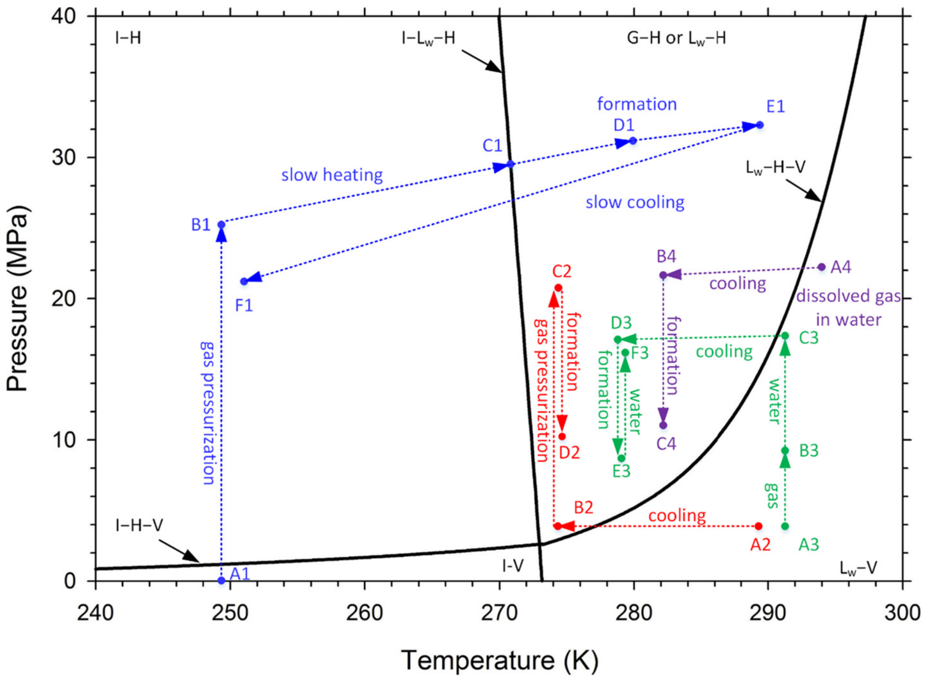

Fig. 2. Schematic *P-T* trajectory during MH formation by various methods in relation to the $CH_4 + H_2O$ + MH phase curve: (i) A1-F1 (in blue) refers to ice-to-hydrate method [57]; (ii) A2-D2 (in red) refers to excess-gas method [59]; (iii) A3-F3 (in green) refers to excess water method [62]; (iv) A4-C4 (in purple) refers to dissolved gas method [67]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)