Development of a Hydrate Inhibition Monitoring System by Integration of Acoustic Velocity and Electrical Conductivity Measurements

a report by

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Hydrate blockage is a major flow assurance issue in the oil and gas industry and inhibitor injection is probably the most popular technique in preventing its occurrence. The amount of inhibitor required is a function of various parameters, including the fluid composition, operating pressure and temperature, types of inhibitor, water production rate, inhibitor partition in hydrocarbon phases, seasonal changes and so on. Currently, inhibitors are injected upstream without any downstream monitoring. Here, we report the development of a novel downstream hydrate inhibition monitoring system. It determines both the inhibitor and salt concentrations, the hydrate phase boundary and therefore, the hydrate safety margin, by measuring the acoustic velocity and electrical conductivity of downstream aqueous samples. It can be used for any inhibition system containing methanol, monoethylene glycol, kinetic hydrate inhibitors, or anti-agglomerants in the presence of salts. Its performance has been extensively evaluated using synthetic samples and real produced water samples by the authors and leading oil companies.

The increasing demand for oil and natural gas has moved the oil industry to deepwater regions worldwide. The high pressure and low temperature conditions in such regions provide favourable conditions for gas hydrate formation. Gas hydrates, apart from waxes, asphaltene and scales, pose serious flow assurance problems to

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deepwater drilling, production and processing, impeding hydrocarbon flow by blocking valves, wellheads and flowlines. It is not unusual for hydrate plugs to form in inaccessible sections of pipelines in deepwater, which leads to the partial loss or complete suspension of gas and oil production.[1,2] In principle, there are two options for avoiding hydrate blockage with regard to the nature of gas hydrate formation.[3] One option is to remove one of the elements that is essential for hydrate formation. For example, the hydrocarbon fluids in a pipeline can be kept outside the hydrate stability zone (HSZ) by thermal insulation or external heating, or by lowering the operating pressure, or by dehydrating the system. However, these techniques might not be feasible and/or economical for some conditions, especially in offshore and deepwater environments, because of the high cost of insulation, heating and dehydration.[4]

Application of hydrate inhibitors is the second option to either prevent or reduce the risk of hydrate blockage. Hydrate inhibitors are divided into two categories: thermodynamic hydrate inhibitors (THIs) and low-dosage hydrate inhibitors (LDHIs). THIs, such as methanol (MeOH) and monoethylene glycol (MEG), are chemical additives that shift the hydrate phase boundary to a lower temperature and/or higher pressure by reducing the water activity. It is not unusual for concentrations of up to 60 mass% of MeOH or MEG in the aqueous phase to be needed for the THI to have a sufficient inhibitory effect. For high water-cut systems, the large volume of MeOH and MEG requires huge storage areas on the platform with limited space and/or a separate pipeline, which can result in significant increases in capital and operating expenditure, as well as negative impacts on the environment.[5,6] As a result, during the past two decades, LDHIs have been developed rapidly.[7] These include kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs).[8–12] It is generally believed that KHIs delay hydrate nucleation and hinder hydrate growth within a certain degree of subcooling, whereas AAs allow hydrate formation but prevent hydrate crystals from agglomeration (i.e. keep the hydrates transportable).

In current industrial practice, the amount of a hydrate inhibitor is determined based on the predicted or measured hydrate phase boundary for the specific fluid composition (gas or oil and water), water-cut, worst temperature and pressure conditions, and the estimated inhibitor loss to non-aqueous phases. In addition to the above, a safety factor is also considered when calculating the inhibitor dosage and/or pump rate. Consequently, an excessive dose of an inhibitor usually has to be applied to minimise the risk of hydrate blockages. This results in unnecessary additional cost and more severe environmental impacts, although other efforts have been made to optimise hydrate inhibitor injections.[13]

Recently, Tohidi et al.[14] reported a freezing point depression method for monitoring the degree of hydrate inhibition. It directly determines the hydrate phase boundary by measuring the freezing point depression

(FPD) of the downstream water samples regardless of the actual composition of those water samples. The FPD technique provides a simple way of optimising the dosage of a hydrate inhibitor. Here, we report the development of anther novel hydrate inhibition monitoring system. It is based on acoustic velocity and electrical conductivity measurements of an aqueous sample and determines not only the hydrate inhibitor and salt concentrations, but also the hydrate phase boundary and the hydrate safety margin, assuming that the hydrocarbon composition, temperature and pressure in the pipeline are known.

Methodology

The hydrate safety margin is defined as the temperature difference between the actual fluid temperature and the hydrate dissociation temperature under pipeline pressure. It was previously reported that the hydrate suppression temperature (i.e. dissociation temperature shift) can be determined by measuring the electrical conductivity of a water sample.[15] Henning et al.[16] developed an acoustic multi-sensor system for accurately measuring the concentrations of chemicals such as MeOH and MEG. However, in most cases, there are salts and at least another artificially added inhibitor in a pipeline. Sandengen and Kaasa[17] developed an empirical correlation that determines MEG concentration and NaCl concentration based on the measurements of density and electrical conductivity of the water samples under examination. However, the requirement of high accuracy of the density measurement reduces its applicability to real produced water samples, which usually contain solid particles (sands and clays) and oil droplets.

**Figure 1: Methodological Chart of the Hydrate Inhibition Monitoring System**
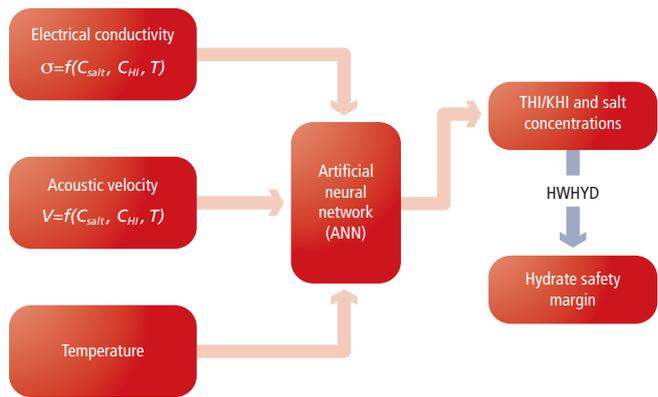
C = concentration; KHI = kinetic hydrate inhibitors; T = temperature; THI = thermodynamic hydrate inhibitor.

Velocity-conductivity Method

To be able to determine both the hydrate inhibitor and salt concentrations simultaneously, at least two physical properties need to be known. The electrical conductivity of liquid solutions depends on the concentration of ions and their activity. For an aqueous solution (usually electrolyte solutions) in a pipeline, its conductivity is proportional to the salt concentration. The activity of the ions will be affected by temperature and impurities, such as non-conductive chemical additives. Therefore, electrical conductivity could directly reflect the concentrations of chemicals such as salts, alcohols and hydrate inhibitors that are normally non-electrolytes. The second
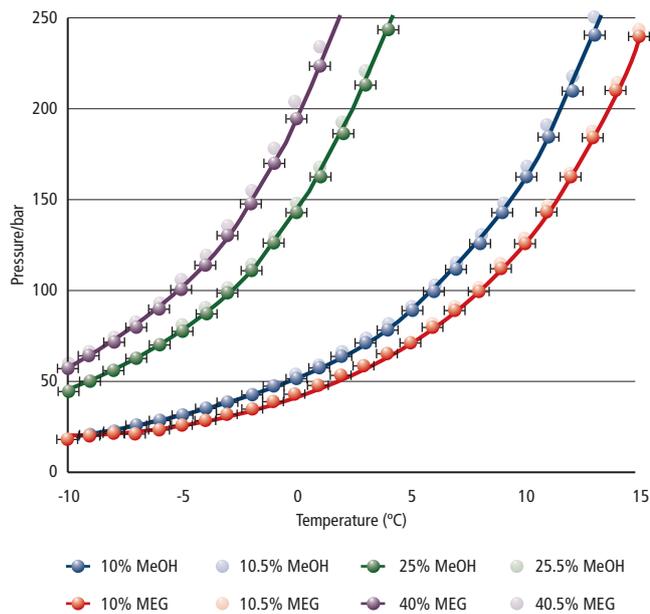
Error bars = ±0.4°C for the curves with 25 mass% MeOH and 40 mass% MEG; ±0.3°C for the curves with 10 mass% MeOH and 10 mass% MEG, in the presence of 5 mass% NaCl. MEG = monoethylene glycol; MeOH = methanol.

Figure 3: Evaluation of the Prototype C-V Device Using Two Real Produced Water Samples Containing Unknown Concentrations of Methanol, a Corrosion Inhibitor and Multi-component Salts in Addition to the Presence of Condensate
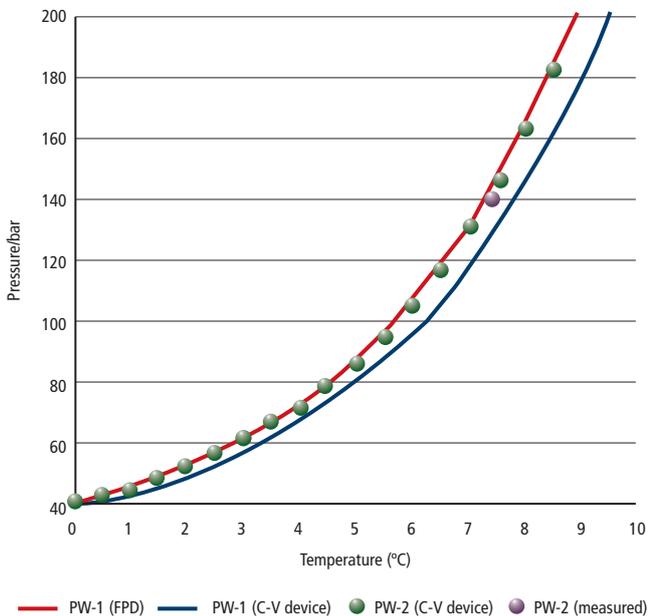
property must be independent of the electrical conductivity in that it is not correlated with the electrical conductivity in any way. Furthermore, it should be sensitive enough to identify changes in hydrate inhibitor and salt concentrations. Ideally, the technique should be robust for potential online application. Acoustic velocity (acoustic property) is such a property. It is well known that the sound propagation can be directly related to salt concentration.[18] In recent years, acoustic velocity has been successfully applied to investigate a variety of situations.[19–23] In addition, ultrasound can penetrate the

metal wall of pipelines and is not easily interfered with by unexpected sound waves, such as common sounds and low frequency vibration. Therefore, measuring ultrasound velocity can be an ideal technique for online applications.

Artificial Neural Network
Here, an artificial neural network (ANN) technique was used to determine the inhibitor and salt concentrations simultaneously using the measured electrical conductivity, acoustic velocity and temperature. An ANN is initially trained using a set of carefully measured data and then validated using another set of independent data. It does not require an analytical formula or understanding of the underlying physical relationships. Therefore, an ANN is especially useful for applications in which multi-parameter correlations are needed but where the interaction and relations between the measured parameters are not well known.[24,25]

Determination of Hydrate Phase Boundary (the Hydrate Safety Margin)
An in-house thermodynamic model, HWHYD,[26,27] was used to determine the hydrate phase boundary (the hydrate phase safety margin). To do so, the salt and inhibitor concentrations (as determined by the ANN) and the composition of the hydrocarbon fluids (oil or gas) are fed into the thermodynamic model.

Figure 1 shows the methodological chart of the hydrate inhibition monitoring system. The acoustic velocity and electrical conductivity are functions of salt concentration, inhibitor concentration and temperature. The velocity, conductivity and temperature of the aqueous sample under examination are measured and fed into a pre-trained/validated ANN correlation. The salt and inhibitor concentrations are determined by the ANN. By loading the composition of the hydrocarbon fluids, the hydrate phase boundary can be determined by the thermodynamic model HWHYD. The hydrate safety margin is determined by superimposing the pipeline temperature and pressure.

Prototype Device

Instrumentation
The C-V prototype device consists of four units: a sample cell, an electrical conductivity measurement unit, an ultrasonic test unit and a PC. The sample cell is a stainless steel container in which the aqueous sample under examination is added. The conductivity measurement unit includes a four-pole conductivity probe and a conductivity meter. One advantage of the four-pole probe is to minimise the effect of polarisation on electrical conductivity measurements, especially for high salinity solutions. The electrical conductivity and the sample temperature are measured by the conductivity meter and fed into the PC. The ultrasonic test unit is composed of two ultrasonic transducers, a pulser/receiver (P/R) and a high-speed data acquisition card (DAC). The two transducers are high-damp transducers with a central frequency of 1MHz. One acts as a transmitter, whereas the other acts as a receiver. The P/R sends a pulse that excites the transmitting transducer, generating an ultrasonic signal. The ultrasonic wave passes through the sample and is received by the receiving transducer. The received ultrasonic signal is sent back to the P/R. The P/R then amplifies the received signal and sends it to the DAC, where the analogue signal is converted into a digital signal and sent to the PC. Specially developed software is installed in the PC. The software integrates three programmes under

one graphic user interface. The first programme is coded for determining the travelling time of the acquired ultrasonic signal and the acoustic velocity (the travelling distance is known). Next, a trained ANN correlation programme is used to determine the salt and inhibitor concentrations using the measured acoustic velocity, the electrical conductivity and the sample temperature. Finally, the determined salt and inhibitor concentrations are fed into the thermodynamic model HWHYD, which determines the hydrate phase boundary once the oil or gas composition is loaded.

Evaluation

A prototype C-V device was developed based on the design described above. Three ANN correlations were initially trained, validated and tested for typical inhibition systems, including salt–MEG systems, salt–MeOH systems and salt–Luvicap EG systems. The prototype can measure salt and inhibitor concentrations and then determine the hydrate phase boundary and the hydrate safety margin given that the composition of the oil or gas and the temperature and pressure in the pipeline are known. The device was extensively evaluated using various solutions containing hydrate inhibitors and salts under both lab and field conditions.

Evaluation with Synthetic Solutions

The evaluation data were generated over a temperature range of 0–25°C for synthetic solutions that contained a wide range of salt (NaCl) and inhibitor concentrations. *Table 1* shows the evaluation results, the measurement ranges and maximum errors. In view of the practical application of the C-V device, it is important to understand how

Table 1: Evaluation Results for the Prototype C-V Device with Synthetic Solutions

Inhibition system	Range* (mass%)		Error (mass%)	
	Inhibitor	Salts	Inhibitor	Salts
MEG	0–60	0–10	0.5	0.2
MeOH	0–25	0–10	0.5	0.2
Luvicap EG®	0–2 (PVCap)	0–7	0.2	0.1

* The measurement ranges can be expanded by the dilution function of the prototype C-V device.
MEG = monoethylene glycol; MeOH = methanol.

Table 2: Results of Kinetic Hydrate Inhibitors Evaluation with Luvicap EG in Produced Water

Inhibition system	Salts (mass%)		PVCs (mass%)	
	Exp	C-V	Exp	C-V
Luvicap EG	4.97	4.83	1.20	1.19
Luvicap EG+SI+CI	4.97	4.86	1.10	1.10

the measurement errors influence the accuracy of the hydrate phase boundary that is determined by the C-V device. For simplicity, the largest shifts in hydrate phase boundary were predicted for methane with two different concentrations of MEG and MeOH in the presence of 5 mass% NaCl, corresponding to the maximum measurement errors of the alcohols. *Figure 2* illustrates the possible shifts in the hydrate phase boundary. It can be seen that, for pressures up to 250 bar, 0.5 mass% of the C-V prototype measurement errors in MEG and MeOH concentrations results in a shift of approximately 0.4°C for systems containing 25 mass% MeOH plus 5 mass% salt and 40 mass% MEG plus 5 mass% salt, approximately 0.3°C for the systems containing 10 mass% MeOH or MEG plus 5 mass% salt.

Development of a Hydrate Inhibition Monitoring System

Evaluation with Produced Water Solutions

Aqueous fluids in oil and gas pipelines usually contain multiple components of salts, such as NaCl, $CaCl_2$, KCl and so on, other contaminants, such as oil droplets and chemical additives, such as corrosion inhibitors (CIs) and scale inhibitors (SIs). To investigate the effect of these factors on the performance of the prototype C-V device, two real produced water samples were used. These samples contained unknown concentrations of MeOH, a CI, multi-component salts and some condensate. The MeOH and salt concentrations were measured using the C-V device. The measurement results showed that the concentrations of MeOH and salt in the first produced water sample (PW-1) were 2.9 and 22.2 mass%, respectively and 3 and 23 mass% in the second produced water sample (PW-2). The reliability of the C-V device measurements was checked in two ways. For PW-1, the hydrate phase boundary was determined by the C-V prototype for a typical natural gas (88.3mol% methane, 5.4mol% ethane, 1.5mol% propane, 0.2mol% isobutene, 0.3mol% normal butane, 0.1mol% isopentane, 0.09mol% normal pentane, 2.39mol% nitrogen and 1.72mol% carbon dioxide) and then compared with that determined by the flame photometric detector (FPD) method for the same natural gas. For PW-2, one hydrate dissociation point was experimentally measured at 7.4°C and 139.4 bar, which was compared with the hydrate phase boundary determined by the C-V device. *Figure 3* shows that the deviation between the C-V device (blue line) and the FPD (red line) is less than 0.5°C for pressures lower than 200 bar and that the measured dissociation point (purple points) is very close to the C-V results (green points). The required dosage of KHIs is relatively low by comparison to THIs such as MeOH and MEG, typically, 1–3 mass% in the aqueous phase. Therefore, it is particularly important to examine the possible influence of other chemical additives and multi-component salts on the accuracy of the C-V device for KHI systems. Produced water taken from a pipeline was used to examine the possible influences. It contained 4.97 mass% of multi-component salts including NaCl (3.11 mass%), $CaCl_2$ (0.16 mass%), KCl (0.34 mass%), $MgCl_2$ (0.33 mass%) and others (1.03 mass%). Two aqueous solutions were made from a KHI (Luvicap EG) and the produced water. One contained 1.2 mass% PVCap (3 mass% Luvicap EG) and the other 1.1 mass% PVCap (2.75 mass% Luvicap EG), 500ppm of a CI and 550ppm of a SI. *Table 2* shows that the presence of multi-component salts and the CI and SI did not have any measurable effect on the performance of the C-V device as long as NaCl was the dominant component.

Evaluation in Field Conditions

The prototype C-V device was also evaluated in field laboratories by leading oil companies, including Total in Pau, France; Statoil in Trondheim, Norway; Dolphin Energy (Total) in Qatar; Petronas in Nouakchott, Mauritania; NIGC (National Iranian Gas Company) in South Pars Gas Complex (SPGC) fields; and Champion Technology, Aberdeen, UK. The evaluation results from Dolphin Energy were reported by Lavallie et al.[28] and demonstrated that the C-V device is a simple and reliable device for monitoring KHI concentration compared with conventional chemical analysis methods. Recently, the C-V technique has been patented[29] and the prototype has been commercialised with a tradename HydraCHEK® by Hydrafact Ltd.

Conclusions

A novel hydrate inhibition monitoring system has been developed based on measurements of acoustic velocity and electrical conductivity of downstream aqueous samples. It determines concentrations of salt and inhibitor (both THIs and KHIs) and the hydrate phase boundary (hence, the hydrate safety margin) given that the gas or oil composition and the temperature and pressure in a pipeline are known. Results of the lab and field evaluations demonstrated that technique can be used for monitoring the hydrate safety margin and optimising inhibitor injection rates, thus improving the reliability and economics of oil and gas production and reducing their impacts on the environment. ■

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