Numerical and Lab Experimental Methods of the Wax Deposition Investigation in Oil Pipelines

R M Karimov¹, R R Tashbulatov¹, A R Valeev¹

¹Lecturer, Department of Oil and Gas Pipeline Transportation and Storage, Ufa State Petroleum Technological University (USPTU, FSBEI HE), 1 Kosmonavtov St., Ufa, 450062, Russia

E-mail: tashbulatovradmir@gmail.com

Abstract. This paper presents results of a comparative analysis of several research methods for oil pipelines waxing process, which are based on the progress made with present-day laboratory equipment and the capabilities of software and hardware computational packages used to simulate properties of multiphase fluids and kinetics of complex multi-factor processes. This paper considers theoretical foundations of proven and substantiated mechanisms of the processes of wax formation and accumulation on the inner surface of oil pipeline walls, including main factors that impact the rate of such processes. The paper also points out disadvantages of the methods of static measurement based only on the diffusion factor of deposition of deposits, predominantly of the paraffin wax type; these static measurement methods preventing from taking into account the impact of other equally significant factors that accelerate and decelerate accumulation of deposits. This work highlights the most accurate methods to determine the chilling point or mass crystallization of paraffin waxes, which are recommended to be used in computerized simulation of the process.

1. Introduction

Paraffin wax deposits in wells, oil pipelines and vessels, caused by natural heat and mass transfer processes, result not only in decreased throughput of the lines and decreased useful volume of vessels, but also often impede ultrasonic diagnostics (they distort data, cause blind spots or even result it stuck in-line devices) [1, 2].

Forecasting of complications associated with waxing is one of the important operational tasks, the solution of which makes it possible to reduce the risks mentioned above and select the most efficient ways to control deposits. The latter can be divided into methods to prevent and remove the deposits. Notwithstanding the great abundance of process methods and technical means for complete removal of deposits both from pipes and vessels, the solution of the first problem — complete prevention of their formation or accumulation — is associated with the need to conduct the entire set of experimental (both laboratory and bench-scale) [1, 2, 3, 4, 6, 11] and computational research [5].

The up-to-date instrumental and software facilities for experimental methods to study waxing processes enable to reproduce both static and dynamic modes of tests that are close to the conditions of real operation of oil pipelines. Flow Loop installations [5, 6] and dynamic simulators of multiphase flow, enabling to evaluate the kinetics of the process of deposit accumulation and removal (resolution, breakaway and washing-off by the flow) [4, 5], hold a special place among them. In both cases, the
primary of the high-priority tasks is to determine the dropout point (temperature and pressure of wax saturation), or, for rougher calculations, the temperature of mass crystallization, at which the process of wax deposition intensifies, thus making it possible to use indirect evaluation methods associated with changes in rheological or physicochemical properties of oil [7].

\[
\frac{dm_w}{dt} = \rho_0 \cdot D_m \cdot A \cdot \frac{dC}{dT} \cdot \frac{dT}{dr},
\]

where \(m_w\) – total amount of paraffin wax deposits, kg;
\(\rho_0\) – initial oil density, kg/m\(^3\);
\(D_m\) – molecular diffusion coefficient of oil paraffin waxes, m\(^2\)/s;
\(A\) – area of the inner surface of the pipeline wall, m\(^2\);
\(C\) – mass concentration of paraffin waxes in oil, mass%;
\(T\) – oil temperature, °C;
\(r\) – radial distance from the pipeline axis, m.

2. **Theoretical basis**

It is believed that deposition, primarily because of crystallization of normal paraffin waxes, occur inside oil pipelines due to the following primary mechanisms and processes:

- molecular diffusion which is the process oil n-alkanes (paraffins of normal structure) moving from the area of high concentrations to the area of low concentrations;
- shear dispersion that depends on the flow velocity gradient determining the movement of solids from the flow to the wall;
- Brownian diffusion (to a lesser extent);
- gravity casing the solid dispersed particles to settle on the lower generating line of the pipeline and the pipeline to sag.

The dominant process among the ones mentioned, as noted in a lot of works [8, 9], is molecular diffusion (Fig. 1), the rate of which can be assessed with Fick’s law:

Numerous studies, by both domestic and foreign scientists, deal with research on determining the value of the molecular diffusion coefficient while offering various experimental techniques and mathematical correlations [8, 12, 13].

![Figure 1. The mechanism of molecular diffusion of paraffin wax molecules. Brownian diffusion makes a far smaller contribution to the waxing process than all the other listed processes, for which reason it is not taken into account in the models to solve practical problems.](image-url)
Random movement of dispersed particles suspended in oil takes place during their colliding with thermally agitated molecules, because of which they move from a warmer area of the flow to a colder one with less agitated molecules, leading to a concentration gradient in the liquid.

In contrast to diffusion mechanisms, shear dispersion, on the contrary, already limits accumulation of deposits on pipe wall. For instance, in a laminar flow regime, the velocity of the flow is highest in the center of the pipe and lowest near its walls where shear stress is highest, which leads to this velocity gradient profile inducing the angular velocity of solid particles in the flow, because of which they move to the wall of the pipe likewise. As velocity of particles and laminar-to-turbulent transition increase, a loose layer of deposits is knocked out and separated from walls.

The action of gravity is a bigger driver of accumulation of inorganic and heavy deposition particles in neckings and sinkings of the pipeline profile.

3. Determining factors

Other factors that determine waxing include, most notably, oil flow composition and conditions (velocity and flow rate, temperature and pressure of the flow, liquid-to-gas ratio), surface properties (wall roughness and material), and — for upstream systems and field gathering and transportation of oil — gas content (gas saturation) of untreated water-oil emulsion.

On the one hand, influence of hydrocarbon and fractional composition of oil on waxing processes is utterly understandable and does not require argumentation but, on the other hand, more in-depth studies became possible not so long ago, after state-of-the-art high-precision laboratory testing tools and powerful programming & computing suites for PVT-modeling and generation of equilibrium phase diagrams emerged in the petroleum industry [3, 4, 14].

It is known that aromatic hydrocarbons serve as solvents for saturated n-paraffin waxes that make up paraffin wax deposits while high-molecular polar components (oil asphaltenes to a greater extent and resins to a lesser extent) can both serve as crystallization nuclei and, vice versa, prevent subsequent growth of druses settling on their surface in a way similar to the way pour point depressants act [15, 16, 17]. High mobility of normal paraffin waxes enables them to gather in clusters easily as their concentration increases and oil temperature decreases. That said, a combination of the following factors will have an impact on intensity of waxing, these factors including weight content of paraffin waxes and their ratio to high-molecular heavy oil components, and solid inorganic impurities in the form of mud and sand particles, emulsified water, corrosion and erosion products [1, 2, 3, 4, 5, 6, 7, 8, 9].

As the driving process of molecular diffusion, temperature is the predominant factor in precipitation of paraffin waxes because of its direct impact on their solubility in oil. It is known that solubility of paraffin waxes increases as oil temperature rises and, vice versa, decreases as it falls. The growth rate of paraffin wax deposits is in a direct relationship to the temperature gradient on the wall surface — the difference between the flow and the ambient temperatures [3, 4]. The notions of the mass crystallization temperature and the wax dropout point (WAT or wax appearance temperature) are used [13, 14] to solve the problems of waxing prediction.

In crude oil production and field gathering systems, in contrast to major pipeline transport of treated dehydrated and degassed commercial product at lower and conditionally stable pressure and temperature conditions, the term of paraffin wax saturation pressure is often used, above which the wax appearance temperature also rises provided that the composition is constant. This phenomenon means that increasing the pressure in a single-phase area above the saturation pressure will facilitate intensification of wax deposition. As noted above, both these dependences and the impact of composition and temperature can be represented in phase diagrams of fluid equilibrium (Fig. 2) [4].
Figure 2. Phase diagram of petroleum fluid equilibrium.

Phase diagrams became widespread mainly in the exploration and production sector. In this way, hydrocarbon gases as lighter low-boiling fractions remain in solution above the pressure of oil saturation with them, which facilitates preservation of n-paraffins in their dissolved state. At a low gas/oil ratio (GOR), the WAT will be lower as long as the flow is in a single-phase state. A high GOR during oil recovery can lead to expansion and further cooling of the flow, which results in a possible increase in the risk of waxing because of decreased system pressure.

The impact of the flow rate and flow conditions is well studied, which is reflected in numerous works [10, 11, 12, 13]. It has been experimentally proven that the rate of deposit buildup is higher in laminar flow. Turbulent flow has an impact on the internal friction force that facilitates movement of the deposit layer from the pipe surface in the direction of the flow. When viscous friction forces exceed the values of static shear resistance, paraffin waxes come back into the oil flow, which slows down the growth rate of the deposits, breaking away and washing them off the wall surface. It is important that this process also leads to hardening of the wall layer, which makes it harder to carry out pigging operations of oil pipelines [1, 2, 3].

A host of works have also been devoted to studies of the impact that wall surfaces have on the processes of deposit accumulation in oil pipelines [18, 19]. More specifically, it has been established that paraffin wax deposits do not attach to the metal itself but cling to rough spots on walls that then serve as nuclei for deposit accumulation thus forming a layer. As roughness, which changes in the course of natural wear and tear, grows, the rate of the deposit accumulation on the walls also grows, and, vice versa, wax deposits do not linger or are completely absent on smooth surfaces. This effect is used in deposit inhibiting, but, in contrast with traditional pour point depressants, surfactant wetting agents are the chemicals used.

4. Static methods
Up-to-date equipment for analysis of the smallest particles makes it possible to determine the value of the wax appearance temperature or wax mass crystallization with varying degrees of accuracy. While mainly direct methods of visual measurement of the medium micro-state and properties (optical permeability, exo- and endothermic processes) became most widespread for measurement of the wax
appearance point for solid oil paraffins, the conditions of mass crystallization of paraffin waxes can be
determined by an even rougher estimation of macroscopic properties (oil viscosity and density) to
solve practical problems. The latter methods, which are less accurate but more accessible, are way
below the former ones in terms of accuracy, and application of the former, along with costly methods
to determine hydrocarbon composition, is a prerequisite for high-precision modeling that enables to
identify modes completely excluding paraffin wax deposition. However, when it is not possible to
eliminate conditions for deposit formation completely due to thermobaric conditions of operation
(temperature and pressure of the flow are much lower than the chilling point of paraffin waxes),
application of rougher methods is also an effective way to take into account negative factors of the
deposit formation and to select effective methods of cleaning or inhibition.

Cross-polarization microscopy (CPM) and differential scanning calorimetry (DSC) have the
highest accuracy among contemporary laboratory methods to determine WAT. Despite the visual
principle of optical measurements and thanks to very high resolutions of contemporary photo/video
recording devices, the first one, which is recognized as the most accurate method (the error in WAT
calculation is less than 0.1 °C), enables to obtain sharp microphotographs, on which one can see
nucleation of the “first” smallest particles of paraffin waxes. The plane of light polarization changes if
crystalline substances are present — the light reflects from the particles transmitting shapes of paraffin
crystals as white dots against a dark background. The first dot appears when the temperature of the
sample reaches WAT (Fig. 3).

![Figure 3. Determination of WAT using the CPM method.](image)

Unlike optical CPM measurement method, differential scanning calorimetry is based on the
difference in heat absorption between the reference (with known properties) and the sample being
tested. The mass fraction of the formed oil paraffin crystals with a known melting enthalpy of the
sample can be calculated using a function of paraffin wax concentration and oil temperature function, the solubility curve. The accuracy of temperature measurement is 0.3 °C, that of enthalpy — 1 J/kg. When measuring, one can observe a sharp change in the heat flux at first due to transitioning from isothermal conditions (the sample is temperature-controlled prior to starting the measurements) to heating the sample. If the sample contains moisture or low-boiling solvents, a peak (an endothermic process) is observed on the DSC curve (Fig. 4) and the sample loses mass. If chemical reactions occur during the measurement, exothermic peaks or endothermic effects can also be observed, and the sample decomposes at high levels of the heating temperature. When samples are cooled, the rate of cooling starts to decrease close to the WAT point as compared with the reference standard because of the heat release from crystallization of paraffin waxes. In this case, the analyzer registers the difference in incoming heat to maintain the exact temperature of both samples. The value of the WAT point is registered in the thermal image as deviation from the straight trend line above its value.

![Figure 4. Determination of WAT using the DSC method.](image)

1 — start of measurements; 2 — evaporation of moisture or solvent; 3 — relaxation peak; 4 — chemical reaction; 5 — start of decomposition

Less accurate, but more accessible even with application of standard equipment of chemical analysis laboratories at enterprises, methods mainly include indirect methods to measure viscosity and density profiles (DMA method), which are based on assessment of shapes of experimental curves where sharp changes in consistency properties are registered, which depend on the structure of oil during crystallization of paraffin waxes in it (Fig. 5).
on the left — viscosimetical method; on the right — DMA method

**Figure 5.** Measurement of the temperature of mass crystallization of oil paraffin waxes by changing viscosity and density profiles.

It should be noted that application of these methods to determine the wax mass crystallization temperature can be effective only for homogeneous media because mixes of oils that are vastly different in density are distinguished by manifestations of oil incompatibility effects [4, 16] associated with sharp changes in viscosity and density due to nanoaggregation of asphaltenes rather than mass crystallization of paraffin waxes.

5. **Dynamic methods**

If it is more than enough to determine the WAT for determination and complete elimination of waxing conditions with computational simulation methods, then it is important in practical problems of oil pipeline operation to study the kinetics of the process over time, which depends on all the above factors. Kinetic studies are based mainly on Cold Finger and Wax Loop bench units (Fig. 6, 7).

on the left — unit with 4 cells; on the right — arrangement of the test cell

**Figure 6.** Cold Finger laboratory unit.
The concept of testing with the dynamic method of Cold Finger is to measure the mass content of deposits that formed in the cell of the device and on the rod surface directly during the test. It should be noted that this method takes into account only the molecular diffusion mechanism, and therefore it became widespread when selecting brands and assessing the comparative effectiveness of paraffin wax deposition inhibitors of the depressant type. The duration of the testing is chosen on a case-by-case basis as are the temperature regimes — the difference between the test sample and the cold rod temperatures, the values of which are set depending on the mass crystallization temperature of oil paraffins or the WAT value previously calculated by one of the methods above. Despite the fact that this method belongs to dynamic types, such studies do not enable to take into account the actual kinetics of the process that takes place during oil pumping in pipelines because the oil sample is unstable in its composition during the test (as it cools and paraffin waxes drop out, the WAT shifts too). There are no such drawbacks in the method that is based on application of laboratory units and test stands of the Flow Loop type, including Wax Loop units, specifically designed to study waxing in oil pipelines, which also enable to solve important practical problems of operation — determination of the starting characteristics of oil pipelines, the time allowed for their safety shutdown and the time to reach the design conditions after long downtimes at low temperatures [20].

6. Conclusions
The suggested analysis of the methods applied to study the conditions, factors and mechanisms of waxing in oil pipelines enables us to make a conclusion that the progress of present-day analytical equipment and software & hardware suites for computational modeling make it possible not only to determine boundaries of hazard modes but also to select the most effective methods to deal with them — to optimize costs for regular cleaning and deposit inhibition with account of the actual kinetics of the process over time, from the startup of the oil pipeline and over a long period of its operation, and to prepare linear sections for inline inspection and scheduled shutdowns if there are risks of complications after a subsequent cold start.

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