Chapter 6
Analysis of the Influence of Wax Precipitation and Paraffin Control Technology on Environmental Protection

Deyin Zhao, Yi Zhao, Rongqiang Zhong, Lirong Yao, and Gaojie Liang

Abstract With the rapid development of deepwater petroleum engineering, the waxing characteristics of waxy crude oil have attracted more and more attention. In order to obtain a more accurate wax precipitation point of waxy crude oil, the test methods of wax precipitation point are summarized and compared. The test methods are classified into conventional and unconventional methods. In terms of test conditions and applicability to gas-bearing crude oil, three conventional methods (microscopic observation method, rheometer method, and differential scanning calorimetry method) were compared. It is pointed out that the test conditions should be formulated according to the actual working conditions when the wax precipitation point is determined, and the test method should be selected according to the wax crystal type and wax content. Wax deposition will block the pipeline, thus reducing the transmission efficiency of the pipeline; the residual paraffin deposit in the scrapped pipeline will penetrate into the earth and pollute the environment. Before the pipeline is scrapped, wax removal measures should be taken to remove the paraffin deposit inside, so as to protect the environment. Therefore, the research on paraffin removal and prevention of crude oil is of great significance to the normal production and environmental protection of oil wells.

Keywords Waxy crude oil · Wax precipitation point · Wax removal · Environmental protection · Pollution prevention

D. Zhao · Y. Zhao · R. Zhong · L. Yao
Sinopec Northwest Oil Field Company, Wulumuqi city, China

G. Liang (✉)
School of Civil and Engineering, Northeast Petroleum University, Daqing 163318, China
e-mail: lljdqpi@126.com

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6.1 Introduction

The wax content of crude oil in my country is very high, most of the oilfields have a wax content of more than 20% (Ye 2016), and some even reach 40% to 50%. Crude oil with a wax content of more than 10% accounts for almost 90% of the output oil fields. The internal factors that affect the waxing of crude oil are the wax, gum and asphaltene content in crude oil. In the process of crude oil pipeline transportation, the pipeline transportation method of mixed transportation is often used, which greatly changes the composition and properties of crude oil, which may directly affect the stable operation of the crude oil pipeline (Xuanfeng and Cheng 2019).

Crude oil is a mixed liquid composed of many components. It is mainly composed of a large amount of hydrocarbons and a small amount of nitrogen, sulfur, and oxygen compounds. In addition, most crude oils also contain a certain amount of asphaltenes and gums. Among them, the hydrocarbons contained in crude oil are mainly:alkanes, aromatic hydrocarbons, and cycloalkanes (Jiaying 2006). The oxygen-containing compounds mainly include: fatty acid, benzoic acid, etc. The asphaltenes and gums are mainly composed of heterocyclic compounds containing nitrogen, sulfur, and oxygen. Asphalt has the highest molecular weight in crude oil, and its molecular weight is more than 1,000, and it may even be as high as 100,000. Molecular weight, and the molecular weight of gum is about 800 to 1200. A large number of research results show that there are many cycloalkane rings, aromatic rings, heterocycles, etc. in asphaltenes and gums.

When waxy crude oil encounters a low temperature environment during pipeline transportation, the wax dissolved in the crude oil will precipitate and deposit on the pipe wall, resulting in a decrease in the circulation area of the pipeline, an increase in transportation pressure, and a decrease in the transportation capacity of the pipeline. If the pigging is not timely, it may cause serious blockage of the pipeline or even the pipeline scrap (Nan 2018). Lead to the leakage of residues in the pipeline, polluting the environment.

6.2 The Wax Precipitation Mechanism of Crude Oil

As the mining conditions continue to change, the phase state of the various components in the crude oil will also change accordingly. The phase state may be a liquid phase, or a gas–liquid two-phase coexistence, or even a gas–liquid-solid phase. Three-phase. The wax in crude oil usually exists in liquid form at the bottom of the well. As the pressure and temperature are reduced and some light components escape in the form of gas, the solubility of wax in crude oil becomes smaller, and some waxes will become The form of crystals gradually precipitates, and continuously aggregates, grows, and deposits, causing wax formation. The changes in the microstructure and quantity of wax crystals in waxy crude oil significantly affect the changes in macro rheological parameters such as the storage modulus and

energy consumption modulus of crude oil (Teng 2013; Wang 2011; Liu 2014; Gao 2007; Lin 2010,1982; Peng 2007).

6.2.1 Composition of Wax Deposits

Paraffin wax is one of the natural components present in crude oil. Paraffin wax is mainly a mixture of a series of normal alkanes. In addition, there are a small amount of aromatic hydrocarbons and paraffinic hydrocarbons in paraffins, but under normal circumstances, the content of these isomeric hydrocarbons is only less than 10%, but it should not be ignored that these isomeric hydrocarbons will be very large. To the extent it affects the physical and chemical properties of paraffin wax.

Pure paraffin wax is a white solid at room temperature, and its crystal lattice shape is mainly diamond-shaped flakes or needles. The proportion of wax deposits in the crude oil is Probably between 40 and 60%. Paraffin entering water source will pollute it, and paraffin volatilizing into atmosphere will pollute the atmosphere. If people inhale high concentration paraffin vapor, they will have headache, dizziness, loss of appetite, cough and other symptoms. Paraffin can accumulate in organisms, especially in fish and seaweed, thus causing damage to the respiratory system of aquatic organisms.

More than 80% of the crude oil mined in China is waxy crude oil, which has a high freezing point and poor fluidity at room temperature, which brings many problems to the production, transportation and storage of crude oil (Wenchao 2019). In order to ensure the normal and efficient exploitation of crude oil in waxy oilfield and the environmental protection treatment of abandoned pipelines, wax removal and control is a very important measure in oilfield exploitation. In China, most of the oil field waste pipeline treatment method is to clean up the residues in the pipeline, and then take on-site burial, so as to reduce the environmental pollution caused by the residues in the pipeline. In order to ensure the safe and economical operation of pipelines, waxy crude oil must be treated with wax prevention and viscosity reduction (Yang 2012).

6.2.2 Waxing Process in Oil Wells

During the flow of waxy crude oil in the pipeline, when the temperature is lower than the wax precipitation point, the paraffin wax crystallites in the crude oil continue to precipitate and aggregate into particles. The particles adsorb each other so that the paraffin wax grows and adheres to the pipe wall, causing The reduction of the pipeline flow area reduces the pipeline transportation capacity, and even blocks the pipeline in severe cases, affecting the safe operation of the pipeline. Therefore, the crude oil pipeline needs to be pigged regularly.

Generally speaking, the waxing process can be composed of three stages: (1) The waxing stage. When the temperature of the crude oil is slightly higher than the cloud

point, wax crystals begin to precipitate from the crude oil; (2) The wax crystal growth stage. When the temperature of crude oil is near the cloud point, the precipitated wax crystals continue to combine with each other, and the aggregation becomes larger, and the speed of their combination will become faster as the temperature decreases; (3) The wax deposition stage. When the temperature of the crude oil is lower than the cloud point, increasing wax crystals gradually deposit on the surface of the tubing, causing wax formation (Guosi 2015).

At the same temperature, the amount of wax crystals precipitated, the number of wax crystals and the area ratio decreased with the increase of the cooling rate. This is because as the cooling rate increases, the wax in the oil is supersaturated but is too late to precipitate, leading to the precipitation of wax crystals and the formation of wax crystal structure lag, that is, the wax precipitation phenomenon of crude oil exhibits "hysteresis". In the case of the same pipe wall temperature, the higher the temperature of the crude oil, that is, the greater the temperature difference between the crude oil and the pipe wall, the wax deposition rate will gradually increase due to the formation of a radial temperature gradient that is conducive to wax deposition (Lilin 2016). At higher temperatures, the wax crystals are dispersed in the crude oil, making the crude oil behave as a Newtonian fluid; as the temperature decreases, the wax crystal concentration increases and the size increases, and the crude oil changes from a sol to a gel state. Its storage modulus and energy consumption the modulus also changes accordingly (Chuanxian 2000; Ming Zhen 2008; Coutinho 2004; Visintin 2005). Therefore, the quantitative description of the relationship between the storage modulus, energy consumption modulus and cumulative wax precipitation of waxy crude oil is very important to further understand the elastic change mechanism of waxy crude oil (Lorge 1997; Kané 2004; Coutinho 2004).

6.3 Crude Oil Wax Precipitation Point Test Method

There are three main methods for testing the wax separation point: microscopic observation method (often using polarizing microscope CPM), viscometer/rheometer method, differential scanning calorimetry (DSC), laser method and ultrasonic method, etc. This article mainly summarizes the test methods of wax precipitation point (Wei 2018), and compares and analyzes three common methods.

6.3.1 Introduction to Conventional Methods

Microscopic observation method. The oil sample is heated until the wax is completely melted, and the temperature at which the wax crystals first appear under the observation of the polarizing microscope during the cooling process is regarded

as the wax precipitation point. The microscopic observation method is the most sensitive and intuitive for the determination of wax precipitation point. With the development of microscopic image acquisition and processing technology, in recent years, the analysis of wax crystal microscopic images has focused on quantitative characterization research, using the first step temperature of the increase in the number of particles to determine the wax-out point; image processing technology enables microscopy The result of observation method is more accurate and reliable.

Viscometer/rheometer method

Rotational viscometer method. After heating the oil sample until the solid wax turns into liquid, record the shear stress or viscosity-temperature curve. When the temperature drops to the precipitation of wax crystals in the crude oil, it will cause a turning point in the viscosity-temperature curve, and the turning point corresponds to the wax precipitation temperature.

Activation energy method. According to the principle that the wax crystals in the dispersed phase appear in the crude oil after waxing, the activation energy of viscous flow is increased, and the waxing temperature is determined by the increase of activation energy.

Differential scanning calorimetry. The oil sample begins to cool down from a certain temperature below its waxing point, and the differential heat flow between the oil sample and the reference substance at each temperature point is drawn into a differential scanning calorimetry curve (DSC curve). The temperature at which wax crystals begin to precipitate in crude oil, that is, when the DSC curve deviates from the baseline to form an exothermic peak, the corresponding starting temperature is defined as the wax precipitation point. DSC method has the characteristics of easy operation, less time-consuming and less sample consumption, fast response and good reproducibility, and is widely used in the wax precipitation point test.

Wax deposition is an important factor affecting the safety and economic operation of crude oil pipelines. It is of great significance to accurately predict the wax content of crude oil and the wax deposition law of the pipeline (Qiyu 2011). Compared with the method of calculating the wax content by the thermodynamic model, the DSC test method is simple and efficient. At present, a large number of experimental studies have proved that the wax content measured by DSC is consistent with the results obtained by other methods. The influence of DSC cooling rate on wax precipitation of waxy oil samples is analyzed here, and the optimal cooling rate is determined to ensure the accuracy of the test results (Nan 2018).

6.3.2 Comparison of Test Conditions

Scholars at home and abroad have conducted a lot of comparative studies on the three conventional methods for testing wax precipitation points (microscopic observation method, viscometer/rheometer method, and differential scanning calorimetry).

Ronningsen, Pedersen, Hansen, Cazaux, etc. all believe that the results measured by the microscopic observation method are more accurate than the viscometer method and the DSC method, but the measurement results depend on the thickness of the test piece and the cooling rate. It is found that when the wax precipitation rate of the measured crude oil is large, the results measured by the three methods are almost the same; the microscopic observation method and the viscometer method are not suitable for measuring the wax precipitation point of the crude oil with a small wax precipitation rate.

6.3.3 Introduction to Unconventional Methods

Unconventional methods include laser method, ultrasonic method, in addition, filter screen pressure difference method and infrared spectroscopy, which can also be used to measure the waxing point.

6.4 Crude Wax Removal and Wax Prevention

The wax in crude oil usually exists in liquid form at the bottom of the well. As the pressure and temperature are reduced and some light components escape in the form of gas, the solubility of wax in crude oil decreases, and some waxes will be The form of crystals gradually precipitates, and continuously gathers, grows, and deposits. Paraffin will deposit on downhole equipment, production casing, around the well wall and oil pipelines and other equipment, causing wax clogging. After the tubing is waxed, the diameter of the tubing is reduced, thereby increasing the oil flow resistance, reducing the production efficiency of the oil well, and having a great impact on oil transportation. In severe cases, it may even block the oil well and stop the exploitation of crude oil. Therefore, in order to ensure the normal extraction of crude oil in waxy oilfields, wax removal and wax prevention are a very important measure in oilfield exploitation (Jiguo 2017).

To ensure the safe and economical operation of pipelines, waxy crude oil must be treated with wax prevention and viscosity reduction. Among them, the advantages of magnetic treatment technology are simple equipment installation, convenient use, non-polluting, low cost, and long duration, which can reduce the viscosity of crude oil and improve the fluidity of crude oil in gathering pipelines (Dirand 1998; Xiubo 2005). At present, in the actual application process, it is found that the viscosity reduction effect of the magnetic processor is unstable, which is due to the insufficient understanding of the key factors that affect the magnetic treatment effect and the viscosity reduction law of the magnetic treatment (Tung 2001; Zhang 2013).

6.4.1 General Rules of Wax Deposition in Oil Wells

Light crude oil group. The wax-dissolving ability in crude oil increases as the light fractions increase, and the lower the wax precipitation temperature, the less likely it is to wax. When natural gas is separated under the bubble point pressure, the wax dissolving ability of crude oil is reduced, the wax precipitation temperature rises, and the wax deposition is intensified. In other words, the wax precipitation temperature changes with the change of the crude oil composition during the mining process (Duntong 2017).

The influence of colloid. The increase in crude oil gum and asphaltene content will change the initial temperature during wax precipitation and the wax properties after condensation. In order to facilitate the study of the influence of gums and asphaltenes on paraffin in crude oil, experiments can be carried out in a kerosene-paraffin system (The research of acoustic wave anti-wax technology has reached the international advanced level 2000).

The influence of temperature and pressure. When the pressure does not change, if the temperature rises above the wax precipitation temperature, the wax in the crude oil will not precipitate. On the contrary, when the temperature drops below the wax precipitation temperature, the wax begins to crystallize. Among the wax prevention technologies used in oil fields around the world today, there are mainly: lined tubing wax prevention, cable wax prevention, strong magnetic wax prevention, ultrasonic composite wax prevention, and chemical wax prevention (Gang 2018).

6.4.2 Wax-Proof Lined Tubing

There are two types of anti-wax technologies for lining tubing: glass tubing and coating tubing (Hongjing 2017). The wax-proof method of glass tubing is to line a layer of about 0.5 to 1.0 mm of industrial glass on the wall of the tubing, and then lower the tubing into the waxing section of the oil well.

The main wax-proof effects of the wax-proof technology for lining tubing are: (1) The lining layer has a good smoothness, and it is difficult for wax crystals to deposit on the pipe wall. (2) The inner lining layer has strong hydrophilicity, and water can form a water film when adsorbed on the surface of the pipe wall. This water film will prevent wax crystals from depositing on the pipe wall surface.

6.4.3 Cable Wax Prevention

The function principle of the cable wax prevention is that the cable is energized to release heat, and the tubing that goes into the well with the cable is heated, and

the temperature of the crude oil in the tubing increases. When the temperature of the crude oil in the tubing rises above the cloud point, the wax in the crude oil the crystals are difficult to precipitate, and they will not be deposited on the wall of the tubing, but will be taken out with the flowing oil, so as to achieve the purpose of wax prevention.

According to the wax-proof effect of the cable wax-proof in the field application: the oil well is obtained under normal production conditions, from the 1000 m section downhole to the wellhead, the cable wax-proof can keep the temperature of the flowing oil above 40 °C, which can achieve good the anti-wax effect.

6.4.4 Ultrasonic Compound Wax-Proof Technology

The combination of ultrasonic oscillator wax-proof and solid wax-removing and wax-proofing agent has formed a new wax-proof technology-ultrasonic compound wax-proof technology (Ying 2013). The theoretical basis of ultrasonic oscillator design is derived from the principle of ultrasonic. When the sonication of oscillation occurs when the oil flow passes through, it can send an effective effect to delay and destroy the crystallization of paraffin, and it can also reduce the surface tension of the crude oil. In addition, it can also make the crude oil and solid wax preventive. The agent can be fully stirred and mixed to improve the wax-proof effect.

6.4.5 Chemical Wax Prevention Technology

(1) The method of surfactant aqueous solution to achieve wax prevention is to adsorb on the surface of the wax crystal or the surface of the wax to make the polarity reversal and form a water film to prevent wax deposition on the surface.
(2) When the wax molecules have not yet precipitated, the wax inhibitor molecules will first precipitate from the crude oil, and a large number of fine and small crystal centers will be produced. At this time, the crystallites formed by the wax crystal modifier will adhere Adding paraffin alkane makes the wax crystals in a dispersed state that cannot be coalesced and increased, so the wax deposition on the surface of the equipment is greatly reduced.

The problems of chemical paraffin inhibitors in paraffin control are: Chemical wax inhibitors have relatively poor adaptability. Due to the different properties of crude oil and wax and the influence of external factors such as temperature and pressure, the choice of wax inhibitors will also change accordingly. Some paraffin removers pollute oil wells and some wax removers have high pour point, which is not suitable for winter use.

Thermal wax removal and anti-wax technology Self-energy hot washing (Hongyan 2016): From 2013 to 2015, this unit has a total of hundreds of wells with self-energy hot washing. After hot washing, the average maximum load of the well decreased by 1.43 kN, and the minimum load increased by 0.52 kN. Reduced by 1.95 kN, the effect of hot washing to remove wax is better.

6.4.6 Acoustic Viscosity Reduction and Wax Prevention Technology

Under the action of the formation pressure of oil well, the velocity of fluid accelerates through the nozzle to excite the reed to vibrate and produce the sound wave with certain frequency and amplitude. With the action of fluid, the device continuously generates sound waves and acts on the fluid. This kind of hydraulic acoustic wave generated by the spring plate by the fluid jet establishes the vibration wave field in the fluid and the surrounding medium, acts on the fluid, achieves the purpose of viscosity reduction and wax prevention, and prolongs the hot washing period of oil wells. Acoustic wax control technology is a new type of advanced technology with high efficiency and low cost. It has the characteristics of simple process, convenient management, strong adaptability, good wax prevention effect and no pollution to the formation. It is a practical technology worthy of promotion.

6.5 Conclusions

By consulting the literature, we know that when testing the wax removal point, special attention should be paid to the choice of test conditions and the choice of test methods. This is due to the close relationship between wax precipitation characteristics and temperature drop rate, and the wax precipitation point can be considered as a conditional parameter. Therefore, there is no need to stick to the specifications for the choice of test conditions. In the choice of test method, a suitable test method should be selected according to the type of wax crystal and wax content, supplemented by other methods for verification. For the problem of paraffin control in oil wells, we should choose the wax prevention and removal methods with the characteristics of simple process, convenient management, strong adaptability, good wax prevention effect and no pollution to the formation according to different geographical, climatic and economic conditions. In order to prevent pollution and protect the environment, the ultrasonic anti wax technology and magnetic treatment anti wax technology have better effect.

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