

Impact of Internal CO₂ Corrosion of Mild Steel Subsea Pipelines on Solid Hydrate Particles

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ABSTRACT

This work focuses on the interplay between protective iron carbonate surface scales and hydrate particles deposition. An iron carbonate layer was formed on API 5L X65 carbon steel in a glass reactor cell under aqueous CO₂ saturated conditions using a three-electrode system. The protectiveness of the surface film was determined in situ using electrochemical techniques, which included open-circuit potential (OCP) and linear polarization (LP) measurements. As expected, the microscopic surface layer acted as a mass-transfer barrier, which reduced the corrosion rate of the carbon steel sample to various degrees depending on the pH of the electrolyte and polarization condition. After testing, the structure and composition of the films were characterized using surface analysis techniques, including, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS). The influence of the surface film on hydrate adhesion was subsequently investigated using a micromechanical force (MMF) apparatus, which indirectly measures the adhesion force between a clathrate hydrate particle and a nominated solid substrate surface. The combination of methods enabled the comparison of how corrosion products and surface film formation affect hydrate deposition tendency. Results indicate that the presence of an iron carbonate layer increases the propensity for hydrate deposition, through both higher growth rates.

Key words: Hydrates, Corrosion, Carbon Steel, Carbon Dioxide, Electrochemistry, Scale.

INTRODUCTION

The development of new long subsea tiebacks will provide crucial infrastructure to bridge the gap between recent energy discoveries and existing offshore and onshore facilities, driving continued production of key energy resources. Looking at the challenges that need to be overcome for future energy production, the safe and reliable transport through subsea networks is one of the main initiatives of the flow assurance community. Additionally, subsea tiebacks provide a critical path to the delivery of the low-emissions future of the energy sector.

There are many challenges related to the production and transportation of oil and gas within subsea pipelines, largely associated to the hostile environment and extreme operation conditions. Particularly, considering that several prominent Australian offshore gas fields produce a significant volume of CO_2 , which may account for up to 14% of recoverable fluid on a molar basis.¹ This CO_2 must be removed from the raw gas stream before reaching gas production facilities, transiting subsea production lines on the order of 100+km before treatment onshore. The fact that subsea pipelines are typically made of carbon steel,² a material prone to internal corrosion when exposed to an aqueous environment containing CO_2 ,³ implies that corrosion is a chief concern for pipeline integrity management.

Similarly, hydrate formation represents a significant flow assurance risk as hydrate agglomeration and deposition can limit and fully block flow inside pipelines. Gas hydrates are solid crystal compounds formed from hydrogen-bonded water molecules that encage small gas molecules such as light hydrocarbons, under high pressure and low temperature conditions. Since the first evidence of hydrate formation in oil/gas production lines in 1934 by Hammerschmidt,⁴ hydrate has been treated with a strategy of avoidance, aimed at preventing solids formation. This is typically done by the addition of methanol or monoethylene glycol (MEG) into flowlines to shift the hydrate phase boundary to a lower pressure and/or higher temperature (Figure 1).

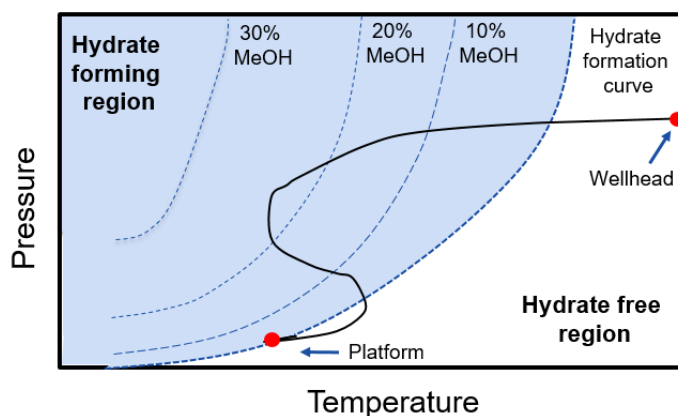


Figure 1: Hydrate formation pressures and temperatures (blue region) as a function of methanol concentration in free water for a given gas mixture. Flowline fluid conditions are shown from wellhead to platform along the bold black line. Adapted from Koh et al.

The mechanism for thermodynamic hydrate inhibition is the inhibitor dissolving in the free water phase thereby reducing the fugacity of water. As water is the principal component of hydrates, reducing the fugacity of water also reduces the tendency of hydrates to form.⁵ However, as new discoveries advance further offshore, the chemical requirements for such prevention strategies in long subsea tiebacks have become expensive, environmentally unacceptable, or both.^{6, 7}

New risk management strategies have arisen since 1990,⁸ largely owing to low dosage hydrate inhibitors (LDHIs). In these techniques, small hydrate particle formation is delayed or tolerated, but

aggregation to large plugs is avoided via kinetic inhibition and agglomeration prevention.^{8, 9} Kinetic Hydrate Inhibitors (KHIs) are low molecular weight polymers, which are dissolved in a carrier solvent and injected into the water phase inside the pipelines. The KHIs mechanism is to prevent hydrate nucleation and inhibit hydrate growth. Furthermore, anti-agglomerants (AAs) are amphiphilic compounds (hydrophilic head group and hydrophobic tail group) that adsorb to the interphases allowing hydrate formation but keeping the particles small and well dispersed preventing hydrate plugging.⁸

Hydrate Agglomeration and Deposition

In subsea oil and gas flowlines, hydrate blockages may occur due to hydrate particle build-up on the interior pipe wall stopping the flow. The exact plugging mechanism for hydrate particles varies depending on the dominant phase (oil, water, and gas) systems present in the flow system.¹⁰ Initially, particle agglomeration and deposition are responsible for large undesired pressure drops, increasing the flow complexity, rendering it unpredictable,¹⁰ and depleting momentum energy resulting in lost production. Eventually, if a deposit is left to ripen over time, it may ultimately lead to the formation of an impermeable plug:¹¹ under favourable hydrate forming conditions, hydrate blockage may occur within minutes.¹²

Oil-dominant systems are typically characterised by a dispersion of water droplets and hydrate particles in a continuous liquid hydrocarbon phase.¹³ The mechanism for hydrate formation and blockage in oil dominant flowlines is well understood and was presented as a four stage model proposed by Turner et al.: (1) emulsification or water entrainment in the oil phase; (2) hydrate growth in both gas and liquid phases; (3) agglomeration between hydrate particles and deposition on pipeline wall; (4) hydrate plugging formation.¹³ The primary blockage mechanism in this model is agglomeration and resultant viscosification,¹⁴ a schematic of the process is shown in **Figure 2**.^{15, 16}

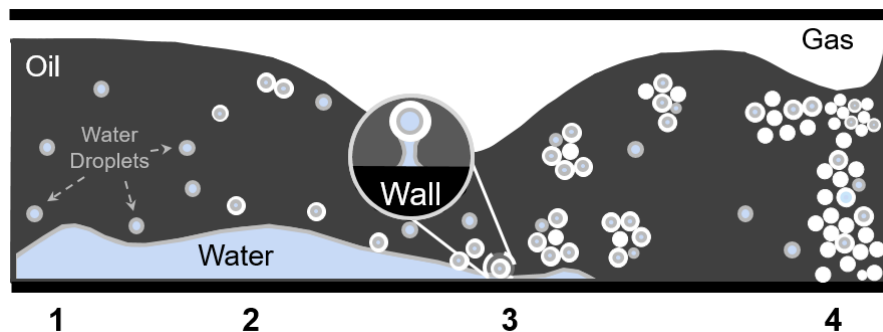


Figure 2: Conceptual mechanism of hydrate deposition and plug formation in oil-dominated flowlines. Adapted from Aman et al.

Extensive research¹⁷ has focused on the measurement of hydrate-hydrate particle cohesion through a capillary bridge mechanism¹⁴ as the primary driver for agglomeration. Rabinovich et al.¹⁸ presented a model to estimate inter-particle cohesive forces, which includes a capillary bridge component. The model have been extended geometrically to account for particle contact with a surface as presented in Equation 1¹⁶

$$F_A = \frac{4\pi R\gamma \cos \theta}{1 + \frac{H}{d}} + 2\mu R\gamma \sin(\theta + \alpha) \left(\sin \alpha - \frac{H}{a + \frac{H_a}{d}} \right) \quad (1)$$

where F_A is the particle-surface adhesive force, γ is the water-oil interfacial tension, H is the separation distance between the particle and surface, d is the immersion depth of the particle in the bridge, θ is the mean wetting angle of water on the hydrate surface, and α is the embracing angle (or functional width

of the liquid bridge). These geometric terms are illustrated in **Figure 3** where the water wetting angle on the surface is a function of different interfacial tensions.¹⁶

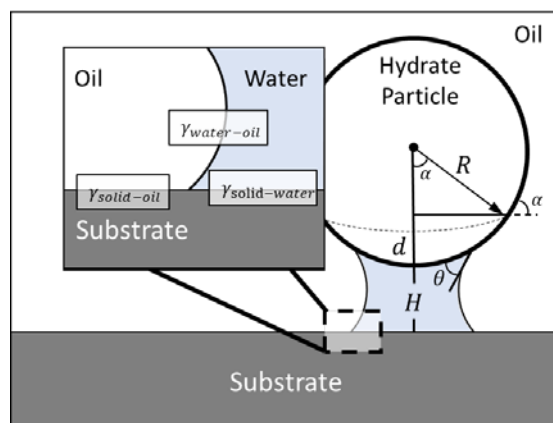


Figure 3: Hydrate particle adhesion to a substrate through a capillary bridge where interactions are dominated by interfacial tensions. Adapted from Aman et al.

The relationship between interfacial tension and contact angle was established by Young¹⁹ and is generally known as Young's equation (Equation 2)

$$\cos \theta = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{wo}} \quad (2)$$

where γ is the interfacial tensions between the three different interfaces solid/oil, solid/water and water/oil. This suggests a strong dependence on the three-phase contact angle θ at the capillary bridge component that is further influenced by the interfacial (surface) free energy loaded into the bridge from both substrate and hydrate particle. Previous work by Aspenes et al.²⁰ showed that the adhesion force between hydrate particles and solid surfaces is highly dependent on the surface material. Solids with low surface free energy (SFE) lead to low hydrate deposition. Substrate surface roughness accounts for another key parameter impacting hydrate deposition. Aman et al.¹⁶ showed how hydrate adhesion force increases with surface roughness modification for different materials (steel, quartz and calcite).

Cross-Interactions Remain an Outstanding Knowledge Gap

Evidence of the extensive understanding about hydrate agglomeration and deposition have been provided above. However, there is a highlight limitation when it comes to hydrate interactions within steel surfaces under 'real conditions'. In this new scenario, where industry is moving away from hydrate prevention allowing hydrate formation to some extent; interactions between hydrate particles and internal corrosion scale products at pipeline walls are expected, and its potential impact on both flow assurance management and corrosion control strategies represent a knowledge gap. In this study, a first approach for a pH control corrosion strategy scenario with hydrate formation from entrained water droplets is considered and new technical insight is sought.

This paper considers the effect of a uniform iron carbonate (FeCO_3) layer formed at a carbon steel sample under aqueous CO_2 -saturated conditions, on cyclopentane hydrate particles. In-situ electrochemical measurements and advance microscopy imaging were used to evaluate the morphology, uniformity and grade of protectiveness of the film. Hydrate deposition tendency at corroded steel substrates was further evaluated.

EXPERIMENTAL PROCEDURE

The objectives of the experimental work were, initially, to form a uniform iron carbonate (FeCO_3) scale layer at the surface of the carbon steel sample while gathering in-situ electrochemical measurements, secondly, to characterize the scale as to protectiveness, morphology and composition, and finally to generate hydrate-steel interaction data and evaluate its effects.

Materials

Carbon steel samples were cut from one section of an API 5L X65 oil & gas pipework. The final size of the tested samples was 10 mm x 10 mm x 3 mm. Chemical composition of the tested material are presented on Table 1.

Table 1
Chemical Composition of Tested Material in Wt%

Element	C	Si	P	S	Mo	Mn	Ni	Nb	V	Fe
Parent Metal	0.15	0.22	0.023	0.002	0.17	1.42	0.09	0.05	0.06	97.81

Prior to the experiment, the samples were wet polish with a P600 and P300 SiC paper, then rinsed with deionized (DI) water and thoroughly cleaned with ethanol and acetone to remove grease and impurities from its surface. Lastly, the samples were dried by flowing compressed air. Wires were soldered to the back of the specimens before embedding them in a non-conducting epoxy resin before immersion in the test solution. Additional samples were placed inside the reactor for further advance microscopy and hydrate adhesion measurements.

Brine Preparation

The brine preparation consisted of a 1 wt% NaCl solution. Before the start of the experiment the vessel was sealed, and brine solution was continuously bubbled with 100% CO_2 for a minimum of 8 h to achieve saturation in the water phase and reduce oxygen concentration. The flow of carbon dioxide continued throughout the experiment to maintain the CO_2 pressure at 1 bar.

CO_2 Corrosion Pre-conditioning Test

Electrochemical measurements were carried out in a modified three electrode reactor cell, consisting of a saturated Ag/AgCl reference electrode, a platinum counter electrode and the carbon steel sample as the working electrode. Due to the possibility of oxygen contamination inside the reactor a dissolved oxygen meter was placed in the cell to control oxygen concentration (below 0.03 ppm) inside the system. The experiments were performed at 80°C and atmospheric pressure, a ceramic heating plate with a temperature regulator was employed to assure constant heating during the experiment. The solution pH was maintained constant at 7.8 and controlled through the addition of 20 ml batches of 1M sodium carbonate solution throughout a burette without opening the system to prevent oxygen contamination. Inlet holes at the top lid of the cell were drilled and secured with Teflon tape for the placements of a pH meter, DO meter and a burette for the Na_2CO_3 addition.

Open circuit potential (OCP) and Linear Polarization (LP) measurements were performed using a single channel potentiostat. For the LP method, the polarization range was ± 5 mV versus the free corrosion potential (E_{corr}) and the B value needed to extract corrosion rates was 26 mV. The data gathered was processed and analyzed with the recorded electrode potentials mentioned in this study, and later converted to the standard hydrogen electrode SHE.