



# Adhesion force between cyclopentane hydrates and solid surface materials

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## ABSTRACT

The mechanisms by which hydrates deposit in a petroleum production line are related to pipeline surface properties, fluid composition and properties, and water cut. In this work, adhesion forces between cyclopentane hydrates and solid surfaces were investigated as a function of the solid material, the presence of water and the presence of petroleum acids in the oil phase. The influence of dissolved water on hydrate adhesion forces was also investigated.

The results show that the adhesion force between hydrates and solid surfaces was dependent on the surface material; solids with low surface free energy lead to the lowest adhesion forces. The adhesion force was strongly dependent on the presence of water in the system. When a water drop was deposited on the solid surface, the adhesion force between the hydrate and the solid surface was more than 10 times larger than hydrate–hydrate adhesion forces. The presence of a water-saturated oil phase also led to an increase in adhesion force between hydrate particles. Adhesion forces were highest when the solid surfaces are water-wet. Addition of petroleum acids to the oil phase drastically reduced adhesion forces.

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## 1. Introduction

Hydrate blockages during deepwater petroleum production is a major flow assurance problem [1]. Hydrates can form when sufficient amounts of gas and water mix under appropriate pressure and temperature conditions [1]. Hydrates resemble ice in physical appearance. The first evidence of hydrates in petroleum production lines was presented in 1934 by Hammerschmidt [2]. Since then, different strategies (e.g. addition of methanol or ethylene glycol to shift the hydrate phase boundary to higher pressures/lower temperatures) have been used to prevent hydrate formation in pipelines. However, these prevention strategies are expensive and/or environmentally unacceptable.

The modern strategy for hydrate mitigation has moved from total prevention (i.e. thermodynamic inhibition) to risk management [3], in which hydrates may be allowed to form as long as the hydrate formation does not lead to plugging. One key aspect leading to hydrate plugs is the agglomeration of hydrate particles. Reduction of the adhesion force between hydrates, or between hydrates and the pipeline wall, will likely reduce the plugging tendency of petroleum production systems.

This work seeks to understand the mechanisms of hydrate deposition on the pipeline wall. There is still some controversy within the

oil and gas industry as to whether hydrate deposition on the pipeline wall occurs in pipelines, though it has been suggested as a plugging mechanism, especially in gas-dominated systems [4].

A number of techniques have been developed in particle technology for investigating particle–particle or particle–surface adhesion, such as optical tweezers [5], micropipette aspiration [6,7], atomic force microscopy [8,9] and micromechanical force measurements [10–13].

Fan et al. [10] have shown, with micromanipulation, that the adhesion force between ice particles increases with particle size and contact time between the particles. Adhesion forces are known to decrease as the temperature is lowered from the freezing point of ice or hydrate particles [11]. Camargo et al. [14] have indicated that capillary attraction dominates hydrate agglomeration in the oil phase and that subsequent freezing of the bridge between hydrates strengthens the hydrate plug.

The present apparatus designed for measuring hydrate–hydrate adhesion force, originally developed by Yang et al. [11], is constantly being improved. Taylor et al. [12] and Dieker [13] describe the use of the micromechanical force apparatus to measure the adhesion force between hydrate particles. Several different hydrate formers have previously been investigated. The adhesion force between tetrahydrofuran (THF) hydrates and ethylene oxide (EtO) hydrates had values up to 100 mN/m [15]. Since these hydrate formers are miscible in water, the bulk fluid was a stoichiometric mixture of cyclic ether and water [15,16]. The adhesion forces between two ice particles on a water saturated decane phase were

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in the same order of magnitude as THF and EtO [16]. This indicated that presence of dispersed water significantly influences the measured adhesion forces. It was suggested that ice contamination increased the hydrate adhesion forces due to increased water available to form a capillary bridge between the particles [15,17]. Cyclopentane was chosen as a more suitable hydrate former because it is immiscible with water and has a hydrate equilibrium temperature at 7.7 °C, which allows measurements to be performed well above the ice point [15].

Nicholas et al. [18] measured adhesion forces between cyclopentane hydrates and a carbon steel surface, discovering that these adhesion forces are much lower than between two hydrate particles. When a water droplet is deposited between the hydrate and the carbon steel surface, the hydrate is unable to be detached from the solid surface, indicating that there are strong capillary forces present [19].

It is known that some crude oils contain natural compounds that can act as anti-agglomerants and reduce the plugging tendency [20]. Petroleum acids have been identified as one type of surface-active compounds that reduce the plugging tendency [21–26]. However, the type of acids present has been suggested to be more important than the amount of acids [26]. Bio-surfactants such as Rhamnolipid have also been shown to have anti-agglomerating properties [22,27,28].

## 2. Materials and methods

### 2.1. Chemicals

Cyclopentane (CyC5) forms Structure II hydrates below 7.7 °C at 1 bar [1], and is thus suitable for laboratory experiments without pressurized equipment. Similar to pipeline hydrate formers, CyC5 is immiscible in water. Due to the relatively high melting point of CyC5 hydrates, measurements can be made above the freezing point of water and assure that ice has not formed [13]. As such, CyC5 hydrates are used in the micromechanical force apparatus for these adhesion force experiments.

The continuous liquid phase used is pure cyclopentane (99% purity) from Sigma–Aldrich/ACROS ORGANICS and (97.28% purity) from OmniSolv. The primary contaminant in CyC5 (97%) is n-pentane. For the experiments with petroleum acids, 10 wt.% of a model oil is added to the pure cyclopentane bath. The model oil is petroleum ether (Mallinckrodt, boiling range 35–60 °C), containing 6000 ppm of commercial naphthenic acids from Sigma–Aldrich (batch number 1331432 11808153, acid number 230 g/mol). The naphthenic acids are produced by acid extraction of crude oils and comprise an isomeric mixture of carboxylic acids containing one or several saturated alicyclic rings [29]. The model oil is added to the pure cyclopentane phase after hydrate formation. Deionized water is used in the experiments to deposit water droplets on the solids.

For the experiments with two hydrate particles in a saturated water-in-decane solution, approximately 10 wt.% of a mixture of decane saturated with water was added to the cell after hydrate formation with pure CyC5. For the system with additional acids, the acids were added to the saturated water-in-decane mixture in a 10 wt.% concentration.

### 2.2. Solid surfaces

The solid surfaces investigated were carbon steel (also used by Nicholas et al. [18]), stainless steel (AISI 316 L), aluminum (EN AW 5052), brass (63% Cu, 37% Zn), glass and an epoxy coating (Epoxy-A). Most of these surfaces are described in a previous work focusing on the wettability of surfaces [30]. The surface free energies for these surface were determined to be 65 mJ/m<sup>2</sup> for glass, 64 ± 5 mJ/m<sup>2</sup> for stainless steel, 59 ± 1 mJ/m<sup>2</sup> for aluminum,

47 ± 5 mJ/m<sup>2</sup> for brass and 33 ± 1 mJ/m<sup>2</sup> for epoxy-A [30]. The surface free energy for carbon steel has been determined in this work to be 61 ± 5 mJ/m<sup>2</sup>. The surface free energy was determined by performing contact angle measurements with different probe fluids according to “the equation of state of interfacial tension” developed by Kwok and Neumann [31]. The probe fluids used were distilled water, a buffer solution, glycerol, formamide, and dimethyl sulfoxide (DMSO) [30].

### 2.3. Adhesion force measurements

The surfaces were thoroughly washed with a detergent (sodosil (RM 01) from Riedel-de Haën), and subsequently rinsed with distilled water, acetone, ethanol and cyclopentane. The surfaces were aged in cyclopentane for at least 24 h prior to the experiments. For experiments with acids, the surfaces were aged in the model oil for at least 48 h prior to the experiments.

The experimental set-up was the same as described by Nicholas et al. [18]. A water droplet was placed at the end of a glass fiber cantilever. The droplet was quenched in liquid nitrogen to create an ice particle and quickly submerged in cooled CyC5 at approximately –5 °C. The temperature of the CyC5 bath was slowly raised above freezing, allowing the ice particle to convert to a CyC5 hydrate particle. The cantilever with a solid surface sample was also placed in the CyC5 bath. The hydrate and solid surface were allowed to reach thermal equilibrium over the course of 30 min. When the pull-off experiments were performed, the hydrate particle appeared to be completely rigid.

Three to four separate experiments, each consisting of 40 pull-offs, were performed for each surface. The average and standard deviation was determined for each set of experiments. Averages of the 40 pull-offs are usually reported because variability between pull-off measurements is expected, due to slightly different alignment of the rough hydrate particle and the surface which leads to slightly different contact areas. The preload contact force (approximately 0.7 N) was held for approximately 10 s. A newly formed hydrate particle was used for each experiment. No trend has been found in the measured adhesion forces during the course of 40 pull-offs for hydrate–hydrate adhesion forces; (i.e. the forces measured were random and a previously-contacted hydrate surface did not seem to influence the subsequent adhesion forces). The same was found for the experiments with solid surfaces. However, when a water droplet was deposited onto the solid surface, the adhesion forces seemed to increase over the 40 pull-offs. This was likely caused by an increase in the hydrate particle size during the pull-offs as some water from the water droplet deposited on the solid hydrate surface and was converted to hydrate. The adhesive force,  $F$ , is calculated from Hooke's law:

$$F = k\delta \quad (1)$$

where  $k$  is the spring constant of the glass fiber and  $\delta$  is the displacement between solid surface and particle after detachment [32]. More details on the calibration of the spring constant can be found elsewhere [12].

The adhesion forces are normalized by the harmonic mean radius to account for different particle sizes. The harmonic mean radius,  $R^*$ , is given by

$$\frac{1}{R^*} = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

where  $R_1$  and  $R_2$  are the radii of the hydrate particle and solid sample, respectively. The radius of the solid sample was considered as infinite both with and without a water droplet deposited on the surface. The same approach was employed by Nicholas et al. [18] for the solid sample.



A liquid bridge is formed between the particle and solid surface according to the Capillary Bridge Theory [17]. The maximum attraction between the two solids is specified by the Laplace pressure. The Capillary Bridge Theory describes the attractive force as

$$\frac{F_{CBT}}{R^*} = 2\pi\gamma_{wo} \cos \theta \quad (3)$$

where  $\gamma_{wo}$  is the water–oil interfacial tension,  $\theta$  the water contact angle on the hydrate surface, and  $R^*$  is the harmonic mean radius as described in Eq. 2.

Four different sets of experiments were performed between solid surfaces and hydrates: solid surface–hydrate (S–H); solid–hydrate with addition of 10 wt.% model oil containing 6000 ppm acids (actual concentration 600 ppm) (S–H acids); solid–hydrate with a water droplet deposited on the solid surface prior to experiment (S–H water); and solid–hydrate with a water droplet on the surface and acids added to the oil phase (S–H water + acids). All measured forces were correlated to the surface free energy of the solids.

Adhesion force experiments between two CyC5 hydrates are analogous to hydrate–solid adhesion force measurements. Detailed information can be found in Taylor et al. [12] and Dieker et al. [15]. To investigate the influence of a water–saturated oil phase, two hydrate–hydrate adhesion force experiments were performed: hydrate–hydrate with addition of approximately 10 wt.% saturated water-in-decane mixture (H–H water) and hydrate–hydrate with addition of approximately 10 wt.% saturated water-in-decane mixture with 10 wt.% naphthenic acids (H–H water + acids).

The measured forces are compared to the adhesion forces measured for CyC5 hydrates (H–H) at the corresponding temperature, 3.2 °C (i.e.  $3.8 \pm 2.3$  mN/m [13]) and the adhesion forces measured between CyC5 hydrates when the same acids are added to the bulk phase (H–H acids) (i.e.  $1.3 \pm 0.4$  mN/m [33]). The error bars in hydrate–hydrate adhesion forces are the standard deviation from 40 pull-off measurements.

### 3. Results and discussion

#### 3.1. Adhesion force between dry solids and hydrates with and without acids

The adhesion forces for CyC5 hydrates on the different solid surfaces, characterized by their surface free energy, is shown in Fig. 1.

The adhesion force between solid and hydrate (S–H) increases with increasing surface free energy of the solids. This is consistent with the findings from Aspenes et al. [30], where it was shown that the adhesion energy between water and solids in the presence of oil increases with increasing surface free energy of the solids, corresponding to more water-wet surfaces.

However, the adhesion forces are approximately 10 times lower than hydrate–hydrate adhesion force [13] value given above. These S–H forces are in the same range as those measured by Nicholas et al. [18]. The low forces indicate that hydrates will not preferentially deposit on the pipeline wall when there is no free water in the system.

The data for glass shows a large standard deviation compared to the other surfaces, which may be due to a less stable surface consisting of a layer of hydroxyl groups that are readily influenced by small variations in its surroundings.

When acids are added to the system, the adhesion force between the hydrate and solid (S–H acids) was too low to be measured, independent of the solid surface, as shown with black triangles in Fig. 2. This could suggest that the acids adsorb to either the hydrate surface, to the solid surface, or to both, reducing the potential for a water layer to be formed between the solid and hydrate. These forces are compared to the hydrate–hydrate (H–H) adhesion forces; they are lower than hydrate–hydrate adhesion forces, as previously mentioned, and are also lower than hydrate–surface forces (without acids) from Fig. 1.

A comparison of the different forces is provided in Fig. 3, where the average force measured for the solids is used. The adhesion force between CyC5 hydrates with acids in the oil phase (H–H acids) is also shown [33]. The forces are highest for hydrates when there are no acids present. Naphthenic acids reduce adhesion forces for both solid surfaces and hydrates. However, the forces between CyC5 hydrates with acids in the system are higher than the adhesion forces between solid and hydrate without acids.

#### 3.2. Adhesion force between hydrate and solid surface with a deposited water drop

The adhesion forces between different solid surfaces and CyC5 hydrates were investigated with a water droplet deposited onto the surface, with the results shown in Fig. 4. The adhesion forces

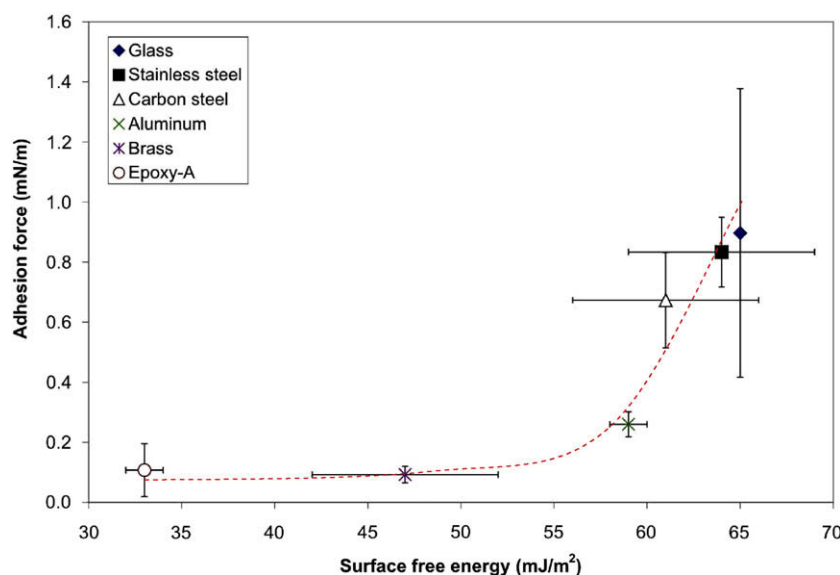
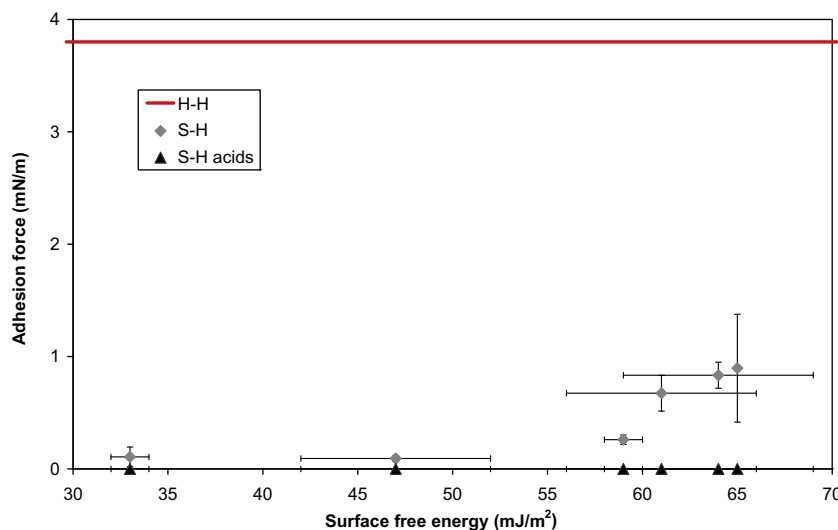
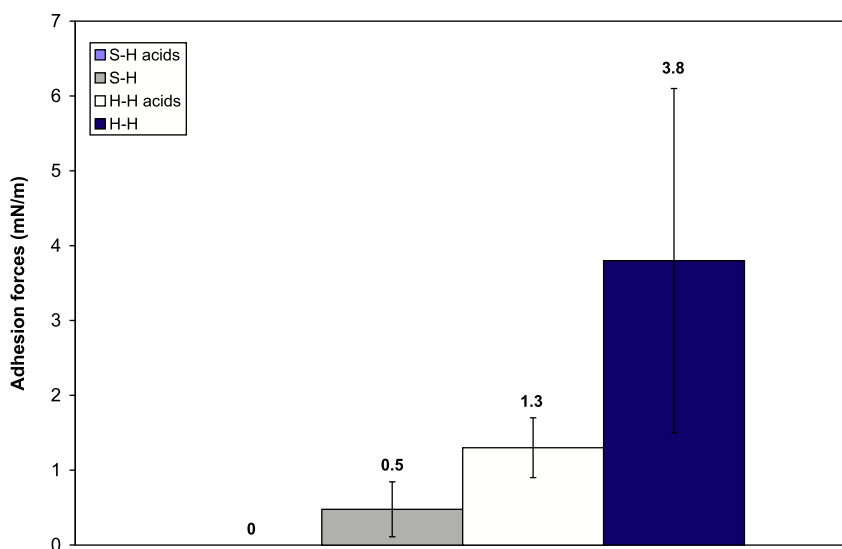


Fig. 1. Adhesion force measurements between CyC5 hydrates and different solid surfaces at 3.2 °C (4.5 °C sub-cooling) correlated to the surface free energy of the solids.





**Fig. 2.** Adhesion force measurements between two cyclopentane hydrates (H–H) [13], solid surfaces and cyclopentane hydrate (S–H), and solid surfaces and cyclopentane hydrate when the system contains 600 ppm of acids (S–H acids). All forces were measured at 3.2 °C (4.5 °C sub-cooling) and are correlated to the surface free energy of the solids.



**Fig. 3.** Comparison of average adhesion forces measured for CyC5 hydrates (H–H) [13], CyC5 hydrates with acids added (H–H acids) [33], solid surfaces and CyC5 hydrates (S–H) and solid surfaces and CyC5 hydrates with acids added (S–H acids). The adhesion forces for (S–H acids) were negligible or too low to be measured. All forces were measured at 3.2 °C (4.5 °C sub-cooling).

were more than 10 times larger than hydrate–hydrate adhesion forces ( $3.8 \pm 2.3$  mN/m).

The adhesion forces increase slightly with increasing surface free energy of the solids. The large forces may indicate that hydrates adhering to a water droplet on the pipeline wall will attach to the wall and lead to deposition.

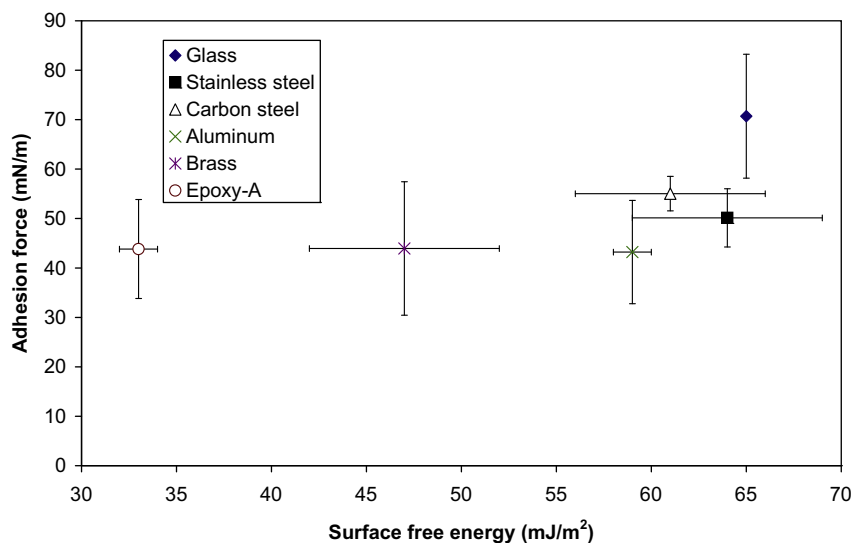
Fig. 5 shows a sample image of the measurements for a hydrate contacting with a water drop deposited onto the solid surface. As clearly seen in the image the water drop stretches before it detaches. It is also observed that some water deposits on the hydrate particle, which likely converts into solid hydrate.

When acids were added to the oil phase the forces decrease compared to the system without acids, as illustrated in Fig. 6. The forces are halved compared to systems without acids, but the forces are still considerably higher than hydrate–hydrate adhesion forces. No trend is observed correlating the measured forces to the surface free energy of the solids. The highest measured adhe-

sion force is still measured for glass, while the lowest measured adhesive forces are for aluminum and carbon steel. These lower forces suggests strong interactions of the solid surfaces with the naphthenic acids, as discussed by Aspenes et al. [30]. Aluminum and iron, in particular which is the most prominent component of carbon steel, are more reactive compared to the surface metals in some of the other alloys. The chemical reaction reduce the oxide layer on the solid surfaces more compared to the other solids leading to a lower interaction between the water and solid.

A different behavior of the water phase was observed for most of the experiments when acids were added to the system, as illustrated in Fig. 7. In these measurements, the water did not appear to wet the hydrate particles, in contrast to the measurements, without acids (Fig. 5). In some other cases where the water did wet the hydrate, the water drop appeared to stretch more, compared with the experiments without acids. The lower adhesive forces with acids can be attributed to several causes:

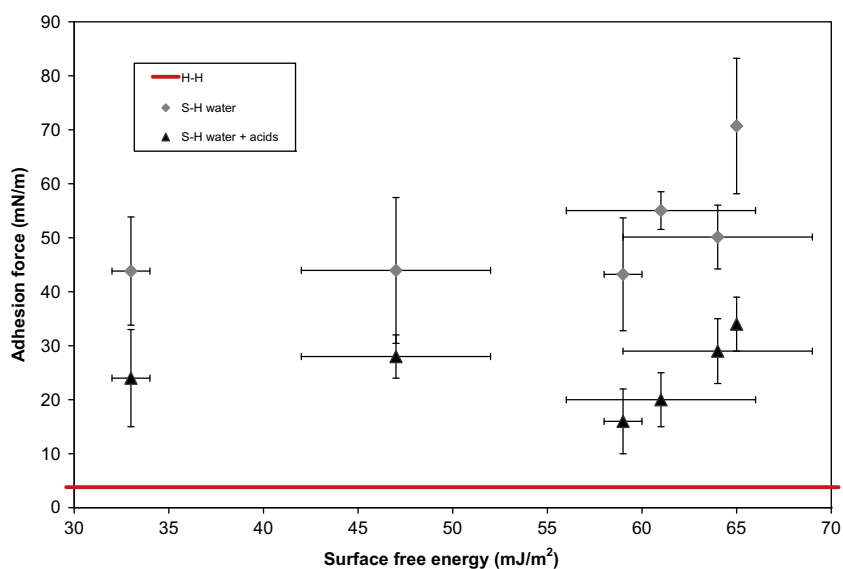




**Fig. 4.** Adhesion force measurements between CyC5 hydrates and different solids with a water droplet at the solid surface at 3.2 °C (4.5 °C sub-cooling) correlated to the surface free energy of the solids.



**Fig. 5.** General experimental image between hydrates and solid surfaces with a water drop deposited on the solid. The water is stretched until the hydrate particle detaches from the solid surface.



**Fig. 6.** Adhesion force measurements between CyC5 hydrates (H–H) [13], solid surfaces and CyC5 hydrates with a water droplet on the solid surface (S–H water) and between solid surfaces and CyC5 hydrates when the system contains 600 ppm of acids and with a water droplet on the surface (S–H water + acids). All forces were measured at 3.2 °C (4.5 °C sub-cooling) and are correlated to the surface free energy of the solids.

- (1) The wettability of both hydrate and solid has been changed due to adsorption of acids to the surfaces, creating more oil-wet surfaces.
- (2) The interfacial tension between the water and oil phase has been reduced.
- (3) The adhesion force of water to the solid has been reduced due to the combination of increased contact angle and

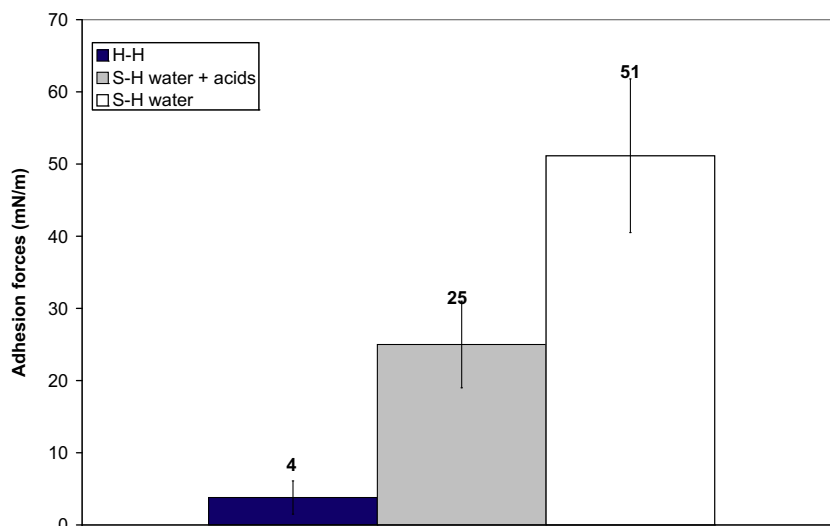
reduced interfacial tension between the oil and water phase, as given by the Young–Dupré equation [17].

The suggestions above are in agreement with those by Anklaam et al. [34], which proposed that anti-agglomerants reduce oil-water interfacial tension and increase water contact angle, in addition to reducing attraction due to adsorption of anti-agglomerants.





**Fig. 7.** When acids are present the water does not wet the hydrate as was seen in the systems without acids. The acids adsorbed to the hydrate surface reduce the water from bridging to the hydrate surface.



**Fig. 8.** Comparison of average adhesion forces measured for CyC5 hydrates (H–H) [13], solid surfaces and CyC5 hydrates when acids are added and a water drop is deposited on the solid (S–H water + acids), and solid surfaces and CyC5 hydrates when a water drop is deposited onto the solid surface (S–H water). All forces are measured at 4.5 °C sub-cooling.

A comparison of the average adhesive forces for the hydrate particles with the solid surfaces when water is added onto the solid surface is shown in Fig. 8. The adhesion force between CyC5 hydrate particles (H–H) is also compared, although this system does not contain water. The adhesive forces are much lower between CyC5 hydrates when there is no water present in the system. Because the adhesive forces are significant, if a hydrate particle comes in contact with a water saturated pipeline wall, it will most likely deposit on the wall.

### 3.2.1. Influence of water

The water droplets were deposited onto the solid surfaces 30 min prior to experimentation. Based on observation, the water was still in the aqueous phase during the experiments. The water droplets were approximately of the same volume ( $0.26 \pm 0.17$  ml) each time and the droplet size was not adjusted for in the calculated adhesion forces. No correlation was found between the measured adhesion force and the volume of the water used.

For systems without acids, the immersion depth of the hydrate particle in the water phase, i.e. the ratio of hydrate particle contained in the water phase (shown in the first picture in Fig. 5), was  $24 \pm 10\%$ . To clarify, a hydrate particle fully immersed in the water phase would have an immersion depth of 100%, whereas a non-wetted particle, as seen in Fig. 7, would have an immersion depth of 0%. The variation in immersion depth did not reflect on the measured adhesion forces for these systems. This is reasonable, since the hydrate surfaces should have a similar wettability in all the experiments with the same components present. For acid-containing systems, the water did not wet the particles in most of the experiments, as is shown in Fig. 7, and the immersion depth was

observed close to zero in these experiments. The radius of the hydrate particles used in these experiments was  $0.003 \pm 0.001$  m. It was previously suggested by Fotland and Askvik [35] that for hydrate particles nucleating and growing at oil/brine interfaces, their positioning at the interface is largely dominated by the wetting state of the system, as long as the particles have radius smaller than 0.01 m. Capillary force was suggested to dominate for particles with a radius smaller than 0.001 m [35]. In this present work, the hydrate particles are mechanically removed from the oil/water interface, overriding the natural force balance of the system, but the observed differences in immersion depth could be argued to be related to differences in wetting state and capillary forces in the systems.

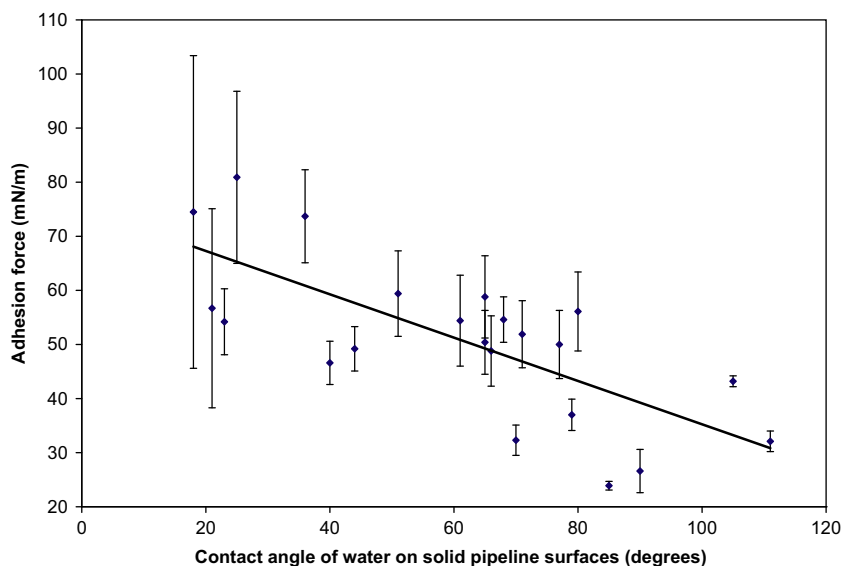
The contact angle measured for the water droplet on the solid surface in the experiments (as seen in Fig. 5) corresponds to the measured adhesion forces, as illustrated in Fig. 9. When the contact angle is large, the adhesion forces are low; when the contact angle is small, the adhesion forces are large.

### 3.3. Hydrate–hydrate adhesion forces with added water

The adhesion forces between two hydrate particles were investigated in the presence of a saturated water-in-decane solution. The addition of acids to the decane was also investigated. These results are presented in Fig. 10.

As seen in Fig. 10, the adhesion force between CyC5 hydrate particles is slightly higher for the system with decane saturated with water (H–H water) compared to hydrate–hydrate adhesion forces (H–H) in pure CyC5. As mentioned previously, increased water available to form a capillary bridge between the hydrate





**Fig. 9.** Correlation between measured adhesion forces between solid surfaces and cyclopentane hydrates when there is a water droplet on the surface (S–H water) and the contact angle of the water drop on the solid surface. Line is shown as a guide only.

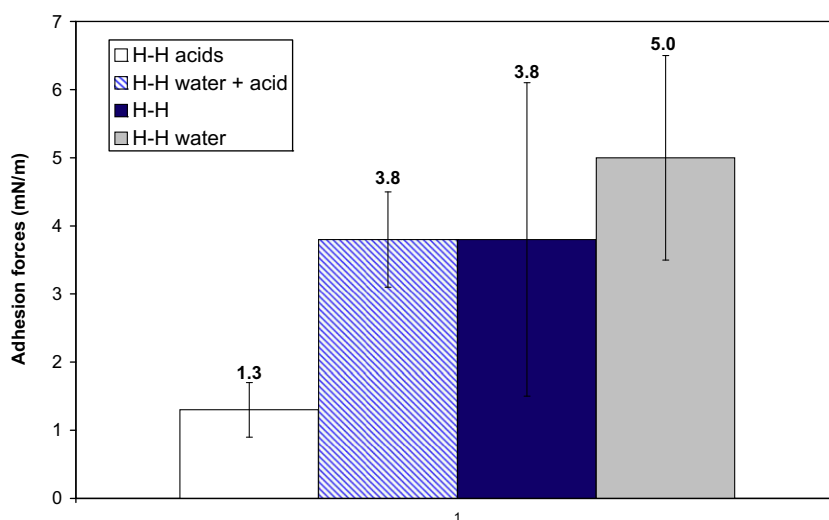
particles leads to an increase in measured adhesion forces [15,17]. It should be kept in mind that only a miniscule amount of water is soluble in pure CyC5; this differentiates CyC5 hydrates from THF and EtO hydrates, in which THF and EtO are completely miscible in water. Therefore, the lower adhesive forces for CyC5 hydrates can be attributed to two reasons: (i) water is immiscible in CyC5 and only tiny amounts of water were present and (ii) the small amount of water in the system tends to deposit onto the hydrate surface and form hydrate instead of creating a liquid bridge (the temperature is within the hydrate formation conditions for CyC5).

For the system with both decane saturated with water and acids (H–H water + acids), the adhesive forces measured are equivalent to the hydrate–hydrate adhesion forces (H–H), but lower than the system with decane saturated with water (H–H water) and higher than the system with acids (H–H acids). These results clearly indicate that the addition of acids leads to a reduction in

the adhesion forces and the presence of dissolved water in the oil phase leads to an increase in adhesion forces.

#### 4. Summary

The results show that the adhesion force between hydrates and solid surfaces is dependent on the surface material. Solids with low surface free energy lead to the lowest adhesion force. The adhesion force is very dependent on the presence of water in the system. When no free water is present, the adhesion force is approximately 10 times lower than hydrate–hydrate adhesion forces. When a water drop is deposited on the solid surface, the adhesion force between the surface and hydrate is more than 10 times larger than hydrate–hydrate adhesion forces, which suggests hydrate deposition on a water-wet pipeline wall may provide part of a mechanism for hydrate blockages. The presence of dissolved water also leads to an increase in adhesion force between hydrate particles.



**Fig. 10.** Comparison of adhesion forces measured for CyC5 hydrates with 10 wt.% addition of water saturated decane (H–H water), CyC5 hydrates (H–H) [13], CyC5 hydrates with 10 wt.% addition of water saturated decane containing 10 wt.% acids (H–H water + acids) and CyC5 hydrates with acids added (H–H acids) [33]. All forces were measured at 3.2 °C (4.5 °C sub-cooling).



Adhesion forces are dramatically reduced when petroleum acids are present in the continuous phase, both between solid surfaces and hydrate, and between hydrates. For a system without free water, the adhesion force between solid and hydrate with acids in the system was too low to be measured. The adhesion force is higher for a water-wet pipeline compared to an oil-wet pipeline.

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