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Hydrate formation and particle distributions in gas–water systems

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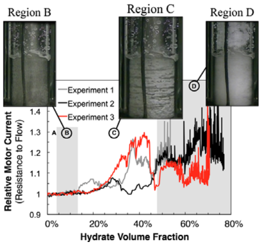
HIGHLIGHTS

- Methane hydrate was formed in a high-pressure visual autoclave.
- A transition from homogeneous to heterogeneous particle distribution was observed.
- The transition points agreed from visual, pressure, and motor current measurements.
- Under-inhibition increased the transition point by approximately 10 vol% hydrate.

GRAPHICAL ABSTRACT

Relative motor current (resistance to flow) increase in high-pressure autoclave as a function of methane hydrate volume fraction, for three repeat trials at an initial Reynolds number of approximately 2460. The regional boundaries (A–D) arise from slope changes in the average hydrate formation rate; resistance to flow was observed to increase only after approximately 14 vol% hydrate, and large fluctuations in motor current were observed after approximately 47 vol% hydrate.



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ABSTRACT

Methane hydrate formation rate and resistance to flow were measured for gas–water systems in a high-pressure visual autoclave over a range of mixture velocities (300–5000 Reynolds number). A transition from a homogeneous to heterogeneous particle distribution, proposed following flowloop studies by others, was observed directly in the autoclave through three independent measurements: motor current increase (resistance to flow), pressure consumption rate (hydrate growth rate), and visual observation. The hydrate volume fraction at the transition, $\phi_{\text{transition}}$, generally increased with increasing turbulence, although the relationship between Reynolds number and $\phi_{\text{transition}}$ was not the same as that observed in flowloop experiments. The addition of a thermodynamic inhibitor below the full inhibition threshold (i.e. under-inhibited) increased the transition point by about 10 vol% hydrate, without affecting the initial hydrate growth rate. A simple mass transport-limited formation model with no adjustable parameters was implemented to enable quantitative predictions of hydrate formation rate. In sufficiently turbulent systems the model's predictions were in excellent agreement with the observed growth rates. At lower Reynolds numbers, two mechanisms are proposed to explain the deviations between the observed and predicted growth rates. Prior to $\phi_{\text{transition}}$ the low shear means that hydrate formation is limited by the rate at which the aqueous phase can be re-saturated with methane. This rate is increased greatly by the formation of a hydrate bed after $\phi_{\text{transition}}$, which increases the gas–liquid interfacial area.

1. Introduction

Clathrate hydrates are crystalline inclusion compounds, where molecular cages of water trap light hydrocarbon species, such as methane (Sloan and Koh, 2008). Hydrates are typically stable at high pressures and low temperatures, and play an important role in global energy systems. Naturally-occurring gas hydrates exist in the region of the seafloor (Kvenvolden, 1994), where thermogenic and biogenic methane sources have generated substantial gas hydrate reserves (Paull et al., 2010). Gas hydrates also form in conventional oil and gas pipelines and pose operational and safety hazards, where high pressures and cool ambient temperatures

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may lead to rapid hydrate growth and complete blockage of the flowline (Davies et al., 2009). Hydrate prevention is most commonly managed by the injection of thermodynamic inhibitors (THIs), such as monoethylene glycol (MEG), which disrupt the hydrogen-bonded water network and shift the hydrate stability zone to lower temperatures (Koh et al., 2002). However, as the quantity of thermodynamic inhibitor required to fully inhibit hydrate formation scales linearly with the volume of water in the system (water cut), requiring up to $30 per barrel of water produced, the operational cost of THI injection may limit the economics of continued production from older reservoirs (Creek et al., 2011).

Over the past two decades, significant progress has been made toward elucidating hydrate plug formation mechanisms. To help simplify the problem of hydrate formation in pipelines, plugging mechanisms may be categorized into oil-, gas- and water-dominated scenarios, based loosely on the most abundant phase (Zerpa et al., 2012). Systems with a dominant gas fraction are the least well-studied and understood; hydrate plug formation may largely be the product of hydrate-wall deposition (through hydrate film growth or deposition from a flowing slurry). Laboratory (Rao et al., 2013) and flowloop (Nicholas et al., 2009) experiments suggest hydrate film growth (Lingelem et al., 1994) directly on the pipeline wall is a dominant effect during the early stages of plug formation, with a maximum (initial) deposition rate of 1 mm per day (Rao et al., 2013).

In oil-dominated systems, Turner et al. (2009) proposed four discrete stages of plug formation based on laboratory and field observations: (i) water droplet dispersion in liquid hydrocarbon (Boxall et al., 2012); (ii) hydrate nucleation and initial shell growth at the water–hydrocarbon interface (Walsh et al., 2009; Taylor et al., 2007); (iii) hydrate particle agglomeration and wall deposition (Aman et al., 2011); and (iv) plug formation, enhanced by jamming-type phenomena of large aggregates (Guariguata et al., 2012). In high water-cut cases (water-dominated systems), where the water-oil emulsion may invert (Moradpour et al., 2011) or the well is producing little-to-no oil, a combined suspension of gas bubbles, hydrate particles and oil droplets flow in an aqueous bulk phase. Hydrate may nucleate and grow along the gas–water interface (Sun et al., 2007; Sakemoto et al., 2010), where continued growth is supported by dissolved methane in water. Aman et al. (2012) reported hydrate interparticle forces to be three to four times smaller in the water phase than in oil, primarily due to a change in cohesive mechanism (particles do not cohere through an aqueous liquid capillary bridge when suspended in the water phase). Consequently, the flowing hydrate particles are unlikely to aggregate unless the shear field is eliminated, after which the particles may start to cohere and begin sintering/growing together or to the wall (Aman et al., 2011).

Joshi et al. (2013) studied high water-cut systems by measuring pressure drops in a four-inch flowloop over a variety of liquid loading and velocity conditions, observing three systematic regions in which pressure drop (i) appeared independent of hydrate fraction during the initial phase, (ii) increased directly with hydrate fraction during the second phase, and (iii) fluctuated significantly with hydrate fraction during the final phase. By drawing analogies with observed flow regimes in ice-water mixtures, Joshi et al. (2013) proposed that these regions corresponded to three distribution states of hydrate particles, as shown schematically in Fig. 1 (Sum et al., 2012): (i) homogeneous particle distribution; (ii) heterogeneous particle distribution (i.e., variable particle concentration in the radial direction), leading to a moving bed-type accumulation (Hernandez, 2006); and (iii) stationary bed formation and catastrophic deposition resulting in plug formation.

Joshi et al. (2013) observed that the transition from the first region (homogeneous distribution) to the second region (heterogeneous distribution) occurred at a repeatable hydrate volume fraction, denoted $\phi_{\text{transition}}$, that increased with the Reynolds number of the mixed flow. Furthermore, the transition was observed to be irreversible with respect to hydrate plugging behavior; it was not possible to revert from region 2 back to region 1 by increasing the velocity of the flow.

In this paper, we report direct observations of hydrate formation and plug formation, and the associated distribution of hydrate particles between the gas and water phases, using a high-pressure visual autoclave cell. In this study, the term hydrate particle distribution refers to the spatial distribution of the hydrate particle number density, principally along the autoclave's vertical axis. The distribution of hydrate particle size (including aggregate diameters) could be considered in future work, once the necessary improvements to the video capture system's resolution are made. Measurements of either type of particle distribution are typically very challenging in flowloop experiments, often requiring flow to be halted during periods of visual observation. Joshi et al. (2013) presented images of the homogenous hydrate distributions that occur prior to the transition. In this work we used a visual autoclave, with a geometry, shear field and other experimental systematics entirely different to those of a flowloop, to obtain information about hydrate formation in gas–water systems from three independent sources: visual observation, hydrate formation rate (calculated from pressure decrease), and resistance to flow. The latter property, which is inferred from the observed pressure drop in flowloop experiments, was measured here by monitoring the motor current required to maintain the visual autoclave's impeller at a constant rotational speed. These new results from bench-top scale experiments provide direct confirmation of the conceptual picture proposed by Joshi (2012) for high water content systems based on flowloop-scale experiments; as the hydrate fraction increases, a clear transition occurs between (i) a regime in which the particles are homogeneously distributed and the resistance to flow is insensitive to the amount of hydrate present, and (ii) a regime in which the particles are distributed heterogeneously and the resistance to flow increases directly with hydrate volume fraction.

In addition, by comparing the observed hydrate formation rates with the predictions of a simple model *containing no adjustable parameters*, further insight was obtained into the mechanisms governing hydrate growth in high water content

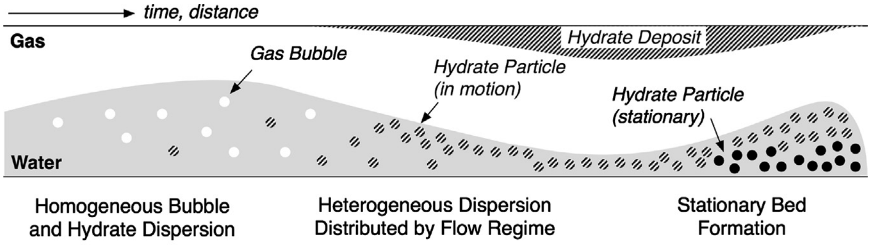

Fig. 1. Conceptual hydrate plugging mechanism for high water content systems, adapted from Joshi et al. (2013).