

New Method to Determine the Strength of Wax Deposits in Field Pipelines

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Abstract

Mechanical pigs are generally used to remove the wax deposit in oil pipelines. A better understanding of the deposit strength is beneficial to make a suitable pigging schedule, preventing the pig from blocking. The previous studies mainly examined the effect of the operating conditions on the thickness and wax content of wax deposit. However, there was little work on the deposit strength, especially the field-deposit strength. This study focuses on a new method to determine the strength of wax deposit in field pipeline. First, the structure of wax deposit obtained from field pipelines and wax deposit formed in laboratory was observed. The results showed that the structure of the field wax deposits is much looser than that of wax deposit formed in lab. The looser structure could result in lower strength. Second, according to analyze, three basic factors contributing to the deposit strength are solid wax content, deposit structure and morphology of wax crystals. Based on above analyzation, a method by preparing model wax-oil gels in the lab instead of field deposit was proposed to measure the field deposit strength indirectly. The model gels were prepared by using the oil obtained from pipeline and a wax. As the structure of field deposit is looser than that of the model gels, a wax was chose to form the smaller size of wax crystals in model gels than that of wax crystals in field deposit for approximately the same strength between field deposit and model gels at the same solid wax content. The strength was measured by using the vane, and the solid wax content was determined by using differential scanning calorimetry (DSC). Third, the accuracy of new method was evaluated. Verification experiments showed that the new method is an effective method for determining the strength of field deposit.

Key words: New method; Wax deposit; Strength; Field pipeline

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INTRODUCTION

Crude oil is a complex mixture containing waxes, aromatics, resins, asphaltenes, and so forth. Waxes, which are the compounds of n-paraffins $(C_{17}-C_{55})$, may cause flow assurance problem during the transportation because of their tendency to deposit on the cold wall of the pipelines. The Fogler group outlined a five step process for wax deposition as below^[1]: (a) formation of an incipient gel layer on the cold surface; (b) convection of n-paraffin molecules with carbon numbers greater than the critical carbon number (CCN) into the gel layer from the bulk fluid; (c) precipitation of the n-paraffin molecules at the interface, increasing the gel layer thickness; (d) penetration of n-paraffin molecules through the liquid phase of the gel matrix and precipitation of the diffused n-paraffin molecules inside the deposit; (e) counter-diffusion of light hydrocarbon components with a carbon number lower than the critical carbon number out of the gel laver.

Wax deposition results in reduction of the flow line section or even blockage of a pipeline. Pigs are commonly used to remove wax deposits^[2]. However, if the wax deposits become too hard, pigs will be unable to break the deposits and will get stuck in pipeline.

The pressure difference before and after the pig makes the pig move along the pipelines. Part of the pressure difference, named Δp_1 , is used to remove the wax deposit. The Δp_1 depends on the deposit thickness (δ) and deposit strength (τ), which could be characterized by the yield stress. Using the finite element method, the previous paper has developed the relationship between Δp_1 and δ and τ , as shown in Equation 1^[3]. However, there was not reported how to determine the deposit strength τ .

$$\Delta p_1 = \frac{\tau}{3.11} \left(\frac{\delta}{D}\right)^{0.5}.$$
 (1)

The deposit strength is associated with several factors such as oil composition, flow rate, oil temperature, and deposition time. The previous studies have widely studied the effect of the operating conditions on the thickness and wax content of wax deposit by using the flow loop or cold finger under laborary conditions^[1,4-11]. It is observed that the smaller difference between oil temperature and surface temperature of cold finger or flow loop^[1,4-7], higher flow rate^[1,4-5,8-11]</sup> and more time for deposition^{<math>[1,5,10]}</sup> result</sup></sup> in higher wax content and therefore the harder waxdeposits. In fact, the deposit strength is dominated by the solid wax content (concentration of precipitated wax) rather than the wax content (total concentration of the dissolved and precipitated wax). Another our published paper has established the relationship between the solid wax content and wax content^[12]. Besides the solid wax content, the deposit strength also depends on the structure of wax deposit and the morphology of wax crystals in wax deposits. However, there was little work on quantitatively determination of deposit strength, especially the strength of deposit in field pipelines.

The objective of this study was to propose a method for determining the strength of wax deposit in field pipelines. The structure of wax deposit formed in flow loop and cold finger was compared with the structure of deposit obtained from the filed pipeline in order to evaluate if the flow loop or cold finger can be properly used to predict the field deposit strength. Based on above results and analyzation of wax deposition process, three basic factors contributing to the deposit strength are identified. Then a method by preparing model wax-oil gels in the lab instead of the field deposit was proposed to measure the field deposit strength indirectly. The accuracy of the new method was evaluated by comparing the field deposit strength with the deposit strength determined by using new method.

1. MATERIALS AND METHODS

1.1 Materials

1.1.1 Wax Deposit

The sample of wax deposit RD was collected from a land and buried pipeline R in single-phase flow. This pipeline is 31 km in long and 515 mm in diameter. The inlet temperature is about 50 $^{\circ}$ C. The thickness of wax deposit is 153 mm at the sampling point. The wax apperence temperature (WAT) and wax content of the deposit sample is 81 $^{\circ}$ C and 42%, respectively. The main procedures of collecting wax deposit were as follows: Plugging the pipelines at the two ends of pipe section that will be cut off; pumping off the crude oil in separated pipe section; cutting off the pipe at the two ends; cutting the wax deposits like "cut cake" with a knife. Due to the field limitation, wax deposit had to be transferred from field to the lab for experiment. In another our published paper, it has demonstrated that deposit properties might not be altered by the temperature changes during the transferring and characterizing them under a probably different temperature conditions from that in the field^[12]. Therefore, the conclusion observed in the lab could represent what happened in the field.

1.1.2 Crude Oil

Crude oil RO was obtained from the inlet of the pipeline R. The desity, WAT and wax content are 857.5 kg/m³, 46 °C and 19.8%, respectively. The solubility curve of wax in crude oil is shown in Figure 1.



Solubility Curve of Wax in Oil 1.1.3 Wax

The wax W was used to prepare model oils. The melting point of this wax is 70-72 °C. The carbon number distribution was measured using the high-temperature gas chromatography (HTGC), as shown in Figure 2.



Figure 2 Carbon Number Distribution of Wax W

1.2 Methods

1.2.1 Yield Stress Measurements

The vield stress was measured by using a stress-controlled rheometer equipped with the vane geometry, which has been widely used to determine the yield stress^[13]. The deposit obtained from pipeline was first kept at 25 °C. The vane was then inserted into the deposit samples, and the shear stress was applied. The results of the yield stress measurements were reproducible within 13 %. One could refer to another our published paper for detail information about determining the yield stress^[12].

1.2.2 DSC

The DSC technique is commonly used to quantify the WAT and the precipitated wax concentration^[14-18]. In this study, tests were performed from 100 °C to -20 °C at a rate of 5 °C/min. The calorimetric signal recorded by the computer was used to determine the WAT and the precipitated wax concentration. The accuracy of WAT measurements and precipitated-wax-concentration measurements was calculated to be within 2 °C and within 5%, respectively.

1.2.3 Optical Microscopy

A polarizing microscope was used to observe the morphology of wax crystals. The observation proceeded as follows. First, the thermal stage of the microscope was preheated to 25 °C. Second, the specimen was spread by a cell scraper onto a preheated glass slide. Third, wax crystals were photographed with a digital charge-coupled device (CCD) color camera. Thirty images were obtained for a specimen to ensure reliability of the observation results. All images were processed and analyzed with the software Image J to extract the parameters of wax crystals.

2. RESULTS AND DISCUSSIONS

2.1 Stucture Comparation Between Field Deposit and Deposit Formed in Labortary

Wax deposition in single phase flow has been studied for several decades. The apparatus used are flowloop or cold finger. By changing one of the operating conditions such as oil temperature, wall surface temperature, and flow rate, the effect of a factor on the deposition was examined. In the laboraty, the temperature difference between oil and wall surface is generally high to reduce the experimental time and form the deposit quickly. However, the wax deposition in filed pipeline is a slow process due to the small temperature difference. Therfore, the properties of wax deposit formed under laboraty conditions may not consistent with that of wax deposit in field pipeline because of the distinction of operating condiction. Figure 3 shows an example of the nature difference of wax deposits under field conditions and under laboraty conditions. As can be seen, the structure of deposit in field pipeline is looser than that of deposit in both cold finger and flowloop.





(c)

Figure 3 Structure Comparison of Wax Deposits Formed: (a) in Cold Finger, (b) in Flowloop, and (c) in Field Pipeline

Another our paper studied the effect of the structure on the yield stress, and some experiment datas are listed in Table 1. It is found that the yield stresses of heated deposits with dense structure are about twice than that of original deposits with loose structure. Therefore, the yield stress of wax deposit in cold finger or flowloop may be great different with that of wax deposit in field pipeline due to the different structure.

Table 1		
Comparison of Yield Stresses	Between	Original
Comparison of Yield Stresses Deposits and Heated Deposits ^[12]		0

Duon ontion	Samples		
Properties	WD1	WD2	RD3
Original deposits (kPa)	23.99	34.51	59.81
Heated deposits (kPa)	45.51	64.20	130.0

2.2 New Method of Determining the Field Deposit Strength

2.2.1 Analysis of Possible Method

The quantitative determination of the strength of wax deposit in pipeline is crucial to make an effective pigging program. The flow loop and cold finger are the primary devices for studying the wax deposition. However, these equipments may be unsuited to indirectly determine the strength of wax deposits in field pipelines. The reasons are summarized as follows:

(a) It takes a long time to form thick deposit for measuring its strength under similar conditions with field pipelines;

(b) The oil temperature may vary along the axial direction of a pipeline, and conducting all experiments under different temperature is an arduous task;

(c) As is discussed above, the structure of wax deposit in laboraty devices and in field pipelines is great different, resulting in the different strength.

Another possible method may be the direct measurement of the strength of wax deposits at different axial positions of a pipeline. However, this is unpractical because it is impossible to cut the field pipeline into several sections and then collect the deposits for experiment.

Therefore, using the flowloop, cold finger, and direct measuring method are unsuitable to determine the strength of wax deposit in field pipeline. It is necessary to seek a feasible method. According to wax deposition mechanism, wax deposit does not consist solely of solid wax particles, but is actually a wax-oil gel consisting of liquid oil that is entrapped by the solid wax particle network. Hence, using the model oil gels instead of wax deposits may be the most effective approach to evaluate the deposit hardness quantitatively. However, there is difference (such as structure) between the wax deposits and wax-oil gels prepared in the lab. How to prepare a model oil gel becomes the key of this approach.

2.2.2 Proposing the New Method

According to analyze, three basic factors contributing to the deposit strength are solid wax content (or precipitated wax content), deposit structure and morphology of wax crystals. And the factor of oil temperature, flow rate, deposition time and so on influences the basic factor essentially and thus affects the deposit strength. When preparing the model oil gels, three basic factors should be mainly considered.

The structure of the model gels is denser than that of wax deposit. Figure 4 shows an example of structure of wax deposit and model gels. The denser structure is expected to result in lager yield stress. Previous studies reported that the size of wax crystals depends on the carbon number distribution of wax, and the smaller size of wax crystals could result in smaller yield stress^[19]. Based on these results, approximately equal strength between field deposit and model gels at the same solid wax content may be achieved by chosing a wax to form the smaller size of wax crystals in model gels than that of wax crystals in field deposit.





It is indicted that the carbon number distribution of the wax in deposit are mainly in the range from C_{17} to C_{35} . The size of wax deposit in field pipelines is in the range of 9.1-14.3 μ m^{2[12]}. Higher cabon number wax tends to form smaller wax crystals^[19]. Therefore, a wax W with more fraction of carbon number greter than C_{35} was

chose to prepare the model gels with smaller size of wax crystals. One can refer to Figure 2 for the carbom number distribution of wax W.

The procedures of model-gel preparation are summarized as follows: The different amount of wax W was respectively added into crude oil obtained from pipeline; the specimen was heated to 80 °C and kept isothermally for 2 hours to completely dissolve the wax into the crude oil; then the sample was cooled quiescently to 25 °C and kept at this temperature for 2 hours. The yield stresses of model gels at 25 °C were measured by using the vane method. The solid wax content of model gels at 25 °C can be determined by using the DSC. Finally, the correlation between the yield stress of model gels and solid wax content can be obtained. In other words, the relationship between the yield stress of wax deposit and solid wax content will be estabilished indirectly by above method.

The correlation (Equation 2) between the solid wax content ϕ_s and wax content ϕ and deposit temperature *T* has been established^[12]. The wax content and deposit temperature along the pipeline can be predicted by using the wax deposition model^[20]. Therefore, the solid wax content of wax deposit can be predicted along the pipeline, and then the yield stress of wax deposit can be calculated by substituting the solid wax content into the correlation between yield stress and solid wax content.

$$\phi_s = (-4.086 \times 10^{-3}T + 0.965 \ 8)\phi. \tag{2}$$

2.3 Evaluation of New Method

Applying the above proposed method, the model gels consisting of crude oil RO and wax W were prepaped to determine the yield stress of wax deposit in a pipeline indirectly. The morphology of wax crystals in both model gels and wax deposit RD from a pipeline is listed in Table 2. As is expected, the size of wax crystals in model gels is smaller than that of wax deposit RD. The smaller crystals, resulting in smaller yield stress, could offset the denser structure which is benefit for the larger value of yield stress. Hence, the approximately equal strength between field deposit and model gels at the same solid wax content can be achieved.

 Table 2

 Properties of Wax Deposit and Model Gels

Samples	Solid wax content at 25 °C (wt.%)	Size (µm ²)
Wax deposit RD	33.0	13.8
RO+30%W	33.2	5.3

The yield stresses of wax depoit RD and model gels were also measured to evaluate the accuracy of poposed method. Figure 5 shows the comparision of yield stress between wax deposit RD and model gels. It is indicated that the deposit strength determined by the proposed method is higher than that of the field deposit at the same solid wax content, and the relative deviation is 34%. When considering the average relative deviation of strength measurement with 13% and solid wax content with 5%, this relative deviation of 34% may be acceptable. However, due to the limitation of the samples of wax deposit, only one wax deposit is used to evaluate this new method. And it should be further evaluated or perfected in the future.



Figure 5 Comparison of Yield Stress Between Wax Deposit in a Field Pipeline and Model Gels Formed by New Method

CONCLUSION

The properties of wax deposit are assotiated with the formation process. The flowloop and cold finger are common apparatus used for studying wax deposition. However, it is indicated that the structure of wax deposit in field pipeline is looser than that of wax deposit in both flowloop and cold finger. And their strength may be also great different.

The quantitative determination of the deposit strength is crucial to make an effective pigging program. According to analyze and base on our previous study, a new method by preparing the model gel in the lab instead of field deposit was proposed to determine the field deposit strength indirectly. The model gel is composed of the crude oil from the pipeline and a wax W.

The yield stresses of model gel and a sample of wax deposit obtained from field pipeline were compared to evaluate the accuracy of the new method. The results showed that the new method is an effective method for determining the strength of field deposit. However, due to the limitation of the sample of wax deposit, only one wax deposit is used to evaluate this new method. In the future, it should be further evaluated or perfected.

REFERENCES

- Venkatesan, R. (2004). *The deposition and rheology of organic gel* (Doctoral dissertation). University of Michigan, Ann Arbor, Michigan.
- [2] Wang, Q., Sarica, C., & Volk, M. (2008). An experimental study on wax removal in pipes with oil flow. J. Energy Resour. Technol., 130, 0430011-0430015.
- [3] Mendes, P. R. S., Braga, A. M. B., & Azevedo, L. F. A. (1999). Resistive force of wax deposits during pigging operations. *Journal of Energy Resources Technology*, *121*(3), 167-171.

- [4] Creek, J. L., Lund, H. J., & Brill, J. P. (1999). Wax deposition in single phase flow. *Fluid Phase Equilibria*, 158-160, 801-811.
- [5] Singh, P., Venkatesan, R., & Fogler, H. S. (2000). Formation and aging of incipient thin film wax-oil gels. *AIChE Journal*, 46(5), 1059-1074.
- [6] Jennings, D. W., & Weispfennig, K. (2005). Effects of shear and temperature on wax deposition: Coldfinger investigation with a gulf of Mexico crude oil. *Energy & Fuels*, 19(4), 1376-1386.
- [7] Banki, R., Hoteit, H., & Firoozabadi, A. (2008). Mathematical formulation and numerical modeling of wax deposition in pipelines from enthalpy-porosity approach and irreversible thermodynamics. *International Journal of Heat* and Mass Transfer, 51(13-14), 3387-3398.
- [8] Singh, P., Venkatesan, R., & Fogler, H. S. (2001). Morphological evolution of thick wax deposits during aging. *AIChE Journal*, 47(1), 6-18.
- [9] Hernandez, O. C. (2002). Investigation of single-phase paraffin deposition characteristics (Master dissertation). University of Tulsa, Tulsa, Oklahoma.
- [10]Tiwary, R., & Mehrotra, A. K. (2009). Deposition from wax-solvent mixtures under turbulent flow: Effects of shear rate and time on deposit properties. *Energy & Fuels*, 23(3), 1299-1310.
- [11]Brown, T. S., Nielsen, V. G., & Erickson, D. D. (1995). Measurement and prediction of the kinetics of paraffin deposition. *Journal of Petroleum Technology*, 47(4), 328-329.

- [12]Bai, C., & Zhang, J. (2013). Thermal, macroscopic and microscopic characteristics of wax deposits in field pipelines. *Energy & Fuels*, 27(2), 752-759.
- [13]Liddel, P. V., & Boger, D. V. (1996). Yield stress measurements with the vane. J. Non-Newtonian Fluid Mech., 63, 235-261.
- [14] Léoffé, J. M., Claudy, P., & Kok, M.V. (1995). Crude oils: Characterization of waxes precipitated on cooling by d.s.c. and thermomicroscopy. *Fuel*, 74, 810-817.
- [15]Li, H., Huang, Q., & Zhang, F. (2003). Determination of wax content in crude oil using differential scanning calorimetry. *Shiyou Daxue Xuebao*, 27, 60-62.
- [16]Yi, S., & Zhang, J. (2011). Relationship between waxy crude oil composition and change in the morphology and structure of wax crystals induced by pour-point-depressant beneficiation. *Energy Fuels*, 25, 1686-1696.
- [17]Li, H., & Zhang, J. (2003). A generalized model for predicting non-Newtonian viscosity of waxy crudes as a function of temperature and precipitated wax. *Fuel*, 82, 1387-1397.
- [18]Juyal, P., Cao, T., & Yen, A. (2011). Study of live oil wax precipitation with high-pressure micro-differential scanning calorimetry. *Energy Fuels*, 25, 568-572.
- [19]Bai, C., & Zhang, J. (2013). Effect of carbon number distribution of wax on the yield stress of waxy oil gels. *Ind. Eng. Chem. Res.*, 52(7), 2732-2739.
- [20]Lee, H. S. (2008). Computational and rheological study of wax deposition and gelation in subsea pipelines (Doctoral dissertation). University of Michigan, Ann Arbor, Michigan.