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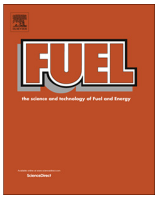

Exploring methane-hydrate formation and dissociation in geologic materials through laboratory experiments: Kinetic behavior and morphology

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HIGHLIGHTS

- A novel apparatus for studying hydrate formation in geologic matrices is presented.
- Kinetics of methane-hydrate formation in sand was investigated.
- Influence of methane injection rate was studied.
- Repeated experiments at constant methane injection flow rate showed different formation patterns.
- Morphology of hydrates in sand–clay mixtures changes with the proportion of clay.

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ABSTRACT

To gain in-depth understanding of natural gas hydrate behavior it is necessary to identify key parameters that affect their formation, distribution and destabilization within sediments. Hydrate formation kinetics in porous media is amongst the aspects which deserve important considerations as it may provide useful information on the formation history and the formation mechanisms of natural gas hydrate accumulations. Yet, it is at its early stage.

In this paper, experiments on methane hydrate formation and dissociation in porous media are reported and discussed. The first part of this work is devoted to the investigation of the kinetics of methane hydrate formation within silica sand using a custom-design apparatus. The latter is suitable for investigating small hydrate-bearing cores. The influence of the methane injection flow-rate is examined, and then a straightforward method is proposed to quantify the amount of hydrate-bound gas. In the second part, three mixtures of clays and sand are used as geologic matrix to study the influence of clay content on the hydrate morphology for a predetermined amount of injected water. Visual observations showed that the morphology shifts from disseminated through massive to moussy hydrates with increasing proportion of clays.

1. Introduction

Natural gas hydrates are crystalline compounds resulting from the enclathration of small molecules, primarily methane, into a water lattice [1–4]. They are found in marine sediments of continental margins and in the permafrost regions [2,5,6], and represent one of the major organic carbon reserves on earth [5,7].

Currently, natural gas-hydrate accumulations are regarded as a double-edged sword: while they are considered as both a potential energy resource [8–13] and huge carbon dioxide-storage reservoirs [14–20], they are also defined as a geohazard [21–25] and often presented as a potential climate-change contributor [26–32]. This makes its study a timely topic as reflected by the increasing number of related articles available from scientific reviews. In fact, the scientifically established literature offers a very broad spectrum of natural gas-hydrate study ranging from field investigations through laboratory experiments to modeling, and from the microscale to the macroscale level (see Sloan and Koh [4], Waite et al. [33] and references herein).

The kinetics of natural gas-hydrate formation within geologic materials is perhaps one of the less studied aspects related to their occurrence in nature. By definition, it deals with the nucleation mechanism and the incipient hydrate-formation time, the

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distribution points of these nuclei and the rate at which hydrates grow within the sediment. Thus, kinetics may provide useful information on the formation history and the formation mechanisms of natural gas-hydrate accumulations. Recently, Sultan et al. [34] have experienced the release of a huge amount of free gas from a gas hydrate-bearing sedimentary interval during the drilling of a giant pockmark in the Gulf of Guinea. They argued that such a coexistence of free gas and gas hydrates is indicative of a deposit where hydrates grow at a rate high enough to trap free gas in between the crystals. In a previous work, Torres et al. [35] proposed the same interpretation to constrain the coexistence of free gas, gas hydrates and chloride-enriched pore fluids at the southern summit of Hydrate Ridge. These two examples illustrate well the influence of the kinetics of formation on the hydrate deposit characteristics. However, when focusing only on the kinetics of hydrate formation in porous media where methane is the guest molecule, one can quickly realize that the available literature is very limited. In a state-of-art review on gas hydrate research, Changyu et al. [36] highlighted the difficulties of investigating hydrate formation kinetics in porous media through laboratory experiments. Those difficulties are mainly related to the control of heat and mass transfers within the porous medium as mentioned by Sun and Mohanty [37]. Accordingly, hydrate-formation kinetics has to be investigated with great prudence due to the implication of many specific factors like the gas transport process, the nature of the geologic matrix, the gas flux intensity when free gas is involved, the pore fluid chemistry, the degree of supersaturation and subcooling which are likely to impinge it [36,38–46]. This makes the evaluation of the relevance of each specific factor very difficult. Hence, well-designed experiments where only one or very few parameters vary whereas the others are kept constant are often required to achieve this goal.

The kinetics of formation may also influence hydrate morphology. The latter is a foundational topic when studying hydrate occurrence and distribution in nature [47]. Field observations highlight that hydrates occur at two different morphologies depending of the nature of the sediments [33]: disseminated in coarse-grained sediments and massive hydrates as lenses and nodules in fine-grained sediments. While disseminated hydrates result from pore-filling, load-bearing or cementing habit, only the latter two lead to massive hydrates. The last recent years, investigators have made a lot of efforts to develop experimental systems to mimic natural gas-hydrate formation in order to either observe or infer the resulting morphology. Laboratory experiments of hydrate formation in coarse-grained sediments from dissolved gas are very time-consuming and often lead to low hydrate saturation levels. Such a formation method leads to pore-filling habit because of the excess water configuration usually applied [33]. However, Spangenberg et al. [48] achieved a saturation level as high as 95% after 55 days of continuous experiment of hydrate formation from dissolved methane in glass bead samples. Priest et al. [49] claimed that with hydrate saturation above 40% the habit changes from pore-filling to frame-building (i.e. load-bearing or cementing hydrates). From a macroscopic point of view the hydrates would appear as disseminated due to the coarse-grained matrix. When the geologic matrix is partially or fully saturated with water prior to free-methane injection, frame-building habit prevails, leading to load-bearing or cementing hydrates [33,49]. Tohidi et al. [45] and Madden et al. [42] have observed the formation of massive hydrates preferentially in areas favorable for gas accumulations. Su et al. [50] drew similar conclusions from experiments performed in a three-dimensional simulation device to investigate hydrate formation and distribution in porous medium. Both experimental results are in agreement with observations reported from natural hydrate settings where massive gas hydrates are found in faulted and fractured sedimentary structures conducive to free-gas accumulation [35,51,52].

This paper reports experimental results from the kinetics of methane hydrate formation in silica sand and the resulting hydrate morphology from their growth in mixtures of sand and clays. Hydrate dissociation pattern is also discussed, together with the quantification of the hydrate-bound methane.

2. Experimental study

2.1. Apparatus

2.1.1. Conception strategy

In nature, the hydrate forming gas is either generated *in situ* or migrates upwards from deeper sources. Therefore, the required apparatus has to be able to simulate natural gas transport processes. It should also allow the study of all aforementioned specific factors influencing the hydrate formation kinetics in a reliable way, through experiments where sediment composition is well controlled and the amount of gas bound within the hydrates fairly estimated. This approach would for instance enable us to identify the critical clay composition for which hydrate morphology moves from disseminate to massive specimens for a matrix made up with sand and clays. Furthermore, it should be possible to retrieve the newly created hydrate-bearing core in a quick and easy way from the high-pressure vessel in order to appreciate both the morphology and the distribution of hydrates from naked eyes without too much disturbance due to depressurization; as it is usually done for cores recovered from natural hydrate settings. This apparatus should also allow the simulation of different hydrate production methods in order to investigate on the system's response to physical and chemical perturbations. Accordingly, it should be versatile enough to be implemented with various (1) analytical instruments such as chromatograph-connected high-pressure sampler to monitor the chemical evolution of both pore fluid and produced gas, (2) sensors such as thermal probe and well-acting tubing to investigate the effects of thermal perturbation or chemical injection on hydrate accumulations.

2.1.2. Description

Following the criteria mentioned above, the apparatus has been designed to create hydrate-bearing cores of 170 mm length and 60 mm diameter from a wide variety of sediments (from pure sand to clay-rich sediments) at most of temperature and pressure conditions encountered in nature. Fig. 1 shows a schematic diagram of the set-up. The heart of the latter is a 316-L stainless-steel high-pressure vessel of ~500 mL from TOP-Industrie (F-77013 Vaux Le Penil, France). It can be operated at pressures up to 22 MPa and for temperatures ranging from 253 to 373 K. It has been mounted vertically to better simulate fluid migration into a sedimentary column. Two flanges, one located at the top and the second one at bottom, ensure for the sealing of the system by mean of a PTFE gasket. Both flanges have five high-pressure fluid ports: four equally distributed over a circle located at the periphery of the vessel chamber for the connection of 1/8″ tubing, and one for the connection of 9/16″ tubing at the center (Fig. 1). The vessel is housed in a thermal jacket and connected to a cooling/heating circulator bath Ministat 230 from Huber capable of thermal regulation between 230 and 473 K, with a claimed temperature stability of 0.02 K. Temperature and pressure are measured with a 150 mm length DMESA thermocouple *K* located at the top of the vessel and a type P-31 pressure transducer from Wika located at the bottom, respectively. Both are connected to a 6100E paperless graphic recorder from Eurotherm for continuous data logging. The uncertainties were less than ±0.2 K and 0.02 MPa for the measurements of temperature