

MITIGATION OF WAX IN OIL PIPELINES

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Abstract: Flow assurance is of great importance in the oil and gas industry, where the main objective is to provide and secure the transport of the well stream fluid from the reservoir to the process facilities. A root cause of many oil industry production and flow problem is paraffin wax especially in cold and deep offshore fields. About 85% of the world's oil suffers when paraffin wax precipitates out and solidifies in the formation pores and fluid flow channels, at the wellbore, on the side walls of wells, in tubing, casing perforations, pump strings, and rods, and the complete oil transfer system of flowlines and pipelines etc. Paraffin wax deposition is costly, causing decreased production, equipment failures, bottlenecks, loss of storage and transport capacity, clogging of refinery pipe work, and loss of efficiency and revenue. In this article, different methodology for remediating wax deposits both in offshore and deep water is presented; focusing on chemical treatment techniques, mechanical treatment techniques, thermal treatment techniques, thermo-chemical and biological methods,

Keywords: Wax, Chemical, Treatment, Well, Deposition, Formation, Remediation, Pipeline.

I. INTRODUCTION

Flow assurance is a critical and expensive task in the oil and gas industry, especially when operating offshore. Flow assurance means to deliver and assure the transport of the well stream fluid from the reservoir to the process facilities. Flow assurance is designed in a way to identify, quantify and minimize the challenges with the flow risks such as solid depositions to avoid the reduction of the well stream flow, or in worst case complete clogging of the flow lines leading to cease production. Severe deposition problem leads to bulk economic effect on the oil companies, hence different prevention and remediation methods for the deposition problems have been developed, and still further research works are going on to find better techniques to improve the situation.

The well stream fluid is a multiphase mixture fluid that mainly consists of oil (liquid hydrocarbons), gas (gaseous hydrocarbons) and water. Production and transport of the multiphase fluid can cause different problems in downhole and in the pipe lines, such as:

- Organic depositions, such as wax and asphaltene.
- Scale deposits caused by different inorganic salts.
- Formation of gas hydrates, due to mixing of water and hydrocarbons.
- Corrosion damage to the pipelines and associated equipment, due to high water cut.

This article focuses on the organic deposition of wax, and the prevention of this problem with the use of chemical wax inhibitors mainly as pour-point depressants, chemical treatment techniques, mechanical treatment techniques, thermal treatment techniques, biological methods and thermos-chemical methods.

II. WAX

The wax present in petroleum crudes primarily consists of paraffin hydrocarbons ($C_{18} - C_{36}$) known as **paraffin wax** and naphthenic hydrocarbons ($C_{30} - C_{60}$). These molecules can be either straight or branched hydrocarbon chains, and can contain some cyclic and/or aromatic hydrocarbons. Hydrocarbon components of wax can exist in various phases either gas, liquid or solid depending on their temperature and pressure. When the wax freezes, it forms crystals. The crystals formed of paraffin wax are known as macrocrystalline wax (figure 1) (Mansoori, 2009). Those formed from naphthenes are known as microcrystalline wax (figure 2). A collection of normal paraffin's, with 16 or more carbon atoms ($\geq C_{16}$) that form crystalline solid substances at cloud point, are known as wax. The severity of the wax deposition problems depends on type of oil and the molecular composition of the wax molecules. The waxes in crude oils are often more difficult to control when compared to condensate, because the alkane chains are often longer in the crude oil than in the condensate, which consists of lighter hence shorter hydrocarbons.

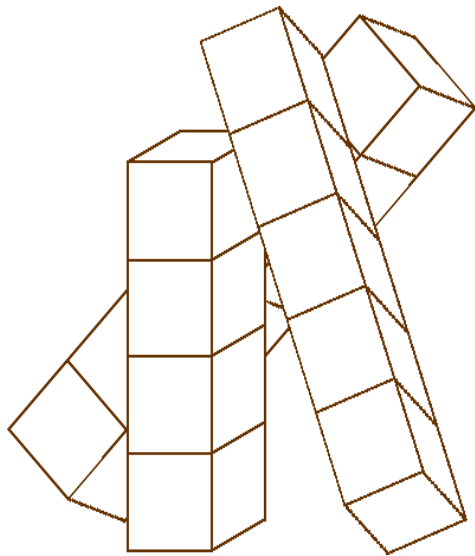


Figure 1: Macrocrystalline [1]

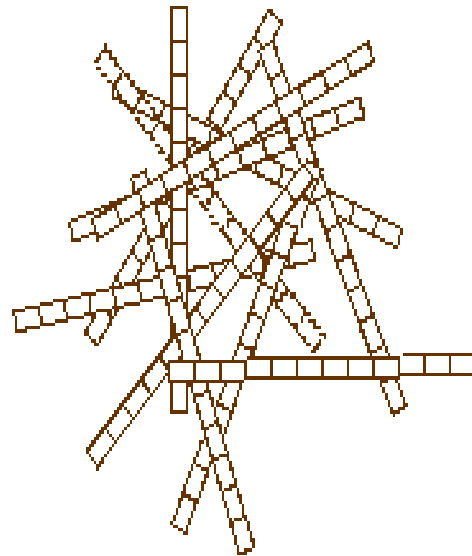


Figure 2: Microcrystalline [1]

A. WAX CRYSTALLIZATION PROCESS

If the temperature of crude oil decreases below the wax appearance temperature (WAT), or sometimes called cloud point, the precipitation of the wax molecules occurs. WAT is the temperature where the first wax crystal begins to precipitate out from the crude oil. The crystallization of the wax molecules can further develop an ordered solid structure, which traps the crude oil causing it to experience a gel consistent with low flow ability. The crystallization process can be divided into two stages called **nucleation** and **growth**.

When the temperature decreases the motion of the molecules in the crude oil reduces due to less energy to move around freely. This makes it easier for the wax molecules to cluster and aligned together, and finally attached to each other and reach a critical and stable size. The cluster of the wax molecules is called nuclei, and the formation process is known as **nucleation**. The nuclei remain stable if the temperature is below the melting point of wax. Once the nuclei are formed and the temperature is kept low, more wax molecules will precipitate and continue to grow on the nucleation site; this is called as the growth process (Dobbs, 1999).

Generally, pressure changes have a very small effect on wax precipitation temperatures and amounts; as pressure decreases below the bubble point, solution gas is liberated, and thus the cloud-point temperature of the oil increases. Wax precipitation doesn't necessarily lead to deposition because individual wax crystals tend to disperse in the fluid instead of depositing on a surface. If the number of wax crystals becomes large enough or if other nucleating materials such as asphaltenes, formation fines, clay, or corrosion products are present, the crystals may collage into larger particles. Then these large particles separate out of the fluid and form solid deposits (PetroWiki)

B. WAX DEPOSITION

In some literature, deposition is switchable with precipitation, but they are different concepts. Wax deposition is the formation of a layer of the separated solid phase, and the eventual growth of this layer, on a pipeline in contact with the crude oil. Wax deposition can be formed from a previously precipitated solid phase (wax) through mechanisms of shear dispersion, gravity settling, and Brownian motion, or from dissolved wax molecules through a molecular diffusion mechanism. There are two stages that are involved in wax deposition:

- Wax gel formation
- Aging

Petroleum wax deposits consists some crude oil, water, gums, resins, sand, and asphaltenes, depending on the nature of the crude oil, which are captured during the crystallization and deposition process. The trapped oil causes diffusion of wax molecules into the gel deposit and counter-diffusion of oil out of the gel deposit, this process depends on the critical carbon number of the oil (Burger, E. D., Perkins, T. K. and Striegler, J. H., 1981). When a hot crude oil coming out from an oil reservoir at a temperature higher than the cloud point, meets a cold sub-sea pipe wall, it instantly precipitates and forms a gel layer on the wall. The trapped oil in the incipient gel deposit is connected to the bulk oil through the gel pores that open at the gel interface. Due to the formation of the solid phase, the trapped oil becomes deleted of certain heavier hydrocarbons as compared to the bulk oil. The minimum carbon number of these heavier hydrocarbons is called CCN (critical carbon number). In the gel deposit, the fraction of molecules with carbon numbers greater than the critical carbon number increases, while that of molecules with carbon numbers lower than the critical carbon number decreases (Singh, P., Youven, A., Fogler, S. H., 2001). The process of diffusion and counter-diffusion leading to hardening of the gel deposit, increase in size of deposit, and increase in the amount of wax in gel deposit, is called aging (hardening), the second stage of wax deposition.

C. FACTORS LEADING TO WAX PRECIPITATION AND DEPOSITION

Temperature: Temperature seems to be the chief and most critical factor in wax precipitation and deposition due to its direct relationship with the solubility of paraffin. Paraffin solubility decreases with decreasing temperature and vice versa. Wax precipitates from crude oil when the operating temperature is at or below the WAT. The ambient temperature around the pipe is generally less than the oil temperature in the pipe because temperature gradient exists between the colder pipe wall and the bulk oil. This temperature gradient leads to wax deposition when the pipe wall temperature falls below the cloud point. The rate of wax deposition is in direct proportion to the temperature difference between the bulk oil and the pipe wall when bulk oil temperature is fixed (Zhu, T., Walker, J. A., Liang, J., 2008).

Crude oil composition: Crude oil is composed of Saturates, Aromatics, Resins, and Asphaltenes (SARA). SARA determines the susceptibility of the crude to deposition of wax solids, and thus the stability of the crude oil. Saturates are flexible in nature; the flexibility is highest in normal paraffin's because they are straight chain compounds, and therefore, easily cluster and crystallize. The iso-paraffin's equally enjoy a high level of flexibility, but form a more unstable wax. Cyclo-paraffin's (naphthenes) are least flexible due to their cyclic nature and do not contribute much to wax deposition. These components are in thermodynamic equilibrium at initial reservoir conditions. It is known that aromatics serve as solvents for high molecular weight saturates, which are the sources of paraffin waxes in crude oil while the polar components, especially asphaltenes, induce wax nucleation. Light ends of saturates equally help to keep the high molecular weight heavy ends in solution. The onset of production results in the loss of these light ends, as they are first to leave the reservoir. This alters the original composition of the oil system, resulting in decreased solubility of the paraffin waxes. This loss of solubility could lead to precipitation and deposition of wax (Zhu, T., Walker, J. A., Liang, J., 2008).

Pressure: Pressure, as a major parameter in the exploitation of reservoir fluids, plays a significant role in wax precipitation and deposition. The pressure profile during oil production is such that the reservoir pressure declines with production, and the pressure of the flow stream drops all the way from the reservoir to the surface. The lighter components of the reservoir fluid tend to be the first to leave the reservoir as pressure depletes. This causes an increase in the solute solvent ratio, since the light ends serve as solvent to the wax components. Hence, the solubility of wax is reduced with the loss of these light ends. The wax appearance temperature increases with increase in pressure above the bubble-point, at constant composition (Seteram). This phenomenon implies that increase in pressure in the one-phase

liquid region (above bubble-point pressure) will favor wax deposition. The situation is different below the bubble-point where there is two-phase existence. Here wax appearance temperature decreases with increase in pressure up to bubble-point pressure due to dissolution of light ends back into the liquid phase (figure 3) (Zhu, T., Walker, J. A., Liang, J., 2008).

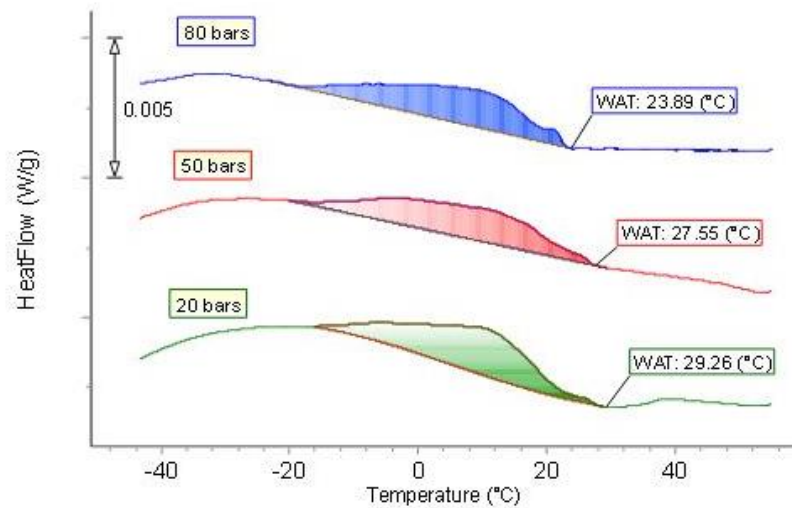


Figure 3: Exothermic effects of wax precipitation [6]

Flow rate: In turbulent flow regime, dynamic forces dominate and the motion is parallel to the pipe axis with mixing occurring between the different layers. In laminar flow regime, viscous forces dominate and there is no mixing between the layers (figure 4).



Figure 4: (a) Turbulent and (b) Laminar flow conditions

Laboratory investigations have revealed that wax deposition is influenced more by laminar flow than when flow is in the turbulent regime occurs (Hsu J. J. C. and Brubaker J. P., 1995).

Gas/oil ratio: This influences wax deposition in a manner that depends on the pressure regime. Above the bubble point, where all gases remain in solution, solution gas helps to keep wax in solution. WAT is high with low GOR (Gas-Oil ratio) Injection of lift gas in a closed loop reduces wax deposition by causing a depression in WAT as a function of pressure. High GOR would result in more expansion and subsequent cooling as pressure of the oil system depletes a situation that can aggravate the wax deposition problem. In a study to reduce WAT by injection of diluents lift gas, noted that good results were not obtained in high GOR wells (Zhu, T., Walker, J. A., Liang, J., 2008).

III. WAX REMEDIATION TECHNIQUES

The success rate of remediation techniques depends on the wax composition and the type of crude oil in the reservoir. In many cases a combination of two or more treatment methods have been used to remove and reduce the wax depositions more efficiently. The wax remediation techniques are divided into three categories, namely: thermal, chemical and mechanical techniques.

A. THERMAL TECHNIQUES

Wax precipitation is highly temperature dependent; therefore, thermal techniques can be highly effective both for preventing and removing wax precipitation problems.

Hot oiling is one of the most popular methods of deposited wax removal in the flow lines and downhole. Hot oil is heated to a temperature above the melting point for wax and then pumped into the well, normally through the annular space. The

circulated hot oil melts and dissolves the wax which allows it to be circulated from the well and the surface producing system. During the hot oil process, a wax dispersant is usually added to the crude oil to boost the dispersion of the melted wax with the crude oil. Higher molecular-weight waxes tend to deposit at the high-temperature bottom end of the well, while lower molecular-weight fractions deposit as the temperature decreases up the wellbore. As the oil proceeds down the well, its temperature decreases and the carrying capacity for wax is diminished. Thus, sufficient oil must be used to dissolve and melt the wax at the necessary depths. (Becker, 2000) This technique should not be applied to wells where the crude is characterized by a low flash point. Reports show that hot-oil has been replaced with steam or hot water to melt the wax in certain operations, but they are rarely used due to risk of emulsion and corrosion problems. The hot-oiling method is not generally used in subsea flow lines, due to the exorbitant cost of heating the oil. There is evidence that hot oiling can cause permeability damage if melted wax enters the formation (Allen, T.O. and Roberts, 1982).

Hot water treatments do not give the solvency effects typical of the hot oiling technique, so surfactants are often added to aid wax dispersion in the water phase. The combined hot water and surfactant method allows the suspension of solids by the surfactant's bipolar interaction at the interface between the water and wax. An advantage of this method is that water has a higher specific heat than oil, and therefore usually arrives at the site of deposition with a higher temperature. Surfactants are discussed under chemical methods.

Direct heating has been regarded as an efficient flow in combating the flow problems associated with wax, due to the advantages to control the temperature above the formation region. The basic principle involves passing a huge quantity of electric current through the pipeline wall to generate heat. It is the most appealing and reliable option for Deepwater field operation of transport flowlines (Nysveen, A., Kulbotten, H., Lervik, J.K., Børnes, A.H., Høyer-Hansen, M. and Bremnes, J.J. (2007): . , Vol. 43, No. 1, J, 2007), (Lenes, A., Lervik, J. K., Kulbotten, H., Nysveen, A., and Børnes, A. H., 2005). The pipe to be heated is an active conductor in a single phase electric circuit with a single core power cable which acts as a forward conductor. Power is supplied from the platform through two riser cables. One of the two single core riser cables are connected to the near end of the pipe, and the other to the forward piggyback cable connected to the far end of the pipe (Lenes, A., Lervik, J. K., Kulbotten, H., Nysveen, A., and Børnes, A. H., 2005). This implies that each pipeline's end is connected to the two cables, creating a closed circuit. As current is added, anionic force is encountered and thus, an energy loss in this process heats up the pipeline (Akpabio, 2013). Direct Heating method is generally designed in a manner that the temperature of the produced fluid is kept above WAT (20°C) during shutdowns, as well as increasing its temperature from ambient temperature (6°C) within a specified period. Thus, during steady state flow, continuous heating may not be required.

B. CHEMICAL TECHNIQUES

Solvent treatments of wax and asphaltene depositions are often the most successful remediation methods, but are also costlier; therefore, are reserved for applications where hot oil or hot water techniques have shown little success. Wax solvents help to resolve the precipitated wax to ease transport of crude oil to the surface (Ferworn, K.A., Hammami, A., and Ellis, H., 1997). Normally the solvents are applied in frequent batch treatments or continuously. Aliphatic and aromatic solvents are the main groups of solvents used in the oilfields. The aliphatic solvents are straight or ring formed hydrocarbons (diesel, kerosene are mostly used), while the aromatic solvents are compounds containing a carbon ring with delocalized electron double bonding, such as xylene and toluene (Figure 20) (Barker, K.M., Newberry, M.E., and Yin Y.R., 2001). Mixing xylene or toluene together with an aliphatic solvent has shown to increase the wax removal efficiency. Addition of surfactants can also serve to enhance the performance of the solvent by increasing the dispersion action on the waxes (Thierheimer Jr., 1990). Other solvents have shown such as benzene, chlorinated hydrocarbons, and carbon disulfide have shown a good level of success. However, many of these solvents are not environmental friendly. Many also possess dangerous risks related to low flash points, such as the aromatic solvents, and corrosion problems, as seen with chlorinated hydrocarbons (Woo, G.T., Garbis S.J., and Gray T.C., 1984).

A green solvent "Terpene", derived from natural and renewable sources has been utilized alternative to the conventional solvents for wax remediation. Terpene is composed of repeating five-carbon isoprene units, grouped as unsaturated aliphatic cyclic hydrocarbon abundant in renewable plant resources such as oleoresins from pine plant (alpha and beta pinene), orange peels (d-limonene) while others include turpentine, citronella, carotene and many more. Terpene has low toxicity, less flammable, rapidly biodegradable and has high solvency for organic deposit comparable to aromatic solvents. Terpene is good surfactant which is environmental friendly. Terpene can be blended with other co-solvents (Okafor, H. E., Ismail, M. S. and Rasidah, M. P., 2014). Comparatively, terpene possess good solvency, it's biodegradable, less toxic and less flammable.

Wax crystal modifiers act at the molecular level to reduce the networking tendency of wax molecules, and prevents them from forming lattice structures within the oil. They reduce oil viscosity and lower the wax gel strength. They are known for high-molecular-weight and thus they have high pour points, so their use can be limited in cold climates (Becker, 2000).

Dispersants are a type of surfactants that acts to disperse the wax crystals into the produced oil or water, thereby preventing wax deposition and effect positively on the viscosity and gel strength. Dispersants breaks up deposited wax into smaller particles capable of being carried in the oil stream. To remediate deposited wax, dispersants can be used continuously or in batch treatments. They generally have a very low pour point making their use suitable for cold climates. These chemicals are used in low concentrations and can be formulated in both aqueous and hydrocarbon solutions, making them relatively safe and inexpensive.

Surfactants are a general class of chemicals that are most often used to clean vessels, tanks, pipes, machinery or any place where wax may deposit. Surfactants or dispersants can also be used in combination with hot oil and water treatments.

C. MECHANICAL TECHNIQUES

These techniques include manual stripping, pigging, mechanical vibrations, etc.

Mechanical/manual stripping is probably the oldest method known for the removal of heavy hydrocarbon deposits. It is done by mechanically scraping the tubing.

Pigging technology is well established, it is most suitable for foams, waxy crude arteries and wax deposit removal. The traditional answer to the problem of wax deposition has been to mechanically clean the pipeline using a pig (figure 5). A pig is an effectively moving piston driven through the pipe by a pressure differential. Pigs are generally designed to push any loose material through the pipeline and to apply a mechanical force between the pig and the pipe wall to remove debris. In the North Sea, this technique is widely used for pipelines with high wax content. Pigging frequencies may range from 2-3 days to 3-4 months (Tordal, 2006). A very important factor for efficient wax pigging is that the pig has small by-pass holes that allows liquid to be 'flushed' through due to the pressure drop across the pig. Before the remediation operation, a pigging program must identify type and numbers of pigs. The use of a non-suitable pig can, in the worst-case scenario lead to full pipeline blockage (Tordal, 2006). As the pig enters the pipeline, it removes the wax deposit on the pipe wall and pushes the wax forward. As the pigging length increase, the volume of wax in front of the pig also increases.

Pigs can also be molded in polyurethane foams of various densities. This type of pig is usually bullet shaped and, if a more aggressive cleaning operation is required, bristles or studs can be molded into a hard gel coat. Very hard deposits such as hard wax and scale require a very aggressive tool; usually a metal-bodied pig with tooling attached with brushes, ploughs, scrapers and pin-wheels to increase the efficiency.



Figure 5: Result of pigging operation

D. THERMO-CHEMICAL PACKAGES

Thermo-chemical packages method utilizes the heat released from an exothermic reaction to melt the wax deposits in downhole or in subsea flow lines. NGS (Nitrogen Generating System) or SGN (expressed in Portuguese as 'Sistema Gerador de Nitrogenio') introduced by Petrobras in 1992, is a thermo-chemical cleaning method. This utilizes the localized mixing of two chemicals to produce an exothermic, effervescent reaction that removes deposits. Two nitrogen salt-containing aqueous solutions are mixed in the affected area of the pipeline to produce Nitrogen gas and heat (figure 6). The NGS process combines thermal, chemical, and mechanical effects by controlling nitrogen gas generation to comprise the reversible fluidity of wax/paraffin deposits. Petrobras pioneered the use of an exothermic chemical reaction between ammonium chloride and sodium nitrite in an acidic pH to generate heat to melt wax deposits in the Campos basin. The Brazilian national oil company successfully removed many blockages by using the NGS (Librino, 2015).

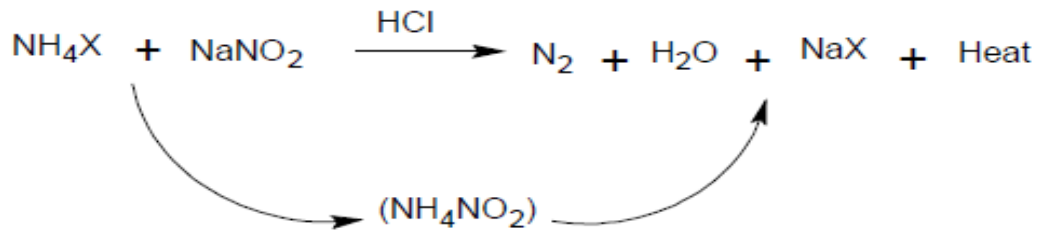


Figure 6: The thermo-chemical reaction used as wax deposition removal

The greatest setback of this technology is that only those areas near the chemical injection point could be treated, because the exothermic reaction would terminate before the chemicals could reach far areas. To overcome this issue, Halliburton developed SureTherm, which controls the onset of the exothermic chemical reaction and generates heat after a calculated delay time (figure 7) (Halliburton, 2012). By delaying the exothermic reaction, sufficient time is available for pumping the chemicals into a flowline to a specified location where the generated heat can be used to melt the wax deposits. The maximum temperatures achievable and the target temperatures employed are dependent upon and controlled by two factors, they are pipeline pressure and the concentration of the reactants used. SureTherm can be used online (with production) or offline (flowline shutdown) and has been successfully used once in a field trial for one of Halliburton's clients in West Africa. The SureTherm treatment generated sufficient heat to remove the wax deposits in the pipeline; the time-delay mechanism worked as expected; and the reaction took place in the wax deposition area (Librino, 2015).

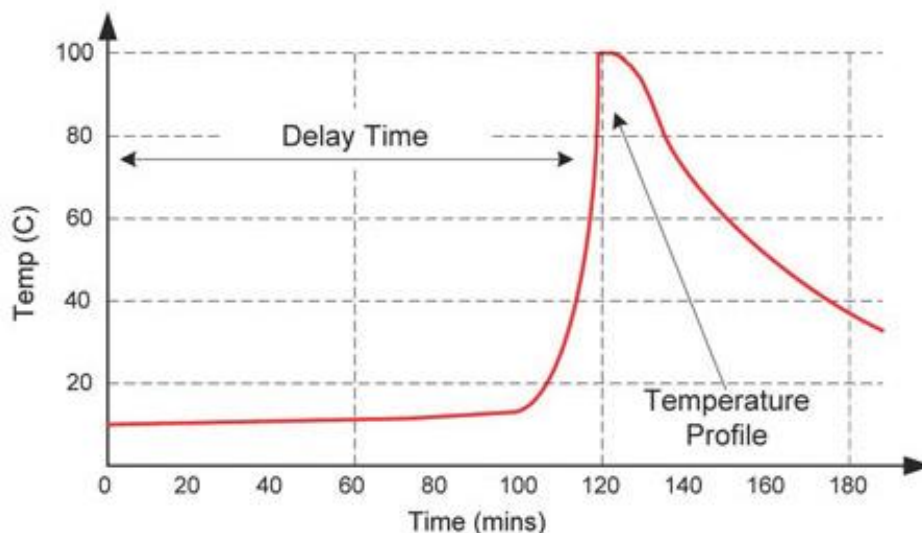


Figure 7: Graph depicting SureTherm temperature versus time [21]

Microbes are routinely used for oil spill remediation. Recently, in Venezuela and Alaska, microbes were successfully used to clean out wellbores. Based on the reported results of these tests, it is conceivable to assume that this method would be successful for paraffin removal from flowlines.

E. CONDITIONS FOR SELECTING THE BEST REMEDIATION METHOD

- For the oil wells with water cut below 50%, wax content less than 30% and Carbon Number distribution of the wax in the range of C₁₃-C₄₀, a good efficiency may be obtained by using chemical removing and inhibiting techniques.
- For the wells with water cut more than 50%, the magnetic paraffin inhibiting technique is generally more economic to apply.
- For the wells with wax content more than 30%, pour point higher than 40⁰C, irrespective of the water cut, the best choice is to adopt chemical paraffin-removal or thermal washing method.
- For the oil wells with very high Carbon Number of wax, pure chemical paraffin removing techniques are ineffective. The best economic choice is to apply chemical paraffin inhibitor or glass/plastic coating or lining of tubing.

IV. CONCLUSION

Deposits of paraffin and asphaltenes containing other resinous and foreign particles in tubing and flow lines poses severe problem. A heavy expenditure is incurred to combat this deposition problem. It also adds losses due to down time and loss of production. For trouble-free operation, a timely corrective action is primary task for the petroleum production engineers.

Any of the methods can be employed after careful consideration of the operating conditions of the well or field; to achieve efficient results.

With sustainability in view, the environmental friendly techniques will be preferred; the green solvent terpene is good example of non-toxic and clean methods.

Microbial treatment has shown very effective results in preventing wax deposition and them method is environmental friendly.

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