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Oil and gas pipelines with hydrophobic surfaces better equipped to deal with gas hydrate flow assurance issues

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ABSTRACT

Gas hydrate deposition can cause plugging in oil and gas pipelines with resultant flow assurance challenges. Presently, the energy industry uses chemical additives in order to manage hydrate formation, however these chemicals are expensive and may be associated with safety and environmental concerns. Here we show the effect of a hydrophobically coated surface on hydrate formation in the presence of an antifreeze protein type I (AFP I) and a biodegradable synthetic polymer (LuvicapBio) in a high pressure crystallizer setup. The hydrophobic surface increased the hydrate induction time and reduced the hydrate growth significantly in pure deionized water (control). Furthermore, in the presence of 0.02 wt% of LuvicapBio or 0.014 wt% AFP I in the hydrophobic coated crystallizer; the hydrate growth was reduced to almost the same level as obtained with 0.20 wt% of LuvicapBio in a stainless steel crystallizer. This indicates that 10 to 14 times less KHI is needed in the presence of a hydrophobically coated surface. These experimental studies suggest that the use of hydrophobic surfaces or pipelines could serve as an alternative or additional flow assurance approach for gas hydration mitigation and management.

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1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds of hydrogen bonded water molecules with enclathrated gas molecules such as methane, ethane, propane and carbon dioxide (Sloan, 2003). Natural gas hydrate formation conditions are frequently encountered in the oil and gas industry, potentially leading to blockage of pipelines with resultant production losses and safety issues (Koh, 2002; Sloan and Koh, 2007). Currently the most applied method in industry is the use of chemicals known as thermodynamic hydrate inhibitors (THIs) such as methanol and glycol which shift the hydrate phase boundary to higher pressure and lower temperature (Englezos, 1993). However, the large amounts of THI required to prevent hydrate formation can cause safety and environmental issues as well as resulting in higher expenses associated with the large amounts of chemicals used, and the need for offshore handling facilities (Frostman et al., 2003).

Consequently, the industry is increasingly looking to low dosage inhibitors such as kinetic hydrate inhibitors (KHIs) which affect the hydrate kinetics by delaying hydrate formation for a certain period of time before hydrates starts forming. These compounds are usually water-based polymers that are used in much lower amounts than THIs (Kelland, 2006). Nevertheless, due to environmental restrictions resulting from the poor biodegradability of KHIs their use is still limited (Villano et al., 2008).

Antifreeze proteins (AFPs) found in certain plants, fish and insects can prevent ice from growing when cooling below the freezing temperature. Recently, AFPs have been studied as a green and environmentally friendly kinetic hydrate inhibitor (Walker et al., 2015). Promising results has been obtained in THF (Gordienko et al., 2010; Zeng et al., 2003, 2006), methane (Al-Adel et al., 2008; Jensen et al., 2010, 2011; Perfeldt et al., 2014) and multi-component gas systems (Daraboina et al., 2011a, 2011b, 2011c; Ohno et al., 2010; Sharifi et al., 2014a, 2014c) showing that AFPs may have potential as gas hydrate inhibitors. Although, AFPs offer potential as KHIs the large-scale manufacturing costs have been a challenge for the transition from research to industrial application (Kelland, 2006). Additional approaches to prevent or delay the hydrate formation are therefore of interest.

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Deposition and plugging of gas hydrates in pipelines are still not completely understood phenomena. The pipeline surface offers several nucleation sites and is the coldest point in the system (Nicholas et al., 2009). Several experimental studies and field trials suggest that hydrate deposition occurs on the pipeline wall. However, hydrate plugging is also considered to be caused by phenomena such as sloughing and jamming (Grasso et al., 2013). Lingelem et al. (1994) proposed (based on experimental studies) that hydrates will start growing where gas molecules are available – at the pipeline wall close to the liquid gas interface or at the gas liquid interface. Austvik et al. (1997) suggested (based on a field trial study at Tommeliten Gamma gas-condensate field in the North Sea) that hydrates may stick to the pipeline wall. Nicholas et al. (2008) experimentally observed (in a single pass condensate flow loop with dissolved water) that cyclopentane hydrates deposited on the pipeline wall. In a high pressure reactor Austvik et al. (2000) found that agglomeration of hydrates was dominated by the stickiness between hydrate particles, by stickiness of hydrate particles to the pipeline wall or a combination of these two effects. In some systems, hydrates form sufficiently fast causing the hydrates to deposit without forming transportable lumps. Hence, the wetting conditions of the pipeline wall were believed to be important for determining the stickiness of hydrates to the wall. As hydrate particles are very hydrophilic, a hydrophobic surface should be able to reduce water bridging to the pipeline wall and thereby have an influence on gas hydrate nucleation (Austvik et al., 2000).

These experimental studies and field trial underline the importance of understanding the hydrate-surface adhesion for ensuring flow assurance. Recently, adhesion has been studied between cyclopentane hydrate particles and solid surfaces using a micromechanical force apparatus (Aman et al., 2014; Aspenes et al., 2010; Nicholas et al., 2009). Nicholas et al. (2009) found that in a water-free environment the forces between cyclopentane hydrates in the bulk phase and carbon steel were lower than the hydrate–hydrate forces. It was hypothesized that the capillary forces between hydrate and carbon steel were dominating; however the forces were insufficient to deposit hydrates on the pipeline wall. Aspenes et al. (2010) studied several different surfaces and found that for cyclopentane hydrates the adhesion force between solid and hydrate increased with increasing surface energy of the solids when no water was present. The surface-hydrate forces were observed to be approximately 10 times lower than the hydrate–hydrate adhesion forces. This indicates that hydrates will not preferentially deposit on the pipeline wall when no free water is present. However, when water was present as a drop on the surface, the adhesion force between the hydrate and the surface were more than 10 times larger than the hydrate–hydrate adhesion forces. This may indicate that hydrates in contact with a water droplet on the pipeline wall would likely stay attached to the wall leading to deposition (Aspenes et al., 2010).

Aman et al. (2014) measured the adhesion forces between cyclopentane hydrate particles and various physically and chemically modified surfaces. The physical surface modification with graphite reduced the hydrate-surface adhesion force by 79% in comparison to the plain steel surface. This was explained to be due to the hydrophobic contact angle of water on the graphite surface. The chemically modified surfaces lead to changes in the growth morphology of the hydrates. However, although a citric acid ester modified surface significantly reduced the adhesion forces between hydrate and the surface, the hydrate growth was accelerated. It was hypothesized that as citric acid ester behaves as a strong surfactant it may weaken the capillary bridge between hydrate and steel surface leading to the reduced adhesion forces. Consequently, due to the strong surfactant properties the interfacial energy barrier for hydrate growth was reduced resulting in rapid growth of hydrates.

On water-wetted surfaces, both the graphite and the citric ester acid modified surfaces were less effective in reducing the adhesive force. This implies that a physically or chemically modified surface may not be sufficient to prevent hydrate formation in pipelines. Recently, Smith et al. (2012) studied THF hydrate adhesion on steel coated with several different hydrophobic surface coatings. It was found that the more hydrophobic the surface was the less the adhesion of THF hydrates to the surface. THF hydrate adhesion was observed to be reduced by more than 4 times for 80%/20% PEMA/fluorodecyl POSS coated surface compared to steel.

These studies suggest that the surface of the pipeline wall can have a significant influence on the adhesion of hydrates and thereby have an impact on the risk of hydrate deposition in the pipeline. However, the qualitative nature of these studies only indicate the influence of the surface as the experimental work (THF hydrates and cyclopentane hydrate particles at low pressure) has not been carried out at conditions close to those found in oil and gas production.

Here we employ pure methane under high pressure and flowing circumstances in order to mimic actual pipeline conditions. The objective is to assess the influence of the hydrophobic surface on hydrate formation and growth. A high pressure setup that consists of two stirred crystallizers was used to examine the performance of both AFP I and LuvicapBio (modified PVCap). We found that the hydrophobic surface increased the nucleation time in the control solution and that the growth was significantly reduced even at very low KHI concentrations.

2. Experimental section

2.1. Materials

The gas was UHP (ultrahigh purity 3.7) grade methane gas from Polar Cryogenics Inc. which forms structure I (SI) hydrates. SI forms a cubic structure which consists of linking vertices of small cavities (5^{12}) that form spaces of larger cavities ($5^{12}6^2$). These cavities can contain small natural gas molecules like methane, ethane or CO_2 (Sloan, 2003).

Two biodegradable kinetic hydrate inhibitors were used: a synthetic inhibitor LuvicapBio from BASF which is a modified PVCap (polyvinylcaprolactam) in water and ethylene glycol and an antifreeze protein from winter flounder fish type I AFP (AFP I; α -helical protein of 3.3–4.5 kDa (most of it at the smaller size); purity 70%; A/F Protein Canada Inc.). Concentration of the AFP I was determined by amino acid analysis (AAA) (Department of Systems Biology, DTU, Denmark). The KHIs were dissolved in deionized water. LuvicapBio was diluted to 0.20 wt% which is in the concentration range used for low-dosage KHIs in the oil and gas industry (Kelland, 2006). AFP I was diluted to 0.014 wt% which is comparable to AFP I amounts used in previous studies within inhibition of methane hydrate formation (Al-Adel et al., 2008). In addition, LuvicapBio was diluted to 0.02 wt% in order to compare the efficacy of LuvicapBio and AFP I as kinetic hydrate inhibitors. Reference liquids for contact angle measurements were glycerol from Sigma Aldrich (purity >99%) and diiodomethane from ACROS Organics (purity >99%).

2.2. Apparatus

A high pressure crystallizer apparatus (Fig. 1) was used to conduct hydrate nucleation and formation experiments under constant pressure and constant volume. The apparatus consists of two stainless steel crystallizers (CR1 and CR2) and one crystallizer coated with hydrophobic material (CR3) which are connected in one parallel experimental setup. The stainless steel crystallizers are

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