

REVIEW OF ONSHORE TEXAS PARAFFIN PROBLEMS AND MITIGATION TECHNIQUES

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Paraffin is one of the major flow assurance problem in west and south Texas. The mitigation techniques for the case of onshore paraffin deposition inside a well and flow line is different from the offshore subsea pipeline case. Chemical treatment is used for the onshore Permian basin wells. The current reliable methods for the onshore Permian basin paraffin treatment in well are (1) downhole chemical injection (continuous/batch/squeeze), (2) solid paraffin inhibitor pumped during hydraulic fracturing, (3) hot water or oil circulation. The magnetic conditioning is also being used in some field, despite the lack in the understanding of this method. This paper reviews the current understanding in paraffin deposition problem (single-phase, oil-water, gas-oil), mitigation technique and its current development.

INTRODUCTION

Paraffin or wax is an interesting phenomenon, and it is also a significant problem for petroleum industry. Researchers try to understand the deposition process for both multiphase¹⁻⁵ and single-phase⁶⁻¹⁰ flow. They try to develop the deposition prevention-mitigation techniques. Paraffin is mainly n-alkane components with the carbon number in the range of 20 or more.⁷ The solubility of wax in crude oil decreases as the temperature decreases. Wax precipitation starts at the temperature called Wax Appearance Temperature (WAT), during the decrease in temperature. The onset temperature required to re-dissolve the precipitated wax particles during a heating process is called Wax Disappearance Temperature (WDT). WDT is higher than WAT.¹¹ WDT represents the true solid-liquid thermodynamic equilibrium of wax in oil (not WAT).¹² This means that to raise the oil temperature back to WAT is not enough to dissolve the precipitated wax particles. Wax precipitation and wax deposition are not the same thing. Wax precipitation or crystallization is governed by the solid-liquid thermodynamic equilibrium of wax in oil and the precipitation kinetics (precipitation rate).

For wax deposition to occur in a pipe or well inner surface, (1) wax deposit must have enough attraction force to the surface to stay on the surface, (2) the surface temperature has to be lower than WAT, and (3) the surface temperature has to be lower than the oil temperature.¹³ The difference in oil and the inner wall surface temperature creates a radial temperature gradient. Wax can dissolve less at the surface and can dissolve more at the bulk oil due to the radial temperature gradient. This difference in the dissolved wax concentration creates a dissolved wax concentration gradient which is the driving force for wax deposition. The flow of oil and the concentration gradient cause the dissolved wax molecules to convectively transfer to the wall. It should be noted that the deposition does not occur by the migration of the precipitated solid particles toward the wall.

Once the first layer of the deposit is formed, the radial temperature gradient across the deposit layer creates the radial concentration gradient of the dissolved wax. This causes wax diffusion inside the deposit. The liquid phase hydrocarbon can be described as wax and non-wax hydrocarbon. The dissolved wax concentration that decreases along the radial direction, causes the non-wax hydrocarbon concentration to increase along the radial direction. This opposite gradient direction of the non-wax hydrocarbon causes the counter-diffusion of non-wax hydrocarbon as explained in Singh et al. study.⁶ The diffusion and counter-diffusion inside the wax deposit is the aging process which harden the deposit layer.

Wax precipitation increases the oil viscosity and causes the oil to be a non-Newtonian fluid. Wax deposition decreases the flow area and can eventually plug pipeline and well tubing. For the offshore case, Lasmo Company (U.K.) had to abandon a platform at a cost of \$100 million due to wax deposition problem in pipeline.⁶ The cost of pigging due to the deferred in revenue is in the order of \$5 to \$25 million per year depending on the pigging frequency.¹⁴ Wax deposition is the major engineering issue for both subsea and onshore oil production.^{15,16} For the onshore case, monthly tubing cleanouts are common if the paraffin inhibitors is not used.¹⁷ The high bottom hole temperature (150°C or 302°F) does not necessarily ensure the prevention of wax deposition. The deposition and well plugging in Mexico by fifty-fifty mixture of paraffins and asphaltenes was reported. This deposit was mitigated by using paraffin crystal modifier. In this case, the bottom hole temperature and the total depth of the well are 150°C and 5,700 meters, respectively, and paraffin deposition was still found.¹⁸ This paper reviews the current understanding

in wax deposition phenomena and the serious wax deposition problems in Eagle Ford south Texas and Permian Basin west Texas.^{19–30}

FIELD CASES REVIEW

As early as 1938, paraffin problems in Permian basin were reported. The general practice at that time is to remove it; (1) from the tubing by scraping and (2) from flow lines by heating.¹⁹ The scraping frequency as high as once a week was observed.¹⁹ In 1988, Thomas²⁹ reported paraffin deposition problem in the tubing of rod-pumped oil wells in West Texas. Laboratory tests, including GC analysis, were performed to select a proper additive (surfactant / dispersant type) to mitigate wax problem.²⁹ In 1992, Brown conducted microbial treatment on 72 producing oil wells in Permian Basin and suggested that microbial treatment can be used to control paraffin deposition in oil wells.²⁰ In 1994, Henson et al.²¹ suggested that the conventional hot oiling/watering and mechanical deposit removal in oil well were not effective. Their study was based on the rod-pumped oil wells testing in Midland County, Texas. Some success in paraffin treatment in rod pumped wells (Midland area) by using tubing injection valves with hot watering was observed, but it was suggested that this method can be costly.²¹

In 1999, Becker.²² invented winterized paraffin crystal modifiers that can be used during winter months to minimize wax deposition in both well and flow line. The field case study of five wells in West Texas showed favorable results for using the winterized paraffin crystal modifier. Becker also suggested the use of organic solvent or solvent/dispersant mixture for well clean-up from paraffin problem.²² Dobbs' study²³ in West Texas wells (Ector County) showed the successful application of squeezing the wax crystal modifier into reservoir. The inhibitor retained in the rock matrix was fed-back slowly and continuously to hinder paraffin deposition.²³ In 2001, Becker showed three field case studies in West Texas (including Levelland area) related to the success in paraffin crystal modifier application in well. The studies suggested that the crystal modifier method was superior to hot oil and hot water-surfactant methods.²⁵ Later in 2009 and 2010, Becker and Brown²⁶ and Brown et al.³⁰ reported the use of VHF (very high frequency) and SHF (super high frequency) radio frequencies (RF) for paraffin problem treatment in field case. Becker and Brown²⁶ reported the increase in oil production and the reduction of pour point in the field test. This test was conducted in more than 30 wells in Permian Basin region.^{26,30} Brown et al.³⁰ also reported the increase in wax solubility after the treatment with radio frequency without the detailed analysis that was needed for their claim. In these RF studies, the mechanism of radio frequency on paraffin deposit was speculated, but it was not proven. More detailed laboratory tests are needed to clarify the impact of RF on wax deposit. Smith et al.²⁷ and Szymczak et al.²⁸ developed and successfully tested a new solid paraffin inhibitor technology in Permian Basin (5 wells) and Eagle Ford (17 wells) fields. The solid inhibitor was prepared by using a proppant-like particle as a solid substrate for a liquid inhibitor to be adsorbed on. Then, the solid paraffin inhibitor substrate was added during proppant addition stages of the hydraulic fracture. This allow a continuous release of the inhibitor inside the reservoir at the temperature above WAT. The solid paraffin inhibitor substrate has been applied in over 2,000 wells, primarily in US and Canada. In all cases, the operators have either reported satisfaction or are waiting for a longer time period to evaluate the performance of the solid inhibitor.^{27,28}

CURRENT UNDERSTANDING AND DEVELOPMENT

In this section, the nature of wax deposition research and its challenges are addressed. Then, the reviews on experimental finding, model development, and paraffin inhibitor are discussed. Several researchers investigated the impact of oil-type and operating condition on paraffin deposition. The number of experimental data is limited in the field of wax deposition, because the time required to obtain one data point is long (hours – days) compared to other fluid flow study (5 – 15 minutes). Detailed analysis of the deposit thickness, deposit wax fraction, and oil collected from the test is also required in addition to the flow loop test. The analysis of oil before and after the test can tell if some n-alkane fraction in oil is depleted and causes wax to stop deposit or not. The analysis of deposit thickness and composition allows the model development to predict these parameters accurately. Moreover, these understandings can also be applied when doing the analysis in the field case. The understanding in the deposit thickness and its composition is explained in the following paragraphs.

The deposit thickness and composition is a function of space and time.^{3,6} The surface roughness of the deposit can also change with the length from the inlet.³¹ The deposit surface in the case of single-phase turbulent flow, water-in-oil dispersed flow, and gas-oil slug flow was found to be mostly smooth for the region away from the inlet.^{2,32} The deposit from single-phase laminar flow tends to be thicker, softer, and trap more oil than the one from the turbulent flow cases.³³ The deposit thickness was found to be thinner as the flow rate increases for both laminar⁶ and turbulent flow^{3,34}, in general. However, Panacharoensawad and Sarica³ showed that initially the deposit thickness increased

with flow rate and the late-time-deposit-thickness decreased with flow rate. This means that the deposit thickness versus time trends of various flow rate cases can cross-over each other at a certain time. It should be emphasized that the actual initial temperature difference between the bulk fluid and the interface temperature was controlled to be constant in the case of Panacharoensawad and Sarica.³ They decreased coolant temperature as the oil flow rate increased to maintain the initial inner wall temperature. Some earlier studies^{35–38} made the comparison between high and low flow rate cases by controlling the coolant temperature (but not the inner wall temperature). This causes the variation in thermal driving force within the comparison domain. In all flow loop experiment^{2,3,34,39–41} (especially turbulent flow cases), the inner wall temperature decreased slightly with time as the deposit form, because the deposit insulated the inner wall surface from the heat from the hot fluid side. For the case of slug flow wax deposition, Matzain⁴² and Rittirong² showed that the deposit at the top wall was thicker than the deposit at the bottom wall for all slug flow cases. Moreover, Matzain⁴² (gas-oil case) and Anosike³⁶ (oil-water case) showed that the deposition phenomenon is a strong function of the flow pattern. Matzain⁴² and Anosike³⁶ showed the crescent deposit shape for stratified flow of gas-oil and oil-water, respectively. For stratified-wavy case, they showed that the deposit at the side of the wall (at either gas-oil or oil-water interface) was thicker than its immediate adjacent area (earmuffs shape was formed). This is probably because the side of the wall contacted with the oil intermittently due to wave motion. More analysis on the composition of the tip of the earmuffs shape will reveal the deposition mechanism due to wave motion. If the deposit composition at the tip is close to the oil case and does not contain a long n-alkane as the rest of the crescent shape, then it indicates that the waxy-oil is just gelling (touch-and-dry or freeze) at the interface.

The deposit thickness was found to increase with the thermal driving force for both laminar^{6,43} and turbulent single-phase flow^{38,44} in many cases. This is because as the thermal driving force increases, the concentration driving force increases, in general. However, there were cases that the concentration driving force decreases as the thermal driving force increases. Paso and Fogler⁴⁵ reported that the deposit mass increased and then decreased with the increase in the bulk oil temperature while the coolant temperature remain constant. Huang et al.⁹ showed experimentally and theoretically that the deposit thickness can both decrease and increase as the thermal driving force increases. They explained the decrease in the concentration driving force with the increase in the thermal driving force through the solubility curve of wax in oil. At the same actual thermal driving force (bulk temperature minus interface temperature), the concentration driving force can be decreased significantly for a highly non-linear solubility curve. Moreover, the deposit can only grow until the deposit interface temperature reaches WAT temperature. This means that the deposit can stop growing due to a temperature limitation for the case where the bulk oil temperature is above WAT. Many models^{2,6–8,32,46} suggested that as the temperature at the deposit interface reaches WAT, the increase in the deposit wax fraction (due to aging) will slightly decrease the interface temperature (through the slightly increase in the deposit thermal conductivity), and allows the deposit to grow slightly more. The maximum deposit thickness based on the thermal restriction can be estimated by using a pure wax thermal conductivity for the deposit layer to calculate the thickness at which its interface temperature reaches WAT. For the case where the bulk oil temperature is below WAT, theoretically, if only the thermal and concentration driving forces are considered without the impact of shear, the deposit can grow until the deposit interface reaches the center of the pipe. However, this was not seem to be the case. This concept motivates researchers^{2,7,32,38,47} to consider the shear reduction concept where shear stress from the fluid can hinder the growth or deposition process.

The deposit solid content increases with time. The n-alkane fraction where the carbon number equal to or above a critical carbon number (CCN) in the deposit increases with time. The n-alkane fraction in the deposit where the carbon number is lower than CCN decreases with time. This aging phenomena with respect to the CCN was found experimentally in all flow patterns including single-phase laminar⁶ and turbulent flow,^{3,41} water-in-oil dispersed flow,³ and gas-oil slug flow². The deposit solid content or wax content in wax deposition research is mainly obtained from HTGC and DSC analysis.^{2,3,6,38,41,47,48} The unknown in the heat of crystallization of the deposit causes an uncertainty in DSC analysis of wax content. A typical value of wax crystallization enthalpy of 200 J/g can be used to estimate the deposit wax content. However, this will cause the difference between the wax content value obtained from DSC and HTGC method.^{1,32} HTGC method (with FID detector) will give the carbon number distribution of n-alkane fraction. However, HTGC does not tell if a certain n-alkane species is in a liquid or solid phase at the in-situ condition. Panacharoensawad and Sarica³ showed a mathematical method to calculate the solid fraction of the deposit by using an n-alkane carbon number distribution of the deposit with the solid fraction information from a precipitation curve. The precipitation curve can be obtained by using an HTGC-centrifuge method proposed in Han et al.⁴⁹ Panacharoensawad and Sarica³ also explained that the deposit wax fraction estimated from CCN plus fraction is approximately the same as the value obtained from the calculation through the composition analysis and the precipitation curve.

The deposit wax fraction was found experimentally to increase with the increase in flow rate in the case of laminar flow,⁶ turbulent flow,^{2,7,32,41} dispersed flow of water-in-oil,³ and gas-oil slug flow². Panacharoensawad and Sarica³ did not find that the deposit solid content trends of various flow rate cases can cross-over each other as in the thickness trends case. They found that the deposit solid content and the average n-alkane chain length in the deposit increases with time and flow rate. In laminar flow case, Singh et al.⁶ showed that the deposit wax fraction increased with flow rate. However, Rittirong² found that the slug flow deposit can have a lower wax fraction than the single-phase flow case even though both cases have the same v_{SL} . The film region of the slug flow (which has lower liquid velocity than the single-phase case) could possibly create the low solid fraction deposit (compared to the single-phase deposit) due to the low actual liquid velocity in that region. Therefore, the mass transfer in the slug body and in the liquid film should be analyzed separately as done previously in Rittirong's² modeling study part. For the case of dispersed flow water-in-oil, Panacharoensawad and Sarica³ observed that the deposit wax fraction either increased, decreased or remained the same as water cut increased. They observed that the initial wax fraction (e.g. after 4 hours of test) formed a single increasing trend with the initial wall shear stress, regardless of water cut.³ The initial deposit composition was more sensitive to the initial wall shear stress compared to the initial radial heat flux.³ For the case of single-phase flow turbulent flow, Panacharoensawad and Sarica³ and Rittirong² showed that the deposit wax fraction and the average carbon number of the deposit increased with velocity for the case of a constant initial effective ΔT (bulk fluid temperature minus the interface temperature).

Model Development

All available models mainly predict wax deposition in pipeline, but not inside a well. For the prediction of wax deposition in a well, the deposition mechanism in pipeline can be applied to the well case by adjusting the thermal boundary condition accordingly. Singh et al.⁶ developed a deposition model for laminar flow thin deposit based on heat and mass balances principles. They showed that the main mechanism for wax to deposit is the diffusion of n-alkane molecules inside the wax deposit. They estimated the rate of n-alkane molecules to be convectively transferred to the deposit interface by using heat and mass transfer analogy method. This estimation is equivalent to the assumptions that (1) the precipitation of wax in oil reaches its equilibrium at the deposit surface and the center of the pipe and (2) the precipitation rate in other part is slow and negligible as pointed out in Venkatesan and Fogler⁵⁰ and Lee⁴⁶ studies. In other words, the radial temperature and concentration profiles in the case of Singh et al.⁶ were assumed to develop individually. Singh et al.⁶ model also contains an unknown physical parameter that is not measurable. This parameter is the wax crystal aspect ratio. They assumed that the effective diffusivity inside the deposit can be approximated to be the diffusion through a membrane with layers of infinitely long rectangular barriers, and they used Cussler et al.⁵¹ correlation in this estimation. Singh et al.⁶ model assumed a linear relationship between the deposit wax fraction and the wax crystal aspect ratio. The slope of this linear function (between wax fraction and crystal aspect ratio) could be affected by flow rate, pipe diameter, and testing temperatures. The closure relationship to determine the slope value with respect to the operating conditions (e.g. flow rate, pipe diameter, temperatures, oil composition) was not given, but it is needed. Thus, Singh et al.⁶ model cannot be directly used to predict wax deposition. Nevertheless, Singh et al.⁶ model served as a core model used in several later developments.^{2,5,8,32} Singh et al.⁵² later developed the deposition model for a thick wax deposition in a laminar flow. More complex calculation is needed in this case because the solid fraction inside the deposit was calculated at each radial location, instead of treating the whole deposit with one average solid fraction. Their simulation results showed the prediction of the wax fraction variation inside the deposit which were validated against their experimental results.

For the case of turbulent flow, Venkatesan,⁷ Panacharoensawad (single-phase and water-in-oil dispersed flow),³² Eskin et al.,^{53,54} and Rittirong (single-phase and gas-oil slug flow)² added a shear reduction term into the mass balance equation. Lee,⁴⁶ Huang et al.⁸ and Zheng et al.¹⁰ did not include the shear reduction term into the model, but they incorporated the precipitation rate parameter to taking into account for the effect of turbulent flow. However, the result from Panacharoensawad and Sarica³ suggested that the early time deposition composition is affected by the shear stress from the fluid. Panacharoensawad's analysis³² also showed that the incoming wax mass flux can be lower than the theoretical solubility limit if shear effect is not considered. In Venkatesan model, the wax concentration was assumed to be at the solubility limit (wax concentration is governed by temperature, solubility method). Without the consideration of the shear effect, the solubility method gives the minimum theoretical incoming wax mass flux limit (wax mass flux from the bulk to the deposit interface). The heat and mass transfer analogy method gives the maximum possible theoretical incoming wax mass flux. Fogler and co-worker^{8,10,46} used the partial precipitation model which give the predicted wax mass flux to be between the solubility limit and the heat and mass transfer analogy limit. As the flow Reynolds number goes toward a low Reynolds number value (somewhere in laminar flow regime) and a high Reynolds number value (somewhere in turbulent flow regime), the precipitation rate goes toward zero and infinity,

respectively.^{8,10,46} However, the Reynolds number values where the precipitation rate should approach zero and infinity was not well defined to be at a particular range of Reynolds number. It is not known if this Reynolds number range for no- and complete- precipitations is a function of operating conditions (such as velocity, pipe diameter, and oil composition) or not. Moreover, the relationship between the precipitation rate and the Reynolds number within the Reynolds number domain of the precipitation rate was not shown. Therefore, the model containing the precipitation rate cannot be used as a predictive tool, at least until the closure relationship for the precipitation rate is available. The closure relationship for the crystal aspect ratio is also needed in Huang et al.⁸ model to determine the effective diffusivity inside the deposit. Panacharoensawad³² and Rittirong² models acknowledged the role of the precipitation rate in the thermal boundary layer and the role of the wax crystal aspect ratio on the effective diffusivity of wax inside the deposit. However, they did not model these parts, and assumed the precipitation to be zero and the slope between the wax crystal aspect ratio and the deposit wax fraction to be one. Then, the uncertainty from these parts were absorbed into the closure relationships of other unknown parameters.

The incorporation of the shear effect allow the prediction of the wax mass flux which is lower than the theoretical solubility limit. Researcher models this term differently. Venkatesan incorporated the shear term to reduce the total incoming wax mass flux. In this model, the shear term is proportional to the power law of the shear stress and unknown constant in the model. Panacharoensawad³² and Rittirong² modeled the shear term by assuming that the maximum shear stress that the deposit can tolerate increases linearly proportional to the solid fraction of the deposit. The probability that the incoming wax mass flux will fail to participate in wax deposition process was depending on the shear stress at the deposit interface and the maximum shear stress that the deposit can tolerate. They^{2,32} developed an empirical closure relationship to determine this maximum tolerable shear stress. Eskin et al.⁵⁴ also incorporate the shear effect through an unknown constant in their model. It should be noted that different investigator incorporate this term differently. Therefore, the direct comparison of the shear term among the model cannot be done, even though they tried to model the same parameter.

From the practical point of view, Zheng et al.¹⁰ model is the only model that give the prediction of the composition of the deposit. It is the collective development which include Singh et al.,⁶ Venkatesan,⁷ Lee,⁴⁶ Huang et al.⁸ and its own development together into one simulator which is called Michigan Wax Predictor (MWP).¹⁰ MWP can predict the overall trend of the shift in the deposit composition distribution as the flow rate change, but their model could not predict the actual average carbon number of the deposit accurately.¹⁰ Zheng et al. model¹⁰ has two unknown-physical-constants inherited from Singh et al.⁶ and Huang et al.⁸ which are for the calculations of wax crystal aspect ratio and wax precipitation rate, respectively. Therefore, MWP¹⁰ is considered as a non-self-sufficient predictor because the closure relationships for the unknowns in MWP are not given. Other models, such as Panacharoensawad,³² Rittirong,² and Eskin,⁵⁴ predict only the total solid content of the deposit, but they do not predict the composition in the deposit. Rittirong modified Panacharoensawad model from the water-in-oil dispersed flow to gas-oil slug flow case. He showed that his model can predict the overall deposit thickness and wax fraction (based on his experimental data alone) with the uncertainties of ± 15 and $\pm 20\%$, respectively. Even though Rittirong provided the closure relationships for two unknown in his model and his model is considered as a self-sufficient prediction (can be used to do the prediction), however, the up-scaling of his model to a larger pipe diameter or other temperature required more development. This is because Rittirong model was not intended to claim the up-scaling ability, at this moment. Nevertheless, MWP and Rittirong model have a potential for up-scaling or extrapolating to the case of other oil. This is because these models are mechanistic model which are based on transport equations. Panacharoensawad model contain two unknown parameters which are (1) the parameter used in the relationship between the maximum tolerable shear stress and the deposit solid fraction and (2) the parameter used to modify the initial aging rate which is to account for the entrapment of solid particles near the deposit interface and the initial transient gelation process. Rittirong model contains two unknown parameters which are (1) the parameter to calculate the maximum tolerable shear stress (the same as in Panacharoensawad model) and (2) the modifier for the upper part wax mass flux. The second parameter in Rittirong model is to account for wax deposition in the upper part during the time that the Taylor bubble moves past by the upper portion of the pipe and the upper pipe is in contact with a thin moving oil film. Eskin et al. model contains five fitting parameters to account for (1) precipitation rate, (2) initial deposit porosity at the wall, (3) initial deposit porosity at the deposit interface, (4) the diffusivity inside the deposit, and (5) shear effect. In all models, the diffusivity of wax in oil was calculated from the model that was developed for an infinitely dilute binary system such as Hayduk-Minhas⁵⁵ correlation, yet multi-component diffusion exists in the actual cases.⁵⁶ Moreover, as pointed out in Hoteit et al.,⁵⁶ Fick's law of diffusion is strictly valid only for an isothermal system, but all models used this law for a non-isothermal cases. Therefore, the unknown constants in all models also absorb the error in the diffusivity calculation and the error from using Fick's law for a non-isothermal system.

Despite the fact that the accurate prediction of wax deposition in the field case is questionable, Eskin et al.⁵³ claimed that fitting parameters in their model can be obtained by conducting test in the laboratory by using a Taylor-Couette high pressure deposition cell. They improved their model and showed in Eskin et al. study.⁵⁴ Their new model eliminated drawbacks in their previous model by (1) allowing the total incoming wax mass flux to be different from the wax mass flux through the deposit layer, and (2) by accounting the dependency of the deposit thermal conductivity on the deposit wax fraction in each deposit layer. Yet, these improvements did not make their claim on the model up-scaling to be valid. Eskin et al.⁵³ referred to their previous publication (Akbarzadeh et al.⁵⁷) that the unknown parameters used in their model can be determined by matching the wall shear stress, pressure, and temperature to the field condition. However, the validity of the parameters obtained from the Taylor-Couette high pressure cell is at least dependent whether the unknown parameters are shear and heat flux dependent at the same time or not. If the unknown parameters are dependent upon the shear and heat flux at the same time, then the value obtained from the test cell will not be valid for directly up-scaling to the field condition. This is because it is possible to match only shear, inner wall temperature, and bulk fluid temperature to the field condition but the test cell cannot provide the same heat flux to the field condition at the same time. For turbulent flow in a pipe, the wall shear stress and Nusselt number can be roughly estimated to be $\tau = \frac{0.046}{2} \left(\frac{\rho v D}{\mu} \right)^{-0.2} \rho v^2$, and $Nu = \frac{hD}{k} = 0.023 \left(\frac{\rho v D}{\mu} \right)^{0.8} \left(\frac{\mu C_p}{k} \right)^{1/3}$, respectively. If the bulk oil temperature and the inner wall temperature are controlled to match the field condition, the heat transfer coefficient has to match the field condition too in order to have the same heat flux ($q = h(T_b - T_i)$). For the same fluid properties, the wall shear stress (τ) is approximately proportional to $D^{-0.2} * v^{1.8}$ and the heat transfer coefficient (h) is approximately proportional to $D^{-0.2} v^{0.8}$. This means that we need to have a constant $D^{-0.2} * v^{1.8}$ for both a large diameter (field case) and small diameter (lab case) cases, in order to have the same wall shear stress for both cases. However, in order to maintain the same heat transfer coefficient (or heat flux for the case of identical T_b and T_i) as the pipe diameter increases the value of $D^{-0.2} v^{0.8}$ needs to remain constant. If $D^{-0.2} * v^{1.8}$ is constant as the diameter increases, $D^{-0.2} v^{0.8}$ will not be constant. Therefore, we cannot match τ and h at the same time in the pipe flow with a difference in pipe diameter, as expected.

For the case of pipe flow and Taylor-Couette flow, Akbarzadeh et al.⁵⁷ estimated the momentum boundary layer thickness from $y^+ = \delta_M \sqrt{\tau/\rho}/v = 5$ and approximate the thermal boundary layer thickness from $\delta_T \approx \delta_M/\sqrt{Pr}$. With this approximation, Akbarzadeh et al.⁵⁷ explained that once the wall shear stress between the pipe flow and Taylor-Couette flow conditions are matched, then the analogy from both system is reached from both hydrodynamic and thermal point of view. If we follow Akbarzadeh et al.⁵⁷ analysis, we will have that the small pipe and large pipe will have the analogous conditions from both hydrodynamic and heat transfer point of view. However, we show here earlier that even for the pipe flow case, we cannot directly up-scale and match the shear stress and heat transfer for the large and the small pipe diameter at the same time. This means that the up-scale from the small Taylor-Couette system to the field case condition will not be as easy as matching the wall shear stress and approximate the heat transfer to match at the same time as in the case of Akbarzadeh et al.⁵⁷. Moreover, Wax deposition phenomenon is dependent upon both heat flux and shear of the system. Panacharoensawad and Sarica³ showed the impact of shear stress on the early time deposit wax fraction. The concentration gradient itself is driven through the temperature gradient.⁶ In general, a larger wax crystal is formed for the case of a slower cooling rate or less heat flux from the system. A high enough shear exerted to the system is expected to crack or deform the newly form wax crystal shape and size.³² Therefore, the crystal size, shape, and the arrangement of the crystal inside the deposit are expected to be a function of heat flux and shear stress. The closure relationship between the effective diffusivity and the deposit wax fraction is directly related to the arrangement, size, and shape of the crystal. Thus, the direct up-scaling of the constant used in this effective diffusivity calculation (the constant n for the case of Eskin et al.⁵³) from the Taylor-Couette system to the field condition without accounting to both heat flux and shear at the same time (as in the case of Eskin et al.⁵³) is invalid.

MITIGATION TECHNIQUES

Several mitigation techniques for paraffin deposition problems are available. These techniques include pigging, chemical additive, heating, and solvent methods. The pigging technique can be used only in the pipeline but not inside a well. Chemical method, hot oiling, hot watering, and other non-conventional mitigation techniques such as radio frequency or magnetic field techniques can be used in both inside the well and flow line. In general, polyethylene (PE) flow line has a limited pressure rating and can has low flow rate which can restrict the direct use of pig. Installation of pig launcher and receiver is also required for a pigging operation. A soft pig with water-jet can be used to clean a PE pipeline. Scraper-type or rigid hard pig can damage PE line and it should be avoided. This article reviews mainly on the mitigation technique that can be used for wax deposition inside an oil well.

Chemical Method

Chemical additive for wax problems can be categorized by its function as wax deposition inhibitor and pour-point depressants. The pour-point depressants main function is to decrease the pour-point temperature of waxy oil (temperature below which oil stop to flow). Some chemical can reduce deposition and pour point at the same time. Three main groups of paraffin or wax deposition inhibitor are wax crystal modifiers, detergents, and dispersants. Chemicals that reduce WAT are usually referred as wax inhibitor or crystal modifier. Detergent and dispersants are primarily surface-active agents such as polyesters and amine ethoxylates. Their main function is to keep wax crystals dispersed as separate particle and not to adhere to solid surface. They can also modify surface of the pipe wall in addition to acting on the wax crystal.⁵⁸⁻⁶⁰ Many effective wax deposition inhibitors creates softer deposit that can be removed easily by shear forces.⁶¹ Paraffin inhibitor typically do not provide 100% inhibition⁵⁹ and they are crude specific. The increase in the deposit hardness can also be found after treating crude oil with an inhibitor.⁶² Therefore, an inhibitor has to be evaluated on a case-by-case basis.^{60,63}

Pour-point depressants and paraffin inhibitor are mainly (1) ethylene polymers and co-polymer and (2) comb-shaped polymers. Ethylene copolymers group includes ethylene/small alkene copolymers, ethylene/vinyl acetate (EVA) copolymers, and ethylene/acrylonitrile copolymers.⁶⁴ Generally, ethylene/small alkene copolymers inhibitor type such as ethylene/butane copolymers (PEB) has a crystalline nonpolar group (polyethylene (PE)) and an amorphous nonpolar group (polybutene (PB)). This type of inhibitor form micelle-like structures and interact with wax molecules by nucleation and co-crystallization resulting in numerous smaller wax crystal.^{65,66} The effectiveness of EVA copolymer is dependent upon the percentage of vinyl acetate in the copolymer. The vinyl acetate content decreases the crystallinity and improve solubility which is necessary to depress WAT. The polyethylene content allows the co-crystallization with wax molecule, so that the vinyl acetate portion can disrupt the crystallinity of wax deposit once the co-crystallization occurs.⁶⁰ The comb-shaped polymers are usually made from methacrylic acid or maleic anhydride monomer, or both and provide improved wax deposition inhibition compared to the ethylene copolymers. One proposed mechanism for the comb polymers to act as a pour point dispersant is by reducing the ability of wax crystals to agglomerate into a gel structure by introducing defects of repulsive force. Their paraffin-like pendant chains provide nucleation sites for wax crystal while a polar backbone impede the formation of an interlocking wax network.^{60,67} Matching the average pendant chain length of the comb-shaped polymers to the paraffin chain length distribution in oil provides greatest pour-point depression and efficient wax deposition inhibition.^{63,68}

Unconventional Method

One way to identify the stages of research and development is to categorize it into the following three stages which are: (1) fundamental pure science research, (2) engineering applied research, and (3) practical application development. In this paper, the unconventional method of wax mitigation technique is defined as the method that has one or more of the aforementioned research stages missing. The proposed unconventional method to mitigate paraffin deposition problem includes (1) pipe wall surface treatment (2) microbial treatment, (3) exothermic reaction, (4) cold flow technology, and (5) ultrasonic wave and electromagnetic field and wave methods. Unconventional methods (1) to (4) has a clear fundamental science concept to support its mechanism of action. The electromagnetic field and wave including a high radio frequency method do not have a firm scientific explanation of its mechanism of action. The ultrasonic wave method has a clearer explanation of its mechanism of action compared to the electromagnetic field and wave method, but there is still some unclear mitigation mechanisms which are required more investigations on this part. The methods (1) to (4) requires more engineering researches and practical developments to establish themselves as a reliable method.

The chemical coated surface allows water to be adsorbed on its surface instead of oil. This water layer repels oil and prevents oil from touching the surface to form wax deposit.⁶⁹⁻⁷¹ The theory supported this anti-wax surface was established, and the testing result showing the performance of the anti-wax surface was obtained.⁶⁹⁻⁷¹ However, it may not be economically feasible to implement the anti-wax surface tubing/pipeline to the field case. Therefore, more development on the practical application of this method is required. The microbial treatment is based on the mechanism that microbe can digest wax molecules and remediate the wax precipitation⁷² and deposition problems. This method is a potential method to mitigate wax deposition problem in an economical and environmental friendly way. However, the reliability of this method can be questionable, even though there are some field case studies^{20,73-76} showed the success in using this method. A detailed study should be conducted to understand the method's limitations and its operating range.

The exothermic reaction technique proposed by Singh and Fogler⁷⁷ is based on the principle that the fused chemical reaction allow the exothermic heat from the reaction to release at the place where wax deposit precisely to dissolved

the deposited wax. The simulation result⁷⁷ was shown, and the experiment⁷⁸ was also conducted to prove that the concept of the fused chemical reaction can be used. Nevertheless, the practical application development of this technique (which can be complicated due to the calculation of the required delay time) has to be completed before this technique can be used in the field case. The cold-flow technology concept is that the produced oil temperature is reduced to precipitate most wax dissolved in oil. Then, the solid-wax-in-oil slurry is safely to flow without producing any wax deposit because the dissolved wax molecule was depleted from the oil already after the temperature reduction.⁷⁹ This method was proposed to be used for the transportation in a pipeline but not to put down hole inside a well. If the Joule-Thomson expansion of gas (Hutton and Kruka technique shown in Garcia and Corraera⁷⁹) is used to cool oil, the flow will be choked and resulted in more pressure drop. The drawback of this method is that the cold slurry of wax-oil mixture has a higher viscosity than the fluid before treatment. More energy is required to pump a more viscous fluid. The practical development of this technique needs to be completed before it can be used as a practical reliable method for a pipeline wax deposition mitigation technique.

An ultrasound wave was found to delay the gel network formation for isothermal condition where the temperature was below the pour point.⁸⁰ The ultrasonic wave was found to be able to remove wax precipitation from the near wellbore formation region based on laboratory result.⁸¹ Bjorndalen and Islam proposed the used of microwave and ultrasonic wave to re-suspend the precipitated wax in horizontal well based on their success laboratory results.⁸² The removal of wax precipitate from a formation shows the potential of this method for wax deposit removal. A patent on the ultrasonic wave application for wax deposit removal in a wellbore is available.⁸³ However, the experimental result⁸⁴ on the impact of ultrasonic wave on wax deposit removal was not quite conclusive and more experimental investigations are required to elucidate this point. For high radio frequency application in wax deposition prevention, there were field case studies indicating the success of this method as discussed previously.^{26,30} However, the proposed mechanism of action for the radio frequency to work is unclear and questionable. A detailed experiment in a controlled environment is required to understand the mechanism of this radio frequency method. The impact of magnetic field on wax deposition is not quite conclusive. The study on this part is scarce. There was a report showing an obvious effect of magnetic field on wax deposition reduction.⁸⁵ Magnetic field was found to be able to reduce viscosity⁸⁶ of some crude oil type⁸⁷ but the theory to explain this mechanism was unclear. Moreover, there was a report that the magnetic field did not do anything on oil viscosity.⁸⁸ There are several magnetic treatment patents⁸⁹⁻⁹¹ available for wax deposition reduction purposes, despite the unproven reduction mechanism. Furthermore, as the viscosity decreases the diffusion increases, theoretically. This promotes more mass transfer and should increase wax deposition.

CONCLUSION

In conclusion, this paper reviews the wax deposition problems in onshore west and south Texas. Several reported field cases are reviewed. The comprehensive views on the current wax deposition phenomena understanding and the deposition model development are given. Flaws and assumptions in wax deposition models are identified and discussed. The conventional and unconventional mitigation techniques for wax problems are summarized and reviewed. The development status of the unconventional methods is briefly discussed.

REFERENCE

- (1) Sarica, C., and Panacharoensawad, E. (2012) Review of paraffin deposition research under multiphase flow conditions, in *Energy & Fuels*, pp 3968–3978.
- (2) Rittirong, A. (2014) Paraffin Deposition Under Two-Phase Gas-Oil Slug Flow in Horizontal Pipes. Ph.D. dissertation, The University of Tulsa, Tulsa, Oklahoma.
- (3) Panacharoensawad, E., and Sarica, C. (2013) Experimental study of single-phase and two-phase water-in-crude-oil dispersed flow wax deposition in a mini pilot-scale flow loop. *Energy and Fuels* 27, 5036–5053.
- (4) Zhang, Y., Gong, J., and Wu, H. (2010) An Experimental Study on Wax Deposition of Water in Waxy Crude Oil Emulsions. *Pet. Sci. Technol.* 28, 1653–1664.
- (5) Huang, Z., Senra, M., Kapoor, R., and Fogler, H. S. (2011) Wax deposition modeling of oil/water stratified channel flow. *AIChE J.* 57, 841–851.
- (6) Singh, P., Venkatesan, R., Fogler, H. S., and Nagarajan, N. (2000) Formation and aging of incipient thin film wax oil gels. *AIChE J.* 46, 1059–1074.
- (7) Venkatesan, R. (2004) The deposition and rheology of organic gels. Ph.D. dissertation, The University of Michigan, Ann Arbor, Michigan.
- (8) Huang, Z., Lee, H. S., Senra, M., Scott Fogler, H., and Fogler, H. S. (2011) A fundamental model of wax deposition in subsea oil pipelines. *AIChE J.* 57, 2955–2964.

- (9) Huang, Z., Lu, Y., Hoffmann, R., Amundsen, L., and Fogler, H. S. (2011) The Effect of Operating Temperatures on Wax Deposition. *Energy & Fuels* 25, 5180–5188.
- (10) Zheng, S., Zhang, F., Huang, Z., and Fogler, H. S. (2013) Effects of Operating Conditions on Wax Deposit Carbon Number Distribution : Theory and Experiment. *Energy & Fuels* 27, 7379–7388.
- (11) Hansen, A. B. (1991) Wax precipitation from North Sea crude oils. 3. Precipitation and dissolution of wax studied by differential scanning calorimetry. *Energy & Fuels* 914–923.
- (12) Ji, H.-Y., Tohidi, B., Danesh, A., and Todd, A. C. (2004) Wax phase equilibria: developing a thermodynamic model using a systematic approach. *Fluid Phase Equilib.* 216, 201–217.
- (13) Svendsen, J. A. (1993) Mathematical modeling of wax deposition in oil pipeline systems. *AIChE J.* 39, 1377–1388.
- (14) Lu, Y., Huang, Z., Hoffmann, R., Amundsen, L., and Fogler, H. S. (2012) Counterintuitive effects of the oil flow rate on wax deposition. *Energy & Fuels* 26, 4091–4097.
- (15) Fan, Y., and Llave, F. (1996) Chemical removal of formation damage from paraffin deposition. Part I- Solubility and dissolution rate, in *SPE Formation Damage Control Symposium, 14-15 February, Lafayette, Louisiana*, p SPE–31128–MS. Lafayette, LA.
- (16) Edmonds, B., Moorwood, T., Szczepanski, R., and Zhang, X. (2008) Simulating wax deposition in pipelines for flow assurance†. *Energy & Fuels* 22, 729–741.
- (17) Ellison, B. T., Gallagher, C. T., Frostman, L. M., and Lorimer, S. E. (2000) The Physical Chemistry of Wax, Hydrates, and Asphaltenes, in *Offshore Technology Conference, 5/1/2000, Houston, Texas*, p OTC–11963–MS.
- (18) Becker, H. L. (2000) Asphaltene : To Treat or Not, in *SPE Permian Basin Oil and Gas Recovery Conference, 21-23 March, Midland, Texas*, p SPE–59703–MS.
- (19) Doherty, W. T. (1938) The Permian Basin and its Drilling and Production Problems, in *38-047 API Conference, Spring meeting Southwestern District, Division of Production, Fort Worth, Texas March 24-25*.
- (20) Brown, F. G. (1992) Microbes: The Practical and Environmental Safe Solution to Production Problems, Enhanced Production, and Enhanced Oil Recovery, in *Permian Basin Oil and Gas Recovery Conference, 18-20 March, Midland, Texas*, p SPE–23955–MS.
- (21) Henson, R. D., Tangen, T. J., and Horne, P. T. (1994) Evaluation of Paraffin-Treating Programs in Rod-Pumped Oil Wells, in *Permian Basin Oil and Gas Recovery Conference, 16-18 March, Midland, Texas*, p SPE–27669–MS.
- (22) Becker, J. R. (1999) Winterized Paraffin Crystal Modifiers. *SPE Annu. Tech. Conf. Exhib. 3-6 October, Houston, Texas* SPE–56811–MS.
- (23) Dobbs, J. B. (1999) A Unique Method of Paraffin Control in Production Operations, in *SPE Rocky Mountain Regional Meeting, 15-18 May, Gillette, Wyoming*, p SPE–55647–MS.
- (24) Herman, J., and Ivanhoe, K. (1999) Paraffin, asphaltene control practices surveyed. *Oil gas J.*
- (25) Becker, J. R. (2001) Paraffin-Crystal-Modifier Studies in Field and Laboratory, in *SPE Permian Basin Oil and Gas Recovery Conference, 15-17 May, Midland, Texas*, p SPE–70030–MS.
- (26) Becker, J. R., and Brown, J. M. (2009) Quantum Effects Imparted By Radio Frequencies as a Stimulation Method of Oil Production, in *SPE Annual Technical Conference and Exhibition, 4-7 October, New Orleans, Louisiana*, p SPE–124144–MS.
- (27) Smith, T. W., Szymczak, S., Gupta, D. V. S., and Brown, J. M. (2009) Solid Paraffin Inhibitor Pumped in a Hydraulic Fracture Provides Long Term Paraffin Inhibition in Permian Basin Wells, in *SPE Annual Technical Conference and Exhibition, 4-7 October, New Orleans, Louisiana*, p SPE–124868–MS. Society of Petroleum Engineers.
- (28) Szymczak, S., Gupta, D. V. S., Steiner, W., Bolton, S., and Romano, J. (2014) Well Stimulation Using a Solid Proppant-Sized Paraffin Inhibitor to Reduce Costs and Increase Production for a South Texas Eagle Ford Shale Oil Operator, in *SPE International Symposium and Exhibition on Formation Damage Control, 26-28 February, Lafayette, Louisiana, USA*, p SPE–168169–MS.
- (29) Thomas, D. . (1988) Selection of Paraffin Control Products and Applications, in *International Meeting on Petroleum Engineering, 1-4 November, Tianjin, China*, p SPE–17626–MS.
- (30) Brown, J. M., Becker, H. L., Darby, G., and Services, B. J. (2010) Quantum Effects Imparted by Radio Frequencies as a Stimulation Method of Oil Production — Part II.
- (31) Panacharoensawad, E., and Sarica, C. Wax Deposit Surface Characteristic under Single-phase and Water-in-Crude-Oil Flow Conditions, in *Offshore Technology Conference, 05-08 May, Houston, Texas*. Offshore Technology Conference.
- (32) Panacharoensawad, E. (2012) Wax Deposition Under Two-Phase Oil-Water Flowing Conditions. Ph.D. dissertation, The University of Tulsa, Tulsa, Oklahoma.

- (33) Hernandez, O. C. (2002) Investigation of Single-Phase Paraffin Deposition Characteristics. M.S. Thesis, The University of Tulsa, Tulsa, Oklahoma.
- (34) Dwivedi, P., Sarica, C., and Shang, W. (2013) Experimental Study on Wax-Deposition Characteristics of a Waxy Crude Oil Under Single-Phase Turbulent-Flow Conditions. *Oil Gas Facil.* 61–73. SPE–163076–PA.
- (35) Matzain, A., Apte, M. S., Zhang, H.-Q., Volk, M., Brill, J. P., and Creek, J. L. (2002) Investigation of Paraffin Deposition During Multiphase Flow in Pipelines and Wellbores—Part 1: Experiments. *J. Energy Resour. Technol.* 124, 180–186.
- (36) Anosike, C. F. (2007) Effect of Flow Patterns on Oil-Water Flow. M.S. Thesis, The University of Tulsa, Tulsa, Oklahoma.
- (37) Bruno, A., Sarica, C., Chen, H., and Volk, M. (2008) Paraffin Deposition During the Flow of Water-in-Oil and Oil-in-Water Dispersions in Pipes, in *SPE Annual Technical Conference and Exhibition, 21-24 September, Denver, Colorado, USA*, p SPE 114747–MS.
- (38) Dwivedi, P. (2010) An Investigation of Single-Phase Wax Deposition Characteristics of South Pelto Oil Under Turbulent Flow. M.S. Thesis, The University of Tulsa, Tulsa, Oklahoma.
- (39) Mirazizi, H. K., Shang, W., and Sarica, C. (2012) Experimental investigation of paraffin deposition under turbulent flow conditions, in *8th North American Conference on Multiphase Technology, 20-22 June, Banff, Alberta, Canada*, pp 151–166. BHR–2012–A010.
- (40) Mirazizi, H. K., Shang, W., and Sarica, C. (2012) Paraffin Deposition Analysis for Crude Oils under Turbulent Flow Conditions, in *SPE Annual Technical Conference and Exhibition, 8-10 October, San Antonio, Texas, USA*, p SPE 159385–MS.
- (41) Singh, A. (2013) Experimental and Field Verification Study of Wax Deposition in Turbulent Flow Conditions. M.S. Thesis, The University of Tulsa, Tulsa, Oklahoma.
- (42) Matzain, A. (1999) Multiphase Flow Paraffin Deposition Modeling. *Multiph. Flow Paraffin Depos. Model.* Ph.D. dissertation, University of Tulsa, Tulsa, Oklahoma.
- (43) Lashkarbolooki, M., Seyfaee, A., Esmailzadeh, F., and Mowla, D. (2010) Experimental Investigation of Wax Deposition in Kermanshah Crude Oil through a Monitored Flow Loop Apparatus. *Energy & Fuels* 24, 1234–1241.
- (44) Lund, H. (1998) Investigation of Paraffin Deposition during Single Phase Liquid Flow in Pipelines. *Investig. Paraffin Depos. Dur. Single-Phase Liq. Flow Pipelines.* M.S. Thesis, The University of Tulsa, Tulsa, Oklahoma.
- (45) Paso, K. G., and Fogler, H. S. (2004) Bulk Stabilization in Wax Deposition Systems. *Energy & Fuels* 18, 1005–1013.
- (46) Lee, H. S. (2008) Computational and Rheological Study of Wax Deposition and Gelation in Subsea Pipelines. Ph.D. dissertation, The University of Michigan, Ann Arbor, Michigan.
- (47) Mirazizi, H. K. (2011) Investigation of Single-Phase Paraffin Deposition Characteristics Under Turbulent Flow. M.S. Thesis, The University of Tulsa, Tulsa, Oklahoma.
- (48) Senra, M., Panacharoensawad, E., Kraiwattanawong, K., Singh, P., and Fogler, H. S. (2008) Role of n -Alkane Polydispersity on the Crystallization of n -Alkanes from Solution. *Energy & Fuels* 22, 545–555.
- (49) Han, S., Huang, Z., Senra, M., Hoffmann, R., and Fogler, H. S. (2010) Method to Determine the Wax Solubility Curve in Crude Oil from Centrifugation and High Temperature Gas Chromatography Measurements. *Energy & Fuels* 24, 1753–1761.
- (50) Venkatesan, R., and Fogler, H. S. (2004) Comments on analogies for correlated heat and mass transfer in turbulent flow. *AIChE J.* 50, 1623–1626.
- (51) Cussler, E. L., Hughes, S. E., Ward, W. J., and Aris, R. (1988) Barrier membranes. *J. Memb. Sci.* 38, 161–174.
- (52) Singh, P., Venkatesan, R., Fogler, H. S., and Nagarajan, N. R. (2001) Morphological evolution of thick wax deposits during aging. *AIChE J.* 47, 6–18.
- (53) Eskin, D., Ratulowski, J., and Akbarzadeh, K. (2013) A model of wax deposit layer formation. *Chem. Eng. Sci.* 97, 311–319.
- (54) Eskin, D., Ratulowski, J., and Akbarzadeh, K. (2014) Modelling wax deposition in oil transport pipelines. *Can. J. Chem. Eng.* 92, 973–988.
- (55) Hayduk, W., and Minhas, B. S. (1982) Correlations for prediction of molecular diffusivities in liquids. *Can. J. Chem. Eng.*
- (56) Hoteit, H., Banki, R., and Firoozabadi, A. (2008) Wax Deposition and Aging in Flowlines from Irreversible Thermodynamics. *Energy & Fuels* 22, 2693–2706.
- (57) Akbarzadeh, K., Ratulowski, J., Eskin, D., and Davies, T. (2010) The importance of wax-deposition measurements in the simulation and design of subsea pipelines. *SPE Proj. Facil. Constr.* 5, 49–57 SPE–115131–PA.
- (58) Pedersen, K. S., and Rønningsen, H. P. (2003) Influence of Wax Inhibitors on Wax Appearance Temperature, Pour Point, and Viscosity of Waxy Crude Oils. *Energy & Fuels* 17, 321–328.

- (59) Jennings, D. W., and Breitigam, J. (2010) Paraffin Inhibitor Formulations for Different Application Environments: From Heated Injection in the Desert to Extreme Cold Arctic Temperatures. *Energy & Fuels* 24, 2337–2349.
- (60) Aiyejina, A., Chakrabarti, D. P., Pilgrim, A., and Sastry, M. K. S. (2011) Wax formation in oil pipelines: A critical review. *Int. J. Multiph. Flow* 37, 671–694.
- (61) Manka, J. S., Magyar, J. S., and Smith, R. P. (1999) Novel method to winterize traditional pour point depressants, in *Proceedings - SPE Annual Technical Conference and Exhibition*, p SPE 56571–MS.
- (62) Wang, K. S., Wu, C. H., Creek, J. L., Shuler, P. J., and Tang, Y. (2003) Evaluation of effects of selected wax inhibitors on paraffin deposition, in *Petroleum Science and Technology*, pp 369–379.
- (63) Manka, J. S., and Ziegler, K. L. (2001) Factors Affecting the Performance of Crude Oil Wax-Control Additives, in *Proceedings - SPE Production Operations Symposium*, pp 639–645, SPE 67326–MS.
- (64) Tinsley, J. (2008) The effect of polymers and asphaltenes upon wax gelation and deposition. Ph.D. dissertation, Princeton University, Princeton, New Jersey.
- (65) Wei, B. (2014) Recent advances on mitigating wax problem using polymeric wax crystal modifier. *J. Pet. Explor. Prod. Technol.* 1–11.
- (66) Yang, F., Zhao, Y., Sjöblom, J., Li, C., and Paso, K. G. (2015) Polymeric Wax Inhibitors and Pour Point Depressants for Waxy Crude Oils: A Critical Review. *J. Dispers. Sci. Technol.* 36, 213–225.
- (67) Soni, H. P., and Bharambe, D. P. (2008) Performance-Based Designing of Wax Crystal Growth Inhibitors. *Energy & Fuels* 22, 3930–3938.
- (68) Jang, Y. H., Blanco, M., Creek, J., Tang, Y., and Goddard, W. A. (2007) Wax inhibition by comb-like polymers: support of the incorporation-perturbation mechanism from molecular dynamics simulations. *J. Phys. Chem. B* 111, 13173–9.
- (69) Guo, Y., Li, W., Zhu, L., and Liu, H. (2012) An excellent non-wax-stick coating prepared by chemical conversion treatment. *Mater. Lett.* 72, 125–127.
- (70) Wang, Z., Zhu, L., Liu, H., and Li, W. (2013) A conversion coating on carbon steel with good anti-wax performance in crude oil. *J. Pet. Sci. Eng.* 112, 266–272.
- (71) Li, W., Zhu, L., Liu, H., and Zhai, J. (2013) Preparation of anti-wax coatings and their anti-wax property in crude oil. *J. Pet. Sci. Eng.* 103, 80–84.
- (72) Etoumi, A., El Musrati, I., El Gammoudi, B., and El Behlil, M. (2008) The reduction of wax precipitation in waxy crude oils by Pseudomonas species. *J. Ind. Microbiol. Biotechnol.* 35, 1241–5.
- (73) Liu, J. H., Jia, Y. P., Xu, R. D., and Zhao, P. J. (2012) A Pilot Test Using Microbial Paraffin-Removal Technology in Daqing Oilfield. *Adv. Mater. Res.* 550-553, 1299–1303.
- (74) He, Z., Mei, B., Wang, W., Sheng, J., Zhu, S., Wang, L., and Yen, T. F. (2003) A pilot test using microbial paraffin-removal technology in Liaohe oilfield. *Pet. Sci. Technol.* 21, 201–210.
- (75) Rana, D. R., Bateja, S., Biswas, S. K., Kumar, A., Misra, T. R., and Lal, B. (2010) Novel microbial process for mitigating wax deposition in down hole tubular and surface flow lines, in *SPE Oil and Gas India Conference and Exhibition, 20-22 January, Mumbai, India*, p SPE-129002–MS.
- (76) Biswas, S. K., Kukreti, V., Rana, D. P., Sarbhai, M. P., Bateja, S., and Misra, T. R. (2012) Application of microbial treatment for mitigating the paraffin deposition in down hole tubulars and surface flow lines of wells - A success story, in *SPE Oil and Gas India Conference and Exhibition, 28-30 March, Mumbai, India*, pp 589–595 SPE 154662–MS.
- (77) Singh, P., and Scott Fogler, H. (1998) Fused chemical reactions: The use of dispersion to delay reaction time in tubular reactors. *Ind. Eng. Chem. Res.* 37, 2203–2207.
- (78) Nguyen, D. A., Fogler, H. S., and Chavadej, S. (2001) Fused chemical reactions. 2. Encapsulation: Application to remediation of paraffin plugged pipelines, in *Industrial and Engineering Chemistry Research*, pp 5058–5065.
- (79) Merino-Garcia, D., and Corraera, S. (2008) Cold Flow: A Review of a Technology to Avoid Wax Deposition. *Pet. Sci. Technol.* 26, 446–459.
- (80) Lionetto, F., Coluccia, G., D'Antona, P., and Maffezzoli, A. (2006) Gelation of waxy crude oils by ultrasonic and dynamic mechanical analysis. *Rheol. Acta* 46, 601–609.
- (81) Roberts, P. M., Venkitaraman, A., and Sharma, M. M. (1996) Ultrasonic removal of organic deposits and polymer-induced formation damage, in *SPE Formation Damage Control Symposium, 14-15 February, Lafayette, Louisiana*, p SPE 31129–MS.
- (82) Bjorndalen, N., and Islam, M. R. (2004) The effect of microwave and ultrasonic irradiation on crude oil during production with a horizontal well. *J. Pet. Sci. Eng.* 43, 139–150.
- (83) Towler, B. F. (2007) System and method for the mitigation of paraffin wax deposition from crude oil by using ultrasonic waves. US 7264056 B2.

- (84) Towler, B. F., Chejara, A. K., and Mokhatab, S. (2007) Experimental investigations of ultrasonic waves effects on wax deposition during crude-oil production, in *Proceedings - SPE Annual Technical Conference and Exhibition*, pp 478–486 SPE–109505–MS.
- (85) Tung, N. ., Vinh, N. ., Phong, N. T. ., Long, B. Q. ., and Hung, P. . (2003) Perspective for using Nd–Fe–B magnets as a tool for the improvement of the production and transportation of Vietnamese crude oil with high paraffin content. *Phys. B Condens. Matter* 327, 443–447.
- (86) Rocha, N., González, G., Marques, L. C. D. C., and Vaitsman, D. S. (2000) Preliminary study on the magnetic treatment of fluids. *Pet. Sci. Technol.* 18, 33–50.
- (87) Gonçalves, J. L., Bombard, A. J. F., Soares, D. A. W., Carvalho, R. D. M., Nascimento, A., Silva, M. R., Alcântara, G. B., Pelegrini, F., Vieira, E. D., Pirota, K. R., Bueno, M. I. M. S., Lucas, G. M. S., and Rocha, N. O. (2011) Study of the Factors Responsible for the Rheology Change of a Brazilian Crude Oil under Magnetic Fields. *Energy & Fuels* 25, 3537–3543.
- (88) Evdokimov, I. N., and Kornishin, K. A. (2009) Apparent Disaggregation of Colloids in a Magnetically Treated Crude Oil. *Energy & Fuels* 23, 4016–4020.
- (89) Harms, H. L., Moeckley, C. R., Reed, D., Reed, A. A., and Kaiser, P. A. (1991) Oil tool and method for controlling paraffin deposits in oil flow lines and downhole strings. US 5052491 A.
- (90) McDonald, W. J., Humphreys, K. J., Humphreys, R. D., Kopecky, K. R., and Adams, G. W. (1998) Apparatus for magnetic treatment of liquids. US 5804067 A.
- (91) Borst, T., Perio, D. J., and Alms, D. S. (2008) Magnetic assemblies for deposit prevention and methods of use. US 7353873 B2.