WAX DEPOSITION IN CRUDE OIL PIPELINES

Pablo Morelato Assunção, pablomorelato@hotmail.com
Lorennzo Marrochi Nolding Rodrigues, lorennzomnr@hotmail.com
Universidade Federal do Espírito Santo / Centro Universitário Norte do Espírito Santo / Engenharia de Petróleo. Rodovia BR 101 Norte, km 60, Litorâneo, São Mateus, ES 29932-540, Brazil

Mao Ilich Romero, mromerov@uwyo.edu
University of Wyoming / Enhanced Oil Recovery Institute. Dept. 4068, 1000 E. University Ave., Laramie, WY 82071-2000, USA

Oldrich Joel Romero, oldrichjoel@gmail.com
Universidade Federal do Espírito Santo / Centro Universitário Norte do Espírito Santo / Engenharia de Petróleo. Rodovia BR 101 Norte, km 60, Litorâneo, São Mateus, ES 29932-540, Brazil

Abstract. *Crude oil is a complex mixture of hydrocarbons which consists of aromatics, paraffins, naphthenics, resins asphaltenes, etc. When the temperature of crude oil is reduced, the heavy components, like paraffin, will precipitate and deposit on the pipe internal wall in the form of a wax-oil gel. The gel deposit consists of wax crystals that trap some amount of oil. As the temperature gets cooler, more wax will precipitate and the thickness of the wax gel will increase, causing gradual solidification of the crude and eventually the oil stop moving inside the offshore pipeline. Crude oil may not be able to be re-mobilized during re-startup. The effective diameter will be reduced with wax deposition, resulting in several problems, for example, higher pressure drop which means additional pumping energy costs, poor oil quality, use of chemical components like precipitation inhibitors or flowing facilitators, equipment failure, risk of leakage, clogging of the ducts and process equipment. Wax deposition problems can become so sever that the whole pipeline can be completely blocked. It would cost millions of dollars to remediate an offshore pipeline that is blocked by wax. Wax solubility decreases drastically with decreasing temperature. At low temperatures, as encountered in deep water production, is easy to wax precipitate. The highest temperature below which the paraffins begins to precipitate as wax crystals is defined as wax appearance temperature (WAT). Deposition process is a complex free surface problem involving thermodynamics, fluid dynamics, mass and heat transfer. In this work, a numerical analysis of wax deposition by molecular diffusion and shear dispersion mechanisms in crude oil pipeline is studied. Diffusion flux of wax toward the wall is estimated by Fick's law of diffusion, in similar way the shear dispersion; wax concentration gradient at the solid-liquid interface is obtained by the volume fraction conservation equation; and since the wax deposition can only occur when the interface temperature is below WAT, the temperature distribution is a necessary information which is obtained by the energy equation. The one-dimensional, transient and laminar flow governing equations are discretized based on the finite volume method, with the upwind scheme to treat the convection term. A totally implicit procedure was employed to handle the time integration term. The set of algebraic equations were solved by the TDMA line by line algorithm. The thickness of the deposited layer is a function of the axial coordinate and presents a monotonic increase at several time instants which is in reasonable agreement whit previous results.*

Keywords*: wax deposition, offshore pipelines, molecular diffusion, shear dispersion, crude oil.*

1. INTRODUCTION

Many studies were conducted in an attempt to understand and solve the problem of paraffin deposition in oil transmission lines. Several studies of experimental and numerical modeling were developed in order to predict the phenomenon of deposition of paraffin. An important feature in the study of paraffin is its solubility in oil. Solubility is a property that is defined the conditions of temperature and pressure at which these compounds precipitate from solution in the form of crystals. Studies show that the solubility of paraffins depends strongly on temperature and decreases with the decrease of the temperature. The pressure on the other hand, seems not to significantly affect the solubility.

In conditions of high temperature and pressure at which oil is found in reservoirs, hundreds of feet into the subsurface, ensure the solubility of paraffins. As shown schematically in Figure 1, the oil taken from the reservoir flows through the column of production to the wellhead where it arrives with temperatures exceeding 40 ° C. It is transported to the platform through the interior of the production lines supported on the seabed where a cold external environment usually 5 ° C prevails in deepwater operations. A heat exchange between the oil at elevated temperature and sea water will occur as a result cooling the oil, reaching a critical temperature known as the initial temperature of appearance of crystals (TIAC), in which the first wax crystals precipitate from the solution. Experimental studies indicate that TIAC is not necessarily a fixed value and may be a function of the cooling rate. Its value can also depend strongly on the experimental method used to measure it. Research shows that the higher molecular weight paraffins precipitate first forming stable crystals, these crystals are interwoven to form a solid matrix on the walls of the lines. Paraffins form predominantly the material deposited on the walls of the ducts, as shown in Fig. 1.

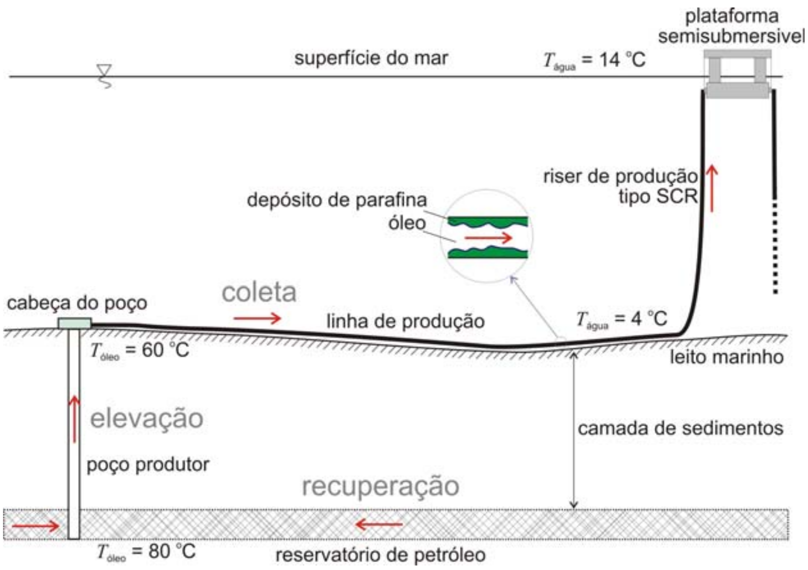

Figure 1: Deposition of paraffin in a production system *offshore*.

The capacity of predicting the phenomenon of paraffin deposition in the walls of the ducts depends crucially on understanding the physical mechanisms governing the deposition. According to the work of Burger et al. (1981) the possible deposition mechanisms were identified as the molecular diffusion, Brownian diffusion, shear dispersion, and deposition by gravitational effects. In addition to Burger et al. (1981), others pioneering studies are Brown et al. (1993), Svendsen (1993), Creek et al. (1999) and more recently Azevedo and Teixeira (2003), Leiroz (2004), Romero (2005), Todi (2005) and Romero et al. (2006) Conducted research in this direction. The present work aims at performing a numerical simulation of the deposition of paraffin in submarine pipelines considering the two main mechanisms in literature; deposition by molecular diffusion and shear dispersion.

The molecular diffusion occurs due to temperature gradient generated in the radial direction of the duct, this caused by the difference between the duct wall temperature and oil flowing inside. Because the solubility of paraffin decreases with temperature, the temperature gradient set, generates a higher concentration of paraffin dissolved in the warmest region which leads to a transport by molecular diffusion in the liquid paraffin into the wall of the duct. The dispersion of shear is also a mechanism that contributes to the deposition of paraffin, where small crystals contained in the oil tend to move in the direction of the flow. However, as the flow velocity is maximum at the center of the tube and zero on the walls, there is a shear that induces motion of the particles, known as shear dispersion. This movement may be responsible for transporting the paraffin precipitated from the fluid in the center of the line towards the wall, where are joined to the existing wax deposits due to the phenomenon of molecular diffusion.

The study of wax deposition in pipelines is a complex subject, its understanding involves many areas of knowledge as are balance and phase transition, thermodynamics, heat transfer, mass transfer, fluid mechanics, among others. The ability to make accurate predictions of deposition rates of paraffin inside ducts is of fundamental importance to assist in the stages of production projects of new fields, as well as in programming interventions for removal of accumulated deposits.

2. METHODOLOGY

One the prediction of deposition rates and spatial distribution of paraffin deposited is knows, this becomes essential information for the design of subsea lines, this work aims at performing a numerical analysis of paraffin deposition process in pipelines using the models of molecular diffusion and dispersion shear, based on the work of Romero (2005) developed by the group of researchers from the Department of Mechanical Engineering, PUC-Rio.

To facilitate the numerical treatment of the problem is considered that the deposition of paraffin on the inside of a pipe is similar to which occurs inside a parallel plate channel. As depicted in simplified form in Figure 2, hot paraffin oil at a temperature T_{oil} flows between two parallel plates separated a distance "*a*" exists externally to the plates with cold water at a uniform temperature T_{oil} , so that $T_{oil} > T_{water}$. The two plates of a thickness determined, have high conductivity allowing heat exchange between oil and the external environment, thereby causing the growth of wax deposit thickness $\delta(x,t)$. It is considered that the paraffin is deposited also in the two inner walls of the channel.

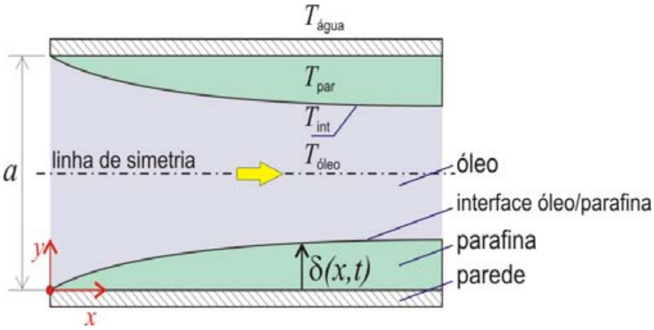

Figure 2: A simplified representation two-dimensional of the process of paraffin deposition in a channel.

A very important parameter for analysis of paraffin is its solubility in oil. Leiroz (2004) experimentally measured the concentration of saturated solution of paraffin / oil (in grams of solute per gram of solution w g / g) as a function of temperature (ºC). The equation that best fits the experimental data used is described by equation 1 and is shown graphically in Fig. 3.

$$w = 1{,}021 \times 10^{-9}\, T^{5{,}133} \tag{1}$$

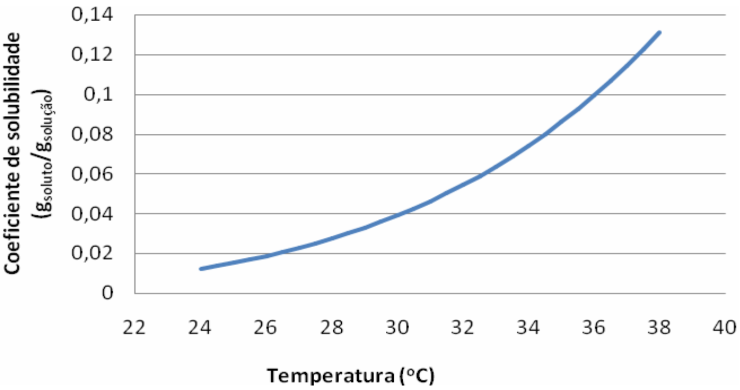

Figure 3: Curve of the solubility coeficient.

The phenomenon of deposition of paraffin belongs to a class of problems called phase change, which has a mobile frontier. The solution of this class of problems involves a difficulty inherent to the process as it relates to movement of the interface between solid and liquid phases. As a result, the location of solid / liquid interface is not known previously, becoming part of the solution.

To write the conservation equations that govern this phenomenon, different hypothesis were used to facilitate the achievement of the solution. The mixture of paraffin oil is composed of hydrocarbons of high molecular weight, but present Newtonian behavior. We opted for simplicity, consider the constant properties, except for the dependence of the solubility of paraffin in the oil with temperature being a critical parameter to evaluate the deposition of paraffin.

The hypotheses were:

- Deposition of paraffin governed by molecular diffusion and shear dispersion,
- Newtonian Fluid,
- Incompressible fluid,
- Thermal conductivity and specific heat at constant pressure of the fluid and paraffin equal and constant,
- Coefficient of molecular diffusion of the paraffin is constant.
- Solubility of paraffin dependent of the temperature,
- Laminar flow,
- Variations in the transverse direction of the flow is negligible,
- Paraffin deposition occurs at temperatures below the TIAC,
- Storage of solid paraffin with constant porosity,
- Diffusion of mass in the solid phase negligible,
- Effect of gravity is negligible.

3. MATHEMATICAL EQUATIONS

It was considered the one-dimensional model, and the deposition of paraffin determined from the temperature field. The geometry and operating conditions were similar to those used by Leiroz (2004) and Romero (2006), aiming to compare the results of the models developed in this work with experimental data and numerical simulations referenced.

In this work the deposition rates were modeled as the sum of the fees generated by molecular diffusion of paraffin dissolved and dispersed by the action of shear. We emphasize that the mathematical development for the two models is similar, so greater emphasis will be given in the derivation of the model of deposition by molecular diffusion.

For the molecular diffusion was considered to Fick's Law (Eq. 2)

$$\frac{dm_p}{dt} = -\rho_m D_m A_d \left.\frac{dw}{dy}\right|_{\text{int}} , \tag{2}$$

where m_p is the mass of wax deposited by molecular diffusion, ρ_m is the density of the mixture, $A_d = b * dx$ is the deposition area, where dx is the length of the elementary volume and b is the channel width. D_m is the diffusion coefficient of liquid paraffin in the mixture, w is the volume fraction of paraffin in the solution and y is the vertical coordinate.

The incorporation of solid particles (crystals) was considered to be proportional to the volume fraction of the paraffin out of solution $C*$, the coefficient of dispersion by shear D_s and the surface area available A_d, Eq 3.

$$\frac{dm_i}{dt} = \rho_r D_s A_d \left.\frac{dC^*}{dy}\right|_{wall} , \tag{3}$$

which m_i is the mass of wax deposited per shear dispersion, ρ_r is the density of the crystals of paraffin.

For a differential volume of paraffin deposited dv, the paraffin's mass m_p of density ρ_p is given by

$$dm_p = \rho_p (1-\phi) dv , \tag{4}$$

ϕ is the porosity defined as the ratio of the volume occupied by liquid in the solid deposit and the volume of solid deposit. You can re-write the infinitesimal volume depending on the thickness of the deposit δ, so that:

$$dv = A_d \frac{\partial \delta}{\partial t} dt . \tag{5}$$

Substituting Eq 5 into eq 4 and deriving with respect to time, we have:

$$\frac{dm_p}{dt} = \rho_p b dx (1-\phi) \frac{\partial \delta}{\partial t} . \tag{6}$$

Equating Equation 6 with Equation 2, we can obtain the thickness variation as a function of time.

$$\frac{\partial \delta}{\partial t} = \frac{-D_m}{(1-\phi)} \frac{\rho_m}{\rho_p} \left.\frac{dw}{dy}\right|_{\text{int}} \tag{7}$$

According to Eq. 7, we must evaluate the gradient of the volumetric fraction of paraffin in the interface $\left. dw/dy \right|_{\text{int}}$. This fraction gradient of concentration is estimated from the temperature gradient at the interface. Due to the symmetry of the problem, we can solve it considering any part of the channel (upper or lower). Through visualization of the elemental control volume it is perceived that it was divided into three distinct regions: the fluid, the paraffin region and the region of copper. For each region, it presents an infinitesimal control volume, which has the same dx and where to applied the equations of mass conservation (Eq. 8), energy (Eq. 9) and volumetric fraction (Eq. 10).

$$\frac{\partial}{\partial t}\int_{VC}\rho dV + \int \vec{u}.\vec{n}dA = 0\,, \tag{8}$$

$$\frac{\partial}{\partial t}\int_{VC}\rho c_p T dV + \int_{SC}\rho c_p T\vec{u}.\vec{n}dA = \int_{SC}\overrightarrow{q''}.\vec{n}dA + \int_{VC}S_t dV\,, \tag{9}$$

$$\frac{\partial}{\partial t}\int_{VC}\rho w dV + \int_{SC}\rho w\vec{u}.\vec{n}dA = \int_{SC}\overrightarrow{m''}.\vec{n}dA + \int_{VC}S_w dV\,, \tag{10}$$

Where ρ is the density of the fluid, $\vec{u}$ the velocity vector, A the cross-sectional area of the pipe is the differential volume, $\vec{n}$ unit vector normal to the control surface, and the variable t denotes the time. T is the temperature of the fluid, c_p is the specific heat at constant pressure of it, $\overrightarrow{q''}$ is the heat flux is diffusive and S_t heat generation per unit volume. $\overrightarrow{m''}$ is the diffusive flux of volume fraction and S_w is the source of volume fraction.

It is considered in the channel's entrance that the field of the mean velocity and mean temperature are known.

4.NUMERICAL METHOD

The governing equations are solved by finite volume method (Patankar, 1980). This method consists of dividing the domain into several control volumes and integrates the equations in time and space in each volume. The main advantage of this procedure is that it ensures the conservation of global quantities of interest. Was chosen the method of dislocated grid where all quantities are stored in the main nodal points, except for speeds that are stored on the faces of control volumes. The values not available in the faces and the nodal points are obtained by interpolation. It is emphasized that the integration of the terms transient was performed with the fully implicit Euler scheme. Figure 4 shows the control volume with the nodal points W, E and P, the *w* and *e* faces, such as the location of the variables.

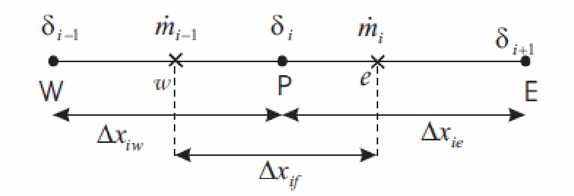

Figure 4: Diagram of control volume.

5. RESULTS

Oil is considered with a volume fraction of paraffin dissolved equals to 10% at a temperature of 40 ºC entering the domain (Romero, 2005). Initially, the external water of the parallel plate is also at a temperature of 40 °C. The analysis begins by cooling the water at 15 ° C. Information on the fluid properties are presented in Table 1. It is noteworthy that, as carried out by Romero (2005), the properties of the oil were obtained from the experimental work of Leiroz (2004), these were considered constant due to a slight variation with temperature of work, except the curve of solubility of paraffin was changed to observe its influence on the deposition rate.

Table 1. Thermophysical properties.

Properties	Oil	Paraffin
Specific Mass, kg/m^3	844	844
Thermal Conductivity, W/(m K)	0,23	0,23
Specific Heat, J/(kg K)	2,018 x 10^3	2,018 x 10^3
Latent heat, J/kg	---	26.440
Porosity,	---	0,86
Viscosity, Pa.s	1,02 x 10^{-2}	---
Molecuar Difusion Coef., m^2/s	Pa.s	---
Molecular Mass, g/mol	2,09 x 10^{-9}	---
	218	

The first analysis was performed to verify the influence of the coefficients of molecular diffusion and shear dispersion coefficient in the deposition of paraffin. To specify the diffusion coefficient we used the correlation proposed by Hayduk and My (1982), which is given by equation

$$D_m = 1{,}33 \times 10^{-7} \frac{T^{1,47} \mu^{\varepsilon}}{V_a^{0,71}}, \tag{11}$$

where T is the absolute temperature in Kelvin, μ is viscosity, V_a is the molar volume of paraffin (cm3/mol), ε is a function of V_a.

For the shear dispersion coefficient correlation proposed by Eckstein and Bailey (1975), according to Eq 12, is used.

$$D_s = \frac{a^2 \gamma C^*}{10}, \tag{12}$$

where a is the particle diameter and γ is the shear rate of oil. To check the influence of both factors, it was proposed an analysis in which the coefficient of molecular diffusion was twice the coefficient obtained with the experimental data Leiroz (2004), and an analysis by varying the shear rate of oil.

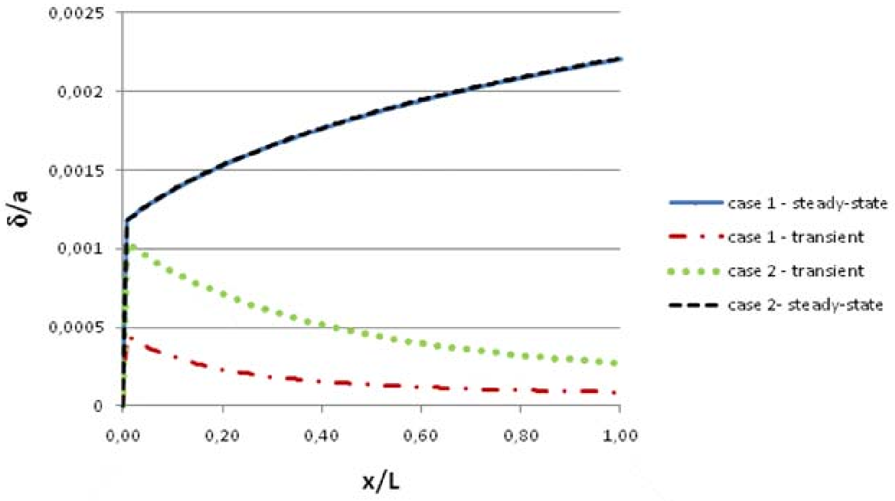

Figure 5: Influence of molecular diffusion coefficient, Re = 856.

In Fig. 5 we can see the influence of molecular diffusion coefficient. Starting with a base case, "*case 1*" and investigated a case with the coefficient with a value twice as great, "*case 2*". We can observe that the coefficient of diffusion will influence the thickness of deposit only during the transient regime, however keep the tendency of the curve. For the steady state, i.e. when the temperature of the mixture is equivalent to TIAC, it is noticed that the final thickness of the deposit is similar for both cases, being so, in principle, that value of the coefficient does not influence the final deposition. Other tests are being conducted to corroborate these findings.

Figure 6 shows the distribution of the deposits in permanently for three Reynolds numbers considering only the influence of molecular diffusion. The model predicts a thinner layer of paraffin as the Reynolds number increases, agreeing with experimental data and numerical simulations of previous work. It is noteworthy that the relative importance of diffusion mechanism in determining the thickness of the deposits and the mechanism associated with the transport of particles depends on the prevailing levels of shear in the fluid. This implies that low Reynolds numbers results in low shear rates, thus the transport mechanism of particles starts to be equally relevant (Burger et al, 1981). Therefore, for a lower Reynolds number it is perceived that the influence of shear dispersion in thick end of the deposit is higher when compared with a higher Reynolds number (Figure 7).

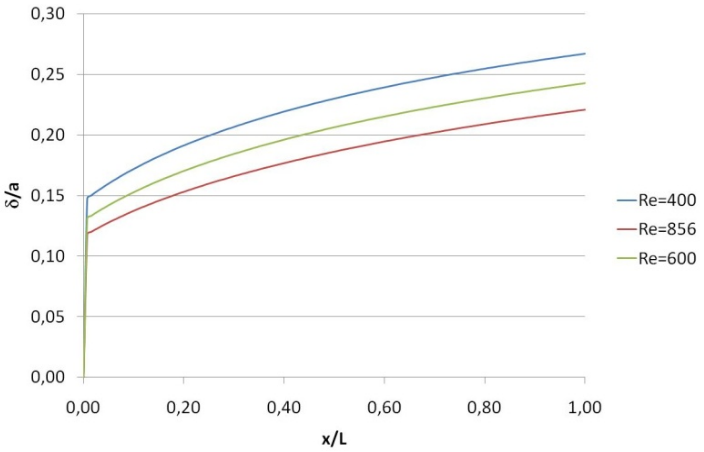

Figure 6: Thickness of paraffin considering only the molecular diffusion

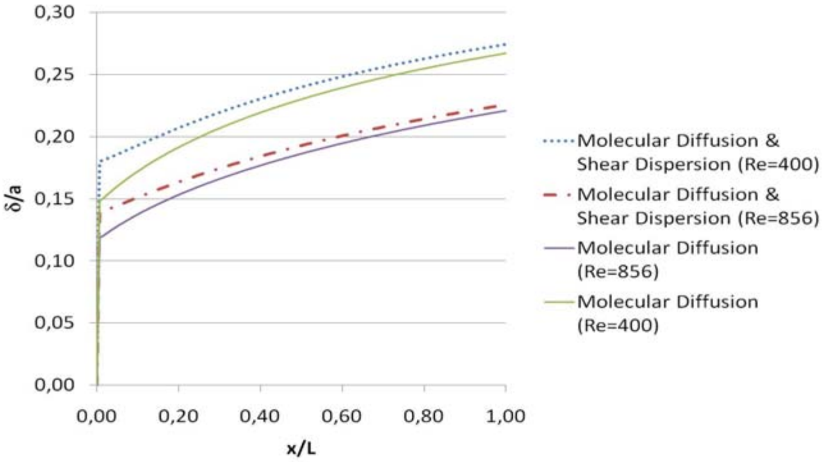

Figure 7: Thickness of the deposit of paraffin considering both mechanisms

Figure 8 shows an analysis of the dispersion coefficient by shear, in which the variation depends, basically, on the value of the shear rate of oil. It was noted therefore that the higher the values of the shear rate of oil, the greater the influence of shear dispersion in the thickness of the deposit. As can be seen, for values γ of higher dispersion by shear will begin to prevail in relation to molecular diffusion.

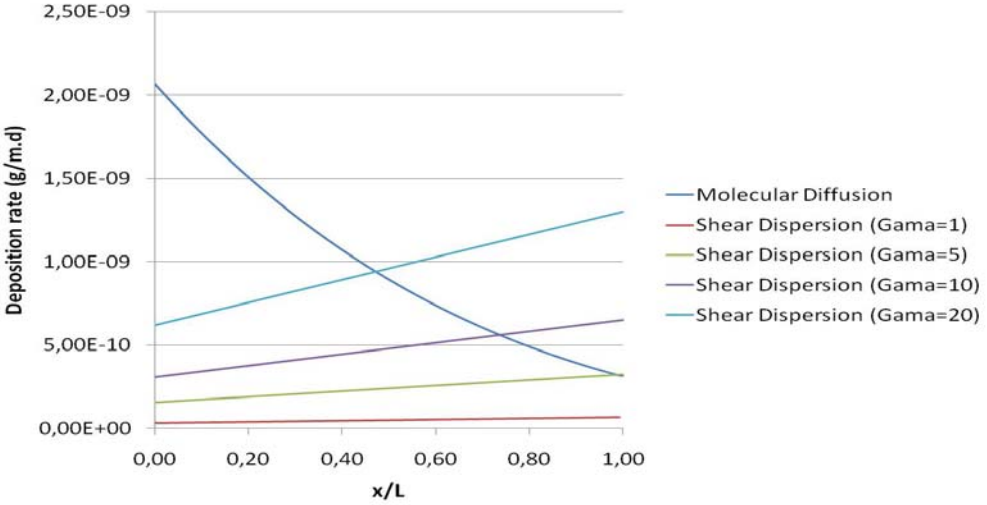

Figure 8: Influence of shear rate for Re = 856.

6. CONCLUSION

The deposition of paraffin in a rectangular duct under laminar flow conditions was analyzed in this work, considering the molecular diffusion and shear dispersion as gifts mechanisms responsible for their deposition on the inner wall of the channel. This research is based on papers published by researchers from the Department of Mechanical Engineering, PUC-Rio. The aim of this study was to evaluate the importance of the diffusive and shear in the process of deposition of paraffin. It was noticed through the results, that the lower the Reynolds number the greater the influence of shear dispersion in the thickness of the deposit. However, in that it can be seen on the results of numerical simulation based on experimental data, there is a predominance of molecular diffusion independent of Reynolds number. It is emphasized that this research is still in early stages in UFES. It was proposed in order to strengthen the newly created research group as well as cooperate with future projects, *offshore* oil production. The necessity of updating the literature on the subject was another goal. It is suggested for realization of future work, the incorporation of other deposition mechanisms and the use of other techniques for dealing with interfaces, such as the method of Elliptic Mesh Generation Method in the context of Galerkin Finite Element.

7. REFERENCES

Azevedo, L. F. A; texeira, A. M. A Critical review of the modeling of wax deposition mechanisms. Petroleum Science and Technology, vol. 21, No 3 e 4, 393-408, 2003.

Brown, T.S., niesen V.G., E erickson, D. D. Measurement and prediction of the kinetics of paraffin deposition. Society of Petroleum Engineers, 26548: 353-368, 1993.

Burguer, E. D., perkins T. K., striegler, J. H. Studies of wax deposition in the Trans Alaska Pipeline. Journal of Petroleum Technology, 1075-1086, 1981.

Creek, J. L., lund, H. J., brill, J. P., volk, M. Wax deposition in single phase flow. Fluid Phase Equilibria, 158-160; 801-811, 1999.

Leiroz, A. T. Estudo sobre a deposição de parafina em linhas de petróleo. Tese de Doutorado, Pontifícia Universidade Católica, PUC-Rio, Rio de Janeiro, 2004.

Patankar, S. V. Numerical heat transfer and fluid flow. Hemisphere, New York, 1980.

Romero, M. I. Avaliação do mecanismo de difusão molecular para a modelagem da deposição de parafina em dutos de petróleo. Dissertação de Mestrado, Departamento de Engenharia Mecânica, Pontifícia Universidade Católica, PUC-Rio, Rio de Janeiro, 2005.

Romero, M. I., Nieckele, A. O., Azevedo, L. F. A. Analysis of two molecular diffusion models for predicting wax deposition in laminar flow. 11th Brazilian Congress of Thermal Sciences and Engineering, 2006.

Svendsen, J. A. Mathematical modeling of wax deposition in oil pipeline system. AIChE J., 39, 1377-1388, 1993.

Todi, S. Experimental and modeling studies of wax deposition in crude oil carrying pipelines. Ph. D. Thesis, The University of Utah, Utah, 2005.

8. RESPONSIBILITY NOTICE

The authors Pablo Morelato Assunção, Lorennzo Marrochi Nolding Rodrigues, Mao Ilich Romero, Oldrich Joel Romero are the only responsible for the printed material included in this paper.