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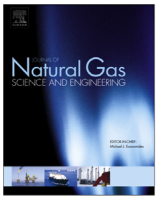

Crystal growth phenomena of $CH_4 + C_3H_8 + CO_2$ ternary gas hydrate systems

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ABSTRACT

Gas hydrates are crystalline solids comprised of a three-dimensional network of water cages that can trap small hydrocarbon molecules at high pressure and low temperature. Formation of gas hydrates can lead to blockages in subsea oil and gas flowlines, where these conditions are readily achieved. As gas reserves mature over time, new CO_2-rich reservoirs can be prolific hydrocarbon producers for markets willing to bear the additional production costs. However, there is a lack of understanding about the formation behavior and growth morphology of CO_2-rich hydrates. In this work, hydrate growth rate and resistance-to-flow (torque) data for a ternary CO_2-rich gas mixture were measured in a high-pressure sapphire autoclave apparatus and were compared with baseline data for a pure methane system. Images of hydrate growth and eventual plug formation were captured for methane hydrate and ternary gas systems, where early hydrate growth in the latter was dominated by an opaque film nucleating at the gas-water-wall interface and growing into both gas and water phases with time. Only 7 vol% methane hydrate was required to increase the motor torque above its baseline value, while at least 20 vol% hydrate was required when formed from the CO_2-rich ternary gas. These new observations provide insight into the effect of guest species solubility on hydrate growth and resistance-to-flow in the resultant slurries, which are key parameters when assessing the risk of hydrate blockage in oil and gas pipelines.

1. Introduction

Gas hydrates are solid inclusion compounds, where a molecular lattice of water molecules surrounds light hydrocarbon species (e.g. methane or carbon dioxide), typically at high pressure and low temperature (Sloan and Koh, 2007). In subsea oil and gas flowlines, the formation of gas hydrates can increase the frictional momentum losses of flow; in the limit of severe hydrate formation, blockages may form and halt flow (Davies et al., 2009). For the past eight decades, the energy industry has used thermodynamic hydrate inhibitors (THIs), which are anti-freeze chemicals such as methanol or monoethylene glycol (Sloan, 2000), to shift the hydrate phase boundary to higher pressure and lower temperature, preventing hydrate from becoming a stable phase in production systems (Kinnari et al., 2015). However, the uncertainty associated with predicting the hydrate phase boundary for complex hydrocarbon gas mixtures can exceed 1 K for many commonly used algorithms (Ballard and Sloan, 2004). When the aqueous phase contains high THI fractions (e.g. 40%), the level of uncertainty in the phase boundary predictions increases further. Recently, Ward et al. (2015). identified similar uncertainty associated with hydrate phase boundary predictions for flowlines containing high fractions of H_2S, which may behave similarly to CO_2 due to the high solubility of both species in the aqueous phase.

Due to either uncertainty in the hydrate phase boundary or malfunction of the THI injection equipment, gas hydrate may form in flowlines containing hydrogen sulfide (H_2S) or carbon dioxide (CO_2). If hydrate does form in the gas or water phases, there is uncertainty as to whether the presence of CO_2 or H_2S may help or hinder the generation of a complete hydrate blockage. The conceptual basis for hydrate blockage formation in systems containing gas and water phases was first proposed by Joshi et al. (2013), and includes three sequential stages shown in Fig. 1: (i) the homogeneous suspension of hydrate particles in the aqueous phase; (ii) the formation of a moving hydrate bed, where hydrate particles are heterogeneously distributed along the radius of the pipeline; and (iii) formation of a stationary hydrate bed, enabling the rapid build-

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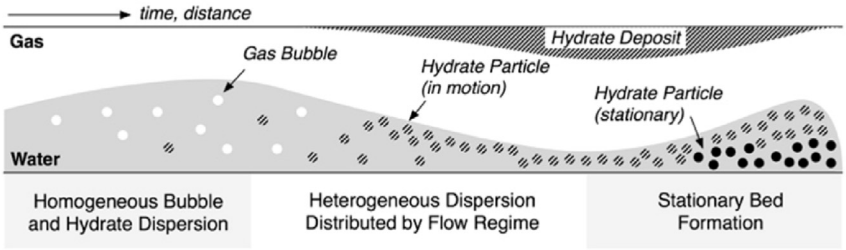

Fig. 1. Conceptual mechanism of hydrate blockage formation in gas-water systems (Joshi et al., 2013), where the hydrate-in-water volume fraction at which the system forms a heterogeneous distribution of hydrate particles was labelled $\Phi_{transition}$; above this volume fraction, hydrate particles may form a moving bed (grey) and, at high volume fractions, result in a stationary deposit (black).

up and collection of hydrate particles. Based on experimental data from a high-pressure recirculating flowloop, Joshi et al. (2013) proposed that the transition from a homogeneous to a heterogeneous particle suspension corresponded to the first measured increase in frictional pressure drop due to hydrate formation; the hydrate-in-water volume fraction at which this transition occurred was denoted $\Phi_{transition}$.

Laboratory studies by Akhfash et al. (2013) and Aman et al. (2015) provided further insight to the nature of $\Phi_{transition}$, which was observed to increase with the degree of mixing in a sapphire autoclave. That is, increasing turbulence allowed the aqueous phase to maintain additional hydrate in a homogeneous suspension; a similar increase in $\Phi_{transition}$ was observed when monoethylene glycol (10 wt%) was added to the aqueous phase. Together with the flowloop results from Joshi et al. (2013), these studies demonstrated an important step needed in the mechanistic description used to predict the onset of hydrate accumulations; this practice is critical to the successful management of hydrate blockages in gas flowlines, especially in the case that the field is operating inside the hydrate stability region (Creek, 2012), or insufficient THI is available to fully prevent hydrate formation (Li et al., 2011; Hemmingsen et al., 2008). To date, estimates of $\Phi_{transition}$ for flowloop and autoclave systems have been empirically correlated with the degree of turbulence in the aqueous phase, but no fundamental basis for this prediction has been established.

In this investigation, we extend the study of $\Phi_{transition}$ to a natural gas containing 40 mol% of CO_2 using a high-pressure sapphire visual autoclave. In addition, this study provides new insight into the effect of CO_2 on the stages of hydrate blockage formation (Fig. 1).

2. Methods and materials

Gas hydrate was formed in a high-pressure sapphire visual autoclave apparatus, described in detail by Akhfash et al. (2013). The apparatus consisted of DB Robinson-type sapphire cell (150 mm length, 38.2 mm outer diameter, 12.8 mm wall thickness), in which fluids were mixed by a vane-and-baffle geometry impeller that was magnetically coupled to a Groschopp direct-drive DC motor capable of providing up to 1750 RPM (Fig. 2); motor speed was monitored by a Dynapar digital tachometer (±17.5 RPM). The motor torque required to maintain constant speed was measured by a ViscoPakt Rheo-57 with 0.04 N·cm resolution. Cell pressure and temperature were measured using an Omegadyne pressure transducer (±0.1 bar) and platinum resistance thermometer (±0.2 K), respectively. The cell was submerged into a glycol bath for temperature control, where heat was continuously removed with a ThermoFisher immersion cooler and heat was intermittently added with a 1100 W cartridge heater; the heater power was controlled by a PID algorithm implemented in LabView, where bath temperature was measured with a second PRT. Visual images of the hydrate cell were captured with a time-lapse camera placed outside the cooling bath, with images collected every 80 s.

Gas hydrate was formed from deionized water and two different gasses: ultra-high purity (99.999%) methane (CH_4) and a ternary gas mixture (55 mol% CH_4, 5 mol% C_3H_8, 40 mol% CO_2, CoreGas Australia). This composition was chosen as a practical upper boundary for oil and gas fields with high CO_2 content, to complement the existing data available for pure methane systems. As mentioned above, the hydrate phase boundary for methane hydrate is well-established (Sloan, 2000), but it is not well-defined for this ternary gas mixture. While thermodynamic phase boundary tests were attempted in this work, the current experiments were designed around the equilibrium boundary predicted by Multiflash 4.1 (Multiflash® for Windows, 2012). In each test, the sapphire cell was loaded with 18 ml of deionized water at atmospheric pressure and 20 °C. The cell was sealed and the gas phase was flushed five times with 20 bar of the feed gas, and then pressurized to the desired experimental pressure; after the cell was pressurized, the mixing system was initiated. The cell was sealed and kept at the target experimental pressure (which varied between 30 and 70 bar for the experiments reported below) and 20 °C for at least 60 min to confirm no leaks were present, after which the bath temperature was decreased at a rate of 1 K/hr towards a target temperature inside the hydrate region (typically 1 °C). As the system was operated isochorically, the cell pressure decreased with temperature; hydrate nucleation was identified by a sharp decrease in cell pressure that deviated from the isochoric cooling curve, and was confirmed visually in each experiment. As discussed by Akhfash et al. (2013) and Aman et al. (2015), the sapphire cell and stainless steel enclosure exchange heat effectively with the glycol bath. As a consequence, hydrate formation typically increased the cell temperature by less than 0.2 K during the first hour of growth, which was readily corrected by the PID algorithm. In the experiments discussed below, hydrate growth was not heat transfer limited in sapphire cell, which is in agreement with previous observations from this autoclave. While always below the hydrate equilibrium temperature for the cell pressure, the final temperature reached in each experiment (prior to intentional dissociation) was usually slightly above the target set point temperature of 1 °C depending on the amount of hydrate formed and the cooling power delivered by the submersible cooler (as discussed below).

The hydrate volume fraction during each test was estimated by calculating the molar volume of the gas, water, and hydrate phases using Multiflash 4.1 (2012) with a cubic plus association (CPA) equation of state; a hydration number of 6.1 was assumed for both gas systems in this study (Sloan and Koh, 2007). The hydration number depends on both the guest species and pressure-temperature conditions, and may be different for the two gasses used in this study. A comprehensive description of this calculation

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