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The Physical Chemistry of Wax, Hydrates, and Asphaltene

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Abstract

Wax, hydrates, and asphaltenes are the three major threats to flow assurance that must be assessed by design teams. These potential problems can dramatically change system selection and operational procedures. If one of them is discovered after the system is under construction or worse after first oil then the whole project may be at risk. Each solid must be well understood by engineers so they can neutralize the threats to system uptime that result from poor solids management. This paper focuses on the problems posed by, and the system implications of, wax, hydrates, and asphaltenes.

Introduction

Flow assurance in subsea systems focuses on preventing solid deposits from blocking the flow path. The principle solids of concern are wax and hydrates.   Sometimes scale and asphaltenes are also a concern. For a given reservoir fluid these solids precipitate at certain combinations of pressure and temperature. Precipitated solids are often carried downstream slurried in the fluid; however precipitated solids can also deposit on the walls of the production equipment, which ultimately causes plugging and flow stoppage. Control of this blockage is the essence of "flow assurance". Solids control strategies involve keeping the system pressure and temperature in a region where the solids are unstable (thermodynamic control) or controlling the conditions of solids formation so that deposits do not form (kinetic control) or allowing solids to deposit, then periodically removing them (mechanical control).

This paper focuses on the thermodynamic and kinetic behavior of wax, hydrates and asphaltenes in reservoir fluids. The emphasis is on solids behavior in subsea systems. So, for each solid we describe the phase envelope, rate of solid formation and system implications.   We also describe physicochemical factors important in solids removal. This is not a comprehensive review of the solids but we will describe their behavior well enough so that the reader can understand why subsea systems are designed and operated as they are.

Wax

Paraffinic hydrocarbon fluids can cause a variety of problems in a production system ranging from solids stabilized emulsions to a gelled flowline.   Problems caused by wax occur when the fluid cools from reservoir conditions and wax crystals begin to form. The temperature at which crystals first begin to form is called the cloud point. At temperatures below the cloud point, crystals begin to form and grow. Crystals may form either in the bulk fluid forming particles that are transported along with the fluid or deposit on a cold surface where the crystals will build-up and foul the surface.

While there are a number of problems that wax may cause in a production system, producers focus on two critical issues. The first issue is gel formation and the second issue is deposition. A crude oil gel forms when wax precipitates from the oil and forms a three dimensional structure spanning the pipe. This does not occur while the oil is flowing because the intermolecular structure is destroyed by shear forces as it is able to form.   However, when the oil stops flowing wax particles will interact, join together and form a network resulting in a gel structure if enough wax is out of solution.

In a pipe, wax deposition results in flow restrictions or possibly a complete blockage. Complete blockage of flow due to deposition is rare. Most pipeline blockages occur when a pig is run through a pipeline after deposition has occurred and a significant deposit has built up. In this situation the pig will continue to scrape wax from the pipe wall and build up a viscous slug or candle in front of the pig. However, if the candle becomes too large there will be insufficient pressure for the pig to move. When this occurs the pig becomes stuck and mechanical intervention to remove the candle will be necessary before the pig can be moved.

Wax in crude oil is comprised primarily of paraffins. Paraffin is a white, odorless, tasteless, chemically inert compound composed of saturated hydrocarbons. The linear paraffins are easily measured by high temperature gas chromatograph (HTGC). The HTGC technique measures the amount of each n-alkane in the sample. The sum of the n-alkanes greater than twenty carbons is reported as the n-paraffin or wax content of the oil. In general the amount of

paraffin in an oil decreases with decreasing API gravity.

Wax varies in consistency from that of petroleum jelly to hard wax with melting points from near room temperature to over 100°C. Wax has a density of around 0.8 gm/cm^3 and a heat capacity of around 0.140 W/mK.

IP 143 (SARA) , true boiling point (TBP), simulated distillation (ASTM D2887), and chromatographic analysis are a few of the methods that are used to characterize hydrocarbon fluids. While all methods provide insight to the fluid composition, the chromatographic analysis is necessary to evaluate potential wax problems. In this method, a small sample of oil is completely vaporized and analyzed for the paraffin, aromatic and naphthenic hydrocarbon groups around each carbon number starting at C6. If a whole oil analysis is needed then a gas analysis is performed and added to the results of the chromatographic analysis. In Figure 1 chromatographs of an asphaltic crude oil (low API) and a paraffinic oil (medium API) are plotted.

With an oil analysis it is possible to predict when crystals will form in the system. Thermodynamic models have been developed using chromatographic data that will adequately predict the vapor-liquid equilibrium and the solid-liquid equilibrium. Therefore, what the models are capable of calculating are the vapor, liquid, and solid fractions and composition of each fraction for any temperature and pressure. What they are not capable of providing directly is physical properties such as cloud point and pour point. However, correlations can be built to make predictions of many oil properties. For example, a thermodynamic cloud point can be defined as the temperature at which a given threshold solid fraction is reached. The solid fraction can be adjusted or tuned to laboratory measurements.

The cloud point can be measured by differential scanning calorimetry (DSC), crossed polarized microscopy (CPM), viscosity, and direct visual measurement. However, CPM seems to give the best results among the above methods. When CPM is conducted with properly conditioned crude oil and run with slow cooling rates, measurements from different labs run by different people on different days agree to better than 1°F. With proper conditioning of waxy crude oils that are greater than 5% wax the other techniques are likely to produce sufficient results.

For live oils measuring a cloud point is significantly more difficult. Most techniques rely on data from a PVT cell and have detection limits are between 0.22 μm and 1 μm. These methods produce valuable data but the experiments are tedious and expensive. Most engineers will use a predicted value from a thermodynamic model for high pressure cloud points.

Wax deposition will occur once the oil has fallen below the cloud point if there is a negative temperature gradient between the bulk oil and a surface. However, Deepstar has shown that wax deposition also can occur above the dead oil cloud point in some systems. Therefore, to prevent wax deposition altogether, the system temperature should remain greater than 9°C above the dead oil cloud point.

Experimentally the tendency of an oil to deposit and the rate of deposition can be measured by placing a cold surface in contact with warm oil. Experimental systems include cold fingers, co-axial shearing cells, and pipe loops. The cold finger consists of a test tube shaped metal finger cooled by flowing chilled fluid through the finger and a heated stirred container for an oil sample. The co-axial shearing cell is similar to a cold finger but the finger rotates to create uniform shear on the surface. Pipe loop is a pipe in pipe heat exchanger where the cold fluid is pumped through the shell side and the oil is heated and pumped through the tube side.

It may seem that the pipe loop would be the preferred method due to its geometric similarity to a pipeline. However, if an actual field sample is to be used, none of the methods properly simulate the system since dynamic similitude is impossible to achieve without building a system of the same size. It is possible to match N_{Re} or wall shear stress for example, but not both. However, each method can be used to measure the wax flux to the surface. With careful analysis the data from any laboratory method can be used to make predictions about field deposition.

The deposition tendency and rate can also be predicted adequately by calculating the rate of molecular diffusion of wax to the wall with equation 1,

$$\frac{dm}{dt} = -\rho \, D_m A \frac{dC}{dr} \tag{1}$$

where m is mass of deposit, ρ is the density of wax, D_m is molecular diffusion constant, A is the deposition area, C is the concentration of wax, and r is the radial position. The radial concentration gradient can easily be calculated if broken into two components with the chain rule as shown in equation 2,

$$\frac{dm}{dt} = -\rho \, D_m A \frac{\partial C}{\partial T} \frac{\partial T}{\partial r} \tag{2}$$

where T is temperature. The concentration gradient may be calculated from the wax concentrations predicted by a thermodynamic model for a range of temperatures.

As oil cools far below the cloud point it may begin to gel. While the amount of wax out of solution needed to form a gel structure varies considerably, 2% paraffin is used as a useful rule of thumb. The typical method of measuring a crude oil pour point is ASTM D-5853-95 which specifies the conditioning required for obtaining reproducible values. Because the cooling rate is not controlled in this method results may vary from lab to lab, but in general the results are accurate to within ±5°F.

While the pour point is a useful value for determining whether or not a crude oil will form a gel, the more important information is the strength of the gel that is formed. The measurement of this value is problematic. Values measured in a rheometer are typically on the order of 50 dyne/cm^2. However, the sample in a rheometer will yield uniformly due to the small gap. In a pipe the sample will not yield uniformly or simultaneously. A pressure front will propagate through the oil and the oil near the inlet will yield and begin to flow

when a line is restarted. Since this problem is not tractable due to the compressibility and non-Newtonian behavior of a crude oil gel, predictions continue to be made from rheometer measurements or short pipe sections.

Start up pressure predictions can be made using equation 3,

$$\Delta P = 4\tau_y\big|_{wall} \frac{L}{D} \qquad (3)$$

where ΔP is the pressure drop, τ_y is the yield stress, L is the length of the pipe, and D is the diameter of the pipe. Equation 3 assumes that the whole line is gelled, will yield simultaneously, and that the yield at the wall is the appropriate parameter to consider. This method typically over predicts the actual restart pressures.

For export pipelines laboratory pour point methods are very good indicators of potential problems since the export pipelines and blown-down flowlines are full of dead crude. If a flowline were not blown down then the gel situation would improve due to an increase in light components in the oil. Unfortunately, predicting the amount of pour point reduction is difficult.

Hydrates

Like wax, hydrates can pose a threat to production systems during both flowing and shut-in conditions. However, unlike wax, hydrates can plug off a flowline during normal production operations, even in the absence of pigging, with little or no warning. More vulnerable are the transient operations, such as shut-in and startup, where temperatures tend to be lower, pressures can be higher, and water has time to accumulate into low spots. In most Deepwater production, the source of the cooling driving hydrate formation is the ambient water temperature. But numerous examples also exist of hydrates forming during Joule-Thomson cooling of gas, for instance as it expands across a valve. Stuck valves, both subsea and on the platform, are a common manifestation of hydrates. In further contrast to the other solids discussed here, hydrates pose significant safety hazards in the oilfield due to the physical properties discussed below. The ever-expanding push toward Deepwater production has led to an increased concern about hydrates, as the high pressures, low ambient temperatures, extended tiebacks, and hilly terrain are ideal for hydrate formation.

Natural gas hydrates can form when water and natural gas contact each other under high pressures and low temperatures. Natural gas hydrates are crystalline water structures with low molecular weight guest molecules. They are often referred to as clathrate hydrates, where clathrate means cages, as crystalline cages of water molecules form around individual gas molecules. The presence of the gas molecules lends stability to the crystalline structure, allowing hydrates to exist at much higher temperatures than ice. For example, at 2000 psi, a typical natural gas hydrate is stable at temperatures up to 70 °F. Hydrate formers include nitrogen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, iso-butane, n-butane, and some branched or cyclic C5-C8 hydrocarbons.

Natural gas hydrates are composed of 85 mol% water and as such have many physical properties similar to those of ice. For instance, the appearance and mechanical properties of hydrates are comparable to those of ice. The latter has implications for safety: if a hydrate plug breaks loose from the pipe walls, it can be propelled down the flowline like an ice bullet, potentially rupturing the flowline at a restriction or bend. The densities of hydrates vary somewhat due to the nature of the guest molecule(s) and the formation conditions, but are generally comparable to that of ice. Thus, hydrates typically will float at the water / hydrocarbon interface. However, in some instances, hydrates have been observed to settle to the bottom of the water phase.

Two factors combine to make hydrate plugs exceedingly difficult to remove: it takes a high amount of energy to dissociate the hydrate and heat transfer through the hydrate phase is slow. Hydrates also concentrate natural gas. A cubic ft of hydrates can contain up to 182 scf of gas. Thus when gas hydrates dissociate, they release large volumes of gas. For comparison, 1 ft³ of dry natural gas at 900 psi and 60 °F will give off 66 scf of gas when depressurized, whereas the same volume of hydrates will give off nearly 3 times as much. This has significant implications for safety in depressurizing hydrate plugs. For a more complete discussion of gas hydrate structures and properties, the reader is referred to the monograph by Sloan[1].

A typical natural gas hydrate stability curve is shown in Figure 2. To the right of the curve, hydrates are thermodynamically unstable. Operating in this region, producers can feel comfortable that their system will be safe from hydrate blockages. To the left of the curve, hydrates are thermodynamically stable and have the potential to form. This does not mean that hydrates will necessarily form. Nor does it imply that if hydrates form they will cause operational difficulties. A term often used when discussing gas hydrates is subcooling. The subcooling of a system is the difference between hydrate stability temperature and the actual operating temperature at a constant pressure. Thus in Figure 2 if the system is operating at 40 °F and 3000 psi, the hydrate formation temperature is 72 °F so the system is experiencing 32 °F of subcooling. Subcoolings in excess of 30 °F are common in the Gulf of Mexico.

The compositions of the gas, oil, and water phases all affect the hydrate stability curve. Figure 3 shows the effect of adding small amounts of certain gases to methane on the hydrate stability curve. Note that propane and H_2S are particularly adept at stabilizing hydrate crystal structures. To get a complete picture of hydrate stability, the characteristics of the condensate/oil must also be accounted for. Figure 4 shows two examples of hydrate stability curves with and without liquid hydrocarbon present. Since liquid hydrocarbons can absorb hydrate-forming gases, the presence of a liquid hydrocarbon phase lowers the temperature at which hydrates are stable. Considering the gas phase only yields too conservative a curve, especially at higher pressures.

The composition of the water phase, particularly the presence of salts or alcohols, has the most dramatic impact on

the hydrate stability temperature. Salts and alcohols, among other compounds, act as thermodynamic hydrate inhibitors, that is they shift the hydrate stability curve to the left. Figure 5 shows the effects of several different substances. On a weight basis, salt is the most effective hydrate inhibitor and so accounting correctly for the produced brine salinity is important in designing a hydrate treatment plan.

Hydrate stability curves can be predicted by a number of means, the most accurate being statistical mechanical routines, which are now available in several commercial software packages. These predictions are often taken for granted, but caution must be exercised in applying them at high pressures, in systems with high concentrations of mixed electrolytes, and in trying to model the presence of both salt and methanol / glycol. In addition, natural gas hydrates typically form one of three crystal structures, depending primarily on the size(s) of the guest molecule(s). All potential hydrate structures must be considered, since different formation conditions can produce different hydrate phases.

While these calculations provide useful information and guidance, they cannot completely describe hydrate behavior, for it is kinetics which often control hydrate formation in real systems. Unfortunately, little in the way of field-verified kinetic models are as of yet available. Despite a lack of quantitative understanding, some qualitative observations are instructive.

As with any crystallization process, hydrate formation is not always spontaneous; there is often a delay time or the temperature must be lowered somewhat below the hydrate stability temperature in order for hydrates to form. The farther the temperature below the hydrate stability temperature, shorter the delay time to nucleate crystals. A useful analogy is that of ice formation. It is often possible to cool water several degrees below its freezing point before the first crystal appears. Once the crystal appears, subsequent growth is typically rapid. The same holds true for hydrates. The ability to subcool a system without hydrate formation leads some to distinguish between a hydrate formation temperature and a hydrate dissociation temperature (which is nearly the same as the equilibrium temperature), calling the region in between the metastable region. Some software packages even attempt to predict this metastable region. These hydrate formation temperatures are often cited as being 3-7 °F below the equilibrium value. Regularly operating within this metastable region is risky. While such differences in hydrate formation and dissociation temperatures are readily observed in the laboratory, the quantitative magnitude of this hysteresis is apparatus and technique dependent. In real systems, factors such as agitation, fluid history, presence of other solids, and differing residence times are unknowns which cannot be fully accounted for.

Assuming hydrates will form in a system, the next concern is whether they will form a restriction or plug. Hydrate plugs can form in just a few minutes, or take several days to block production. There are two views of plug formation, one in which hydrates slowly build up on the bottom of the pipe, gradually restricting flow, and the other in which hydrates agglomerate in the bulk fluid, forming masses of slush which bridge and eventually block the flow. Both mechanisms have been observed in the field, though the latter is believed to be more prevalent.

Hydrate problems can appear during normal production, but transient operations are often more vulnerable. For instance, during a shut-in, the temperature of the subsea line drops to that of the surrounding environment (typically 40 °F). Given sufficient time under these high pressures and low temperatures, hydrates will form. The extent to which the gas, oil, and water partition during shut-in somewhat limits the growth of hydrates; though direct contact between the gas phase and the water phase is not needed for hydrate formation, an intervening oil layer slows transport of the hydrate forming molecules. Additionally, hydrates typically form in a thin brittle layer at the water / oil interface, which impedes further contact between the water and gas molecules. Most often, lines do not plug when shut-in. However, when the well is restarted, the agitation breaks the hydrate layer and allows good mixing of the supercooled water and gas. Rapid hydrate formation ensues, sometimes called a "snowball" effect, and often leads to a blockage downstream of where water tends to accumulate (i.e., low spots).

Plugging tendency increases as the water cut increases, since there is a higher likelihood that sufficient hydrate particles will contact each other and stick together. It follows that just downstream of low spots is a common location to find hydrate plugs. Other typical locations include flow restrictions and flow transitions (e.g., elbows and riser bases). Often, multiple plugs have been recorded, further complicating remediation efforts. Once a hydrate plug forms, it is not a static entity. The often rapid growth of hydrates leads to a porous structure with high volumes of occluded water. These initial plugs can be permeable to gas, but not usually to liquids. Transmission of gas through the hydrate deposit can lead to Joule-Thomson cooling and further conversion of water to hydrates. Thus deposits can ripen to denser, less permeable plugs.

While the extent of wax and asphaltene problems varies enormously from project to project, gas hydrate problems are nearly universal in Deepwater production. The vast majority of hydrate blockages reported have occurred in gas or gas condensate systems[2]. Even gases dried below 10 lbs water / mmscf of gas can form hydrate plugs, especially if there are points in the system where condensed water can accumulate.

In some instances, there is still a misconception that hydrate plugs do not occur in black oils. This myth has arisen from two factors: a lack of experience and the phenomena of "non-plugging" oils. Most Deepwater black oil systems are simply not producing significant volumes of water yet. As water cuts rise, the incidence of hydrate plugs in black oil lines will most certainly increase. It is well known that some black oils have a tendency not to plug, even when hydrates are formed. Rather, the hydrates remain small particles dispersed in the liquid phase and are readily transported through the flowline. Though often referred to as non-plugging oils, these oils will eventually plug with hydrates if the water cut gets

high enough (occasionally as high a 45% water cut). There are several known instances where hydrate plugs have occurred in black oil systems, some reported to have water cuts of less than 1%. Plugging tendency appears to be a characteristic of each oil, and at present, only extensive, large scale flowloop testing has shown promise in predicting plugging tendencies. A further complication is that the water cut observed on the platform may not be indicative of the water cut at local points along the flowline due to differences in water and oil hold-ups or hydrate deposition. These uncertainties require producers to use conservative designs and operating procedures to guard against potential hydrate blockages.

There is only one universal truth about hydrate dissociation: operators seldom have the patience to wait for it to happen. Like the kinetics of hydrate formation, this is a poorly understood subject and translating laboratory observations to field predictions has proven difficult. Part of the problem is the complicated interplay of heat transfer, mass transfer, and kinetics in addition to phase equilibria. Intuitively, one expects the dissociation behavior to depend on the size, porosity, permeability, volume of occluded water, "age" of the deposit, and local conditions such as temperature, pressure, fluids in contact with the plug, and insulation on the pipe.

Hydrate dissociation is highly endothermic. If heat transfer from the surroundings is limited, the temperature near a dissociating hydrate can drop rapidly. In addition, as gas is evolved during hydrate dissociation, Joule-Thomson cooling of the expanding gas is possible. By either of these mechanisms, additional hydrates and / or ice can form during the dissociation process, so that freeze/thaw cycles may delay the time to remove a plug.

Asphaltenes

In general asphaltenes cause little to no operational problems since the majority of asphaltic crude oils have stable asphaltenes. Typically only downstream problems occur due to blending or high heat. Crude oils with unstable asphaltenes suffer from some severe operational problems most of which are fouling related and affect valves, chokes, filters, and tubing. Asphaltenes become unstable as the pressure of the well decreases and the volume fraction of aliphatic components increases. If the aliphatic fraction of the oil reaches a threshold limit then asphaltenes begin to flocculate and precipitate. This pressure is called the flocculation point.

One method of characterizing an oil is with a SARA analysis. This method breaks the oil down into four pseudo components or solubility classes and reports each as a percentage of the total. The four pseudo components are saturates, aromatics, resins, and asphaltenes. The asphaltene fraction is the most polar fraction and is defined as aromatic soluble and n-alkane insoluble. Asphaltenes are condensed polyaromatic hydrocarbons that are very polar. Whereas wax has a hydrogen to carbon ratio of about 2 asphaltenes have a hydrogen to carbon mole ratio around 1.15[3]. The low hydrogen content is illustrated in Figure 6, which is a drawing

of a hypothetical asphaltene molecule.

Asphaltenes appear as black crumbly coal like solids that do not melt but, break down before they vaporize, and have a density of around 1.3 g/cm^3. Often iron sulfide and heavy wax are misidentified as asphaltenes but these can be differentiated with melting and weak acid solubility tests. In production systems the asphaltenes are often found mixed with wax or oil which contributes to some of the confusion.

It is likely that the primary fouling mechanism in production systems involves adhesion of precipitated particles. Therefore, the amount of asphaltenes that can deposit is limited to the precipitated fraction, which is significantly smaller than the total asphaltenes in the crude oil.

There are two mechanisms for fouling that occur in the formation. The first involves acid; the second is adsorption to formation material. Acidizing is one of the most common well treatments and can cause severe damage to a well with asphaltic crude oil. The acid causes the asphaltenes to precipitate, sludge and form rigid film emulsions which severely affects permeability, often cutting production by over 50%. Formation material, particularly clays, contain metals that may interact with the asphaltenes and cause the chemisorption of the asphaltenes to the clay in the reservoir.

A SARA screen, aliphatic hydrocarbon titration, or depressurization of a bottom hole sample are used to determine if asphaltenes are unstable in a given crude. One SARA screen is the colloidal instability index (CII)[4]. The CII is the ratio of the unfavorable components to the favorable components of the oil as shown in Equation 4,

$$CII = \frac{S + As}{R + Ar} \qquad \textbf{(4)}$$

where S is the percentage of saturates, As is the percentage of asphaltenes, R is the percentage of resins, and Ar is the percentage of aromatics in the oil. If the CII is greater than one then amount of unfavorable components exceeds the amount of favorable components in the system then the asphaltenes are likely to be unstable.

There are several aliphatic hydrocarbon titrations that can be used to assess the stability of asphaltenes in a dead crude oil. One method in particular involves the continuous addition of an aliphatic titrant to oil and the measurement of the optical density of the solution. In this method the precipitation point of asphaltenes is detected by monitoring changes in transmission of an infrared laser. The instrument is referred to the asphaltene precipitation detection unit (APDU). As the hydrocarbon is added to the oil the optical density decreases and the laser transmittance through the sample increases. At the point when enough titrant has been added to the sample that asphaltenes become unstable and precipitate the optical density drops dramatically. This point is called the APDU number which is defined as the ratio of the volume of titrant to the initial mass of crude oil.

Depressurization of a live bottom hole sample provides the most direct measure of asphaltene stability for production systems. During depressurization, the live oil flocculation point or the pressure at which asphaltenes begin to precipitate

in the system is determined by monitoring the transmittance of an infrared laser which passes through the sample. Onset of flocculation will produce a noticeable reduction of light transmittance. If an oil has a flocculation point then the asphaltenes are unstable at pressures between the flocculation point to just below the bubble point. Many oils are unstable only near the bubble point which has led many engineers to believe that problems only occur at the bubble point. However, there are oils that have an instability window of several thousand pounds per square inch. In figure 7 an asphaltene solubility curve is depicted. The onset or flocculation point, saturation pressure, and asphaltene saturation point are indicted with dashed lines while the unstable region is indicated by a shaded area between the asphaltene saturation point and the solubility curve. As shown on the curve the region of instability is from 2600 psi to 3800 psi.

After the bubble point has been reached the mass of precipitated asphaltenes and the mass of asphaltenes deposited in the cell is measured. These two measurements provide a means to assess the likely hood of problems due to deposition. We have observed that only a small percentage of total asphaltenes will adhere to a surface during an experiment. Based on these observations we would expect only about 5% of the total asphaltenes to play a role in asphaltene deposition. The mass of deposited asphaltenes can be used to predict the mass of deposition in a production system. While this number is likely to be an overestimate it is a good number for design purposes and for contingency planning.

System Implications

Systems can be designed either to let the solids deposit then remove them or to prevent deposition altogether. Usually the prevention strategy results in high capital costs while the "deposit then remove" strategy yields lower capital but higher operating costs. Often a risk analysis is required to determine which strategy to employ. Sometimes the choice of strategy is obvious based on some characteristics of the deposition of solids.

Wax deposits slowly. Often weeks are required to deposit a significant amount of wax. Insulation and wax inhibitors can stretch the time for a significant deposit to many months. This characteristic invites a system design to allow wax to deposit then remove it. This is the usual approach to managing wax in flowlines. They are designed to permit wax removal by round trip pigging from the host platform. Two flowlines are required for round trip pigging.

Subsea pig launchers installed at the tree permit pigging of a single flowline. In another approach, Petrobras sends soft foam pigs down a small gas lift line to remove wax in the larger flowline as the pig returns to the host facility. This does not remove all the wax so they periodically treat the lines with chemically generated heat. An electrically heated flowline could also be used to manage wax in a single flowline system.

Wax management in the wellbore is usually accomplished by preventing deposition altogether. A "deposit then remove" strategy results in either a costly TFL system or in periodic

wax cutting from a floating rig. Neither is desirable. Wax deposition in the wellbore is prevented by conserving heat with insulated tubing or maintaining a minimum flow rate to keep the temperature above the wax deposition temperature. It is now recognized that in the Gulf of Mexico insulated tubing is probably not worth the cost in reduced wellbore size, dollars, rapid cool-down times and long procurement times. However, insulated tubing may have a place where reservoir temperatures are low.

Hydrate plugs form quickly. In gas systems it is not unusual for plugs to form within a few hours of failure of the hydrate control systems. A plug requires heat to melt and the heat transfer rate is often the rate-limiting step in melting. It requires much longer to melt a plug than to form it; thus, the appropriate design premise is to prevent hydrate deposition altogether. Producers cannot afford the down time associated with constant plug remediation.

Hydrate control strategies for gas and oil systems are different. Gas systems are designed for continuous injection of a hydrate inhibitor. Water production is small, typically only the water of condensation. Inhibitor requirements are thus relatively small, on the order of 1-2 bbl MeOH/mmscf. Oil systems produce free water. Continuous inhibition is generally too expensive so some alternative control system is adopted. Insulation is often used to control hydrates during normal production and some combination of blow down and methanol injection used during start-up and shutdown. Flowline insulation is costly but the more serious drawback may be lengthening the hydrate plug remediation time in the event of plug formation. Insulation limits the heat transfer required to melt the plug.

If the system produces a "non-plugging oil", insulation may not be required, at least early to mid-life. However, late in life when the water cut rises, even non-plugging oils will require either insulation or continuous inhibition treatment. Thus installing uninsulated lines can limit field life to moderate water cuts. Choosing to design an uninsulated flowline based on the assumption that the oil will be non-plugging is risky given the difficulties in predicting plugging tendencies.

Reservoir engineers and flow assurance engineers distinguish differently between gas and oil systems. A reservoir engineer relies primarily on a GOR cutoff to characterize a gas or oil system. The flow assurance engineer is primarily concerned with water production. Will the water be water of condensation or is significant formation water expected? These differing perspectives can lead to communication issues amongst the different specialties.

Asphaltene problems occur infrequently offshore but can have serious consequences on project economics. Since asphaltene deposition is most likely as the produced fluid passes through the bubble point, the deposition often occurs in the tubing. Subsea systems designed to mitigate asphaltene problems generally rely on bottom hole injection of an inhibitor with provision to solvent treat the wellbore when required. In the absence of inhibitors, monthly tubing cleanouts are not uncommon onshore. This frequency would

be intolerable in a subsea system making effective inhibitors essential to the development.

Conclusion

Flow assurance threats can be identified and handled with if they are discovered early and proper system design and operation procedures are implemented. Meeting the stretch goal of a 100 mile single flowline tieback will require increasing confidence in and continuous improvement of flow assurance technology.

To select and deploy an appropriate flow assurance strategy a fundamental understanding of each solid's characteristics is essential. Otherwise, minimizing capital and operating expenditures while minimizing risk is difficult.

A good strategy for deepwater subsea system would include the following rules of thumb:

- Prevent wax deposition in the wellbore
- Mitigate wax deposition in the flowline and pig
- Continuously treat for pour point problems
- Prevent hydrates deposition everywhere
- Mitigate asphaltene deposition and do not pig

To determine which problems may affect a given system quality oil samples are needed for analysis and testing. And finally, always design for the worst case because early samples may not be entirely representative of the produced fluids due to contamination or fluid changes. If the produced fluids are more problematic than anticipated then chemical solutions may be the only alternative.

Nomenclature

A = deposition area
Ar = percentage of aromatics in the oil.
As = percentage of asphaltenes
C = concentration of wax
CII = colloidal instability index
D = diameter of the pipe
D_m = molecular diffusion constant
L = length of the pipe
m = mass of deposit
R = percentage of resins
r = radial position
S = percentage of saturates
ΔP = pressure drop
ρ = density of wax
τ_y = yield stress

Acknowledgements

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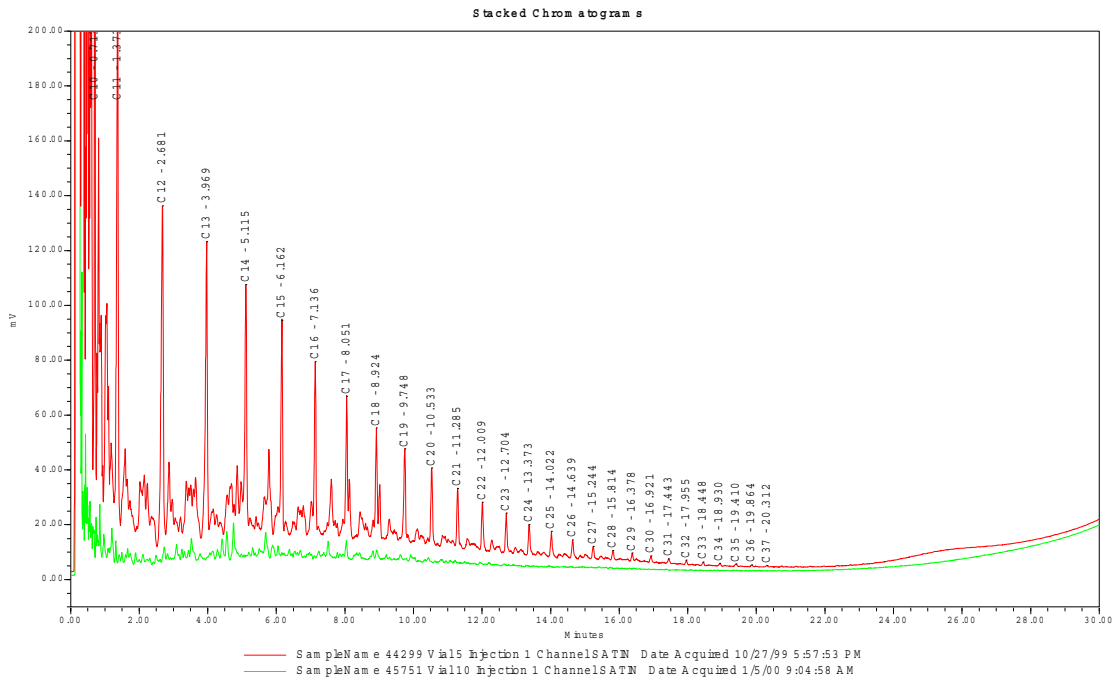
Figure 1: Chromatogram of a waxy crude oil (top) and an asphaltic crude (bottom)
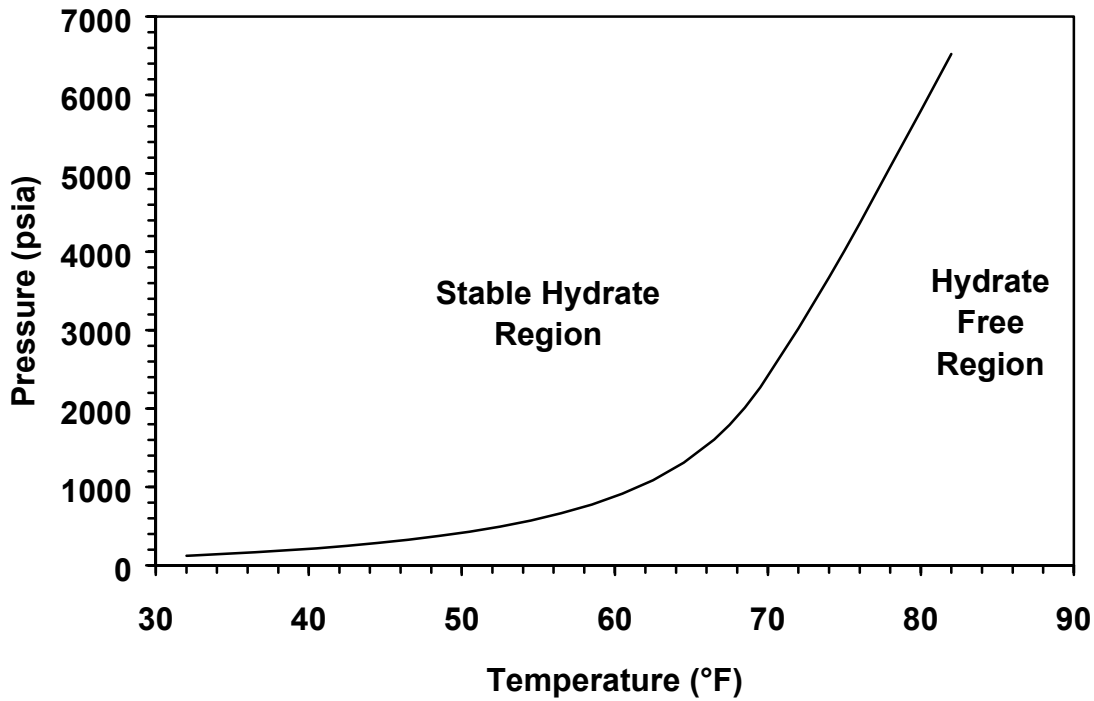

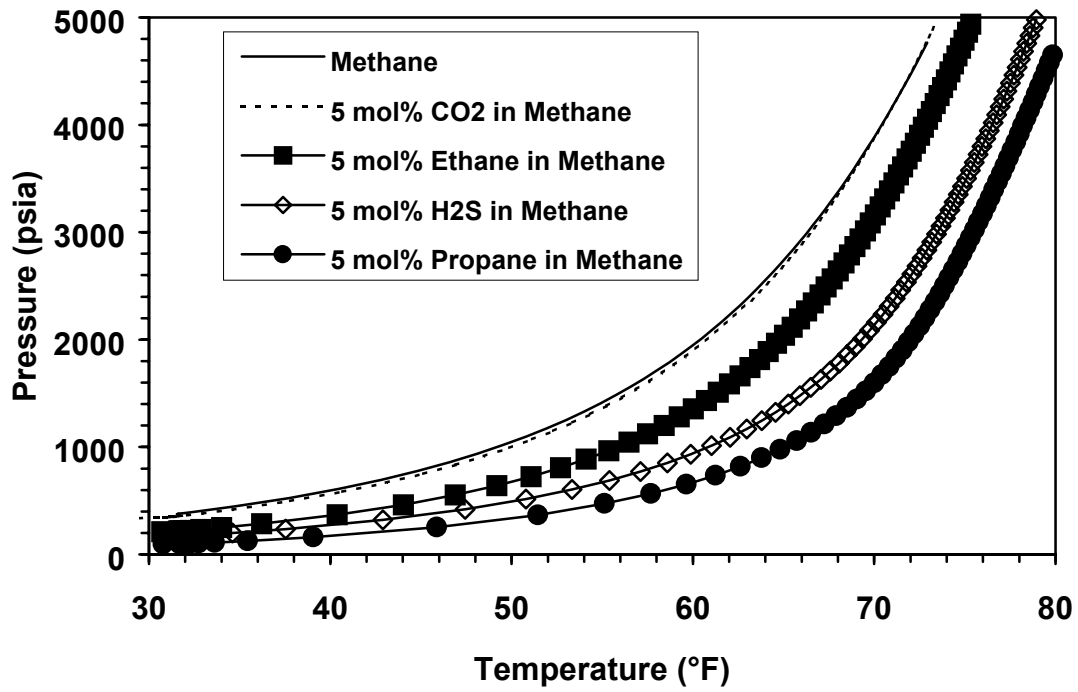**Figure 2: Hydrate stability curve for a typical GOM gas condensate**

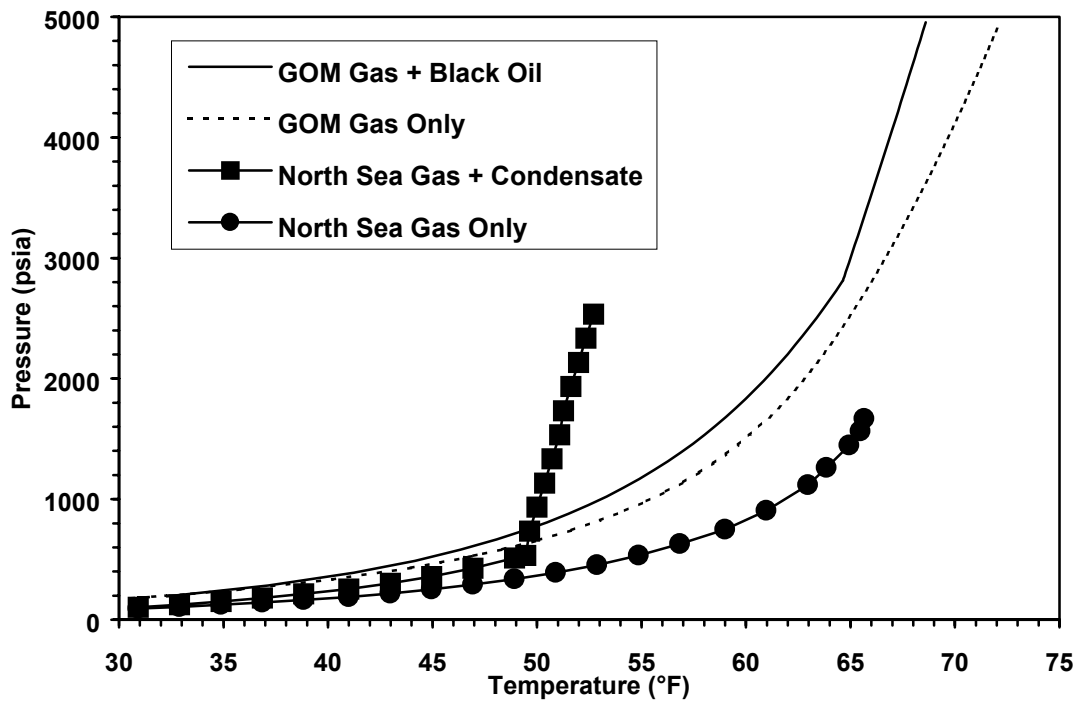Figure 3: Effect of gas composition on hydrate stability

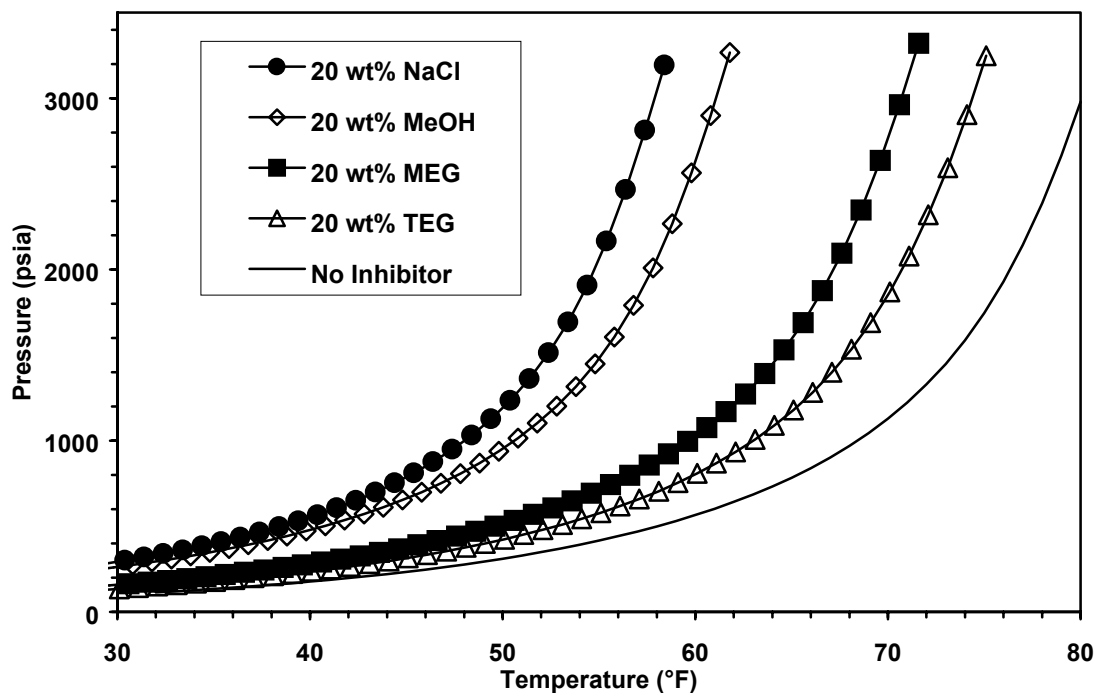Figure 4: Effect of liquid hydrocarbons on hydrate stability

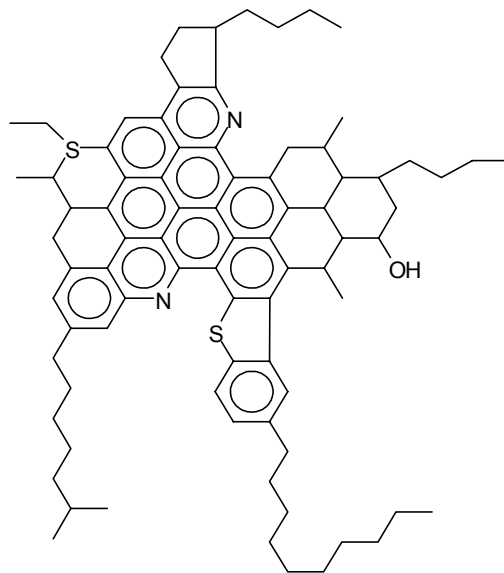**Figure 5: Effect of thermodynamic inhibitors on hydrate stability**
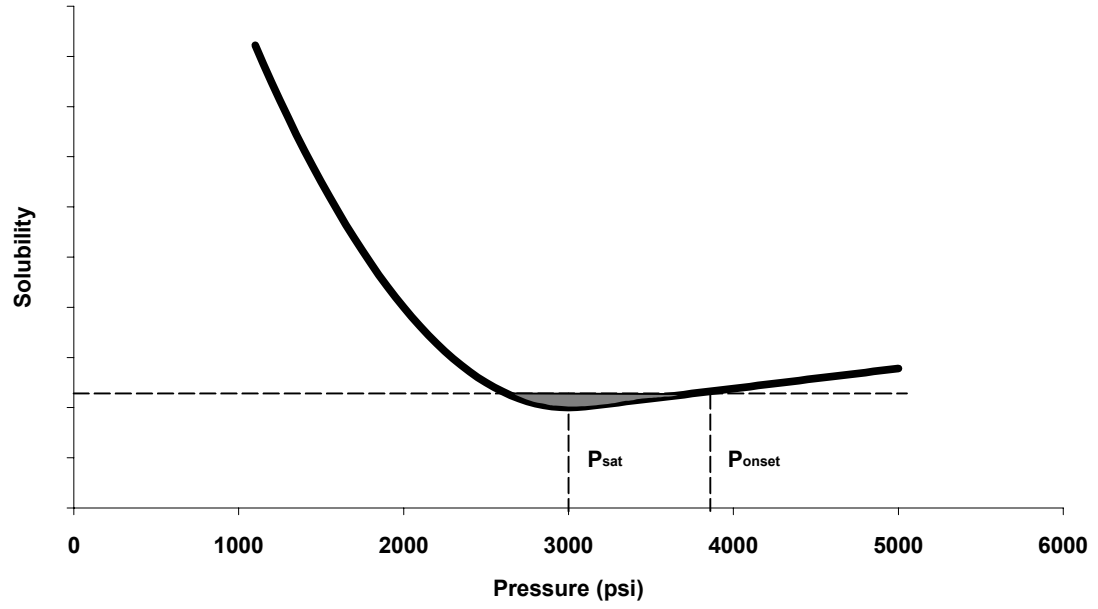

Figure 6: Hypothetical asphaltene molecule

Figure 7: Asphaltene solubility as a function pressure