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Research Article

Major factors influencing the generation of natural gas hydrate in porous media☆

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Abstract

Current researches related to natural gas hydrate mainly focus on its physical and chemical properties, as well as the approaches to the production (decomposition) of hydrate. Physical modeling of the flow process in hydrate deposits is critical to the study on the exploitation or decomposition of hydrate. However, investigation of the dynamic hydrate process by virtue of porous media like sand-packed tubes which are widely used in petroleum production research is rarely reported in literature. In this paper, physical simulation of methane hydrate generation process was conducted using river sand-packed tubes in the core displacement apparatus. During the simulation, the influences of parameters such as reservoir temperature, methane pressure and reservoir model properties on the process of hydrate generation were investigated. The following results are revealed. First, the use of ice-melted water as the immobile water in the reservoir model can significantly enhance the rate of methane hydrate generation. Second, the process driving force in porous media (i.e., extents to which the experimental pressure or temperature deviating those corresponding to the hydrate phase equilibrium) plays a key role in the generation of methane hydrate. Third, the induction period of methane hydrate generation almost does not change with temperature or pressure when the methane pressure is above 1.4 folds of the hydrate phase equilibrium pressure or the laboratory temperature is lower than the phase equilibrium temperature by 3 °C or more. Fourth, the parameters such as permeability, water saturation and wettability don't have much influence on the generation of methane hydrate.

Keywords: Methane hydrate; Porous media; Formation process; Gas hydrate deposits; Physical modeling; Factor; Induction period; Ratio of formation

1. Introduction

Current researches related to natural gas hydrate mainly focus on its physical and chemical properties, as well as the approaches to the production (decomposition) of hydrate [1−5]. The common experimental method in studying hydrate formation-decomposition is to directly utilize a autoclave to form massive hydrate [6,7], or to put some sands, quartz, core powder or other similar materials in a autoclave to provide a porous media environment [2,8−13]. However, the flow process and kinetic feature of fluid in porous media cannot be simulated only with the autoclave, and the flow process is critical for studying the producing methods of hydrate [5]. In the petroleum industry, the common and mature reservoir models for physical simulation of formation fluid include sand-packed tube and cemented core, etc. [14−16]. Such models are rarely used in studying hydrate [17].

The hydrate formation−decomposition process is affected by pore sizes in porous media. Anderson et al. [18−21] worked a lot on this aspect, and found that the porous media size presents similar inhibition to the hydrate generation

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process to that of the thermodynamic inhibiting agent (inorganic salt). Схаляхо et al. [14,15] studied the influence of hydrate generation on the permeability values of the sand-packed tube and cemented core, and found that the permeability of the porous media decreases as the water converts to methane hydrate. Essentially, hydrate grains are generated within the center of the porous channels, not on the rock surfaces [22].

Pilot experiment results show that the induction period of hydrate generation under similar experimental conditions may be vary in a ten-fold range, and the repeatability of hydrate generation process under a porous media condition is not ideal, thus it is hard to conduct effective physical simulation on methane hydrate formations. It is necessary to improve the synthesis method of methane hydrate in porous media. For accelerating the process of methane hydrate generation, agitation is usually adopted in the reaction kettle. Besides, surfactant is usually added [1], which, however, may affect the wettability of the porous media surface, and air bubbles may be generated when gas flows through the porous media. Therefore, surfactant is not recommended in the reservoir model. Huang Duzi et al. [23] and Li Jinping et al. [6] studied the contribution of temperature vibration and pressure disturbance to the process of hydrate generation in the autoclave.

As a part of the basic studies on the development methods of natural gas hydrate [5], hydrate synthesis methods under laboratory conditions are intended to be improved. In this paper, the authors illustrate why the study on hydrate dynamic process is necessary and how to quickly prepare the reservoir models considering different hydrate content. They intend to (1) find an experimental method that can improve the repeatability of methane hydrate generation process and reduce the induction period in porous media; (2) determine an experimental method that can quickly compose methane hydrate with high conversion rate; and (3) identify the influence of temperature-pressure condition, initial water saturation, permeability and wettability on the methane hydrate generation process under experimental conditions (sand-packed tube) of this study. This study is just exploratory, so it was conducted not relying on specific hydrate deposits conditions, but using river sand-packed tube as the reservoir model.

2. Experiment

2.1. Reservoir model and its preparation

The reservoir model used in this study is a sand-packed tube in Ref. [5]. The packed media include river sands with quartz and clay minerals, with similar components to natural hydrate formations [9,10,18]. The sand-packed tube is a stainless steel tube with its ends sealed and threads on inner wall (to prevent fluid slippage along the inner wall), 3 cm in ID, and 19.5 cm and 34.5 cm in length respectively. The preparation of the reservoir model is described in Ref. [5], with properties shown in Table 1.

2.2. Hydrophobic treatment

Before the sand-packed tube was prepared in No. 13 experiment, the sands were hydrophobized with fuel oil (M100) weighted at the ratio of 1 g oil and 100 g sands. Then, it was heated and dissolved in a small amount of petroleum ether (with boiling point ≤70 °C). After that, it was blended with sands and stirred. The solvent was evaporated by using a rotating evaporation device; the sands were scattered on filter paper to remove the residual oil, and finally dried at 90 °C.

2.3. Experimental apparatus and reagents

The major experimental apparatus is the automatic core flooding system УИК-5. Its structure is provided in Ref. [5]. A high-pressure piston intermediate container was used to store methane. The reagents are methane (with purity of 99.99%) and fresh distilled water.

2.4. Experimental steps

1) Purge and fill the reservoir model with methane gas at room temperature in order to remove the air in it.
2) Cool the reservoir model and generate methane hydrate. The whole process was controlled at constant pressure, during which methane was injected continuously to timely supplement the consumption during hydrate generation.

Table 1
Parameters of the reservoir model of a sand-packed tube.

Experiment No.	Gas permeability/D	Initial water saturation	Pore volume/mL	The tube length/cm
22/2	2.060	65.6%	79.0	34.5
22/3	2.060	58.5%	79.0	34.5
33	1.140	60.1%	82.6	34.5
9/3	0.334	28.6%	40.5	19.5
9/2	0.334	48.9%	40.5	19.5
9/1	0.334	62.0%	40.5	19.5
13[a]	1.400	33.0%	59.2	19.5
10	1.400	34.8%	44.0	19.5
14	2.050	32.2%	45.5	19.5

Note.
[a] The porous media is hydrophobic.

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