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Physical properties of wax deposits on the walls of crude pipelines

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Abstract: Wax deposits on the wall of a crude oil pipeline are a solid wax network of fine crystals, filled with oil, resin, asphaltene and other impurities. In this paper, a series of experiments on wax deposition in a laboratory flow loop were performed under different conditions (flow rate, temperature differential between crude oil and pipeline wall, and dissolved wax concentration gradient), and the wax deposits were analyzed, so quantitative relationships among wax content, wax appearance temperature (WAT), shear stress, and radial concentration gradient of dissolved wax at the solid/liquid interface were obtained. Finally, a model was established to predict WAT and the wax content of the deposit.

Key words: Crude oil, wax deposits, pipeline, wax content, wax appearance temperature (WAT)

1 Introduction

During wax deposition in crude oil pipelines, oil can be trapped in the deposit. The trapped oil is quantified by the oil content of the deposit. Burger et al (1981) concluded that a sloughing mechanism was a possible explanation for the reduction in deposition. Hsu et al (1994) revealed that flow turbulence or shear dispersion effects suppressed wax deposition significantly due to sloughing. Agarwal et al (1990) deduced that turbulence was the main factor for the decrease in deposition with increasing flow rate, while diffusion was responsible for the increase in deposition with increasing flow rate in the laminar region. Matzain (1996) and Lund (1998) confirmed that wax thickness was greater in laminar flow than in turbulent flow, and decreased with increasing Reynolds number in turbulent flow. Hamouda and Ravnϕy (1992) revealed by experiments at a fixed pipe wall temperature that the higher the oil temperature, the higher the content of long-chain paraffins in the deposit. Brown et al (1993) proposed that the wax deposits formed at a high-speed shear rate on the wall were much harder than that formed at a low-speed shear rate. Creek et al (1999) reported that when the flow regime and the shear rates on the pipe wall were kept unchanged, the wax deposits formed at higher temperature gradients were softer than those formed at lower temperature gradients. Singh et al (2000) investigated the carbon distribution in wax deposits formed under different experimental conditions, and confirmed that the wax content of deposits was qualitatively related to thermal and hydraulic conditions. By considering the effect of duration factors on the wax content of the deposit, this paper further states that the wax content of the deposit increased with shear rate, wall temperature (at a fixed oil temperature) and oil temperature (at a fixed wall temperature).

In this study, laboratory flow loop experiments are performed to acquire data on the wax content, wax appearance temperature (WAT) under different thermal conditions (oil temperature, wall temperature, difference in temperature between oil and pipe wall), and hydraulic conditions (shear rate or shear stress on pipe wall). Furthermore, a model is established to predict the wax content of the deposit, WAT, shear stress, and concentration gradient of wax molecules on the wall.

2 Experimental

The oil samples studied were taken from Luliang crude oil, Xinjiang Oilfield, China. A series of wax deposition experiments were performed in a laboratory flow loop to investigate the WAT and wax content of the deposit formed under different conditions. The samples of the deposits from each test section were collected and analyzed at the end of each test to determine the wax content and the wax appearance temperature of the deposit. Table 1 shows the properties of Luliang crude oil.

Table 1 Properties of Luliang crude oil

Gelling point ºC	Density at 20 ºC g/cm^3	WAT ºC	Wax content %
18	0.852	29	9.26

2.1 Experimental apparatus

A laboratory flow loop was designed and installed to measure the deposition of wax, as shown schematically in Fig. 1. The flow loop has four characteristics: 1) Wax deposits

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can be formed under flowing conditions. 2) Experimental data are collected and recorded automatically by computer. 3) The wax thickness can be calculated from pressure drop data between the reference section and the test section, while the flow of crude oil in pipelines is monitored by pressure drop in the reference section. 4) The test section in the flow loop is removable (demountable), which makes it easy to measure the physical properties of wax deposits.

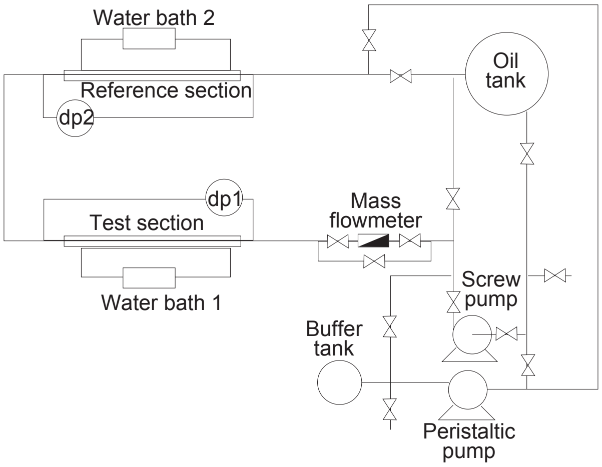

Fig. 1 Schematic diagram of the flow loop system used to measure wax deposition

2.2 Determination of wax content and wax appearance temperature of the deposit

Several thermodynamic models have been proposed to describe wax precipitation. Computational tools based on regular-solution theory of mixtures as well as on equations of state have been proposed to model wax precipitation (Won, 1989; Hansen et al, 1988). Lira-Galeana et al (1996) assumed that precipitated wax consisted of several solid phases, and each solid phase was described as a pure component or pseudo-component that did not mix with other solid phases. Liquid-phase properties were obtained from an equation of state. Coutinho et al (1995, 1999) proposed two new solid phase models. These new models allowed the calculation of multiphase equilibria, overcoming one of the main limitations of the Wilson equation. It was shown that the limits of solubility predicted by these models were in agreement with those presented by other authors.

A differential scanning calorimeter (TA2000/MDSC2910) was used to measure the WAT and wax content of the deposit. Air, without phase change and with a small enthalpy, was chosen as the reference sample. In the programmed cooling range, the temperature of the test sample tended to be higher than the reference sample because of the release of latent heat during wax crystallization. In this process, the temperature difference ΔT turned from zero to non-zero, and then less heat influx would be needed than the reference to maintain both at the same temperature. Thermal spectra, which are curves of heat influx versus temperature, were collected. In the thermal spectra, the heat flux curve of the test sample deviated from the reference baseline to form a heat peak, due to the release of latent heat during phase change. Both the heat released due to phase change and the temperature difference dropped until the two curves coincides when the wax crystallization was finished. The temperature, at which the curve deviated from the baseline, was the wax appearance temperature, and the curve peak was taken as the wax peak temperature. The curve could be used to calculate the average latent heat of wax crystallization by integrating the peak corresponding to the phase change. The wax content of the sample could be obtained with the average heat of wax crystallization.

3 Experimental results and discussion

3.1 Influence of shear stress on physical properties of wax deposit

High flow rate means a high shear stress on the pipe wall when the oil and wall temperatures remain unchanged in the experiments. Therefore, the influence of wall shear stress on wax content and WAT of the deposit can be studied by changing the oil flow rate. Fig. 2 shows the wax content of the deposit formed on the wall at different shear stresses. Fig. 3 shows the WAT of the deposit formed on the wall at different shear stresses.

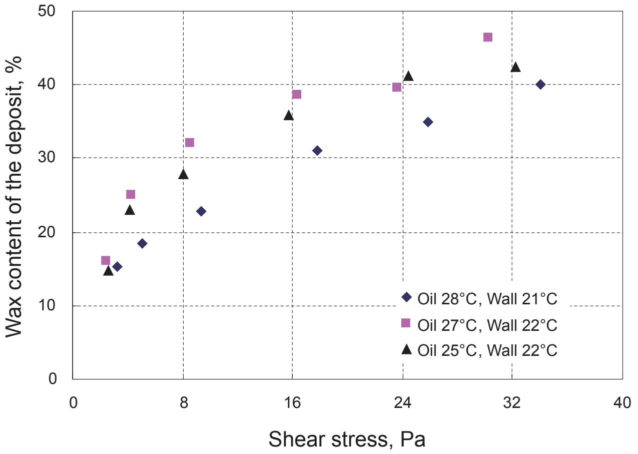

Fig. 2 Wax content of the deposit formed at different shear stresses

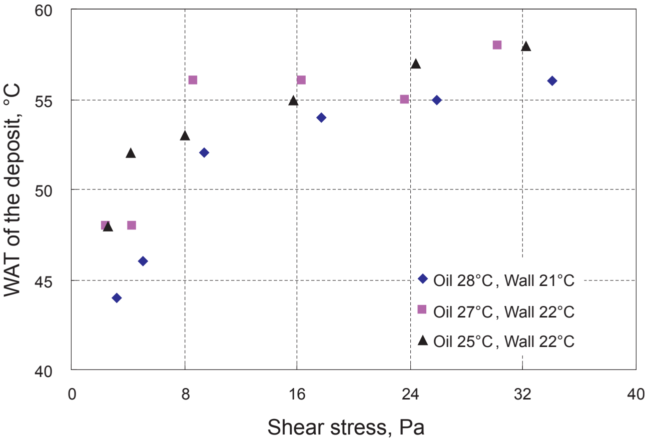

Fig. 3 WAT of the deposit formed at different shear stresses

Fig. 2 indicates that the wax content of the deposit increases with increasing shear stress on the wall at different oil and wall temperatures. Fig. 3 indicates that the WAT of the deposit formed on the wall also increases with shear stress under the same experimental conditions.

3.2 Influence of radial temperature gradient on physical properties of wax deposit

Creek et al (1999) proposed that when the flow regime and wall shear stress remained unchanged in the experiments, the wax content of the deposit was very low at relatively high temperature gradients. However, the radial temperature gradient will lead to a dissolved wax concentration gradient between the bulk oil and pipe wall, and this dissolved material will be transported toward the wall by molecular diffusion. Creek et al neglected the influence of the dissolved wax concentration gradient on the wax content of the deposit, so he did not really understand the influence of temperature gradient on wax content. In our experiments we took special measures to eliminate the influences of shear stress and concentration gradient of dissolved wax at the solid/liquid interface. To minimize the influence of wall shear stress on physical properties of the deposit, the oil temperature was specified at 22-27 ºC, at which oil viscosity changed slightly; and the wall temperature was fixed at 22 ºC, indicating a stable gradient of the concentration of dissolved wax, to eliminate the influence of concentration gradient of dissolved wax at the solid/liquid interface. When wall temperature and oil flow rate were kept unchanged, the temperature gradient on the wall increased with the temperature difference between oil and pipe wall. Figs. 4 and 5 show the wax content and WAT of the deposit formed at different temperature gradients on the wall.

Figs. 4 and 5 show that temperature gradient on the wall had no effect on the wax content and WAT of the deposit when the shear stress and radial concentration gradient of dissolved wax at the solid/liquid interface remained unchanged.

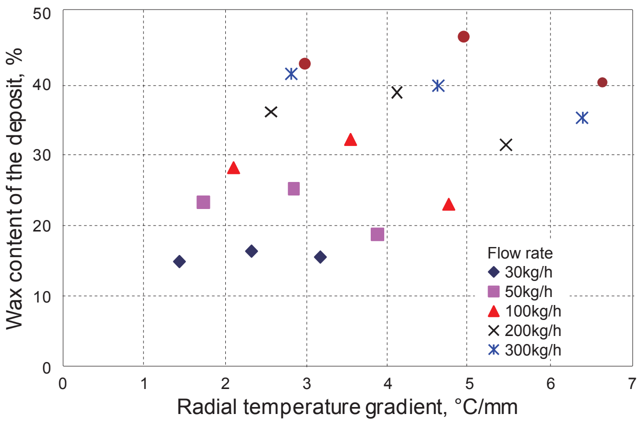

Fig. 4 Wax content of the deposit formed at different radial temperature gradients on the wall

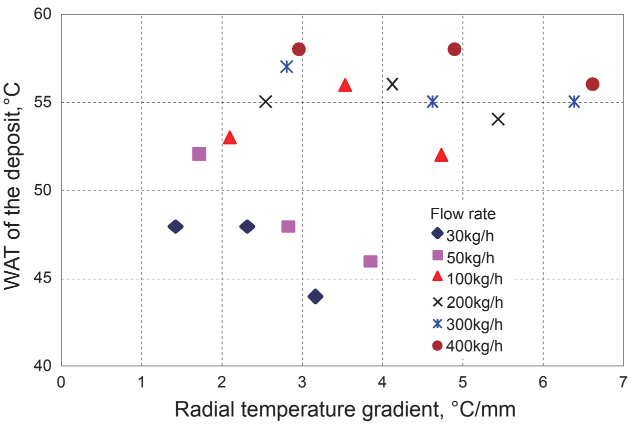

Fig. 5 WAT of the deposit formed at different radial temperature gradients on the wall

3.3 Influence of dissolved wax concentration gradient on physical properties of wax deposit

To investigate the effect of the dissolved wax concentration gradient on the physical properties of wax deposit, the flow rate and the temperature difference between oil and pipe wall were kept unchanged, but the oil and wall temperatures were changed simultaneously to obtain a specified temperature difference. The mass flow rate was 100 kg/h. Table 2 lists the oil and wall temperatures adopted in experiments. The shear stress and temperature gradient on the wall underwent only a slight change under these conditions. Therefore, the change in the physical properties of the deposit was mostly due to the concentration gradient of dissolved wax at the solid/liquid interface. Figs. 6 and 7 show the wax content and WAT of the deposit formed at different dissolved wax concentration gradient.

Table 2 Oil and wall temperatures adopted in experiments

Wall temperature, ºC	20	22	24	26
Oil temperature, ºC	23	25	27	29

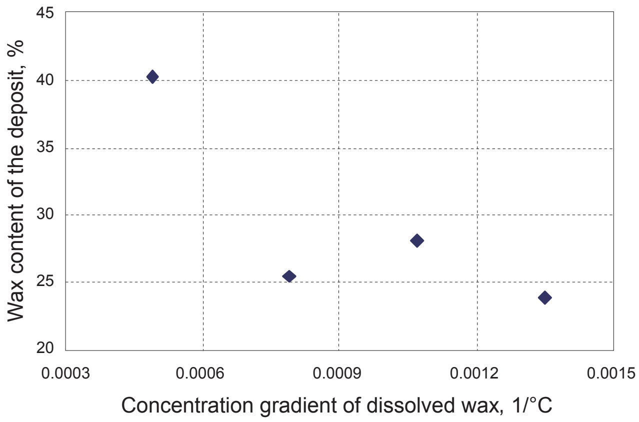

Fig. 6 Wax content of the deposit formed at different concentration gradients of dissolved wax

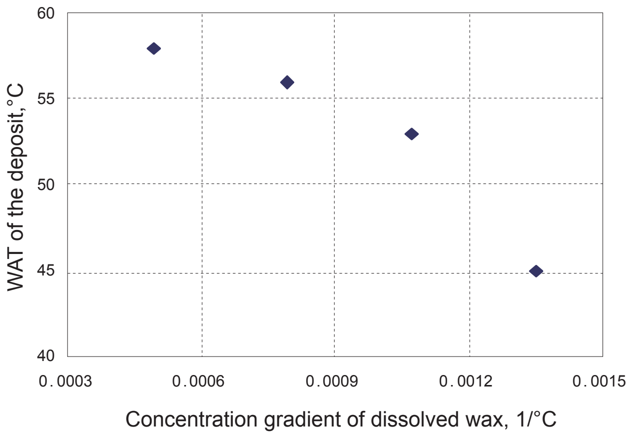

Fig. 7 WAT of the deposit formed at different concentration gradients of dissolved wax

Figs. 6 and 7 indicate that a higher concentration gradient of dissolved wax at the solid/liquid interface might produce a lower wax content of deposit as well as a lower WAT of the deposit under the conditions of a specified temperature difference and oil flow rate

4 Prediction model for wax content and WAT of the deposit

Laboratory results (Figs. 2-7 and Table 3) showed that for Luliang crude oil, the shear stress and concentration gradient of dissolved wax at the solid/liquid interface were the major factors influencing the wax content and WAT of the deposit. Both the wax content and WAT of the deposit increased with increasing shear stress, but decreased with increasing concentration gradient of dissolved wax at the solid/liquid interface. For other crude oil samples, the effect of the shear stress and dissolved wax concentration gradient on the physical properties of wax deposit could be studied with the same method. For Luliang crude oil, a model for predicting the wax content and WAT of the deposit can be written as follows:

$$\varphi_{\text{total}} = k\tau_{\text{w}}^{m}\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)^{n} \tag{1}$$

$$T_{\text{WAT}} = k'\tau_{\text{w}}^{m'}\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)^{n'} \tag{2}$$

where φ_{total} is the total wax content of the deposit, %; T_{WAT} is the wax appearance temperature of the deposit, ºC; τ_{w} is the shear stress on the pipeline wall, Pa; $\frac{\mathrm{d}C}{\mathrm{d}T}$ is the dissolved wax concentration gradient between bulk oil and pipeline wall, i.e., the change of dissolved wax concentration with temperature, 1/ºC, $\frac{\mathrm{d}C}{\mathrm{d}T}$ can be calculated from DSC curve (Huang, 2000); C is the dissolved wax content.

Table 3 Wax content and wax appearance temperature in different experiments

Temperature, ºC		Flow rate kg/h	$\frac{\mathrm{d}C}{\mathrm{d}T}$ 1×10^{-3}/ ºC	τ_{w} Pa	Wax content, %		Relative error %	WAT, ºC		Error ºC
Wall	Oil				Measured	Predicted		Measured	Predicted	
21	28	30	1.09	3.24	17.4	17.8	2.1	43	46.8	3.8
21	28	50	1.09	5.11	18.6	21.2	14.0	45	48.5	3.5
21	28	100	1.09	9.42	25.4	26.7	4.9	52	50.9	-1.1
21	28	200	1.06	17.76	31.0	34.6	24.7	54	54.1	0.1
21	28	300	1.08	25.84	36.7	39.3	7.0	55	55.4	0.4
21	28	400	1.09	34.03	43.6	43.3	-0.7	56	56.5	0.5
22	27	30	0.99	2.43	16.1	17.0	5.7	48	46.9	-1.1
22	27	50	1.00	4.29	25.1	21.0	-16.1	48	49.0	1.0
22	27	100	1.05	8.61	36.6	26.4	-28.0	55	51.1	-4.0
22	27	200	1.00	16.39	37.7	34.8	-7.7	54	54.5	0.5
22	27	300	1.00	23.65	39.6	40.2	1.4	55	56.2	1.2
22	27	400	1.00	30.21	46.4	44.1	-5.0	58	57.3	-0.7
22	25	30	1.09	2.61	17.1	16.4	-3.9	48	46.0	-2.0
22	25	50	1.09	4.21	23.1	19.7	-15.0	53	47.8	-5.2
22	25	100	1.07	8.03	25.6	25.4	-0.7	50	50.5	0.5
22	25	200	1.07	15.77	35.9	32.8	-8.6	55	53.3	-1.7
22	25	300	1.07	24.37	38.0	38.6	1.4	57	55.2	-1.8
22	25	400	1.06	32.23	42.5	43.4	2.1	58	56.7	-1.3
20	23	100	1.35	10.65	23.8	24.1	1.4	45	48.5	3.5
24	27	100	0.79	6.75	32.1	29.3	-8.7	55	54.2	-0.8
26	29	100	0.49	5.79	40.2	38.5	-4.2	58	61.3	3.3

In the above equations, k and k' , m and m' , n and n' stand for constants that are determined by the physical properties of the oil. These constants are independent of the experimental conditions and can be obtained by regression of experimental data.

To improve the precision of the proposed prediction model, and to verify its applicability in a wide range, 21 sets of wax deposition experiments were performed on Luliang oil samples under different conditions. Table 3 shows the measured and predicted wax content and wax appearance temperature under different conditions. Regression results from these data are as follows:

$$\varphi_{\text{total}} = 12.025\tau_{\text{w}}^{0.382}\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)^{-0.686} \tag{3}$$

for wax content of the deposit formed from Luliang crude oil, and

$$T_{\text{WAT}} = 44.367\tau_{\text{w}}^{0.077}\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)^{-0.248} \tag{4}$$

for WAT of the deposit.

Of all the 21 sets of oil samples, the average error of wax content is 7.8%, with a maximum of 28.0%. The average error of WAT is 1.8 ºC, with a maximum of 5.2 ºC.

5 Conclusions

Experimental results and theoretical analysis helped us arrive at the following conclusions about the factors affecting wax content and WAT of the deposit.

1) Wax content and WAT of the deposit increased with increasing shear stress on the wall at different oil and wall temperatures.

2) The radial temperature gradient on the wall had no effect on wax content and WAT of the deposit when shear stress and concentration gradient of dissolved wax at the solid/liquid interface remained unchanged.

3) A higher concentration gradient of dissolved wax at the solid/liquid interface might produce a lower wax content and a lower WAT of the deposit under the conditions of a specified temperature difference and oil flow rate.

4) A model was established to predict the wax content of the deposit. Of all the 21 samples of Luliang crude oil, the average error of wax content was 7.8%, with a maximum of 28.0%. The average error of WAT was 1.8 ºC, with a maximum of 5.2 ºC.

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