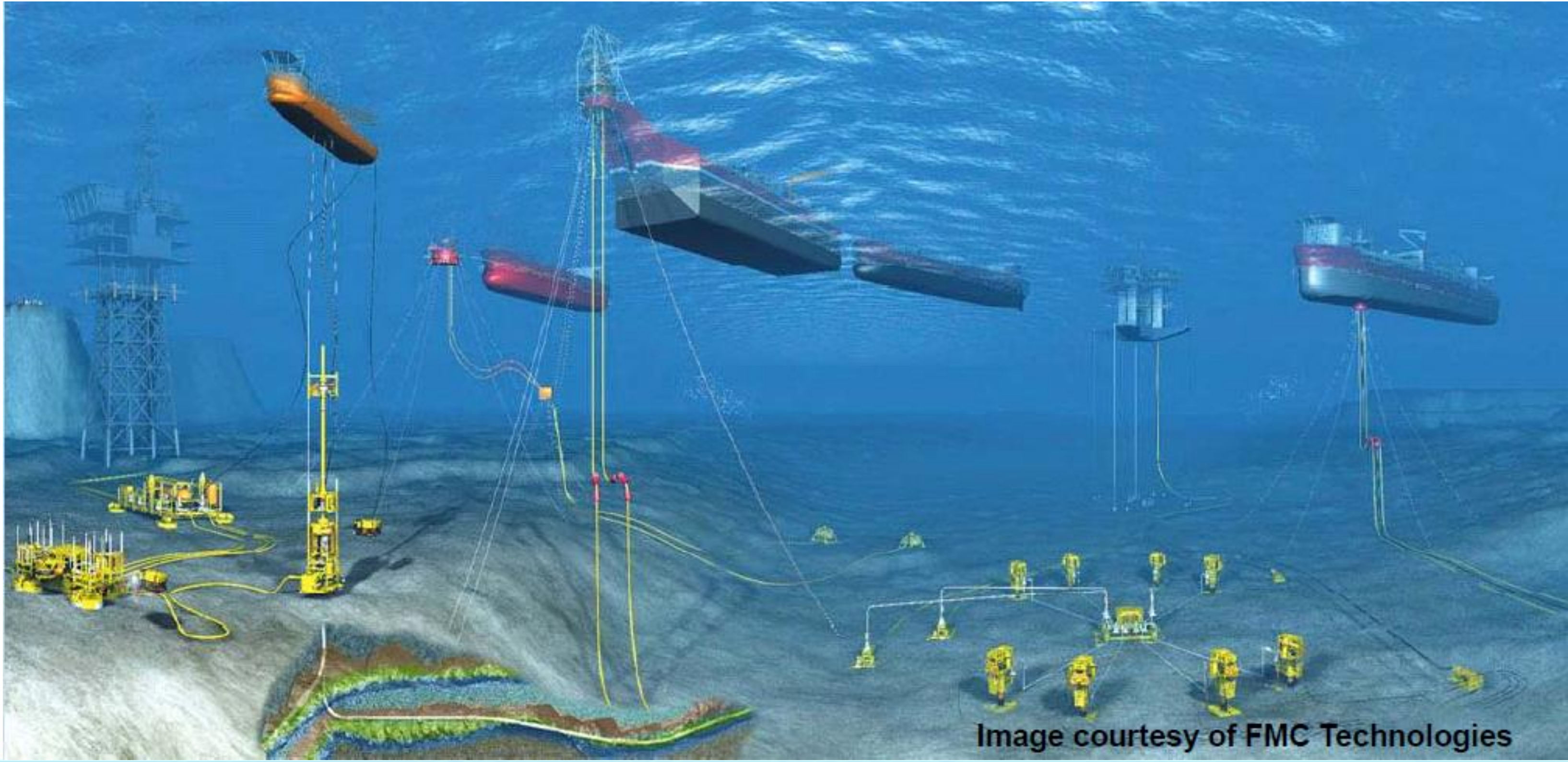


Image courtesy of FMC Technologies

Flow Assurance

서유택

Wax

Wax

- Paraffinic hydrocarbons

  : A solid paraffinic hydrocarbon which precipitate from a produced fluid

  : Forms when the fluid temperature drops below the Wax Appearance Temperature (WAT)

  : Melts at elevated temperature (20^{o}F above the WAT)

- Control strategy

  : Rate of deposition can be predicted to calculate pigging frequency

  : Flowline insulation

  : Wax inhibitor

  : Major factors

    - WAT
    - Fluid temperature
    - Overall U-value
    - Deposition rate

- WAT or cloud point

  : The temperature at which crystals first begin to form is called the cloud point or wax appearance temperature (WAT)

  : 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.

  : WAT does not indicate the amount of wax that will be deposited or the rate at which it will be deposited.

- Pour point

  : The pour point temperature is the temperature at which the oil stops flowing and solidify into a gel.

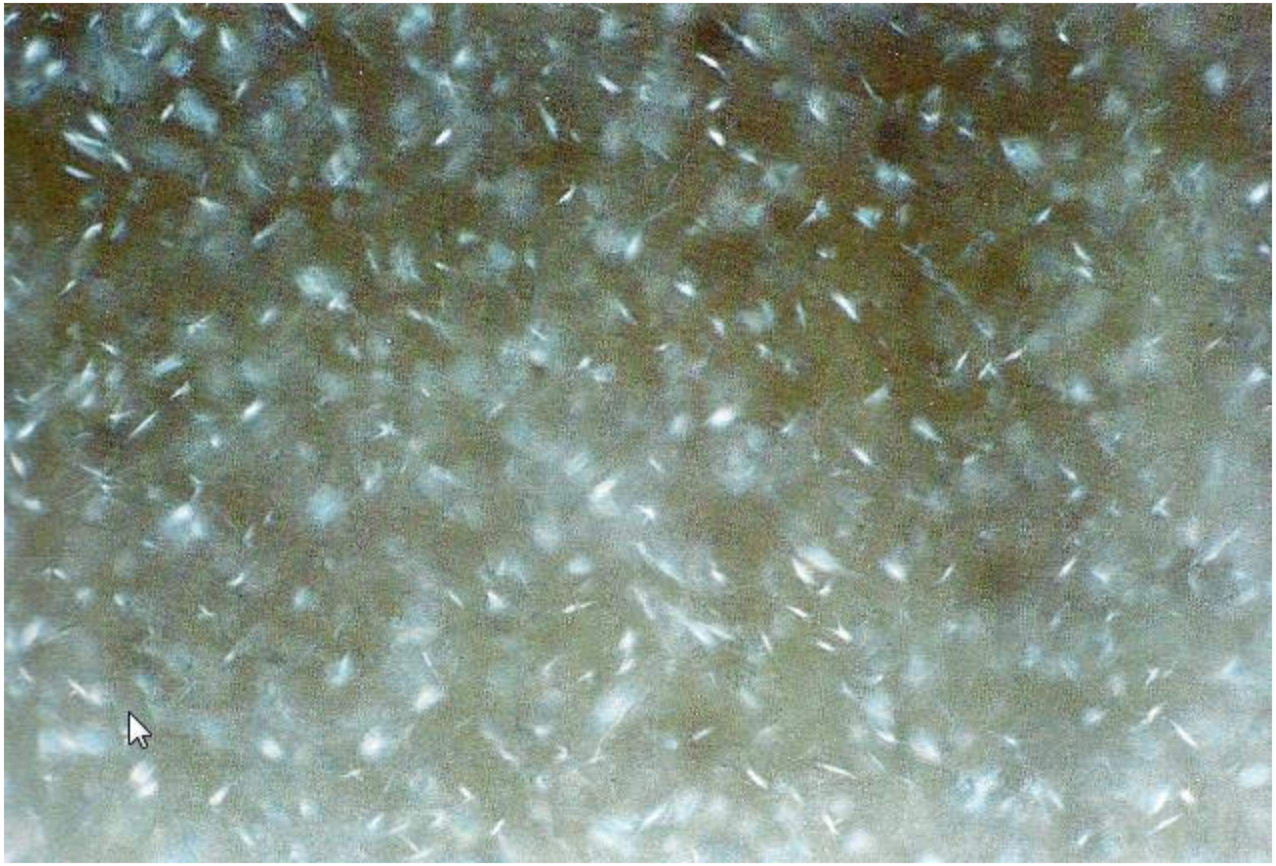
  : A crude oil gel forms when wax precipitates from the oil and forms a 3D structure spanning the pipe.

  : This does not occur while the oil is flowing because the intermolecular structure is destroyed by shear forces. 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.

WAT determination

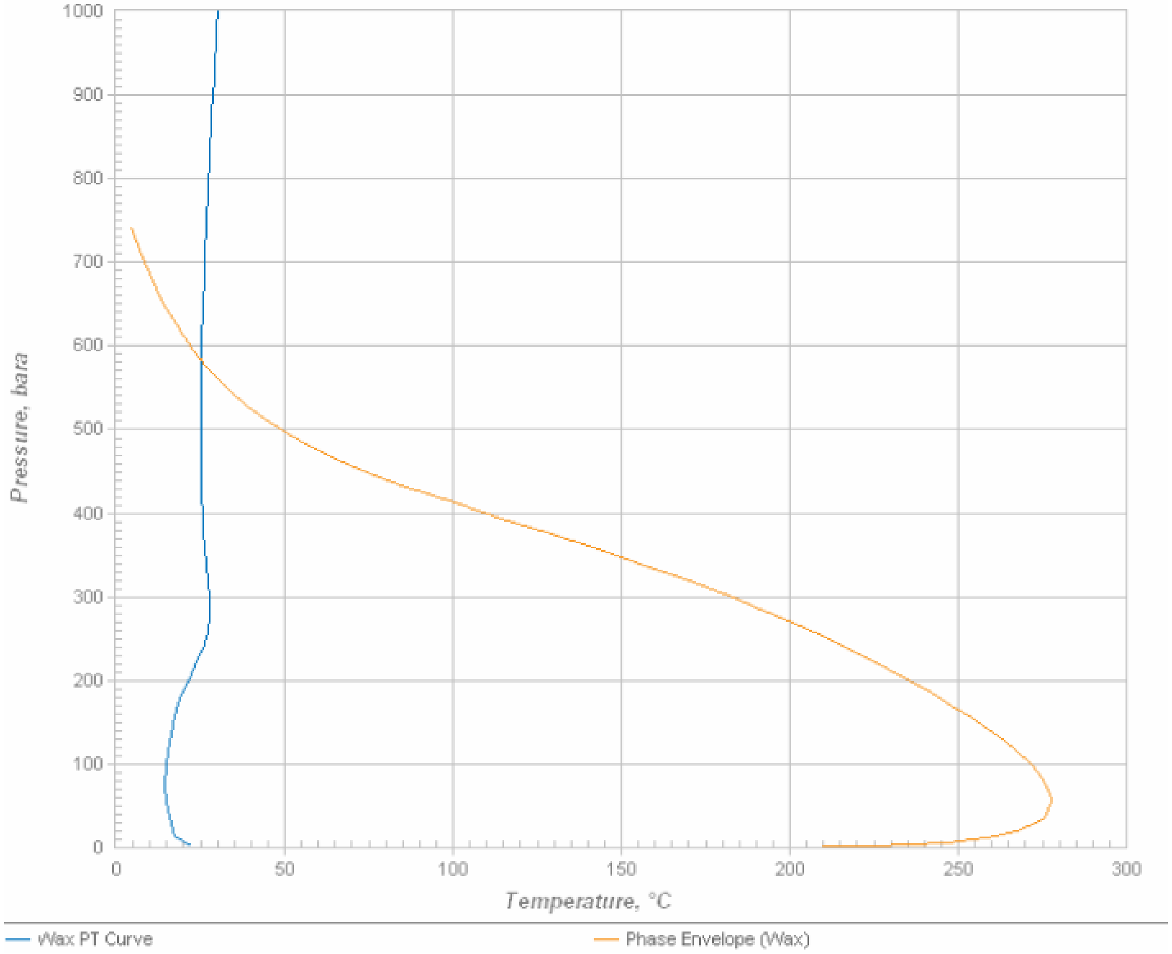
- The wax appearance temperature (WAT) or cloud point is the most important parameter relating to wax formation.
    - CPM - Cross Polarized Microscopy
    - NIR - Near Infra Red Absorption Reflection
    - DSC - Differential Scanning Calorimetry
    - Cold Finger
    - Filtration
- WAT is a crystallization temperature and therefore kinetics will influence any measurement. Thus, it is strongly recommended that cloud point be determined using two different techniques. With care, the cloud point can be determined to an accuracy of 5 ^{o}F.

WAT by Cross Polar Microscopy



- Thermodynamic models can predict wax appearance Temperature (WAT) with
  - Detailed compositional analysis of oil
  - Quantitative n-paraffin analysis using high temperature (HTGC technique, C90+)
- The thermodynamic model may be combined with the model of flowline using software such as PIPESIM or OLGA to predict where wax deposits will occur, how fast wax will accumulate, and the frequency at which the line must be pigged.

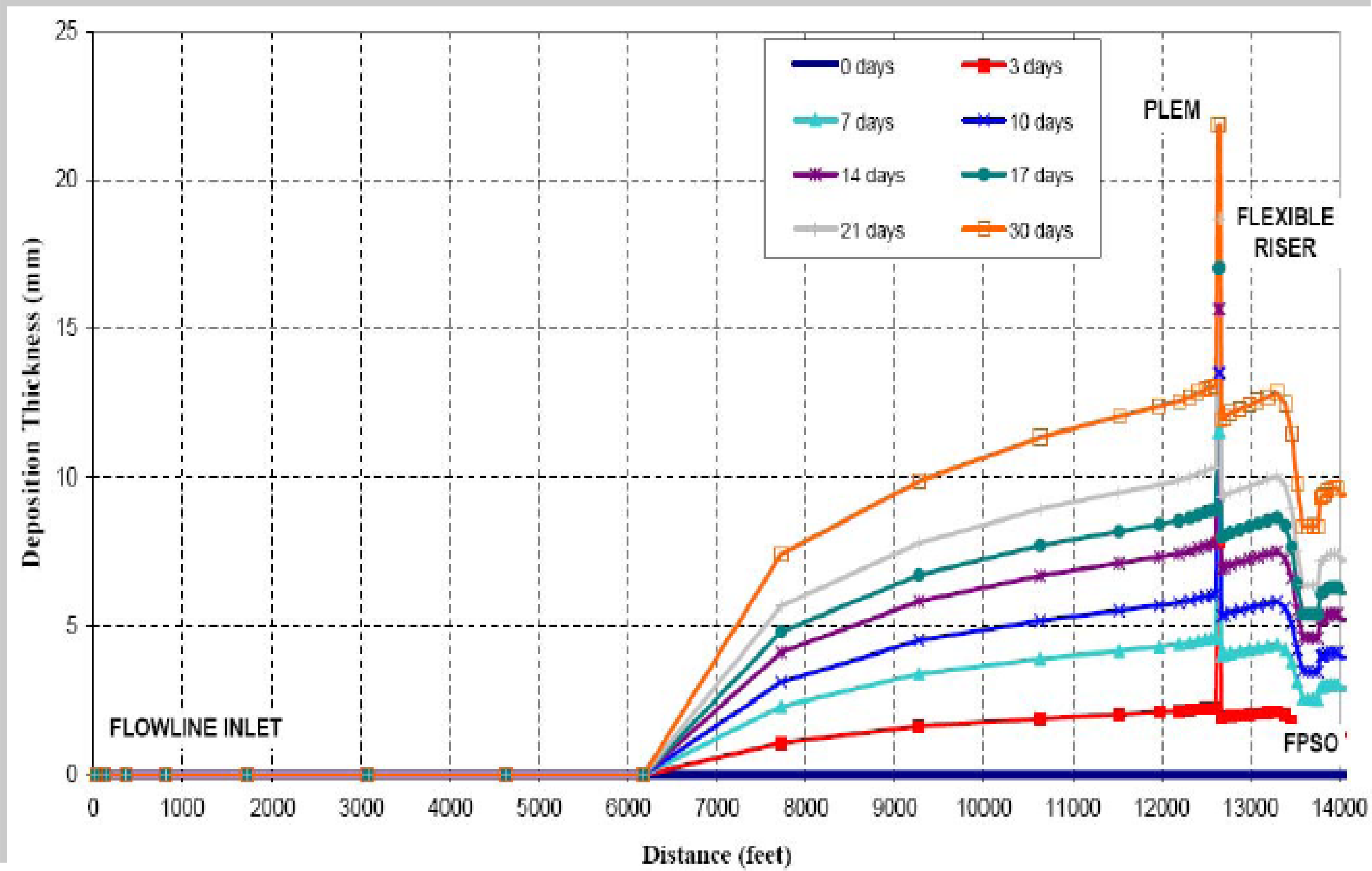
- PVTSim prediction: Wax phase diagram



Impact on production

- Deposition in flowlines is gradual with time but can block pipelines.
- Gelation of crude oil can occur during shutdown.
- High start-up pressures and high pumping pressures occur as a result of the higher viscosity.
- Insulation for pipeline increases capital expenses.
- Wax inhibitors increase operational expenses.
- Pigging operation in offshore environment is more difficult than that in onshore.
- Wax handling in surface facilities requires a higher separator temperature.

Wax deposition in a flowline



Wax Management

- Thermal insulation and pipeline heating

  : Good thermal insulation can keep the fluid above the cloud point for the whole flowline and thus eliminate wax deposition. However this can be a problem once the fluids cool down during shut-in.

- Inhibitor injection

  : Suppresses cloud point, modify wax crystal structure, coat wax crystals, or co-crystalize with wax

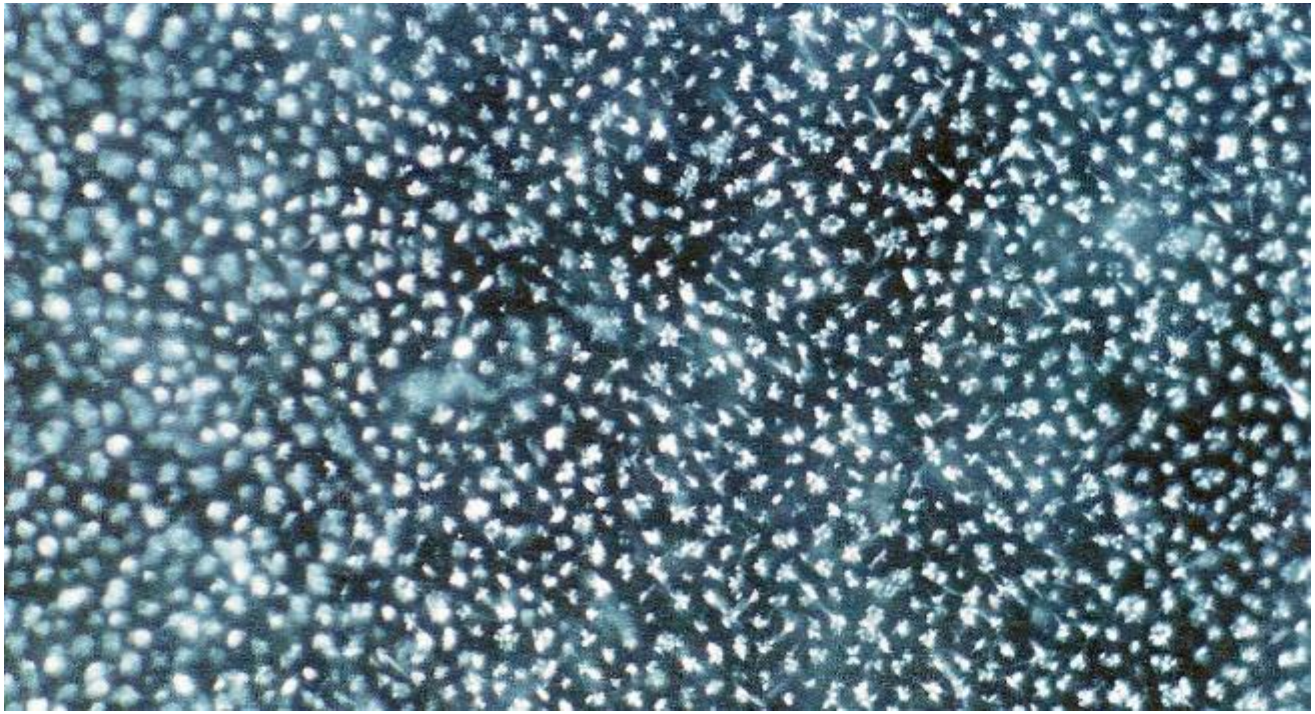
  : The chemicals must match the chemistry of the oil, at the operating conditions, to be effective.

Wax inhibitors

- Wax Inhibitors
  - Thermodynamic wax inhibitor
  - Crystal Modifiers: weaken adhesion
  - Dispersants/Surfactants: prevent growth
  - Pour Point Depressants: reduce viscosity

- Chemistry
  - High molecular weight polymers/co-polymers (such as ethylene vinyl acetate)
  - Esters (olefin/maleic;C18-30+)
  - Surfactants

Modification of Wax Crystals in STO by a Wax Inhibitor



Effectiveness of Chemical Inhibitors

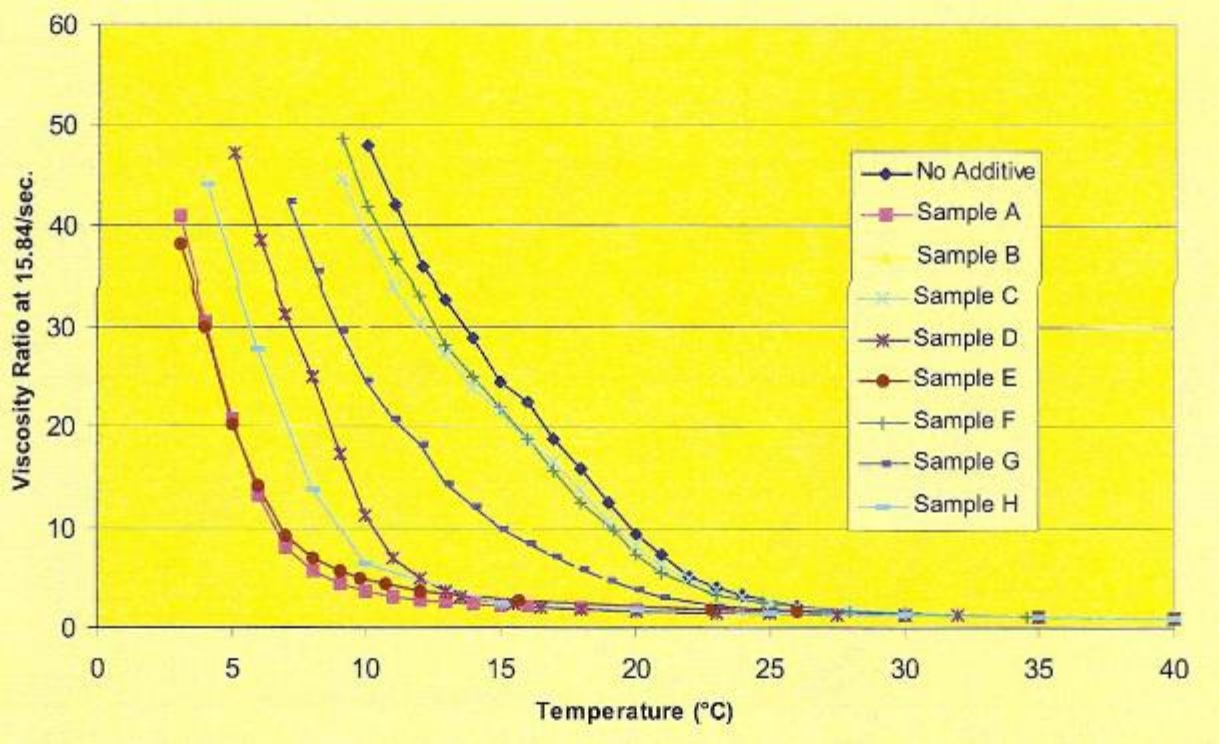
- Can reduce deposition rates but rarely eliminate deposition
  - There is no universal wax inhibitor
  - Pigging capabilities needed as secondary or backup

- Test chemical inhibitors at expected operating temperatures conditions with representative oil
  - Must match the composition of the specific live oil at applicable operating conditions

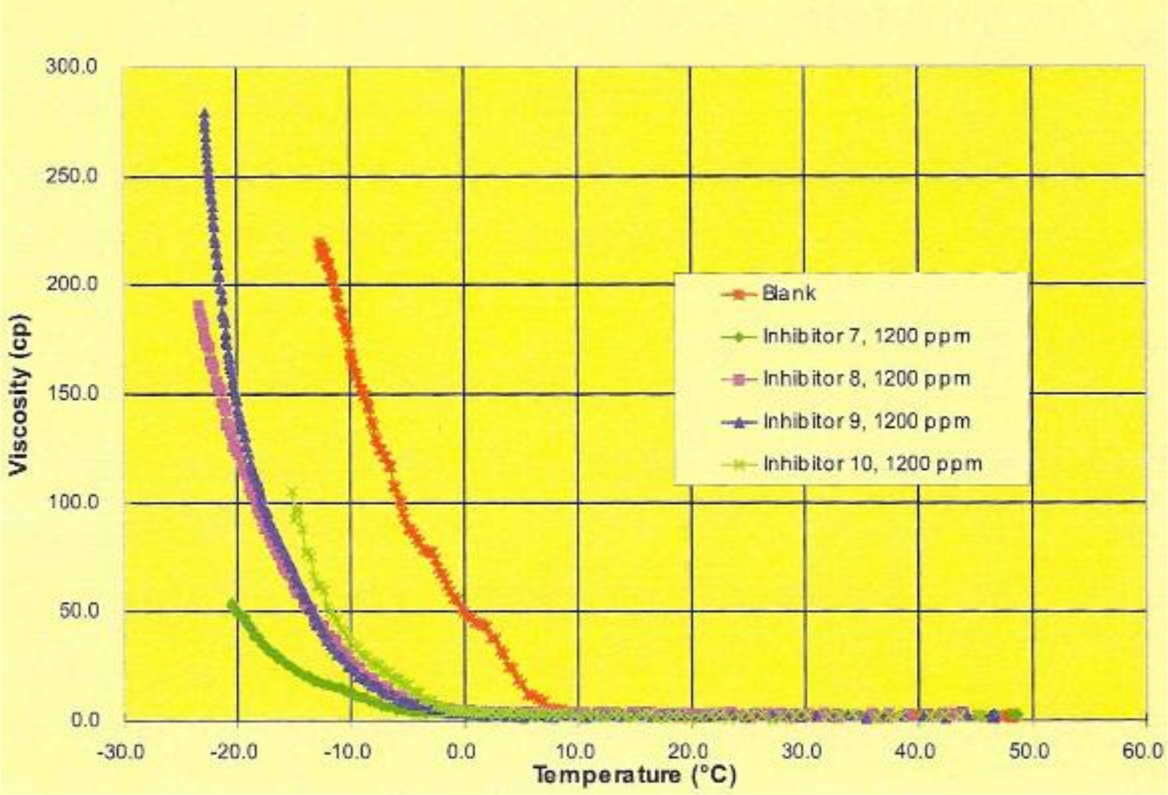
- Optimum wax inhibitor concentration
  - Higher concentration can reduce effectiveness
  - Injection rates: less than 50 to over 1500 ppm, depend on additive and system operating conditions

- Inhibitor should be injected above the cloud point to be effective

Wax Inhibitor Effectiveness - Crude Oil



Wax Inhibitor Effectiveness - Condensate



Remediation of a Wax Plug

- Mechanical means

  : Pigging (expect 1~3 days down time)

  : Pressure surging

  : Coiled tubing

- Heating (at least +12 ^{o}C WAT)

  : Hot oil, hot water, or steam circulation

  : Electric heating

- Solvent Flushing

  : Often the most successful remediation methods, but also the most expensive.

  : When solvents contact the wax, the deposits are dissolved until the solvents are saturated.

Wax Control Design Philosophies

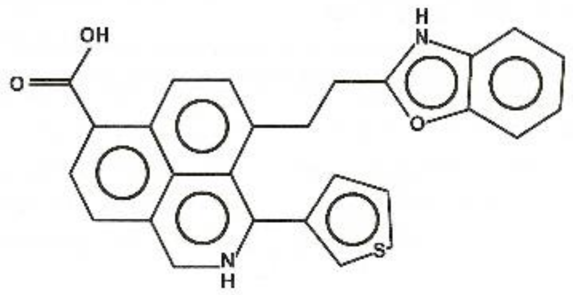
- Design the subsea system to operate above the WAT by thermal insulation.
- Operate the well at sufficiently high production rates to avoid deposition in the wellbore and tree.
- Remove wax from flowlines by pigging, and pig frequently enough to ensure that the pig does not stick.
- Utilize insulation and chemicals to reduce pigging frequency.
- Identify and treat high pour point oils continuously.

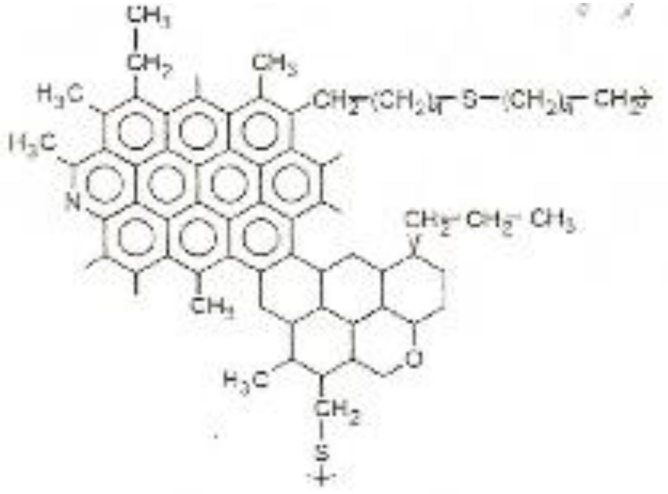
- In steady-state operation, heat retention (pipeline insulation) is used to maintain temperatures above WAT along the pipeline, especially in the deepwater section. Regular operational pigging will be needed throughout life to remove wax deposition.
- In transient operations, gelling is the issue. For planned shutdown and start-ups, inject inhibitors; for unplanned shutdown, focus on restarting the system within the cooldown time of pipeline insulation; if this is not possible, use export pumps to move the gelled plug as early as possible. The required cool-down time has yet to define by operations.

Asphaltene

Asphaltenes

- Asphaltenes are the most heavy polar/aromatic compounds. They are not really soluble in most oils but exist as colloidal suspensions in the oil phase under reservoir condition.
- Asphaltenes carry the bulk of the inorganic component of crude oil, including sulfur and nitrogen, and metals such as nickel and vanadium.
- All oils contain a certain amount of asphaltene. Asphaltenes only become a problem during production when they are unstable.





Asphaltenes Properties

- The ASTM 0-3279-90 (IP143/90) defines asphaltenes as solids that precipitate when an excess of n-heptane or n-pentane is added to a crude oil.
- Asphaltenes do not have a single, unique structure or molecular weight. Unlike waxes, asphaltenes do not melt. Consequently, thermal methods do not work to prevent or remediate asphaltene deposition.

- H/C = 0.8 - 1.4

- Molecular weight:

  depends on solvent and concentration

  monomer = 500 - 1000

  micelles = 1000 - 5000

- Heteroatoms: acting as polar functional group

  C=80-85wt% (50-60 wt% aromatics), H=7-10 wt%, S=0.5-10 wt%; N=0.6-2.6 wt%; O=0.3-4.8 wt%

- Metal elements: Ni, V, Fe

Differences between wax and asphaltene

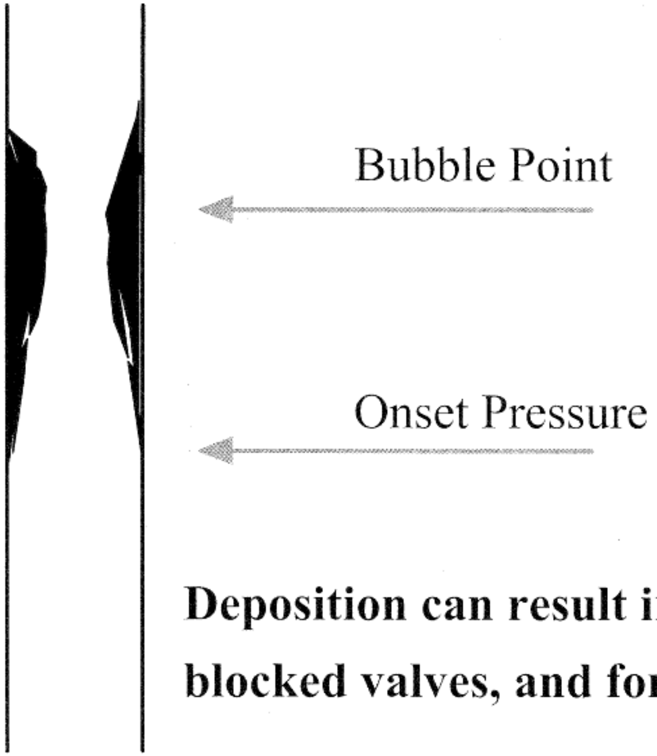
	Asphaltene	Wax
Dissolved in heptane	No	Yes
Crystalline	No	Yes
Melting point	No	Yes

Asphaltene Precipitation/Deposition

- Asphaltenes can deposit in reservoirs, wellbore tubing, flowlines, separators, etc. The deposits can interrupt and potentially stop production due to the formation of plugs.
- Asphaltenes are suspended by resins as micelles in the crude oil. Resins are chemically similar to asphaltenes on one end and similar to alkanes on the other.
- 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*.
- At the bubble point, gas breakout occurs, where lighter gases such as methane, ethane, and propane are lost from the oil. These are the very species which remove the stabilizing resins from asphaltene, destabilizing them and leading to precipitation.

Downhole deposition

- However, the loss of these alkanes increases the solvency of the crude for asphaltenes, and no further precipitation would be expected once pressure fall below the bubble point

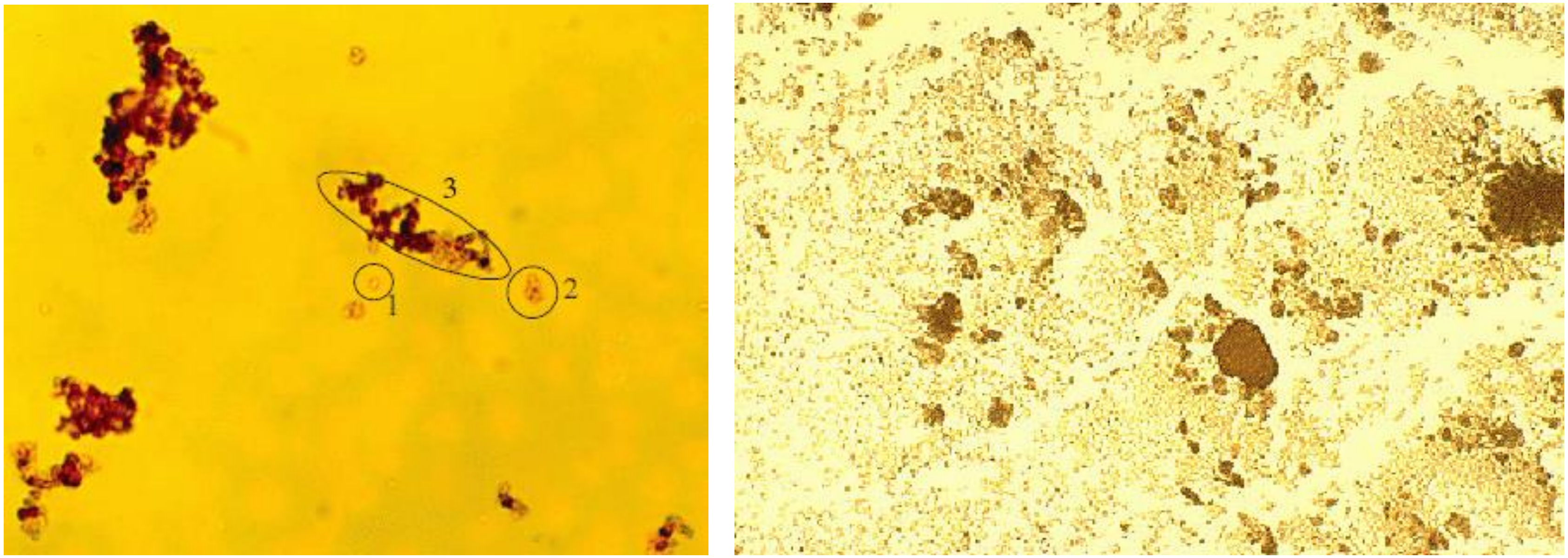


Deposition can result in stuck tools blocked valves, and formation damage

Assessment of Asphaltene Problem

- One method of characterizing oil is with a SARA (saturates, aromatics, resins, and asphaltenes) analysis.
- This method breaks the oil down into four pseudo-components or solubility classes and reports each as a percentage of the total. The asphaltene fraction is the most polar fraction and is defined as aromatic soluble and *n*-alkane insoluble.
- Depressurization of a live bottomhole sample provides the most direct measurement 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 that passes through the sample.

Asphaltene flocculates under microscope



Treating Asphaltene Problems

- Chemical treatment

  : Dissolving precipitated asphaltenes with hot aromatic solvents such as xylene

  : Injecting asphaltene inhibitors such as polymeric asphaltene dispersant chemical

- Plastic coating

  : Epoxy resin coatings may stop asphaltenes from sticking and building up into a deposit

- Engineering solutions

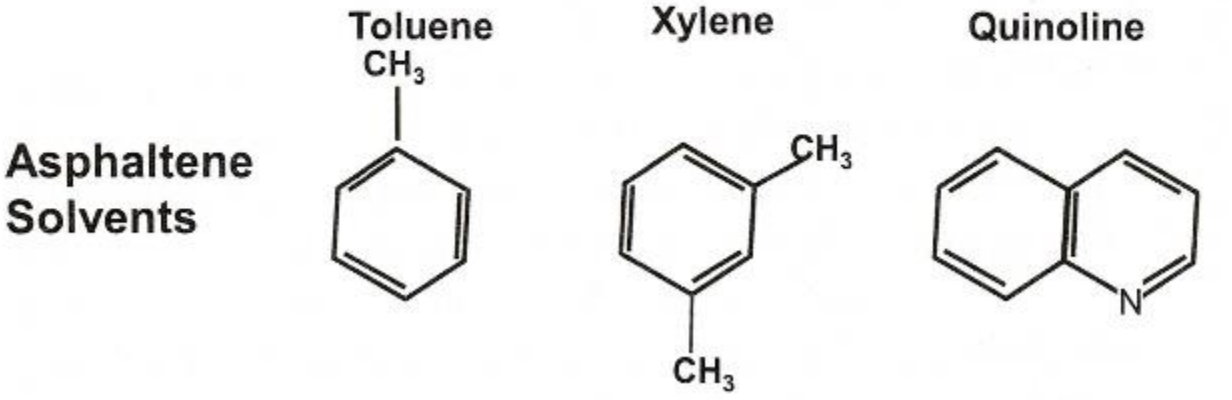
  : Dual completions to allow the injection of Xylene directly into the production stream. Coiled tubing can be used to inject asphaltene solvents.

- Operational changes

  : The greatest risk occurs at pressures just above the bubble point. The reservoir pressure can be reduced by rapid depletion such the bubble point occurs away from the production tubing.

Asphaltene Inhibition/Remediation

- Addition of chemicals that are similar to the asphaltene stabilizing resins and aromatics in crude oil.



Asphaltene control design philosophies

- Inject an asphaltene dispersant continuously into the wellbore (injection must be at the packer to be effective).
- Install equipment to facilitate periodic injection of an aromatic solvent into the wellbore for a solvent soak.
- Be financially and logistically prepared to intervene with coiled tubing in the wellbore to remove deposits.
- Control deposition in the flowline with periodic pigging with solvents.

Scale

Scale

- Scale is a deposit from precipitated mineral components in formation water. This is in contrast with waxes and asphaltenes, which deposit from crude oil.

- Solids may precipitate and deposit from the brine once the solubility limit is exceeded, which is caused by one of following ways.

  : (Solubility) Due to the change of temperature or pressure for brine during production, the solubility of some of the inorganic constituents will decrease and result in the salts precipitating.

  : (pH) As pressure decreases, CO_2 and H_2S (acid gases) vaporize from the water phase, which increases the pH. Minerals are generally less soluble at higher pH.

  : (Incompatible fluids) When two incompatible waters (such as formation water rich in calcium and seawater rich in sulfate) are mixed. Scales formed under these conditions are generally sulfate scales.

Common Scaling Minerals in Reservoirs

- Calcium Carbonate (calcite)
- Calcium Sulfate (gypsum)
- Barium Sulfate (barite)
- Strontium Sulfate (celesite)

Scale: Saturation Index (SI)

- The solution is said to be saturated when the concentration of the solute is high enough such that it will no longer remain in solution at a specified temperature and pressure.

- The saturation index is defined as: SI = log([Me][An]/Ksp)

  SI<0: Non-Scaling, SI=0: Equilibrium, SI>0: Scaling Tendency

  Where:

  [Me] = molality of: Ca^{2+},Mg^{2+},Ba^{2+}, Sr^{2+} or Fe^{2+}

  [An] = molality of CO_3^{2-}, SO_4^{2-}, or S^{2-}

  Ksp= solubility product = product of moralities at saturation

Common type of scale

- Calcium Carbonate
  - Scaling conditions usually occur from loss of CO_2 upon production.
  - Scaling can also occur from incompatible waters mixing.
  - Higher solubility at lower temperatures.
  - Precipitation is slow to start after scaling conditions reached
- Calcium Sulfate
  - Scaling usually occurs due to pressure reduction; but also mixing waters.

- Barium Sulfate (usually with a small amount of Strontium Sulfate)

  - Scaling conditions can occur due to temperature drop during production.

  - Scaling can also occur due to mixing of incompatible waters(water floods).

  - Amounts of scale are relatively small, compared to calcium carbonate, but precipitation occurs rapidly once scaling conditions are encountered.

  - "Impossible" to dissolve once formed

- Iron Carbonate

  - Usually are produced by production process rather than as an inherent part of reservoir chemistry (except reservoir souring results in FeS scale)

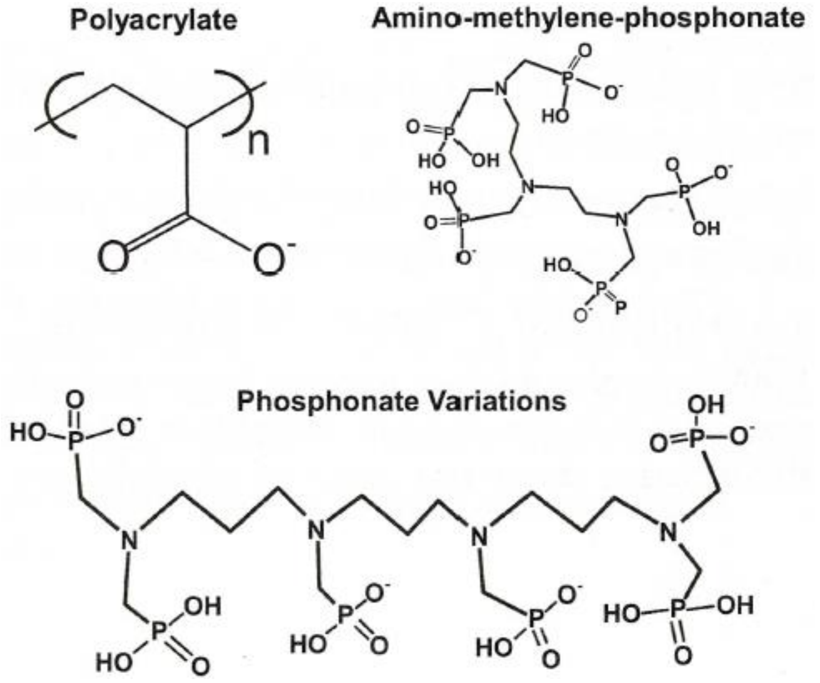
  - Iron scales, especially iron carbonate, inhibit corrosion

Scale Mitigation and Remediation

- Mitigation: As is true in most cases, prevention is much easier than the cure. Scale deposition is inhibited by chemical injection downhole
- Remediation: Acid treatments with sequestering agents are used to dissolve scale and keep it solubilized while it is flushed out of the flow system. The downside to acid treatments is the corrosion that is caused on metal surfaces that are contacted.
- Barium Sulfate scale is almost impossible to dissolve.

Scale Inhibitors

- Barite inhibitors are usually amino methylene phosphonates
- Carbonate inhibitors may be phosphonates, polyphosphates or polymeric anions.
- Time Dependent - Threshold Inhibition
  - Inhibitors are used as a much lower dosage than required to keep all scale in solution. Inhibition is designed to delay the onset of precipitation.



Polyacrylate

Amino-methylene-phosphonate

Phosphonate Variations

Corrosion

Corrosion

- Loss of metal

  : Metal loss caused be corrosive water

  : Fe = Fe^{++} + 2e-

  : Variables

    - Material
    - H_2S and CO_2 level in fluids
    - Water composition

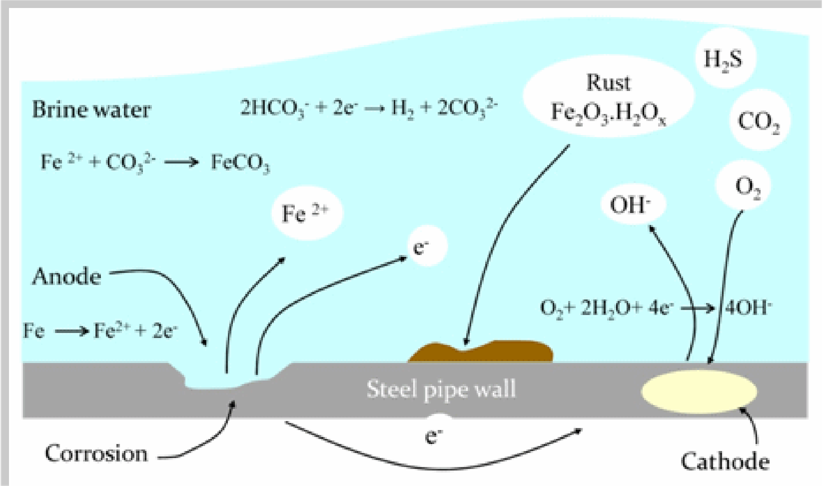
- Control strategy

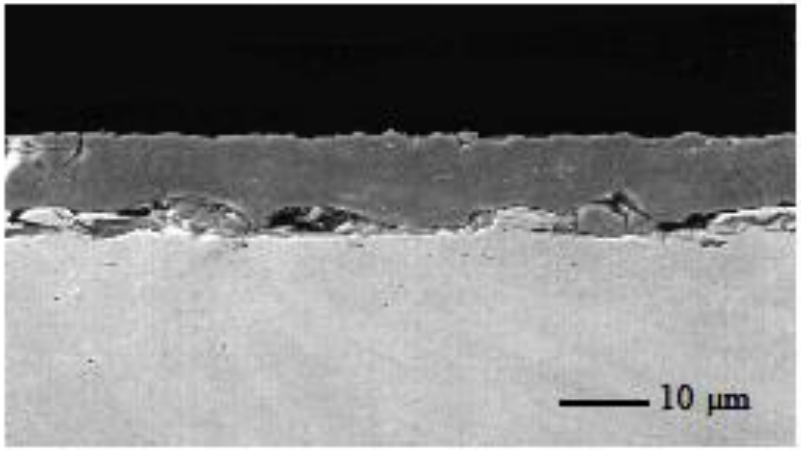
  : Alter chemical environment

    - Oxygen scavengers
    - Sulfide scavengers

  : Alter reactive surface of metal

    - pH control to form protective film
    - Corrosion inhibitors
    - Polymeric liners to flowlines





protective iron carbonate film formed at high pH (right).

Pipeline corrosion examples

Sweet corrosion: CO_2

- Dry CO_2 gas is itself not corrosive at the temperatures encountered with oil and gas production. It needs to be dissolved in an aqueous phase through which it can then promote electrochemical reaction between steel and the contacting aqueous phase.
- CO_2 dissolves in water to give carbonic acid:

$$\mathrm{CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3{}^-}$$

  : H_2CO_3 provides a source of H+ ions leading to the normal cathodic hydrogen evolution reaction and to the metal loss.

  : The concentration of dissolved CO_2 in solution have a critical bearing on corrosion rate.

- Areas where CO_2 corrosion is most common include flowing wells, gas condensate wells, areas where water condenses, tanks filled with CO_2, saturated produced water, and pipelines, which are generally corroded at a slower rate because of lower temperatures and pressures.

Corrosion Predictions

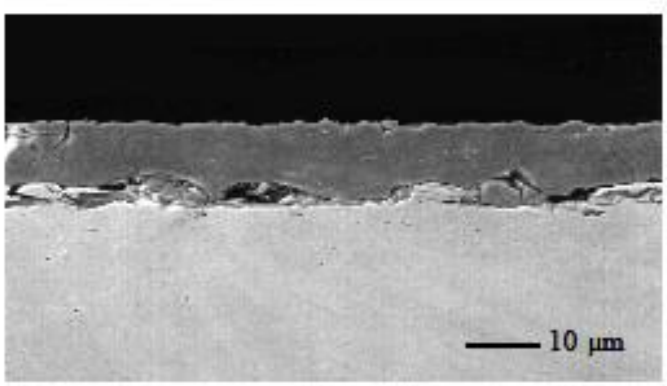
- Temperature;
- CO_2 partial pressure;
- Flow (flow regime and velocity);
- pH;
- Concentration of dissolved corrosion product ($FeCO_3$);
- Concentration of acetic acid;
- Water wetting;
- Metal microstructure (welds);
- Metal prehistory.

Reducing Corrosion

- Alter chemical environment
  - Oxygen Scavengers
  - Sulfide Scavengers/Biocides
  - Limit exposure to oxidizing Agents
- Alter reactive surface of metal
  - Corrosion Inhibitors: applicable primarily to sweet corrosion
  - Polymeric Liners to Flowlines

Corrosion control – using protective film

- The pH stabilization technique based on precipitation of protective corrosion product films on the steel surface by adding pH-stabilising agents to increase the pH value of the water phase in the pipeline.
- A major application for the pH-stabilisation technique has been the Troll pipelines. It was decided to increase the pH value in the pipeline to 7.4. This was done by injecting a sodium-hydroxide solution into the lean glycol tank
- The concentration of dissolved iron, which has the potential to form scale in the process equipment was reduced from around 100ppm to less than 5ppm after six weeks



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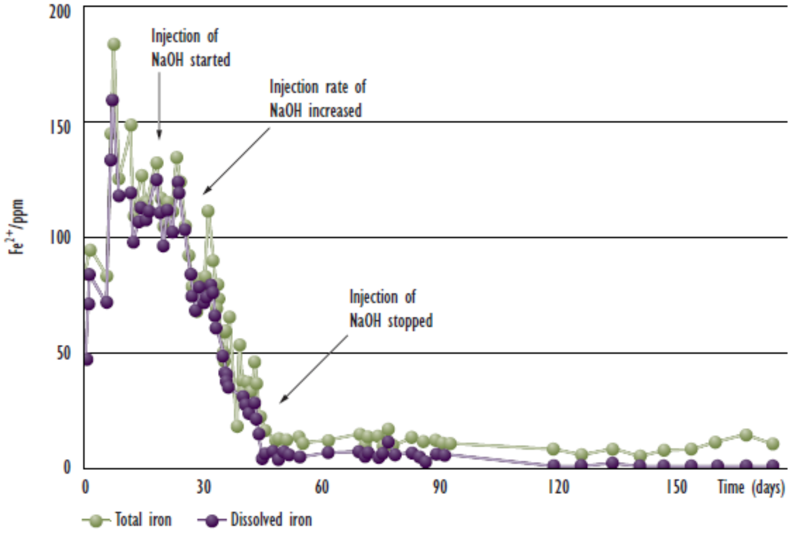

Corrosion Monitoring

- Corrosion Coupons (must be in the flow stream)
- Produced water analysis for iron
- Smart Pigging

- Common design

  : Maximum corrosion allowance is 0.1 mm/yr

Wax, Asphaltene, Scale, Corrosion, Erosion …

Species	Flow Situation	Mitigation methods
Wax	Steady state	Insulation, Chemicals, Pigging
	Shutdown, Start up	NA, except if T < gel point
Asphaltenes	Steady state	Downhole chemicals, Pigging
	Shutdown, Start up	NA
Scale	Steady state	Downhole chemicals
	Shutdown, Start up	NA
Corrosion	Steady state	Chemicals, Cathodic protection
	Shutdown, Start up	NA
Erosion	Steady state	Flow velocity and solids control
	Shutdown, Start up	NA

Example treating chemicals properties and levels

Treating Chemical (& Injection location)	Viscosity at 40 oF (cP)	Density at 14.7 psia (g/cc)	P50 Treatment levels	
			(ppm-V)	basis
Paraffin Inhibitor (at tree)	4.1@ 14.7 psia 8.2 @ 10,000 psia	0.879 @ 60 oF	150	Oil
Scale Inhibitor (down hole)	37.8 @14.7 psia 41.5@10,000 psia	1.324@ 77oF	20	Water
Asphaltene Inhibitor (downhole)	12.4 @ 14.7 psi 35.3 @ 10,000 psi	0.926@ 60oF	250	Oil
Corrosion Inhibitor (at tree)	83.1 @ 14.7 psia 187.7 @ 10,000 psia	0.999@ 70oF	25	Oil + Water

Note: Treating chemicals from different suppliers (and different formulations from the same supplier, for the same function) can have greatly different physical properties and treatment levels.