Tool for Predicting Wax Deposition Rate at Different Operating Conditions: A Penetration Theory Approach

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Abstract: Solid crystals may deposit when the thermodynamic conditions of the temperature, pressure or composition changes in the process of oil production. This crystalline solid (wax) may block the pores in the formation and significantly affect the oil productivity. Several studies have been conducted on the mechanism of wax deposition in and around the wellbore. Experimental measurements have shown that most of these previous analytical models under-estimate elemental Wax build up rate at different radial distance around the wellbore while the minimum blockage time was over-estimated. This paper presented an improved analytical model for predicting the rate of deposition of wax inside a wellbore or pipeline from a crude oil at different operating temperatures, which also allows the selection of the temperature with minimum deposition rate as system or operating temperature, by assuming an equimolecular counter-diffusion condition at the interface between the solute (solid phase) and the solvent (liquid phase), this is known as Penetration theory. Using a Penetration theory to predict wax deposition rate will be a new dimension in wax deposition modelling, since most of the researchers depend solely on using steady state Fick’s first law of molecular diffusion, chain’s rule and thermodynamic models for their predictions whereas Penetration theory is based on using circulating or eddy currents present in a turbulent fluid (eddies diffusion), combining with unsteady state Fick’s second law, without the inclusion of chain rule.

Keywords: Penetration theory, Equimolecular counter-diffusion, thermodynamic model, Chain’s rule

1. Introduction

Wax (solid) in crude oil is comprised primarily of paraffins. Paraffin is a white, odorless, tasteless, chemically inert compound composed of saturated hydrocarbons. Waxes are essentially mixtures of long-chain hydrocarbons (n-paraffins) with carbon chain lengths ranging from C15 to C75. Wax varies in constituents from that of petroleum jelly to hard wax with melting points from near room temperature to over 100°C. Wax has a high density of around 0.8 g/cm³ and a heat capacity of around 0.140 W/m K. They are crystalline in nature and tend to crystallize / precipitate from crude oils at and below their cloud points. Under the most favourable conditions, n-paraffins form clearly defined orthorhombic crystals, but unfavourable conditions and in the presence of impurities lead to hexagonal and/or amorphous crystallization. Crystallization is the process whereby an ordered solid structure is produced from a disordered phase; such as a melt or dilute solution (e.g. crude oil). It usually involves two distinct stages, namely nucleation and growth which may be considered separately. (Coutinho et al., 2000, 2001).

As the temperature of the liquid solution or melt is lowered to its WAT, the energy of molecular motion becomes increasingly hindered, and the randomly tangled molecules in the melt tend to move closer together and form clusters of adjacently aligned chains. The paraffin molecules continue to attach and detach to and from these ordered sites until the clusters reach a critical size and become stable. This process is termed ‘nucleation’ and the clusters are called nuclei. These nuclei are only stable below the melting/dissolution temperature of the wax as they are disrupted by thermal motion above this temperature. Once the nuclei are formed and the temperature is kept at or below the WAT, additional molecules are laid down successively on the nucleation sites and become part of the growing lamellar structure. This mechanism is called the ‘growth process’. Nucleation can be homogeneous, meaning that the sample is pure and the nucleation sites are time dependent or heterogeneous, which implies that all nucleation sites are activated instantaneously. The latter type is the most common in crude oils where impurities such as asphaltenes, formation fines, clay and corrosion products act as nucleating materials for wax crystals.

Wax deposition mechanism from crude oil during transportation has been studied recently1-7. It has been reported that there are three mechanisms on wax deposition during transportation of crude oil2, namely, molecular diffusion, shear dispersion, and Brownian diffusion. Experimental measurements8,9 have shown that the shear dispersion mechanism does not have an important contribution in wax deposition, especially in high temperature and heat flux conditions3. The effect of Brownian diffusion is also negligible. Therefore, molecular diffusion is the dominant mechanism in wax deposition. One of the other mechanisms that affect the amount of deposited wax is sloughing mechanism. Experimental results have shown that sloughing effect is an important mechanism due to the shear effect of fluid during turbulent flow that must not be neglected in wax deposition modelling2,8,9. Wax deposition rate increases with increasing flow rate during laminar flow, whereas due to shear effect contrary trend was observed during turbulent flow8,9. Existing models deal with laminar flow and there is no attempt to model the sloughing effect on wax deposition. Therefore, these models can not be used in the turbulent flow regime. An ideal design should use an accurate mathematical model that includes all salient features of wax deposition and waxy crude transport.
In this paper, a comprehensive mathematical model both in laminar and turbulent flow regimes is developed. The rate of deposition of wax inside a pipeline from a waxy crude was predicted by assuming an equimolecular counter-diffusion condition at the interface between the solute (solid phase) and the solvent (liquid phase). Both the deposition mechanism and the sloughing effect were considered for wax deposition during turbulent flow. The deposition mechanism is supposed to be molecular diffusion. Fick’s law along with two film theory, was applied to predict wax deposition rate. In the transport part, steady state analytical or numerical approach can be used for prediction of temperature profile in laminar flow. A turbulent flow model and energy equation was used to predict velocity and temperature distributions in the turbulent flow regime.

2. Model Formulation

A simple analytical model was developed for the rate of deposition of wax inside a pipeline from a waxy crude by assuming an equimolecular counter-diffusion condition at the interface between the solute (solid phase) and the solvent (liquid phase), this is known as Penetration theory.

(A) Deposition Rate Model Development

Equimolecular counter-diffusion occurs when mass transfer rate of two components across an interface are equal and opposite. i.e. there is no net transference of molecules at the interface, then the rate of transfer on each side of the interface will be the same, indicating there is no accumulation at the interface and since there is no accumulation at the interface, there will be no or low resistance to transfer at the interface, then the molar concentration at each side will be constant.

Therefore by measuring the change in molar concentration in either of the phases at both sides of the interface with time, the molecular mass deposition rate of wax at the wall can be predicted.

Unsteady state mass transfer

In many practical mass transfer processes, unsteady state conditions prevail. Thus consider an element of liquid of cross-sectional area \( A \) and the thickness \( \delta y \) in the direction of mass transfer in which the concentrations \( C_A \) and \( C_B \) of the components \( A \) and \( B \) are a function of both position \( y \) and time (Fig. 3.1), then if the mass transfer flux is composed of two components, one attributable to diffusion according to Fick’s law and the other due to a bulk flow velocity \( U_F \), the fluxes of \( A \) and \( B \) at a distance \( y \) from the origin may be taken as \( N_A \) and \( N_B \), respectively. These will increase to

\[
N_A' = N_A + \left( \frac{\partial N_A}{\partial y} \right) \delta y \quad \text{and} \quad N_B' = N_B + \left( \frac{\partial N_B}{\partial y} \right) \delta y
\]

at distance \( y + \delta y \) from the origin. At the position \( y \), the fluxes \( N_A' \) and \( N_B' \) will be given in table 3.1. At a distance \( y + \delta y \) from the origin, that is at the further boundary of the element, these fluxes will increases by amounts shown in the lower part of the table 3.1.

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**Figure 3.1:** Unsteady state mass transfer

Thus, for \( A \):

\[
\text{Moles IN/unit time (at} \ y \text{)} - \text{Moles OUT/unit time (at} \ y + \delta y \text{)} = \text{Rate of change of concentration in element volume}
\]

\[
\left\{ D \frac{\partial C_A}{\partial y} + u_F C_A \right\} A = \left\{ -D \frac{\partial C_A}{\partial y} + u_F C_A + \frac{\partial}{\partial y} \left[ -D \frac{\partial C_A}{\partial y} + u_F C_A \right] \right\} A
\]

Simplifying:

\[
\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} - \frac{\partial (u_F C_A)}{\partial y}
\]

For component

\[
B \frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial y^2} - \frac{\partial (u_F C_B)}{\partial y}
\]

adding:

\[
\frac{\partial (C_A + C_B)}{\partial t} = D \frac{\partial^2 (C_A + C_B)}{\partial y^2} - \frac{\partial (u_F (C_A + C_B))}{\partial y}
\]

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**Table 3.1:** Fluxes of liquid mixture

<table>
<thead>
<tr>
<th>Diffusional Flux Flux due to bulk flow Total flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-D \frac{\partial C_A}{\partial y} u_F C_A) and (-D \frac{\partial C_B}{\partial y} u_F C_B)</td>
</tr>
<tr>
<td>(-D \frac{\partial^2 C_A}{\partial y^2} u_F C_A) and (-D \frac{\partial^2 C_B}{\partial y^2} u_F C_B)</td>
</tr>
</tbody>
</table>

Changes in fluxes over distance \( \delta y \):

\[
- \frac{D \partial^2 C_A}{\partial y^2} \delta y \frac{\partial (u_F C_A)}{\partial y}
\]
Since for an idea gas \( C_A + C_B = C_T = \text{Constant} \)

\[
0 = 0 \frac{\partial}{\partial y} (u_F C_B) + \frac{\partial}{\partial y} (u_F C_A) = 0
\]

and:

\[
\frac{\partial}{\partial y} (u_F) = 0
\]

Where \( u_F \) is independent of \( y \). Thus equation 2 can be written:

\[
\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} - u_F \frac{\partial C_A}{\partial y}
\]

(5)

For equimolecular counterdiffusion, \( u_F = 0 \) and equation 3.5 simplifies to:

\[
\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2}
\]

(6)

Equation 6 is referred to as Fick's second law. This also applies when \( u_F \) is small, corresponding to condition where \( C_A \) is low. This equation represents the diffusion of solute A away from the interface (y-direction). This equation can be solved for a number of important boundary conditions.

The following boundary conditions apply:

\[
t = 0 \quad 0 < y < \infty \quad C_A = C_{Ao} \\
 t > 0 \quad y = 0 \quad C_A = C_{Ai} \\
 t > 0 \quad y = \infty \quad C_A = C_{Ao}
\]

where \( C_{Ao} \) is the concentration in bulk of the phase, \( C_{Ai} \) is the equilibrium value at the interface.

It is convenient to work in terms of a 'deviation' variable \( C \) as opposed to \( C_A \), where \( C \) is the amount by which the concentration of A exceeds the initial uniform concentration \( C_{Ao} \). This change allows some simplification of the algebra.

With the substitution:

\[
C = C_A + C_{Ao}
\]

Equation 3.6 becomes

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2}
\]

(8)

Because \( C_{Ao} \) is a constant with respect to both \( t \) and \( y \); the boundary conditions are then:

\[
t = 0 \quad 0 < y < \infty \quad C' = 0 \\
 t > 0 \quad y = 0 \quad C' = C_{Ai} - C_{Ao} \\
 t > 0 \quad y = \infty \quad C' = 0
\]

These boundary conditions are necessary and sufficient for the solution of equation 8 which is first order with respect to \( t \) and second order with respect to \( y \). This equation is most conveniently solved by method of Laplace transforms.

By definition, the Laplace transform \( \mathcal{L} \) of \( C \) is given by:

\[
\mathcal{L}C = \int_0^\infty e^{-pt} C \, dt
\]

(9)

Then:

\[
\frac{\partial C}{\partial t} = \mathcal{L}C = \int_0^\infty e^{-pt} C \, dt
\]

(10)

Integrating by parts using a standard Laplace format, we have

\[
= \left[ e^{-pt} C \right]_0^\infty + \int_0^\infty e^{-pt} C \, dt
\]

(11)

from above boundary conditions, when \( t=0 \), and equation 11 becomes zero but when \( t=\infty \), the solution becomes

\[
= p\mathcal{L}C
\]

(12)

Since Laplace transform operation is independent of \( y \):

\[
\frac{\partial C}{\partial t} = \mathcal{L}C = \frac{\partial^2 \mathcal{L}C}{\partial y^2}
\]

(13)

thus taking Laplace transforms of both side of equation 3.8

\[
p\mathcal{L}C = D \frac{\partial^2 \mathcal{L}C}{\partial y^2}
\]

(14)

Equation 8 has therefore been converted from partial differential equation in \( C \) to an ordinary second order linear differential equation in \( \mathcal{L}C \). Since equation 3.13b has a real root, that is:

\[
\pm \sqrt{\frac{p}{D}}
\]

Thus:

\[
\mathcal{L}C = B_1 e^{\sqrt{\frac{p}{D}} y} + B_2 e^{-\sqrt{\frac{p}{D}} y}
\]

(15)

When

\[
y = 0 \quad C_A = C_{Ai}, \quad \text{and} \quad C' = (C_{Ai} - C_{Ao}) = C_i
\]

and when

\[
y = \infty \quad C_A = C_{Ao}, \quad \text{and} \quad C' = 0
\]

Hence

\[
B_2 = 0
\]

and:

\[
\mathcal{L}C = B_1 e^{\sqrt{\frac{p}{D}} y} = \mathcal{L}C_i e^{\sqrt{\frac{p}{D}} y}
\]

(16)

Taking the inverse transform (see Appendix), then:

\[
\mathcal{L}C = \int_0^\infty e^{-pt} C \, dt = \int_0^\infty (C_{Ai} - C_{Ao}) e^{-pt} \, dt = \frac{1}{p} (C_{Ai} - C_{Ao}) e^{\sqrt{\frac{p}{D}} y}
\]
\[ C = (C_{Ai} - C_{Ao}) = (C_{Ai} - C_{Ao}) erfc \left( \frac{y}{2\sqrt{D}t} \right) \]

or:
\[ \frac{C_{A} - C_{Ao}}{C_{Ai} - C_{Ao}} = erfc \left( \frac{y}{2\sqrt{D}t} \right) = 1 - erf \left( \frac{y}{2\sqrt{D}t} \right) \]  

(17)

This expression gives concentration \( C_A \) as a function of position \( y \) and time \( t \).

\( erf\ X \) is known as error function and values are tabulated as for any other function of \( X \); \( erf\ X \) is the complimentary error function \((1 - erf\ X)\).

By definition
\[ erf\ X = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-x^2} \, dx \]  

(18)

since:
\[ \int_{0}^{\infty} e^{-x^2} \, dx = \frac{\sqrt{\pi}}{2} \]  

(19)

\( erf\ X \) goes from 1 to zero as \( x \) goes from 1 to \( \infty \)

The concentration gradient is then obtained by differentiation of equation 3.17 with respect to \( y \). Thus
\[ \frac{1}{C_{Ai} - C_{Ao}} \frac{\partial C_A}{\partial y} = \frac{\partial}{\partial x}\left[ \frac{2}{\sqrt{\pi}} \int_{\frac{y}{2\sqrt{D}t}}^{\infty} e^{-x^2/4Dt} \, dx \right] \]

(20)

\[ \frac{\partial C_A}{\partial y} = -(C_{Ai} - C_{Ao}) \frac{1}{2\sqrt{\pi} \sqrt{D} t} e^{-y^2/4Dt} \]

(21)

The mass transfer rate at any position \( y \) at time \( t \) is given by:
\[ (N_A)_t = -D \frac{\partial C_A}{\partial y} \]

\[ = (C_{Ao} - C_{Ai}) \frac{D}{\pi t} e^{-y^2/4Dt} \]  

(22)

(23)

The mass transfer rate per unit area of surface is then given by:
\[ (N_A)_{t, y=0} = -D \left( \frac{dC_A}{dy} \right)_{y=0} \]

\[ = (C_{Ao} - C_{Ai}) \frac{D}{\pi t} \]  

(24)

The point value of the mass transfer coefficient is therefore
\[ \sqrt{\frac{D}{\pi t}} \]

\( N_A \) = The mass deposition rate per unit area of surface per unit time \((kg/m^2 s)\)

\( C_A \) = The concentration of wax forming compound in the solvent at time \( t \) \((kg/m^3)\)

\( C_{Ao} \) = initial uniform concentration of wax forming compound in the bulk fluid \((kg/m^3)\)

\( D \) = Diffusivity of wax (solute) in the solvent (lighter component) \((m^2/s)\)

\( t \) = flowing time (s)

3. Model Validation

In this section, the models are applied to fluids which have been characterized experimentally and in which other models had been applied. The results of the models are compared with experimental results to validate it; and are equally placed in contrast with the results of other models to justify its position with regards to the existing models.

In equation 3.24, data needed in addition to Wax concentration for the computation of deposition rate is the liquid phase molecular diffusivity for different temperatures. Diffusivity of wax in oil is obtained from the work of Fogler et. al\(^{10}\) where the solubility of wax in a solvent at difference temperature under WAT \((40°C)\) was tabulated and shown graphically and the values of corresponding molecular diffusivity of wax oil was stated (based on equation 3.25) as tabulated below:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility (kg/m(^3))</th>
<th>Diffusivisity (m(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>5</td>
<td>1.45x10(^{-10})</td>
</tr>
<tr>
<td>10°C</td>
<td>20</td>
<td>1.48x10(^{-10})</td>
</tr>
<tr>
<td>20°C</td>
<td>25</td>
<td>1.52x10(^{-10})</td>
</tr>
<tr>
<td>30°C</td>
<td>35</td>
<td>1.60x10(^{-10})</td>
</tr>
</tbody>
</table>

Therefore the mass rate of deposition at different temperatures is then calculated by using equation 3.24, following the data supplied by Fogler et. al\(^{10}\) as shown in the table below:

AT 10°C (283\(^{1}\)K)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{Ao} )</td>
<td>170 (kg/m(^3))</td>
</tr>
<tr>
<td>( C_{Ai} )</td>
<td>5 (kg/m(^3))</td>
</tr>
<tr>
<td>( T )</td>
<td>30 days</td>
</tr>
<tr>
<td>( D_{WO} )</td>
<td>1.45x10(^{-10}) (m(^2)/s)</td>
</tr>
</tbody>
</table>

AT 14°C (287\(^{1}\)K)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{Ao} )</td>
<td>170 (kg/m(^3))</td>
</tr>
<tr>
<td>( C_{Ai} )</td>
<td>20 (kg/m(^3))</td>
</tr>
<tr>
<td>( T )</td>
<td>30 days</td>
</tr>
<tr>
<td>( D_{WO} )</td>
<td>1.48x10(^{-10}) (m(^2)/s)</td>
</tr>
</tbody>
</table>

AT 20°C (293\(^{1}\)K)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{Ao} )</td>
<td>170 (kg/m(^3))</td>
</tr>
<tr>
<td>( C_{Ai} )</td>
<td>20 (kg/m(^3))</td>
</tr>
<tr>
<td>( T )</td>
<td>30 days</td>
</tr>
<tr>
<td>( D_{WO} )</td>
<td>1.48x10(^{-10}) (m(^2)/s)</td>
</tr>
</tbody>
</table>
The output of the model (equation 3.4) obtained at varying temperatures (as tabulated above) are then tabulated as shown below, which is also plotted in figure 4.1.

Table 4.2: Wax deposition rate @ different Temperatures (Model output)

<table>
<thead>
<tr>
<th>Flowing time (days)</th>
<th>Deposition rate (kg/m²/s) @ different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>283°K (10°C)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>1.8047</td>
</tr>
<tr>
<td>60</td>
<td>3.6094</td>
</tr>
<tr>
<td>90</td>
<td>5.4142</td>
</tr>
<tr>
<td>120</td>
<td>7.2189</td>
</tr>
<tr>
<td>150</td>
<td>9.0236</td>
</tr>
<tr>
<td>180</td>
<td>10.8283</td>
</tr>
</tbody>
</table>

Table 4.3: Wax deposition rate @ different Temperatures (Laboratory Results)

<table>
<thead>
<tr>
<th>Flowing time (days)</th>
<th>Deposition rate (kg/m²/s) @ different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>283°K (10°C)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>1.7910</td>
</tr>
<tr>
<td>60</td>
<td>3.4094</td>
</tr>
<tr>
<td>90</td>
<td>5.1922</td>
</tr>
<tr>
<td>120</td>
<td>7.0234</td>
</tr>
<tr>
<td>150</td>
<td>8.9872</td>
</tr>
</tbody>
</table>

Figure 4.1: A plot showing variation in deposition rate for different operating temperatures

4. Discussion of Result

From Table 4.1 above, it can be seen that when temperature was 10°C (283 K) the concentration of wax in the flowing fluid was 5 kg/m³ and when the temperature was 30°C the concentration was 35 kg/m³. This shows that wax concentration is a thermodynamic property i.e. it varies with changes in temperature. It can therefore be deduced that Wax solubility in a solvent increases with increase in temperature.

Also from Table 4.1 it can be seen that when temperature was 10°C (283K) the Diffusivity of Wax in oil was 1.45x10⁻¹⁰ m²/s and when the temperature was 20°C Diffusivity increased to 1.52x10⁻¹⁰ m²/s. This shows that Diffusivity of wax in oil is a thermodynamics parameter which increases with increase in temperature.

It can be seen from Table 4.2 that for a flowing time of 3 months, the Deposition rate was 1.8047 kg/m²/s at 283K and 1.5511 kg/m²/s at 303K. This shows that the rate of Deposition of wax along pipeline wall reduces with increase in temperature; this is also confirmed in figure 4.1 with temperature of 303K showing the lowest deposition rate. Therefore figure 4.1 serves as a tool for determining the deposition rate at different operating temperatures and which would allow the selection of the temperature with minimum deposition rate as system or operating temperature.

Comparing table 4.2 (model output) and 4.3 (experimental results), it was observed that at the flowing time of 30 days at operating temperature of 10°C (283 K) the deposition rate was 1.7910 kg/m²/s for laboratory result and at the same operating condition it was 1.8047 kg/m²/s for model result. This shows a very high predictive accuracy of the model since the percentage difference is negligible. This trend can also be seen at other operating conditions 287 K, 293 K and 303 K respectively.

5. Conclusion

The approach employed in this work is easily accessible since the application requires constant thermodynamic data (properties that varies with temp) and rheological properties of the crude. The following conclusion can be deduced from this research work.

1. A new model for prediction of wax deposition during turbulent and laminar flow of crude oil in pipeline using penetration theory has been developed.

2. A tool for determining the deposition rate at different operating temperatures and which would allow the selection of the temperature with minimum wax deposition rate as system or operating temperature has been developed.

References


