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An Overview of Wax deposition in the Pipeline

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ABSTRACT

Paraffin deposition is one of the major production related issues which incurs huge financial losses to petroleum industry worldwide. The aim of this paper is to provide in-depth knowledge of paraffin deposition issues. Paraffins are responsible for deposition in pipeline during production and transportation along with mechanism of paraffin deposition and factors affecting wax formation are also critically reviewed. Efficient and cost-effective solutions of paraffin deposition are analyzed and supported by some experimental data.

*KEY WORDS:*Crude oil, Paraffin deposition, Pour point, Paraffins, Wax removal

INTRODUCTION

Paraffin deposition in one of the major flow assurance issues causing production and transportation related problems viz reduced operation efficiency, interruptions in production or shutdowns, costly and technically challenging removal especially in deep water pipelines, etc. In depth understanding of such problems is prerequisite for oilfield operators for economic solutions. This paper discuses fundamental aspects of wax deposition.

WAX (PARAFFIN)

Crude oil contains components such as saturates (paraffins), aromatics, asphaltene and resins along with metals such as Nickel, Vanadium and Iron. Paraffin responsible for deposition in pipeline are long chain hydrocarbons (n-alkanes) with the general formula C_nH_{2n+2}. On the other hand, long chain hydrocarbons (iso-alkanes and cycloalkanes) with the general formula C_nH_{2n+2} are microcrystalline waxes mainly present in tank bottom sludge. Structures of paraffins are given below in Fig.1.

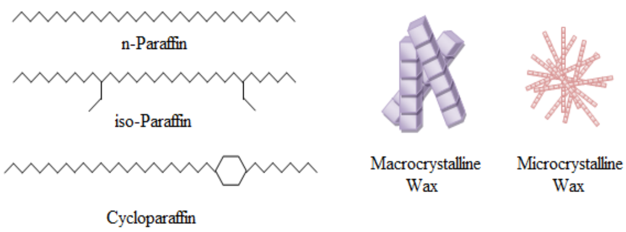

Fig. 1. Structure of Paraffin

WAX DEPOSITION

Wax deposition is one of the main flow assurance issues which causes several pipeline issues during production and transportation of crude oil. Initially, paraffin wax is present in dissolved form in crude oil at reservoir conditions. In other words, above cloud point, the wax is in soluble form in crude oil. Cloud point or Wax appearance temperature (WAT) is the temperature atwhich precipitation of components occurs and crude oil shows cloudy appearance. Due to lowering of temperature in the pipeline, low molecular weight hydrocarbons start evaporating due to which the solubility of wax decreases in crude oil. As the temperature reaches below the cloud point, thecrystallization of wax takes place which is known as nucleation. Crude oil from the reservoir contains asphaltenes, clay and corrosion products which act as a nucleating agent and hence, in crude oil, mainly heterogeneous nucleation takes place. Asphaltenes and other elements present in crude oil either promote or suppress the formation of wax crystals during production and transportation. Gradually, these nuclei agglomerate to form bigger clusters. This process is known as agglomeration. These agglomerates settle down on the pipeline and further growth deposition of wax molecules takes place which is known as growth process as shown in fig.2.

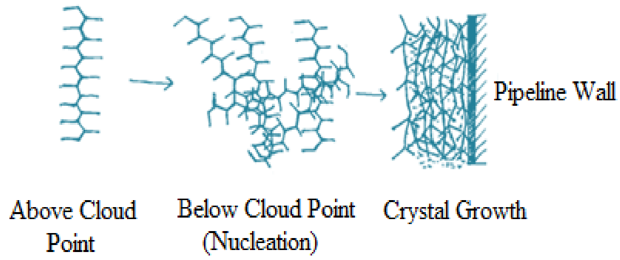

Fig. 2. Mechanism of Wax deposition

The wax deposits could be present as soft mush to a hard, brittle material. Wax deposits will be harder if high molecular weight n-alkanes deposit in pipeline. Wax deposition could damage formation near the wellbore. The adverse impact of wax deposition on formation leads to reduction in permeability, changes in composition and rheology of fluid in the reservoir. Pour point for crude oil is the minimum temperature at which crude oil continues to flow during cooling. Below pour point, crude oil fluidity reduces because of wax precipitation, and on further reduction in temperature, crude oil stops flowing and blockage in pipeline occurs. As a result, the production of crude oil cannot be operated smoothly. The wax deposition in pipeline during transportation of crude oil is shown in fig. 3.

Figure 3. Wax deposition in pipeline

DETECTION OF BLOCKAGE AND WAX DEPOSITION

Chen et al(2007) developed pressure echo technique which is used to find the location of a blockage in pipeline. In this method, the time for a pressure wavewhich reflects back along the pipeline from the point of blockage is measured.

Sarmento et al(2004)developed atechnique in which the pressure in pipeline is increased and then external diameter of a pipeline is measured with the help of a tool with caliper and video camera on a remotely-operated submersible.

Pigging is one method in the volume of wax inside measured by removing a section of pipeline. Pressure drop and heat transfer methods are indirect methods for detection of wax deposition.

Zaman et al(2004) developed a method which is efficient of detecting extremely small wax deposition. However, this method is efficient on laboratory samples only.

WAX DEPOSITION MECHANISMS

There are six wax deposition mechanisms namely, molecular diffusion mechanism, Soret diffusion, Brownian diffusion mechanism, Gravity settling mechanism, Shear diffusion mechanism and Shear stripping mechanism. However, first three mechanisms are well accepted by most of the researchers. The most dominant deposition mechanism is molecular diffusion. Molecular diffusion mechanism, Soret diffusion, Brownian diffusion and Shear dispersionmechanism are discussed briefly below.

A. Molecular diffusion

Crude oil in pipeline flows in laminar flow. The crude oil in the pipeline experiences a radial thermal gradient. This is because the temperature of crude oil near the pipeline wall has lower temperature compared to that at the center of the pipeline. In other words, there is a temperature gradient across the laminar sub-layer. At cloud point, the crystallization of wax takes place near the pipeline wall which results the change in the equilibrium of the liquid and solid phases. At one stage, the liquid will be saturated with dissolved wax crystals. As the temperature decreases, the solubility of wax decreases in the fluid and a concentration gradient is established by the temperature gradient within the pipeline. The concentration of wax molecules is lower near the wall of the pipeline and higher in the central region. Thus, molecular diffusion of wax takes place from bulk to the pipeline wall. Wax deposition takes place in following two steps: wax gel formation and aging of the deposited wax gel. During wax deposition, crude oil, water, gums, resins, sand and asphaltenes present in the oil are entrapped in the wax crystals depending on the nature of the crude oil which results diffusion of wax molecules into the gel deposit and counter-diffusion of oil out of the gel deposit, as shown belowFig.4.

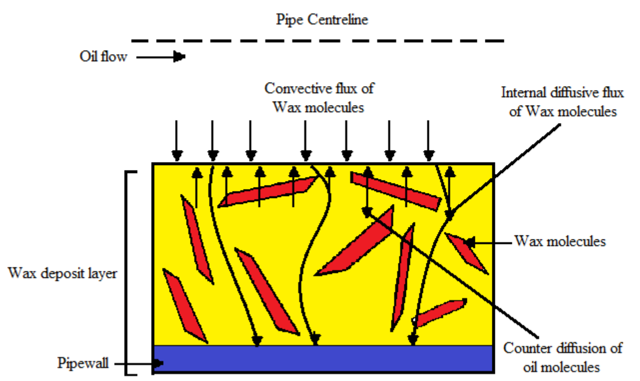

Fig. 4. Molecular diffusion

In the process of aging, hardening of the gel deposit, increase in the size of the deposit and increase in the amount of wax in the gel deposit result due to the diffusion and counter-diffusion. Thus, molecular diffusion is crucial for aging and hardening of wax gel deposits. As suggested by Azevedo and Teixeira (2003), the mass flux of the wax can be calculated by Fick's Law. The mathematical expression for Fick's law is given below:

$$\frac{dm_m}{dt} = \rho_d D_m A \frac{dc}{dr} \qquad (1)$$

Where, m_m is the mass of deposited wax, ρ_d is the density of the solid wax, D_m is the diffusion coefficient of liquid wax in oil, A is the surface area over which deposition occurs, C is the concentration of wax in solution (volume fraction), and r is the radial coordinate. With decrease in temperature in the radial direction of the pipe, the viscosity of the oil increases and the diffusion coefficient of the wax in oil decreases which can be shows that molecular diffusion is the main mechanism for wax deposition in which diffusion of the dissolved molecules of the waxy components takes place toward the wall.

B. Soret diffusion

Soret diffusion leads to thermal diffusion because of the temperature gradient in the pipeline because of distribution of wax crystals in the fluid near the wall and in the bulk. Soret diffusion takes place when both large and small molecules are dispersed under thermal gradient regions.

C. Brownian diffusion

This mechanism explains the collision between wax crystals in the crude oil and the excited oil molecules which can be represented by Fick's Law as shown in mathematical equation below:

$$\frac{dm_B}{dt} = \rho_d D_B A \frac{dc^*}{dr} \qquad (2)$$

Where, m_B is the mass of wax deposited by Brownian motion, D_B is the Brownian motion diffusion coefficient of the solid wax crystals andC^* is the concentration of solid wax out of solution.

D. Shear dispersion

The lateral movement of wax particles is known as shear dispersion which is predominant where the temperature decreases below cloud point. The shearing of the fluid usually occurs close to the pipe wall. The wax crystals flow in the direction of oil with mean speed in the flowing oil. These wax crystals move towards the wall because of their low velocity near the wall due to wax deposition. The wall shear rate, the amount of wax out of solution and the shape and size of the wax particles are the factors affecting shear dispersion.

FACTORS AFFECTING WAX DEPOSITION PROCESS

Wax deposition in petroleum pipelines is affected by factors such as temperature, pressure, the composition of crude oil, rate of cooling, flow rate and pipeline properties. The factors affecting wax deposition process are discussed below.

A.Temperature

With decrease in temperature, wax deposition increases. This is because increase in the temperature difference between the inner solution and the pipeline wall which is considered as one of the main reason for wax deposition by many researchers. Wax deposition will occur below the cloud point. **In cold environment, the temperature of pipeline wall decreases and hence, the temperature difference between that of the pipeline wall and the solution in the pipeline increases. Wax deposition starts taking place at the inner surface of pipeline wall as it has lower temperature compared to central solution.** The inlet coolant temperature plays is very critical as wax deposition occurs if the inlet coolant temperature is low despite the temperature of the solution is above WAT. When the temperature difference between pipeline wall and that of solution is high, the rate of wax deposition is high. However, with more and more wax deposition on the wall, the thickness of the wax layer increases which acts as thermal insulation and reduces the temperature difference between pipeline wall and the solution. With decrease in the temperature differential the wax formation also decreases. The following plotted graph in Fig.5 of paraffin wax deposition of waxy crude oil under various temperatures represents the correlation between temperature differential with wax deposition. The results showed that with increase in temperature, the paraffin wax deposition decreases. This drop in wax deposition rate with increasing in temperature difference is attributed to the extra heat gained or added in the solution, which move the solution away from its cloud point. Thus, the process of wax crystal formation and wax deposition is a function of temperature differential (Norman 1989).

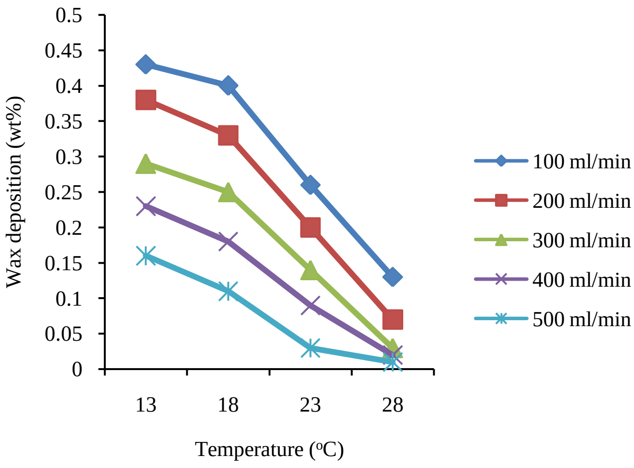

Fig. 5. Effect of temperature differential on wax deposition

B. Rate of cooling

Cooling rate plays an important role in deciding size and number of wax crystals. At a higher cooling rate, large number of smaller wax crystals is formed because of availability of large number of crystallization sites and at a lower rate cooling rate, uniform wax crystals are formed which possess small surface area. Usually, higher cooling rate is observed when the temperature differential is high which generates mixture of both high melting and low melting waxes.

C. Crude oil composition

Crude oil contains different types of molecules such as asphaltenes, clay, resin, and salts, etc. which either promotes or inhibits wax deposition. The concentration of above materials in crude oil impacts the amount of deposited wax in the crude oil.

D. Flow rate

Wax deposition increases with decrease in flow rate in laminar flow and it increases with increase in flow rate in turbulent regime. In laminar flow, more particles are available for deposition due to which wax deposition is high when laminar flow rate is low. However, when turbulent flow is high, because of increase in shear dispersion, wax deposition decreases. Wax crystals generally stick to the wall of pipeline during wax deposition. When the flow rate is high, the wax crystals break into smaller particles and prevent the process of wax deposition on pipeline. On the other hand, when the flow rate is low, the wax molecules get longer residence time which favors decrease in oil temperature and promotes wax precipitation and deposition. The minimum flow rate in the experimental rig to avoid deposition is 0.56 ft/ sec.**Several experiments have been performed to find the correlation between flow rate and wax deposition. The following graph in Fig.6 represents the relation between flow rate and wax deposition at a constant temperature of 15⁰C, oil inlet temperature of 45⁰C and volumetric flow rate of 31/min. It is evident from below graph that wax deposition is inversely proportional to flow rate. In other word, as flow rate increases, wax thickness decreases.**

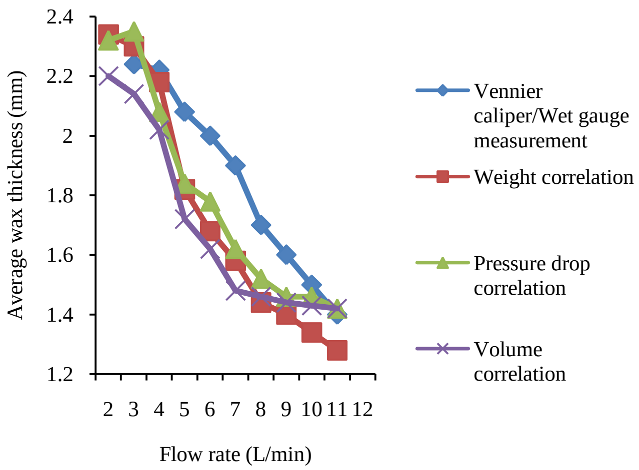

Figure 6. Effect of flow rate on wax deposition

E. Pressure

When the pressure decreases, lighter hydrocarbons evaporate from the reservoir which decreases the solubility of wax molecules in crude oil and hence, wax deposition occurs. With increase in pressure, the WAT increases with above the bubble point pressure (the pressure at which the first gas bubble appears while decreasing pressure on a fluid sample)due to which wax deposition decreases whereas the WAT decreases with decrease in pressure above the bubble point pressure due to which wax deposition increases for a constant composition. However, below the bubble point, where the oil has two-phases, the WAT decreases with an increase in the pressure up to the bubble point pressure. This is because lighter hydrocarbons tend to dissolve again in the crude oil which affects the wax deposition.The graphical plot in Fig. 7 indicates that the maximum amount of wax is deposited at 1 MPa to 2 MPa and decreasefrom 2 MPa to 6 MPa. However, with variation in wax content, the pressure corresponding to the maximum wax deposition also changes.

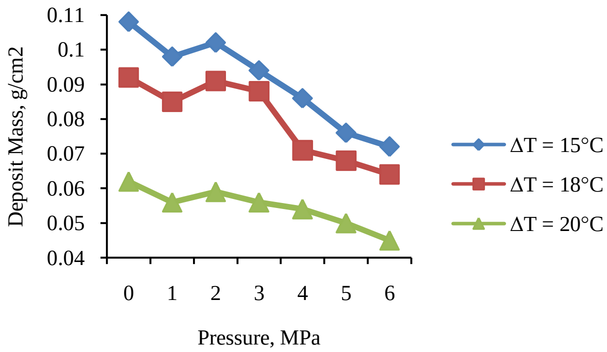

Figure 7. Effect of pressure on wax deposition

F.Pipe surface properties

During wax deposition, wax crystals adhere to the inner wall of the pipeline. Thus, surface property can also be considered as a factor affecting wax deposition. There is no direct correlation between wax deposition and surface roughness but in case of rough surface, the total contact area for wax molecules is high which favors wax deposition because the adhesion bond at a surface is directly proportional to the total contact area. Wax molecules adhere at the wall via diffusion. Low friction also discourages the adhesion of wax molecules on pipeline wall. Thus, it can be concluded that at increased surface roughness highly favors wax deposition and causes pipeline blockage and even production shutdown.

PREVENTION AND REMOVAL METHODS OF WAX DEPOSITION

Wax deposited in pipeline wall can be removed mainly thermal, chemical and mechanical methods. Among these methods, chemical method is preferred by the industry. The methods used for removal of wax deposition are discussed below.

A.Thermal methods

Wax deposition takes place at higher temperatures. With increase in temperature, deposited wax can be easily removed. Thus, thermal methods are found to be an effective remedy to wax deposition and its prevention. Thermal methods for removal of wax deposition include hot watering and hot oiling. Hot watering is not as effective as hot oiling. In hot oiling method, hot oil is pumped which increase the temperature in the well and due to increase in temperature, wax is melted. During hot oiling method, hot oil is pumped down the well but as the oil moves down, its temperature decreases and hence, its capacity of removing deposited wax also decreases. Thus, sufficient hot oil is required for wax removal up to required depth. However, there is a drawback of this method. If melted wax enters the formation then there can be permeability damage if to the well.

B.Chemical methods

Different types of chemical methods used are solvents, wax dispersant, pour point depressant (PPD), and wax crystal modifier.

1)Solvents

Solvents such as chlorinated hydrocarbons and aromatic hydrocarbons are excellent solvents for wax removal. However, these solvents are toxic and they are difficult to process due to which they have limited applications. Solvents are mainly used in large batch treatments.

2)Wax Dispersant

Wax dispersants are surfactants such as alkyl sulfonates and fatty amine ethoxylates which adsorb on the wall of the pipeline and inhibit the wax deposition on the wall. Wax dispersants either form a thin layer on pipeline wall or get adsorbed onto wax crystals, andhinder the wax particles to deposit on the wall which ultimately delays the formation of wax crystals. Surfactants with longer chain esters have better performance at reducing pour point, altering the morphology and reducing co-crystallization. Wax dispersants generally have a very low pour point making due to which they can be used in cold climates. They need low dosage and can be formulated in aqueous as well as hydrocarbon solutions which make them inexpensive and safe.

3)Pour Point Depressant (PPD)

Pour point depressants do not inhibit the crystallization of wax but they inhibit the growth of wax crystals by interfering during wax crystallization process. Thus, pour point depressants decrease pour point of the crude oil but they do not alter wax appearance temperature of the crude oil.

Pour point depressants are generally polymeric compounds containing non-polar alkyl chain and polar moiety. The polymeric chain of PPD interacts with long chain of paraffin wax by Vander Waals interaction and increases the solubility of wax in oil. However, the non-polar long alkyl chain of PPD interacts with the long-chain paraffin wax and reduces pour point of the crude oil due to alteration in wax crystallization pattern. Some commonly used pour point depressants are polyethylene vinyl acetate (EVA), methyl methacrylate (MMA), olefin-maleic anhydride copolymer (MAC), and diethanolamine (DEA).Pour point depressants inhibit the growth of wax crystals by following three mechanisms:

4)Wax Crystal Modifier

Wax crystal modifiers interfere with wax crystals during the nucleation process and alterthe growth and surface characteristics of the crystals. Thus, Wax crystal modifier inhibits wax crystals to form lattice structure which results reduction in viscosity and pour point of the crude oil. Some examples of wax crystal modifiers are polyalkyl methacrylate, polymeric fatty ester, methacrylic acid ester, and crystalline-amorphous copolymers such as polyethylene–polyethylene propylene (PE-PEP) and polyethylene butene (PEB). Wax crystal modifiers have a high-molecular-weight and high pour points due to which they cannot be used in cold climates.

C. Mechanical

Scrapers and cutters are commonly used mechanical techniques for removal of wax deposited on wall. Scrapers contain a sucker road attached to it which scratches wax deposited on the wall. Soluble pigs (composed of naphthalene or microcrystalline wax) and insoluble pigs (made of plastic or hard rubber) can also be used to remove the wax deposits on surface of pipeline by forcing them. Another method is use of plastic coated and low friction pipelines which reduces the chances of wax deposition because of smooth surface.

CONCLUSIONS

Paraffin deposition is one of the major flow assurance issues. Paraffin waxes crystallize because of decreases in pressure and temperature. A decrease in pressure causes loss of light ends, which act as natural solvents for waxes. Number of methods have been used to predict paraffin problems. The need of the hour is to standardize these methods for better technical/economic mitigation.

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