COMPATIBILITIES AND INTERACTIONS

SECTION B13
HYDRATE INHIBITION

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B13.1 Introduction

Gas hydrates (or clathrate hydrates) are ice-like crystalline solids formed from mixtures of water and natural gas, usually methane. The water (host) molecules, upon hydrogen bonding, form lattice structures with several interstitial cavities. The guest gas molecules occupy the lattice cavities, and when a minimum number of cavities are filled, the crystalline structure becomes stable and solid gas hydrates form, even at temperatures well above the melting point of water ice. The schematic in Figure 1 shows a single hydrate cage with a single gas molecule.
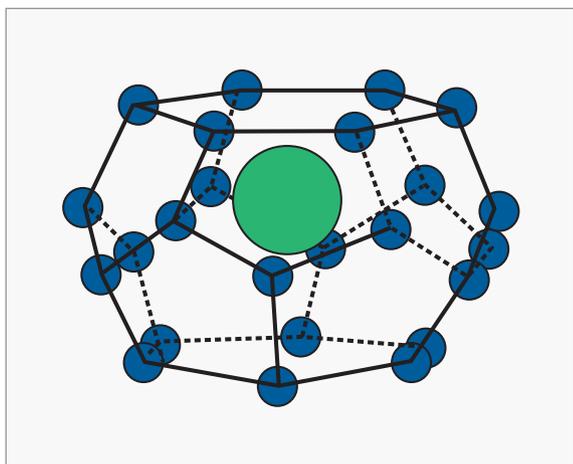

Figure 1 Gas hydrate. The black lines represent hydrogen, the blue spheres oxygen, and the green sphere in the middle is a methane gas molecule.

Gas hydrates form where pressure, temperature, gas saturation, and local chemical conditions combine to make them stable. In oilfield operations, especially in deep-water, gas hydrate formation has serious economic and safety impact. Low seabed temperatures combined with high fluid pressures promote formation of gas hydrates in both well construction and production.

During drilling and completion with water-based fluids gas hydrates can form in the event of a gas kick. This can cause serious well safety and control problems during containment of the kick. Two cases have been reported in the literature where losses in rig time were 70 and 50 days [1].

The formation of gas hydrates in water-based drilling and completion fluids can create significant problems [1]:

1. Gas hydrates can form in the drill string, completion string, drilling and production annuli, blow-out preventer (BOP) stack, choke, and kill lines. This can result in potentially hazardous conditions,

i.e. flow blockage, hindrance to drill string movement, loss of circulation, and even abandonment of the well.

2. As gas hydrates consist of more than 85 % water, their formation could remove significant amounts of water from the drilling fluids, which changes fluid properties. This could result in salt precipitation, an increase in fluid weight, or the formation of a solid plug.

Hydrate formation depends on composition of the kick gas as well as the pressure and temperature of the system. It also depends on the concentration and type of water-soluble salt(s) dissolved in the fluid. As a rule of thumb, the inhibition effect of a traditional saturated salt (*NaCl*) mud or brine is inadequate for avoiding hydrate formation in water depths greater than 1,000 m. Therefore a combination of salts and chemical inhibitors, which can provide the required inhibition, is frequently used to deter hydrate formation.

When using water-based well construction fluids it is therefore vital that they have adequate hydrate inhibition properties. These could be inherent properties of the fluid or gained by additives.

B13.2 Hydrate inhibition by formate brines

Concentrated brines are known to be very good inhibitors for gas hydrate formation. They are so-called inert inhibitors, i.e. inhibitors that do not enter the gas hydrate phase, but influence the thermodynamic equilibrium through their effect on water activity. The brines' ions interact with the dipoles of water molecules with a much stronger bond than the van der Waals forces, which cause clustering around apolar solute molecules [2]. This clustering also causes a decrease in the solubility of potential hydrate molecules in the water (a phenomenon known as 'salting-out') as a secondary effect. Both of these effects combine to require substantially more cooling to overcome the structural changes that cause hydrates to form.

The effect of brines on hydrate formation temperature can be estimated using their freezing-point depression data. Formate brines are known to have substantial effects on the freezing point of water (Section A3, Water Activity and Colligative Properties and Section A5, Crystallization Temperature).

There is a simple rule of thumb for predicting the brine's effect on hydrate formation temperature for any natural gas [3]:

$$HET_{BRINE} = HET_{WATER} - 0.8 \times FPD_{BRINE} \qquad (1)$$

where

HET_{BRINE} = Hydrate equilibrium temperature for brine
HET_{WATER} = Hydrate equilibrium temperature for water
FPD_{BRINE} = Freezing-point depression for brine

This simple rule of thumb is very helpful in predicting HET (hydrate equilibrium temperature) in low-concentration brines where freezing-point data is available, i.e. the left side of single-salt TCT curves in Section A5, Crystallization Temperature. In higher concentration brines, where no freezing-point data exist (the right side of the TCT curve), there is no simple way of estimating HET. In blends of concentrated brines, such as cesium / potassium formate brine blends, no freezing-point data is available as the whole TCT curve represents crystallization temperature.

Consequently, there is no simple way to predict HET for concentrated brines. We do, however, know that one factor influencing HET is water activity. Brines with low water activity can therefore be assumed to have good hydrate-inhibiting properties.

Divalent halide brines have been used as gas hydrate inhibitors for many years, and models have been developed to predict HET in these brines as a function of brine concentration and thermodynamic properties (pressure, temperature, and gas composition). An example of such hydrate prediction packages is WHyP from Intertek Westport Technology Center in Houston, USA.

Concentrated formate brines, due to their very low water activities, are expected to be just as good hydrate inhibitors as divalent halide brines. The water activity of concentrated cesium formate brine, concentrated potassium formate brine, and their blends is as low as 0.3 (see Section A3, Water Activity and Colligative Properties).

In spite of the increased popularity of formate brines as well construction fluids over the past ten years, no hydrate prediction model has yet been developed for these brines.

A limited number of measured hydrate equilibrium temperatures in formate brines are available and presented here.

B13.3 HET measurements in formate brines

13.3.1 HET measurements with GoM gas

Two studies have been carried out by Intertek Westport Technology Center, Houston, USA to measure the inhibitive effect of formate brines on gas hydrate formation with Green Canyon gas [4][5], a typical gas from the Gulf of Mexico (GoM).

High-density cesium and potassium formate brines

Samples of buffered concentrated potassium formate brine (1.560 g/cm^3 / 13.0 lb/gal) and cesium formate brine (2.198 g/cm^3 / 18.3 lb/gal) were tested at Intertek Westport Technology Center [4]. These fluids were evaluated for hydrate equilibrium temperatures (HETs) in a high-pressure stirring autoclave system at constant pressure conditions of 10,000, 7,000, 4,000, and 1,000 psig using a Green Canyon gas mixture. The composition of the Green Canyon gas used for this study is shown in Table 1.

In order to compare the performance of the formate brines with well-known and respected hydrate inhibitors, hydrate equilibrium curves were simulated using Westport's Hydrate Prediction modeling software (WHyP) for water, 30 %w/w $CaCl_2$, 32 %w/w $ZnBr_2$, 40 %w/w $CaBr_2$, 40 %w/w $MeOH$, and 40 %w/w MEG.

Measured hydrate equilibrium curves for concentrated potassium and cesium formate brines are plotted in Figure 2 along with simulated curves for well-known hydrate inhibitors. Results obtained from this evaluation indicate that performance of both formate brines were comparable to the simulated performance of 40 %wt $MeOH$ and 40 %wt MEG inhibited water systems. These are both known to be excellent hydrate inhibitors.

The measured curves for the two formate brines have a different shape than the other curves. This could be due to salt crystallization as the fluids tested were close to saturation point. Crystallization of salts changes the inhibition properties of the solution and thereby increases the temperature required for complete dissolution of hydrate crystals. This issue is being investigated further.

Table 1 Composition of Green Canyon gas used for HET testing.

Component		Mole %
N2	Nitrogen	0.14
C1	Methane	87.48
C2	Ethane	7.58
C3	Propane	3.08
i-C4	Isobutane	0.51
n-C4	N-Butane	0.80
i-C5	Isopentane	0.20
C5	Pentane	0.20

Table 2 Composition of simulated Gulf of Mexico gas used for hydrate inhibition testing.

Component		Mole %
N2	Nitrogen	0.409
C1	Methane	87.202
C2	Ethane	7.590
C3	Propane	3.100
i-C4	Isobutane	0.503
n-C4	N-Butane	0.793
i-C5	Isopentane	0.203
C5	Pentane	0.200

Low-density sodium and potassium formate brines

Laboratory testing was performed by Westport Technology Center International, Houston, USA to measure hydrate-phase equilibrium conditions for three diluted formate brines and distilled water [5]:

1. Distilled water (baseline)
2. 1.06 g/cm^3 / 8.86 lb/gal KFo – buffered
3. 1.05 g/cm^3 / 8.76 lb/gal NaFo – buffered
4. 1.21 g/cm^3 / 10.1 lb/gal NaFo – unbuffered

The gas used for testing was a typical Gulf of Mexico gas mixture shown in Table 2.

The fluids were tested in the range 1,500 – 5,000 psig apart from 1.05 g/cm^3 / 8.76 lb/gal buffered sodium formate brine that was tested up to 8,500 psig.

Hydrate equilibrium curves for 1.06 g/cm^3 / 8.86 lb/gal potassium formate brine, 1.05 g/cm^3 / 8.76 lb/gal sodium formate brine, and distilled water are shown in Figure 3. The 1.05 g/cm^3 / 8.76 lb/gal sodium formate brine had approximately twice the hydrate suppression as the same density potassium formate brine. This is not surprising as sodium formate has a lower freezing point than potassium formate (see Section A5, Crystallization Temperature) and also lower water activity (see Section A3, Water Activity and Colligative Properties). The 1.21 g/cm^3 / 10.1 lb/gal sodium formate brine did not form hydrates under any of the pressure temperature conditions tested (temperature down to -1°C / 30°F and pressure 34.5 MPa / 5,000 psig).

13.3.2 HET measurements with Marnock North Sea gas

A detailed study has been conducted on gas hydrate formation using simulated Marnock North Sea gas [6]. Due to high risk of gas hydrate formation in the BP-operated Marnock field, a series of tests were conducted to compare and predict the degree of inhibition from cesium formate and zinc bromide brines.

HET was measured at four pressures up to 10,000 psia. The gas mixture used is shown in Table 3. Measurements were taken for the following four aqueous solutions:

1. De-ionized water

2. 1.91 g/cm^3 / 15.9 lb/gal $ZnBr_2$ / $CaBr_2$ / $CaCl_2$
   (12.44 %wt $ZnBr_2$ + 38.7 %wt $CaBr_2$
   + 15.29 %wt $CaCl_2$)

3. 1.98 g/cm^3 / 16.5 lb/gal buffered cesium formate

4. 1.98 g/cm^3 / 16.5 lb/gal buffered cesium / potassium formate

Measured HET curves for distilled water and $ZnBr_2$ / $CaBr_2$ / $CaCl_2$ brine are shown in Figure 4. Neither of the formate brines tested formed gas hydrates, even when the samples were held for eight hours in the pressure range 34 – 38 MPa / 5,000 – 5,500 psia and at a temperature of 15°C / 59°F.

Table 3 Composition of simulated Marnock gas used for HET testing.

Component	Mole %
Nitrogen	0.070
Carbon dioxide	0.681
Methane	78.446
Ethane	7.288
Propane	3.402
Isobutane	0.720
N-Butane	1.274
Isopentane	0.676
N-Pentane	0.711
Hexanes	0.545
Benzene	0.062
Hephanes	0.783
Toulene	0.138
Octanes	0.856
Nonanes	0.739
Decanes	0.605
Undecanes	0.430
Dodecanes	0.331
Tridecanes	0.320
Tetradecanes	0.269
Pentadecanes	0.226
Hexadecanes	0.181
Heptadecanes	0.159
Octadecanes	0.146
Nonadecanes	0.127
Eicosanes	0.103
Henicosanes	0.088
Docosanes	0.077
Tricosanes	0.067
Tetracosanes	0.059
Pentacosanes	0.053
Hexacosanes	0.046
Heptacosanes	0.041
Octacosanes	0.037
Nonacosanes	0.033
Triacontanes	0.209
C 12+	0.573

13.3.3 HET measurements with methane gas

Norsk Hydro has evaluated use of potassium formate as a replacement for traditional hydrate inhibitors used in gas transport pipelines [7]. In this connection, the inhibitive effect of various concentrations of potassium formate brine (10, 20, and 30 %w/w) was measured along with that of distilled water, methanol (*MeOH*) and *MEG*. The HET curves from this testing are shown in Figure 5.

The study concluded that the hydrate inhibitory effect of 10 %w/w *KFo* (1.06 g/cm^3 / 8.84 lb/gal) is approximately equal to the effect of 7.5% *MeOH* or 12.4 %w/w *MEG*. The effect of 30 %w/w *KFo* (1.19 g/cm^3 / 9.92 lb/gal) is approximately equal to the effect of 25.5 %w/w *MeOH* or 37.1 %w/w *MEG*.

B13.4 Recommendations

The effective hydrate inhibiting effects of formate brines have been established through a few simple experiments. No hydrate predication simulation model exists for formate brines today.

The test results available give some good indicators for the expected performance of formate brines compared to other well-known hydrate inhibitors. For critical operations, testing under exact operating conditions is recommended.

With increasing use of formate brines for drilling and completion operations, development of a hydrate prediction simulation tool is recommended. Such a prediction tool should be developed as a joint-industry project.

The good hydrate inhibiting effect of formate brines make them suitable for hydrate dissolution applications. Cesium formate brine has been successfully used twice to dissolve hydrate plugs. More information about this application can be found in Section C5, Other Applications.

References

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[3] Howard, S.K., Houben, R.J.H., Oort, E. van, Francis, P.A.: "Report # SIEP 96-5091 Formate drilling and completion fluids – Technical manual", Shell International Exploration and Production, August 1996.

[4] "Potassium and Cesium Formates. Hydrate Equilibrium Evaluation. Cabot Specialty Fluids Inc.", Intertek Westport Technology Center, Report # WTC-08-000933, 6 October, 2008.

[5] "Hydrate Phase Equilibrium Tests Supporting BP Devenick Field", Westport Technology Center International, Report # DT-01-XXX, February 2001.

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[7] Fadnes, F.H., Jakobsen, T., Bylov, M., Holst, A., and Downs, J.D.: "Studies on the Prevention of Gas Hydrates Formation in Pipelines using Potassium Formate as a Thermodynamic Inhibitor", SPE 50688, 1998.
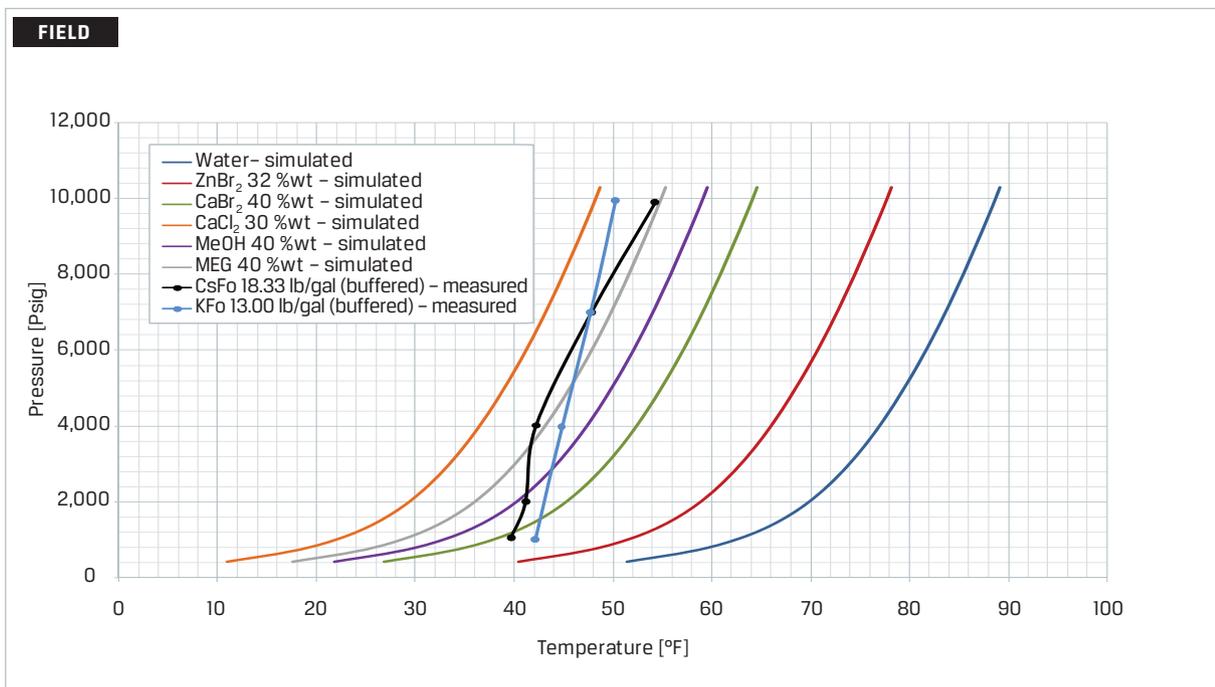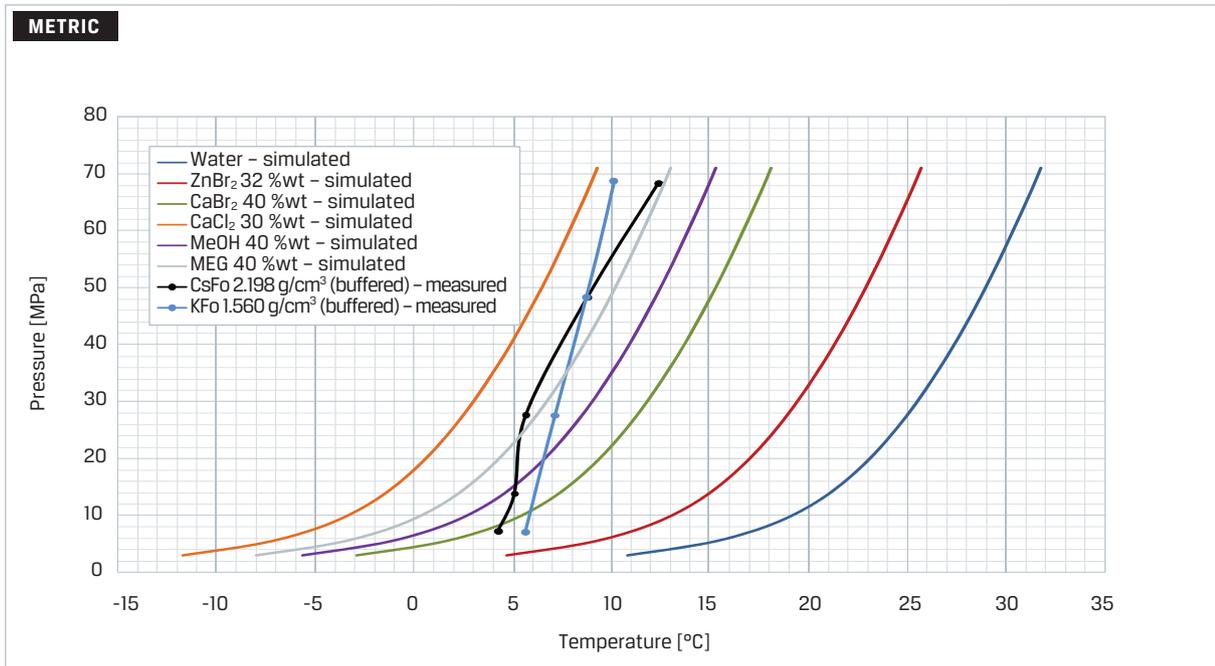
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Figure 2 Hydrate equilibrium curves for buffered concentrated potassium formate brine (1.560 g/cm³ / 13.00 lb/gal) and cesium formate brine (2.198 g/cm³ / 18.33 lb/gal), along with simulated hydrate equilibrium curves for other well-known and respected hydrate inhibitors. The tests were conducted with typical GoM (Green Canyon) type gas. The different shape of the formate brine curves is currently not understood. This could be related to crystallization in these highly concentrated brines.
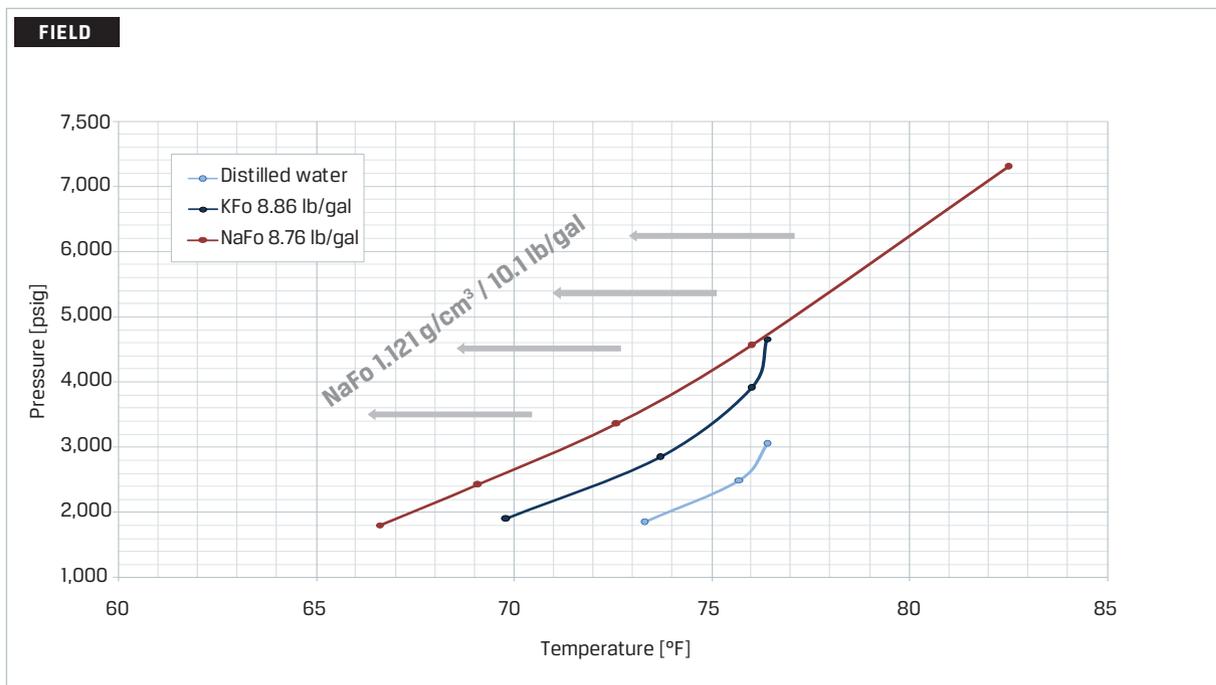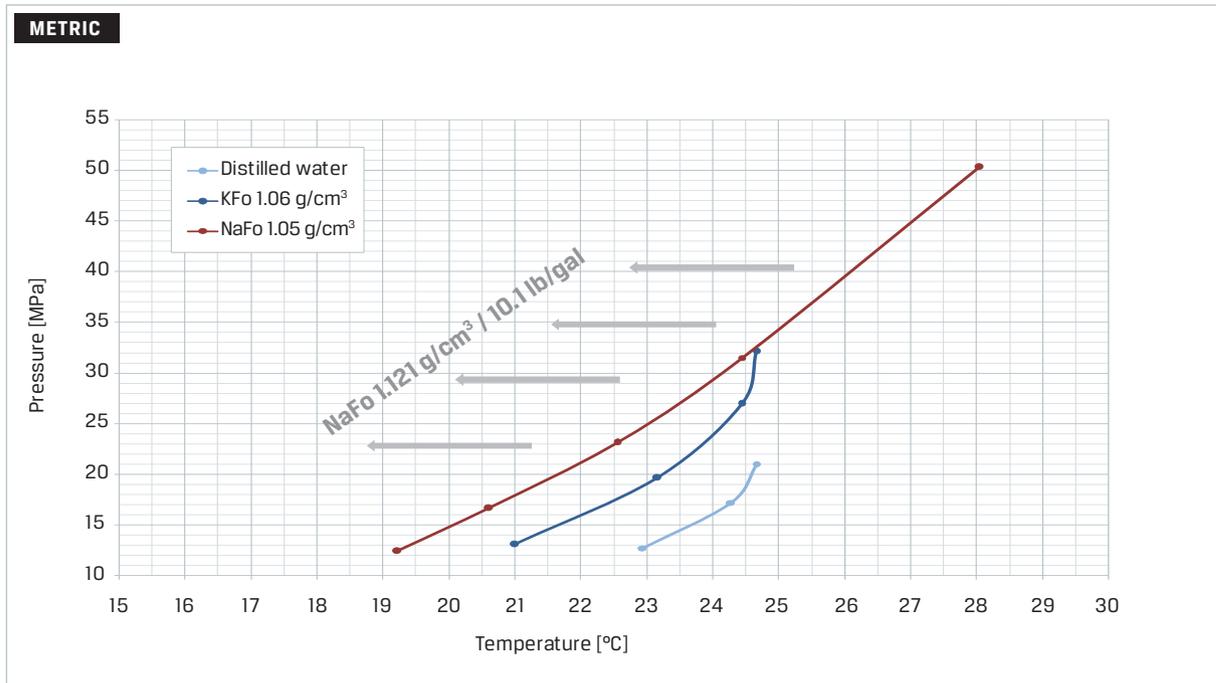
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Figure 3 Measured hydrate equilibrium curves for distilled water, buffered diluted potassium formate brine (1.06 g/cm³ / 8.86 lb/gal), and buffered diluted sodium formate brine (1.05 g/cm³ / 8.76 lb/gal). The gas was a simulated typical GoM type gas. The 1.21 g/cm³ / 10.1 lb/gal sodium formate brine did not form hydrates at the highest pressure it was tested – 34.5 MPa / 5,000 psig with temperatures down to 15.6°C / 30°F.
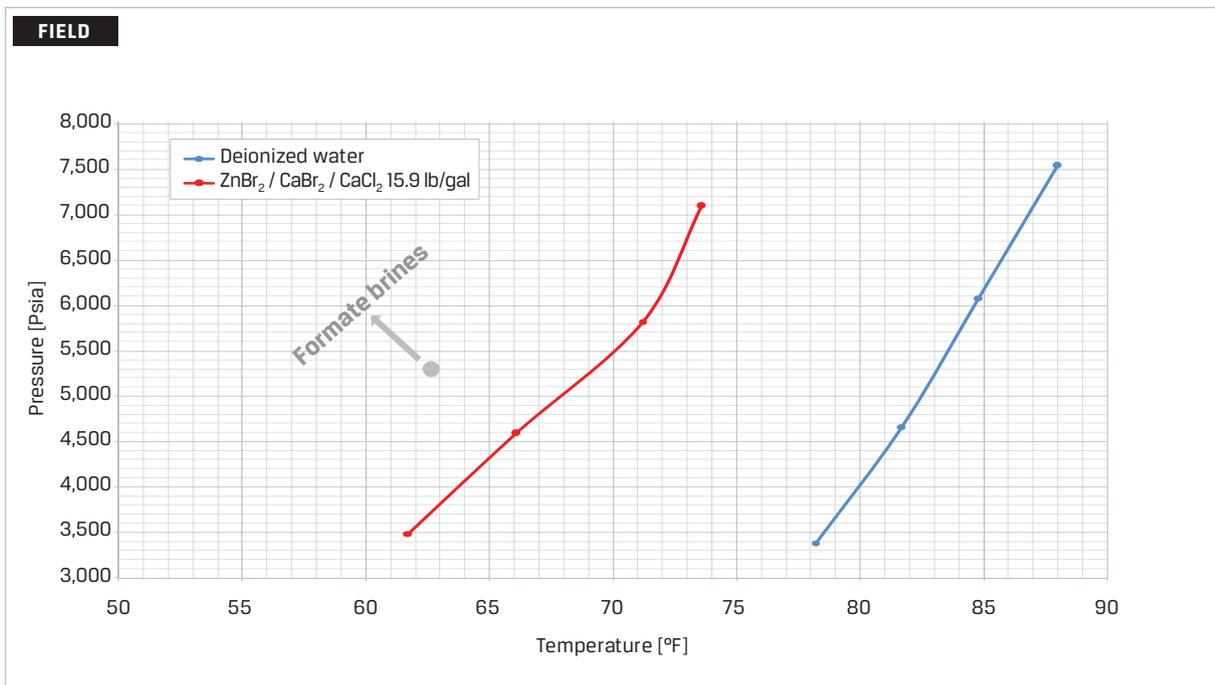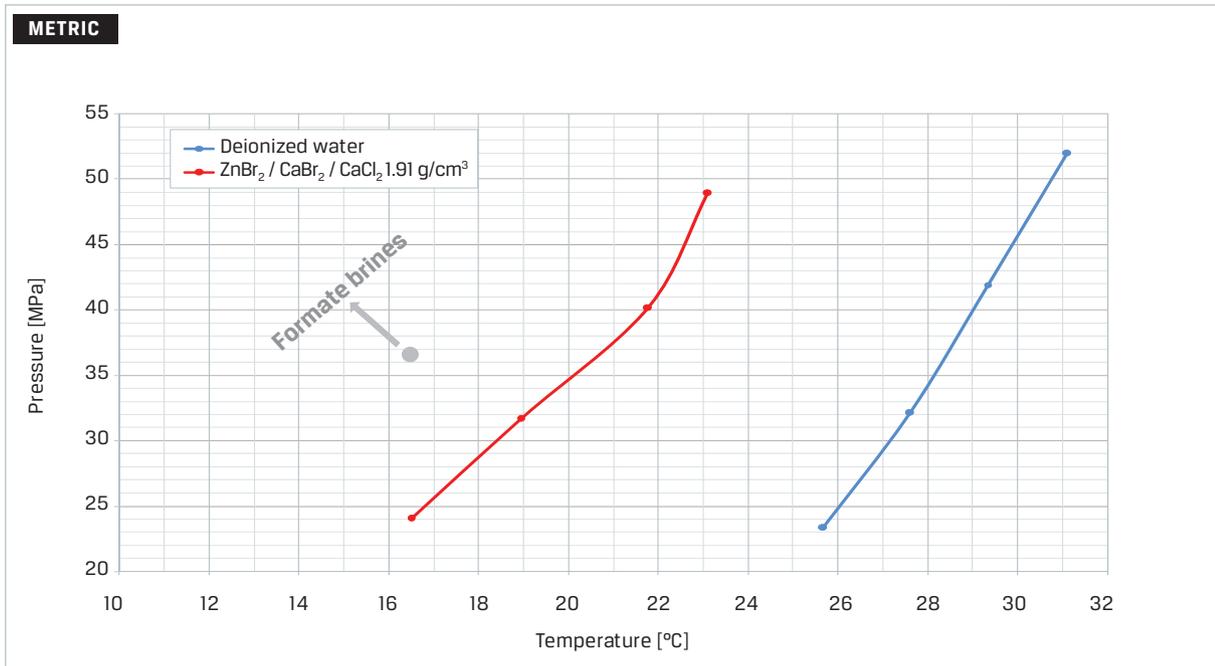
Figure 4 Measured hydrate equilibrium curves for distilled water and 1.91 g/cm^3 / 15.9 lb/gal *ZnBr$_2$ / CaBr$_2$ / CaCl$_2$* brine with simulated North Sea Marnock gas. The 1.98 g/cm^3 / 16.50 lb/gal cesium formate brine and the 1.98 g/cm^3 / 16.50 lb/gal cesium / potassium formate brine blend did not form hydrates within the pressure and temperature range of the test conditions.
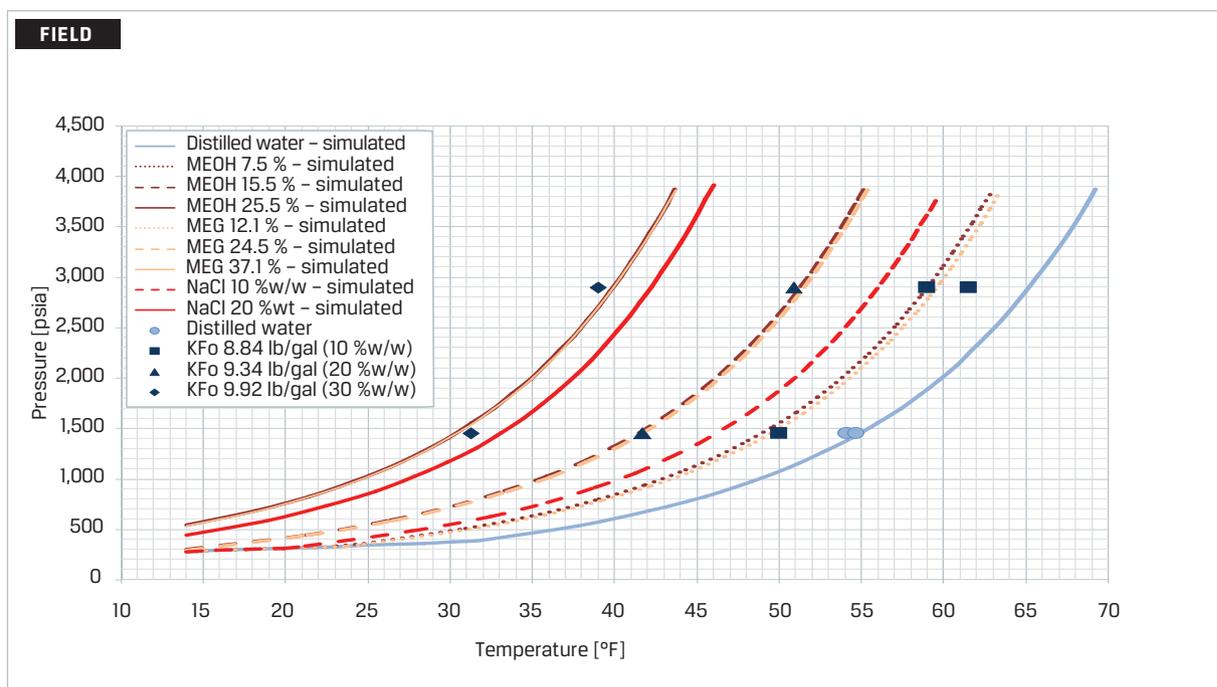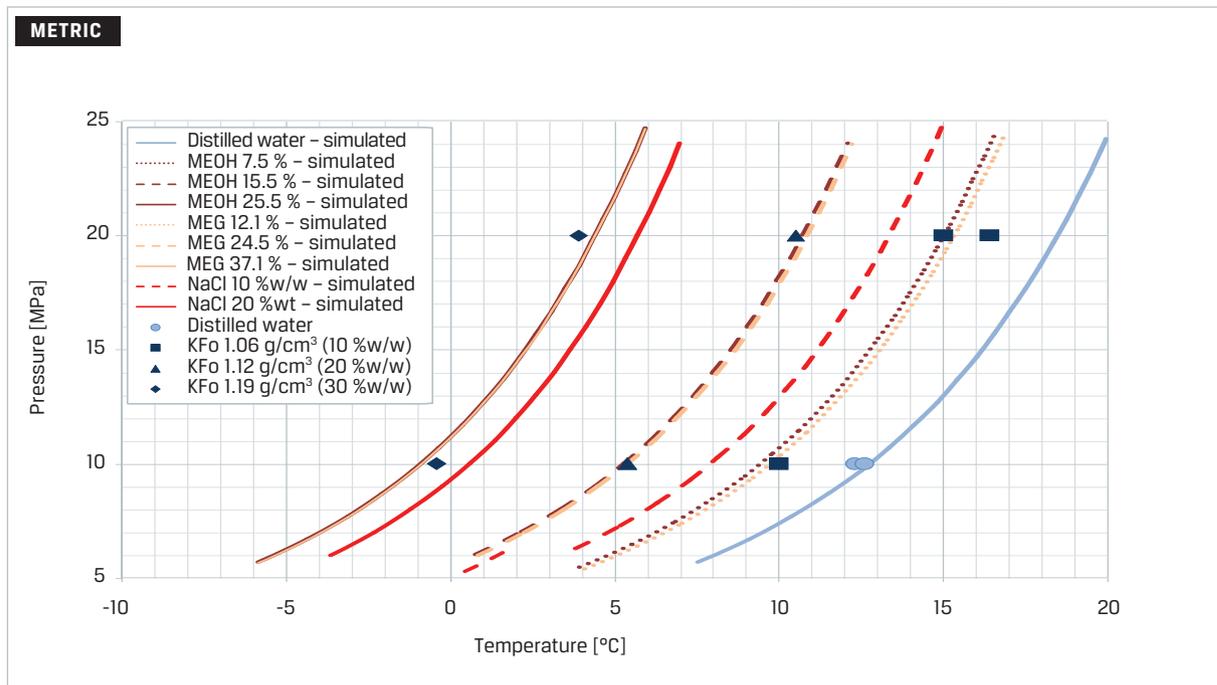
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Figure 5 Hydrate equilibrium curves for distilled water and 10%w/w potassium formate brine, 20%w/w potassium formate brine, and 30%w/w potassium formate brine, along with simulated hydrate equilibrium curves for other well-known and respected hydrate inhibitors. The tests were conducted with methane gas.