PARAFFIN TREATMENT IN THE WELL SERVICE INDUSTRY

James M. McCall, Jr.
Richard L. Johnson II
NOWSCO Services

ABSTRACT

Paraffin problems exist in the majority of petroleum producing areas. The chemistry of paraffin and methods of analysis are discussed. Asphaltenes are also described and differentiated from paraffin. Three types of chemical treatment for paraffin problems are compared: paraffin inhibitors, paraffin dispersants, and paraffin detergents. Each has advantages, and factors are given which would influence the choice of one method over the other. Recent developments and possible pitfalls in paraffin treatment are discussed.

INTRODUCTION

Paraffin problems exist in many petroleum producing areas including offshore Louisiana and areas of West Texas.

Paraffin is a waxy solid substance naturally occurring in petroleum which causes production problems in several ways. Paraffin can deposit in the well tubing, flowline and other surface equipment. This deposition can cause restriction or plugging which may be difficult to remove. Paraffin can also interfere with the mechanism of emulsion breaking, causing stable emulsions, and interfering with surface treatment of the petroleum. Paraffin can even deposit in the pore spaces of the producing formation causing permanent damage and decreased production. Precipitation of paraffin can cause increased viscosity and therefore problems in pumping and distribution of the produced petroleum. Paraffin deposition can also be a major problem in gas wells if the condensate contains paraffin compounds.

Producing wells can be damaged by the introduction of cold fluids during stimulation treatments. Relatively cold stimulation fluids used for squeeze treatments, acidizing and fracturing can cause precipitation of paraffin in the pore spaces of the formation if the fluid in the formation is cooled below the cloud point.[1] Paraffin can also interfere with proper contact of the acidizing solution with scale or formation material. Similar problems can occur in oils containing high concentrations of asphaltenes. Asphaltene sludge is caused by contact of hydrochloric acid and some asphaltic crude oils.

CHEMISTRY OF PARAFFIN

Paraffin is a waxy solid substance naturally occurring in petroleum. The chemical structure is characterized as a straight or branched chain saturated hydrocarbon with the molecular formula usually written:

$$C_nH_{2n+2}$$

The number of carbon atoms, n, is 18 to 60 for paraffin wax.

Paraffin belongs in the chemical classification of hydrocarbons named alkanes which all have similar structural formulas as shown above. These compounds are chemically non-reactive under usual conditions. Lower molecular weight alkanes containing one to four carbon atoms are gases at normal room temperatures. Alkane compounds with five to sixteen carbon atoms are liquids at normal room temperatures. These fractions are normally present in gasoline, kerosene and other fuel oils. Alkanes with structures containing eighteen to sixty carbon atoms are designated paraffin wax. Figure 1 depicts a paraffin molecule with n = 18.

Further distinction can be made between macrocrystalline and microcrystalline paraffin waxes. Macrocrystalline paraffin consists of mixtures of saturated straight chain compounds with eighteen to thirty carbon atoms having a molecular weight range of 250 to 450. Melting points of these compounds are generally between 100 and 140 degrees Fahrenheit. Crystals are typically very large with plate or needle shaped structures. Microcrystalline waxes form much smaller crystals which consist mainly of compounds having forty to sixty carbon atoms with complex branched chain and cyclic structures. These paraffins have higher average molecular weights than the macrocrystalline compounds with melting points in the 140 to 190 degrees Fahrenheit range.[2]

Typical paraffin deposits consist of mixtures of both linear and branched chain hydrocarbons and may also include other organic and inorganic materials including scale, formation materials and asphaltic compounds. The melting point of deposited paraffin is typically in the range of 120 to 140 degrees Fahrenheit. Since paraffin is a saturated hydrocarbon, it is soluble in solvents with similar chemical properties such as pentane and gasoline. Paraffin is relatively insoluble in aromatic solvents such as benzene and toluene. These solubility characteristics are one way of distinguishing paraffin from other common solids found in the oilfield such as asphaltenes, scales and formation fines.

Initially paraffin occurs as a component of petroleum before the petroleum is produced from the formation. When the petroleum is produced, changes in temperature and composition of the petroleum occur which can lead to deposition of the paraffin. Since paraffin is typically less soluble in crude at lower temperatures, precipitation can occur in the well tubing as the temperature drops from the formation temperature. Also as the pressure decreases from the initial formation pressure to atmospheric pressure, the crude oil tends to lose the lower weight hydrocarbons due to evaporation. Loss of these compounds (light ends) decreases the ability of the crude to hold the paraffin in solution and increases the possibility of precipitation. Since the pressure drop is most drastic in the wellbore area, precipitation is likely to occur there. Precipitation of the paraffin occurs by physical mechanisms including molecular diffusion and agglomeration of previously precipitated paraffin crystals. Paraffin content of crude oil is considered to be low to moderate if in the concentration range of 1 to 10 percent. High paraffin content, above 10 percent, can cause severe deposition and flow problems.

Two commonly used measures of paraffin content are cloud point and pour point. The cloud point is the temperature at which paraffin first begins to precipitate. This causes the oil to appear cloudy. Since most crude oil is opaque, this is often difficult to observe. However, this point can be measured by several other means in the laboratory such as viscosity changes when temperature is decreasing, or differential thermal analysis.

Pour point is measured as the lowest temperature at which oil will pour or flow in the absence of shear. This temperature will typically be in the range of 40 to 100 degrees Fahrenheit. Solidification of the oil due to paraffin can be distinguished from that due to asphaltenes. High asphaltene content causes the oil to become highly viscous (viscous pour point) but the oil does not solidify as with paraffin. Paraffin causes the oil to solidify due to the formation of an interlocking network of fine sheets of paraffin crystals. These crystals form cage-like structures which can trap the unsolidified oil and water. Thus the oil appears to be solid at lower temperatures. GLC (Gas Liquid Chromatography) is also a useful tool to study the composition of paraffin. The range and distribution of molecular weight are an indication of the type of paraffin that will be deposited.[3,4]

Asphaltenes are aromatic based hydrocarbons of amorphous structure and high molecular weight. Asphaltene deposits generally appear to be black, brittle and hard. Asphaltene content generally increases with decreasing API gravity. Asphaltenes do not melt, but decompose at temperatures above 300 degrees Fahrenheit. Effective solvents for asphaltenes are aromatic types such as toluene and xylene. Compounds which are used for removal or inhibition of paraffin are totally ineffective for asphaltenes. Precipitation of asphaltenes can be caused by physical changes in the composition of the oil or flow related effects. The use of hydrochloric acid during acidizing can cause the formation of precipitated asphaltic sludges as mentioned previously.

Paraffin can be identified in the field and distinguished from asphaltenes as well as other types of solid inorganic material by several tests. If the deposit dissolves in hot xylene, then the deposit is organic in nature. Scales and other inorganic formation material will not dissolve in xylene. If the deposit is organic (dissolves in xylene) and is also soluble in hot pentane, then the deposit is paraffin. If the deposit is not soluble in pentane then it is asphaltic. Asphaltic deposits must be handled differently from paraffinic deposits since their solubility characteristics are totally different. Table 1 shows methods of identifying deposits by solubility and other physical characteristics.

CHEMICAL TREATMENT OF PARAFFIN

There are three main catagories of chemicals used for treatment of paraffin deposition problems. These chemicals are classed as paraffin inhibitors, paraffin dispersants and detergents. These chemicals may be used individually or as a mixture of several different types in the treatment of paraffin problems.

PARAFFIN INHIBITORS

Paraffin inhibitors generally consist of high molecular weight copolymers, for example copolymers of ethylene vinyl acetate, which have enough structural similarity to paraffin to enter into the paraffin crystallization process. The molecular weight of inhibitor compounds ranges from 1500 to 100,000. Paraffin inhibitors function by modifying or blocking the formation of large paraffin crystals, which lowers the pour point or decreases viscosity at lower temperatures. The effectiveness of an inhibitor can be measured by the extent to which the pour point is lowered for each crude oil being treated. This may vary for each crude oil source. However, an inhibitor may lower the pour point of a crude oil only slightly and still reduce viscosity and improve the flow characteristics significantly.[5] Typical treating concentrations range from 0.02 to 0.2 percent by weight of produced oil.

There are several factors which may affect the response of a particular inhibitor chemical. To be effective, the inhibitor must be able to chemically combine with the paraffin molecules or otherwise modify the formation of the large paraffin crystals. By chemically combining with the paraffin, the inhibitor modifies the structure of the crystal and inhibits the growth of the large cellular structures.[6] Therefore the response to an inhibitor will vary, depending on the average molecular weight and distribution of molecular weights of the paraffin molecules. An inhibitor may be selective for paraffin in a particular molecular weight range, leaving paraffin of a different molecular weight unaffected. This can be a particular problem when the inhibitor is selective for lower molecular weight paraffins, allowing the higher molecular weight paraffins to be deposited which are more difficult to remove. Inhibitor response is also affected by other components in the crude oil. There is no universal inhibitor which is effective in all cases.

Most paraffin inhibitors are high molecular weight compounds which exist as solids or viscous liquids. This makes them difficult to handle and place. The response of a crude oil to a paraffin inhibitor cannot be predicted with certainty without testing. The cost effectiveness of the inhibitor must be carefully evaluated. Most importantly, to be effective, an inhibitor must be added to the crude oil before extensive growth of the paraffin crystals, usually 10 to 15 degrees Fahrenheit above the pour point. Optimum conditions for use of paraffin inhibitors occur in the producing formation, away from the wellbore. Paraffin inhibitors are available in solid form, consisting of 100 percent active ingredient, which can be placed in the formation during fracture treatments. In cases where paraffin has already accumulated, inhibitors are usually used in combination with other removal methods.

PARAFFIN DISPERSANTS

Paraffin dispersants are compounds that have the ability to chemically coat small particles of paraffin, decreasing their tendency to agglomerate and form layers on pipe surfaces. Chemically, paraffin dispersants work by neutralization of the attractive forces between paraffin particles and binding agents which hold them together.[4] These products are chemically structured so that one end of the molecule is attracted to the paraffin crystal and the other end is soluble in either oil or water, depending on which phase the paraffin is to be dispersed. Ideally the dispersant will possess enough penetrating power to break up accumulated masses of paraffin. Other chemicals are often added to aid in the penetration and solvation. These products may be designed for continuous injection in systems where the concentration of water is low. Other dispersants are designed to be used in squeeze treatments.

DETERGENTS

Detergents are surface active compounds that reduce the surface tension of water and solvate the paraffin crystals (paraffin particles can become water wet). These compounds are normally used in hot water or other solvents to clean up existing paraffin accumulations in well tubing or surface facilities.

Detergent molecules have both an oil soluble end and water soluble end. This dual solubility enables the molecule to align at the interface between the oil soluble paraffin phase and the water phase. Detergents are commonly classified into three groups depending on the charge of the water soluble end. Detergents are anionic, cationic and non-ionic. The water soluble end of an anionic molecule is negatively charged. Conversely the water soluble end of a cationic molecule is positively charged. Non-ionic detergents do not ionize into charged species, although they still have the dual solubility character. The choice of the proper ionic nature of the detergent is important for several reasons. First, the detergent must be compatible with other additives which may be in the same treatment solution. Also the ionic nature of the detergent should be selected to insure leaving the formation in the proper "water wet" state. Leaving the tubing and formation in a "water wet" state promotes better production of oil and lessens the chance of further deposition of paraffins. It has been shown that paraffin is less likely to accumulate on water wet surfaces.[7]

USE OF PARAFFIN CHEMICALS IN WELL STIMULATION

Paraffin dispersants and detergents should be considered for removal of paraffin deposits prior to well stimulation procedures such as acidizing and fracturing. The removal of these deposits will aid in the contact of the acid with the scale deposits and formation material, and help leave the formation "water wet" for better production after the treatment. Also removal of these deposits will avoid the possibility of pushing additional paraffin into the formation during the treatment. In addition, paraffin can be a stabilizer for emulsions, and adding paraffin compounds to the acidizing solution often helps control emulsifying tendencies of the returning acid.

The use of hot fluids is recommended to increase the effectiveness of the chemicals and to help avoid any additional precipitation of paraffin in a wellbore treatment. The solvent of choice is usually hot water (cold water requires as much as ten times the concentration of chemical). Water is preferred for paraffin removal due to factors such as availability, cost, the ability to form surfactant solutions, and the ability to penetrate high levels of oil in the annular space of a well. Product concentrations recommended for paraffin removal range from 0.1 percent to 5 percent depending on the severity of the deposition and temperature of the treatment fluid.

Products are best selected using tests with samples of the paraffin to be removed. Care must be taken to be sure that the paraffin sample is representative of the paraffin which has accumulated. The activity of the paraffin compound is evaluated by use of a "flask test" using various concentrations of the chemicals in contact with samples of the paraffin under the expected temperature of use. Each product is rated for paraffin break up and dispersion. The solution that gives the smallest particle size but still maintains the paraffin in a "water wet" state is judged the best.[3] If other treatment chemicals are also being used (for example scale inhibitors or corrosion inhibitors) the compatibility of the paraffin product should be tested. In this case, the use of the other products would be greatly enhanced by removal of the paraffin in advance, rather than combining these treatments into one solution. The products chosen may vary depending on production zone and method of production. A sufficient concentration of the dispersants and detergents should be used to insure an adequate clean up. Also sufficient contact time with the paraffin is important.

It is also very important to check for compatibility of the paraffin control compound with the produced fluids from the well. Emulsification tendencies should be tested with produced oil and water. Ions in the produced water, for example calcium and magnesium ions, can form insoluble precipitates with anionic surfactants. The use of fresh water is preferred to avoid interferences that are seen with high dissolved solids in produced water. KCl can be added where clay swelling is a problem.

Paraffin inhibitors can be placed into formation fractures during hydraulic fracturing treatments. Physically the compounds look like small beads or pellets. The pellets are oil soluble and dissolve over a period of several months as the crude oil is produced around them. The paraffin treatment is placed in the fracture with the normal proppant. The rate of dissolution depends on the formation temperature and production rate of the well. An effective concentration would be 100 ppm or higher. Consideration of the formation temperature and the proper placement of the beads is very important. Care must be taken that the treatment is placed properly with the proppant, so that the treatment chemical is located in the central part of the proppant pack. The advantage to this type of treatment is that the compound is 100 percent active rather than a partially active solution of the compound in a solvent. High molecular weight paraffin inhibitors are difficult to handle and inject properly, so this method also eliminates these problems. The paraffin inhibitor is placed in an area where it will do the most good, before the wellbore area where the most drastic pressure drop occurs.

SUMMARY OF IMPORTANT FACTORS IN PARAFFIN TREATMENT

I. Identify the Depositing Material

- A. Organic
    1. Paraffin
    2. Asphaltene
- B. Inorganic
    1. Scale, Iron Oxide, Iron Sulfide (Acid Soluble)

2. Clay, Drilling Mud (Acid Insoluble)

II. Test Paraffin Treatment Compound

A. Detergents and Dispersants - Test for effectiveness in breaking up and dispersing paraffin sample (Bottle Test)

B. Paraffin Inhibitor - Test for pour point depression and effectiveness in inhibition of paraffin deposition.

C. Compatibility - Test all selected paraffin compounds for compatibility with treating fluids and produced fluids.

D. Test paraffin product for emulsifying properties with produced fluid.

III. Application

A. Insure adequate contact time with the paraffin deposit.

B. Check for proper concentration and mixing of additives in the treatment fluid.

C. Preclean the system of paraffin deposits if possible before other treatments for scale or corrosion.

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STRAIGHT CHAIN:

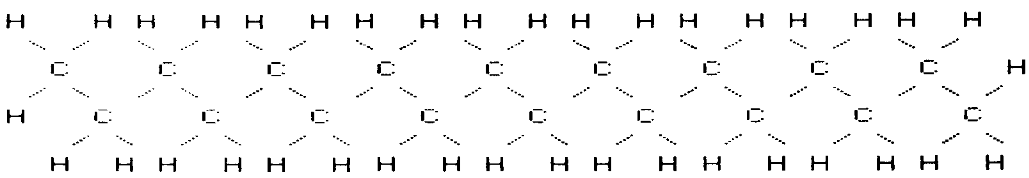

Figure 1 - Paraffin molecule with 18 carbon atoms (n = 18)

Table 1
Field Identification of Deposits