A COMPARISON OF HOT OILING TO VARIOUS TYPES OF CHEMICAL TREATMENTS TO CONTROL PARAFFIN PROBLEMS

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ABSTRACT

Hot oil treatment of flowline and downhole paraffin problems is still common in the oilfields of North America. The use of chemical programs has been growing but often the industry is unsure which type of treatment should be done and if these programs are more cost effective than hot oiling. This paper will attempt to show, based on the paraffin problems being experienced, which type of chemical treatment would be most cost effective. Case histories of economic treating programs will be presented.

INTRODUCTION

Paraffin is a major constituent in most crude oils > 20" API. In many fields these paraffin constituents cause plugging, congealing or settling problems that require some type of treatment to maintain hydrocarbon production. In a vast number of fields the preferred solution involves the use of hot oil or water to reduce the problems to a manageable level regardless of cost. In many instances other chemical treatment programs would be much more cost effective. The following information is presented in an attempt to help the industry understand the limitations of hot fluids and help discover other potential treatment methods that may be more cost effective.

CHEMISTRY OF CRUDE OIL

The paraffin series of compounds or n-alkanes contain only hydrogen and carbon'. The number of carbon atoms can range from 1 to >100. The ratio of carbon to hydrogen atoms can be shown by the formula $C_n H_{2n+2}$. This means that for every carbon atom we will have twice as many hydrogen atoms plus two.'

| <u>Compound</u> | <u>Formula</u> | Melting Point °F | Boiling Point °F |
|-----------------|----------------------------|------------------|-----------------------|
| Methane | СН | -296 | <u>@ 1 atm</u> 250 |
| | | | -259 |
| Ethane | CH | -297 | -127 |
| Propane | $C^{2}H^{6}$ | -305 | -44 |
| Butane | $C^{3}H^{8}$ | -217 | 31 |
| Pentane | $C^{4}H^{10}$ | -201 | 96.8 |
| Hexane | $C^{5}H^{12}$ | -137 | 156 |
| Heptane | $C^{6}H^{14}$ | -131 | 209 |
| Octane | $C^{7}H^{16}$ | -70 | 258 |
| Nonane | $C^{8}H^{18}$ | -65 | 303 |
| Decane | $C^9 H^{20}$ | -21.5 | 345 |
| Undecane | $C^{10}H^{22}$ | -14 | 385 |
| Pentadecane | $C^{11}H^{24}$ | 50 | 519 |
| Eicosane | $C^{15}H^{32}$ | 97.5 | NA |
| Triacontane | $C^{20}H^{42}$ | 150 | 579 |
| Tetracontane | $C^{30}H^{62}$ | 178 | NA |
| Pentacontane | $C^{40}H^{82}$ | 198 | 790 |
| Hexacontane | $C^{50}H^{102}$ | 210 | NA |
| Heptacontane | $C^{60}H^{122}$ | 221 | NA |
| Hectane | $C_{100}^{70}H_{202}^{42}$ | 239 | NA |

PHYSICAL CHARACTERISTICS OF SOME N-ALKANES IN CRUDE PETROLEUM

The cloud point is the temperature at which the longest chain length paraffin present in a particular oil becomes insoluble in that oil. The cloud point indicates the temperature at which paraffin deposition will start. If the formation or equipment surface reaches the cloud point temperature of the oil, paraffin deposition will start even though the bulk oil is still above the cloud point. As the surface temperatures of the equipment drops below the cloud point shorter chain paraffins will start to precipitate and deposit. The type of paraffin depositing will change as the oil progresses downstream through the system. The melting point of the deposits will change as the type of paraffin changes. If the system cools sufficiently paraffins of < C36H74 will start to precipitate and will cause the congealing of the crude oil itself. Many times congealing oil will be misidentified as paraffin deposition. The only difference between deposited paraffin and deposited congealed oil will be the melting point of deposit itself. A rule of thumb of the author is that if the deposit melts at < 120°F it is probably a congealing oil problem.

It should be noted that no two oils are exactly alike in paraffin distribution. The cloud points will vary from well to well in a field, viscosities will vary, production levels and the temperatures of the fluids will vary. These differences between wells will cause the problems to vary enormously from well to well within a field.

CAUSES OF PARAFFIN PROBLEMS

All paraffin problems occur because the oil contacts a surface that is cooler than the cloud point of the oil in the system. Paraffin problems can occur from the formation to the refinery in any kind of production system. Cooling of the oil and surrounding environment is caused by a number of well and fluid characteristics. A number of the possible reasons are listed here.

Geothermal Gradient

The natural cooling of the oil as it is carried to the surface may allow it to reach its cloud point. If the equipment surfaces cool to the oils cloud point deposition of paraffin will occur. The location may vary from the formation to the pipeline or anywhere in between.

Gas Expansion Cooling

In humid regions of the world it is not usual to see ice form on the body of a choke in an oil and gas production system. The reason this ice forms is the rapid expansion of gas molecules across the choke. This expansion is due to the pressure drop across the choke. It is not unusual to see 2000 psig upstream of the choke and 100 psig downstream of the choke. This 1900 psig pressure drop causes a 95°F temperature drop in the choke, or 1°F per 20 psig. In this example the body of the choke is cooled 95°F, and if the temperature drops below 32°F, ice forms. The cooling associated with pressure drop takes places wherever a pressure drop occurs; permeability in formation rock, perforations, across pumps, chokes and separators⁶.

The first time that a well is tested using a pressure drawdown test, paraffin will start to damage the most open flow paths (permeability) in the formation. If the formation temperature is below the melting point of the paraffin that has been deposited, permanent damage has occurred.

Oil Volume

The more gas, oil or condensate that an oil well makes, the more paraffin is being carried through the system. It never sounds like very much when you say an oil contains 2% paraffin by volume until you realize that this is 2 barrels out of every 100barrels of oil production. The more oil a well makes the faster the deposition will be and the more frequent the problems. The higher the volume of oil produced, the warmer the oil will reach the surface. This will reduce downhole problems, but may not eliminate them.

Loss of Gas Liquids

As gas is separated from the crude oil during production the paraffin content is going up. The crude oil with the least paraffin by volume is the crude oil in the formation. The formation crude is at a high temperature and pressure and has the lowest cloud point it will ever have. As methane, ethane, propane and butane are lost from the crude the $>C_{20}H_{42}$ paraffins are increasing in volume compared to the rest of the crude. The cloud point will also increase as the gas and gas liquids are lost. The most paraffinic crude oil in any system is that crude oil in the sales tank near the bottom of the tank.

Cold Fluids

In many operations in the oilfield we have to pump large volumes of fluid into the tubing or annulus. Reasons that we may do this include; killing a well to work on it, acidizing or fracturing the well. If the volume of fluid is larger than the shut in fluid level some of the fluid will go into the formation. If the fluid is pumped at >5 bbl per minute the fluid will reach the formation at near its surface temperature. If a 70°F fluid is pumped from a truck on the surface at 5 barrels per minute it will reach 5000 feet down a well and only be 75°F. If pumped at 50 bbl per minute it will still be 70°F when it reaches the formation. The situation gets much worse if it is January in Texas and the fluid is only 20°F in the truck. If the flow paths in a formation are cooled to 20°F and the cloud point of the oil in the formation is 90" paraffin deposition will occur as the produced fluid are being produced and warmed up the near wellbore area. The melting point of the paraffin can be high enough to permanently damage the formation.

Water Injection

Water injected into the producing formation to maintain formation pressure and push oil to the producing well can cool the fractures in the formation. Papers have been written that theorize that paraffin will deposit on the surface of these cooled fractures as the new oil enters the fracture. As this process continues the fracture becomes paraffin damaged, new oil does not enter the fracture and oil is left trapped in the formation.

Gas Injection

Gas injection to maintain or increase formation pressure, whether it is methane, CO, or NGL's can cause cooling at the production well when the gas starts to break out of solution. The 1°F cooling for 20 psig applies in these systems. The gases do a good job of increasing production, but can cause cooling in the largest permeability leading to the wellbore.

Hot Oiling

As has been written before hot oiling is a major cause of paraffin formation damage in many wells. Use of tank bottoms containing the highest quantity of the highest melting paraffin in a system to clean a well on a monthly basis makes no sense. Hot oiling down the tubing pushing hundreds of pounds of paraffin into the formation in order to pull a pump makes little sense if the formation is eventually plugged causing the abandonment of the well. Hot oiling is cheaper than many other paraffin treatments, but is not worth what it costs.

HOT OIL/WATER TREATMENT PROCEDURE

Hot treatments are used to melt the paraffin deposit or congealed oil from its original location in the system and to carry it through the system by diluting it in the produced oil. Hot oiling is used in all kinds of production from flowing wells to beam pump. The procedure that is followed is fairly simple. A hot oil truck is loaded with up to 70 barrels of produced oil from the sales tank or produced water from a water tank. A vacuum truck may be used to carry additional fluid if larger quantities are needed. Chemical or solvent may or may not be added to the oillwater at the discretion of the producer^{2,3}.

The fluid is carried by the truck to the injection location, hoses are hooked up, pumping of the fluid is started then the burners are turned on. The fluid is heated to an exit temperature that should be greater than the melting point of the paraffin that is to be removed. The hot fluid is pumped until the desired amount has been injected into the system then the burner is turned off and the fluid is pumped until the burner has cooled. The pumps are then turned off and the hoses are disconnected from the system.

This procedure is repeated on some kind of schedule from once every day to once a year based on the determined severity of the individual well's problem. The type, quantity of fluid, rate and temperature can be varied to generate a successful job. Usually one size treatment will be used in a field at a set interval.

Hot oil is still used in many locations especially if the formation is thought to be sensitive to water. Solvents or dispersants are sometimes added to hot oil but usually only a few gallons to a truck load. Hot water is used in some locations both with and without chemical. If chemical is added to hot water it is usually added at a rate of 200-5000 ppm. The rate may be determined using a hot flask test.

TYPES OF PARAFFIN PROBLEMS TREATED WITH HOT OIL/WATER

Paraffin problems do not just happen, they are caused. They are predictable if we understand the causes. All paraffin problems occur because of the cooling of a surface below the oil's cloud point⁵. Once a surface cools below the oil's cloud point deposition will occur. Hot fluids have been used to remove paraffin from the following locations⁷:

Formation, Perforations and Pumps

If production goes down and paraffin deposition is suspected in the formation, perforations or pump, hot oil or water are usually the first thing tried. This treatment is relatively inexpensive compared to stimulation treatments and is usually done as a first means of remediation⁴.

The problem with this treatment is that no heat will reach the formation so no paraffin is melted from these areas of the well. Hot fluids pumped at 1.5 - 2 barrels per minute reach the formation at the formation temperature. This means that 250° F oil or water reach the bottom of a well with a 105° FBHT at $<105^{\circ}$ F. This means that the only stimulation seen is probably that caused by back flushing the formation or displacement of solid particles from the perfs or pump. If the oil used contains chemical from the sales tank you may accidentally break an emulsion or reduce surface tension to allow gas to break out of solution. Any of these may cause an increase in production. Use of the small amount of chemical in hot water may help de-oil solids but usually the amount used is not sufficient to remove paraffin from surfaces or solid particles.

Oil from the stock tank may also contain high amounts of very high melting paraffin that have collected in the tank as tank bottoms. If these bottoms are melted into the oil pumped down the casing or tubing this oil may actually deposit paraffin in the casing or tubing as it cools to the formation temperature on the way down the well. Tank bottoms may also cause pump plugging instead of the cleaning that is expected.

Tubing

Most hot oil/water jobs done today are used to try to remove paraffin from the tubing of wells to maintain production, keep the rods free and allow the well to be pulled if needed⁹. Based on previous work we know that heat only removes paraffin from the tubing by melting it into the fluids in the tubing. These fluids will carry it out of the well. Usually all the wells in a field will be treated and the treatments will all be similar in size. Small amounts of chemical may be mixed with the oil or water treatments to increase their effectiveness. The only time that hot fluids can totally clean a well is if the paraffin present in the tubing has a low melting point and deposition or congealing is only occurring in the upper 500 feet of the tubing. In some flowing wells hot oil may be pumped down the tubing to remove paraffin.

The problem is again that the heat is lost in the first 400-700 feet of the casing and the hot fluids returning up the tubing have cooled to the normal production temperatures. If oil is used it may actually deposit paraffin in the tubing instead of removing it¹⁰. The small amount of chemical in hot water may work when the water is hot, as in the bottle test, but when it is cool returning up the tubing it will not remove the paraffin present. You can determine that your hot treatments are not working if you are sticking pumps when you try to pull them. If a treatment is leaving paraffin in the tubing it is not effective and cannot be cost effective.

Pulling Jobs

Another type of hot oil job is that done to remove paraffin during a pulling job to get the pump from the hole. In some fields before any pump is pulled a hot oil job is done down the tubing to remove the paraffin present so no extra time will be required for the pulling rig. It is not known on a particular well if the pump would have stuck in paraffin but historical problems have been enough so that a policy of hot oiling before pulling has been instituted. After hot oiling it is assumed that the paraffin was successfully removed when the pump comes out of the hole without getting stuck.

The problem with this treatment is that it shows that the producer knows that his normal (down the casing) hot oil treatment is not successful since he expects paraffin to be present in the tubing even if it is only a week since the well was hot oiled". The biggest problem is all the paraffin removed from the tubing is carried into the casing and formation and since the oil is not hot when it reaches the bottom of the well plugging should be expected. If you melt a thousand pounds of high melting paraffin into 70 barrels of oil you create a new oil that has a much higher cloud point. This oil is in the formation and casing waiting for a new pump to be run. This extremely high paraffin content oil is the first oil that has to be pumped through the new pump. In some cases plugging of the new pump occurs requiring a repeat of the hot oil/pump pulling procedure. Formation damage and loss of production is a likely result of this down the tubing hot oil procedure.

Flowline

In many systems, paraffin deposits in the flowlines or gathering lines carrying fluids to the batteries. Hot oil/water treatments are frequently used to melt this paraffin out of the flowlines. The hot oil/water needs to be heated to a temperature higher than the melting point of the paraffin being removed. It should also be realized that the temperature of the hot fluids need to be above the melting point of the paraffin at the exit end of the flowline. Chemical is sometimes added to

the oil or water to help remove or disperse the melted paraffin as it is carried out of the flowline. Usually only low quantities (>5000 ppm) of chemical is used as it is usually believed that the heat will do the removal and carry the paraffin from the flowline. The treatments can be on a regularly scheduled basis (once a week to once a year) or on demand when the flowline pressure reaches a predetermined level. Usually in a field that is on a regularly scheduled treatment program all flowlines will be treated the at the same interval and with the same size treatment.

The problem with hot fluid flowline programs is that no two wells have the same type paraffin problem. The melting point of the paraffin will vary from well to well. The rate of deposition will vary based on where the flowline is in the field and the amount and type of paraffin in a particular well. Some flowlines will be under standing water either all the time or after rainstorms. Some flowlines will run uphill or downhill. Some fluids may be emulsified causing more severe paraffin deposition. Flowlines with free water may be water wet and not experience any paraffin deposition. Trying to get the entire flowline to a temperature above the melting point of the paraffin present in that line with hot fluids may be impossible. Few fields ever measure the temperature at the exit end of a line during a heat treatment. The length of flowlines in a field will vary a great deal from well to well requiring that the treatments be of varying volumes.

Separation Vessels and Tanks

If paraffin interfaces or tank bottoms are encountered during production operations hot oiling is used to melt or disperse them back into the produced oil. It is hoped that by heating the oil in the tank above the melting point of the paraffin that they will stay dispersed until the fluids can be sold. In many systems with low melting paraffin, no emulsions and few solids this heat treatment may be successful.

Problems will be encountered if the melting point of the paraffin in too high, too many solids are present and/or it takes too long a period of time before the heated oil can be sold. Heating the oil may make the problem worse if a large volume of gas is driven off during the heating process which will increase the paraffin content of the oil remaining in the tank. It is also possible to melt so much paraffin into solution that the oil will actually go solid in the tank as the heat is slowly lost.

CHEMICAL TREATMENTS FOR PARAFFIN PROBLEMS

Paraffin problems can be treated in a number of different ways but all of the possible treatments can be divided into either inhibition treatments or removal treatments. An inhibition treatment is one that prevents the paraffin from depositing. A removal treatment is one that allows the paraffin to deposit but then on a periodic basis removes it. Usually hot oiling or hot watering are used as removal treatments. In a few instances hot oil equipment or line heaters have been installed to keep systems hot on a continuous basis to solve a paraffin problem. Usually this is when an oil is experiencing a congealing oil problem in the winter months. Hot or warm water with low ppm levels of chemical have also been injected continuously in an attempt to keep a system water wet so that paraffin deposition did not occur. In every case where this heat approach was tried it was abandoned as not cost effective. For a batch hot treatment to be effective it has to remove all the paraffin so that the system is completely clean every time. If the system is not cleaned totally, paraffin will slowly accumulate and eventually allow something to plug or stick. As we have discussed hot fluids, in many cases, do not do a complete job and therefore leave room for more cost effective treatments. In the next few paragraphs chemical treatments will be presented to treat the paraffin problems occurring in the various parts of the system.

Chemical treatments are also confined to either batch removal treatments or continuous injection inhibition treatments.

<u>Continuous treatments</u> either require that a pump be set up to inject chemical down the casing, down a capillary tube or into the flowline or surface equipment. Cost of pumping equipment for every well and the manpower to maintain the pump and monitor chemical levels in chemical tanks makes this a very costly treatment method. Usually this is used only on inaccessible, large systems or the most severe, frequent paraffin problems in order to be cost effective. Another method of treating continuously involves a squeeze treatment of a crystal modifier (PPD) paraffin inhibitor into the formation of the well. Squeezes have to be done on a periodic basis but return chemical continuously to inhibit deposition of paraffin or congealing oil. Trial and error is required on each well treated as the rate of return of chemical from the formation of a particular well is impossible to predict. Again, squeeze treatments because of their cost should only be used on certain severe, frequently occurring paraffin problems that are affecting oil production levels. Batch removal treatments are used on a majority of the paraffin problems that are treated with solvents or chemicals. Batch treatments may be solvent or condensate treatments¹², solvent or condensate with added chemicals, batch treat-

ments of neat chemical down the casing, mixtures of hot waterlchemical and/or mixtures of cold waterlchemical. Any of these batch treatments can be effective if conditions are right and it is applied in the correct manner. The selection of the most cost effective chemical treatment will be based on the location of the problem.

Formation, Pumps and Perforations

To treat problems in this area of the system where hot fluid treatments are not effective requires that the treatment be sized to penetrate and displace fluid from the bottom of the wellbore. Continuous treatments will not be able to solve this type of problem because chemical will be carried back up tubing before reaching the bottom of the well. Usually large solvent or condensate treatments with added chemicals are required to remove old damage of very high melting paraffin¹³. If the treatment is successful (cost effective) increased production can result which pays for the treatment in < 100 days. If the production drops following this treatment it may because of redeposition of paraffin from the produced oil. If this occurs and a second batch treatment again restores production it may be cost effective to try a squeeze treatment to inhibit reoccurring paraffin deposition. If higher production can be maintained for an extended period of time (>3 months) the squeeze treatment will be the most cost effective treatment you can do as it will help maintain production and reduce deposition of paraffin throughout the system.

Tubing

As discussed above continuous applications for downhole problems will be very expensive and can only be afforded on remote, inaccessible (subsea) problems or ones that occur very frequently (< monthly). Gas production up the casing may make it impossible for the chemical to get to the bottom of the casing. Batch treating has been preferred method with hot oiling or hot watering the predominate methods tried. We have discussed how these methods are ineffective as stripping jobs or stuck pumps are still occurring because the treatments do not totally clean the systems. Hot oiling down tubing to get pumps out of tubing is an indication of an ineffective paraffin program. Heat cannot be carried more than 500 feet down the casing of a well in most fields.

Other types of treatments that are possible are squeeze treatments on paraffin problems that occur very frequently or batch treatments with cold water and chemical. Batch cold water treatments have been found to be the most cost effective treatment in many fields with tubing deposition problems.

Cold water batch treatments consist of using a sized treatment based on a wells total fluid production. Instead of using 40-70 barrels of water as most hot water treatments only 3-20 barrels of water and chemical are required. The amount of chemical required is based on cold flask testing using the produced water and paraffin from the system. The amount of chemical required may be greater in volume in a specific well treatment but can be less than the amount used on a hot treatment. For example, a hot treatment of 70 barrels of water with 10 gallons of chemical may fail because the heat does not remove paraffin below 500 feet from the tubing. The 10gallons/70 barrel mixture may not be strong enough, chemically, to remove paraffin left in the tubing by the heat as it returns up the tubing. A cold treatment on the other hand may only require 10 gallons of chemical in 10 barrels of water to totally remove the paraffin from the tubing. It is a stronger chemical mixture that does the removal job at less cost without killing the well with a large volume of water. Smaller treatments allow for more treatments per hour also reducing cost. Cold water treatments can be monitored by catching samples of the treatments as they return to the surface carrying large quantities of paraffin.

Pulling Jobs

If cold treatments are used as discussed above pumps should be able to be pulled without resistance caused by paraffin. Cold batch treatments can be totally effective at removing paraffin from the tubing. This allows the pulling job to be used as a monitoring technique to find problem wells.

Flowlines

Flowline treating with hot oil or hot water is still common today. Many flowlines are still being treated with oil even when water and chemical is used downhole. Hot oiling or hot watering may be effective if the temperature of the exit end of flowline is raised above the melting point of the paraffin. If the exit temperature is not checked paraffin may be left behind to cause the problem to reoccur sooner. Again the hot treatment may not be doing a complete job leaving room for more cost effective treatments. If the problem occurs every week or daily in cold weather continuous treatment of a line may be effective if it is only required for short periods of time. Cold batch treatments can again be an option as smaller batch size will allow more treatments per day, the cost of propane is saved, less water needs to be handled in the separation equipment and smaller amounts of paraffin could be handled on a more frequent basis at the same cost.

Separation Vessels and Tanks

Interfaces and tank bottoms can be treated with batch treatments of chemical. These problems are usually caused by the paraffin depositing upon solids or water droplets. Use of a good dispersant in a batch treatment will separate the paraffin from the solids and water allowing the paraffin to redisperse into the oil. Hot oiling in many fields is making interfaces and tank bottoms worse by moving the paraffin and solids down the line together. If the paraffin cools it becomes solid again and redeposits on the solids. The solids cause the paraffin to resettle to interface or tank bottom. Continuous treating is also possible if the problems are usually server but this is usually not cost effective.

CONCLUSIONS

- 1) Hot oil or water treatments are used to treat paraffin problems in almost every area of the production system.
- 2) Hot treatments are greatly limited because the treatments cannot stay hot as they travel through the system.
- 3) Hot treatments may actually be a cause of paraffin damage under certain application conditions.
- 4) Other chemical treatments such as Solvent, Squeeze, Continuous and Cold Water Treatments may be much more cost effective in removing paraffin from production systems.

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