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Paraffin Wax Deposition: Mitigation & Removal Techniques

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Abstract

Flow assurance is critical and difficult for deepwater pipeline since the seawater temperature, surrounding pipeline, is usually much colder than the surface air temperature. In the deepwater, the fluid heat can be quickly lost to the water if there is no thermal insulation layer surrounding the pipe wall. When the inner wall temperature falls below the crude oil cloud point temperature, wax deposition occurs. Such problem starts when paraffin components in crude oil precipitate and deposit on the cold pipeline wall. Whereas wax precipitation during oil flow results in wax deposition and flow restriction, wax precipitation during a production shutdown results in problems when attempting to restart the flow.

In this review, wax deposition problem in flow and during the shut-in conditions are discussed. Also, proposed wax deposition physics and mechanisms are outlined. Furthermore, different wax deposition mitigation techniques are explained. These techniques include: Cold Flow, Chemical Additives and Different Pipes and Coatings Techniques. In addition, different wax deposition removal techniques are reviewed. These techniques include: Fused Chemical Reaction, Mechanical Techniques, Heat Application, Chemical Additives, Magnetic Fluid Conditioning (MFC) technology and Use of Microbial Products.

Introduction

Risks associated with the transportation of multiphase fluids are the most critical operational hazards of offshore pipelines. When water, oil, and gas are flowing inside the pipeline simultaneously, few potential problems can occur. Such problems include, but not limited to: wax and asphaltene can deposit on the wall and may eventually block the pipeline. In addition, water and hydrocarbon fluids can form hydrate and block the pipeline, Furthermore, with high enough water cut, corrosion may occur. Also, scales may form and deposit inside the pipeline and restrict the flow. Moreover, with pressure and temperature changes along the pipeline and/or with incompatible water mixing and severe slugging may form inside the pipeline and cause operational problems to downstream processing facilities. The challenge that engineers will face is, thus, how to design the pipeline and subsea system to assure that multiphase fluids will be safely and economically transported from the bottom of the wells all the way to the downstream processing plant. (Guo et al., 2005)

The practice of identifying, quantifying, and mitigating of all the flow risks associated with offshore pipelines and subsea systems is called flow assurance (Guo et al., 2005). Flow assurance is tedious for deepwater pipeline and system operations. In deepwater, the seawater temperature is usually much colder than the surface air temperature. If the fluid temperature inside the pipeline becomes too low due to the heat loss, water and hydrocarbon (oil and gas) may form hydrate and block the flow. Furthermore, if the fluid temperature is low enough, wax may start to precipitate and deposit on the pipe wall. Thus, effective protection of fluid heat is one of the most important design parameters for offshore pipeline (Guo et al., 2005). In this review, wax deposition problem in flow and during the shut-in conditions, proposed wax deposition mechanisms, wax deposition mitigation and removal techniques are highlighted.

Wax deposition occurs when paraffinic components in crude oil (alkanes with carbon numbers greater than 20) precipitate and deposit on the cold pipeline wall when the inner wall temperature falls below the cloud point temperature (solubility limit). If preventive methods for wax deposition (e.g. insulation of pipeline, injection of wax inhibitor, or combination of both) are not successful, a wax gel layer grows rapidly in thickness and slows down the flow of oil due to the flow restriction, as shown in **Figure-1**. In the Lasmo field in the UK, wax deposition was so severe and frequent that the entire field was abandoned at a cost of over $100,000,000 (Singh et al., 2000; Nguyen et al., 2001).

Whereas wax precipitation during oil flow results in wax deposition and flow restriction, wax precipitation during a production shutdown results in problems when attempting to restart the flow. If the transportation in a pipeline is stopped due to a planned maintenance or an emergency situation such as severe weather conditions on the off-shore platforms (Fung et al., 2006; Thomason, 2000), the temperature and solubility of wax decreases and wax molecules precipitate out of liquid phase in a static condition.

In the absence of flow, the precipitation of wax molecules leads to the formation of a wax-oil gel (Lee, 2008) that could include the entire cross-section of the pipe. In order to restart flow and to recover the steady state flow, this wax-oil gel in the pipeline must be broken. This restart flow problem is especially challenging when the ambient temperature is below the pour point temperature (ASTM D 5853) or the gelation temperature (Venkatesan et al., 2002), which indicates the lowest temperature at which oil is pumpable. In order to prevent this risk and to enhance the restart ability after shut-in, chemical agents, which can depress the pour point temperature and/or weaken the strength of the wax-oil gel, are used. In addition, it is necessary to estimate the pressure required to break the plug of wax-oil gel. This pressure is proportional to the strength of the gel (yield stress) and the aspect ratio of the pipeline.

Physics of Wax Deposition Phenomenon

Wax precipitation during crude oil flow causes wax deposition and flow restriction. Wax deposition during the flow of waxy crude oils through subsea pipelines occurs as a result of the precipitation of wax molecules adjacent to the cold pipe wall. Thus, wax deposition can only occur when the inner pipe wall temperature is below the cloud point temperature. The precipitated wax molecules near the pipe wall start to form an incipient gel at the cold surface. The incipient gel formed at the pipe wall is a 3-D network structure of wax crystals and contains a significant amount of oil trapped in it. The incipient gel grows as time progresses while there are radial thermal and mass transfer gradients as a result of heat losses to the surroundings as shown in **Figure-2**.

The ability of solid particles to diffuse towards the cold wall is a critical issue with respect to the formation of stable cold slurry that will not adhere to the walls. The main proposed mechanisms of transport of solids inside a fluid stream were reported by Merino-Garcia and his team (2008). These mechanisms include: shear dispersion, Brownian diffusion, gravity, thermophoresis and turbophoresis.

All those mechanisms (Borghi et al., 2005) would tend to drive particles towards the wall, but it was concluded that their contributions were small compared to the other two mechanisms. Without temperature gradients, liquid molecules do not participate in deposition. Due to the fact that only negligible deposition is observed, solids are considered to essentially remain in the bulk and not deposit. This negligible quantity that does deposit may come from the waxes that were in direct contact with the wall, so that diffusion was not needed to transport them.

Problem Solutions

Paraffin wax deposition causes severe operational problems in the oilfield leading to decreased production rates, equipment break down and production shut dawns. Therefore, Wax deposition must be mitigated in first place and the paraffin wax must be removed when it already deposited. Paraffin wax treatment methods can be divided into two main categories: mitigation of deposition and removal of paraffin wax deposits.

1. Mitigation Techniques

1.1. <u>Cold Flow:</u>

Figure-3 displays a schematic design of the Cold Flow process. It is claimed that, if solid slurry is formed in the first section of the pipe, it will be transported in a stable way without further solid deposition. At the exit of the process, the oil is at the same temperature as the external water and all potential waxes have been precipitated. The idea of Cold Flow is based on the pioneering work of Coberly (1942). He showed that the presence of foreign particles decreased the tendency of wax crystals to deposit. They acted as nucleation sites which made wax solids precipitate in the bulk, limiting the amount of solids that actually adsorbed to the wall surface. Merino-Garcia et al., (2008) claimed that in order to validate the feasibility of Cold Flow, temperature gradient between hot oil and cold wall should be eliminated. Also, all waxes have precipitated and are transported as a solid dispersion. The solid slurries can be created by different methods as shown in the below sections.

A) *Cold seeding* (NEI, Calgary, Canada, and Marathon Oil, Houston, Texas):
Nenniger (1991) showed that wax deposition rates could be reduced by seeding crude oils with waxy solids. Further investigations in a one-pass system with controlled temperature and shear stress were published (Nenniger, 2001).

B) *The wax eater* (Kellogg, Brown, and Root, Halliburton):
The oil enters a loop in which the external temperature is below WAT to encourage the formation of solids (**Figure-4**) and cool the oil to the seabed temperature (Benson, 2000; Fung et al., 2003; Amin et al., 2000) and the amount of re-circulating fluid must be much greater than the amount of oil that enters the loop (Merino-Garcia et al., 2008).

C) *High-shear heat exchanger* (Kellogg Brown and Root, Halliburton):
Fung et al. (2003) proposed the use of an extra pressure source to increase the speed of the oil stream through a heat exchanger so that the solids are rapidly formed and scratched from the wall by the shearing effect of the extremely high velocity reached. In principle, the use of high speed would imply an increase in size of the heat exchanger as the time to transfer heat is reduced by the high flow rates.

D) *Pressure surges* (Kellogg Brown and Root, Halliburton):
Fung et al. (2003) proposed to combine the pig action with induced pressure surges. The discontinuous release of pressure courses at sonic conditions is supposed to aid in the release of the deposited solids.

E) *Flash cooling* (Shell Western E&P Inc., Houston, Texas):
The oil is mixed with a gas and a choke is used to cause a sudden pressure drop that leads to the precipitation of waxes in the bulk (Knowles, 1986; **Figure-5**). The idea behind this work is to use the cooling motivated by the Joule-Thomson effect to precipitate the waxes.

F) *Oil or solvent injection* (C-FER Technologies, Edmonton, Canada):
C-FER proposes cooling by addition of a re-circulating current of cold oil or solvent (**Figure-6**). Nenniger (2001) has proposed using cold oil in his cold seeding equipment.

G) *Magnetic conditioning* (Magwell, Boerne, Texas, and Halliburton, Dubai):
The device is installed to reduce or eliminate the buildup of paraffin deposits. There is an interesting work by Evans (1997) that studied the effect of magnetic devices in the deposition in a laminar flow system.

1.2. Wax Deposition Reducing Chemicals

Following chemicals are used in the industry to mitigate the paraffin wax deposition or at least reduce it: crystal modifiers, deposition inhibitor surfactants and polymer additives. Wax crystal modifiers incorporate themselves with the growing wax. Surfactants are mainly to sufficiently disperse the wax particles to affect aggregation and reduce their deposition. It should be noted that combinations of these types of chemicals can be employed. Polymers can mitigate or at least reduce the problem by different mechanisims as going to be discussed later.

A) *Crystal modifiers:*
Paraffin deposition is thought to occur in following way. Paraffin comes out of solution in crystals and then it agglomerates around the nucleus to form significantly larger particles which are capable of depositing on a solid surface. Wax crystal modifiers are believed to interfere with the crystal growth and agglomeration processes and therefore minimize paraffin wax deposition.

Allen and Roberts (1993) reported that the removal of the nucleating material leads to the elimination of the process of agglomeration of wax crystals and to the subsequent deposition on solid surfaces. This process is perfectly illustrated on **Figure-7**. A major disadvantage of crystal modifiers is that they are not universally effective in each case of paraffin problems and thus a trial and error method is required to find the proper product.

B) *Deposition inhibitor surfactant:*
The use of these surfactants has been limited to a few areas. One of the applications is to water-wet the pipe surface in order to prevent the adhesion of paraffin to it. Additional volumes of surfactant must be fed into the system to maintain the water film, which prevents paraffin contact with the pipe. Also, some surfactants may actually solubilize the nucleus and thus prevent the paraffin agglomeration.

C) *Polymer additives:*

Polymer additives may work by a number of mechanisms. ((Pedersen et al., 2003), (Wang et al., 2003)) They may serve as nucleating agents if they self-assemble or aggregate above the precipitation temperature of the wax. Facilitating nucleation can lead to a higher wax precipitation temperature. However, a lower precipitation temperature may result if there are many small nucleation sites that are not large enough to be detected. Such a condition can also prevent significant precipitation if the clusters are less than the critical size required for growth. (Wang et al., 2003)

Polymers may also incorporate into growing crystal faces. In this way they disturb growth at these growing edges ((Wang et al., 2003), (Holder et al., 1965)) or at dislocations. This relies on the ability of the polymer to co-precipitate with the wax. In sequestration the additives bind to the surface of the wax particle and prevent molecular addition of more wax.

Polymers may also bind to larger crystals and prevent particle-particle interactions from forming aggregates, volume spanning networks, or deposits. This can be termed steric stabilization or adsorption. The method by which a polymer acts can also be a combination of such mechanisms. Thus, polymer additives do not work by changing the amount of wax that comes out of solution ((Holder et al., 1965), (Pedersen et al., 2003), Ronningsen et al., 1991) but by altering the crystal growth and structure.

Polymer positive effects of on viscosity, cloud point and pour point were reported. ((Garcia, et al., 2001), (Holder et al., 1965), (Pedersen et al., 2003), (Gentil et al., 2005)) Of these, gelation is the most relevant to the restart problem. Reduction in yield stress due to the polymer addition was also reported (Lee, 2008).

1.3. Application of Different Pipe Materials and Pipe Coatings:

Plastic pipes or plastic-coated pipes have been proposed to reduce wax deposition. However, currently they are mainly used to eliminate corrosion. Despite that, the rate of paraffin deposition on plastic pipes is slower than on steel, but the accumulation of wax deposits will progress with the same rate as on steel surfaces after the plastic pipe has been covered with a certain layer of paraffin wax. But deposits must be cleaned out from plastic or plastic-coated steel pipes, and cleaning problems must be considered. Paraffin cleaning techniques such as hot oiling or solvents use may damage PVC type pipes.

2. Removal Techniques

2.1 Fused Chemical Reaction:

Another notable remediation technique is to use a fused chemical reaction with controlled heat emission (Singh and Fogler, 1998; Nguyen et al., 2001, 2003, 2004; Nguyen and Fogler, 2005) to remove the wax deposit as shown in **Figure-8**. However, in order to successfully use this technique, it is critical to know the thickness profile and the wax fraction of the deposit as a function of axial location and time. If this technique were to be used based on inaccurate information on the location of wax deposit and its wax fraction, there could be unwanted local high temperature in the pipeline due to the failure of re-dissolving wax deposit.

The wax deposition management cost to the petroleum production industry is huge and will increase both in terms of capital costs (e.g. preventive methods) and operating costs (e.g. corrective methods) (Paso, 2005). It is widely recognized that tremendous savings could be realized from accurate wax prediction in offshore systems (Majeed et al., 1990). As a result, a fundamental understanding of wax deposition phenomena and a comprehensive wax deposition model based on this fundamental understanding is strongly necessary in order to overcome the challenges in production and transportation of subsea pipelines.

2.2 Mechanical Removal:

Several paraffin deposit removal techniques are available in the industry. In the early stages of solving the paraffin wax problems only *mechanical* methods were used. In the well tubing part of the production system, usually scrapers and cutters are used in order to effectively remove paraffin. Principles of operation of such devices is the same in all cases and consists of physical scraping of paraffin deposits from the tubing wall while the well is still producing. Application of these devices is considered economical but they may result in limited formation damage. But when it is required to circulate scraped paraffin through the well annulus it may lead to plugging of perforations. If paraffin problems in the well are extensive and requires frequent cleanest operations, mechanical wax removal may become costly.

Another method of scraper application is also widely used in the oilfield. Flowing and gas-lift wells and also wells produced with downhole centrifugal pumps utilize a scraper attached to a wire line or a scraper operating with the oil and gas stream energy. However, a scraper attached to a wire line usually creates a local hydraulic resistance and at certain conditions its utilization is counterproductive. During cleanest operations the wireline may break and the scraper will be stuck in the well. Also, to operate a wireline scraper, special surface equipment and trained personnel are required. Usually wireline scrapers are operated manually but some units are controlled automatically by a timing device. Devices such as free pistons are installed in gas-lift wells to improve the efficiency of gas lift by removing the paraffin from the tubing. Scrapers also are installed on sucker rods to remove paraffin while the well is pumped.

In surface pipelines, pigging is one of the most commonly used techniques used in the fields as a method of paraffin wax removal. In pigging, a pig (a solid object with the diameter smaller than the inner diameter of the pipe) passes through the pipeline to scrape off the wax deposit as shown in **Figure-9**. However, the pigging method can not efficiently be utilized without a proper wax deposition prediction. For example, pigs at times get stuck inside the pipeline in the presence of thick hard deposits making the situation worse, which occurred in a Gulf of Mexico pipeline (Fung et al., 2006). In the worst cases, production must be stopped in order to replace the plugged portion of the line, which is estimated to cost approximately $40,000,000 per incident as reported by Elf Aquitaine.

2.3 Heat Application:

Before thinking on how to apply heat, consider should be taken to know how to keep the oil temperature as it was in the reservoir. This can be achieved by proper insulation. Another popular method of paraffin removal is *heat application*. Heat is applied by various techniques such as *hot oil* or *hot water* injection, *steam* injection and an *electrical pipe heating*. Heat treatment should be applied as early as possible, before large paraffin wax deposits are accumulated in the production equipment.

2.4 Wax Removing Chemicals:

Two types of chemicals are used to remove the paraffin deposits from the equipment surface: solvents and dispersants.

A) Solvents:

Use of solvents to remove the paraffin is quite common in the industry. But care must be taken when solvents are selected and applied. *Carbon tetrachloride* and *Carbon disulfide* have been pronounced as the universal solvent. Solvents such as *kerosene*, *condensate* and *diesel oil* are used to dissolve the low asphaltene content paraffin deposits.

B) Dispersants:

Industry utilizes the water-soluble dispersants to remove the paraffin deposits. This dispersant does not actually dissolve paraffin but breaks up and disperses the wax particles to be carried with the producing flow. The Tretolite Company produces an *alkylaryl sulfonate* product called *Parod PD-33* which is an excellent dispersant for sandstone squeeze jobs and for general use. The effectiveness of dispersants is partially a function of formation permeability because dispersants rely on minimizing the size of paraffin wax crystals.

2.5 Magnetic Fluid Conditioning (MFC) technology:

Devices utilizing magnetic fields are called *Magnetic Fluid Conditioners* or Stabilizers. However, this technology has created considerable controversy.

2.6 Use of Microbial Products:

Use of microbial products has been proposed as an attractive and encouraging technique to tackle the paraffin deposition problem. It is been found that naturally occurring marine micro-organisms, which have the ability to absorb paraffin, are able to remove effectively paraffin deposits or at least reduce the deposition over a certain time period. Application of micro-organisms is a popular technique because they are non-pathogenic, non-carcinogenic, and non-combustible and are environmentally safe. Generally, in the oilfield, the microbial products are batch treated and injected into the well-bore annulus. New batches are injected periodically in order to maintain the size of the microbial colony.

Conclusion

Pipelines wax deposition is a critical problem in oil pipeline transportation and its severity increases in offshore pipelines. Wax deposition occurs when paraffin components in crude oil precipitate and deposit on the cold pipeline wall when the inner wall temperature falls below the cloud point temperature or wax appearance temperature. Different wax deposition mechanisms, mitigation and removal techniques were reported. In the worst cases, when no of such techniques is feasible to be used, production must be stopped in order to cut and replace the plugged portion of the line.

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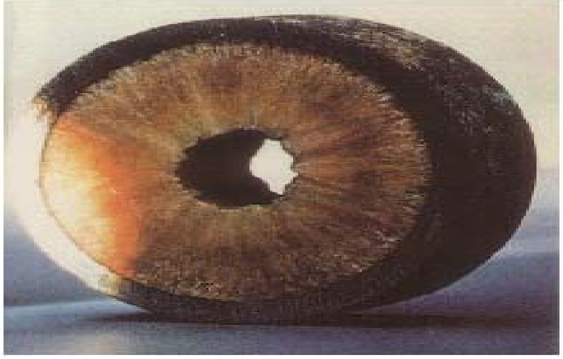

Figure-1 Wax deposit reducing the effective diameter in a retrieved pipeline (Singh et al., 2000)

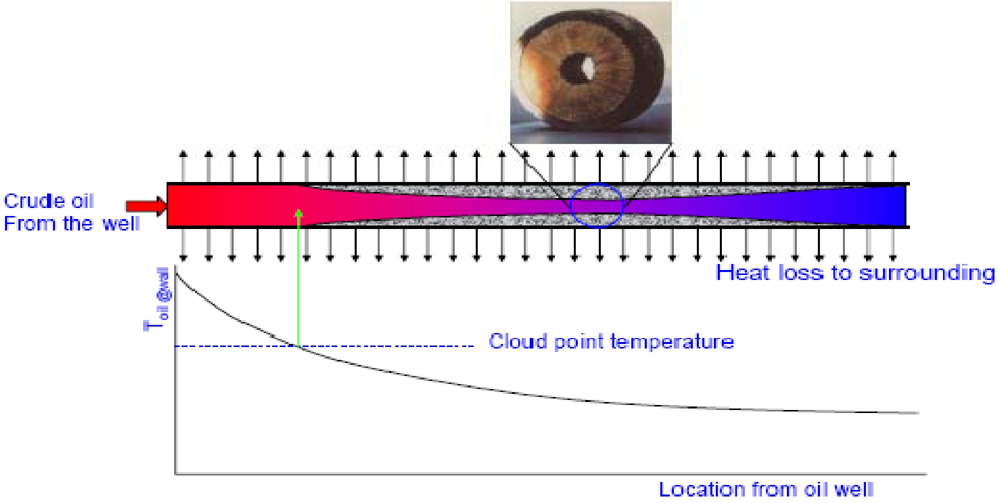

Figure-2 Wax deposition occurs when the inner wall temperature is below the cloud point temperature (Lee, 2008)

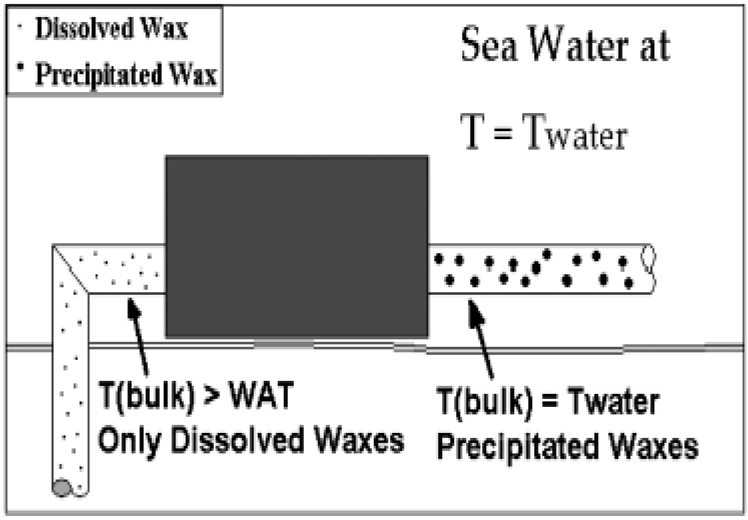

Figure-3 Cold Flow Scheme (Merino-Garcia et al., 2008)

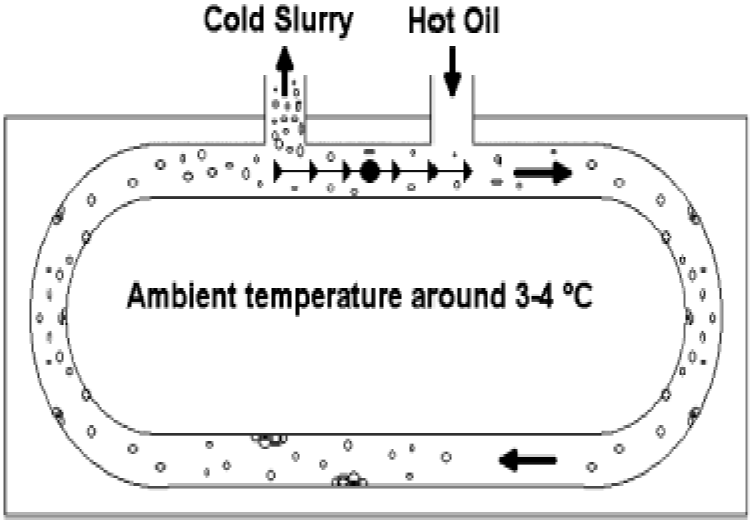

Figure-4 The Wax Eater (Merino-Garcia et al., 2008)

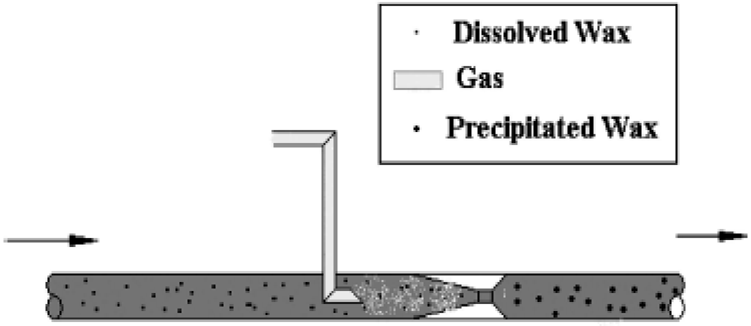

Figure-5 Flash cooling device proposed by Shell Western E&P Inc. (Merino-Garcia et al., 2008)

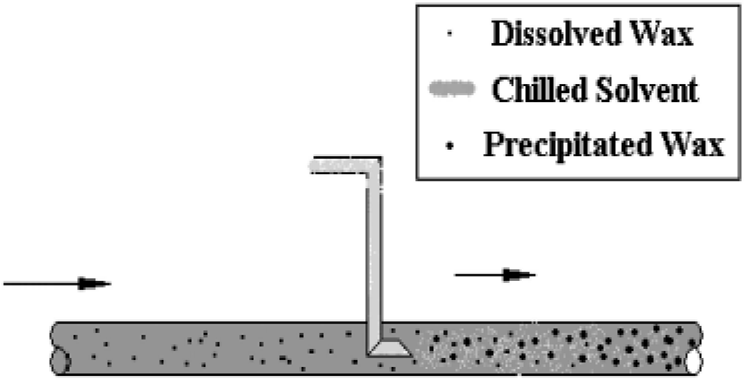

Figure-6 Solvent injection device proposed by C-FER Technologies (Merino-Garcia et al., 2008)

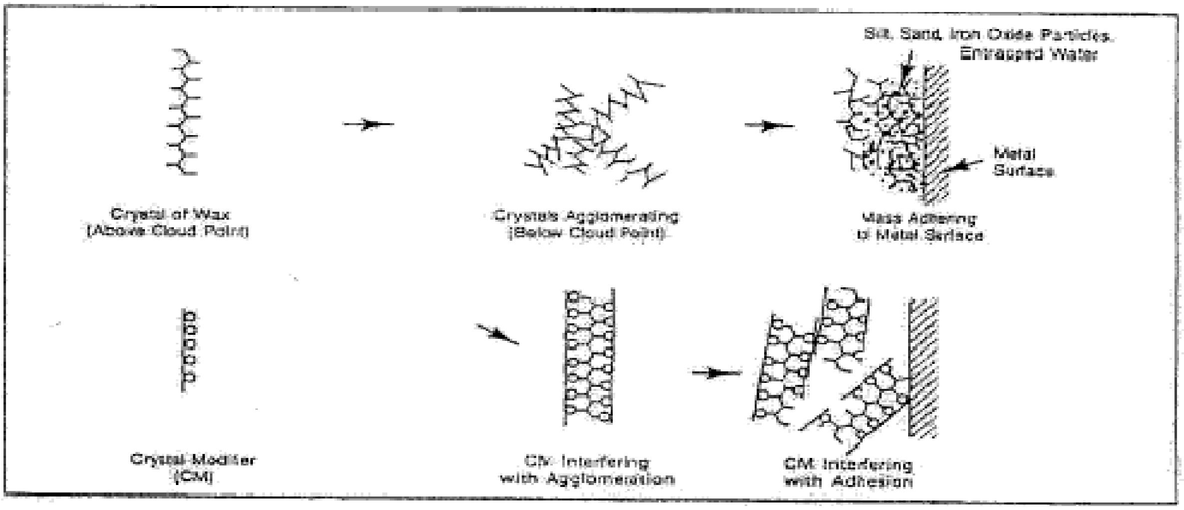

Figure -7 Effects of crystal modifiers on paraffin wax deposition (Allen and Roberts, 2003)

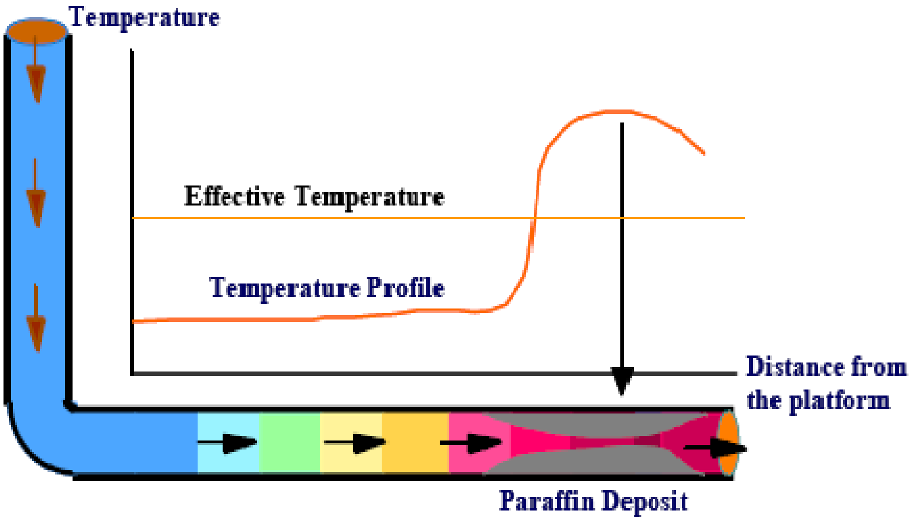

Figure-8 Usage of a fused chemical reaction to remediate the paraffin plugging in subsea pipelines (Nguyen, 2004)

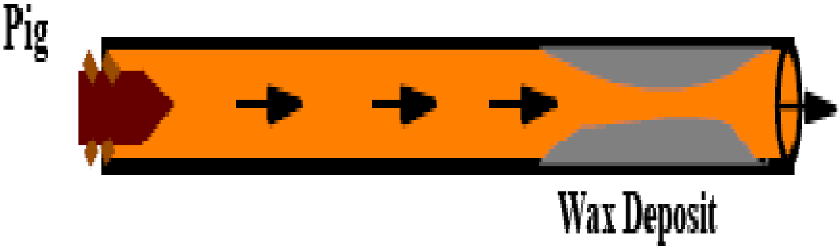

Figure-9 Pigging method to remove wax deposits from pipelines (Nguyen, 2004)