# MODELLING WAX DIFFUSION IN CRUDE OILS: THE COLD FINGER DEVICE

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#### Abstract

In this paper we show how to obtain wax diffusivity and solubility in crude oils from deposition measurements in the cold finger device with stirring. We present a mathematical model in which the physical quantities are assumed to be space-independent in the bulk region of the device, because of agitation. Comparison with available laboratory results is provided, showing that the wax diffusivity values obtained in simulations are in agreement with data of field experiments.

### 1 Introduction

Waxy crude oils (WCOs) are mineral oils with high molecular weight paraffinic components (from C17 on) which below the so-called *Cloud Point* temperature (denoted by  $T_{cloud}$ ) may separate as a wax phase, causing a series of severe problems during transportation along pipelines. One of the most important is certainly the formation of a solid deposit on pipeline walls, (wax deposition). This phenomenon is of crucial importance in oil industry because it can cause the partial or total blockage of a line, causing production to decrease or halt.

Since pipeline blockage removal can be very expensive (for instance in submarine ducts) many industries are interested in having a good understanding in wax precipitation and deposition processes.

Laboratory devices like test loops or the cold finger (a thermally controllable device used to simulate deposition in static and dynamic conditions, see [3], [4], [6], [5]) are set up in order to simulate wax deposition in pipelines. They can be used both for predicting the amount of deposit under specific physical conditions and for determining the main physical parameters like solubility and diffusivity.

Wax deposition is the result of different mechanical and thermal processes which occur under specific physical conditions (for a general overview we refer the reader to [1], [2]). Here we will investigate deposition in the cold finger device (with stirring) when deposition is due only to molecular diffusion, a deposition mechanism induced by the presence of a thermal gradient in the oil (see [1]).

Of course, the phenomenon differs from the one observed in the static case (see [3], [4]). This is basically due to the fact that agitation homogenizes all the relevant physical quantities, so that temperature and concentrations can be considered uniform except for some boundary layers near the walls.

The experimental apparatus consists of a cylindrical thermostatic bath in which the oil is kept at a desired fixed temperature until a metallic probe (mantained below the cloud point) is introduced and placed at the axis of the cylinder. More precisely, the oil is initially charged in the bath and warmed over the cloud point. Then its temperature is gradually lowered to a temperature  $T_e$  which will be kept fixed throughout the experiment. At this point the cold probe (which is at temperature  $T_i < T_e$  with  $T_i < T_{cloud}$ ) is co-axially inserted in the bath. Simultaneously a mixer placed at the bottom begins to stir the oil. When the vicinity of the cold finger is saturated by wax the presence of a thermal gradient near the cold wall (in the bulk, temperature is homogeneized because of the stirring) induces a concentration gradient. The latter, by Fick's law, produces mass transfer of dissolved wax towards the cold finger, and thus deposition.

In [4] we have studied the case when the oil is static (no stirring). In that case we have observed that, in case of initial complete saturation, the system evolves through three stages: i) complete saturation, ii)

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partial desaturation, iii) complete desaturation, the second stage being characterized by the presence of a desaturation front moving from the warm wall towards the cold finger.

In the stirred case, because of homogenization, stage two cannot exist and the system evolves from complete saturation to complete desaturation. This is because in the bulk the parameters describing the wax content are independent of the radial coordinate.

In this paper we will present and analyze a mathematical model that that can be used for determining both wax diffusivity and solubility starting from deposition measurements. Conversely, the model allows to predict the amount of deposit once such parameters are known.

On the basis of available experimental data we will see that the wax diffusivity values that will be obtained are in the range of the ones usually found in the literature (derived from classical correlations).

In this conceptual model we will suppose that the following simplifying assumptions are satisfied:

- i) deposition is due only to molecular diffusion,
- ii) the saturation concentration  $C_s$  (solubility) is a linear function of temperature T. We denote by  $c_{tot}$ ,  $c_{tot}^*$ , c, G,  $T_{cloud}$  total wax concentration, initial total wax concentration, dissolved wax concentration, segregated wax concentration and cloud point respectively,
- iii) oil and wax have the same constant density  $\rho$ .

# 2 The mathematical model

We present here the mathematical model for wax deposition for the cold finger with stirring. Due to the large thermal diffusivity, we assume that an equilibrium temperature profile is reached instantaneously. The latter is characterized by a bulk zone at constant temperature  $T_b$  and two boundary layers near the walls.

The system evolves through two stages. In the first stage the deposition rate is constant and mass grows linearly with time, while in the second deposition rate tends asymptotically to zero (exponential decay).

Mass diffusion takes place in the boundary layer near the cold wall, where a thermal gradient is present. As long as the bulk remains saturated the loss of wax due to deposition is balanced by dissolution of segregated wax. When desaturation is achieved the deposition rate starts to decrease and wax concentration in the bulk tends to the saturation concentration corresponding to the cold finger temperature.

The deposit is formed by oil and wax and the wax fraction  $\phi$  is assumed to be independent of time. The value of  $\phi$  is expected to be larger than in the static device and closer to the ones found in pipeline deposits [8]. Anyway, we shall see that  $\phi$  has no influence on the final determination of wax diffusivity.

#### 2.1 The thermal profile

Let us denote by  $r = R_i$  and  $r = R_e$  the cold and warm wall radii. As stated above temperature is constant except in two boundary layers near the walls. The thickness of the boundary layers is constant and denoted by  $r_i - R_i$  (cold wall) and  $R_e - r_e$  (warm wall). The bulk temperature  $T_b$  is uniform, while in the boundary layers T has a steady profile

$$T(r) = T_i + \frac{T_b - T_i}{\ln\left(\frac{r_i}{R_i}\right)} \ln\left(\frac{r}{R_i}\right), \qquad R_i \le r \le r_i,$$
(2.1)

$$T(r) = T_e + \frac{T_b - T_e}{\ln\left(\frac{r_e}{R_e}\right)} \ln\left(\frac{r}{R_e}\right), \qquad r_e \le r \le R_e,$$
(2.2)

where  $T_i < T_e$  are the temperatures at the inner and outer wall respectively (see Fig. 1).

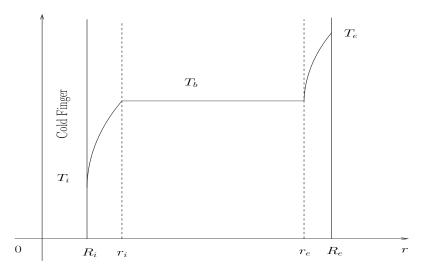


Figure 1: Geometry of the system

To evaluate the thickness of the boundary layers we consider the heat flux per unit height through the boundary layer  $R_i \le r \le r_i$ 

$$q_i = 2\pi R_i h_i (T_b - T_i), (2.3)$$

where  $h_i$  is the heat transfer coefficient at the cold wall. The flux  $q_i$  has to be equal to

$$2k\pi R_i \frac{dT}{dr}(R_i),\tag{2.4}$$

where k is thermal conductivity and dT/dr is given by

$$\frac{dT}{dr}(R_i) = \frac{T_b - T_i}{\ln\left(\frac{r_i}{R_i}\right)} \frac{1}{R_i}$$
(2.5)

Imposing (2.3) equal to (2.4) we get

$$r_i = R_i \exp\left\{\frac{k}{h_i R_i}\right\},\tag{2.6}$$

which relates the boundary layer thickness to the heat transfer coefficient  $h_i$ . In an analogous way we can show that

$$r_e = R_e \exp\left\{-\frac{k}{h_e R_e}\right\},\tag{2.7}$$

where  $h_e$  is the heat transfer coefficient at the warm wall. We may assume  $h = h_i = h_e$  where h can be computed (see [6]) using

$$h = \frac{k}{R_i^{1-m}} \left(\frac{\rho\omega(R_e - R_i)}{2\mu}\right)^m,$$
(2.8)

 $\omega$  being the rotational speed,  $\mu$  the viscosity and m = 0.628. Assuming typical values

$$\mu = 30 \ cP, \qquad \omega = 500 \ rpm, \qquad \rho = 800 \ \frac{Kg}{m^3},$$
(2.9)

$$k = 0.1 \frac{\mathrm{W}}{\mathrm{m} \cdot {}^{o} \mathrm{K}}, \qquad R_{i} = 0.05 \mathrm{m}, \qquad R_{e} = 0.12 \mathrm{m}, \qquad (2.10)$$

we get

$$h = 20 \; \frac{W}{m^2 \cdot {}^o K},\tag{2.11}$$

$$r_i - R_i = 5.3 \times 10^{-3} \text{ m},$$
 (2.12)

$$R_e - r_e = 4,9 \times 10^{-3}$$
 m. (2.13)

The bulk temperature  $T_b$  can be obtained imposing that the incoming heat flux entering  $r = R_e$  is equal to the outgoing heat flux in  $r = R_i$ , that is

$$R_i(T_b - T_i) = R_e(T_e - T_b).$$

We get

$$T_b = \frac{R_e T_e + R_i T_i}{R_e + R_i}.$$
 (2.14)

In expressions (2.1) and (2.2)  $T_b$  has to be replaced by (2.14), while  $r_i$  and  $r_e$  by (2.6) and (2.7). The complete temperature profile becomes

$$T = T_i + \frac{hR_iR_e}{k}\frac{(T_e - T_i)}{(R_e + R_i)}\ln\left(\frac{r}{R_i}\right), \qquad R_i \le r \le r_i,$$
(2.15)

$$T_b = \frac{R_e T_e + R_i T_i}{R_e + R_i}, \qquad r_i \le r \le r_e, \qquad (2.16)$$

$$T = T_e + \frac{hR_iR_e}{k}\frac{(T_e - T_i)}{(R_e + R_i)}\ln\left(\frac{r}{R_e}\right), \qquad r_e \le r \le R_e.$$
(2.17)

## 2.2 Evolution of the segregated phase and estimate of the desaturation time

We recall that we are assuming that  $C_s$  depends linearly on T (see [4] for a justification) that is

$$C_s(T) = C_s(T_i) + b_w(T - T_i).$$
(2.18)

The parameter  $b_w$  can be obtained using asymptotic mass measures. We consider the relation

$$m_{w\infty} = m_{\infty}\phi = (c_{tot}^* - C_s(T_i))\frac{(R_e^2 - R_i^2)}{2R_i},$$
(2.19)

where  $m_{\infty}$  is the asymptotic deposit (per unit surface) and  $m_{w\infty}$  is the asymptotic mass of wax in the deposit. From the knowledge of  $\phi$  and of two measures  $m_{\infty}^1$ ,  $m_{\infty}^2$  (or alternatively from  $m_{w\infty}^1$ ,  $m_{w\infty}^2$ ) relative to two different cold finger temperatures  $T_1$ ,  $T_2$ , from (2.18) and (2.19) we get

$$\frac{[m_{w\infty}^1 - m_{w\infty}^2]2R_i}{(R_e^2 - R_i^2)(T_2 - T_1)} = \phi \underbrace{\frac{[m_{\infty}^1 - m_{\infty}^2]2R_i}{(R_e^2 - R_i^2)(T_2 - T_1)}}_{=b} = \frac{C_s(T_2) - C_s(T_1)}{T_2 - T_1} = \phi b = b_w.$$
(2.20)

Notice that this formula does not contain the initial concentration  $c_{tot}^*$ .

Because of stirring, segregated wax concentration G can be considered to be spatially uniform and we shall write G = G(t). Let us suppose that the solution is initially saturated<sup>1</sup>, that is  $c_{tot}^* > C_s(T_e)$ .

The thermal gradient in the region  $R_i < r < r_i$  will induce the migration of dissolved wax towards the cold finger. When dissolved wax reaches the cold surface it segregates and adheres to the surface forming a solid deposit. At the same time G is depleted because the segregated phase is dissolved to replace the wax that has deposited.

Mass growth rate (per unit surface) at the cold wall is given by

$$\dot{m}_w = D_w b_w \left. \frac{dT}{dr} \right|_{r=R_i},\tag{2.21}$$

<sup>&</sup>lt;sup>1</sup>From experimental measures (see [3]) we know that the thickness of the deposit does not appreciably modify the geometry of the system. When dealing with G we may reasonably identify  $r_i$  and  $r_e$  with  $R_i$  and  $R_e$ , since the thickness of the boundary layers are much smaller than the gap  $R_e - R_i$ .

where  $D_w$  is wax diffusivity and

$$\left. \frac{dT}{dr} \right|_{R_i} = \frac{hR_e}{k} \frac{(T_e - T_i)}{(R_e + R_i)} \tag{2.22}$$

is obtained from (2.15). We write the mass balance

$$\pi \dot{G}(R_e^2 - R_i^2) = -2\pi R_i D_w b_w \frac{hR_e}{k} \frac{(T_e - T_i)}{(R_e + R_i)}.$$
(2.23)

The left hand side of (2.23) represents the rate at which segregated phase is dissolved, while the right hand side the deposition rate (both per unit height of the cylinder). Integrating (2.23) with the initial datum  $G(0) = G_o = c_{tot}^* - C_s(T_b) < \rho$  we get

$$G(t) = G_o - Bt,$$

where

$$B =: \frac{2D_w b_w h R_i R_e}{k} \frac{(T_e - T_i)}{(R_e + R_i)(R_e^2 - R_i^2)}$$

The desaturation time  $t_o$  is obtained imposing  $G(t_o) = 0$ , that is

$$t_o = \frac{G_o}{B}.\tag{2.24}$$

We remark that the ratio  $\dot{m}_w/b_w$  (and hence  $D_w$ ) is the same as the ratio  $\dot{m}/b$  evaluated using the mass of the deposit with oil inclusion. Thus the coefficient  $\phi$  has no influence in the computation of  $D_w$ .

## 2.3 Evolution of solute concentration c

Recall that  $c_{tot} = G + c$ . Due to agitation the solute will be uniformly distributed in the bulk and we write c = c(t), in the global balance neglecting the slight (and opposite) corrections in boundary layers. During the interval  $[0, t_o]$   $c = C_s(T_b)$ , with  $T_b$  given by (2.14). For  $t > t_o$  the solution is unsaturated (G = 0,  $c = c_{tot}$  in the bulk) and the mass transport law (2.21) has to be changed to account for the effects of depletion (see [7] p. 99). Depletion, i.e. wax transfer from the oil to the deposit, will be considered as the only mechanism driving to the asymptotic limit, neglecting the influence of the deposit on the geometry and on the the thermal field.

We denote the asymptotic value of the solute concentration by  $c_{\infty} =: C_s(T_i)$ . Mass growth rate (per unit surface) at the cold wall is

$$\dot{m}_w = \lambda (c - c_\infty), \tag{2.25}$$

where  $\lambda$  is a positive parameter (with the dimension of a velocity) to be determined. Mass balance is expressed by

$$\dot{c}\pi(R_e^2 - R_i^2) = -2\pi R_i \lambda(c - c_\infty).$$
(2.26)

Since at time  $t = t_o$  we have  $c(t_o) = C_s(T_b)$ , integrating equation (2.26) we obtain

$$c(t) = c_{\infty} + (C_s(T_b) - c_{\infty}) \exp\left\{-\frac{2\lambda R_i}{(R_e^2 - R_i^2)}(t - t_o)\right\},$$
(2.27)

that provides the solute concentration for  $t \ge t_o$ . Obviously (2.27) requires the knowledge of  $c_{\infty}$ ,  $C_s(T_b)$  and  $\lambda$ . Total wax concentration can be written in the following way:

$$c_{tot}(t) = \begin{cases} G(t) + C_s(T_b), & 0 \le t \le t_o \\ c(t), & t \ge t_o \end{cases}$$
(2.28)

The function  $c_{tot}$  is continuous in  $t = t_o$ . In the next section we will see how to determine  $\lambda$ .

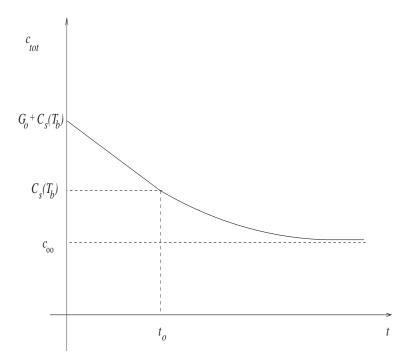


Figure 2: Plot of total wax concentration as a function of time

## **2.4** The parameter $\lambda$

Extending the validity of (2.25) to the saturation stage amounts to requiring that  $c_{tot}(t)$ , given by (2.28), is continuously differentiable in  $t = t_o$ . Accordingly, we impose

$$G(t_o) = \dot{c}(t_o)$$

that is (see (2.23) and (2.26))

$$\frac{2D_w b_w h R_i R_e (T_e - T_i)}{k(R_e + R_i)(R_e^2 - R_i^2)} = \frac{2R_i \lambda (C_s(T_b) - c_\infty)}{(R_e^2 - R_i^2)}.$$
(2.29)

Recalling (2.14) and (2.18) we get

$$C_s(T_b) - c_{\infty} = \frac{b_w R_e(T_e - T_i)}{(R_e + R_i)},$$
(2.30)

which substituted into (2.29) provides

$$\lambda = \frac{D_w h}{k}.\tag{2.31}$$

The plot of  $c_{tot}(t)$  will be like the one shown in Fig. 2, with a linear behaviour up to the desaturation time  $t_o$  and with an exponential decay for subsequent times.

Obviously the plot in Fig. 2 shows the evolution of the solute concentration as well. We notice that the latter is  $C_s(T_b)$  up to time  $t = t_o$  and then decreases exponentially to  $c_{\infty}$ .

#### 2.5 The deposit and its evolution

Let us now consider the formation of the solid deposit layer on the cold wall. Denoting, as usual, by  $m_w(t) = \phi m(t)$  the deposited wax mass per unit surface (m(t) is the total deposited mass), we have

$$\dot{m}_w = D_w b_w \left. \frac{\partial T}{\partial r} \right|_{R_i} = \frac{D_w b_w h R_e}{k} \frac{(T_e - T_i)}{(R_e + R_i)} = \lambda (C_s(T_b) - c_\infty), \qquad 0 \le t \le t_o, \qquad (2.32)$$

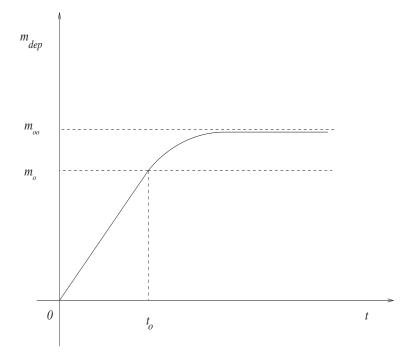


Figure 3: Plot of the deposit as a function of time

$$\dot{m}_w = \lambda (C_s(T_b) - c_\infty) \exp\left\{-\frac{2\lambda R_i}{(R_e^2 - R_i^2)}(t - t_o)\right\}, \qquad t > t_o,$$
(2.33)

where the right hand sides of (2.32),(2.33) are the mass fluxes for the saturated and unsaturated stages respectively. Integrating (2.32) with the initial datum  $m_w(0) = 0$  we find

$$m_w(t) = \lambda (C_s(T_b) - c_\infty)t, \qquad 0 \le t \le t_o, \tag{2.34}$$

that indicates that the deposit grows linearly with time during the interval  $[0, t_o]$ . At the desaturation time  $t_o$ , we have (see (2.24) and (2.30))

$$m_w(t_o) = \frac{[c_{tot}^* - C_s(T_b)](R_e^2 - R_i^2)}{2R_i}.$$
(2.35)

Integrating (2.33) with the initial datum  $m_w(t_o)$  we obtain

$$m_w(t) = m_w(t_o) + \frac{(R_e^2 - R_i^2)(C_s(T_b) - c_\infty)}{2R_i} \left[ 1 - \exp\left(-\frac{2\lambda R_i}{R_e^2 - R_i^2}(t - t_o)\right) \right].$$
 (2.36)

From (2.35) and from (2.36) we see that the asymptotic value  $m_{w\infty}$  of deposited mass per unit surface is

$$m_{w\infty} = \frac{[c_{tot}^* - c_{\infty}](R_e^2 - R_i^2)}{2R_i} = \frac{[c_{tot}^* - C_s(T_i)](R_e^2 - R_i^2)}{2R_i},$$
(2.37)

as stated in (2.19). The plot of deposited mass of wax as a function of time is sketched in Fig. 3. The curve shows a linear growth up to time  $t_o$  and then it tends asymptotically to  $m_{w\infty}$ . The total mass of deposit m is obtained dividing  $m_w$  by  $\phi$ .

#### 3 Comparison with experimental data

Here we determine  $D_w$  and  $b_w$  from some laboratory measurements and we compare our model with the available field data. In fig. 4 some deposition measurements and wax fraction of the deposit obtained with

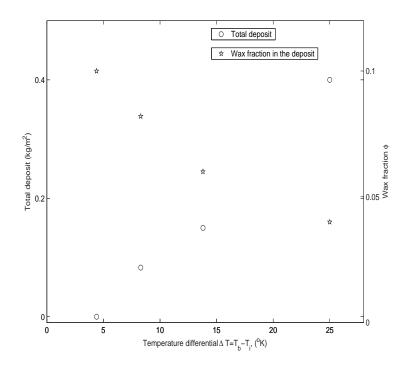


Figure 4: Deposited mass m and wax fraction  $\phi$  as a function of  $\Delta T = T_b - T_i$ . Measurements are taken after 16 hours.

a cold finger with stirring are reported. The experimental data are taken from [6] and represent the total deposited mass m and the wax fraction after 16 hours, for some temperature difference  $\Delta T = T_b - T_i$ .

In the experiment bulk temperature is kept constant

$$T_b = 313.5 \ ^{o}K,$$

and the cloud point is

$$T_{cloud} = 320.2 \ ^{o}K.$$

In the linear growth phase deposition rate is constant and is given by

$$\dot{m}_w = D_w b_w \left. \frac{\partial T}{\partial r} \right|_{R_i}$$

Thus

$$D_w = \frac{m_w^*}{t^*} \frac{1}{b_w \left. \frac{\partial T}{\partial r} \right|_{R_i}},$$

where  $m_w^*$  is deposited wax during a time interval  $[0, t^*]$  with  $t^* < t_o$ . From (2.22)

$$D_w = \frac{m_w^*}{t^*} \frac{k(R_e + R_i)}{b_w h R_e (T_e - T_i)}.$$
(3.1)

From (2.14)

$$T_b(R_e + R_i) - R_i T_i = R_e T_e,$$
  
$$T_e = \frac{1}{R_e} [T_b R_e + T_b R_i - R_i T_i - R_e T_e],$$
  
$$T_e - T_i = \frac{1}{R_e} [(R_e + R_i)(T_b - T_i)],$$

so that

$$T_e - T_i = \frac{1}{R_e} \left[ (R_e + R_i) \Delta T \right]$$

Formula (3.1) becomes

$$D_w = \frac{m_w^*}{t^*} \frac{k}{b_w h \Delta T} \tag{3.2}$$

To determine  $D_w$  we need to know  $\Delta T$ , k, h,  $b_w$  and a deposition measure  $m_w^*$  at some time  $t^* \leq t_o$ .

# 3.1 Evaluation of $b_w$ through asymptotic mass measures

In fig. 4 the wax fraction in the deposit is also plotted, so that we know deposit wax  $m_w$ . The parameter  $b_w$  can be evaluated by means of (2.20) in the following way. We consider

$$\Delta T^o = T_b - T_o,$$
  
$$\Delta T^1 = T_b - T_1,$$

where  $T_o$  and  $T_1$  are two different temperatures of the cold finger. We have

$$\Delta T^1 - \Delta T^o = T_o - T_1.$$

From (2.20)

$$b_w = \frac{[m_{w\infty}^1 - m_{w\infty}^o]2R_i}{(R_e^2 - R_i^2)(\Delta T^1 - \Delta T^o)}.$$
(3.3)

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Assuming that after 16 hours and for sufficiently large  $\Delta T$  the deposit no longer grows (asymptotic stage), we need two deposited mass values relative to different  $\Delta T$ . From the plot we may choose

$$\Delta T^{1} = 25^{o}K \qquad \longrightarrow \qquad m_{w\infty}^{1} = 0.018 \frac{Kg}{m^{2}} \qquad (\phi = 0.07),$$
  
$$\Delta T^{o} = 13.8^{o}K \qquad \longrightarrow \qquad m_{w\infty}^{o} = 0.012 \frac{Kg}{m^{2}} \qquad (\phi = 0.05).$$

In the experiment  $R_i = 0.017m$  and  $R_e = 0.043m$ . From (3.3)

$$b_w = 0.014 \ \frac{Kg}{m^3 \cdot {}^o K}$$

# **3.2** Evaluating $D_w$

We recall that deposited wax at the desaturation time  $m_w(t_o)$  is given by (2.35). Since we are supposing that  $C_s$  is linear in T we have

$$c_{tot}^* = C_s(T_{cloud})$$

and

$$c_{tot}^* - C_s(T_b) = b_w(T_{cloud} - T_b).$$

This yields

$$m_w(t_o) = \frac{b_w(T_{cloud} - T_b)(R_e^2 - R_i^2)}{2R_i}.$$
(3.4)

Asymptotic mass is given by

$$m_{w\infty} = \frac{(c_{tot}^* - C_s(T_i))(R_e^2 - R_i^2)}{2R_i} = \frac{b_w(T_{cloud} - T_i)(R_e^2 - R_i^2)}{2R_i}.$$
$$m_{w\infty} = m_w(t_o) + \frac{\Delta T b_w(R_e^2 - R_i^2)}{2R_i}.$$

Using the data of fig. 4 when  $T_b$  is fixed we obtain

$$m_w(t_o) = 0.038 \, \frac{Kg}{m^2},$$
(3.5)

and

$$\frac{m_w(t_o)}{t_o} = \frac{b_w \Delta T h D_w}{k}$$
$$t_o = \frac{m_w(t_o)k}{b_w \Delta T h D_w}.$$

and

The desaturation time 
$$t_o$$
 depends on  $D_w$ . The greater is  $D_w$ , the smaller is  $t_o$ . The knowledge of  $D_w$  requires the knowledge of  $t_o$ , or at least a measure of the deposited mass taken at  $t \leq t_o$ . If we now consider in the plot of fig. 4 a  $\Delta T$  such that  $m_{w\Delta T}$  relative to  $\Delta T$  is smaller than  $m_w(t_o)$  then we are sure that after 16 hours we are still in the linear growth regime. In this case (3.2) holds true and

$$D_w = \frac{m_{\widehat{\Delta T}}}{16h} \frac{k}{b_w h \widehat{\Delta T}},\tag{3.6}$$

For example for  $\widehat{\Delta T} = 4.4^{\circ} K$  we have

$$m_{\widehat{4.4^o\,K}} = 0.030\,\frac{Kg}{m^2} < m(t_o) = 0.038\,\frac{Kg}{m^2}$$

Recalling the typical values for k and h in (2.10)-(2.11) we get

$$D_w \approx 4.4 \times 10^{-9} \frac{m^2}{s}.$$
 (3.7)

At this point we may use the values of  $b_w \in D_w$  to plot the mass growth vs time for a specific  $\Delta T$ . We make use of (2.36), that is

$$m_w(t) = m_w(t_o) + \frac{b_w(R_e^2 - R_i^2)(T_b - T_{cloud})}{2R_i} \left[ 1 - \exp\left(-\frac{2D_whR_i}{k(R_e^2 - R_i^2)}(t - t_o)\right) \right].$$
 (3.8)

Growth curves for four different  $\Delta T$  are shown in figures (5-8). Continuous lines are plotted using (3.8), while stars represent experimental mass measures at 16 hours. The intersection of the horizontal line and the curve represent is the point  $(t_o, m(t_o))$ , where  $t_o$  is the desaturation time and  $m(t_o)$  is mass deposited during the linear growth regime. We notice that only the measure for  $\Delta T = 4.4^{\circ} K$  is in the linear stage and that the desaturation time decreases as  $\Delta T$  increases.

Other experimental data, unfortunately limited to the unique measure for a temperature difference between the warm and the cold wall of 17  ${}^{o}K$  can be found in [7]. Of course  $b_w$  cannot be evaluated since we need at least two different asymptotic mass measures. However, if we use a typical value  $b_w \approx 0.03 \ Kg/(m^3 \cdot {}^{o}K)$  we find  $D_w \approx 2 \times 10^{-9} \ m^2/s$ .

## 4 Conclusion

We have presented a model for wax deposition in a cold finger device with oil stirring. The transfer of dissolved wax towards the cold finger wall (driven by molecular diffusion) takes place in a boundary layer where the temperature profile is calculated in terms of the geometry of the device and of the heat transfer coefficient (expressed as a function of the stirring speed and of the physical properties of the oil).

The formation of the deposit is discussed as a two-stage process. In the first stage the oil is saturated by wax and in the second stage is not. The model predicts that the deposition rate is constant during the first stage and allows to compute the time of transition to the second stage. The evolution of wax concentration during the unsaturated regime is calculated, showing that the mass of solid wax deposited tends exponentially to its asymptotic limit. Using some experimental data available in the literature we deduce a reliable value for wax diffusivity, on the basis of which the growth of the deposit is predicted in various experimental conditions.

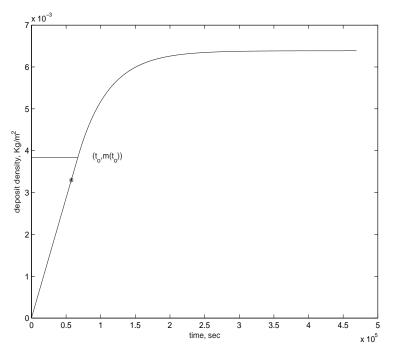


Figure 5:  $\Delta T = 4.4^{\circ}K$ ,  $t_o \approx 18h$ 

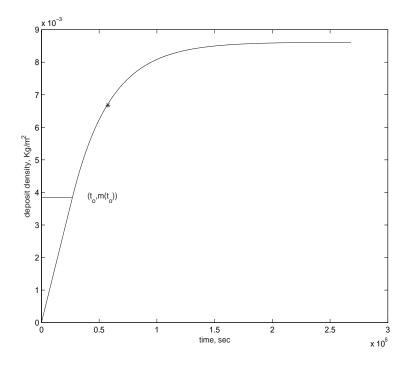


Figure 6:  $\Delta T = 8.3^{o}K$ ,  $t_o \approx 7h$ 

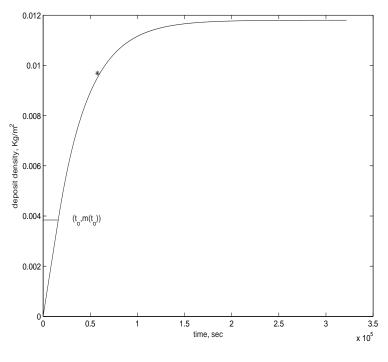


Figure 7:  $\Delta T = 13.8^{o}K$ ,  $t_o \approx 4h$ 

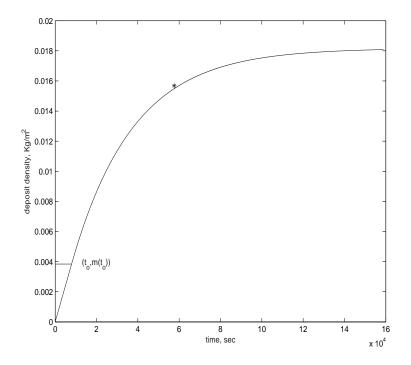


Figure 8:  $\Delta T = 25^{o}K$ ,  $t_o \approx 2h$ 

#### References

- L.F.A. Azevedo, A.M. Teixeira, A critical review of the modeling of wax deposition mechanisms, Petroleum Science and Technology 21 (3&4): 393-408, 2003
- [2] E.D. Burger, T.K. Perkins, J.H. Striegler, Studies of wax deposition in the trans Alaska pipeline, Journal of Petroleum Technology, 1075-1086, (June 1981).
- [3] S. Correra, M. Andrei, C. Carniani, Wax diffusivity: is it a physical property or a pivotable parameter?, Petroleum Science and Technology, 21(9), 1539-1554, (2003).
- [4] S. Correra, A. Fasano, L. Fusi, M. Primicerio, F. Rosso, Wax diffusivity under given thermal gradient: a mathematical model, to appear
- [5] Chien-Hou Wu, J.L. Creek, Kang-Shi Wang, R.M. Carlson, S. Cheung, P.J. Shuler, Yongchun Tang, Measurments of wax deposition in paraffin solutions, prepared for presentation at the 2002 Spring National Meeting, New Orleans, March 10-14, Wax Thermodynamic and Deposition
- [6] ) K. Weispfennig, D.W. Jennings, Effects of shear and temperature on wax deposition: cold finger investigation with a GOM crude oil, The 5th International Conference on Petroleum Phase Behaviour and Fouling, June 13-17, (2004).
- [7] K. Weispfennig, D.W. Jennings, Paraffin deposition modeling using benchtop deposition tests, AIChE Spring National Meeting, New Orleans LA, March (2002).
- [8] P. Singh, R. Venkatesan, H. Scott Fogler, N.R. Nagarajan, Morphological evolution of thick wax deposits during aging, AIChE Journal, vol. 47, N. 1, 6-18 (2001).