PHASES TRASITION IN PRODUCING GAS WELLS.

Abstract Number: 790.

Sonatrach – First Calgary Petroleums

Algeria

BOUCHAREB RAFIK.

JUNE 2014

INDEX

1. ABSTRACT.
2. INTRODUCTION.
3. PROBLEMATIC.
4. RESULTS AND DISCUSSION.
5. CONCLUSION.

Abstract:

By definition the oil & gas industry is used to handling fluid phases, vapour and liquid, as the wells produce always water gas and oil in very different proportions. But in addition under certain circumstances solid phases could appear in different locations (reservoir, pipe-lines or in the process facilities), for instance we could have appearance and deposit of ice, gas hydrates, wax, mercury, sulfur or solid CO2. Most of the time the operating conditions of the fields will be chosen in order to avoid any solid particle in the fluids that could have dramatic consequences on the installations but it is not always possible. Anyway, the simulators used for designing the future installations or assisting the engineers in charge of the production should detect the presence of solid phases. It means that there is a crucial need of predictive, reliable and robust thermodynamic models that can perform calculations of complex equilibrium with 3 fluid phases combined with several solid phase and provide their properties (density, thermal conductivity, heat capacity,…), for instance gas-oil water-gas hydrates-wax. We will present the situations where solid phases can appear in the oil & gas installations their impacts, the current available thermodynamic models and our expectations for the future. In addition, we will imagine how we could react to this problem to avoid any accident that can be happened and can be with fatal consequences, and to avoid unproductive time.

Properties of crude oil and natural gas are fundamental for Designing and analysing oil and gas production systems in Petroleum engineering: Pressure, Temperature (t), Bubble point pressure, Stock tank oil gravity, Solution gas oil ratio (Rs), Gas specific gravity ….

Hydrate formation in one of the most problem occurred in gas production, caused by the transformation of water to glace with the decreasing of temperature, this example illustrate the importance to avoid the appearance of solid particles in the fluid phase.

Once formed, hydrates can block pipeline and processing equipment. They are generally then removed by reducing the pressure, heating them, or dissolving them by chemical means (methanol is commonly used). Care must be taken to ensure that the removal of the hydrates is carefully controlled, because of the potential for the hydrate to undergo a phase transition from the solid hydrate to release water and gaseous methane at a high rate when the pressure is reduced. The rapid release of methane gas in a closed system can result in a rapid increase in pressure.

Salt formation during production is a serious problem occurred in Oil and Field, caused by the temperature and pressure change during production of gas and oil. We will try to focus to this two principal problem, identify the problem and try to find solution will be our objective.

Introduction:

Gas hydrates are ice-like crystalline structures with gas components such as methane and carbon dioxide as guest molecules entrapped into cavities formed by water molecules.

Whenever a system of natural gas and water exists at specific conditions, especially at high pressure and low temperature, we expect the formation of hydrates. In the oil and gas industry, gas hydrates are a serious problem in production and gas-transmission pipelines because they plug pipelines and process equipment. By applying heat, insulating the pipelines, and using chemical additives as inhibitors, we can keep the operating conditions out of the hydrate-formation region.

The most common inhibitors are thermodynamic inhibitors such as methanol and glycols; however, produced water that contains electrolytes also has inhibiting effects. To remediate problems caused by hydrates, it is important to calculate the gas-hydrate formation temperature and pressure accurately; this is more complex when the system includes alcohols and/or electrolytes. Hammerschmidt1 first found that the formation of hydrates could block natural gas-transport pipelines. Since then, the oil and gas industry has been more willing to

Investigate the problem. My work focuses on gas-hydrate formation in three-phase equilibrium (liquid water, hydrocarbon gas, and solid hydrate) with the objectives of developing practical solution to remove this problem.

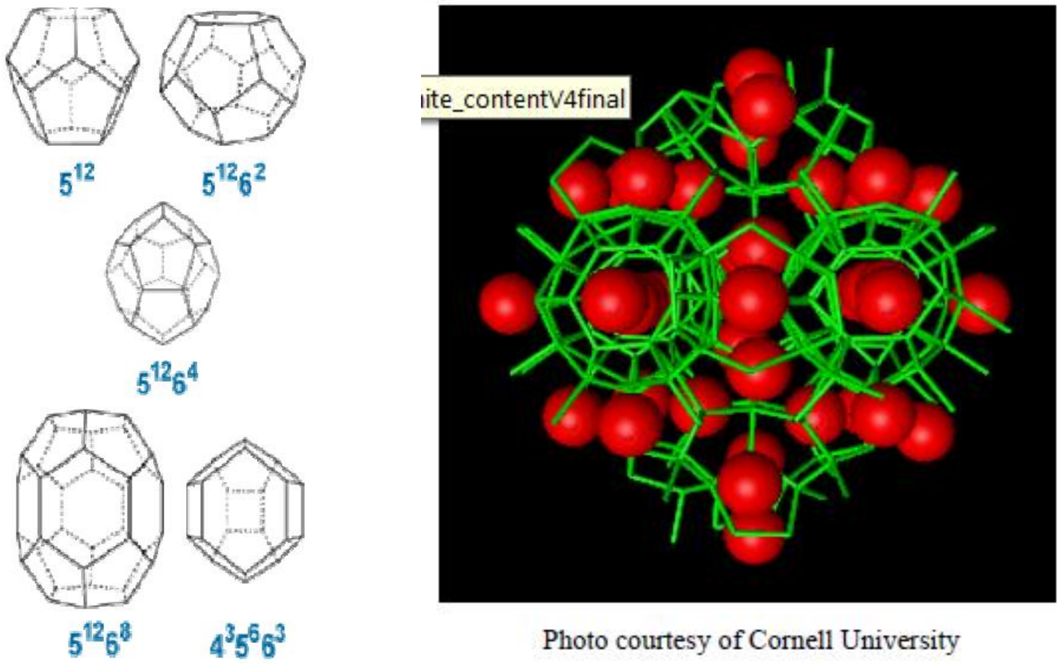


Photo courtesy of Cornell University

Cavities and structure of Hydrate.

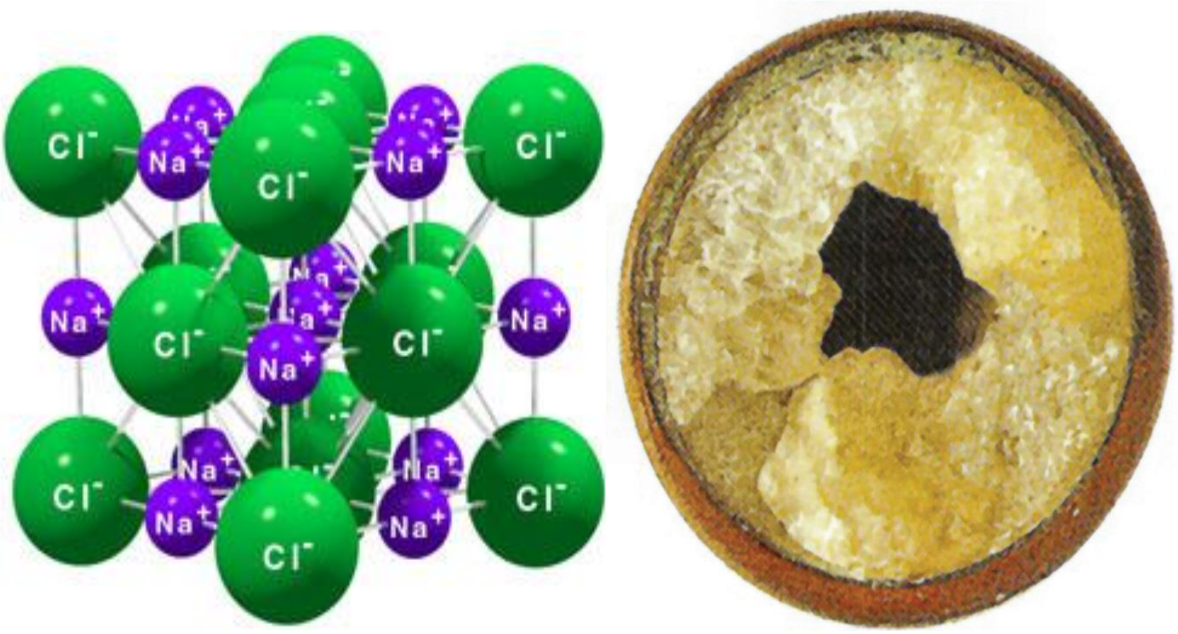
Salt precipitation from the reservoir water is observed to an increasing extent as recovery progresses. This phenomenon likewise occurs during the injection of dry gas into porous aquifers. Salt deposits can form in the production string as well as in the perforation zone. It may be assumed that the surrounding formation is also affected by salt precipitation in the proximity of the well. In the area of an aquifer employed for gas storage. Nacl precipitates have been detected during well testing by pressure drawdown. This deposit had resulted from filling of the pores with saturated brine.

During production, the precipitation of salt results in a significant decline in productivity, which may culminate in total plugging and ultimately in the abandonment of wells, for the elimination of deposits as well as the prevention of salt precipitation in the vicinity of the wells, fresh water treatments are applied in production operations. In addition to the mechanical removal of halite scale from the tubing and perforation zone with the use of scarpers. The object of all such measures is to maintain or restore the original permeability conditions. (Halite is commonly known as rock salt, is the mineral form of sodium chloride NaCl. Halite forms isometric crystals).

Salt Deposition: Sodium chloride is not strictly a scale. Most oilfield scales are formed by the mixing of incompatible waters. Salt, however, is a self-scaling phenomenon requiring only changes in physical conditions to precipitate. It is also, generally, a gas well problem, for reasons that become apparent when looking at the mechanism of salt deposition.

There are two mechanisms working to cause precipitation of salt; firstly, evaporation of fresh water from formation brine
Into the producing gas which increases brine salinity, and secondly, changes in pressure and temperature which can reduce the
solubility of the salt in the brine. Either or both can result in the brine becoming salt saturated so that the salt precipitates out.

Precipitated salt is generally nearly 100% NaCl. Throughout the text this is referred to variously as salt or halite, the terms being used interchangeably.



Salt Deposit.

Problematic:

Well-A is Gas producer vertical well.
This well presented Hydrate problem and a PVT (Pressure-Volume-Temperature) were made to evaluate and analyse the problem.

Sampling type	**Separator**
Number of samples:	**2 sets**
Reservoir Fluid Nature	**Gas Condensate.**
Reservoir pressure [bara]	**384.65**
Reservoir temperature [°C]	**118.0**
Separator pressure [bara]	**21.03**
Separator temperature [°C]	**32.78**
Gas Cyl #	**1881-C1-F**
Liquid Cyl #	**5268-M1-F**
Recombination data	
Lab-corrected GOR @ sep cond [v/v]	**8,256**
Separator Gas Gravity at SC [air=1]	**0.692**
Separator Oil Density at ST [°API]	**55.2**
Reservoir Fluid Sums (%mol)	
C1	**80.826**
C7+	**1.275**
C7+ Mol Weight [g/mol]	**143**
Reservoir Fluid Comp (%mol)	
N_2	**0.062**
H_2S	**0.000**
CO_2	**1.493**
nC1	**80.826**
nC2	**10.432**
nC3	**3.518**
iC4	**0.512**
nC4	**0.947**
neo-C5	**0.011**
iC5	**0.313**
nC5	**0.295**
C6	**0.316**
Benzene	**0.024**
C7	**0.269**
Toluene	**0.058**
C8	**0.242**
Ethylbenzene	**0.005**
Meta and Para Xylenes	**0.047**
Ortho Xylene	**0.012**
C9 - C30	**0.618**
Total	**100.000**
Whole Fluid Mol Weight [g/mol]	**21.70**
C12+ Mol Weight [g/mol]	**228.0**
C12+ Density [g/cm3]	**0.841**

Analyze:

Following PVT Data we have the following figures:

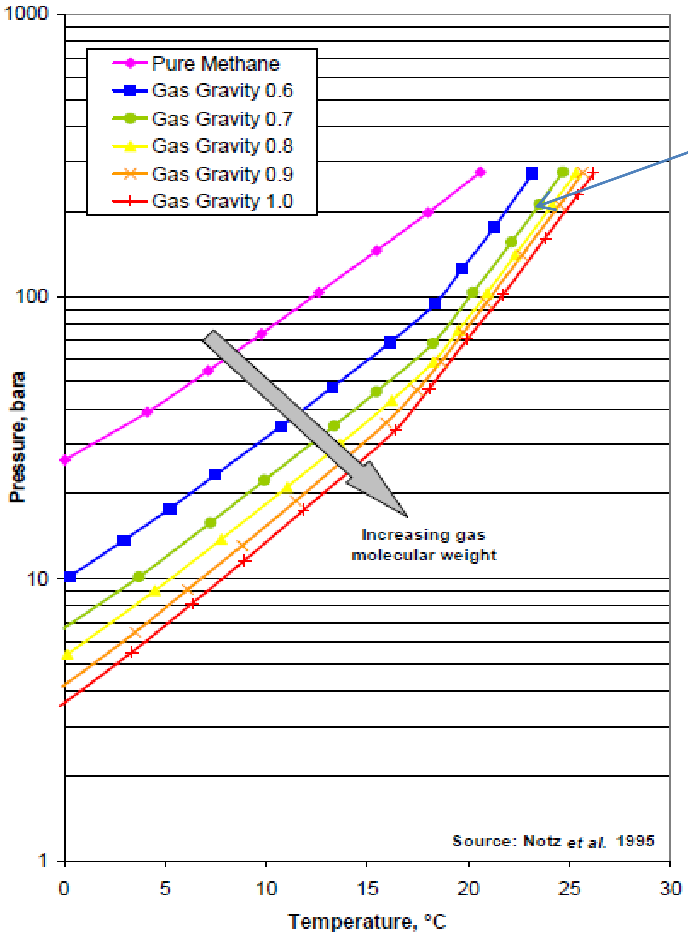


Figure 1.

Figure1: Effect on gas gravity on Hydrate formation.

Figure 2.

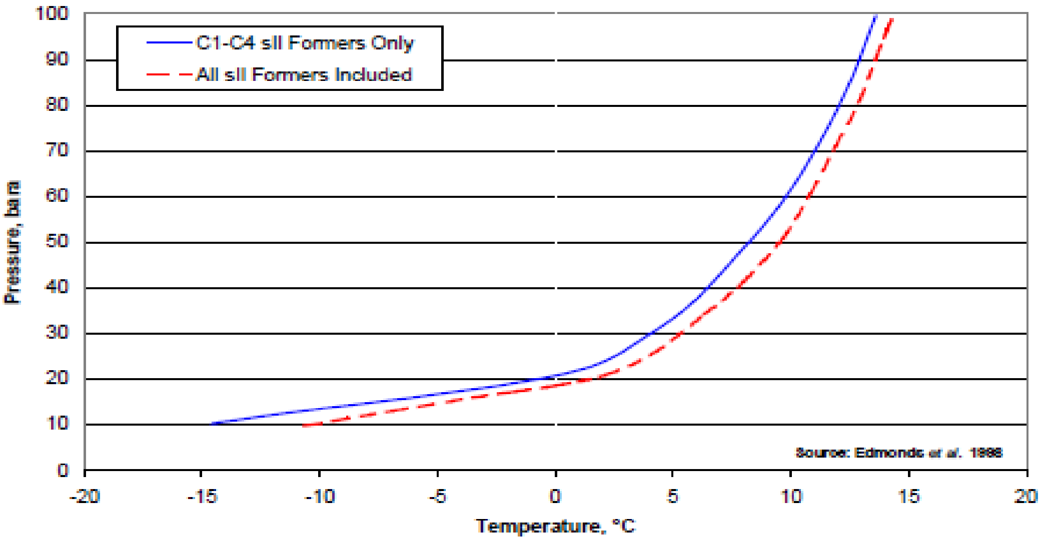


Figure 2: Effect of sII Formers on sII stability boundary.

Figure 1 present the result reported by Katz (1945) and shows that the hydrate dissociation curve is displaced towards lower pressures and higher temperatures as the gas gravity or molecular weight increases.
Edmonds and Al (1998) also illustrates the effect of increasing gas molecular weight, they reported prediction from their hydrate dissociation model. They demonstrated the effect of including higher molecular weight sII formers on the position of the sII hydrate stability. Boundary. These predictions are reproduced in figure 2. And show that the inclusion of the higher molecular weight sII formers shifts the stability curve towards lower pressures and higher temperatures.

Hydrate formation combined to salt formation problem:

For any given organic inhibitor concentration, the saturated salt concentration (i.e., the maximum possible amount of salts in aqueous organic inhibitor solution before salt precipitates) gives the maximum inhibition effect for gas hydrate. Since there are different saturated concentrations of salts and organic inhibitors in the aqueous solutions, inhibition effects will have different values. Consequently, investigation on the inhibition effect locus in these cases could be very important in finding the best and the most effective saturated concentration of salts and organic inhibitors. In fact, the latter investigation should help to distinguish the border between salt precipitations and hydrate formation events in the system. Furthermore, it is necessary to take into account the effect of pressure and temperature on the maximum inhibition locus. The HWHYD thermodynamic model which was recently extended to systems containing salts and/or organic inhibitors (Masoudi et al., 2004b, Masoudi et al., 2004c and Masoudi et al., 2005) has been utilized to predict the hydrate inhibition effects of salts and organic inhibitors. First, the effect of salt-organic inhibitor interactions on gas hydrate inhibition has been investigated and described. Next, the model was employed to examine the maximum inhibition locus in aqueous solutions of salts and organic inhibitors.

The previously developed thermodynamic model has been applied to obtain better understanding of the effects of various salts and organic inhibitors on hydrate stability zone in petroleum exploration and production.

The above model was used to develop guidelines for maximum hydrate inhibition effect of salts and organic inhibitors without any salt formation problem. It was discovered that higher concentrations of organic inhibitors rather than salts is better for hydrate prevention.

The effect of salt-organic inhibitor interactions on hydrate inhibition has been investigated. It was found that the reliability of the hydrate model in the presence of thermodynamic inhibitors is strongly related to salt-organic inhibitor interactions. That means predictive models should take into account the interaction between electrolytes and organic inhibitors in order to accurately predict hydrate inhibition effects.

Results and Discussions:

The following are the thermodynamic ways to prevent the hydrate formation:
1. Reducing the water concentration from the system.
2. Operating at temperatures above the hydrate-formation temperature for a given pressure by insulating the pipelines or applying heat.
3. Operating at pressures below the hydrate-formation pressure for fixed temperature.
4. Adding inhibitors such as salts, methanol, and glycols to inhibit the hydrate formation conditions and shift the equilibrium curve to higher pressure and lower temperature.

Inhibitors are added into processing lines to inhibit the formation of hydrates. There are two kinds of inhibitors: thermodynamic inhibitors and low-dosage inhibitors. The thermodynamic inhibitors have been used for long time in the industry and act as antifreeze. The low-dosage inhibitors have recently been developed and their usage modifies the rheology of the system rather than changing its thermodynamic states. These inhibitors work at low concentrations, lower than or equal to 1 wt%; therefore, the use of this technique reduces the environmental concerns and since no regeneration units are required, it results in reduction of capital cost.

The low-dosage inhibitors are divided into **Kinetic** inhibitors and **antiagglomerants**. The kinetic inhibitors are commonly water-soluble polymers delay the nucleation and growth of hydrate crystals, while the antiagglomerants are usually surfactants and miscible in both hydrocarbon and water, so they impede the agglomeration of hydrate crystals for a period without interfering with crystal formation.

Inhibitors such as ethylene glycol, methanol, and electrolytes inhibit hydrate formation. It is important to determine the inhibition effects of these additives to avoid hydrate formation and select the best inhibitor for a given system and operating conditions.

Bishnoi and Dholabhai obtained experimental hydrate equilibrium conditions for propane hydrate with single and mixed electrolytes. Their work included electrolytes such as NaCl, KCl, and CaCl2 at pressure and temperature ranges of 133 to 500 KPa and 263 to 276ºK. The results of this work show that for the same concentrations of electrolytes (5 and 10 wt% in this case), sodium chloride has a greater inhibition effect than potassium and calcium chlorides.

Bishnoi and Dholabhai5 obtained the hydrate-equilibrium conditions for a ternary mixture of methane (78 mol %), propane (2 mol%) and carbon dioxide (20 mol%) and a natural gas mixture in pure water and solutions containing methanol and electrolytes for a temperature range of 274 to 291ºK and a pressure range of 1.5 to 10.1 MPa. They observed systems that contain the same total wt% of the inhibitor, for example systems with 10 wt% of either methanol or sodium chloride and 20 wt% of either methanol or sodium chloride, 15 wt% of methanol + 5 wt% of sodium chloride, and 5 wt% of methanol + 15 wt% of sodium chloride. For a given pressure, they reported that the incipient hydrate-equilibrium conditions for such systems are close to each other, within 3 to 5ºC (**Figs. 3 and 4**); one can also conclude from these two figures that sodium chloride has higher inhibition potential than methanol with the same wt%, a result is more pronounced at higher pressures. Even in the presence of mixed inhibitors, the inhibitor with a higher wt% of sodium chloride is more effective than the one with higher wt% of methanol.

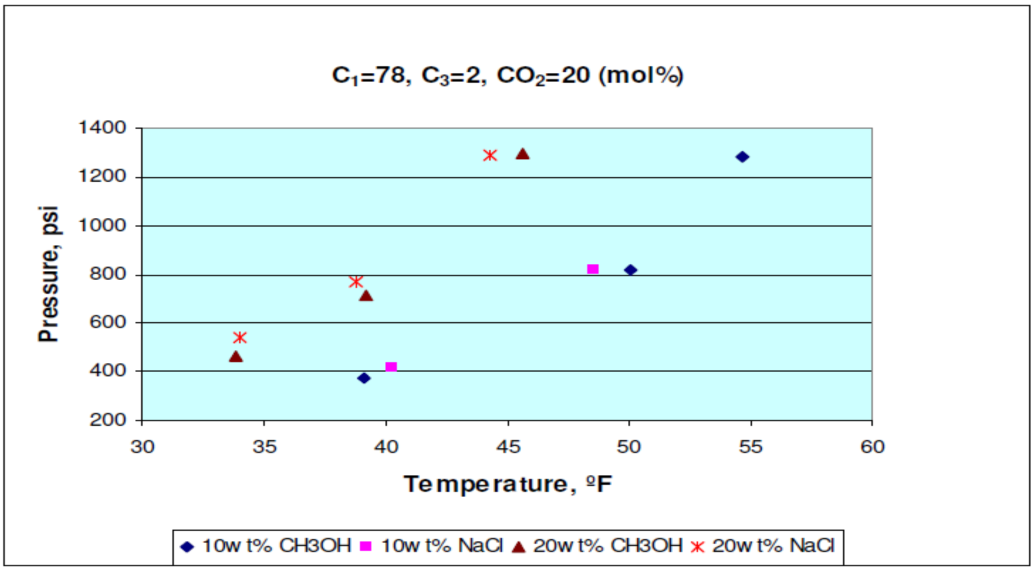


Figure 3: Experimental hydrate equilibrium conditions for the ternary mixture.

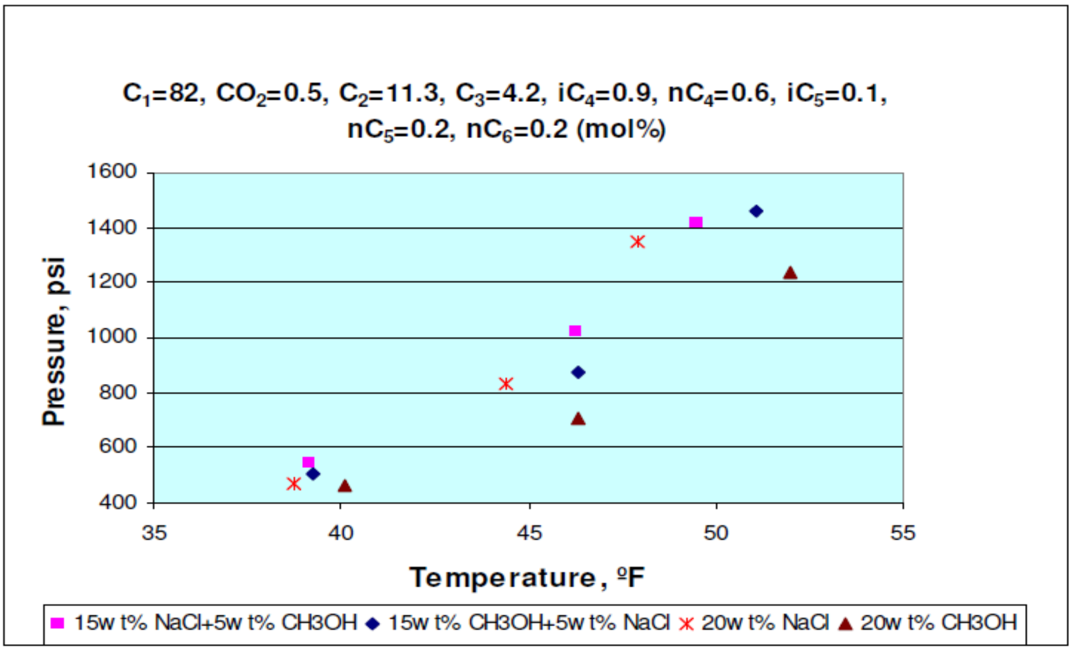


Figure 4: Experimental hydrate equilibrium conditions for the natural gas mixture.

Conclusion:

Hydrate and salt formation is common in oil and gas fields and can be catastrophic if not controlled.

Hydrate control uses a combination of thermal, operational and chemical approaches.

Our field used Methanol as Thermodynamic hydrate inhibitor to prevent formation of hydrate in wells and surface equipment.
It is important to determine the inhibition effects of these additives to avoid hydrate formation and select the best inhibitor for a given system and operating conditions. The use of Methanol is due to their properties to adapt in high concentration with the salt inhibitor used (the presence of thermodynamic inhibitors is strongly related to salt-organic inhibitor interactions).
The use of fresh water to dissolve salt crystals is strongly recommended because of his non-interaction result with Hydrate inhibitor but the use of water may be difficult to control in low temperature system (Hydrate formation).