Measurement of Wax Deposition in Paraffin Solutions

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Wax deposition from crude oil poses problems in the production, transportation, and refining of crude oil (Misra et al., 1995). As oil development sites move to deeper and therefore colder water, the appearance of wax deposition on pipe walls has become inevitable. Wax deposits can restrict the flow of oil and cause the plugging of pipelines. Maintenance operations can lead to frequent production interruptions. The cost of remediation increases with water depth. Finding economic and technical solutions for the prevention, management, and remediation of wax deposition problems has become a hurdle for producing new deep-water resources. Therefore, eliminating or avoiding deposited wax remains a key factor in deep-water flow assurance strategies.

Petroleum waxes (that is, carbon numbers ranging from 18 to 90) have been characterized into two major categories: macrocrystalline (*n*-alkanes) and microcrystalline (*iso*-alkanes and *cyclo*-alkanes) (Srivastava et al., 1993). The chemical composition of precipitated waxes is different from that of solid deposits in crude oils, because the deposits contain enhanced amounts of *n*-paraffins compared to the precipitate recovered from the oil. The high molecular weight (> 280 Daltons) paraffin components in crude oils are soluble in the oil at reservoir conditions.

Many of the techniques used presently in the industry to study wax deposition and develop chemical inhibitors required a day or more per test and more than 0.5 L of fluid per test. The objective of this research was to develop a simple, reliable device to conduct the screening experiments in paraffin deposition. In this article, the verification of the performance of a new "Cold Disk" wax deposition (CoDWaD) apparatus by replicating flow loop performance in terms of the variation of the rate of paraffin deposition with temperature difference and flow velocity was investigated. Initial verification was performed with a binary mixture of decane containing 5 wt. % of *n*-tetracosane ($C_{24}H_{50}$). The performance was further confirmed with a North Sea crude oil. The data obtained from these experiments provided deposition comparable to those reported for flow loops, which required much more time and fluid to operate (Creek et al., 1999).

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Experimental Methods

Materials

All reagents used in this study were reagent grade or GC grade: *n*-heptane (99%, Mallinckrodt); *n*-octane (99 + %, Mallinckrodt); *n*-decane (99 + %, Aldrich); *n*-undecane, *n*-tricosane, and *n*-tetracosane (99%, Aldrich); *n*-tetracosane-d50 (MSD isotopes). A 41° API North Sea crude oil was also studied.

Instrumentation

The experimental apparatus, a "cold disk" wax deposition (CoDWaD) apparatus, was designed and used to measure wax deposition rates, as shown in Figure 1. This apparatus is a cylindrical vessel with a polished stainless steel disk imbedded in the wall. This vessel contains a rotating impeller connected to a spinning rotor. The rotating impeller circulates the solution concentrically along its axis and then tangentially past the nearby cold disk at different rates. The deposits were extracted from the disk with *n*-heptane and subsequently analyzed with an HP 5880A Gas Chromatography operated in the splitless mode using an 60 m $\times$ 0.25 mm ID fused silica HP-5 column, having a phase thickness of 0.25 μm equipped with a flame ionization detector (FID).

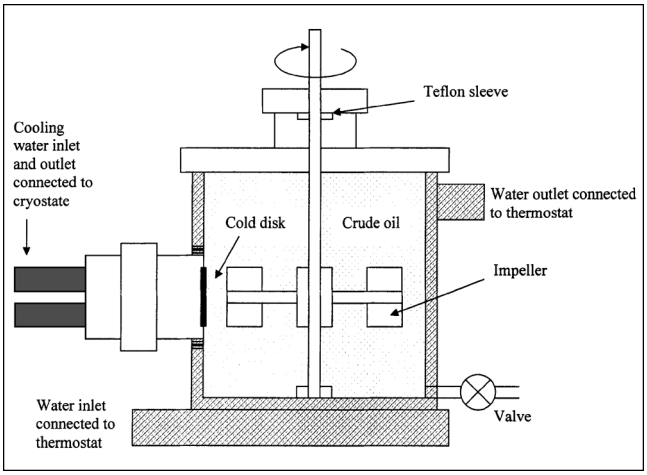

Figure 1. Cell used in this study.

Cylinder vessel was made of copper with a high thermal conductivity ensuring an isothermal surface. The cold steel disk was insulated from the cylinder vessel with epoxy composite to maintain constant low temperature.

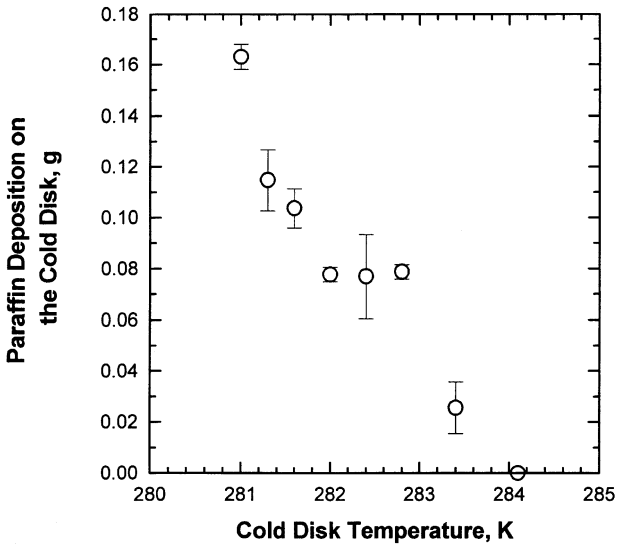

Figure 2. Effect of cold disk temperature on deposition for a sample with 5 wt. % n-$C_{24}H_{50}$ in n-decane solution at 288.1 ± 0.1 K for 30 min.

Flow velocity was maintained at 37 m/min.

Sample preparation

The volume of sample solution used in each experiment was 115 mL. The temperatures of the cold disk and the bulk solution were maintained constant throughout each experiment with Lauda RE 206 refrigerated circulating baths. The surface temperature of the cold disk was monitored by Anritsu Meter Co. Model 529K low heat conducting thermocouple, read with a Cole-Parmer Instrument Co. Model 2186-10A, digital thermometer to ±0.1°C. The agitation was accurately controlled within ±5% with a Talboys Engineering Corp. Model 34-1 with a variable speed motor and shaft connected to the impeller in the solution studied. At the completion of each test, the vessel was disassembled and the sample solution completely drained from the vessel, while the cold disk temperature was maintained unchanged. 4.0 mL of n-heptane was used to wash out and dissolve the paraffin deposit on the cold disk. After the complete dissolution of the paraffin deposit in the vessel, a 5 μL aliquot of the n-heptane extract was withdrawn and mixed with a 995 μL internal standard solution of n-undecane and n-tricosane (or deuterated tetracosane for crude oil samples) in n-heptane in capped vials. A 1 μL aliquot of the mixture was then withdrawn with a syringe and injected into a GC for analysis.

Results and Discussion

Effect of temperature

The Wax Appearance Temperature (WAT) of the sample solution (5 wt. % n-tetracosane in n-decane) was 287.7 ± 0.1 K. This was determined using the ASTM D2500-88 visual method. As long as operating temperatures remain above the WAT, wax deposition will not occur. Therefore, the temperature of the bulk solution was maintained at 288.1 ± 0.1 K, slightly above the WAT in all experiments. Figure 2 shows a plot of the amount of paraffin deposited after 30 min vs. the surface temperature of the cold disk. As expected, the amount of paraffin deposits decreases as the cold disk temperature approaches the WAT. This indicates that the rate of deposition increases as the temperature difference between the bulk solution and the surface of the cold disk increases. Figure 3 shows the effect of disk surface temperature on the composition of paraffin. The composition of deposits appears to depend upon the cold disk temperature. This is an unexpected result, since each experiment was run for the same duration and the velocity of fluid flow across the cold disk is constant for the series of experiments. This result supports the idea that the aging of the deposit is driven by the heat flow through the deposit. Such heat flow would increase as the tempera-

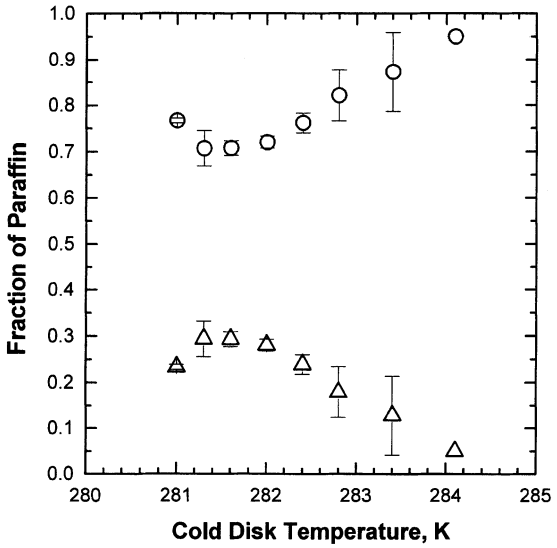

Figure 3. Composition of the paraffin deposition under various cold disk temperatures.

Symbols "O" and "Δ" represent the fraction of n-decane ($C_{10}H_{22}$) and n-tetracosane ($C_{24}H_{50}$) in the paraffin deposit, respectively.

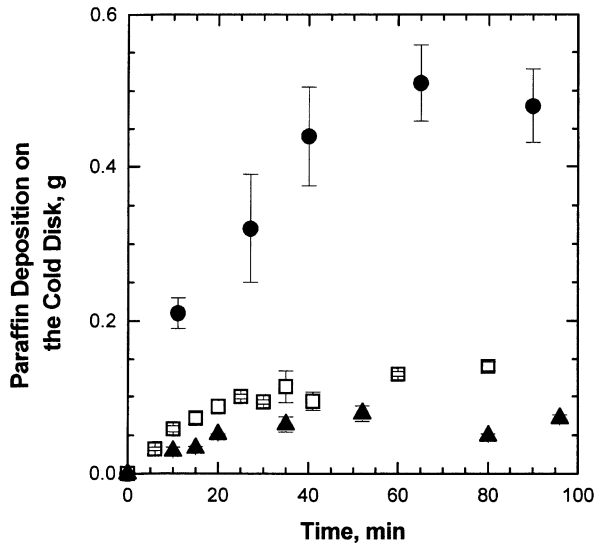

Figure 4. Experimental data for paraffin deposition vs. time of 5 wt. % *n*-tetracosane solutions in *n*-decane at 288.1 ± 0.1 K at varying flow velocities: 0 m/min (●), 12 m/min (□), or 37 m/min (▲).

Cooling water bath was maintained at 280.2 ± 0.1 K.

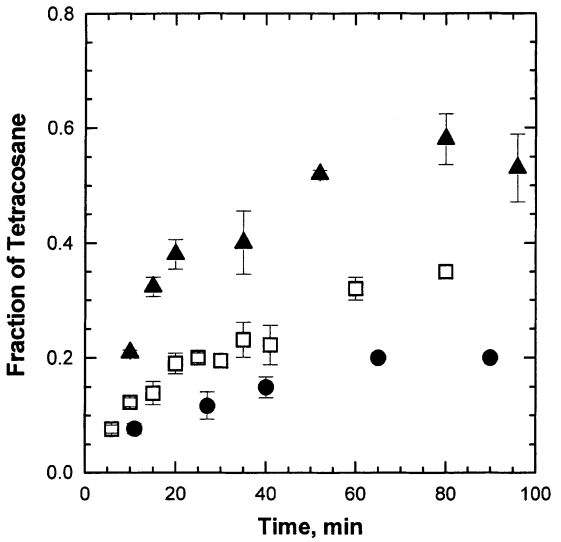

Figure 5. Composition of the paraffin deposition vs. time under various flow velocities: 0 m/min (●), 12 m/min (□), or 37 m/min (▲).

ture difference between the bulk fluid and cold disk increases. This has been demonstrated elsewhere by operating with the same temperature difference between the WAT and the cold disk, while increasing the difference between the bulk temperature and the cold disk (Effner, 1998).

Effect of flow velocity

The flow velocity is a major factor affecting paraffin deposition. Figure 4 shows paraffin deposition as a function of time at a variety of liquid flow velocities over the cold disk. Velocities of 12 and 37 m/min refer to the tip speed of the stirring impeller in the bulk fluid adjacent to the cold disk. The amount of wax deposit on the cold disk increases with time in any one experiment. As the flow velocity increases, the deposition rate apparently decreases. At a higher flow velocity, the temperature difference between the bulk solution and the cold disk approaches the temperature of the bulk solution. With this decrease in the deposition driving force, the observed deposit grows more slowly. Other research groups have made similar observations with flow loop deposition tests (Creek et al., 1999; Singh et al., 2000).

The fraction of $C_{24}H_{50}$ in the deposit is also increasing with time in these experiments, as shown in Figure 5. In fact, both the flow velocity and time appear to affect the deposit composition. At a 12 m/min flow velocity, the deposits were soft, porous, and have a spongy-like structure containing a great amount of solvent $C_{10}H_{22}$. At 37 m/min, the deposits were hard, with a consistency similar to the wax in shoe polish. These harder deposits contained mainly $C_{24}H_{50}$. It appears from these experiments that the reduction in deposit mass is due to the reduction in solvent in the deposit as the flow velocity increases. This is consistent with results from flow loop tests.

Effect of aging

The effect of deposit aging can easily be studied with the cold disk apparatus because of the relatively short run time required to form a credible deposit. Figure 5, shows the fraction of $C_{24}H_{50}$ in the deposit increases gradually with run time. A North Sea crude oil sample was also tested with similar trends. Figure 6 shows the test results for the North Sea oil as a function of deposition time. The ratio shown in Figure 6 is the ratio of heavy to light fraction of the oil ([C_{24}-C_{34}]/[C_8-C_{13}]). These tests show the expected increase in de-

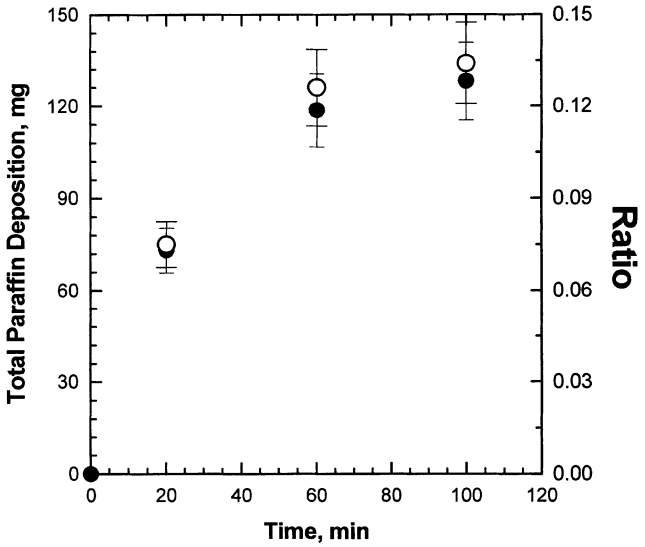

Figure 6. Experimental data for paraffin deposition vs. time of 41° API North Sea Crude Oil at 288.1 ± 0.1 K at flow velocity 37 m/min.

Cooling water bath was maintained at 280.2 ± 0.1 K. Left axis: The total paraffin deposition is represented as dark circle "●". Right axis: C_{24}-C_{34}/C_8-C_{13} ratio of the paraffin deposition is marked as "○" with increasing time.

posit mass with time, as well as a decreased fraction of entrained oil in the deposit. This result is consistent with the observations of Singh et al. (1999). This also confirms that the experimental work on the simple mixture is representative of an oil system. In addition, the key data were obtained in only 100 min compared with the 100 h that would be required to determine similar data with a flow loop.

Two interesting results shown in Figures 4 and 5 are the "zero" flow tests. In these tests the fluid in the apparatus was not stirred and, therefore, had an apparent flow velocity of 0 m/min. The bath and cold disk temperatures were maintained at a constant. Deposit growth with time occurred in the same way as observed in the test where the liquid was flowing across the cold disk. This potentially indicates thermal mass transfer of material is dominant as not enough time has elapsed for mass diffusion driven deposition to occur.

Conclusions

The new "Cold Disk" Wax Deposition (CoDWaD) apparatus was shown to give wax deposition results analogous to those obtained in flow loop experiments with a fraction of the material and in a fraction of the time required for loop deposition. The quality of the deposits was analogous to field deposits. The conclusions were supported by tests on the variation of the deposit magnitude and composition as a function of flow velocity, temperature difference between the bulk fluid and the cold disk, and the time of deposition. Further, "zero flow" tests were observed to produce deposits consistent with those developed during normal flow. These results indicate thermal mass transport, as well as mass diffusion should be considered in this problem.

Acknowledgments

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