

## CRYSTALLIZATION OF PARAFFIN FROM THE OIL IN A PIPE AND DEPOSITION OF ASPHALTENE–PARAFFIN SUBSTANCES ON THE PIPE WALLS

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*Problems associated with the crystallization of paraffin from the oil in conveying pipes and pipes of heat-exchange apparatus and with the deposition of paraffin particles on the inner surface of these pipes are considered. Diffusion models of the kinetics of crystallization of paraffin and its deposition under the indicated conditions are proposed. A comparison of the results of calculations by these models with corresponding experimental data has given positive results.*

**Keywords:** asphaltene–paraffin substances, crystallization, deposition, deposits, diffusion kinetics.

**Introduction.** The formation of a solid substance in a pipe as a result of the crystallization of paraffin from the oil or oil products in it at a low temperature and the deposition of this substance on the inner surface of the pipe are undesirable effects influencing the parameters of the flow in the pipe. Deposits are formed on the inner surface of a pipe in which oil flows as a result of the crystallization of paraffin from the oil at a low temperature and the growth of paraffin crystals and crystals of asphaltene–resin substances on the pipe surface contacting with the oil, i.e., in the bulk of the boundary layer of the oil flow in the pipe and then on the surface of the resin–paraffin layer formed on the pipe walls. A number of works were devoted to experimental investigation and empirical simulation of the crystallization of paraffin from the oil and oil products flowing in pipes under different conditions [1–5]. It should be noted that in the boundary diffusion layer of the oil flow in such a pipe there exists a radial temperature gradient giving rise to a concentration gradient of the paraffin dissolved in the oil and, consequently, to molecular and turbulent diffusion flows of paraffin particles to the walls of the pipe. When paraffin particles reach these walls or the boundary of the solid deposit on them, they crystallize, separate from solution, and deposit on these walls. The main reasons for the formation of paraffin particles in a pipe in which oil flows and for the deposition of them on the inner surface of the pipe are the decrease in the oil temperature to the temperature of crystallization of paraffin and formation of its particles, an increase in the velocity of the oil flow in the pipe, the formation of coagulation structures in the layers of deposited particles, and the roughness of the pipe surface. The crystallization of paraffin from the oil in a conveying pipe and the deposition of it on the pipe walls is also determined by the density and viscosity of the oil and the weight content of the paraffin compounds and asphaltene–resin substances in it.

The aim of the present work is to develop diffusion models of crystallization of paraffin from the oil in a pipe and of its deposition on the pipe walls as well as to investigate the influence of the thickness of the deposit layer formed on the inner surface of the pipe on the hydrodynamic parameters of the pipe and the heat and mass transfer in it.

**Diffusion Kinetics of Paraffin Crystallization.** The crystallization of paraffin from the oil flowing in a pipe begins with the formation of nucleation centers, i.e., solid asphaltene particles of size about 1 nm. Unlike [2], where an empirical model was used for definition of the crystallization and deposition of paraffins, we have developed diffusion models of crystallization of paraffin from the oil and its deposition on the pipe walls. Crystallization of paraffin from the oil flowing in a pipe is a diffusion process in which the following conditions are fulfilled on the surface of the nucleation centers:

$$-D \left. \frac{\partial C}{\partial r} \right|_{r=R} = \beta_m (C - C^*), \quad (1)$$

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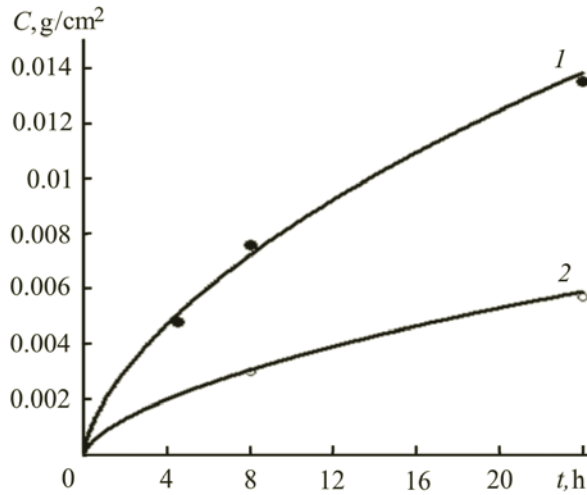


Fig. 1. Crystallization of paraffin from the oil in a pipe at  $\Delta T = 37$  (1) and  $27^\circ\text{C}$  (2).

where  $R$  is the radius of the pipe with deposits and  $r$  is the radial coordinate. In the case where  $dr = Vdt$ , the equation for the kinetics of paraffin crystallization takes the form

$$\frac{dC}{dt} = -K(C - C^*) . \quad (2)$$

Here,  $K = V\beta_m/D$  is the rate constant of the paraffin crystallization dependent on the temperature  $T$  of the oil flow,  $C$  is the concentration of paraffin in the bulk of the boundary layer of this flow, and  $C^*$  is the equilibrium temperature-dependent concentration of paraffin in the liquid and solid phases. A solution of Eq. (2) can be represented in the form

$$C(t) = C^* \left[ 1 - \exp \left( -\int_0^t K dt \right) \right] \quad (3)$$

or in the form

$$C(t) = C^*(T) \left[ 1 - \exp(-\beta_0 t^n) \right] . \quad (4)$$

It follows from Eq. (4) that, in the case where  $t \rightarrow \infty$ ,  $C(t) \rightarrow C_\infty$ , where  $C_\infty$  is the limiting equilibrium concentration of paraffin on the surface of the boundary layer, corresponding to the paraffin layer of maximum thickness on the inner surface of the pipe.

If the maximum thickness of the paraffin layer formed on the walls of a pipe is equal to the pipe radius, the pipe becomes completely plugged. Using experimental data from [2], we defined the function  $C^*(T)$  involved in Eq. (4) as  $C^*(\Delta T) = 1.2 \cdot 10^9 \exp(-7473.5/\Delta T)$ , where  $\Delta T$  is the absolute difference between the surface temperature of the pipe and the crystallization temperature of paraffin. Calculations have shown that, in the temperature range being considered, the exponent  $n$  changes insignificantly, and the value  $n = 0.65$  can be used. Experimental data on the crystallization of paraffin from the oil in a pipe and results of calculations of this process by formula (4) are presented in Fig. 1. It follows from this figure that the concentration of paraffin in the oil tends to an equilibrium value with time.

**Mass Transfer of Paraffin Particles in the Boundary Layer.** The calculations were performed with the following assumptions: a) paraffin particles are crystallized from the oil in a pipe in the diffusion boundary layer of the oil flow at a low temperature, b) the crystallization of paraffin in a laminar oil flow is isothermal, and c) the thickness of the boundary layer is much smaller than the pipe radius, which makes it possible to consider the crystallization process on a plane surface. The velocity of the laminar oil flow in the pipe was determined by the expression

$$V = V_{\max} \left( 1 - \frac{r^2}{R^2} \right) ,$$

where  $V_{\max}$  is the maximum velocity of the flow at the center of the pipe. Since the thickness of the diffusion layer is small compared to the radius of the pipe, we introduce the variable  $y = R - r$  ( $y \ll R$ ) and represent the flow velocity in the form  $V \approx V_{\max} 2y/R$  [7]. In view of the above assumptions, the equation for the diffusion transfer of paraffin particles in the laminar flow in the pipe takes the form [7]

$$\frac{2V_{\max}}{R} y \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial y^2},$$

$$y \rightarrow 0, \quad C = C_0, \quad y = 0, \quad C = C_p, \quad (5)$$

where  $C_0$  is the concentration of paraffin particles in a unit volume of the boundary layer of the oil flow and  $C_p$  is the concentration of paraffin particles on the inner surface of the pipe determined by the kinetics of their formation. We introduce the variable

$$\eta = \left( \frac{V_{\max}}{DR} \right)^{1/3} \frac{y}{x^{1/3}}$$

and, using it, rewrite Eq. (5) as

$$\frac{d^2 C}{d\eta^2} + \frac{2}{3} \eta^2 \frac{dC}{d\eta} = 0. \quad (6)$$

The general solution of Eq. (6) has the form

$$C = A_0 \int_0^\eta \exp\left(-\frac{2}{9} \eta^3\right) d\eta + A_1.$$

Taking into account the boundary conditions of the problem, we write the final solution of Eq. (4):

$$C = C_p + \frac{(C_0 - C_p) \int_0^\eta \exp\left(-\frac{2}{9} \eta^3\right) \eta^3 d\eta}{\int_0^\infty \exp\left(-\frac{2}{9} \eta^3\right) \eta^3 d\eta}. \quad (7)$$

The diffusion flow on a unit surface of the pipe is determined from the expression

$$J = D \left( \frac{\partial C}{\partial y} \right) \Big|_{y=0} = D(C_0 - C_p) \left( \frac{V_{\max}}{DRx} \right)^{1/3} \frac{1}{\int_0^\infty \exp\left(-\frac{2}{9} \eta^3\right) d\eta}.$$

The total diffusion flow on the surface of the pipe is equal to

$$I = 2\pi(R_0 - \delta) \int J dx = 0.7(C_0 - C_p) D \left( \frac{V_{\max} x^2}{DR} \right)^{1/3} (R_0 - \delta), \quad (8)$$

where  $R_0$  is the radius of the pipe with no deposits and  $\delta = C_0 - C_p$ . The function  $I$  related to a unit paraffin mass represents the number of collisions of paraffin particles with the pipe walls. As the thickness of the deposit increases, the number of these collisions decreases. Assuming that the oil flow in the pipe is continuous and using the expression  $R_0 - \delta$  instead of the parameter  $R$ , in view of the pressure drop in the pipe with a layer of deposited particles  $\Delta P = \Delta P_0 \left(1 - \frac{\delta}{R_0}\right)^2$ , we express the maximum velocity of the oil flow in the pipe with deposits in terms of the maximum velocity of this flow in the clean pipe

$$V_{\max} = \frac{R^2 \Delta P}{4\eta_{\text{med}} L} = V_{0\max} = \left(1 - \frac{\delta}{R_0}\right)^4. \quad \text{In this case, we may write}$$

$$I = I_0(1 - \delta/R_0)^2, \quad (9)$$

where  $I_0 = 2\pi\alpha_0^{1/3}\Delta CDR_0\left(\frac{x^2}{R_0^2}\right)^{1/3}$   $Pe^{1/3}$  is the diffusion flow in the pipe with no deposits and  $Pe = \frac{V_0R_0}{D}$  is the Peclet number. The Sherwood number is determined as

$$Sh = \frac{I}{\Delta CDR_0} = 2\pi\alpha_0^{1/3} Re^{1/3} Sc^{1/3} \left(\frac{x}{R_0}\right)^{1/3} \left(1 - \frac{\delta}{R_0}\right)^2,$$

where  $Re = VR_0/v_{med}$  is the Reynolds number and  $Sc = v_{med}/D$  is the Schmidt number.

**Model of Formation of a Dense Layer on the Pipe Walls.** The mass of the paraffin deposited on the walls of a cylindrical pipe was determined on geometrical grounds:

$$m = \pi\rho_d(R_0^2 - (R_0 - \delta_d)^2)L = \pi\rho_{med}(2R_0\delta_d - \delta_d^2)L. \quad (10)$$

Using expression (10), we define the change in the mass of the paraffin deposit as

$$\frac{dm}{dt} = \frac{I_0}{R_0^2} (R_0 - \delta_d)^2. \quad (11)$$

Differentiation of (10) with account of (9) gives the following expression for the change in the thickness of the paraffin layer formed on the pipe walls:

$$\frac{d\delta_d}{dt} = \frac{I_0}{2\pi\rho_dR_0^2L} (R_0 - \delta_d). \quad (12)$$

Solution (12) at the initial conditions  $t = 0$  and  $\delta_d(t) = 0$  (the pipe with no deposits) has the form

$$\delta_d(t) = R [1 - \exp(-m_0t)], \quad (13)$$

where  $m_0 = \frac{I_0}{2\pi\rho_dR_0^2L}$ . Unlike the paraffin particles formed in the bulk of the boundary layer of the oil flow in the pipe, asphaltene–resin substances are present in the free state in the oil. Experimental investigations on the deposition of asphaltene–resin substances in the pipes of heat-exchange apparatus [8] have shown that the thickness of the deposit on the walls of such a pipe can be defined by expression (13) in which  $R$  is replaced by the quantity  $\delta_\infty$  defining the steady thickness of the deposit layer depending on the velocity of the oil flow in the pipe:

$$\delta_d(t) = \delta_{max} [1 - \exp(-m_0t)].$$

Figure 2 shows the dependence of the thickness of the deposit on the walls of the round pipe on the time of its formation, the temperature of the oil flow in the pipe, and the velocity of this flow. Experimental investigations have shown that the limiting thickness of the deposit on the walls of a pipe is determined by the temperature and velocity of the oil flow in it [8]. On the basis of experimental data, we write the following empirical dependence for the limiting thickness of the deposit layer on the walls of a pipe at  $T = 53^\circ\text{C}$  and  $T = 106^\circ\text{C}$ :

$$\delta_{max} = 0.011 \left(\frac{T^2}{V}\right)^{6/7}.$$

The relaxation time of the deposition of particles on the walls of the pipe is equal to  $\tau_r = m_0^{-1} = (\delta_d V k)^{-1} \approx 40\text{--}65$  s. As is seen from Fig. 2, the limiting thickness of the deposit layer decreases with increase in the velocity of the oil flow in the pipe and increases with increase in the temperature of this flow.

**Discussion of Results.** In the diffusion models for the kinetics of crystallization of paraffin from the oil in a pipe (13) and its deposition on the pipe walls, of importance is both the diffusion of paraffin from the liquid to the solid phase and the diffusion transfer of paraffin particles to the pipe walls. The formation of a dense layer of paraffin particles in a

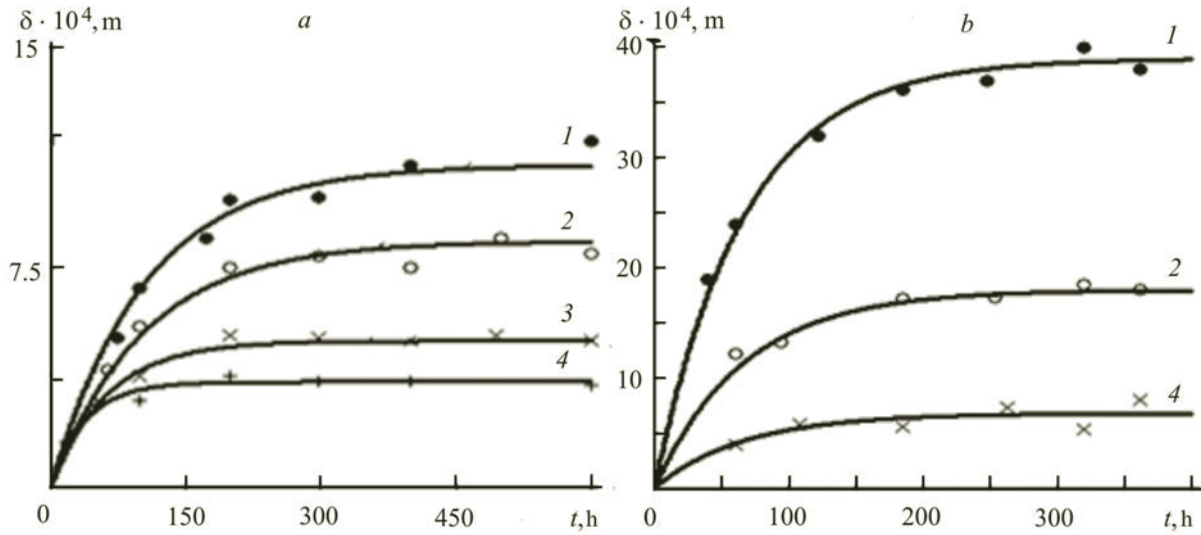


Fig. 2. Time change in the thickness of the asphaltene-paraffin substances on the surface of the pipe at  $T = 53$  (a) and  $106^\circ\text{C}$  (b) and different velocities of the oil flow: 1)  $V = 0.5$  m/s; 2) 1.0; 3) 2; 4) 3.

pipe in which oil flows is determined by a large number of factors, among which are the hydrodynamic, mass-exchange, and thermodynamic conditions in the pipe, the rheological properties of the dispersion medium, the adhesion compatibility of the paraffin particles with the pipe surface over which oil flows, the orientation of this surface, the physicochemical transformations in the boundary layer of the oil flow, and the sizes and concentration of the paraffin particles. An analysis of the indicated processes has shown that the formation of a deposit on the inner surface of a pipe with oil in the form of a dense layer of particles with a low heat conductivity deteriorates the heat exchange of the pipe with the environment, with the result that the coefficients of heat elimination and heat transfer of the pipe decrease.

Defining the dimensionless thickness of the deposit in a pipe as  $\beta = 1 - \delta_d/R_0$ , for the case where the thickness of the deposit layer in the pipe is small ( $\delta_d \leq 0.2(\delta_d/R_0)$ ), we write the following expressions for the main transfer parameters of the pipe:  $\alpha/\alpha_0 \approx \beta^{-1.8}$  and  $\alpha/\alpha_0 \approx \beta^{-3/2}$  for the coefficients of heat elimination in the turbulent and laminar flows in the

pipe, respectively,  $K \sim \frac{1}{\lambda_{\text{med}}} \ln \beta^{-1}$  for the heat-transfer coefficient,  $V/V_0 = \beta^{-2}$  for the velocity of the flow in the pipe,

$\xi_{\text{lam}}/\xi_{\text{lam}0} = \beta$  and  $\xi_t/\xi_{t0} = \beta^{1/4}$  for the drag coefficients in the laminar and turbulent flows, respectively, and  $\text{Re}/\text{Re}_0 = \beta^{-1}$ . It follows from these formulas that, in the case of laminar flow in the pipe, an increase in the thickness of the deposit layer in it disturbs the hydrodynamic stability of the pipe. In the case of turbulent flow in the pipe, an increase in the deposit thickness leads to an increase in the dissipation energy, a decrease in the scale of turbulence, and, consequently, a decrease in the turbulence intensity.

**Conclusions.** The crystallization of paraffin from the oil in a pipe and the deposition of asphaltene and paraffin particles on the inner surface of the pipe with formation of a dense deposit layer on it deteriorate the hydrodynamics of the oil flow in the pipe and the heat and mass transfer in it. If the temperature at the core of the oil flow in the pipe decreases with time, the paraffin particles formed in combination with asphaltene particles exert a marked influence on the structure of this flow and, consequently, on the rheological properties of the oil [9, 10].

## NOTATION

$C$ , concentration,  $\text{kg}/\text{m}^3$ ;  $D$ , molecular-diffusion coefficient,  $\text{m}^2/\text{s}$ ;  $I$ , total diffusion flow on the surface of a pipe,  $\text{kg}/\text{s}$ ;  $J$ , diffusion flow on a unit surface of the pipe,  $\text{kg}/(\text{m}^2 \cdot \text{s})$ ;  $K$ , heat-transfer coefficient,  $\text{W}/(\text{m}^2 \cdot \text{K})$ ;  $L$ , length of the pipe,  $\text{m}$ ;  $m$ , mass,  $\text{kg}$ ;  $\Delta P$ , pressure drop,  $\text{Pa}$ ;  $R$ , radius of the pipe,  $\text{m}$ ;  $T$ , temperature,  $^\circ\text{C}$ ;  $t$ , time,  $\text{s}$ ;  $V$ , velocity of an oil flow,  $\text{m}/\text{s}$ ;  $\alpha$ , heat-elimination coefficient,  $\text{W}/(\text{m}^2 \cdot \text{K})$ ;  $\beta_m$ , mass-transfer coefficient,  $\text{m}/\text{s}$ ;  $\delta_d$ , thickness of the deposit layer,  $\text{m}$ ;  $\eta_{\text{med}}$ , dynamic viscosity of a medium;  $\text{Pa} \cdot \text{s}$ ;  $\lambda_d$ , heat conductivity of the deposit layer,  $\text{W}/(\text{m} \cdot \text{K})$ ;  $\nu_{\text{med}}$ , kinematic viscosity of the

medium,  $m^2/s$ ;  $\zeta$ , drag coefficient;  $\rho_d$ , density of the deposit layer,  $kg/m^3$ ;  $\tau_r$ , relaxation time, s. Subscripts: d, deposit; p, paraffin; med, medium; lam, laminar; max, maximum; m, mass transfer; 0, initial value of a parameter in the pipe with no deposits; r, relaxation; t, turbulent.

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