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Gas hydrate powder formation – Ultimate solution in natural gas flow assurance

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HIGHLIGHTS

- We demonstrate gas hydrate powder formation for the first time.
- Hydrate volume fraction can be as high as 95% with fluidity features.
- The new anti-agglomerant shows kinetic inhibition effect.
- We propose a mechanism for the formation of hydrate powders.

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ABSTRACT

Gas hydrates may plug hydrocarbon flowlines even at low hydrate volume fraction due to agglomeration. Anti-agglomeration is perhaps the most effective approach for flow assurance. An effective anti-agglomerant (AA) can prevent gas hydrate particles from sticking together by lowering of the water–oil interfacial tension and increase of the contact angle of water on hydrate surface. In a recent work, we have introduced a new AA formulation which is effective; it forms hydrate slurry over a broad range of oil to water ratio. In this study, we introduce a modified chemical formulation effective at extreme conditions when hydrate powders are formed from two different gases. The formation of hydrate powders has not been reported in the literature. The powders flow readily in rocking cells. The hydrate fraction can be as high as 95% with fluidity behavior. The AA effectiveness reported in this study is much higher than the past work. A new anti-agglomeration mechanism is also proposed. The gas hydrate powder formation may have applications not only in flow assurance, but also in energy storage.

1. Introduction

Gas hydrates are ice-like crystalline solids, in which small gas molecules are trapped inside the cages formed by water molecules [1]. The hydrate surface is inherently hydrophilic [2]. A thin layer of liquid water film is present on the hydrate surface [3], which leads to a capillary bridge between hydrate particles [2,4]. The strong capillary force holds the particles together, causing agglomeration and high risks of pipeline blockage in hydrocarbon production. Gas hydrate formation has been a major challenge in flow assurance, especially at high pressure and low temperature typically in seabed conditions [5].

The capillary force (F_C) in the liquid bridge between two hydrate particles depends on water–oil interfacial tension (σ) and contact angle (θ_p) of the capillary liquid on the hydrate surface as described by [5]

$$\frac{F_C}{r} = 2\pi\sigma\cos\theta_p$$

where r is the hydrate particle radius, assuming hydrate particles are spheres. Anti-agglomerants (AAs) reduce the capillary force by lowering the water–oil interfacial tension and increasing contact angle [6–9]. When the capillary force is weaker than the shearing force in the flow, hydrate particles are carried by the liquid as a slurry. In a recent work [10], we have compared few AAs that all reduce the water–oil interfacial tension significantly. However, the performances are very different. The contact angle of water on

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Abbreviations: AA, anti-agglomerant.

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hydrate surface is close to 0 [6]. Adsorption of AA molecules increases contact angle and alters the surface to less water-wetting. The chemical structure and functional groups of AAs determine the binding force onto hydrate particles, which affect the contact angle and AA performance. An effective AA keeps hydrates as slurry in water or in hydrocarbon phase. The hydrate slurry turns into a paste as the hydrate volume fraction increases, as observed in our recent study [10] and the work of others [2,11]. Blockage occurs when the hydrate particles are closely packed, reaching maximum packing fraction. The close-packing of equal-size spheres has a volume fraction of 0.74. The maximum packing fraction in hydrate systems is believed to be 0.6–0.7 [2]. However, plugging could occur at lower hydrate volume fraction in reality [11,12]. When gas hydrates form in a pipeline, the crystalline particles stick together and turn into large aggregates with a fractal structure. They trap the aqueous phase and liquid hydrocarbon phases in the internal pores [1,2]. Effective AAs prevent agglomeration, thus allowing formation of a hydrate slurry. When the hydrate volume fraction is high (e.g., >0.50), no slurry can be formed at the usual hydrophilic conditions. When all the water is converted into hydrates and the liquid condensate or the oil phase is small, no solution to hydrate flow assurance by anti-agglomeration has been discussed in the literature.

Matsumoto et al. have reported slush ice with ice packing factor (IPF) higher than 70% by using silane-couplers and silicone oil [13]. They have added 4% silane-coupler into a mixture of 90% water and 10% silicone oil (volume basis) and cooled the mixture while stirring at 200 rpm. The ice surface is covered by silane-couplers and oil. Capillary bridge formation among ice particles is probably prevented. To the best our knowledge, no hydrate powder formation in flow assurance has been reported. Hydrate powder formation is perhaps the only solution with AA at the conditions that all the water is converted to hydrates and the amount of the condensate liquid or the oil phase is small.

There are three types of instruments for hydrate formation and inhibition tests: rocking cells, autoclaves and flow loops [14]. Flow loops are closest to field conditions. However, they require large amount of fluids and gases; the requirement limits their applications. Autoclaves are temperature-controlled steel cell with stirring. They usually require several hundred milliliters of fluids for each test. High pressure rocking cells use small sapphire cells as reactors, which normally require no more than 50 milliliters per test. A stainless steel ball in the cylindrical cell provides agitation during rocking. Clear sapphire tubes allow direct visual observations during tests. Rocking cells are considered a conservative test because of the low shearing force during rocking compared to the other two methods. We employ rocking cells due to simplicity and the ability for visual observation.

In this work, we report the formation of hydrate powders from two different gases and our new AA formulation at a hydrate volume fraction as high as 0.95. We also suggest a new mechanism for the hydrate powder formation.

2. Material and methods

A rocking cell instrument is used for gas hydrate tests as described in our recent work [10,15]. A schematic diagram and image of the setup is shown in Fig. S1 of the Supplementary Information. The cells are closed during rocking. In all tests, water content is low, 2 or 3 mL H_2O along with 0.02–2 mL *n*-octane. The fluids are loaded in the 20-mL sapphire cells. All the water converts to gas hydrates in the cell. Two difference gases are used as hydrate formers: a mixture of methane and propane (Gas 1), and a natural gas (Gas 2) containing 81.0% methane, 8.3% ethane, 4.8% propane, 2.4% CO_2 and 3.5% other species (by mol). For Gas 1, the cell is charged with propane first to the initial watercut before being charged with methane to a desired initial pressure. The rocking frequency is set to 15 times/min. The bath temperature, pressure and ball running time during rocking are recorded. At the start after charging the cells with test mixtures, they are rocked at 20 °C (24, or 28 °C) for half an hour to reach equilibrium. This is set as the initial condition of the closed cell test. Then the water bath is cooled from room temperature to 2 °C for Gas 1 (4 °C for Gas 2) at rate of either −2 °C/h or −10 °C/h, while the cells are being rocked. They are then kept at 2 °C for Gas 1 (4 °C for Gas 2) for a period of time allowing the gas hydrates to fully develop before the temperature ramps back to the initial temperature. Sharp pressure changes indicate hydrate formation/dissociation. A long ball running time implies high viscosity in the cell. The steel ball stops running when hydrate plugging occurs. The effectiveness is evaluated by visual observations and by ball running time. It should be noted that all the water turns into gas hydrates in our tests at the low testing temperature.

The hydrate tests for Gas 1 are listed in Table 1. Under test conditions, the sII hydrate forms. Our AA (from Lubrizol Corporation) contains 80–89% cocamidopropyl dimethylamine (as the effective component), 5–10% glycerin, small amount of free amine and water. AA dosage is 0.5 wt% in water in all tests. The initial pressure varies from 40 to 100 bar. After charging the cells with gas, the initial watercut is estimated to be in the range of 25–66% by considering the formation of liquid condensate. The hydrate volume fraction at 2 °C is higher because some of the condensate species become part of the hydrates; the hydrate density is less than water density.

3. Results and discussion

3.1. Gas hydrates from Gas 1

In all the tests, our AA shows both anti-agglomeration and kinetic inhibiting effects during hydrate formation. The mixture in the cells flows in the form of hydrate slurry, or hydrate powders when the hydrate volume fraction is high. The hydrate dissociation temperatures are above 15 °C, indicating a large subcooling since the testing temperature is low at 2 °C. The low hydrate formation temperatures at high pressure in all the tests demonstrate the kinetic effect. Let us describe Test 12 in Table 1 in which the initial mixture consists of 2 mL of water at 0.5 wt% concentration of AA, 0.02 mL *n*-octane and 1 mL propane liquid. This gives approximate initial watercut (water volume% in total liquid) of 66%. The initial pressure is 100 bar at 28 °C. Hydrate starts to form at 18.8 °C and 93.7 bar indicated by the sudden pressure drop during cooling, shown in Fig. 1. The pressure drops to 78 bar at 2 °C, 17 °C below the hydrate formation temperature. There is no decrease of pressure at 2 °C which indicates no further hydrate formation. All the water is converted into hydrates at this condition. The ball running time is low throughout the test (red[1] curve in Fig. 1).

Hydrate powders are observed instead of hydrate slurry in Test 12. Fig. 2 shows that the hydrate powders move along with the stainless steel ball (in blue circle) during rocking. Four pictures are taken in 1 s. There is no free water left in the cell. The hydrate powders are loosely packed. They flow in the cell as shearing force is applied. Hydrate content in the mixture is estimated to be higher than 66%. To the best of our knowledge, this is the first report of anti-agglomeration of hydrates in the form of powders. A microscope picture (Fig. 3) shows most of the hydrate particles are smaller than 5 μm. Upon heating, the hydrates start to dissociate at 23.8 °C and 92.0 bar during warming, which is 5 °C higher than

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[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.