Mathematical Modeling of Wax Deposition in Oil Pipeline Systems

John A. Svendsen
Dept. of Chemical Engineering, Hydro Research Centre, N-3901 Porsgrunn, Norway

Deposition of wax on the wall of oil pipelines is often regarded as a problem since the tube diameter is reduced. Consequently, more power is needed to force the same amount of oil through the system. A mathematical model for quantitative prediction of wax deposition for each hydrocarbon component has been developed. Each component is characterized by weight fraction, heat of fusion, and melting point temperature. A model explains how a phase transition in the flow from liquid oil to waxy crystals may create a local density gradient and mass flux, which depends on the local temperature gradient. The model predicts that wax deposition can be considerably reduced even when the wall temperature is below the wax appearance point, provided the liquid/solid phase transition, expressed by the change in moles of liquid with temperature, is small at the wall temperature. Deposition as function of time has been obtained as a solution of differential equations derived from the principles of mass and energy conservation and the laws of diffusion.

Introduction

Deposition of solid material on pipe walls is frequently observed in fluid flow systems. In the North Sea for instance, where oil is transported through long pipelines, wax frequently deposits on the pipe wall and must be removed periodically, which in the long run becomes expensive. Full-scale experimental measurements of wax deposition are scarce, however, Burger et al. (1981) measured wax deposition in the Trans Alaska Pipeline and in laboratory experiments. They also referred to Hunt (1962) and Eaton and Weeter (1976) who experimentally studied wax deposition at zero heat flux conditions and concluded that no measurable wax deposition occurred.

Precipitation of wax out of solution has been studied by for example, Won (1986) and Hansen et al. (1988) who presented models for calculation of the wax appearance point (WAP) for several oils. For hydrocarbons Won (1986) presented a correlation between melting point temperature and molecular weight, which was slightly modified by Hansen et al. (1988). Won also obtained a correlation between heat of fusion and molecular weight.

Deposition can be viewed from many scientific disciplines. The objective of this article has been to focus on deposition from a multidiscipline point of view. Hence, the derived mathematical model combines the theory of phase equilibria, phase transition, thermodynamics and fluid mechanics.

Both open and closed systems have been modeled. In a closed fluid flow system, the volume of the fluid reservoir is finite, and the fluid is recirculated. This is in contrast to an open system, such as for example, a North Sea oil pipeline system, where oil enters the pipe at one end and leaves at another.

Assumptions

Conditions for wax deposition

Certain conditions must be fulfilled if wax deposition shall occur. The best known are

(a) Measurable wax deposition will occur only if the wall temperature T_1 is below the precipitation temperature T_p of the particular oil (WAP).

(b) A negative radial temperature gradient must be present in the flow. A zero gradient implies that approximately no deposition will occur.

(c) Wall friction must be so large that wax crystals can stick to the wall.

In the following it is assumed that conditions a, b, and c are fulfilled simultaneously.

Assumptions related to flow

In addition to the conditions above, the following assumptions have been made about the fluid and the flow.

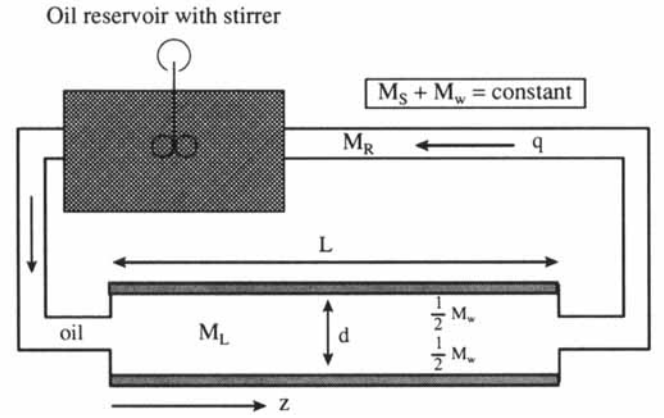

Figure 1. Wax deposition in a closed system.

Control systems are not shown, $M_S = M_L + M_R$.

- Waxy oils are non-Newtonian fluids at temperatures below the WAP and Newtonian fluids at temperatures above the WAP, Wardhaugh and Boger (1991). It is assumed that the viscosity can be adequately described by a power-law model, which is often used for non-Newtonian fluids, and that viscosity varies with temperature according to de Guzman-Andrade equation.
- Since both viscosity and wax thickness may change considerably along the pipeline, a transition from turbulent to laminar flow or vice versa is possible.
- It is further assumed that the wax/oil boundary moves so slowly that a quasi steady-state model is applicable for all rate processes concerning energy and mass.
- Heat associated with frictional heating, axial thermal diffusional and phase transitions is supposed to be negligible compared to heat of convection.

System Description

The fluid

The fluid consists of n hydrocarbon components where in the following, petroleum oil is considered. It consists of vapor, solid and liquid phase, which in equilibrium at the given temperature T and pressure P exactly defines the state and composition of the mixture. The solid phase of the mixture is referred to as wax particles or crystals. If waxy crystals stick to the inner pipe wall, wax deposition occurs. The first compounds to freeze out from a crude oil when temperature decreases are paraffins and naphthenes according to Hansen et al. (1988). It is very complicated to state exactly the flow properties of waxy oil, since the oil viscosity is both time, temperature and shear history dependent, as reported by for example, Wardhaugh and Boger (1991). When oil was cooled they observed a tenfold or more increase in the viscosity exactly at the WAP with a further increase at lower temperatures.

The closed system

An example of a closed small-scale system is shown in Figure 1. It consists of a test tube of length L with inner radius R_0. The volume of the reservoir is V_r. Oil is recirculated in the system by a pump. For wax deposition to occur the local wall temperature must be below the WAP of the particular oil. The tube wall in the test section L is therefore assumed to be kept at sufficiently low temperature. When oil flows in the tube, wax particles move radially towards the wall by diffusion and eventually deposit on the wall. Wax deposition is assumed to take place only on the wall on the test tube of length L. Control systems are not shown in Figure 1.

Solid/liquid Equilibrium

Won (1986) and later Hansen et al. (1988) used the following expression for the K values to determine the equilibrium state between the solid and liquid phase for a mixture of n hydrocarbon components:

$$K_i = \frac{s_i}{x_i} = \frac{\gamma_{xi}}{\gamma_{si}} \exp\left[\frac{\Delta H_{fi}}{RT}\left(1 - \frac{T}{T_{fi}}\right)\right], \quad i = 1,2, \ldots, n \quad (1)$$

For component i, the equilibrium constant is K_i, and the mole fractions in the solid and the liquid phase are respectively s_i and x_i, with activity coefficients γ_{si} and γ_{xi}. The heat of fusion is ΔH_{fi}, and R is the gas constant. Furthermore, T is the local temperature, while T_{fi} is the melting point temperature of component i.

A rigorous treatment of the equilibrium state must also include the gas phase. In that case a three-phase flash calculation must be performed. The vapor/liquid equilibrium constant G_i is expressed by the relation:

$$G_i = \frac{y_i}{x_i}, \quad i = 1,2, \ldots, n \quad (2)$$

where y_i is the mole fraction of component i in the vapor phase. Let the number of moles in the vapor phase, the liquid phase and the solid phase in one mole of feed be L_y, L_x, and L_s respectively, where L_x, L_y and L_s each holds a value between zero and one. The mole fraction of component i in the mixture is:

$$z_i = L_y y_i + L_x x_i + L_s s_i, \quad i = 1,2, \ldots, n \quad (3)$$

where

$$L_y + L_x + L_s = 1 \quad (4)$$

One way of characterizing the mixture is to calculate the weight fraction of each component i in the feed, w_i, where

$$w_i = \frac{z_i M_i}{\sum_{p=1}^{n} z_p M_p} \quad (5)$$

The following property yields for z_i, y_i, x_i, s_i and w_i:

$$\sum_{i=1}^{n} z_i = \sum_{i=1}^{n} y_i = \sum_{i=1}^{n} x_i = \sum_{i=1}^{n} s_i = \sum_{i=1}^{n} w_i = 1 \quad (6)$$

The weight fraction of component i which is in the solid phase is w_{ti}. It is expressed as:

$$w_{ti} = \frac{L_s s_i M_i}{z_i M_i} = \frac{\frac{L_s}{L_x} \cdot \frac{s_i}{x_i}}{1 + \frac{L_y}{L_x} \cdot \frac{y_i}{x_i} + \frac{L_s}{L_x} \cdot \frac{s_i}{x_i}} = \frac{\frac{L_s}{L_x} \cdot K_i}{1 + \frac{L_y}{L_x} \cdot G_i + \frac{L_s}{L_x} \cdot K_i} \tag{7}$$

The weight fraction of component i in the solid phase in the mixture is w_{si}, where

$$w_{si} = \frac{L_s s_i M_i}{\sum_{p=1}^{n} z_p M_p} = \frac{w_i L_s s_i M_i}{z_i M_i} = w_i w_{ti} \tag{8}$$

To illustrate the principles in a simple way, it is assumed in the following that the temperature T and the pressure P is such that the vapor phase can be neglected. This means that z_i now is the mole fraction of component i in a stabilized liquid/solid mixture. Substituting $L_y = 0$ into Eq. 7 yields:

$$w_{ti} = \frac{L_s s_i M_i}{z_i M_i} = \frac{\theta K_i}{1 + \theta K_i} \tag{9}$$

where

$$\theta = \frac{L_s}{L_x} = \frac{(1 - L_x)}{L_x} \tag{10}$$

The total weight fraction of wax crystals in the mixture, w_s, can then be expressed as a function of the K values:

$$w_s = \sum_{i=1}^{n} w_{si} = \sum_{i=1}^{n} w_i \frac{\theta K_i}{1 + \theta K_i} \tag{11a}$$

The total weight fraction of liquid in the mixture is:

$$w_x = \sum_{i=1}^{n} w_{xi} = \sum_{i=1}^{n} (w_i - w_{si}) = \sum_{i=1}^{n} \frac{w_i}{1 + \theta K_i} = 1 - w_s \tag{11b}$$

If w_{si} is large, then component i is very waxy at the given temperature T and pressure P. Notice that w_i is a mass property of the particular oil component, independent of temperature T, while w_{ti} depends on both T and P, although P does not appear explicitly in Eq. 9. The change of w_{ti} with respect to T is expressed as:

$$\frac{\partial w_{ti}}{\partial T} = \frac{K_i \frac{\partial \theta}{\partial T} + \theta \frac{\partial K_i}{\partial T}}{(1 + \theta K_i)^2} = \frac{-\left[(1 + \theta)^2 \frac{\partial L_x}{\partial T} + \theta \frac{\Delta H_{fi}}{RT^2} \right] K_i}{(1 + \theta K_i)^2} \tag{12}$$

where the ratio γ_{xi}/γ_{si} is assumed to be constant in Eq. 1. It then follows that:

$$\frac{\partial w_{si}}{\partial T} = w_i \frac{\partial w_{ti}}{\partial T} \tag{13}$$

In the section "The radial mass flux" it is shown that the wax deposition rate can be expressed as a function of the dimensionless functions σ_i, defined as:

$$\sigma_i = -T \frac{\partial w_{si}}{\partial T} = \frac{w_i \left[T(1 + \theta)^2 \frac{\partial L_x}{\partial T} + \theta \frac{\Delta H_{fi}}{RT} \right] K_i}{(1 + \theta K_i)^2} \tag{14}$$

If Eq. 10 is substituted for θ, the only unknowns in Eq. 14 are L_x and its derivative $\partial L_x/\partial T$. They are generally calculated from a three-phase flash or, in our special case, from a two-phase liquid/solid flash. Flash calculations are usually solved numerically, but an analytic solution can be obtained for a two-component mixture. Combining Eqs. 1, 3, 4 and 6, and remembering that $L_y = 0$, the analytic result for L_x is:

$$L_x = \frac{b}{a}, \quad (0 < L_x < 1) \tag{15a}$$

where

$$a = 1 + K_1 K_2 - K_1 - K_2 \tag{15b}$$

$$b = K_1 K_2 - z_1 K_2 - z_2 K_1 \tag{15c}$$

Equation 15a is valid if $K_1(K_2 - 1)/(K_2 - K_1) < z_1 < (K_2 - 1)/(K_2 - K_1)$, and $z_1 + z_2 = 1$, where $0 < K_1 < 1$ and $K_2 > 1$. The derivative of L_x with respect to T can be written:

$$\frac{\partial L_x}{\partial T} = \frac{\sum_{i=1}^{2} \{ [(b - a)K_i + (az_i - b)] \Delta H_{f3-i} K_{3-i} \}}{RT^2 a^2} \tag{16}$$

where constant z_1 and z_2 have been assumed. If V is the volume occupied by one mole of the solid/fluid mixture, a well known formula for w_s appears:

$$w_s = \frac{\frac{1}{V} \sum_{i=1}^{n} L_s s_i M_i}{\frac{1}{V} \sum_{i=1}^{n} z_i M_i} \approx \frac{\rho_s}{\rho_m} \tag{17}$$

Here, ρ_s is the mass density of the solid phase, and ρ_m is the density of the mixture. The mass density of the liquid phase is:

$$\rho_x = \rho_m - \rho_s \tag{18a}$$

For oil, ρ_m is approximately a linear function of temperature. The same model is used for ρ_w, the density of wax deposition. Hence, one may write:

$$\rho_m = a_m (T - T_r) + \rho_{ma} \tag{18b}$$

$$\rho_w = a_w (T - T_r) + \rho_{wa} \tag{18c}$$

where a_m, ρ_{ma}, a_w and ρ_{wa} must be determined experimentally for each oil, and where T_r is a reference temperature.

Correlations

Won (1986) used a correlation between T_{fi} and M_i which has been modified by Hansen et al. (1988). The modified correlation yields:

$$T_{fi} = 402.4 - 0.01896 M_i - \frac{27{,}109}{M_i} \qquad (19)$$

Hansen et al. (1988) have shown that this correlation is good for naphthenes but it does not represent the melting point of paraffins and aromatics with the same accuracy. If T_{fi} is known, an estimate of the corresponding molecular weight M_i is found when solving Eq. 19 for M_i. The result is:

$$M_i = \frac{(402.4 - T_{fi}) - \sqrt{(402.4 - T_{fi})^2 - 2{,}055.95}}{0.03792} \qquad (20)$$

The enthalpy of melting is expressed by the correlation suggested by Won (1986):

$$\Delta H_{fi} = 0.597 M_i T_{fi} \qquad (21)$$

where ΔH_{fi} is measured in J/mol in Eq. 21, while Won gives ΔH_{fi} in cal/mol and uses the constant 0.1426 instead of 0.597.

The radial mass flux

It is assumed that the radial mass flux can be expressed by Fick's law. Also, since both w_s and ρ_m depend on $T(r, z)$, the radial flux in position (r, z) can be expressed as:

$$\begin{aligned} j &= -D_m \frac{\partial \rho_x}{\partial r} \\ &= -D_m \rho_m \left[-T \frac{\partial w_s}{\partial T} + (1 - w_s) \frac{T}{\rho_m} \frac{\partial \rho_m}{\partial T} \right] \frac{1}{T} \frac{\partial T}{\partial r} \end{aligned} \qquad (22)$$

where D_m is the average diffusion constant, and where Eqs. 17 and 18a have been used in deriving Eq. 22. When Eqs. 11b and 14 are substituted into Eq. 22, the radial mass flux yields:

$$j = \sum_{i=1}^{n} j_i = -D_m \rho_m \left[\sum_{i=1}^{n} \sigma_i + (w_i - w_{si}) \frac{T}{\rho_m} \frac{\partial \rho_m}{\partial T} \right] \frac{1}{T} \frac{\partial T}{\partial r} \qquad (23)$$

or

$$j = \sum_{i=1}^{n} j_i = -D_m \rho_m \left[\sum_{i=1}^{n} \omega_i \right] \frac{1}{T} \frac{\partial T}{\partial r} = -D_m \rho_m \omega \frac{1}{T} \frac{\partial T}{\partial r} \qquad (24)$$

where

$$\omega = \sum_{i=1}^{n} \omega_i = \sum_{i=1}^{n} (\sigma_i - \epsilon_i) = \sigma - \epsilon \qquad (25)$$

The dimensionless functions ϵ_i, which are due to the change in ρ_m with temperature are expressed as:

$$\epsilon_i = -(w_i - w_{si}) \frac{T}{\rho_m} \frac{\partial \rho_m}{\partial T} = (w_i - w_{si}) T \alpha_t = \frac{w_i T \alpha_t}{1 + \theta K_i} \qquad (26)$$

where α_t is the coefficient of thermal expansion for the mixture at constant pressure, which can be calculated if a_m and ρ_{ma} are known in Eq. 18b. Since $\partial \rho_m / \partial T < 0$ for oils, ϵ_i is a positive function which reduces ω_i. The temperature where $\omega_i = 0$ is found by a numerical or graphical solution of Eq. 25. Wax deposition of component i can be inhibited if $\sigma_i \leq \epsilon_i$ is possible, or equivalently if

$$\frac{\partial w_{si}}{\partial T} \geq -(w_i - w_{si}) \alpha_t \quad \text{or } \alpha_t \geq \frac{\left[(1 + \theta)^2 \frac{\partial L_x}{\partial T} + \theta \frac{\Delta H_{fi}}{RT^2} \right] K_i}{(1 + \theta K_i)} \qquad (27a)$$

Since α_t is positive for oil, deposition of component i can be inhibited even when $\partial w_{si} / \partial T < 0$ according to inequality in Eq. 27a. Consequently, there may be a temperature interval where inequality in Eq. 27a is satisfied for some components, but not necessarily for all. In that case a radial separation of components may be possible; a result which is probably valid for liquid/solid phase transitions in general and not restricted to wax. No net deposition occurs if the total flux $j \leq 0$, which occurs if $\sigma \leq \epsilon$, or equivalently if

$$\frac{\partial w_s}{\partial T} \geq -(1 - w_s) \alpha_t \text{ or } \alpha_t \geq \frac{\displaystyle\sum_{i=1}^{n} \frac{w_i \left[(1 + \theta)^2 \frac{\partial L_x}{\partial T} + \theta \frac{\Delta H_{fi}}{RT^2} \right] K_i}{(1 + \theta K_i)^2}}{\displaystyle\sum_{i=1}^{n} \frac{w_i}{1 + \theta K_i}} \qquad (27b)$$

The limiting cases $\theta \rightarrow \infty$, $\theta \rightarrow 0$ and $\partial L_x / \partial T \approx 0$ deserve attention. Using Eq. 14 for σ_i and Eq. 26 for ϵ_i, Eq. 25 simplifies to:

$$\omega_i \approx \frac{w_i T}{K_i} \frac{\partial L_x}{\partial T}, \qquad (\text{if } \theta \rightarrow \infty) \qquad (28a)$$

$$\omega_i \approx w_i T \left(K_i \frac{\partial L_x}{\partial T} - \alpha_t \right) + \theta K_i w_i T \left[2(1 - K_i) \frac{\partial L_x}{\partial T} + \frac{\Delta H_{fi}}{RT^2} + \alpha_t \right], \quad (\text{if } \theta \rightarrow 0) \qquad (28b)$$

$$\omega_i \approx \frac{w_i T}{1 + \theta K_i} \left[\frac{\theta K_i}{(1 + \theta K_i)} \frac{\Delta H_{fi}}{RT^2} - \alpha_t \right], \qquad \left(\text{if } \frac{\partial L_x}{\partial T} \approx 0 \right) \qquad (28c)$$

$$\omega_i \approx \frac{w_i T}{\theta K_i} \left(\frac{\Delta H_{fi}}{RT^2} - \alpha_t \right), \qquad \left(\text{if } \frac{\partial L_x}{\partial T} \approx 0 \text{ and } \theta K_i >> 1 \right) \qquad (28d)$$

$$\omega_i \approx w_i T \left(\frac{\theta K_i \Delta H_{fi}}{RT^2} - \alpha_t \right), \qquad \left(\text{if } \frac{\partial L_x}{\partial T} \approx 0 \text{ and } \theta K_i << 1 \right) \qquad (28e)$$

The ω function related to phase transitions plays very much the same role as the thermal diffusion ratio k_T which appears in the theory of thermal separation processes where no phase transition takes place. Equation 24 is consistent with the conclusion that no measurable deposition occurs at zero heat flux as mentioned in assumption b earlier. If the θ term in Eq. 28b is negligible, the flux j_i becomes:

$$j_i \approx -D_m\rho_m w_i\left(K_i\frac{\partial L_x}{\partial T}-\alpha_t\right)\frac{\partial T}{\partial r},\quad \left(\text{if } T<T_p \text{ and } \theta\approx 0\right) \tag{29a}$$

where no deposition of component i occurs ($j_i\leq 0$) if $\theta\approx 0$ and $\partial L_x/\partial T<\alpha_t/K_t$. If θ is exactly zero, then $\partial L_x/\partial T=0$ and

$$j_i = D_m\rho_m w_i\alpha_t\frac{\partial T}{\partial r},\qquad (\text{if } T\geq T_p\text{, that is, } \theta=0) \tag{29b}$$

Since $\alpha_t>0$ and $\partial T/\partial r<0$, every flux j_i is negative in Eq. 29b, and the wax deposition starts dissolving into the liquid flow if $\theta=0$, in agreement with assumption (a) in the beginning. Whether Eq. 29b holds good must be determined experimentally. When $\theta>0$, any possible negative fluxes j or j_i are generally found from investigation of Eq. 25 or Eq. 27a and 27b. Examples of ω_i-functions are shown graphically and discussed further in the section "Computer Simulations and Discussion."

Burger et al. (1981) reported that Nathan (1955) started with the formula of Wilke and Chang

$$D_m = 7.4\times 10^{-8}\,\frac{T(\Psi M)^{1/2}}{\mu V^{0.6}} \tag{30a}$$

and found that $V^{0.6}$ was proportional to T. Here, D_m is in cm^2/s, μ is in 10^{-3} Pas and V in cm^3/mol. Since both the association parameter Ψ and the molecular weight M are constants, D_m was expressed as:

$$D_m = \frac{C_1}{\mu} \tag{30b}$$

where C_1 is a constant to be determined for each oil, and u is the dynamic viscosity of the mixture. For the oil studied by Burger et al. $C_1 = 2.4\times 10^{-12}\,N$, when D_m is in m^2/s, and μ is in Pas. The viscosity μ depends strongly on temperature. One correlation which is often used for μ is the de Guzman-Andrade equation:

$$\mu = A\cdot\exp(B/T) \tag{31}$$

where A and B are constants to be determined for each oil.

Determination of wax weight fraction as function of z

The weight fraction w_i as function of distance from inlet, z can be determined from a mass balance on a pipe segment between z and $z+\Delta z$, where z is an arbitrary position in the pipe. The mass flow rate of each component i in the position z at time t is $\rho_i\,(z,\,t)q$ where q is the volumetric oil flow rate, assumed to be approximately constant. The mass balance for component i over Δz is:

$$\rho_i(z+\Delta z,\,t)q-\rho_i(z,\,t)q = -2\pi R_w j_i\Delta z \tag{32}$$

where R_w and j_i are both functions of z and t. After division with Δz and taking the limit $\Delta z\rightarrow 0$, one obtains:

$$\frac{\partial\rho_i}{\partial z} = \frac{-2\pi R_w j_i}{q} \tag{33}$$

Also the density of the mixture has changed from z to $z+\Delta z$. This is expressed as:

$$\rho_m(z+\Delta z,\,t) = \rho_m(z,t) - \sum_{i=1}^{n}\frac{2\pi R_w j_i\Delta z}{q} \tag{34}$$

The weight fraction of wax in position $z+\Delta z$ then yields:

$$w_i(z+\Delta z,\,t) = \frac{\rho_i(z+\Delta z,\,t)}{\rho_m(z+\Delta z,\,t)} = \frac{\rho_i(z,\,t)-\dfrac{2\pi R_w j_i\Delta z}{q}}{\rho_m(z,\,t)-\displaystyle\sum_{p=1}^{n}\frac{2\pi R_w j_p\Delta z}{q}} \tag{35}$$

which can be written:

$$w_i(z+\Delta z,\,t) = \frac{w_i(z,t)-\dfrac{2\pi R_w j_i\Delta z}{q\rho_m}}{1-\displaystyle\sum_{p=1}^{n}\frac{2\pi R_w j_p\Delta z}{q\rho_m}} \tag{36}$$

where the substitution $\rho_i(z,\,t) = w_i(z,\,t)\rho_m(z,t)$ has been used. The overall weight fraction of wax in position z at time t is:

$$w_s(z,t) = \sum_{i=1}^{n} w_{si}(z,t) = \sum_{i=1}^{n} w_i(z,t)\,w_{ti}(z,t) \tag{37}$$

Closed and open systems

It is necessary to discriminate between closed and open systems because the inlet weight fractions $w_i(0,\,t)$ are different in these two kinds of systems. In an open system $w_i(0,\,t)$ is constant since fresh oil always appears at the inlet. In a closed system where the oil is recirculated, $w_i(0,\,t)$ will decrease in the feed at every next return to the inlet if deposition occurs ($j_i>0$) in the test tube of length L. The inlet weight fraction $w_i(0,\,t)$ is now calculated for both closed and open systems.

Closed systems

The total mass of moving wax crystals in the closed system is $M_s=M_L+M_R$, where M_L is the mass contained in the test section, and M_R is the remainder, both observed at time t, as shown in Figure 1. The global mass balance yields:

$$M_s = w_{s0}\rho_{ma}V_r - M_w \tag{38}$$

where $\rho_{ma}V_r$ is the initial total mass of the mixture in the whole system, and w_{s0} is the initial wax weight fraction:

$$w_{s0} = \sum_{i=1}^{n} w_{i0}w_{ti0} \tag{39}$$

which depends on temperature T. To estimate the maximum wax deposition that can occur in a closed system the lowest temperature in the system should be substituted for T in Eq. 7. In many cases this is the inner pipe wall temperature T_1.

The mass of deposited wax at time t is M_w, the sum of the contribution from each component i, and yields:

$$M_w=\sum_{i=1}^{n}M_{wi} \tag{40}$$

which leads to a definition of the average weight fraction w_{sa} of moving wax crystals in the closed system at time t:

$$w_{sa}=\frac{M_s}{\rho_{ma}V_r}=w_{s0}-\frac{M_w}{\rho_{ma}V_r} \tag{41}$$

Since $w_{sa}\geq 0$, the maximum wax deposition that can occur is:

$$M_{w\infty}\leq w_{s0}\rho_{ma}V_r \tag{42}$$

If V_r is very large compared to M_w/ρ_{ma}, then w_{sa} is nearly independent of time t. Therefore, a closed system approaches an open system if $V_r\rightarrow\infty$ which implies that w_{sa} is constant and equal to w_{s0} in open systems. The inlet weight fraction of wax in a closed system, as shown in Figure 1, is given by:

$$w_s(0,t)=w_{s0}, \qquad t<t_r \tag{43a}$$

$$w_s(0,\ t)=w_s(L,\ t-t_r), \qquad t\geq t_r \tag{43b}$$

where t_r is the residence time in the system from the pipe outlet back to the inlet. It is expressed as:

$$t_r=\frac{V_r}{q}-\frac{L}{v} \tag{44}$$

It is required that the time step Δt in the simulation is less than or equal to t_r to obtain a very accurate calculation of $M_w(t)$. In that case $w_s(0,\ t)$ is calculated from Eqs. 43a-b. If however, $\Delta t>t_r$ has been chosen to reduce computer time, one can approximate $w_s(0,\ t)$ with $w_s(0,\ t)\approx w_{sa}(t)$, where $w_{sa}(t)$ is given by Eq. 41, but at the expense of some loss of accuracy. In both cases $w_s(z,\ t)$, for $z>0$, is calculated from Eq. 37.

Open systems

Since the inlet wax fraction by weight in an open system is constant, given steady-state conditions, it follows that:

$$w_s(0,\ t)=w_{s0}\quad \text{(constant)} \tag{45}$$

Calculation of Deposition and Wax Thickness

Let $M_w(z,\ t)$ be the total amount of deposition at time t on the distance from the inlet $z=0$ to $z=z$. This is expressed as:

$$M_w(t,\ z)=\sum_{i=1}^{n}M_{wi}(t,\ z)=\sum_{i=1}^{n}2\pi\int_0^t\int_0^z R_wj_i dz dt \tag{46}$$

The increase in amount of deposition per m pipeline at time t is $\partial M_w/\partial z$. It is the derivative of Eq. 46 and yields:

$$\frac{\partial M_w}{\partial z}=\sum_{i=1}^{n}\frac{\partial M_{wi}}{\partial z}=\sum_{i=1}^{n}2\pi\int_0^t R_wj_i dt \tag{47}$$

It is also possible to express $\partial M_w/\partial z$ at time t as:

$$\frac{\partial M_w}{\partial z}=\frac{\partial M_w}{\partial z}\bigg|_{t-\Delta t}+\pi(R_w^2|_{t-\Delta t}-R_w^2)\rho_w \tag{48a}$$

where ρ_w is given by Eq. 18c using wax temperature $T=T(R_w,\ z)$. If the average wax density ρ_{wa} is substituted for ρ_w, Eq. 48a simplifies to:

$$\frac{\partial M_w}{\partial z}=\pi(R_0^2-R_w^2)\rho_{wa} \tag{48b}$$

The solid wax deposition is somewhat compressed, so $\rho_w>\rho_m$. Solving Eq. 48a for $R_w(z,\ t)$ yields:

$$R_w=\left[R_w^2|_{t-\Delta t}-\frac{1}{\pi\rho_w}\left(\frac{\partial M_w}{\partial z}-\frac{\partial M_w}{\partial z}\bigg|_{t-\Delta t}\right)\right]^{1/2} \tag{49a}$$

which becomes:

$$R_w=\left(R_0^2-\frac{1}{\pi\rho_{wa}}\frac{\partial M_w}{\partial z}\right)^{1/2} \tag{49b}$$

If ρ_{wa} is used. The corresponding wax thickness $h(z,\ t)$ is calculated from

$$h=R_0-R_w \tag{50}$$

Since R_w depends on $\partial M_w/\partial z$, Eq. 47 is an implicit integral equation and will be solved numerically. The total deposition rate is the derivative of Eq. 46 and yields:

$$\frac{dM_w}{dt}=\sum_{i=1}^{n}\frac{dM_{wi}}{dt}=\sum_{i=1}^{n}2\pi\int_0^L R_wj_i dz \tag{51}$$

To calculate j, the temperature gradient $\partial T/\partial r$ at the wall must be known. It is therefore necessary to derive the temperature distribution in the flow.

Temperature Distribution

The oil flow temperature distribution $T(r,\ z)$ depends on the velocity profile $v_z(r)$. In the following it is assumed that the system is operating at approximately steady-state thermal conditions.

Velocity profiles

The temperature distribution $T(r,\ z)$ is derived for a steady-state, laminar, non-Newtonian power-law flow with velocity profile $v_z(r)$ expressed as:

$$v_z(r)=\frac{m+3}{m+1}\,v\left[1-\left(\frac{r}{R_w}\right)^{(m+1)}\right]$$

$$=v_{\max}\left[1-\left(\frac{r}{R_w}\right)^{(m+1)}\right] \tag{52}$$

where $v_{\max}$ is the maximum velocity. For a Newtonian fluid $m=1$. If frictional heating and axial thermal diffusion can be ignored, the energy equation to be solved is:

$$v_z(r)\,\frac{\partial T}{\partial z}=\alpha\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{q_h}{k}\right) \tag{53}$$

where $\alpha=k/\rho_{ma}c_p$ is the thermal diffusivity of the fluid with thermal conductivity k and specific heat capacity c_p, and q_h is a heat source term associated with phase transition from the liquid to the solid state. It is assumed in the following that q_h is so small compared to heat of convection that it can be neglected. At least that should be the case when the temperature of the flow is so high that $L_x >> L_s$.

Constant temperature at the boundary

Assume that the physical inner steel pipe wall (not the wax deposition/fluid interface) is kept at approximately constant temperature T_1. In that case the boundary conditions are

$$T(R_0, z)=T_1 \text{ (constant)}, \qquad z>0 \tag{54a}$$

$$T(0, z)=\text{finite}, \qquad z\geq 0 \tag{54b}$$

This may be a good approximation when the tube is clean, that is, free of deposition ($R_w=R_0$). If the thermal conductivities, k, of wax and oil are approximately equal, then Eq. 54a may hold good even after deposition has started. That situation is discussed further in the section "Computer Simulations and Discussion." The initial condition of the problem is stated as:

$$T(r, 0)=T_0 \text{ (constant)}, \qquad 0\leq r\leq R_0 \tag{55}$$

For the given conditions the analytical series solution of Eq. 53 is reported by several authors, for example, Lyche and Bird (1956), but will not be repeated here.

Solution for small values of z

A practical solution for $T(r, z)$ when z is small is described by Pigford (1955) and Bird et al. (1976). It is repeated here since it is used in the section "Computer Simulations and Discussion" at the end of this article. The solution is valid if the Graetz number $Gz = \rho_{ma}qc_p/kL$ is large, that is, if heat convection is much larger than heat conduction and yields:

$$T(r, z)=T_0+\frac{T_1-T_0}{\Gamma(4/3)}\int_\eta^\infty \exp(-\eta^3)d\eta \tag{56}$$

where

$$\eta=\frac{R_0-r}{\sqrt[3]{9\beta z}}, \qquad \beta=\frac{\alpha R_0}{2v_{\max}}, \qquad \Gamma(4/3)=0.893 \tag{57}$$

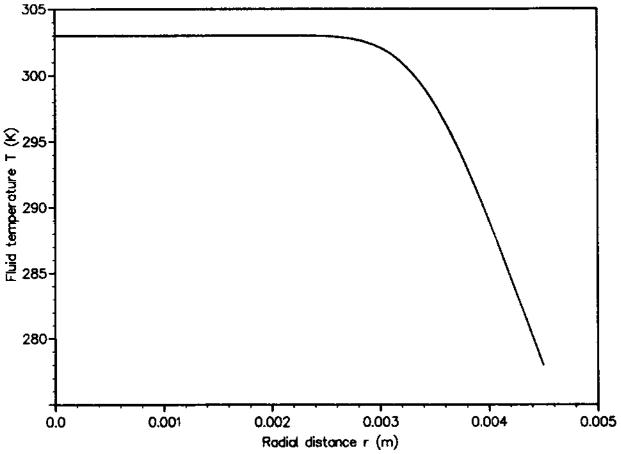

Figure 2. Fluid temperature as function of radial distance at $z=0.5$ m.

Input data from Table 1, small-scale closed system.

The temperature gradient in position (r, z) is then

$$\frac{\partial T}{\partial r}=\frac{T_1-T_0}{\Gamma(4/3)}\frac{1}{\sqrt[3]{9\beta z}}\exp(-\eta^3), \qquad z\neq 0 \tag{58}$$

An example of a radial temperature distribution in a small-scale closed system is shown in Figure 2 based on Eq. 56 for $m=1$, that is, laminar, Newtonian flow. The length of the tube is only $L=1.0$ m, which justifies the use of Eq. 56.

Mixed boundary condition

If the heat-transfer coefficient u between the inner wall and ambient is known, a commonly used boundary condition is:

$$\frac{\partial T}{\partial r}=-\frac{u}{k}\,[T(R_0, z)-T_a], \quad \text{at } (R_0, z) \tag{59}$$

where T_a is a constant ambient temperature. The solution of the problem for a laminar power-law fluid has been obtained by for example, Schenk et Laar (1958) for constant $R_w = R_0$. The general solution is not very practical. However, the solution of the special case $m = \infty$ in Eq. 52, that is, plug flow, can be expressed by Bessel functions as shown in for example, Carslaw and Jaeger (1959) or Crank (1989). A brief summary of the plug flow problem is shown in the following. If the initial condition is expressed by Eq. 55, the solution of Eq. 53 with $q_h=0$ is:

$$T(r, z)=T_a+2(T_0-T_a)\sum_{p=1}^{\infty}$$

$$\times\frac{BiJ_0(\lambda_p r)}{[\lambda_p^2R_0^2+Bi^2]J_0(\lambda_p R_0)}\exp(-\alpha\lambda_p^2 z/v) \tag{60}$$

where $Bi = uR_0/k$ is the Biot number and the eigenvalues λ_p, $p = 1, 2, \ldots, \infty$, are the solutions of

$$\frac{\lambda_p R_0}{Bi} = \frac{J_0(\lambda_p R_0)}{J_1(\lambda_p R_0)}, \quad p = 1, 2, \ldots, \infty \tag{61}$$

Initially $R_w = R_0$, but since R_w decreases with time the λ_ps should be updated regularly, unless $T(r, z)$ is only slightly changed when deposition occurs. The corresponding temperature gradient at a point (r, z) is:

$$\frac{\partial T}{\partial r} = -2(T_0 - T_a)\sum_{p=1}^{\infty} \times \frac{\lambda_p Bi J_1(\lambda_p r)}{[\lambda_p^2 R_0^2 + Bi^2] J_0(\lambda_p R_0)} \exp(-\alpha \lambda_p^2 z/v) \tag{62}$$

If R_w/R_0 is not close to one, then u is a function of $h(z)$. Equations 59 to 62 are valid for constant R_0, but at regular time intervals one should substitute R_0 with R_w. In that case the thermal conductivity k of wax must be known, which is probably close to that of oil as explained later. When deposition occurs, the flow velocity v increases, which makes $T(r, z)$ actually time dependent. How to obtain a quasi time dependent solution for $T(r, z, t)$ is shown in the next section.

Table 1. Input to the Two Examples

Parameter		Example 1	Example 2
t_s	(h)	80	720
Δt	(s)	140	3,600
Δz	(m)	0.02	100
L	(m)	1.0	5,000
R_0	(m)	$4.5 \cdot 10^{-3}$	0.15
V_r	(m^3)	$2.0 \cdot 10^{-3}$	∞
q	(m^3/h)	0.05	500
Re		193	57,970
m		1	∞
A	(Pa·s)	$1.056 \cdot 10^{-7}$	$1.056 \cdot 10^{-7}$
B	(K)	3,429.5	3,429.5
a_m	($kg/m^3 \cdot K$)	−0.65	−0.65
ρ_{ma}	(kg/m^3)	855	855
a_w	($kg/m^3 \cdot K$)	−0.5	−0.5
ρ_{wa}	(kg/m^3)	885	885
M_1	(kg/kmol)	215	215
M_2	(kg/kmol)	530	530
w_1		0.85	0.85
w_2		0.15	0.15
T_0	(K)	303	303
T_1	(K)	278	278
T_r	(K)	293	293
k	(W/m·K)	0.134	0.134
c_p	(J/kg·K)	1,920	1,920
T_{f1}	(K)	272	272
T_{f2}	(K)	341	341
ΔH_{f1}	(kJ/mol)	34.9	34.9
ΔH_{f2}	(kJ/mol)	107.8	107.8

Numerical Solution

The analytical solution for $\partial T/\partial r$ for the steady-state case is expressed by either Eq. 58 or 62, depending on the choice of method, and the mass flux j is expressed by Eq. 24. However, since R_w decreases with time so will w_s, because the surface temperature $T(R_w, z)$ of the solid wax deposition increases when R_w decreases.

It is hard to obtain a time-dependent analytic solution for $M_w(t)$. Therefore, a combination of analytical and numerical methods is proposed in this article to derive an approximate solution of the problem.

The following scheme is used:

(1) Choose a reasonable time step Δt and length step Δz.

(2) Determine the constants and parameters in Table 1 and initialize variables and parameters.

(3) Increment time $t = t + \Delta t$.

(4) Increment position $z = z + \Delta z$.

(5) Calculate $T(r, z)$ and $\partial T/\partial r$ using $r = R_w(z)$.

(6) Calculate L_x and $\partial L_x/\partial T$.

(7) For each component determine j_i from Eq. 23 or 24.

(8) Update $\partial M_{wi}/\partial z$ for each component from Eq. 47, that is,

$$\frac{\partial M_{wi}(t+\Delta t, z)}{\partial z} = \frac{\partial M_{wi}(t, z)}{\partial z} + 2\pi \int_t^{t+\Delta t} R_w(z, t) j_i(z, t)\, dt.$$

(9) Update $w_{si}(z + \Delta z, t)$ from Eq. 37.

(10) Update $R_w(z)$ from Eq. 49 and $h(z)$ from Eq. 50.

(11) Go to (4) if $z < L$, otherwise,

(12) Calculate the mass of deposited wax for each component along the pipe at time $t + \Delta t$

$$M_{wi}(t+\Delta t) = M_{wi}(t) + \int_0^L \frac{\partial M_{wi}(t+\Delta t, z)}{\partial z}\, dz$$

from Eqs. 46 and 47.

(13) Calculate the total amount of wax on the wall at time $t + \Delta t$

$$M_w(t+\Delta t) = \sum_{i=1}^{n} M_{wi}(t+\Delta t).$$

(14) The amount of deposition per square meter clean wall surface is

$$m_w(t+\Delta t) = M_w(t+\Delta t)/A_0, \text{ where } A_0 = 2\pi R_0 L.$$

(15) If the system is closed calculate $w_s(0, t)$ from Eqs. 43a and 43b.

(16) Go to (3) until $t > t_s$, where t_s is the length of the simulation.

Computer Simulations and Discussion

The theory presented requires a lot of input data, ranging from fluid composition, equilibrium data, flow properties and thermal data. It has not been possible to compare the theory directly with experiments reported in the literature, because the theory introduces so many parameters and variables which have not been measured simultaneously. However, the theory matches the qualitative experimental facts as mentioned in the "Assumptions" section earlier.

Two cases, with input from Table 1, have been simulated on a VAX-6410 computer with constant wall temperature as a boundary condition for the temperature distribution. The initial temperature distribution $T(r, z)$ can be used even when deposition takes place if the thermal conductivity, k, is approximately the same for oil and wax. That is probably the case if the wax deposition is very porous with pore spaces filled with liquid oil, as suggested by Burger et al. (1981). Consequently, the solid wax surface temperature is calculated from $T(r, z)$ using $r = R_w$. If, however, the thermal conductivity of the deposition is very different from that of oil, one can use the boundary conditions for $T(r, z)$, as defined by Eq. 59, to account for the wax deposition layer and the thermal conductivity of the pipe wall when the heat-transfer coefficient u is calculated. Petroleum oil is a mixture of many components, but for the sake of simplicity only two pseudo hydrocarbon components have been used in the simulations to demonstrate the principles. Their molecular weights are $M_1 = 215$ kg/kmol and $M_2 = 530$ kg/kmol respectively. From Table 1 the heat of fusion is $\Delta H_{f1} = 34.9$ kJ/mol and $\Delta H_{f2} = 107.8$ kJ/mol, and the melting temperatures are $T_{f1} = 272$ K and $T_{f2} = 341$ K. The physical properties k, ρ_m and μ are data for "BP Transcal LT" oil, VDI-Wärmeatlas (1988, page Dd 25) and that oil was chosen rather arbitrarily. The parameters A and B of Eq. 31 were estimated based on these tabulated values for μ. In this example μ is independent of shear rate. Consequently, it is implicitly assumed that the fluid is Newtonian, which is not necessarily correct at all positions along the pipe.

The ω_i-functions for this mixture, defined by Eq. 25, are plotted as function of temperature in Figure 3, assuming $\gamma_{xi}/\gamma_{si} \approx 1$ for both components in Eq. 1. In our case $\alpha_t \approx -a_m/\rho_{ma} = 7.6 \cdot 10^{-4}$ K^{-1} is too small to obtain any $\omega_i \leq 0$, so both components move towards the wall. The ω_i-functions depend on L_x and $\partial L_x/\partial T$, which are plotted in Figures 4 and 5, where the solid line represents the temperature interval 278 K $\leq T \leq$ 303 K. The local temperature of the oil flow is within that interval in the simulations. Notice that the lightest component contributes more to the deposition rate than the heaviest component in that temperature interval. This is because the weight fraction of component 1 is much higher than that of component 2, and also because component 1 precipitates easier out of solution than component 2 at these temperatures which follows from Eqs. 12-14 and Figure 3.

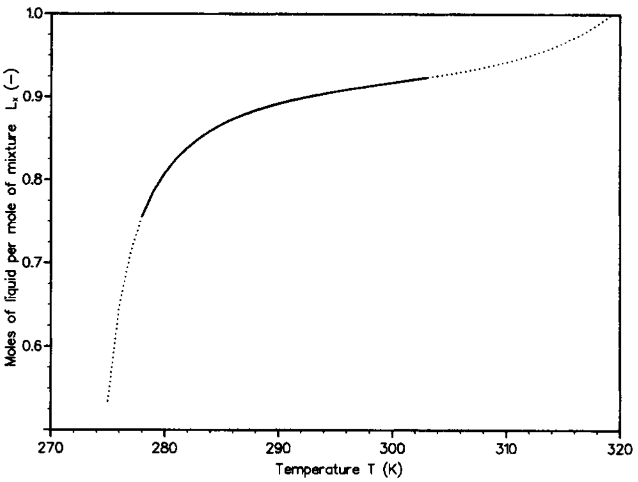

Figure 4. L_x as function of temperature for the two-component mixture.

The K_2 values vary strongly with temperature. In our example $K_2 \approx 5{,}600$ at $T = 278$ K, but only $K_2 \approx 23$ at $T = 315$ K. On the other hand, K_1 is confined to the small interval $0 < K_1 < 1$. This big difference between K_1 and K_2 implies that $\omega_1 >> \omega_2$ at low temperatures as explained from Eq. 28a. Hence, ω_i and $\partial L_x/\partial T$ are proportional at low temperatures, which implies that ω_1 and $\partial L_x/\partial T$ have similar shape at low temperatures, as shown by comparison of Figures 3 and 5. Also ω_2 is then proportional to $\partial L_x/\partial T$, but $w_2 T/K_2 << 1$, since $K_2 >> w_2 T$ in Eq. 28a. Hence, ω_2 is negligible at low temperatures. Figure 5 shows that $\partial L_x/\partial T$ is small in the temperature interval 292 K $< T <$ 303 K. In that case both ω_1 and ω_2 are small, as shown in Figure 3 and explained from Eqs. 28c, d and e. Consequently, if the wall temperature is about 300 K in our case, wax deposition can be considerably reduced even if $T < T_p$, provided that $\partial T/\partial r$ is small or moderate. When $\theta \rightarrow 0$ then $\omega_2 > \omega_1$, as shown in Figure 3. This can for instance be explained from Eq. 28b with $\theta = 0$, and knowing that $w_2 K_2 > w_1 K_1$. When $T > 319$ K, the mixture is completely in the liquid phase, that is, $L_x = 1$, as shown in Figure 4. Hence, $T_p = 319$ K is the Wax Appearance Point (WAP) of the mixture. At temperatures

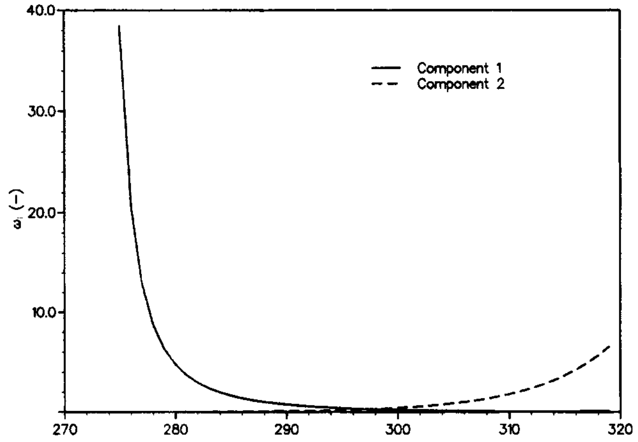

Figure 3. ω_i functions for the two components in Table 1.

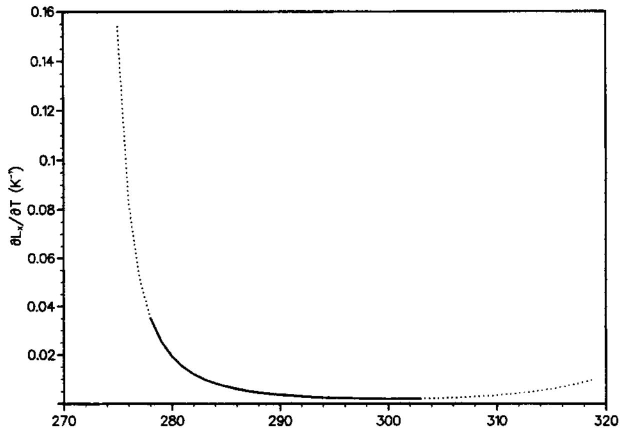

Figure 5. $\partial L_x/\partial T$ as function of T for the two-component mixture.

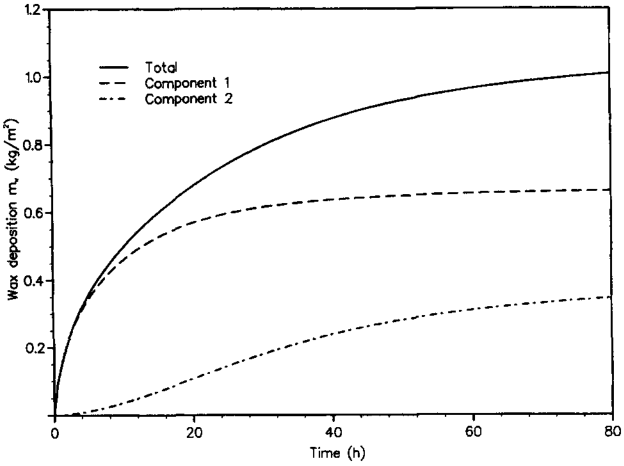

Figure 6. Wax deposition in a small-scale closed system.

Data from Table 1.

above the WAP, ω_i and j_i are both negative and no deposition occurs according to Eq. 29b. Instead, the wax deposition begins to dissolve into the oil flow.

Example 1: Deposition in a small-scaled closed system

In Figure 6 is shown an example of predicted wax deposition as function of time in a narrow and short test tube for a closed system with a modest reservoir of size V_r, as shown in Figure 1. Deposition occurs only in the test tube, since it is assumed that the inner wall of the rest of the system is kept at a temperature above the wax precipitation temperature. The inner steel wall temperature T_1 is assumed to be almost constant, which is obtained by water-cooling of the outer wall. When $z<0.1$ m the step $\Delta z=0.005$ m, but otherwise $\Delta z=0.02$ m. The Reynolds number $\rho_m v d/\mu$ depends on temperature. It is assumed here that the fluid is Newtonian, but if the power-law parameters are known for the particular oil, the fluid should be modeled as non-Newtonian. From Table 1, $Re=193$ is calculated at $T=303$ K for initial v and $R_w=R_0$. Hence, the flow is laminar with $m=1$ (Hagen-Poiseuille flow). The length of the simulation is 80 hours. Deposition as function of time is shown in Figure 6, and the wax thickness after 80 hours is shown in Figure 7 with a maximum thickness of about 1.6 mm. The temperature distribution is calculated from Eq. 56 which is valid for short tubes if the Graetz number $Gz=\rho_{ma}qc_p/kL$ is large. In our case $Gz=170$, which is decided to be sufficiently large. In the first hours the wax deposition is entirely due to the lightest component, as shown in Figure 6. This is because the temperature of the deposition/fluid interface $T(R_w, z)$ is low, that is, close to $T_1=278$ K. At that temperature ω_1 is much larger than ω_2, as shown in Figure 3. Hence, j_1 is much larger than j_2. When $T(R_w, z)$ increases due to increasing h, ω_2 becomes comparable with ω_1. After about 30 hours $T(R_w, z)$ is so high that j_1 is almost negligible. From Figure 3 it is seen that ω_2 dominates over ω_1 at $T>298$ K.

Example 2: Deposition in a large-scale open system

It is assumed that the system is open ($V_r=\infty$), and that the oil composition is the same as in Example 1. The length and diameter of the pipe have been increased and correspond to an oil pipeline with a reasonable flow rate.

To simulate constant wall temperature $u=\infty$ has been chosen in Eq. 59, which implies $T_1\approx T_a$. This situation corresponds to an uninsulated pipe, therefore representing a worst case (large deposition), and has been chosen for that reason. The flow is turbulent with initial $Re=57{,}970$. To simulate plug flow, $m=\infty$ is used in the velocity profile. Since the system is open, the weight fraction of wax at the pipe inlet, w_{s0}, can be regarded as constant. Other temperature distributions valid for turbulent flow may of course be used.

Deposition as function of time is shown in Figure 8, and the wax thickness as function of position z, after 30 days of deposition, is shown in Figure 9. There is no deposition at $z=0$ due to the initial condition $T(r, 0)=T_0$ for $0\le r\le R_0$, which implies $\partial T/\partial r=0$ at the pipe inlet. In this example $\Delta z=25$ m when $z<500$ m, and $\Delta z=100$ m when $z>500$ m. The maximum wax thickness of about 5 mm appears at $z\approx 700$ m.

It is the lightest component which contributes almost entirely to the deposition in this example, because the temperature of

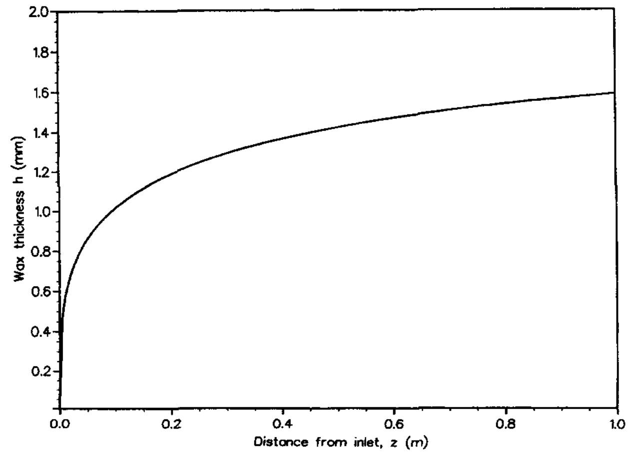

Figure 7. Wax thickness distribution in the small-scale closed system.

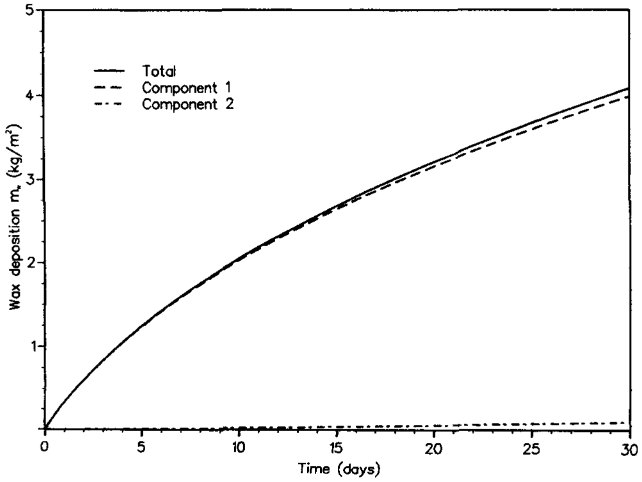

Figure 8. Wax deposition in a large-scale open system.

Data from Table 1.

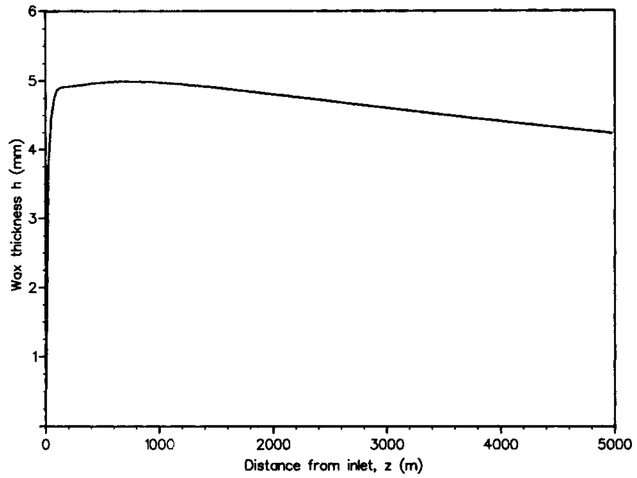

Figure 9. Wax thickness distribution in the large-scale open system.

the deposition/fluid interface is close to $T_1 = 278$ K, since h is small compared to R_0.

Conclusions

A mathematical model for prediction of wax deposition in both open and closed pipeline systems has been developed using a combination of analytical and numerical methods. The model includes several scientific disciplines such as phase equilibria, phase transition and fluid dynamics.

It is known from published experiments that measurable wax deposition will occur if the wall temperature is below the precipitation temperature of the particular oil (WAP) and if simultaneously there is a negative radial temperature gradient present in the flow. The amount of deposition also depends on the oil composition. The model is consistent with these experimental observations.

In any case the model predicts that wax deposition can be considerably reduced even when the wall temperature is below the WAP, provided the liquid/solid phase transition expressed by the change in moles of liquid with temperature, $\partial L_x/\partial T$, is small at the wall temperature.

If, in addition, the coefficient of thermal expansion, α_t, is sufficiently large, some components may separate and move in opposite radial directions at temperatures below the WAP. If a separator of that kind works, it can probably be used in other industrial processes as well.

The proposed combined phase-transition and mass-flux model is perhaps quite generally valid and not restricted to oil and wax. Whether the derived theoretical results hold good must be determined experimentally.

Notation

a = help variable
a_m = parameter in oil density model (kg/m^3·K)
a_w = parameter in wax density model (kg/m^3·K)
A = first parameter in viscosity equation (Pa·s)
A_0 = surface area of clean inner pipe wall (m^2)
b = help variable
B = second parameter in viscosity equation (K)
Bi = Biot number, $Bi = uR_0/k$
C_1 = parameter in diffusion constant model (N)
c_p = specific heat capacity of the mixture (J/kg·K)
d = inner diameter of the tube (m)
D_m = diffusion constant (m^2/s), but (cm^2/s) in Eq. 30a
h = wax thickness (m)
G = gas/liquid equilibrium constant
Gz = Graetz number, $Gz = \rho_m q c_p/kL$
ΔH_f = heat of fusion (J/mol)
j = mass flux of wax (kg/s·m^2)
k = thermal conductivity of the mixture (W/m·K)
k_T = thermal diffusion ratio
K = liquid/solid equilibrium constant
L = tube length (m)
L_x = number of moles in liquid phase per mole mixture
L_y = number of moles in gas phase per mole mixture
L_s = number of moles in solid phase per mole mixture
m = parameter in power-law flow model
m_w = wax deposition per m^2 clean wall at time of measuring (kg/m^2)
M_i = molecular weight of component i (kg/kmol)
M_L = mass of wax crystals which flow in the test tube of length L at time of measuring (kg)
M_R = mass of wax crystals which flow outside the tube of length L at time of measuring (kg)
M_S = mass of wax crystals which flow in the whole closed system at time of measuring (kg)
M_w = mass of wax deposit on the tube wall at time of measuring (kg)
n = number of components
P = pressure (N/m^2)
q = volumetric flow rate (m^3/s)
q_h = heat source (J/s·m^3)
r = radial distance (m)
R = gas constant = 8.3143 (J/mol·K)
R_0 = inner radius of the clean tube (m)
Re = Reynolds number, $Re = \rho_m v d/\mu$
R_w = time dependent inner radius of the tube (m)
s_i = mole fraction in solid phase
t = time (s)
t_r = residence time in closed systems (s)
t_s = length of simulation (s)
T = temperature (K)
T_0 = tube inlet temperature (K)
T_1 = inner wall ("steel") temperature (K)
T_p = precipitation temperature of wax formation (K)
T_r = reference temperature (K)
u = heat-transfer coefficient (W/m^2·K)
v = average axial velocity (m/s)
$v_{\max}$ = maximum axial velocity (m/s)
V = molar volume of mixture (m^3)
V_r = volume of the closed system (reservoir) (m^3)
x_i = mole fraction in liquid phase
y_i = mole fraction in gas phase
z_i = mole fraction in mixture
z = distance from pipe inlet (m)
w = weight fraction
WAP = Wax Appearance Point (K)

Greek letters

α = thermal diffusivity, $\alpha = k/\rho_{ma} c_p$ (m^2/s)
α_t = coefficient of thermal expansion $= -(1/\rho_m)[(\partial \rho_m)/(\partial T)]$ (K^{-1})
β = parameter (m^2)
γ = activity coefficient
ϵ = dimensionless weight function
η = dimensionless length
θ = $(1 - L_x)/L_x$
μ = dynamic viscosity (N·s/m^2)
λ_p = eigenvalues (m^{-1})
π = 3.14159
ρ_m = density of fluid mixture (kg/m^3)
ρ_w = density of solid wax deposition (kg/m^3)
σ = dimensionless weight function
ψ = association parameter
ω = dimensionless weight function

Subscripts

a = average or ambient
f = fusion
i = component
m = mixture
p = help index
0 = initial
1 = wall
t = in solid phase
x = liquid
y = vapor
s = solid

Functions

exp = Exponential function
Γ = Gamma function
J_0 = Bessel function of first kind and order zero
J_1 = Bessel function of first kind and order one

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