Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5574-5578

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18158

Scaling and Wax Deposit Mechanisms of FRP Oil Pipelines†

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AJC-15747

Crude oil occasionally has properties of high wax precipitation temperatures, elevated pour points and high viscosity and this can easily lead to severe wax deposit problems in transport and ultimately result in blockages of the pipeline. There are methods of heating the oil to solve these circumstances. However, the temperature increase aggravates the scale buildup amounts and results in a higher salinity in the water that is produced and low temperatures generate wax precipitation. To deal with these problems, there is a need to study scaling and wax deposit mechanisms of FRP oil pipeline through produced liquids physical property analysis. After experimental analysis, it was discovered that the recommended inlet oil temperature should be 35-40 ºC and in order to reduce the wax and scale buildup amounts, the transportation temperature of XX FRP pipeline is recommended to be 25-30 ºC.

Keywords: Crude oil, FRP, Wax deposit, Scaling, Mechanism.

INTRODUCTION

Waxy crude is a complex mixture of hydrocarbons and non-hydrocarbon compounds, which consist of wax, aromatic hydrocarbons, light hydrocarbons and asphaltene. Under normal temperatures and pressure, crude oil is the coexistence of gases, liquids and solid-phase colloidal suspension systems. The content ratios of the dispersed phase and dispersion medium are related to external factors, such as temperatures and pressures. In the production process and transportation of crude oil, any thermal effect, force effect, electrical effect or any other physical or chemical change may cause deposition of the solid phase and usually results in paraffin and asphaltene deposits.

During transportation of highly waxy crude oil, the temperature difference between the FRP and the external environment causes the oil temperature along the pipeline to gradually drop, which results in wax precipitation. Wax adhering to the pipe walls can decrease the pipe diameter and increase friction and can ultimately affect the safe operation of the pipeline. In order to fix this problem and determine the optimum pigging period, a study on the mechanism of wax deposition needs to be carried out[1-3].

The higher salinity of the water produced during transport causes the temperature to increase, aggravating the scale buildup amounts. A study on the mechanisms of scaling also needs to be done in order to determine an appropriate temperature range in which wax deposition and scaling is unlikely to occur.

EXPERIMENTAL

Physical properties analysis of crude oil and analysis of produced water quality: The physical properties of crude oil have a great impact on the wax build-up and scaling. In the interest of research, collecting sediments in the pipeline (Fig. 1) and analyzing them requires a variety of methods and instruments in order to determine the parameters like the essential components of crude oil, density, DSC (differential scanning calorimetry), viscosity-temperature characteristics *etc*. Tables 1 and 2 listed the determination methods, instruments and results.

Through the produced liquid quality analysis, it was proved that the water type is $NaHCO_3$. Under the transporting conditions of the crude oil at normal temperatures, the XX FRP pipeline could have the potential to develop $CaCO_3$.

Study on wax deposits and scaling mechanisms

Wax deposit mechanisms: The wax residue of the XX pipeline has two main aspects: the thickness of the wax and the wax deposit rate. Actual circumstances of the initial oil

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

TABLE-1
PHYSICAL PROPERTIES OF CRUDE OIL

Physical properties	Experimental methods (or apparatus)	Results	Remarks
Essential component	Wax, colloid and asphaltene content meter	Wax content: 2.76 % Colloid content: 15.62 % Asphaltene content: 0.59 %	SY/T 7550 Determination of wax, resins and asphaltenes in crude oil
Hydrocarbon component analysis	SHIMADZU gas chromatograph	Hexane and heavier hydrocarbon content is higher, about 97.1 %	
Density (10-40 ºC)	The glass float gauge densitometer	0.85-0.87 kg/L	GB/T 1884 Crude petroleum and liquid petroleum products--Laboratory determination of density--Hydrometer method
DSC	Swit Mettler Toledo Company DSC821e	Wax precipitation point is 23ºC and Wax precipitation range is 10-23 ºC.	Accuracy of heat is lower than 0.7 µW and temperature control precision is 0.2 ºC
Viscosity-temperature characteristics	HAAKE MARS III Rotational rheometer	Abnormal point is 21 ºC and wax precipitation point is 23 ºC.	Measurement temperature drops from 60 ºC to 7 ºC with a step of 5 ºC, setting four shear rates at each temperature. (Viscosity-temperature curves are shown in Fig. 2)
Pour point	Pour point measuring instrument	8 ºC	–

TABLE-2
PHYSICAL PROPERTIES OF CRUDE OIL

Test items	Analysis results (mg/L)	Test philosophy
Cl^-	9372.45	$Ag^+ + Cl^- \rightarrow AgCl\downarrow$; $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow$
CO_3^{2-}, HCO_3^-, OH^-	CO_3^{2-}: 116.49, HCO_3^-: 1127.19, pH: 7.96	$OH^- + H^+ \xrightarrow{\text{Phenolphthalein indicator}} H_2O$; $CO_3^{2-} + H^- \xrightarrow{\text{Phenolphthalein indicator}} HCO_3^-$; $HCO_3^- + H^+ \xrightarrow{\text{Methyl orange indicator}} H_2CO_3$
SO_4^{2-}	16.03	$Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$; $Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$; $I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$
Degree of mineralization	16478.58	$Mg + EBT \rightarrow M-EBT$, $M + Y \rightarrow MY$, $M-EBT + Y \rightarrow MY + EBT$
Na^+, K^+	Na^+: 5057.626, K^+: 73.74	Charge conservation of anion and cation

Fig. 1. Sediments in pipeline

delivery systems might be unknown and might use a combination of methods, so the use of a dynamic differential pressure method to calculate the thickness of the wax is appropriate[4-6].

Under stable working conditions, the friction loss between the pipe ends is h_{fi} at i moment and relatively, h_{fi-1} at i_{-1} moment. During crude oil transportation, the length of the pipeline remains unchanged, but the flow rate, friction loss, oil viscosity and density fluctuate over time. The ratio of friction loss at different moments can be calculated by formula (1):

$$\frac{h_{fi}}{h_{fi-1}} = \left(\frac{Q_i}{Q_{i-1}}\right)^{2-m} \left(\frac{v_i}{v_{i-1}}\right)^{m} \left(\frac{D_{i-1}}{D_i}\right)^{5-m} \quad (1)$$

Thus, the average internal diameter of an effective pipe at i moment can be calculated as:

$$D_i = D_{i-1} \times \left(\left(\frac{Q_i}{Q_{i-1}}\right)^{2-m} \left(\frac{v_i}{v_{i-1}}\right)^{m} \frac{h_{fi-1}}{h_{fi}} \right)^{\frac{1}{5-m}} \quad (2)$$

When fluid in the pipeline is Newtonian fluid, formula (3) is adopted to calculate viscosity:

$$\frac{v_1}{v_2} = e^{-u(T_1 - T_2)} \quad (3)$$

where v_1, v_2 = Kinematic viscosity at oil temperature T_1, T_2, respectively; u = Viscosity index.

When the fluid in the pipeline is Newtonian fluid turbulence, the effective average internal diameter of the pipe at i moment can be calculated as:

$$D_i = D_{i-1} \left(\left(\frac{v_i}{v_{i-1}}\right)^{0.25} \left(\frac{Q_i}{Q_{i-1}}\right)^{1.75} \frac{h_{fi-1}}{h_{fi}} \right)^{\frac{1}{4.75}}$$

$$= D_{i-1} \left((e^{-0.25u(T_i - T_{i-1})} \left(\frac{Q_i}{Q_{i-1}}\right)^{1.75} \frac{h_{fi-1}}{h_{fi}} \right)^{\frac{1}{4.75}} \quad (4)$$

At each moment, the average wax deposit thickness in the pipe is calculated by:

$$\delta = \frac{D_0 - D_i}{2} \quad (5)$$

where D_i = Internal diameter of the pipe before the formation of wax deposits; D_0 = Effective average pipe internal diameter at i moment after the formation of wax deposits.

Scaling mechanism: Through the produced water quality analysis, it was proved that the main component of the scale is $CaCO_3$. The following procedure for the formation of calcium carbonate scale was analyzed separately[7-9].

The scaling of $CaCO_3$ is primarily attributed to variations in temperature, pressure, pH, salinity and other related thermodynamic conditions. These changes result in ionic balance state changes, decreasing the solubility of scale-forming components and forming precipitation. Its reaction equations are as follows:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \quad (6)$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O \quad (7)$$

Both reactions are associated with pH. When the pH value is below 7.5, only a small amount of HCO_3^- is dissociated into CO_3^{2-} and the reaction of the Ca^{2+} combines with the CO_3^{2-} to create lime deposits, which means reaction (7) occurs more commonly. When the pH value is above 7.5, reaction (6) generally occurs. Through water quality analysis, the measured pH value was 7.96 and the main reaction was eqn. 6.

The composition of the samples taken of the scaling was very complex. Besides the organic substances contained in the medium (H_2S, CO_2, ions, bacteria and sand), there are many external factors that can affect the scaling, such as temperature, pressure, flow rate, madefaction and adhesion. After analysis, the influence of temperature on the scaling was the biggest and the rest had small effects on scale formation. So, further analysis about how temperature influences scale buildup needs to be done.

Taking into account the simplicity and science of scale buildup predictions, the Davis-Stiff saturation index method and Ryznar stability index method were applied to predict the XX FRP pipeline produced water scaling trend.

Relations of scale amounts and temperatures: Scale amounts vary with temperature, so chemical experiments were adopted to explore the differences. The scale amounts at different temperatures (25-45 ºC) were recorded. The experimental reagents and materials are shown in Tables 3 and 4.

The viscosity-temperature curves of crude oil in XX pipeline is shown in Fig. 2.

TABLE-3
EXPERIMENTAL REAGENTS

$NaHCO_3$ (g)	NaCl (g)	$CaCl_2$ (g)	$MgCl_2$ (g)	KCl (g)
20	60	10	5	2

The experiment was divided into five steps: (1) The conical flasks were dried and its initial mass was weighed. (2) The filter paper was dried and its initial mass weighed. (3) 200 mL prepared water samples were put into eight conical flasks, then put into a thermostatic water tank for 1, 2, 3, 4, 5, 6, 7 and 8 h, respectively. (4) The conical flasks were removed from the thermostatic water tank and the water inside the flasks was filtered. Then the filter papers were dried and their masses weighed. This mass is the filter papers' final weight. (5) The conical flasks were each dried and their masses weighed. These masses are the conical flasks' final weights. The difference between the initial mass and the final weight is the weight of the scale.

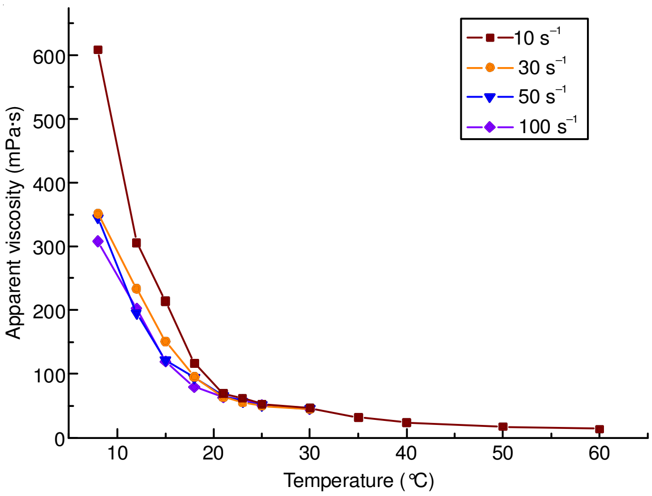

Fig. 2. Viscosity-temperature curves of crude oil in XX pipeline

RESULTS AND DISCUSSION

Wax deposit analysis: The determination of the amount of wax is based on records of the experiments. The pipeline outlet temperature was less than 23 ºC (wax precipitation point temperature) and wax crystals began to precipitate. Referring to the normal temperature delivery parameters of the XX FRP pipeline in October 2013, the dynamic differential pressure method was adopted to calculate the wax deposit amounts for the days of October 6-16 during which the normal transportation temperature was gradually replaced by heated transportation. The effective average inner diameter was back-calculated by friction loss from the initial station to the terminal station. And the overall wax deposit trend within the specified time was also estimated with the friction loss data, so as to predict the wax deposit distribution situation along an actual pipeline, as shown in Fig. 3. Table-5 presents the physical property parameters of crude oil.

Scale analysis: The Davis-Stiff saturation index method and the Ryznar stability index method were used to make predictions of the XX FRP pipeline scaling trend. The predicting outcomes indicated a scaling phenomenon had appeared (Table-6). Severe scaling would occur if the pipeline temperature was greater than 40 ºC and the inlet temperature fluctuation range of the XX FRP pipeline was 20-40 ºC. The scaling trend gradually decreased when the operating temperature decreased.

TABLE-4
EXPERIMENTAL APPARATUS

Conical flask	Graduated cylinder	Filter flask	Filter paper	Funnel	Glass stirring rod	Electronic balance	Thermostatic water tank	Drying oven
8	1	2	60	2	2	1	1	1

TABLE-5
PHYSICAL PROPERTY PARAMETERS OF CRUDE OIL

Pipe inner diameter D_0	0.19 m	Pipe length L	31.7 km
Density under 30 ºC ρ_{30}	0.8673 kg/L	Dynamic viscosity under 23 ºC μ_{23}	56.56 mPa·s
Density under 20 ºC ρ_{20}	0.8731 kg/L	Dynamic viscosity under 21 ºC μ_{21}	65.60 mPa·s

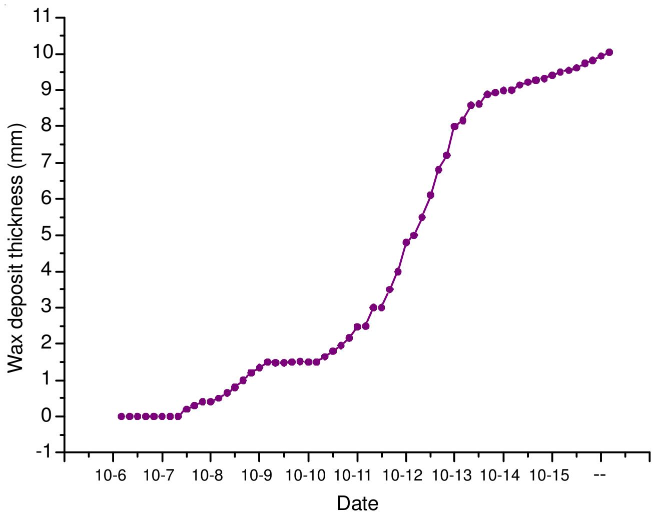

Fig. 3. Average wax deposit thickness in XX pipeline

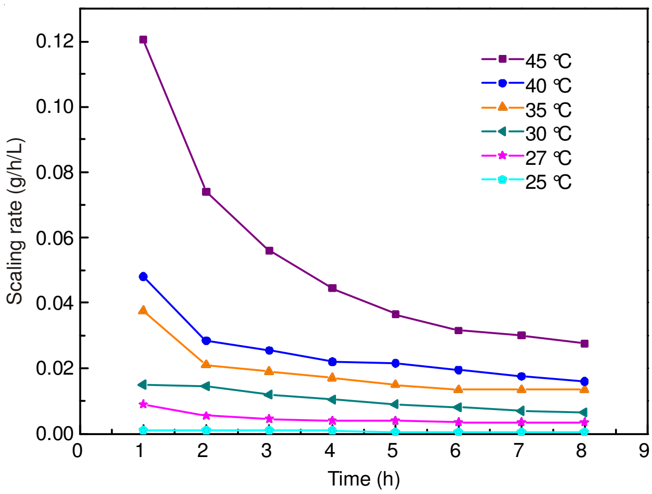

Fig. 5. Relative curves of temperatures and scaling rates

Based on the comparison between predicted results and practical investigation data, it can be deduced that the actual scaling trend coincides with the predictions, indicating the research methods are of high feasibility.

Temperature and scale build-up amounts: According to the experimental data, relative curves of temperature-scale amounts and temperature-scaling rates have been plotted and shown in Figs. 4 and 5.

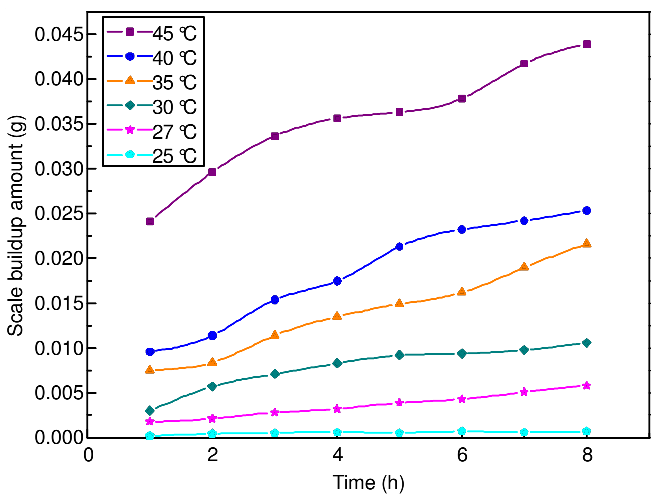

Fig. 4. Relative curves of temperatures and scale amounts

As can be seen in Fig. 4: (1) The scale build up amount increases with the increase of temperature and time. (2) At 25 ºC, scale scarcely builds up. At 30 ºC, trace amounts of scale begin to emerge. At 35 ºC, a small amount of scale has built up. When the temperature is higher than 40 ºC, the scale buildup amount increases and so does the growth rate. At 45 ºC, more scaling appears. Therefore, it is advantageous to keep the transportation temperature of the pipelines below 40 ºC, or severe scaling is likely to occur. (3) Below 30 ºC, there are small amounts of scaling and there is almost no scale at 25 ºC. Therefore, if the specific temperature of normal transportation is controlled within 25-30 ºC, the wax would not precipitate in this case. (4) When the temperature is above 40 ºC, scale buildup amounts increase rapidly.

As can be seen in Fig. 5: (1) The scaling rate varies with temperature and increases with the increase of temperature. (2) At the same temperature, the scaling rate decreases with the increment of time until reaching zero. That is, the calcium and magnesium ions in the water samples almost completely precipitate. (3) At 30 ºC, the scaling rate presents a linear distribution. A sharp decline in the scaling rate appears when it is above 30 ºC. This indicates that at higher temperatures, the scale mainly builds up in short periods and the increment of time does not cause much influence on scale buildup amounts.

TABLE-6
SCALING TREND PREDICTION OF XX FRP PIPELINE

Temperature (ºC)	Related data of XX FRP pipeline	K	SI	SAI	Scaling trend
40	Ca^{2+} = 0.0052 mol/L HCO_3^- = 0.0185 mol/L, μ = 0.28	2.5	1.43	4.9	Severely scaling
35		2.7	1.33	5.3	Slightly scaling
30		2.8	1.23	5.5	Slightly scaling
25		2.9	1.13	5.7	Slightly scaling
20		3.1	0.93	6.1	Trace amount of scale

Notes: The criteria of the Davis-Stiff saturation index method are: SI < 0, no scaling trend; SI = 0, in a state of equilibrium; SI > 0, there is a scaling trend. The Ryznar stability index method criteria are: SAI > 6, no scaling trend; 5 < SAI < 6, there is a scaling trend; SAI < 5, severe scaling.

Conclusion

By studying scaling and wax deposit mechanisms of FRP oil pipeline, this study can be summed up as follows:

The dynamic differential pressure method was adopted to calculate the XX pipeline wax thickness and deposit rate. It was proposed that the high-temperature wax melting process and pipeline pigging process should be applied to remove wax residue. Combined with scaling and wax precipitating characteristics and following the priority to inhibit scaling, the inlet oil temperature range of 35-40 ºC was determined.

The Davis-Stiff saturation index method and Ryznar stability index method were used to make predictions of the XX FRP pipeline scaling trends. It was discovered that severe scaling would occur if the pipeline temperature was greater than 40 ºC.

The relationship between temperature and the amount of scale buildup was studied with chemical experiments and it is recommended that the specific temperature of normal transportation be controlled to within 25-30 ºC to avoid wax deposits.

FRP pipeline has a small surface friction coefficient and slight inner wall roughness, so based on these characteristics, descaling can be done with regular pigging. The pigging period can be determined according to the operation plan and scaling rate.

ACKNOWLEDGEMENTS

This research is supported by Sichuan Provincial Key Disciplinary Development Project Fund (SZD0416).

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