A UNIQUE METHOD OF PARAFFILN CONTROL IN PRODUCTION OPERATIONS

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Abstract

Many oil-producing areas suffer from troublesome paraffin deposition in production and transportation operations. The use of paraffin inhibitors, which are sometimes referred to as wax crystal modifiers or pour point depressants, have been effective at reducing plugging caused by paraffin deposition. To be effective these materials must be applied at a point before the paraffin falls out of solution and they must be present on a continuous basis. This presentation describes a technique for squeezing inhibitor into the reservoir rock matrix to get a slow consistent return of inhibitor provide an extended treatment for controlling deposition.

Introduction:

In common oilfield terminology, the term paraffin is often loosely applied to mean any heavy organic fraction of crude oil which, given the right conditions, can separate or precipitate from solution to form troublesome deposits or sludges. In reality, these deposits may contain a mixture of true paraffin waxes, resins, gums, asphaltic compounds, emulsions, and other components. Fortunately, the analytical tools are now at hand that can identify these components and treatments are available to help alleviate most of the trouble caused. This publication reports on a method of wax control, but recognizes that the problem is rarely a single component problem, and sometimes companion treatments are required to control overall deposition problems.

Definitions:

The true paraffin waxes belong to a family that contains only carbon and hydrogen in the molecular structure, and are sometimes referred to as alkanes. The simplest alkane or paraffin is methane, which has one carbon atom and normally exists as a gas. Paraffins with **6** to 12 carbon atoms (C_6 to C_{12}) are liquids. When the molecular size is **16** to 25 carbons (C_{16} to C_{25}), soft mushy waxes are observed. Hard crystalline waxes have 25 to 50 or more carbons (C_{25} to C_{50}) in the chain.

The melting point of the paraffins increases as the size (length of carbon chain) of the molecule increases. Generally, the higher the melting point of the wax, the more difficult it is to keep the paraffin from forming deposits. Temperature and the availability of lighter hydrocarbons to act as solvent affect the tendency to form deposits.

Causes Of Wax Deposition:

Paraffin is generally assumed to be in solution in the oil under reservoir conditions. However, when these conditions are altered, such as changes in temperature and/or pressure, paraffin will precipitate and adhere to surfaces in the surrounding environment. Several different factors can influence precipitation:

- Temperature reduction of the oil.
- Loss of volatile components that act as solvents.
- Foreign matter that makes a nucleus for deposition.
- Surface conditions of the equipment.

Temperature is the primary factor of paraffin deposition in production equipment. **As** the temperature is reduced, the higher molecular weight wax becomes less soluble, solidifies and separates from the liquid phase. As the crystals come together and adhere, deposits grow

Where The Problems Occur

Since temperature is the prime cause of paraffin deposition, look for problems to occur where there is a drop in temperature. Temperature reduction in crude oil or condensate can occur due to expansion of gas at a point of pressure reduction. Temperature can also drop as the fluids cross a cold water zone, or be lowered by the transition of fluids being produced uphole to the surface. Surface equipment is subject to atmospheric cooling in winter months. Offshore production often flows through a gathering line on the seabed, and fluids are cooled a short distance from the production platform. In summary, paraffin problems can and do occur throughout the production system, in and around the pump, in the tubing, through the flow lines, in the flow lines, at the interface in the gunbarrel or separator, and on the walls of the stock tank. The severity of the problem varies with the system and can be any thing from a nuisance to a major plugging of the system that shuts down operations.

Asphaltene Relationships

Asphaltenes can be and are frequently found deposited with paraffin. Mechanisms of deposition are different, and methods of control are quite different. Small amounts of asphaltene can often act as an inhibitor for paraffin deposition. If the asphaltene deposition is minimal compared to the paraffin deposits, the methods of paraffin control will frequently also control asphaltene problems.

Wax and Paraffin Predictions;

Wax or paraffin problems are usually readily evident when they occur. However, there are programs and methods of predicting deposition problems. These are especially useful in planning new installations. Installation of equipment is normally more economical if it is planned in advance and installed in the initial construction.

Hanssen, J. H., *et al*[1]; Calange, S[2]., *et al*, and others have studied methods predicting paraffin deposition from crude oil. These have mostly been thermodynamic approaches and within limits of component identification, give a reasonable picture of problems to be expected.

Commercial computer models are available on the market. These models predict when, where, and how much deposit will occur. They also predict effects of variables on deposition. Some of these variables are controllable by non-chemical means.

Wax and Paraffin Analysis:

For wax and paraffin control, it is important to know what deposits are to be controlled. For example, inclusions of elevated amounts of asphaltene may require a different treatment approach. Likewise, molecular weight distribution of the wax being deposited. can affect the method of inhibition and the selection of chemical inhibitors.

Therefore laboratory analysis of deposit samples can identify the root-cause of the problem and methods of control can be established. Some of the more common test methods used for paraffin analysis are:

Pour Point: The pour point gives a reference to solidification temperature. This is a test that can be readily repeated with chemical additives to measure lowering of the pour point to a level that will allow production or transportation to continue without deposits.

Cloud Point: The cloud point can be determined by any of several methods including; polarized light microscopy, rheology, differential scanning calorimetry, and frequently with a cold finger apparatus. These tests measure the temperature at onset of paraffin appearance. These data can aid in prediction of paraffin deposition and perhaps suggest where it is likely to occur in the system.

High Temperature Gas Chromatography. This provides a carbon number distribution in the crude mixture. The selection of inhibitor may be dependent on the molecular weight of the wax causing the deposition problems.

Paraffin Inhibitors

Chemicals that prevent the deposition of wax deposits in the system are commonly referred to as "paraffin inhibitors." In reality there are at least three classes of chemical materials that are used to reduce or eliminate build-up of waxy deposits. These are:

- Solvents
- Dispersants
- Crystal Modifiers

Solvents are added to restore solvency to the crude that may have been lost due to escape of dissolved gasses or reduction in temperature. Some examples of solvents that have been used are: produced condensate, casing head gasoline, pentane, butane, xylene, toluene, chlorinated hydrocarbons (like carbon tetrachloride), carbon disulfide and terpenes. The chlorinated hydrocarbons are good solvents, but have been banned, even in small quantities, because of damage to refinery catalysts. Carbon disulfide, is an extremely good paraffin solvent, but has such a low flash point as to be a major hazard. The types of solvent most commonly used today include: aromatic compounds, such as toluene and xylene, white or unleaded gasoline, and terpenes derived from pine trees.

The preventative performance of paraffin solvents does vary with the type of deposit and large volumes of solvent may be required. Therefore, most often the solvents are used in some type of paraffin removal service. However, in cases where solvency can be restored to the crude, solvents work well. They are usually applied in frequent batch treatments, or continuously.

Dispersants work by neutralizing the attractive forces that bind the paraffin particles together[3]. The dispersants are chemically structured so that one end of the molecule is attracted to the paraffin, while the other end is soluble in either oil or water, depending on the phase in which the paraffin is to be dispersed. The dispersants cause the paraffin particles to be physically separated in the produced fluids so they can be kept moving with the fluid flow.

Dispersants are formulated from such materials as: sulfonates, alkyl phenol derivatives, ketones, terpenes, polyamides, and naphthalene. Dispersants can be used for removal of some deposits as well as in a preventative mode. Application can be made in batches, continuous and sometimes as a squeeze into the matrix rock.

Paraffin Crystal Modifiers are materials that have a similar molecular structure to the wax that is precipitating. The crystal modifier co-precipitates or co-crystallizes with the wax by taking the place of a wax molecule on the crystal lattice. However, it also places a steric hindrance on the paraffin crystal that interferes with proper alignment of new incoming paraffin molecules and growth terminates[3]. This prevents the paraffin crystals from adhering together and sometimes prevents sticking to pipe walls. Paraffin deposition is reduced or eliminated and frequently the pour point of the crude is actually reduced.

Typical crystal modifiers are polymeric in nature. They include polyethylene, copolymer esters, ethylene/vinyl acetate copolymers, olefin/ester copolymers, ester/vinyl acetate copolymers, polyacrylates, polymethacrylates, and alkyl phenol resins.

Applications

Paraffin crystal modifiers, have two criteria for being effective: the inhibitor must be present on a continuous basis and it must be in the crude oil before paraffin deposition begins. Batch treatments have been used, but are marginally effective unless they are pumped into a holding reservoir such as into a column of fluid standing in the annulus of a well. The most successful applications have been continuous. In producing wells, chemical injection into the annulus and flushed with a slipstream of produced fluid works well. The use of a capillary string or chemical injection string is much better, because the chemical placement is positive and controllable. Formation squeeze techniques have been used, and when properly designed they have proven very effective.

Formation Squeeze Technique

This work reports a successful application for squeezing the wax crystal modifier inhibitor into the reservoir. The inhibitor is retained in the rock matrix to be fed-back slowly and continuously. While this technique is not new, there are some refinements to the squeeze technique that raises the success ratio and extends effective treatment life. Since the paraffin crystal modifiers are of necessity very similar to the naturally occurring paraffins, they have little affinity to adsorb in the reservoir rock and therefore tend to return rapidly when the well is returned to production. This creates a short effective treatment life.

This presentation describes a unique application procedure that creates an artificial adsorption/desorption mechanism that controls treatment return and produces an effective longer lasting treatment life.

Typical Treatment Design Procedure:

Product Selection:

Product selection for this procedure begins with testing of the crude in question. A carefully collected and transported sample is tested for wax content, asphaltene content and pour point. Next a determination is made of the type (molecular weight) of wax that is causing the deposition problem. This is determined by placing a sample of the crude in a “cold finger” apparatus and collecting a sample of the depositing wax. The scraping is analyzed by gas chromatography. The chromatograph of the crude itself may not identify a significant concentration of high molecular weights. However, the analysis of the cold finger scrapings will yield an instrumental concentration peak for the molecular weight of the wax casing the problem (Figure 1). Re-testing of the crude with various paraffin inhibitors will show this same concentration peak, but it will be reduced by the application of proper inhibitor. (Figure 2). The best inhibitor will be the one that reduces the peak to its lowest volume. This is because the paraffin inhibitor interferes with the wax crystallization and deposition does not occur. The heavy paraffins are still in solution. This then becomes the product selected for the squeeze treatment.

Treatment Procedure:

One successful design approach has been to use a treatment size calculation that will predict an average concentration of inhibitor in a specific volume of produced crude oil. That is, calculate a treatment size based on oil production and the concentration of inhibitor required for inhibition. This is followed by a calculated volume of overflush to place the treatment into the reservoir rock and away from the wellbore. If the inhibitor is displaced too far, the rate of inhibitor return will be low. If it is not placed far enough, there is a tendency for the inhibitor to be returned rapidly in the early production.

It is important to control wettability in the pre-pad before the inhibitor stage and in the overflush fluids. Changes in the relative permeability to oil can reduce productivity when production is resumed.

Inhibitor treatment volumes can be estimated by the following equation.

$$\text{Gal of paraffin inhibitor} = \frac{(\text{ppm})(\text{days})(\text{BOPD})(42\ \text{gal/bbl})}{(\text{f})(1{,}000{,}000)}$$

ppm = Parts per million treating level for specific inhibitor (usually 50 to 200 ppm inhibitor)
days = Days of treatment life (typical 180 to 240 days)
BOPD = Barrels of oil production to be treated per day
f = Ideality factor, estimated 0.55 to **0.6** depending on ability to control flow-back.

This volume of paraffin inhibitor is typically diluted with diesel or clean lease crude to a 20% concentration.

The displacement or overflush fluids are designed to displace the treatment 3 to 4 feet into the reservoir rock. This volume is calculated as follows:

$$\text{Barrels of overflush} = V_1 + (\pi)(r^2)(h)(P)(0.18\ \text{bbl/cu.ft.})$$

Where:
V_1 = Volume of well tubulars (Tubing or Annulus)
π = 3.14
r = radius of displacement (3 to 4 feet)
h = Height of producing zone or perforated zone (in feet)
P = formation porosity expressed as a decimal. (Porosity is usually expressed in percent 20% = 0.2)

Field Applications

West Texas – Permian Basin Application

Most of the wells in a field in Ector County experienced paraffin deposition in the tubing. Production of 25 to 30 BOPD would drop to a point that the well was plugged. Over a period of time, Field Operations determined that a hot oil truck should treat the well when the production dropped to a 5 to 8 BOPD level. If the wells were not treated at this point, they had to pull the rods and pump and run a paraffin scrapper in addition to the hot oil treatment. This occurred at least once a month and sometimes more often.

Two wells were selected for a paraffin inhibitor squeeze. Each well was thoroughly cleaned with a solvent soak to remove paraffin deposition. The wells were then squeezed with a wax crystal modifier before production was resumed.

The treatment procedure followed these general steps. Four drums of inhibitor activator were blended in 20 barrels of clean lease crude, and injected into the well. This was followed by a 10 barrel pad of clean lease crude. The following inhibitor stage was composed of 3 drums of inhibitor mixed in 20 barrels of clean lease crude. The overflush volume was 120 barrels of produced water containing a surfactant to control wettability, followed by a tubular volume of water to displace the treatment from the wellbore. The well was shut in for 24 hours to allow the inhibitor to glaze onto the formation rock. (This provided the artificial adsorption/desorption mechanism to control feedback rates.) The well was returned to production.

Both wells responded in a similar fashion. Immediately the wells returned to the normal production of 25 to 30 BOPD. Six months later the wells were still producing above the 5 to 8 BOPD level that determined the need for wellbore cleaning. After the seventh month the wells were re-squeezed (Figure 4). Not only was the cost or frequent hot oiling eliminated, the wells produced at a higher level of production for an extended period. This translated to more overall production from the well. Subsequently, other wells in the field were squeezed, and performed at similar levels of sustained production without the frequent paraffin removal cleaning procedures.

New Mexico Field Application

A producing well was experiencing production loss due to severe paraffin plugging. The well was being stripped (scrapped and hot oiled) frequently in order to restore production. Production averaged 247.3 BOPD and 226 MMCF of gas per day (or 287.8 BOE) over a period of 117 days prior to application of a paraffin inhibitor squeeze. During this time the use of striping, swabbing and hot oiling occurred almost weekly and the average cost was $140 per day, not including the loss of production.

The solution to the troublesome paraffin problem was the application of a paraffin inhibitor squeeze treatment, utilizing the following procedure:

- Clean tubing thoroughly of all solids. (Use scrapper, solvent soak, and/or hot oil or hot water).
- Mix 4 drums of inhibitor activator in 20 bbls of clean crude and pump down the tubing.
- Pump 10 bbls of crude down tubing as a pad.
- Mix 4 drums of wax crystal modifier in 20 barrels of lease crude and pump down the tubing.
- Overflush and displace with 117 barrels of lease crude
- Shut-in well for 24 hours before returning to production.

For the next 129 days the well needed no stripping, hot watering or hot oiling. The production averaged 430 BOPD and 927 MMCF of gas (or 585.4 BOE) (Figure 5). This is an increase of 297.6 BOE over the previous normal production. At $20/barrel for West Texas Intermediate crude, this is $767,808 in increased revenue for the customer without any other operational costs, except the cost of the squeeze.

Conclusions:

Paraffin inhibitor squeeze treatments can be an effective tool to reduce the operational cost of remedial paraffin work. Field applications have shown that careful attention to treatment design can control paraffin and not be detrimental to oil production. Two important aspects to control are wettability and design for a sufficient concentration level of residual inhibitor in the produced fluids. Changes in wettability can reduce relative permeability to oil and lower productivity. Inhibitor feed back at a low concentration can be ineffective for paraffin deposition control. **A** high residual concentration of inhibitor can reduce treatment life. Proper treatment design can provide an effective treatment life in excess of 6 months.

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GAS CHROMATOGRAPH ANALYSIS

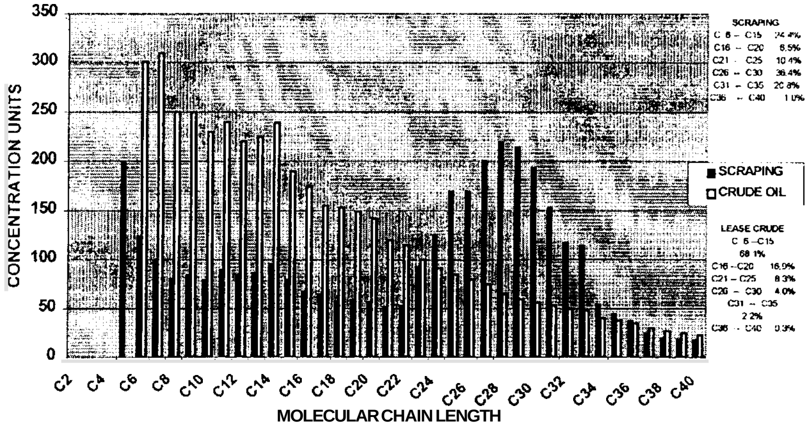

Figure 1 - Chromatogram Showing
Paration Mole Weight that will Deposit

GAS CHROMATOGRAPH ANALYSIS

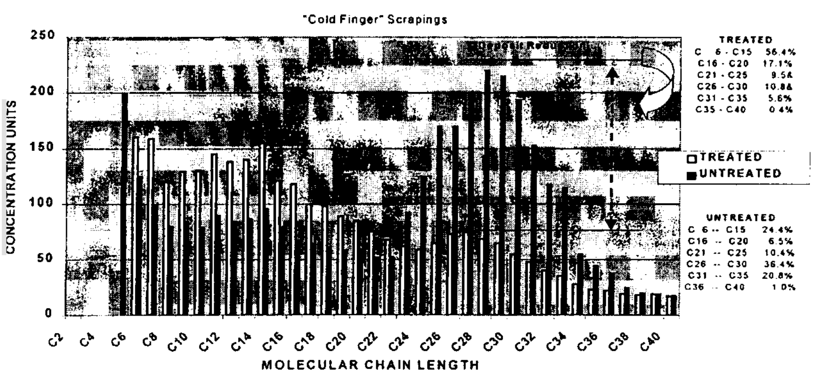

Figure 2 - Chromatogram Showing Effect of Inhibitor
to Hold Paraffin in Solution

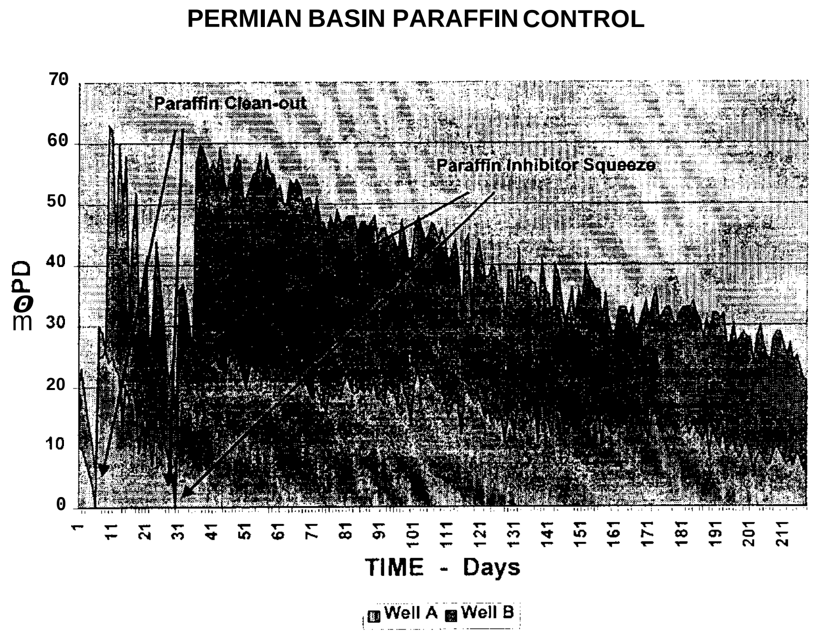

Figure 3 - Production Before and After Paraffin Inhibitor Squeeze Treatment - Permian Basin Wells

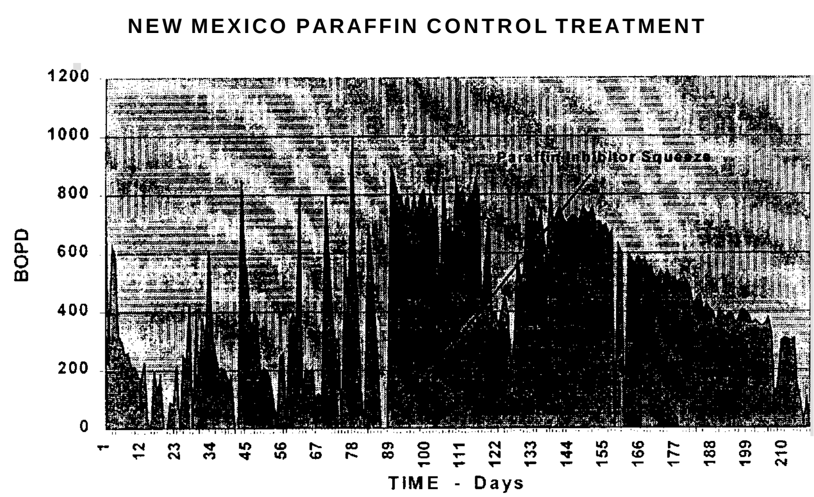

Figure 4 - Production Before and After Paraffin Inhibitor Squeeze - New Mexico