

PARAFFIN DEPOSITION IN A STAGNANT FLUID LAYER INSIDE A CAVITY SUBJECTED TO A TEMPERATURE GRADIENT

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Deposition of high molecular weight paraffins on the inner wall of subsea production and transportation pipelines continues to be a critical operational problem faced by the petroleum industry. The accumulation of the deposited material on the inner wall of the lines may lead to increased pumping power, decreased flow rate or even to the total blockage of the line, with loss of production and capital investment. In the present work a critical review of the literature on wax deposition was conducted leading to the conclusion that there is not enough experimental evidence to determine which are the relevant mechanisms responsible for wax deposition.

Based on the conclusions of the literature search, a research program was initiated with the aim of identifying the relative importance of the wax deposition mechanisms. To this end, simple, basic experiments were designed and complemented by numerical simulations. The present paper is part of this ongoing research program and reports on experiments on deposition in cavities containing a stagnant solution of paraffin and solvent and submitted to a transverse temperature gradient. The experiments yielded temporal distributions of paraffin deposits. A molecular-diffusion-based model developed underestimated the evolution of the deposit thickness for the stagnant cavity. The results obtained were not sufficient to corroborate the widely accepted hypothesis that the wax deposition process is controlled by molecular diffusion.

Keywords. Wax deposition, stagnant layer, pipelines

1. Introduction

Nearly half of the sedimentary basins that offer good petroleum prospects are located offshore, at long distances from the coasts. Today, the most active offshore production areas are the Gulf of Mexico, the North Sea, China Sea, West Africa and the coast of Brazil. The drive toward production at deep waters in these areas is evidenced by the evolution of the world records in sub-sea production. In 1983 production was conducted at 208 m water depth, while in 1999 petroleum was being produced at 1853 m (Machado, 1999). The production in deep waters involves specially designed equipment and costly, complex operations. Even so, due to the steady investment in technology, the cost of production of the petroleum barrel has dropped steadily.

Among the several challenges in deep water petroleum production, the deposition of wax in the interior of production and transportation pipelines is one of the most critical operational problems faced by the industry. The crude oil flows out of the reservoir at, typically, 80 °C into the production pipelines. These lines carry the oil to the platforms and from the platforms to shore. At large water depths, the ocean temperature at the bottom is of the order of 4 °C. The solubility of wax in the oil is a decreasing function of temperature. As the oil flows, it loses heat to the surrounding water. If the crude oil temperature falls below the wax appearance temperature, the wax may precipitate and deposit along the inner walls of the pipeline. The accumulation of the deposited material may lead to increased pumping power, decreased flow rate or even to the total blockage of the line with loss of production and capital revenue.

Once the solubility limit for a particular temperature of an oil is reached, it is expected that precipitation would immediately occur. In general, however, a certain degree of super saturation is necessary to trigger the crystallization process (Bott, 1997). The temperature at which the first wax crystal appears is known as Cloud Point or Wax Appearance Temperature (WAT).

The temperature distribution in the pipeline will determine the location where precipitation of wax crystals will take place. If the region of super saturation is at the pipe wall, deposits will form there. The WAT can also occur in the bulk of the fluid. In this case, the crystals formed may migrate to the wall as particles and form the softer, solid deposits. These crystals formed in the bulk of the liquid can also be carried by the mean or fluctuating components of the flow to regions where the concentration of the solution is below the saturation level, being redissolved. The formation of crystals may be aided by the presence of nucleation sites such as solid impurities in suspension or sites at the pipe wall (Bott, 1997).

There are traditional methods of prevention and remediation of wax deposits employed by the industry. These methods include, among others, the use chemical inhibitors, heating of the lines by electrical or chemical means or mechanical removal (McCaflin et al., 1984). The cost of utilization of these methods, however, increases steeply with water depth, being crucial to the economical viability of offshore petroleum production.

A significant research effort has been devoted to the understanding and modeling of the wax deposition problem. This is a complex problem that involves several disciplines such as thermodynamics, heat transfer, mass transfer, crystal growth and fluid dynamics. An accurate prediction of the deposition rates along the pipeline would be invaluable information that would help in the design stages of the field, as well as in the scheduling of interventions in the pipeline, in order to assure the flow of oil at the desired rates (Misra et al., 1995).

Thermodynamic models have been proposed for predicting the onset of crystallization (i.e., the cloud point) and solid-liquid phase equilibria for hydrocarbon systems (e.g., Butler and MacLeod, 1961; Won, 1986; Hansen et al., 1988; Won, 1989; Pedersen et al., 1991; Erickson et al., 1993; Svendsen, 1993; Pan et al., 1997; Coutinho and Daridon, 2001 and Pauly et al., 2001). Although these models predict reasonably well the thermodynamics of hydrocarbon solutions, the main question to be answered is whether deposition will take place for a particular crude and pipeline operating conditions. Also of interest, are the amount of deposited material and the spatial and temporal distributions of the deposits. Knowledge of the chemical and mechanical properties of the deposited material can also be relevant for the proper design of wax removal operations.

A detailed critical review of the literature was prepared as part of a research project on wax deposition (Azevedo, 2003). One of the key works analyzed in this review was that of Burger et al. (1981) where the possible mechanisms responsible for wax deposition were identified. These mechanisms are molecular diffusion, Brownian diffusion, shear dispersion, and gravitational settling. Among those, it is accepted that gravitational settling does not seem to be a relevant mechanism. For completeness, a brief review of these mechanisms is presented.

2. Deposition by Molecular Diffusion

Molecular diffusion is a possible mechanism responsible for the transport of wax toward the cold pipe wall in its liquid phase. The temperature gradient in the oil/wax mixture induces a concentration gradient that drives the mass flux of liquid paraffin to the wall where the crystals come out of solution and adhere to the wall, forming the deposit. A transport equation in the form of Fick's law of diffusion was proposed for modeling the wax mass flux toward the wall (Burger et al., 1981).

$$\frac{d m_m}{d t} = \rho_d D_m A \frac{d C}{d r} \quad (1)$$

where m_m is the mass of deposited wax, ρ_d the density of the solid wax deposit, D_m is the diffusion coefficient of liquid wax in the oil, A is the area of deposition, C is the volume fraction concentration of wax in solution and r is the radial coordinate.

An expression for the molecular diffusion coefficient was also proposed where the coefficient is inversely proportional to the mixture viscosity,

$$D_m = C_1 / \mu \quad (2)$$

Equation (2) has been employed in several models developed to predict wax deposition (e.g., Weingarten and Euchner, 1986; Majeed et al., 1990; Souza Mendes and Braga, 1996 and Creek et al., 1999). In fact, the constant C_1 has been widely used as an adjusting parameter for fitting experimental deposition data. In our view, this practice has contributed to the general acceptance of molecular diffusion as the mechanism responsible for wax deposition. For instance, the deposition model proposed by Brown et al. (1993) underpredicts the experimental deposition rates by a factor of 3 to 5 when an independent correlation for the molecular diffusivity is used. This is an indication that mechanisms other than molecular diffusion may be in action. However, the authors switched to a model based on Eq. (2), adjusting the constant to fit the data.

3. Deposition by Brownian Diffusion

It is possible that some regions of the oil flowing in the pipeline be at temperatures below the cloud point. In this case, wax crystals will precipitate out of solution and will be suspended in the oil. The wax crystals suspended in the oil will collide with thermally agitated oil molecules, giving rise to an irregular wiggling motion of the crystals. In the presence of a concentration gradient of solid crystals, there will be a net transport of these crystals in the direction of decreasing concentration. This process is characterized by a particle (crystals) Brownian diffusion coefficient and the flux of the particles will be given by,

$$\frac{d m_B}{d t} = \rho_d D_B A \frac{d C^*}{d r} \quad (3)$$

where m_B is the mass of deposited wax, ρ_d the density of the solid wax deposit, D_B is the Brownian diffusion coefficient of solid wax crystals in the oil, A is the area of deposition, C^* is the volume fraction concentration of solid wax out of solution and r is the radial coordinate.

It is interesting to note that Brownian diffusion has not been considered as a relevant deposition mechanism by several authors (e.g. Hunt, 1962; Burger et al., 1981; Weingarten and Euchner, 1986; Majeed et al., 1990; Brown et al., 1993; Ribeiro et al., 1997; Hsu et al., 1998; Singh et al., 1999 and Weispfening, 2001). We do believe, however, that there is not sufficient experimental evidence to support this conclusion.

4. Wax Deposition by Gravity Settling

Wax crystals tend to be denser than the solvent oil, therefore, gravity settling is a possible mechanism for deposition. Studies conducted by Burger et al. (1981) under centrifugal fields determined typical size distributions of crystals and terminal settling velocities. For typical operating conditions encountered in pipelines, these velocities were found not to significantly contribute to the formation of wax deposits. Further experimental studies conducted by the same authors confirmed these predictions. In these studies, laboratory deposition experiments were conducted in horizontal and vertical pipes under the same flow and heat transfer conditions, for the same oil. The results revealed that, within the experimental uncertainty levels of the experiments, there was no difference on the amount of wax deposited for the two configurations. Recently, Leiroz (2004), conducted deposition experiments in a horizontal channel with the top and bottom walls cooled. Visualization of the deposited layers formed at each wall demonstrated perfect symmetry, indicating that gravity was not a relevant mechanism.

5. Wax Deposition by Shear Dispersion

Wax deposition by shear dispersion, as well as Brownian diffusion, is a mechanism of cross-stream transport of solid particles in suspension. The motion of the solid particles depends on their size, relative density and concentration. Several studies on concentrated suspensions indicate that the lateral motion of particles immersed in a shear flow is in the direction of decreasing shear (e.g. Hampton et al., 1997 and Tetlow et al., 1998). In our case, this would lead to a motion of crystals away from the wall, where shear is maximum. There have been studies, however, that report a migration of solid particles toward an intermediate region between the pipe centerline and the pipe wall (Segré and Silberg, 1962). Since the wax crystals may have shapes that differ significantly from the spherical particles considered in the studies mentioned, it is not possible to use the results from spherical particles as an indication of the motion of wax crystals under a shear gradient.

6 Wax Deposition Under Zero Heat Flux

Several studies were conducted in wax deposition loops under zero heat flux conditions (e.g., Burger et al., 1981 and Weingarten and Euchner, 1986). In these studies oil and wax mixtures were pumped through pipes, having inlet temperatures below the cloud point. The pipe wall was either maintained isolated or kept at the same temperature as the fluid, so as to guarantee that there would be no heat flux from the wall to the fluid. Under such conditions, it was expected that solid crystals would be present throughout the flow and available for deposition. Since the heat flux is zero, there can be no means for the molecular diffusion mechanism to act. Also, since there is no radial heat flux and, consequently, no radial diffusion of liquid wax, there will be no concentration gradient of solid particles close to the pipe wall. We conclude that, under zero heat flux conditions, the deposition would only be possible due to a flow-induced mechanism, such as shear dispersion.

All the experimental results available in the open literature, however, have shown no deposition under zero heat flux conditions. We are lead to the conclusion that shear dispersion is not relevant to the deposition of wax crystals. Shear can be, however, relevant as a deposit removal mechanism (e.g., Creek et al., 1999).

7. Rate of Incorporation of Solid Particles

All works available in the literature that have studied the wax deposition process, have employed the hypothesis that wax crystals out of solution at the solid-liquid interface as a result of molecular diffusion, are completely incorporated into the solid deposit. In the case of solid crystals transported by either Brownian diffusion or shear dispersion (if indeed this mechanism is relevant), a mechanism for incorporation of the solid particles into the deposit solid layer was proposed and widely accepted.

Again, it is in the work of Burger et al. (1981), that this incorporation mechanism is proposed. The authors considered that the rate of incorporation of solid particles, dm_i/dt , would be proportional to the concentration of solid particles at the solid-liquid interface, C_w^* , to the wall shear rate γ , and to the surface area available, A , that is,

$$\frac{d m_i}{d t} = k^* C_w^* \gamma A \quad (4)$$

k^* is the deposition rate constant.

For a balanced situation, the rate at which solid particles are brought to the interface by Brownian diffusion or shear dispersion should equal the rate of incorporation of solid particles given by Eq. (4). In the case of an imbalance, the mechanism presenting smaller rates will be the controlling mechanism of deposition. In other words, if the Brownian and shear dispersion mechanisms provide a higher flux of particles than what can be incorporated at the wall, the growth of the deposit will be controlled by the rate of incorporation mechanism given by Eq. (4). On the other hand, if the rate of incorporation at the wall is larger than the Brownian and shear transport mechanisms, the rate of growth of the deposit will be controlled by the rate of combined transport by Brownian diffusion and shear dispersion. Burger et al. (1981) state that experimental studies, for the conditions of operation of the particular pipeline that was the object of their study, demonstrated that the rate of incorporation of the solid deposits, Eq. (4), was the rate controlling mechanism.

According to this assumption the total rate of wax deposition at the pipe wall, dm_T/dt , is given by the sum of the contributions of molecular diffusion and the rate of incorporation of solid deposits at the wall, that is,

$$\frac{d m_T}{d t} = \rho_d D_m A \left(\frac{d C}{d r} \right) + k^* C_w^* \gamma A \quad (5)$$

It is worth noting that, for unknown reasons, the rate of incorporation of solid deposits given by Eq. (5) has been used in the literature as a model for the shear dispersion mechanism (Wiengarten and Euchner, 1986 and Kok and Saracoglu, 2000). Even the authors Burger et al. (1981) who proposed Eq. (5) use the term shear dispersion to label a curve that represents the predictions of Eq. (5) (see figures 11,12 and 13 of their work). This is not just a nomenclature issue since, as already mentioned, the experimental evidences available indicate that shear dispersion is probably not relevant as a mechanism for particle deposition.

The present paper is part of an ongoing research effort aimed at understanding the basic mechanisms responsible for wax crystals deposition at the pipe inner walls. The strategy adopted was to conduct simple experiments and simulations with well defined initial and boundary conditions and employing fluids with known properties, so as to allow the assessment of the relative importance of the deposition mechanisms. In this first step reported here, experiments were conducted using a sealed cavity containing a stagnant solution of wax and oil subjected to a temperature gradient. The test section designed for the experiments allowed the measurement of the growth of the deposited layer and the visualization under a microscope of the formation of wax crystals. Also as part of the work, a simple model was proposed to simulate the growth of the deposited layer. A comparison of experiments and computations would allow the verification of the deposition mechanisms proposed. Next, a description of the test section constructed is presented.

8. Experiments

The test section where the deposition experiments were conducted was designed to allow the study of wax deposition in a stagnant solution. Figure (1) presents a schematic cross section view of the test section constructed. The cavity was formed by two, 2-mm-thick, vertical copper walls and two horizontal glass walls. The copper walls were fins attached to copper hollow blocks. Each copper block was connected to a temperature controlling and water-circulating bath. The lower horizontal glass wall was formed by a sandwich of two glass layers so as to decrease the internal thickness of the cavity to a dimension of 0.5 mm. This small dimension was necessary to eliminate any natural-convection induced motion in the cavity. Two vertical, lateral walls and rubber gaskets sealed the cavity. In one of the lateral walls small holes were present to allow the filling of the cavity with the working fluid and the removal of the trapped air. A hypodermic needle and syringe was used in the filling operation. A fine-gauge thermocouple was installed inside each copper fin, close to the surface that was exposed to the fluid inside the cavity. These thermocouples were used to monitor the temperature history of the two surfaces that limit the cavity. The final internal dimensions of the cavity were 10 x 30 x 0.5 mm (width x length x thickness). A view of the assembled cavity is shown in Figure 4.

A digital camera with resolution of 640 x 480 pixels and equipped with a 18 – 108 m zoom lens was mounted vertically with its axis orthogonal to the horizontal glass wall of the cavity. Back, white illumination was employed. The camera was connected to a video recorder to capture the evolution of the wax deposition front. The videos recorded were digitized and an image processing software was used to measure the thickness of the deposited layer as a function of time. In order to control the temperature of the external environment, the cavity was housed in a styrofoam box that only allowed access to the camera lens and back illumination. The internal temperature within the box was monitored by a liquid-in-glass mercury thermometer. For some runs, the spatial and temporal temperature distribution of the fluid in the cavity was measured. To this end, six fine-gauge thermocouples were installed through holes provided in the

lateral wall of the cavity opposite to the wall equipped with the filling tubes. The thermocouples were evenly distributed along the length of the cavity, penetrating about 10 mm into the cavity. A data acquisition unit was employed to register the thermocouples readings.

The preparation for a data run was initiated by filling the cavity with the paraffin solution to be tested. In the tests presented in the present paper a 10% in volume solution of refined paraffin with carbon numbers between C_{21} and C_{38} dissolved in n-paraffin (C_{13} to C_{16}) was used. The WAT for the solution utilized was measured to be of the order of 27 °C by viscosimetry at CENPES. Prior to the filling operation the water circulating units were set to a temperature above the WAT of the solution to be tested. This way, unwanted depositions in the filling tubes and inside the cavity were avoided. Next, the cavity filled with the solution was positioned horizontally and the temperature of the water baths were set to the highest temperature of the test to be conducted. This temperature was always above the WAT for the solution being tested. After a steady state condition was verified by the thermocouples, a step change in the temperature of one of the walls was imposed. This was achieved by a fast connection of one of the copper walls to a circulating water bath that was previously equilibrated at the lower temperature desired for the test. This lower temperature was lower or equal to the WAT for the solution tested. The evolution of the deposition front was continuously recorded in video until a steady state position of the front was reached. After the test was finished, the temperature of both copper walls were elevated above the WAT in order to dissolve all the deposited wax, thereby preparing the test section for a new data run.

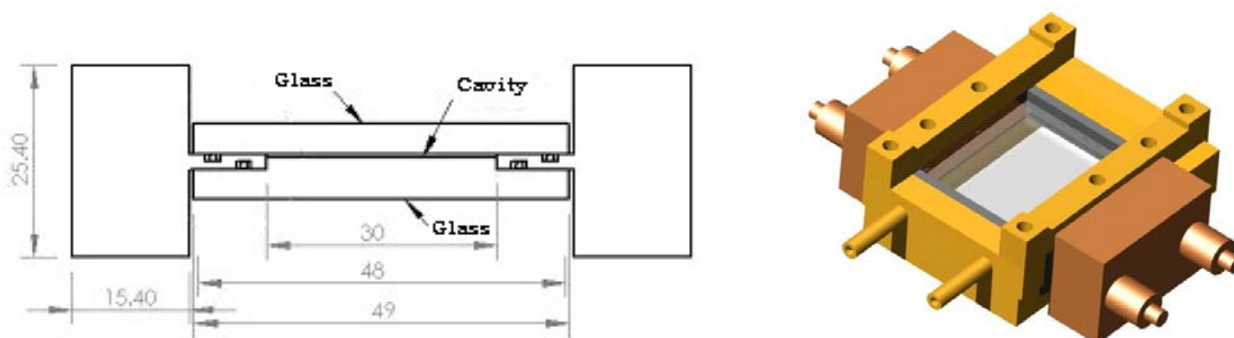


Figure 1. Schematic view of the test section constructed for visualization of wax deposition. (measurements in mm)

9. Numerical Solution

The objective of the numerical solution developed in the present work was to help identify the relative importance of the wax deposition mechanisms proposed in the literature as mentioned before. The idea was to develop a simple model using molecular diffusion as the only mechanism responsible for deposition. The results obtained would then be compared with the experimental results, and the level of agreement observed would be used as a measure of the importance of that particular deposition mechanism.

The simulation of the deposition in a stagnant layer assumed the following hypothesis:

- (i) One dimensional heat conduction and mass diffusion
- (ii) Constant properties. Thermal conductivity, specific heat and density are the same for liquid and solid phases
- (iii) Saturated liquid at the solid/fluid interface

With the assumptions listed above, the energy equations for the liquid and solid phases can be written as,

For the solid region:

$$\frac{\partial^2 T_s}{\partial y_s^2} = \frac{1}{\alpha} \frac{\partial T_s}{\partial t} \quad (6)$$

For the liquid region:

$$\frac{\partial^2 T_l}{\partial y_l^2} = \frac{1}{\alpha} \frac{\partial T_l}{\partial t} \quad (7)$$

At the solid/liquid interface, a energy balance yields:

$$k \frac{\partial T_s}{\partial y_s} - k \frac{\partial T_l}{\partial y_l} = \phi \rho_w L \frac{dS(t)}{dt} \quad (8)$$

In the above equations T_s and T_l are, respectively the temperatures in the solid and liquid phases, y_s and y_l are spatial coordinates of the solid and liquid phases, $S(t)$ is the position of the interface, t is the time, α is thermal diffusivity, and ϕ is the solid deposit porosity defined as the ratio of the liquid to the total mass of solid and liquid. The density of the solid paraffin is ρ_w , while its latent heat of fusion is L .

The solute (paraffin) mass fraction distribution is governed by,

$$\frac{\partial^2 w_w}{\partial y_l^2} = \frac{1}{D} \frac{\partial w_w}{\partial t} \quad (9)$$

At the interface, a mass balance produces a relation for the velocity of the interface,

$$\frac{dS(t)}{dt} = \frac{D}{(1-\phi)} \frac{\rho_T}{\rho_w} \frac{\partial w_w}{\partial y_l} \quad (10)$$

In the equations above, w_w is the mass fraction of paraffin in the liquid phase, D is the molecular diffusion coefficient, and ρ_T is the density of the solution. By assuming thermodynamic equilibrium at the interface the mass fraction at the interface is determined as a function of the interface temperature by means of a solubility curve determined experimentally ($w_w = 0,0004.T^2 - 0,0086.T + 0,0653$).

As initial condition, the solution is assumed to be at a uniform elevated temperature, T_q . For $t > 0$, a colder temperature, T_f , is imposed at the cold wall, $y = 0$, while the hotter wall at $y = H$, is maintained at T_q . The initial mass fraction w_{w0} is imposed as equal to 1 in the solid phase ($0 < y < S(t)$) and equal to 0,1 in the liquid phase ($S(t) < y < H$). The hotter wall at $y = H$ was considered impermeable, so $\partial w_w / \partial y = 0$. At the solid/liquid interface, $y = S(t)$, the solid and liquid temperatures were equal, i.e., $T_l(y,t) = T_s(y,t)$, and the mass fraction was the equilibrium mass fraction for the interface temperature, $w = w_{int}$.

The governing equations were written in dimensionless form using the following dimensionless variables: $y^* = y/H$, $S^* = S(t)/H$, $t^* = t\alpha/H^2$, and $\theta = (T - T_f)/(T_q - T_f)$. The dimensionless parameters governing the problem are the Stefan number, $Ste = C_p(T_q - T_f)/L$, the Lewis number $Le = \alpha/D$, the ratio of the solid paraffin to the solution density, $\rho = \rho_w/\rho_T$, and the porosity, ϕ .

The set of equations described together with initial and boundary conditions were solved by a finite difference method (Pletcher, 1984). Since the paraffin deposition is a moving boundary problem, a coordinate transformation was employed to transform the variable physical domain in a fixed computational domain. Details of the transformation employed and of the implementation of the numerical method can be found in Leiroz (2004).

10. Results and Discussion

The presentation of the results is initiated with the measured temperature profiles within the cavity. Figure (2) presents the temperature results obtained with the fine gauge thermocouples inserted into the lateral wall of the cavity. The ordinate represents the temperature in degrees Celsius, while the abscissa represents the spatial coordinate along the length of the cavity, with the origin located at the cold wall. The hot wall is located at 30 mm, the total length of the cavity. Temperature profiles are presented for six different values of time, counted from the moment the step change in temperature is imposed on the cold wall. The walls were maintained at 30 °C until a steady state condition was verified. After that, water at 20 °C was circulated through one of the walls while the other wall was kept at 30 °C. Since the solution employed in the experiments presented a WAT of 27 °C, deposition of wax crystals was expected to occur.

An observation of the temperature profiles of Figure 2 shows the fluid in the cavity initially at a uniform temperature of approximately 30 °C. After the step change in temperature is imposed, the evolution of the profile can be observed. A linear temperature profile is attained at about 20 minutes after the start of the run. The linear profile is an indication that there was no fluid motion within the cavity and that heat transfer is dominated by conduction, as desired for the stagnant fluid experiment. The dashed horizontal lines in the figure mark the region where the WAT is expected to lie. As will be seen shortly, nearly half of the cavity is filled with deposited wax. The fact that the steady state linear temperature profile does not present any inflection is an indication that the thermal conductivities of solid and liquid paraffin should be similar, as assumed in the numerical model proposed.

The deposition data obtained will now be commented. Figure 3 presents representative images of the evolution of the deposition front in the cavity. Although the figures are presented in the vertical position, the actual experiments were run with the cavity positioned horizontally, as mentioned in the Experiments Section. Figure (3a) presents the moment at which the experiment is started by the lowering of the cold wall temperature. No deposition is present. As time passes, a uniform layer of deposited paraffin is observed to grow. Images like those presented in Fig. (3) were digitized and processed to obtain the deposit thickness as function of time.

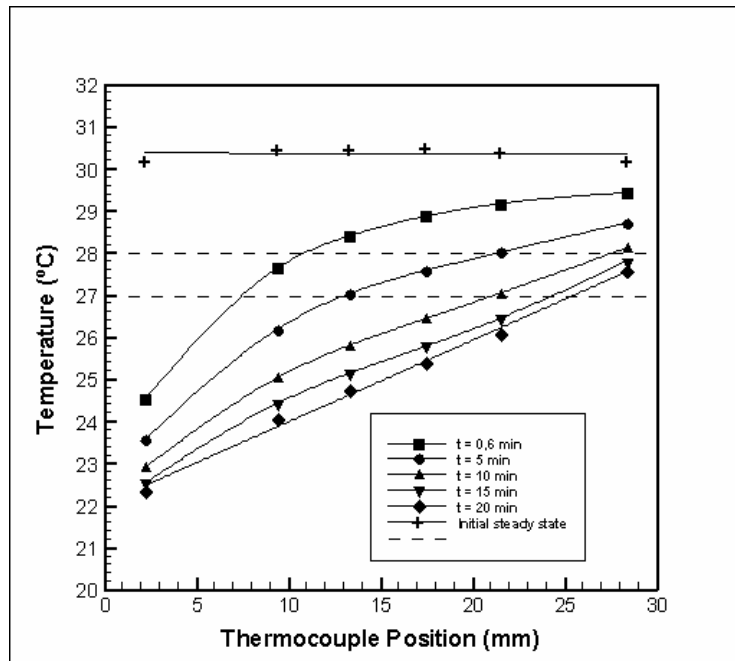


Figure 2. Time variation of temperature profiles for stagnant fluid within cavity. Hot and cold wall temperatures equal to 30°C and 20°C. WAT equal to 27°C.

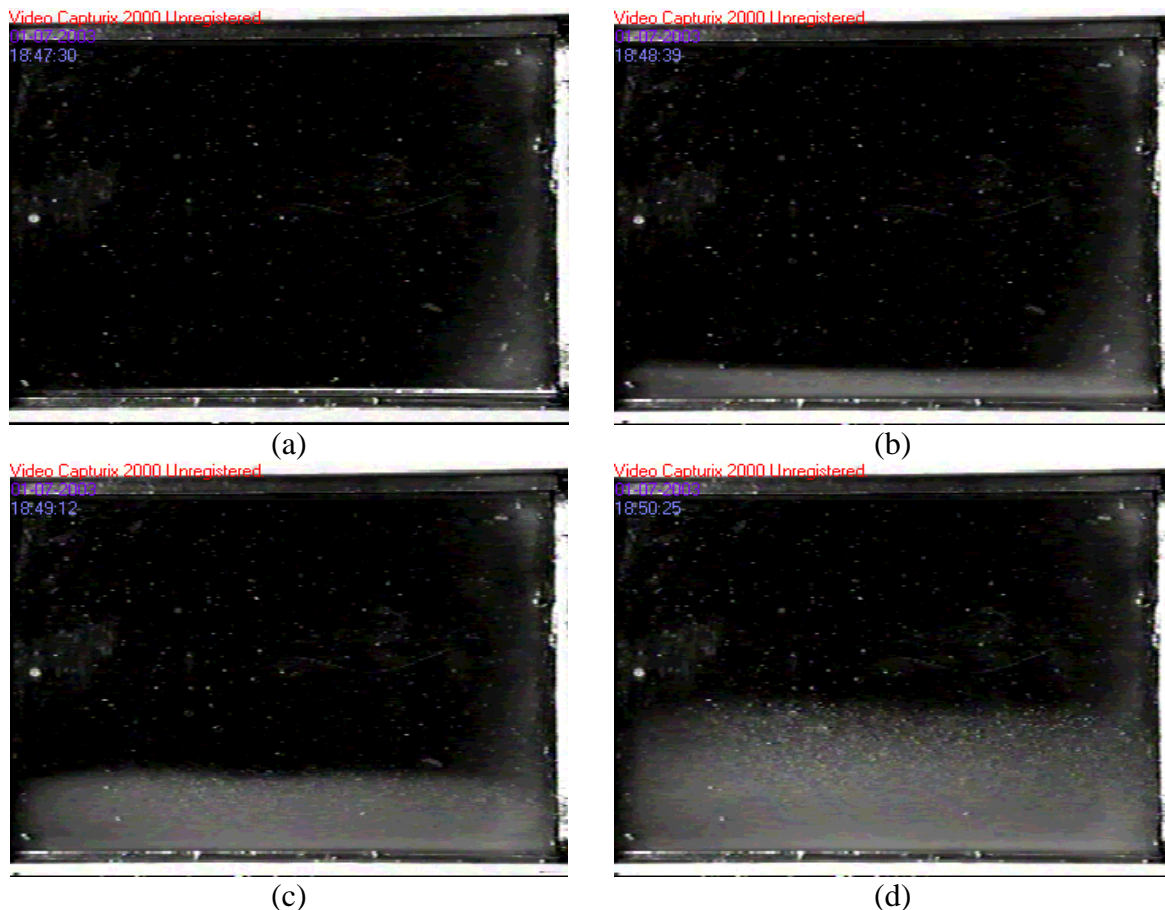


Figure 3. Evolution of deposited wax within cavity. Hot and cold wall temperatures equal to 32°C and 12°C. External ambient temperature equal to 25°C. Images represent intervals of 0, 15, 48, and 125 seconds after cooling starts.

Figures (4a) and (4b) present the evolution of the deposit thickness measured from the captured digital images. The deposited thicknesses given in millimeters are plotted as function of the time in seconds. Figure (4a) represents the

experiments conducted for a 20-degree-temperature difference between the hot and cold walls, while in Fig. (4b) the temperature difference was equal to 30 °C. In dimensionless terms, this temperature differences translate to Stefan numbers of, respectively, 0.19 and 0.29. Eight sets of thickness data are presented in each figure. They represent experiments conducted at the different temperatures of the ambient around the cavity that are labeled in the figures.

An observation of Fig. (4a) shows that the deposit layer grows at a faster rate at the beginning of the experiment, leveling off to reach an asymptotic value for longer times. During the initial transient a spread in the data can be noticed, indicating that the external temperature is influencing the rate of deposit growth. The lower the external temperature the higher the heat losses from the cavity what causes an increase the deposit growth rate. Although there is a sensitivity of the deposit layer to the heat losses during the initial transient, the asymptotic value attained is not influenced by the heat losses, as can be verified in the figure. The spread of the data in the initial transient is less pronounced in the case of the larger temperature difference shown in Fig. (4b). In this case the steady state position of the deposition front reaches about the mid-length of the cavity, i.e., about 15 mm. In the case of Fig. (4a) the deposited layer reaches about 27 mm. A shorter deposited layer offers a smaller lateral area for heat transfer with the external environment, what explains the lesser sensitivity to the external temperature displayed by the data.

The information on the temperature profiles of Fig. (2) combined with the deposition data of Fig. (4), shows that the steady state deposition thickness coincides with the steady state position of the isotherm corresponding to the WAT of the solution. Indeed, for the case of Fig. (4a), the steady state deposit thickness is of the order of 27 mm, the same position obtained for the steady state position of the WAT isotherm in Fig. (2).

Figure (4a) and (4b) also display curves that represent the predictions of the evolution of the deposited layer obtained with the numerical model developed. Three curves are presented for different values of the Lewis number, namely, 2.96, 29.6, and 296. The value of Lewis number equal 296 was obtained employing the actual properties of the solution utilized in the tests. The calculations with the other two values of Lewis were conducted to assesses the sensitivity of the solution to this dimensionless parameter.

A general observation of Fig. (4a) and (4b) shows that the numerical solutions under predict the experimental data by, respectively, 30 and 20 %. The influence of the Lewis number does not seem to be significant. The results presented in Fig. (4) seem to be the first comparison available in the open literature between measured and predicted paraffin deposition. As already commented in the Introduction, all the models available in the literature make use of adjustments of solution properties – mainly the coefficient of diffusion – in order to better reproduce the experimental data. In the present research, the use of actual properties allows the assessment of the use of molecular diffusion as the only mechanism responsible for wax deposition. The fact the diffusion-based model under predicts the deposition thickness is an indication that other deposition mechanisms may be present. Other factors no related to the deposition mechanisms may be affecting the agreement between experiments and predictions. Heat losses from the glass and lateral walls of the cavity have not been considered in the one-dimensional model developed. At the time this article was being prepared, heat losses mechanisms were being included in the model developed.

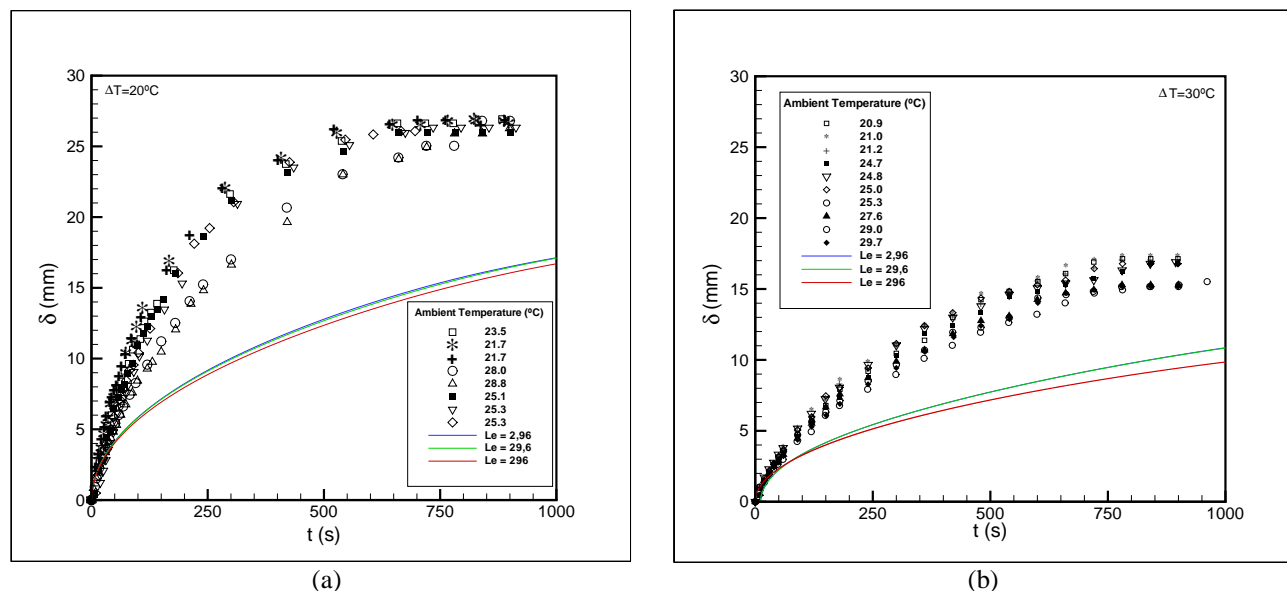


Figure 4. Measured and predicted time variation of wax deposit thickness in a stagnant cavity.

11. Concluding Remarks

The present work describes the first part of a broader, ongoing research project aimed at studying the mechanisms responsible for wax deposition in petroleum pipelines. A detailed review of the literature revealed that the accepted wax deposition mechanisms are molecular diffusion, Brownian diffusion and shear dispersion. Gravity settling does not

seem to be a relevant mechanism. In our view, the experimental evidence available in the literature does support the widely accepted conclusion that molecular diffusion is the dominant deposition mechanism. The fact that all the simulation models available in the open literature make use of molecular diffusion as the only deposition mechanism and rely on adjustment of the fluid properties to fit the available experimental data seems to be an indication that the correct deposition mechanism might not have been included in the modeling.

The strategy followed in the present work was to conduct simple experiments with known boundary and initial condition and utilizing simple fluids with known properties. In parallel, simple simulation models were conducted and its predictions were compared to the experimental data.

The experiments conducted generated, seemingly for the first time, time resolved data for the wax deposition front in a stagnant fluid layer submitted to a temperature gradient. The diffusion based, one-dimensional model developed under predicted the deposition thickness by about 25%. These results are an indication that deposition mechanisms other than molecular diffusion might be acting. Further developments are needed in the numerical model to allow the inclusion of lateral heat losses that might have been present in the experiments. Only after the inclusion of such heat loss components a definitive assessment of the relative importance of the wax deposition mechanisms can be obtained.

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