



Successful Deployment of a Novel Hydrate Inhibition Monitoring System in a North Sea Gas Field.

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Abstract

Nuggets is a Northern North Sea lean gas reservoir with a methanol injection system for preventing gas hydrate problems. In general, the amount of methanol injected is calculated based on worst case conditions (temperature and pressure) and is related to gas composition, water content and the amount of inhibitor lost to non-aqueous phases.

To ensure this risk is monitored effectively, methanol content from a produced water sample on the platform is measured on a daily basis. A coulometric Karl Fischer (KF) technique is used as an indirect method of quantifying methanol, by determining the water content and assuming the remainder of the solution is methanol. Although this method is a well-known technique within the industry, there is limited opportunity to optimise hydrate inhibitor dosing rates completely as there is no measurement of the amount of salt present in the samples.

As a result of a joint industry project, a novel device based on measuring electrical conductivity and acoustic velocity (C-V) has been developed by Hydrafact Ltd and Heriot-Watt University to determine the hydrate safety margin, reduce the risk of hydrates and optimise inhibitor injection rates. The system quantifies the amount of inhibitors (i.e. salt, KHI, methanol, MEG, etc.) present in the aqueous phase which can then be used to determine the hydrate stability zone. Superimposing the operating conditions, the system can determine the hydrate safety margin, hence allowing an opportunity to optimise the inhibitor injection rates.

The device was deployed on the North Alwyn platform in April 2011 to determine the methanol and salt content in the produced water from the Nuggets field.

The results of the trial are detailed in this communication.

Keywords: Gas hydrate; Flow assurance; Hydrate phase boundary; Hydrate inhibition; Acoustic velocity; Electrical conductivity, Hydrate monitoring

1. Introduction

The oil & gas industry faces increasingly difficult challenges related to hydrate deposits in pipelines as hydrates often form at inaccessible locations. Pressure and temperature conditions favourable for gas hydrate formation are commonly encountered during winter in onshore and in shallow water offshore fields, and regularly in deepwater fields offshore. Hydrates can not only form in transfer lines and tiebacks, but they can also form across gas expansion valves (rapid cooling) and during drilling following a gas kick. One of the problems other than blockage is the movement of the hydrate plugs in the pipeline at high velocity which can cause rupture in the pipeline. Any blockage in an oil/gas pipeline due to hydrate is a serious threat to the economic and cost effective strategy and also personnel safety.

Gas hydrate flow assurance methods can be categorised into two main groups as follows:

- Avoiding hydrate formation
- Controlling hydrate formation by means of Low Dosage Hydrate Inhibitors (LDHIs)

The traditional gas hydrate flow assurance methods rely on removing or modifying one of the essential elements required for hydrate formation, i.e. water or conditions suitable for hydrate formation. Hydrate formation can be avoided by dehydration, which reduces the amount of water available for hydrate formation, or by keeping operating pressure and temperature outside the hydrate formation region. The latter method is based on shifting the hydrate phase boundary outside the operating conditions (pressure and temperature of production facility) during normal production. This can be achieved by either pushing the hydrate phase boundary of the system to lower temperatures by adding chemical compounds such as thermodynamic inhibitors, e.g. methanol and mono ethylene glycol (MEG), or by shifting the operating line to higher temperatures by heating and/or insulating the flow line. It may also be possible to shift the operating conditions outside the hydrate stability zone by controlling the operation pressure (though this option is normally used for hydrate plug dissociation by depressurisation).

New methods used in gas hydrate flow assurance are based on delaying / inhibiting hydrate formation by means of kinetic hydrate inhibitors (KHIs) and/or preventing hydrate agglomeration by controlling solid hydrate particle sizes by means of Anti-Agglomerants (AAs).

However, thermodynamic inhibitor (methanol or glycols) injection is probably the most popular technique in preventing gas hydrate blockage. The amount of required inhibitor is usually measured in the laboratory or predicted using thermodynamic models for the specific fluid composition, water-cut and worst operating conditions. The loss of inhibitor to the hydrocarbon phases and a safety factor should be considered in determining the required inhibitor dosage. Despite considering a safety factor, hydrate blockages occur due to changes in the system conditions, equipment malfunction or human error. This problem can be addressed by controlling the inhibitor concentration measured downstream. Recently, Tohidi et al. (2009)¹ reported a freezing point depression method for monitoring degree of hydrate inhibition. It directly determines the hydrate phase boundary of the system by measuring the freezing point depression of the downstream aqueous samples; however, it cannot determine the concentration of the inhibitor and/or salt in the aqueous phase. The technique reported in this paper is another novel hydrate inhibition monitoring system developed to determine not only the hydrate phase

boundary of the system, but also the concentration of the hydrate inhibitor and salt in aqueous phase.

The Nuggets development consists of five gas bearing, Eocene accumulations located between 40 and 70 kilometres south of the North Alwyn installation in the UK sector of the North Sea. The Nuggets reservoir is located at a depth of approximately 1650m. Well fluids from the Nuggets development are produced via subsea wells and tied back to the North Alwyn B Platform (NAB). The development is made up of five subsea production wells, NGA, NGB, NGC, NGD & NGE. A common manifold, N1 collects fluids from NGA and NGB plus a series connection to the N3 manifold, which collects fluids from NGC, NGD & NGE wells.

Table1: Hydrocarbon Composition

Component	Mass %
N ₂	1.34
CO ₂	0.46
C ₁	97.77
C ₂	0.16
C ₃	0.00
iC ₄	0.02
nC ₄	0.02
iC ₅	0.02
C ₆₊	0.21

Table 2: Water Composition

Ion	Formation Water (mg/L)
Na ⁺	17,500
K ⁺	144
Ca ²⁺	1,483
Mg ²⁺	402
Ba ²⁺	124
Sr ²⁺	164
Fe ²⁺	0.5
Cl ⁻	28,712
SO ₄ ²⁻	0
HCO ₃ ⁻	308

The hydrocarbon produced from the five wells is a lean gas, as shown in Table 1. The water produced from the five wells varies from condensed water to formation water resulting in variable water salinity at surface. The water composition shows a degree of variability as operating conditions and well behaviour changes.

As the operating conditions (Maximum Pressure = 150 barg and Minimum Temperature = 4 °C) are within the hydrate formation zone there is a requirement to continuously inject methanol in order to prevent hydrate formation in the subsea system.

In order to effectively manage the treatment process it is necessary to sample the produced water and monitor the methanol concentration and brine composition. A daily produced water sample is taken and analysed by KF as an indirect method of methanol determination, by measuring the water content of the sample and assuming the remainder of the solution is methanol. The chloride content of the produced water sample is also measured, by Mohr titration, to give an indication of the salinity. The Mohr titration uses silver nitrate solution to react with the chloride, forming insoluble silver chloride. Samples are sent onshore for ion analysis to track the split of condensed and formation water being produced.

2. Methodology and Prototype Device

The integrated C-V method is based on the measurements of the electrical conductivity and acoustic velocity of the aqueous fluid under examination.

Electrical conductivity of aqueous fluids in pipelines depends on the concentration and activity of ions in the fluids. Pipeline fluids are typically electrolyte solutions where ion concentration is proportional to salt concentration. Ion activity is strongly related to temperature, and impurities like non-electrolyte chemical additives. Therefore, electrical conductivity can be used as a parameter directly reflecting the concentrations of salts and hydrate inhibitors that are normally non-electrolytes.

Acoustic velocity is measured and used together with the measured conductivity for determining both inhibitor and salt concentrations in aqueous pipeline fluids simultaneously. It is well known that sound velocity in fluids is directly related to the fluid density, and the fluid density depends on the concentrations of salts and chemical additives (Clay and Medwin, 1977)². As a result, acoustic velocity has been successfully used to investigate a variety of solutions and composition of binary gas mixtures (Jerie et al., 2004; Vibhu et al., 2004; Goodenough et al. 2005; Vyas et al. 2006)³⁻⁶. Sandengen and Kaasa (2006)⁸ presented a successful application of a technique combining density and conductivity measurements for determination of both monoethylene glycol concentration and salt concentrations. However, their method requires a high accuracy of 0.0005 g/cm³ in density measurement, which significantly limits its feasibility for pipeline fluid conditions, especially for online application.

Artificial neural network (ANN) correlations are widely used to correlate such parameters. It is well known that ANN is a useful approach for correlating a limited quantity of experimental data with required variables in some specific cases where there is a temporary lack of fundamental understanding of the necessary relationship between the variables under examination, or the analytical or empirical correlation to be applied is unconventional. ANN is also even more powerful for multi-parameter correlations (Sundgren et al. 1991)⁷. By means of ANN correlations the concentrations of thermodynamics inhibitors/KHI/AA and salts can be determined simultaneously using the measured electrical conductivity, acoustic velocity, and temperature.

An in-house thermodynamic model called HYDRAFLASH (Tohidi et al.; 1995 and 1996)⁹⁻¹⁰ was employed to determine the hydrate phase boundary. For this purpose, the salt and inhibitor concentrations (as determined by the ANN), and the composition of the hydrocarbon fluids are fed into the thermodynamic model.

The C-V prototype device consists of the following units: sample cell, electrical conductivity measurement unit, ultrasonic test unit and a computer. The sample cell is a stainless steel container in which the aqueous sample under examination is added. The conductivity measurement unit includes a 4-pole conductivity probe and a conductivity meter. The ultrasonic test unit is composed of two ultrasonic transducers, a pulser/receiver and a high-speed data acquisition card. A specific programme has been developed to calculate the sound velocity (by analysing wave data) and to gather electrical conductivity and temperature data and feed them to the ANN. In the other words, this programme integrates the measured data and the hydrate thermodynamic model/correlation and shows the degree of the inhibition of the system. Figure 1 shows a graphical demonstration of the prototype.

The C-V device was developed within a JIP at the Heriot Watt University (HWU) of Edinburgh and is now commercialised by HYDRAFACT, a spin-out company of HWU.

The device has previously been field trialled for the determination of KHI on the Dolphin field in Qatar and was shown to be both reliable and accurate (Lavallie et al., 2009)¹¹.

In this paper, it is field tested for Methanol and salinity monitoring.

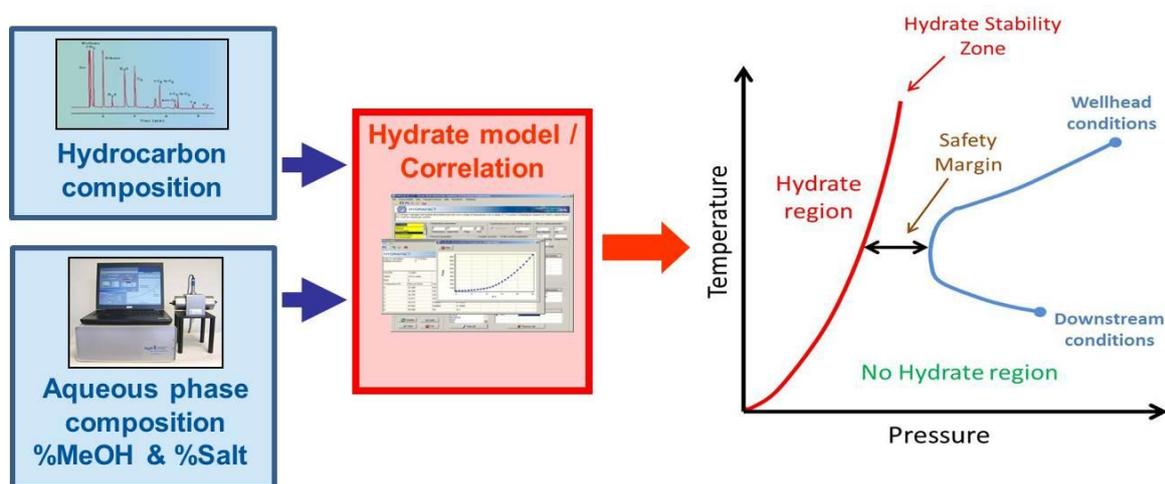


Figure 1. Integrated conductivity-velocity (C-V) device principle

3. Results and Discussions

The device was extensively evaluated using various solutions containing hydrate inhibitors and salts in both laboratory and field conditions. The device was evaluated over a temperature range of 0 to 25 °C, salt (NaCl) concentration of 0 to 10 mass% and MEG concentration of 0 to 60 mass%. The results show 0.5 mass% deviation for MEG and 0.2 mass% for NaCl. The developed prototype was also tested for a system containing 0 to 10 mass% NaCl and 0 to 25 mass% Methanol. The results show the same accuracy as MEG-NaCl system. To evaluate applicability of the device for KHI-salt systems, systems containing 0 to 2 mass% of Luvicap-EG and 0 to 7 mass% NaCl have been tested. The results show 0.2 mass% deviation for Luvicap EG and 0.1 mass% deviation for NaCl.

After successful laboratory evaluation, the developed C-V prototype was tested on North Alwyn alongside the existing monitoring techniques.

As mentioned the incumbent technique for determination of methanol concentration uses the coulometric Karl-Fischer technique. After homogenising the sample, a weighed aliquot is injected into the apparatus. The iodine required for the Karl Fischer reaction, is generated coulometrically at the anode, and the reaction progresses until all the water has been titrated. From the reaction stoichiometry, one mole of iodine reacts with one mole of water, and the quantity of water is proportional to the integrated current required to produce the iodine. Excess iodine is detected by an electrometric detector and the titration is terminated. (An alternating current is applied to a pair of indicator electrodes, and the alternating voltage thus generated decreases drastically if traces of iodine are present.) As large quantities (relative to the intended use) of water are titrated the reaction can take a considerable length of

time to fully titrate, resulting in the requirement to exchange the solution on a regular basis.

The chloride content of the produced water sample is measured by the Mohr Titration. The Mohr titration uses silver nitrate solution to react with the chloride, forming insoluble silver chloride. When all the chloride has been used in this manner, any excess silver titrant added reacts with the potassium chromate indicator, to give a brick red complex. The titration should ideally be carried out between pH 6.5 and 9, as below this pH, the indicator is hydrolysed, and above this range, the silver may react with hydroxide ions. Samples are also sent onshore for ion analysis to track the water breakthrough of the field. Onshore analysis is for full water composition and this is done by ICP (Inductively Coupled Plasma Emission Spectroscopy.)

Both of the above methods rely on the use of chemicals to determine the concentration of methanol and chloride. While the volumes of chemicals required are small any technique which negates this requirement offers an occupational health improvement for those working in the laboratory. The time required to prepare and run both techniques is significant (particularly when the time to exchange Karl Fischer solutions is considered) when compared to the C-V device, affording the laboratory technician time to work on other activities.

3.1 Pre-evaluation of the C-V device in Lab

Before evaluating the C-V device in the field, the device was lab-tested using actual produced water from the field. These results were confirmed using various techniques including gravity method, freezing point method and FTIR (Fourier Transform Infrared). Additionally, the device was tested and the results validated against known samples. These results are presented in Table 3 below.

Table 3. Pre-evaluation results of the C-V device in the lab (mass %)

Solution	Concentration	C-V	Error
NaCl	4.5	4.57	0.07
Methanol	7.5	7.41	0.09
NaCl	3.0	3.00	0.0
Methanol	10.0	10.1	0.1
NaCl	7.0	7.1	0.1
Methanol	15.0	14.96	-0.04
Field Samples	FTIR/Gravity/ Freezing point	C-V	Deviation
NaCl	4.6	4.53	0.07
Methanol	7.6	7.47	0.13
NaCl	4.38	4.45	0.07
Methanol	7.7	7.61	0.09

As can be seen from the results, the maximum deviation observed is around 0.1 mass% in both NaCl and methanol concentration and were in close agreement with the other methods.

3.2 Field evaluation of the C-V device in Nuggets Field

The following figures show the field data obtained over a 7 month period, from May 2011 to November 2011, this includes the planned summer shutdown which took place between 4th June and 21st July. Figure 2 shows the comparison of methanol content measured by KF and by the CV device. Figure 3 shows the comparison between the salt content measured by the CV device and the TDS measured onshore.

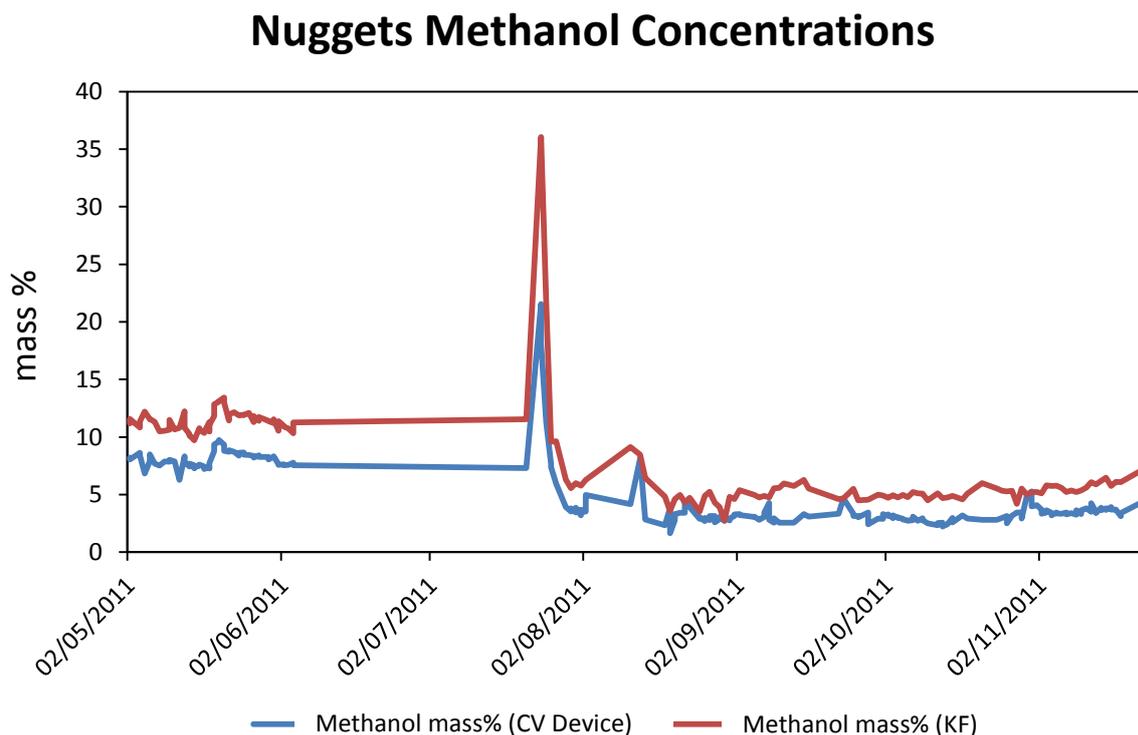


Figure 2. Comparison of methanol concentrations measured by KF and the CV device.

The data presented in Figure 2 in the period up to the shutdown on 4th June shows a consistent trend between both measuring methods. The difference between the two methods is due to the error when measuring methanol by KF in the presence of salt. The large spike in methanol concentrations on start up is due to the injection of additional methanol while starting production after the shut down and was observed by both methods. After the shutdown the target methanol concentration was reduced and both methods followed this trend consistently through the trial period.

The data presented in Figure 3 shows a consistent trend through the entire trial period for the salt content measured by the CV device in the field laboratory when compared to the salinity determined by the samples shipped onshore for ion analysis.

Nuggets Salt Concentrations

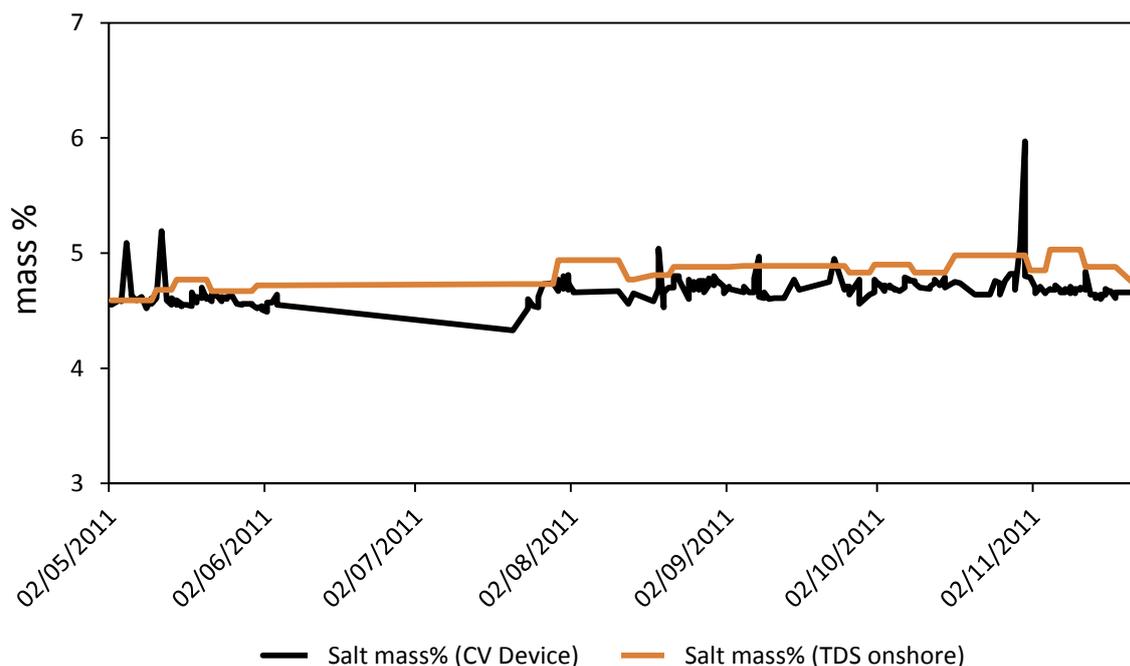


Figure 3. Comparison of Salt concentrations.

3.3 Predicting hydrate phase boundary and optimization suggestions

Based on these results and the provided field data (gas composition, pressure and temperature profile), the C-V device has been used to predict the hydrate phase boundary. Figure 4 below shows the predicted hydrate phase boundary.

In this figure, four hydrate phase boundaries have been plotted.

1. The red dotted curve represents the hydrate phase boundary for deionized water.
2. The orange dashed curve shows the actual hydrate phase boundary for the system determined using the C-V device. This curve indicates that the system with its current methanol injection rate is in the hydrate safe zone.
3. The blue solid curve is the predicted phase boundary curve based on the concentrations determined using the KF method. As expected, this hydrate phase boundary has been shifted to lower temperatures (left side) due to the error in methanol concentration measurements using the KF technique. In other words, this system mistakenly shows that the system is safer than it actually is. For example, if the operating temperature falls to 2°C or below, the system will be inside the hydrate risk zone while the KF method shows it is in the safe zone. As can be seen from this figure, the operating condition is about 4°C outside hydrate phase boundary with the current methanol injection rate meaning that the system is safe, possibly over inhibited.
4. The green dashed curve shows the new phase boundary with the proposed optimised injection rate.

The black points are the pipeline temperature and pressure operating conditions. As can be seen, the system is in the hydrate risk zone in the absence of methanol and salt. When operating the field a +3°C margin is also added to the hydrate curves.

This is done not to take into account the accuracy of thermodynamic models, but to account for the uncertainty of the thermal calculations of flow models like OLGA or LEDA. While the T&P values are known at certain locations within the system i.e. well-heads, manifold and reception facilities they are not defined in between and this uncertainty carries risk especially during transient flow conditions.

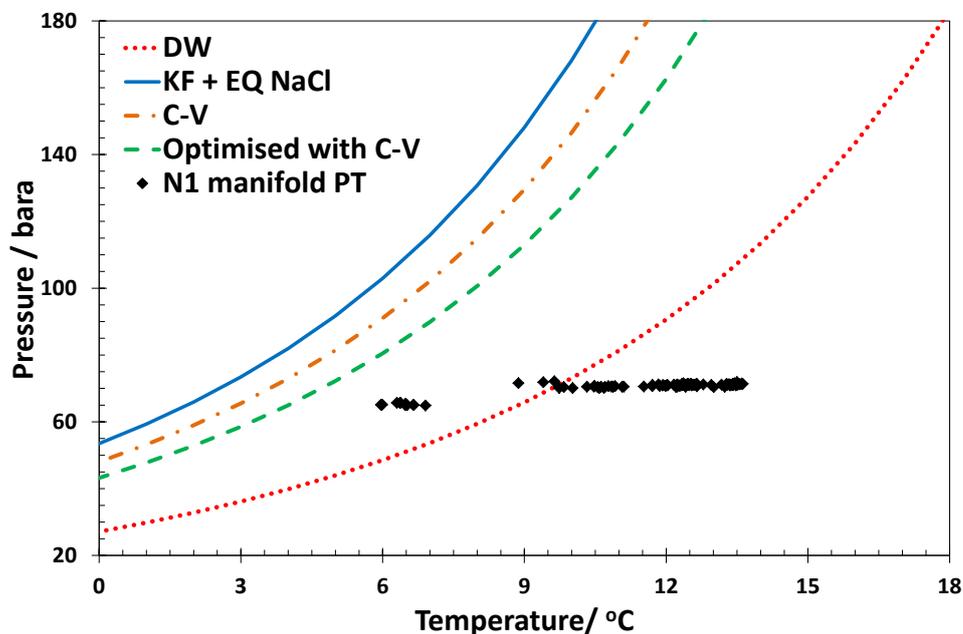


Figure 4. Comparison of C-V and Karl-Fischer measurements during the evaluation time.

4. Conclusions

This paper presents Nuggets field data for a novel laboratory technique which monitors the methanol and salt concentrations in produced waters. The C-V technique combines the measurements of water conductivity and ultrasonic sound velocity with analysis by Artificial Neural Network (ANN). This technique has been compared to those usually applied for methanol and salinity. Both techniques have been used in parallel to field prove the technique over an extended period. Results show that the C-V technique reported more accurate measurements of methanol and allowed for real time determination of salt content in the field laboratory. Furthermore the C-V technique was faster compared to manual techniques and eliminated the requirement for chemical reagents. The C-V technique has allowed North Alwyn to rapidly monitor the degree of hydrate inhibition present in the Nuggets produced waters at reception facilities, leading to an increased confidence in optimising the hydrate treatment.

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