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Full Length Article

Kinetics of methane gas hydrate formation with microscale sand in an autoclave with windows

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ABSTRACT

During the exploitation of subsea natural gas hydrate (NGH) deposits, the muddy silt from marine sediment is carried by the fluid inside the wellbore. Furthermore, NGH is readily formed inside the wellbore when the fluid is in a hydrate formation area. Once NGH has formed inside the wellbore, the exploitation operation will be hindered, or shut down, due to the blockage. Understanding the kinetic characteristics and morphology of NGH formation is important to prevent its occurrence. To this end, a high-pressure autoclave system was designed and constructed in this work. Experiments were conducted to determine the mechanism of sand aggregation, the effect of sand on the kinetic characteristics and the morphology of hydrate formation. Additionally, models of hydrate particle formation with sand and sand aggregation, and structure of wall-attached hydrate layer growth were proposed. The results showed that sand could promote the growth of hydrate and the wall-attached hydrate layer. Additionally, it was observed that hydrate particles were formed with and without sand, and that the wall-attached hydrate layer presented a sandwich structure. The rolling and colliding implantations of hydrate particles were also observed experimentally. Sand aggregation was caused by hydrate particle implantation and the carrying sand effect. Hydrate particle formation with sand can be divided into four stages: nucleation, surface growth, shell formation, and shell growth. The sand aggregation process can also be divided into four stages: hydrate film formation, rupture of hydrate film, particle aggregation, and hydrate layer sintering. For structure of wall-attached hydrate layer growth, the growth front of the hydrate layer was concave-upward.

1. Introduction

Natural gas hydrates (NGH) are nonstoichiometric crystalline cage compounds composed of water and small-molecule gases, such as methane, ethane, and carbon dioxide [1]. At conditions of high pressure and low temperature, the exploration of subsea oil and gas resources is adversely affected by hydrate plugging. Therefore, determining the kinetic characteristics of NGH is important for flow assurance in deepwater oil and gas pipelines [2–7].

The formation mechanism of hydrate particles in oil-water systems has been determined previously. A hydrate crystal nucleus is formed on the surface of a water droplet. Then, the hydrate shell is formed along the water droplet surface until the water droplet is eventually completely converted into a hydrate particle [8,9]. In conditions of high and medium water content, the shell was shown to grow outward. Conversely, in conditions of low water content, the shell was found to grow inward [10]. The process of hydrate film formation on a gas-liquid interface was divided into three stages: loose and thin hydrate film formation, hydrate film growth to the interior of the liquid phase, and the formation of dense hydrate film [11]. This process has also been observed using computed tomography [12]. The hydrate plugging process in gas dominated systems was divided into four stages: hydrate formation, hydrate annulus growth, hydrate sloughing off, and pipe plugging [13], as illustrated in Fig. 1.

The plugging process in oil-dominated systems was also divided into four stages: water entrainment, hydrate shell growth, hydrate particle agglomeration, and pipe plugging [14], as illustrated in Fig. 2.

It was observed that hydrate can form on all oil-water interfaces, and that water can be separated from the oil phase.

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Nomenclature

L	axial thickness of the wall-attached hydrate layer, cm
NGH	natural gas hydrate
$n_{methane}$	consumption of methane gas, mol
P_0	initial pressure of the formation stage, MPa
P_t	pressure of the formation stage at time t, MPa
R	universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
T_0	initial temperature of the formation stage, K
T_t	temperature of the formation stage at time t, K
V_0	volume of the gaseous phase, m^3
$V_{hydrate}$	volume of gas hydrate, m^3
V_{water}	volume of water, m^3
x	horizontal distance between the highest point and the other points of the growth front curve, cm
y	distance between the initial position of hydrate formation and the growth front curve, cm
Z_0	initial compressibility factor of the formation stage
Z_t	compressibility factor of the formation stage at time t
Φ	hydrate volume fraction

Superscript

methane	methane gas
0	initial point of the formation stage, min
t	formation stage at time t, min

In addition, oil can be separated from the water phase after hydrate formation on a continuous oil-water interface [15]. In water dominated systems, the flow regime in the pipe is converted gradually from a homogeneous flow to a heterogeneous flow. Plug flow and a static bed are also formed in the pipe until the pipe is eventually plugged by hydrate [16], as illustrated in Fig. 3.

The transition of flow regime [16] was observed using a high-pressure visual autoclave [17], which showed the proposed plugging mechanism [16] was reasonable.

In conclusion, researchers have mainly focused on the kinetic characteristics of hydrate formation in deepwater oil and gas pipelines. However, during the exploration of hydrate, only sand (>44 μm) can be filtered out, and microscale sand (<44 μm) always flow with the exploiting materials, which can affect the formation of hydrates and blockages in the pipeline. However, the kinetic characteristics of hydrate formation in wellbores with microscale sand have not previously been reported. In the present study, the kinetic characteristics of hydrate formation with microscale sand in an autoclave with windows were investigated.

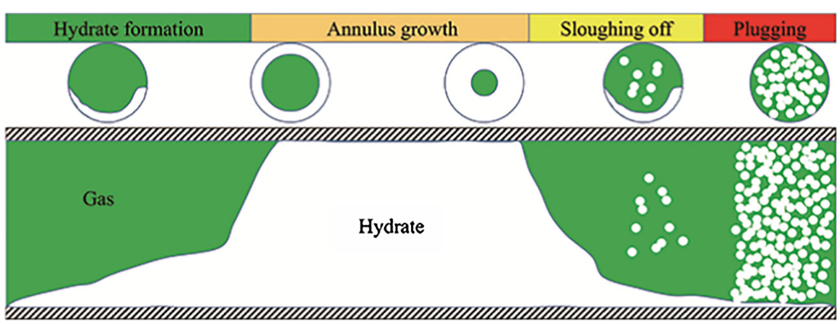

Fig. 1. Schematic illustration of hydrate plugging in gas dominated system, adapted from Sloan [13].

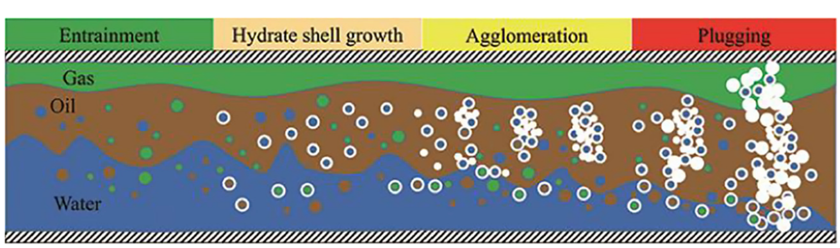

Fig. 2. Schematic illustration of hydrate plugging in oil dominated system, adapted from Turner [14].

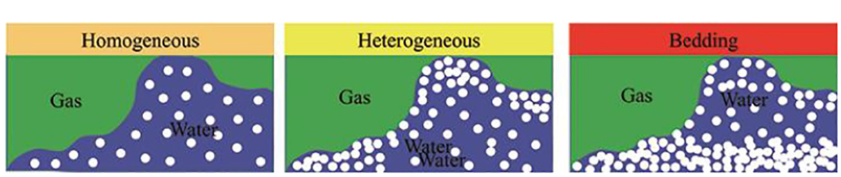

Fig. 3. Schematic illustration of hydrate plugging in water dominated system, adapted from Joshi [16].