Gas hydrate plug formation in partially-dispersed water–oil systems

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HIGHLIGHTS

- New data for hydrate plug formation in partially dispersed water–oil systems are presented.
- A visual autoclave was used to measure hydrate growth and transportability.
- Hydrate particles grow slowly but eventually disrupt the interface leading to rapid growth.
- A new conceptual mechanism for hydrate plug formation in partially dispersed systems is presented.

ARTICLE INFO

ABSTRACT

The formation of gas hydrate plugs in deep water oil and gas flowlines poses severe operational and safety hazards. Previous work has established a mechanism able to describe plug formation in oil-continuous systems, which relies on the assumption that all the water remains emulsified in the oil phase. However, light hydrocarbon fluids, including condensates, may not stabilize water-in-oil emulsions, and the current mechanistic model cannot reliably assess the risk of plug formation in this scenario. This study presents a comprehensive set of experiments conducted in a high-pressure sapphire autoclave apparatus using 10 to 70 vol% water in partially-dispersing mineral oil at three fixed rotational speeds: 300, 500 and 900 RPM. Pressure and temperature were monitored continuously in the autoclave, providing direct estimates of hydrate growth rate, alongside measurements of the motor torque required to maintain constant mixing speed. A new conceptual mechanism for plug formation has been developed based on the visual observations made during these experiments, where a small hydrate fraction (2–6 vol%) in the oil phase was observed to disrupt the stratified water–oil interface and help disperse the water into the oil. This disruption was followed by an increase in the hydrate growth rate and particle agglomeration in the oil phase. In the final stages of hydrate growth for systems with low turbulence and high watercut, hydrate particles in the visual autoclave were observed to form a moving bed followed by full dispersion of water and oil, rapid hydrate growth and deposition on the wall. These rapid hydrate growth and deposition mechanisms significantly increased the maximum resistance-to-flow for partially-dispersing systems in comparison with mixtures that are fully dispersed under similar conditions.

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1. Introduction

Gas hydrates are ice-like solids, where a molecular lattice of water surrounds light hydrocarbon species (e.g. CH_4) at high pressure and low temperature (Sloan and Koh, 2007). These conditions may be readily achieved in subsea oil and gas flowlines, due to high reservoir pressures and heat exchange with cool

seawater. The nucleation and growth of gas hydrates in the flowline may readily lead to a pipeline blockage, resulting in severe economic, operational and safety hazards. Significant effort has been expended over the past decade to identify the critical path of hydrate plug formation in systems where crude oil is the dominant phase. Turner et al. (2009) presented a four-step mechanism (Fig. 1) to describe hydrate plug formation in oil-continuous systems: (i) water droplets are emulsified in the oil phase; (ii) hydrate nucleation at the interface between emulsified water droplets and oil results in the formation of a hydrate shell with an internal
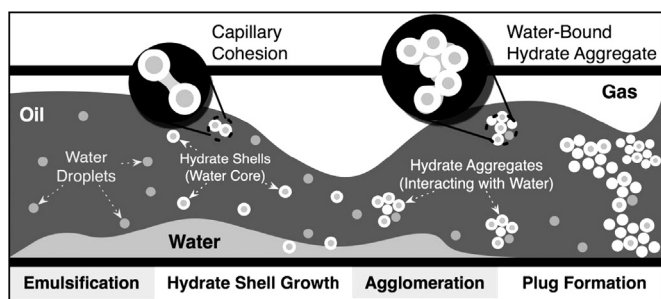
Fig. 1. Conceptual picture of hydrate plug formation mechanism in oil-continuous systems, adapted from Turner et al. (2009).

water core; (iii) the cohesive interaction between hydrate shells/particles results in the formation of multi-particle aggregates; and (iv) the resultant increase in viscosity decreases the velocity of flow, enabling localized particle build-up and jamming-type failure.

The required emulsification of water droplets in a liquid hydrocarbon phase was studied extensively by Boxall et al. (2012), who developed a predictive model for mean droplet size based on flowloop and autoclave measurements. The model balances the shear stress exerted by the continuous phase on the droplet against interfacial restorative forces (Janssen et al., 1994) with consideration for two distinct regimes: (i) inertial breakup, where droplet diameters exceed the length scale of the smallest turbulent eddies in the system; and (ii) viscous breakup, where droplets are smaller than those turbulent eddies and breakup is governed by sub-eddy scale viscous stresses exerted by the continuous phase on the interface. The mean droplet size predicted by both breakup modes is directly proportional to continuous phase density and inversely proportional to the water–oil interfacial tension (Boxall et al., 2012). When compared to typical crude oil properties (Sjöblom et al., 2010), condensate-type hydrocarbon liquids have lower densities, lower viscosities and higher interfacial tensions with water. When compared to crude oil, these condensate properties result in the generation of small water droplet sizes during mixing, with a greater amount of total energy required to maintain the dispersion compared to a crude oil. For these reasons, the maintenance of emulsified water droplets in a condensate fluid generally requires substantial and continuous kinetic energy input (i.e. highly turbulent conditions). Under lower turbulence conditions, or at moderate-to-high watercuts, condensate fluids tend to exhibit partially-dispersing behavior through the formation of a separate, free water phase.

The oil-continuous conceptual model for hydrate formation (Fig. 1) assumes gas hydrate will nucleate at the interface of the emulsified water droplets in the oil, where both water and gas molecules exist in substantial quantities (Walsh et al., 2009). After nucleation, hydrate will spread across and form a shell around the water droplet surface at a rate that depends on guest size (Aman et al., 2011), due to the availability at this interface of both water and dissolved hydrocarbon species. The thickness of the initial hydrate shell was reported by Taylor et al. (2007) to be on the order of 50 microns, which has recently been confirmed via magnetic resonance measurements by Haber et al. (2015). Continued growth of the hydrate shell is limited by the diffusion of either guest or water molecules across the crystal lattice (Davies et al., 2010). However, in a partially-dispersing system, it is currently unclear whether hydrate will nucleate and grow primarily by forming shells around the limited water dispersed in the oil phase, or instead within the continuous water phase where the availability of guest species is limited by the solubility and diffusion of light gases in the aqueous phase (Skovborg and Rasmussen, 1994). Answering this question is one of the primary motivations for the present investigation.

In water-continuous systems, Joshi et al. (2013) suggested that the primary mechanism of hydrate plug formation was related to the formation of a moving hydrate bed at the water–gas interface. This bed functions to retard the local fluid velocity, resulting in the buildup of hydrate particles and eventual formation of a stationary bed that simultaneously restricts the flow channel and enables wavy- or slugging-type hydrodynamic behavior (Hernandez, 2006). Akhfash et al. (2013) confirmed this interpretation using a high-pressure sapphire autoclave, which allowed direct observation of the transition in hydrate particle distribution throughout the aqueous phase from homogeneous to heterogeneous, whereupon a hydrate bed formed. These visual observations regarding the change in spatial distribution of the hydrate particles occurred concurrently with the first significant increase in the motor torque required to continue mixing the hydrate slurry at constant rotational speed above its baseline value.

Small quantities of hydrate particles (e.g. < 3 vol% of the liquid phase) have been demonstrated to have a negligible impact on the apparent viscosity of either the oil (Sinquin et al., 2004) or water (Akhfash et al., 2013; Joshi et al., 2013). However, as hydrate continues to grow, interparticle and particle–wall interactions respectively enable the formation of large agglomerates and wall deposits. Aman et al. (2011) described a model for cohesive interactions between cyclopentane hydrate particles in a continuous oil phase, which includes contributions from both capillary bridge cohesion (enabled by the presence of unconverted water) and interparticle growth/sintering. Further studies revealed that the cohesive force between cyclopentane hydrate particles in a continuous aqueous phase was approximately a factor of three less than the cohesive force in a continuous oil phase (Aman et al., 2012); this result was invoked by Joshi et al. (2013) to interpret the results of large-scale flowloop experiments. Although hydrate-wall adhesive forces have not been measured in systems with a continuous water phase, studies by Aspenes et al. (2010) of oil-continuous systems demonstrated the important role of capillary bridges to the adhesive force mechanism. Hydrate-wall sintering was subsequently observed by Aman et al. (2013) with calcite and quartz surfaces in liquid cyclopentane, suggesting a secondary mechanism by which hydrate particles may deposit on the flowline wall. By analogy with the observed cohesive interactions, it is likely that hydrate-wall adhesion forces may be significantly reduced by the presence of an aqueous phase.

In partially-dispersing systems, the primary phase in which hydrate formation occurs will inform whether particle agglomeration/deposition or moving bed formation mechanisms control resistance-to-flow behavior. Sohn et al. (2015) reported autoclave torque (resistance-to-flow) measurements of mixed gas hydrate slurries in mineral oil at 20–100% watercut at the same rotational velocity; the study reported the most severe torque increases were associated with systems containing watercuts of 40 and 60%, where stratified oil and water phases were likely to be stable in the blind autoclave. Laboratory experiments capable of decoupling these steps are required for the development of a generalized conceptual model that describes both fully-dispersing and partially-dispersing systems. Such laboratory-based studies would help improve the capacity of risk-based hydrate assessment in partially-dispersing systems, calculations of which currently assume a behavior identical to fully-dispersing systems. This work thus seeks to address two knowledge gaps. First, do partially-dispersing systems follow the same pathway to hydrate plug formation as oil-continuous systems, or are different phenomena observed? Second, can hydrate growth in partially-dispersing systems be reliably estimated with a kinetic-type equation (Davies et al. 2009), such as is used for fully-dispersed systems? To help achieve these objectives a sapphire visual