ANALIZA OBRADE VISOKOPARAFINSKIH NAFTI DODATKOM MODIFIKATORA REOLOŠKIH OSOBINA

ANALYZING THE PROCESSING OF HIGH PARAFFIN OILS BY ADDITION OF MODIFIERS OF RHEOLOGICAL PROPERTIES

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Parafini i parafinski voskovi su hemijski stabilni. Iz tog razloga za mnoge tipove nafti primenjuje se obrada visokoparafinskih nafti dodatkom modifikatora reoloških osobina. Na osobine proticanja visokoparafinskih nafti utiče broj nastalih kristala parafina i njihov oblik. Postupak modifikacije reoloških osobina visokoparafinskih nafti, sastoji se u dodavanju određenih aditiva, čime se omogućava promena morfologije kristala parafina. Dodavanje adidtiva u naftu je najefikasnije na pritisku i temperaturi na kojima još nije započela kristalizacija parafina. Postoji veći broj aditiva koji imaju različite primene. Jedan od njih je i aditiv koji se koristi za sniženje tačke stinjavanja i napona smicanja, a naziva se depresant stiništa. U sirovoj nafti ukupan sadržaj parafina i raspodela parafina, značajno varijaju. Zbog toga se za svaku naftu posebno iznalazi i razvija najefikasniji depresant tačke stinjavanja. Ostali aditivi su: parafin inhibitori, odstranjivači parafina i poboljšivači protoka. Primena modifikatora reoloških osobina ima značaj u rešavanju problema protoka visokoparafinskih nafti. Ovom metodom, u bušotini se rešava problem protoka u tubingu, bušotinskim vodovima, procesnim sudovima i naftovodu.

Ključne reči: *visokoparafinska nafta; kristalizacija; tačka stinjavanja; modifikator*

Paraffins and paraffin waxes are chemically stable. For that reason, for many types of oil, the treatment of high-paraffinic oils is conducted with the addition of modifiers of rheological properties. The flow properties of high paraffin oils are affected by the number and shape of formed paraffin crystals. The process of modifying of rheological properties of high paraffin oils consists of adding certain additives, which enable a change in the morphology of paraffin crystals. Adding additives to oil is most effective at pressures and temperatures at which paraffin crystallization has not yet occured. There is a large number of additives that have different applications. One of them is an additive that is used to lower the melting point and shear stress, and it is called a melting depressant. In crude oil, the total content of paraffin and the distribution of paraffin vary significantly. Therefore, for each type of oil the most effective melting point depressant is invented and developed separately. Other additives are paraffin inhibitors, paraffin removers and flow enhancers. The application of modifiers of rheological properties is important in solving the problem of flow of high paraffin oils. With this method, the problem of flow in the tubing, well lines, process vessels and oil pipeline is solved in the well.

Key words: *high paraffin oil; crystallization; pouring point; modifier*

1 Introduction

Paraffins and paraffin waxes are chemically stable. This is why the chemical process of decomposition of paraffin and paraffin waxes present in high paraffin oils has not found application. Very successful applications for many types of oil are modifiers of rheological properties. It was noted in

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earlier that the flow properties of high paraffin oils are affected by the number and shape of formed paraffin crystals. The biggest problem are long chain paraffin crystals. The basis of the process of modifying the rheological properties of high paraffin oils is the addition of certain additives which enable the change of the morphology of paraffin crystals. This way, it is more efficient to add additives to the oil at a pressure and temperature at which paraffin crystallization has not yet occurred. [1]

Today, there is a large number of known additives, which are produced by several main manufacturers. These various types of additives have different purposes. The first group of additives, that are used to lower the melting point and shear stress, is called melt depressants. Another group of additives, that have the role to prevent or reduce the release and deposition of paraffin waxes, is called paraffin inhibitors. The third group of additives, that are used to remove deposited paraffin wax from the pipe walls or vessels, is called paraffin removers. The fourth group of additives, that are used to modify or regulate viscosity, is called flow improvers. There are additives that have combined properties, and multi-purpose application. For example, these additives have the properties of depressants and paraffin inhibitors. [2]

Further, for modifying paraffin wax crystals, special polymers are applied. These special polymers, which are effective as modifiers of wax crystals, contain "paraffin chains" in their molecular structure and co-crystallize more easily with paraffins due to their similarity to the structure of wax crystals. The polymer through co-crystallization inhibits further three-dimensional growth of paraffin crystals. As a result there are many small crystals instead of several large ones, thus preventing the formation of network structures of agglomerated crystals. [1]

2 Materials and methods

2.1 Oil exploitation methods

We distinguish two ways of oil exploitation: direct and auxiliary. The direct method includes the eruptive method of oil exploitation, exploitation by lifting (gas lift or aero lift) and the method of exploitation of oil by deep pumping (pumps with rods and pumps without rods). The auxiliary method includes the water injection method, compressed air injection method, and the underground mining method (an auxiliary method applied in Canada).

2.2 Transport of high paraffin oils

Crude oil with a higher content of paraffin, due to their physical and chemical properties, can lead to certain difficulties and pose a challenge during transport. Problems are evident and are expressed in the transport process of high paraffin oil with solid alkane (paraffin) content above 15% by weight. Problems occur due to high pour point temperatures (the lowest temperature in °C, at which the sample no longer flows, when cooled under specified conditions), which lead to difficult flow through pipelines at temperatures close to the cooling temperature. These types of oils are also called heavy oils, and often contain significant amounts of asphaltene in addition to paraffin. [1]

Paraffins with a low molecular weight have a low melting point. The melting temperatures of paraffin increase significantly as the number of carbon atoms increases. When temperatures are above the melting point, then paraffins in the oil are in a liquid state. Through the cooling process of the oil, the first crystals are formed which originate from paraffin. Through further cooling, new solid paraffins are formed, which cause a change in the shape of the formed solid particles, as they deposit on them. At this point in the process, the oil is gelled. [2]

Paraffin waxes can lead to crystallization in the form of needle crystals, irregular crystals, plate crystals and microcrystals. These different types of crystals are presented on Figure 1.

The amount of paraffin in oil has a very significant influence on the properties of high paraffin oils. Further, research of oil samples with different amounts of paraffin showed that alkane content has a significant influence on the melting point.

Oil pipelines for the transport of heated oil can be constructed in two ways. The first is that the heating process of oil takes place along the entire length of the oil pipeline. In the second approach the oil heating process takes place only at certain intervals. For example, at the beginning of the pipeline and at intermediate stations. When oil is heated along the entire length of the pipeline, its

temperature does not change along the pipeline. In the second approach where the heating of oil takes place only at certain locations/intervals, the temperature along the pipeline decreases after the heating point. [3]

When there is no flow through the pipeline, the pipeline is filled with light oil that does not cool down nor freeze. During the transport of high paraffin oil, the cooled pipeline and its surroundings are heated with light oil which is taken from the tank and which is heated before being pumped into the pipeline. [3]

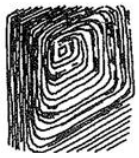
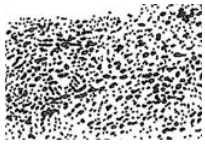
Plate crystals	Needle crystals	Irregular crystals	Microcrystals
			

Figure 1: Types of paraffin crystallization

During the construction and instalment of oil pipelines for heated oil transport, it is necessary to take into consideration that in the future the amount of transported oil can change, which affects the flow through the pipeline.

Flow properties of crude oils with a high paraffin content, high viscosity, and oils prone to gelling can be improved flow mixed with oils of lower viscosity, or if mixed with petroleum products such as gasoline, kerosene or diesel fuel. Additionally, laboratory tests are required to determine the mixing ratios of the noted fluids. The mixing of crude oil with oil of lower viscosity, gasoil or kerosene, is determined by laboratory means.

2.3 Oil temperature in the pipeline at flow interruption and stop of oil flow

It is very important to know the temperature of the fluid along the pipeline when flow stagnation occurs. More precisely, it is important to know how fluid temperatures change depending on the stagnation time, and how fast the fluid cools. Szilas proposed a model for predicting the change in oil temperature in the pipeline as a function of the length of the time interval after the oil flow stops.

2.4 Rheology and viscosity

Rheology is a part of classical mechanics that deals with the study of deformation and the flow of matter. When a force acts on the body, it causes its deformation, and with liquids (liquid fluids) such force causes flow. The name *"rheology"* was given by Eugene Bingham in 1920 inspired by Heraclitus' saying *"panta rei"* (everything flows). [4]

The name itself comes from the Greek words *rheos* (meaning flow, current, flowing) and *logos* (meaning science). Rheology describes in detail the deformations of a fluid under the influence of shear stress. Ideal liquids and gases are deformed irreversibly, and reversibly. More precisely, they flow and the energy is dissipated inside the liquid and cannot be restored by removing the stress alone. Rheology deals with materials whose mechanical properties cannot be described by classical theories of elasticity and Newtonian fluid mechanics. It also deals with the flow of viscous fluids and deformations of colloids that deviate from the classical laws of hydrodynamics. Rheology helps us to predict the mechanical behavior of materials. Through these analyses and predictions conclusions can be drawn about the structure of materials. [5]

Viscosity is defined as the internal resistance of a fluid to flow, or, more precisely, as the resistance to shear (tangential) deformation of fluid particles. The magnitude of the viscosity of oil is influenced by various factors including temperature, chemical composition, pressure, gas content in oil, etc. Due to a large number of influencing factors, viscosity of oil varies widely. Heavy oils usually have high viscosity, and as the temperature rises the oil becomes less viscous. [6]

The viscosity and rheological properties of crude oil are determined by a viscometer. It measures oil shear stress at different shear sizes, as well as the shear limit stress. Haak and Faan

viscometers are standard viscometers in the oil industry. The viscosity of oil can also be determined using empirical correlations, given graphically or analytically.

3 Results and discussion

3.1 Paraffin inhibitors

Paraffin inhibitors modify paraffin wax crystals and crystal growth. The interaction of wax crystals, which form the paraffin network and agglomerated waxes, is reduced and the formation of paraffin precipitate is under control. Inhibitors are used to prevent or reduce the deposition of paraffin on the walls of oil pipes or vessels.

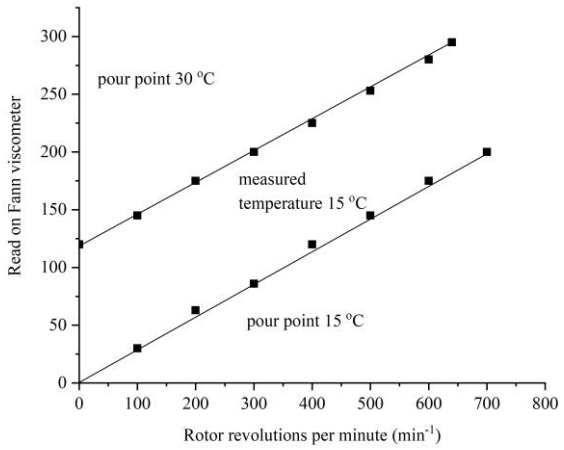


Figure 2: FANN viscometer measurement data

Crude oil has a pour point of 30 °C, and crude oil with a Sepaflux ES-3187 inhibitor from BASF has a pour point of 15 °C. The percentage reduction in the mass of the deposits is equal to the difference in the mass of the deposits between the sample of oil without inhibitor and the sample of oil treated with inhibitor, divided by the mass of deposits of the sample of oil without inhibitor. Figure 2. presents the measurement data on oil samples treated with the subject inhibitor.

In a study conducted in a laboratory, the efficacy of tested pour point depressants, flow enhancers, paraffin inhibitors, and paraffin removers was demonstrated.

These laboratory tests can also include tests for various combinations of additives with the goal to find the optimal solution. The concentration of added additives, their price and application effects are the basis for determining the optimal techno-economic additive for a specific type of oil.

3.2 Application of modifiers of rheological properties

The application of modifiers of rheological properties as a possible solution to solve the problem of flow of high-paraffin oils, is advantageous compared to other methods. Its application in the oil well solves the problem of flow in the tubing, well lines, process vessels and oil pipeline. Other methods have limited application and shortcomings.

Working with modifiers always requires adequate preparation for application. This includes the process of dissolving in water or a solvent and obtaining a certain concentration of the solution that is used for dosing. Dosing into the oil well can be performed with a pump, where a certain amount of solution is continuously injected into the annular space. Dosage can also be discontinuous, where the dosing is applied in certain time intervals. In this case, there is a certain specified amount of solution injected into the annular space.

The prepared solution can also be injected directly into the layer in a certain amount. The return of the injected solution from the layer is conducted very slowly, and this has a dosing effect. The efficacy of the additive varies and it depends on the conditions the additive is dosed as well as other

factors. One portion of 1-2 m^3 of injected solution solves the problem of inflow from the oil well to the collection station for a period of two to six months.

When searching for an adequate modifier of rheological properties, in order to define the parameters and parameters of operation of the pipeline, it is necessary to conduct tests on the model of the pipeline. This is presented on Figure 3.

This model consists of a vessel in which a sample of oil is placed. The vessel is located inside the tempered bathroom through which the oil is cooled. The oil sample is transferred from this vessel to the pipeline model using nitrogen pressure. The pipeline model is also immersed in a tempered bathroom. After filling the pipeline, the system is further subjected to cooling according to the established cooling program.

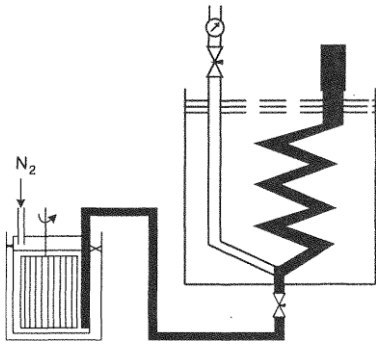


Figure 3: Pipeline model

4 Conclusion

Paraffin, as well as other impurities, are an undesirable occurrence during the exploitation of hydrocarbon deposits, and during their transport. Therefore, it is extremely important to recognize, repair or at least mitigate the negative effects in a timely and effective manner. Paraffin can cause large losses due to reduced well supply, difficult transport, etc. This problem requires significant investment in preventing their occurrence due to the need to adapt to oil well conditions by changing the chemical properties of the fluid or ultimately additives must be used to remove it, such as modifiers of rheological properties (which are described in the previous text). When deciding how to deal with these problems and issues, it is necessary to make a detailed analysis of the situation on site, and choose the best option according to the economic analysis of profitability with the fastest return on investment (ROI). The application of modifiers of rheological properties as a possible way to solve the problem of high-paraffin oil flow is advantageous compared to other methods. Its application in the oil well solves the problem of flow in the tubing, well lines, process vessels and oil pipeline.

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