FORMATION OF GAS HYDRATE BLOCKAGES IN UNDER-INHIBITED CONDITIONS

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ABSTRACT
The prevention of natural gas hydrate blockages in pipelines is of great importance due to the severe financial penalties as well as significant personnel and facility risk during removal, thus considerable effort is made to prevent their occurrence. The majority of oil and gas pipelines at risk from hydrate formation utilise thermodynamic hydrate inhibitors to prevent the occurrence of hydrates, mono-ethylene glycol (MEG) and methanol being the most common inhibitors. MEG systems deliver and recycle large quantities of inhibitor to deep-water pipelines which represent a significant fraction of the total investment required for field development. However, problems may occur where the injection rate of inhibitor falls below the required dose rate due to human error or mechanical failure. In such instances there is anecdotal evidence to suggest that the presence of inhibitor may actually accelerate the agglomeration of hydrate particles into plugs. Conversely, in certain circumstances a self-inhibiting system may result when formation of a small volume of hydrate extracts water molecules from the mixture, reducing the volume fraction of water and raising the inhibitor concentration above the critical level. The effect that this has on blockage formation for both of these phenomena is very poorly understood.

A new facility for studying the formation of natural gas hydrates has been development at UWA: a high pressure – low temperature autoclave cell named the high pressure hydrate agglomeration dynamometer (HPHAD).

Keywords: gas hydrates, plug formation, kinetic hydrate inhibitors

INTRODUCTION
Natural gas hydrates remain the largest concern for flow assurance engineers during oil and gas production from the well to process facility. Mitigating the risk of a hydrate blockage results in substantial capital (CAPEX) and operating (OPEX) expenses, and getting it right is paramount due to the severe consequences of a blockage – which can take weeks or even months to clear. A study by Sloan suggests that hydrates are the single greatest problem in pipeline flow assurance [1].

Hydrates require four ingredients to form: (1) water, (2) hydrate forming molecules (<9 Å, such as methane, ethane, propane etc.) [2], (3) low temperature, and (4) high pressure. In the past hydrate prevention methods have been approached with an “avoid at all costs” attitude typically by avoiding the temperature range at which they form through insulation or adding thermodynamic hydrate inhibitors (THIs) such as methanol or mono-ethylene glycol which suppress the temperature at which hydrates are stable. Figure 1a illustrates these four ingredients as a "hydrate prevention box". The figure includes the measures that can be taken to prevent hydrate formation: separation of gas (although not completely effective as hydrates can still form from a liquid hydrocarbon phase), dehydration of water, and...
insulation or inhibition as described above. Reducing the pressure is often not a viable method as

![Figure 1. (a) The hydrate prevention box, (b) The hydrate management diamond.](image)

A problem that can occur when using hydrate inhibitors such as MeOH or MEG is that if the injection rate of inhibitor falls below the required level (because of human error or mechanical failure). In such systems there is evidence that the presence of inhibitor can actually accelerate the agglomeration of hydrate particles into plugs [14]. As Hemmingsen [14] and his colleagues describe, the potential for hydrate plugs to form in these ‘under-inhibited’ systems is maximised by the presence of 10 to 15 wt% methanol or MEG. However, this phenomenon is still very poorly understood. Most oil and gas pipelines in Western Australia with the risk of forming hydrates utilize thermodynamic hydrate inhibitors (recirculated MEG) [15], and the systems needed to deliver and recycle the large quantities of MEG to deep-water pipelines represent a significant fraction of the total investment needed for the development. Thus an improved understanding of the formation and agglomeration of hydrates into plugs under these conditions will benefit both local gas producers and the global petroleum industry.

Applications of kinetic hydrate inhibitors as the hydrate control strategy are often limited to moderate subcoolings (8-10 °C) for a 24 - 48 hr delay in hydrate onset. However, it is becoming more common to combine a THI and KHI, for increased subcooling performance [4]. However, if the KHI was to fail (i.e. nucleation and growth of hydrate) the system would still have some protection from the presence of the THI albeit...
under-inhibited. The consequence of this scenario has not yet been established. A better understanding of this consequence could allow for more accurate risk analysis modeling.

**EXPERIMENTAL APPARATUS**

Figure 2 illustrates the high pressure hydrate agglomeration dynometer (HPHAD) experimental setup. The apparatus consists of a sapphire cell, for visual observations, and a magnetically-coupled mixer (Dyna/Mag®) that allows high pressure operation. In addition to the standard pressure and temperature instrumentation, the HPHAD consists of a direct-drive motor (incorporated into the magnetically-coupled mixer), to allow determination of the power required to mix the slurry. The reactor is attached to a pressure manifold to supply a constant formation pressure through a pneumatically operated (normally closed) valve and metering valve. Hydrate formation rate will thus be determined from the decrease in pressure of the high pressure reservoir. The reactor and pressure manifold are all submersed in a temperature controlled glycol/water bath.

![Figure 2. Experimental set-up for the high pressure hydrate agglomeration dynamometer (HPHAD)](image)

The reactor is a DB Robinson type Sapphire cell with a 25.4 mm ID and 150 mm height. The cell is rated to 210 bar operating pressure. The contents are mixed by a 4-blade flat impeller. The temperature is measured using a PRT fed through the bottom of the cell. The gas can be added either through the bottom of the cell, i.e. bubbled through the liquid or into the gas space at the top of the cell.

![Figure 3. DB Robinson type sapphire cell rated to 3000 psi (210 bar)](image)

Crucially, the HPHAD allows the amount of power required to mix the hydrate slurry to be measured directly. This quantity can be related to the potential to form a blockage [16]. In this work a Dyna/Mag mixer (Figure 4) is used from PPI, model number MM-T06 with direct drive motor (1/15 HP). The motor includes a variable speed drive, with speeds up to 1750 RPM, and a DTA-108 digital tachometer.

![Figure 4. Dyna/Mag® mixer](image)

**EXPERIMENTAL APPROACH AND DISCUSSION**

Initially, the effect of hydrate volume fraction on condensate-water-hydrate slurry transportation must be studied. This is an area that is still poorly understood. It has been reported that a hydrate blockage can be seen with as little as 4 vol% hydrate [17]. A major component of the initial work is to determine the critical hydrate fraction, when the slurry displays blockage characteristics. The factors that can affect this critical hydrate...
fraction include sub-cooling/driving force, shear rate, hydrate formation rate (controlled by either injecting the gas through the liquid – fast, or to the top of the cell – slower). These experiments provide a base line measurement for subsequent experiments using the HPHAD.

The ongoing experimental work consists of under-inhibited MEG and/or salt systems, where hydrate formation will become self-limiting. A major goal for this work is to determine the relationship between the level of under-inhibition (difference in concentration of inhibitor to fully inhibit hydrate formation and the experimental concentration) and the potential of the system to form a blockage. Achieving a suitable driving force for hydrate formation is essential for these experiments. If the driving force is too low (Figure 5b) the hydrate equilibrium will be reached with very little hydrate formation through the concentration of the remaining aqueous phase. The driving force can be either manipulated by pressure or gas composition. We typically fix the operating temperature of experiments at 4 °C for hydrate flow assurance work, to match typical sea floor temperatures.

![Figure 5](image)

Figure 5. Pressure / temperature diagram illustrating hydrate stability regions and the effect of increased inhibitor concentration

The apparatus is also suitable for the study of alternative techniques for hydrate prevention i.e. low dosage hydrate inhibitor (LDHI) systems including: kinetic hydrate inhibitors (KHIs), and anti-agglomerates (AAs) and synergies of THIs and LDHIs as well as other oil field chemicals such as corrosion inhibitors (CIs).

Experimental data on hydrate plugging phenomena is also an important step for the development of predictive models that could be used in hydrate management strategies. Kinnari et al. (2008) [18] describes the need for such models and how they can be utilized from an industrial stand-point. Boxall et al. (2009) [19] describes the development of one such model.

**CONCLUSIONS**

A new visual autoclave cell facility for studying the formation and agglomeration of natural gas hydrates has been development at UWA. The development of experimental techniques for determining the critical hydrate volume fraction and the effect of this in under-inhibited MEG systems will be presented.

**REFERENCES**