A UNIQUE APPLICATION FOR EFFECTIVE PARAFFIN TREATING IN THE TEXAS PANHANDLE

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ABSTRACT

The crude oil produced by a Major Oil Company in the Texas Panhandle is very paraffinic and has caused paraffin problems in formation, pumps, tubing, casing, flow lines and separators for years. Cost of production had been increasing because of lost production, plugged pumps, workover problems and stripping jobs. Many different types of treatments including cutting, solvent/chemical treatments, hot oil and hot water/chemical had been tried but all had been unable to reduce the problems or reduce costs. A unique application in this field has been found to cost effectively remove paraffin with cold water and chemical. This paper will discuss the application method, how it was tested and benefits resulting from its use.

INTRODUCTION

Paraffin is a major constituent in most crude oils $> 20^{\circ}$ 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 carbon⁸. 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_nH_{2n+2} . This means that for every carbon atom there will be twice as many hydrogen atoms plus two.^{1,8}

<u>Compound</u>	<u>Formula</u>	Melting Point °F	Boiling Point °F @ 1 atm
Methane	CH_4	-296	-259
Ethane	C_2H_6	-297	-127
Propane	C_3H_8	-305	-44
Butane	$C_{4}H_{10}$	-217	31
Pentane	$C_{5}H_{12}$	-201	96.8
Hexane	$C_{6}H_{14}$	-137	156
Heptane	$C_{7}H_{16}$	-131	209
Octane	$C_{8}H_{18}$	-70	258
Nonane	$C_{9}H_{20}$	-65	303
Decane	$C_{10}H_{22}$	-21.5	345
Undecane	$C_{11}H_{24}$	-14	385
Pentadecane	$C_{15}H_{32}$	50	519
Eicosane	$C_{20}H_{42}$	97.5	NA
Triacontane	$C_{30}H_{62}$	150	579
Tetracontane	$C_{40}H_{82}$	178	NA
Pentacontane	$C_{50}H_{102}$	198	790
Hexacontane	$C_{60}H_{122}$	210	NA
Heptacontane	$C_{70}H_{142}$	221	NA
Hectane	$C_{100}H_{202}$	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 particular oil becomes insoluble in that oil. The cloud point indicates the temperature at which paraffin deposition will start. If the formation rock or equipment

surfaces reach the cloud point temperature of the oil, paraffin deposition will start even though the bulk oil is still above its cloud point.² As the surface temperature of the equipment drops below the cloud point of the oil shorter chain paraffin 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 paraffin 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.

PARAFFIN PROBLEMS IN THE FIELD

The oilfield of 154 rod pump wells produces oil, water and gas from the marmaton formation. The wells are ≈ 5500 ft deep, with a bottom hole temperature of 120°F and produce 35°API crude oil. Of the 154 active producers 46 have paraffin problems that are being treated for paraffin deposition or congealing oil. Deposition occurs in the formation,¹³ pumps, tubing, annulus, flowline and separators in these wells.

The oil varies from well to well within the field with paraffin content being measured from <1% to >10% by weight C20H42 n-alkanes and greater. Paraffin deposits have melting points from $<160^{\circ}$ F to $>200^{\circ}$ F. The cloud point of the oils vary from $<82^{\circ}$ F to 111°F from well to well. ASTM maximum pour points of the oils can vary from $<0^{\circ}$ F to $>80^{\circ}$ F. The paraffin found in the tubing in early 2002 was dehydrated, hard paraffin with consistent melting points $>190^{\circ}$ F.^{5,8}

Operational problems resulting from paraffin deposition have been severe in the problem wells.⁷ Formation damage from hot oiling down the tubing has caused rapid production declines in some wells.¹¹ Stuck pumps have resulted in well workovers, including stripping jobs and pump replacement. Stuck rods and plugged tubing have resulted in rod stress, rod breaks, the need for hot oil or hot water treatments, toluene treatments, mechanical cutting, well workovers requiring stripping jobs and lost production due to extended shutins. Flowline treatments including hot oil and hot water to remove paraffin deposits have resulted in plugged separation equipment and treater upsets. Large quantities of paraffin, water and solids removed by hot treatments required extra heating and chemical/solvent treatment to resolve emulsions, interfaces and tank bottoms in the separation equipment.¹²

HOT CHEMICAL TREATMENT PROGRAM

Hot treatments have been the standard for years in the field. In recent years prior to July 2002 Hot Water Treatments were the accepted best practice and were relied upon to remove paraffin from the wells. The produced water in this field had a Total Dissolved Solids (TDS) content of 240,000 making it very difficult to disperse chemical into the water. The best hot water treatment was a mixture of 3 parts of surfactant to disperse 1 part of paraffin dispersant and solvent into 70 barrels of produced water. The chemical was pumped into the truck then the water was loaded to mix the chemical into the water. The load of 60-70 barrels containing the chemicals was then driven to the well to be treated and was then heated to between 180°F - 225°F depending upon the well to be treated. Severe paraffin problem wells were being treated weekly, some bi-weekly and some monthly. Thousands of barrels of produced water containing chemicals were being pumped down wells every month.

It is normally expected that these large amounts of hot water containing chemicals will solve the paraffin problem by removing it and leaving the well clean with each treatment. The "hot flask" test is used to show how small amounts (0.7%) of chemical mixed with hot water and melted paraffin will keep the paraffin broken up into small particles as the water cools. If this worked in a well the water would have to go down the casing hot and return up the tubing at a temperature above the melting point of the paraffin in the tubing. It would melt all the paraffin and as the water exited the tubing into the flowline you would have dispersed paraffin in the to il in the tank with no emulsions and solids dropped into the water phase in the separator. All you would have to determine is how often you needed to treat to keep the paraffin buildup at a minimal amount so wells could be easily pulled. If this worked in this way you would have no stripping jobs, no stuck pumps, clean flowlines and no separator problems.

In actual practice in the field, with 46-60 hot water treatments a month down the annulus the field still had a .4 failure/well/year rate. This indicates that the hot water treatments are not successfully removing paraffin.^{24,7,9,1011} Wells are still being stripped, pumps are still sticking, flowlines are still plugging and interfaces are a problem. If we use the Heat Transfer Program developed by Sandia National Laboratory we can understand part of the problem.⁹ The 225°F water is actually only removing paraffin from the tubing down to ≈ 600 - 1,000 feet. Paraffin is depositing below 2,500 feet on many wells. (See Graph 1) This means that the heat isn't cleaning the well and the water reaches the bottom of the well near the

formation temperature of 120°F. This means that the 20 gallons of surfactant/dispersant/solvent chemical added to the water better be doing a good cleaning job as it is produced back up the tubing for 3-4 hours after the heat is gone. Unfortunately the 240,000 TDS water being used did not help the chemical remove paraffin. This high TDS water actually made it almost impossible to get the paraffin removal chemical to disperse at all.

In April, 2002 when the chemical vendor was changed we tried to make the hot water treatments work with new chemicals. Almost immediately trouble was encountered getting the chemical to disperse in the hot oil trucks. Interfaces of emulsified chemical would develop when the chemicals were mixed with the water in the truck and it was driven to the well for application. Stripping jobs were still occurring indicating that the treatments were not effective. Hot Flask Tests indicated that once the chemical emulsified and separated even 225°F heating and agitation would not disperse the emulsified chemical. After three months of changing the chemical ratio, adding more surfactant to disperse the dispersant it was decided that something different was needed. A test was set up to see if the current hot water treatment program was effectively removing paraffin from the wells.

A Technical Service field trip was made to observe the treatments being done in the field. The loading procedures and treating procedures were observed and appeared to be basically in order. Care was observed in the loading and treating procedures, the water was heated and pumped at best rate possible. Bottle tests of the chemical were made separately and mixed. It was noted that when the chemical was initially mixed with the produced water that it would stay mixed as long as it was agitated. If the chemical and water were allowed to sit the chemical would separate to the top of the water and slowly gel. It was decided that a treatment needed to be monitored to see if it was removing paraffin. Well C-2 producing 11 BOPD and 89 BWPD was chosen as a good candidate. The hot oil truck had about 2 barrels of fluid present in the truck. Ten gallons of paraffin dispersant and 10 gallons of surfactant were pumped into the truck then the truck was pumped full of 70 bbl of produced water. The well was placed on manual and the truck was hooked up, pumping of water started at 1:30PM with the water slowly heated to 225F after 5 minutes. Samples were caught from the flowline at the wellhead before, during and after the hot water treatment with the following results:

1:25PM	Before Hot Water Job	90% Water 10% Oil - No Paraffin - No chemical
1:30PM	Start Treatment	90% Water 10% Oil - No Paraffin - NC
1:36PM	Hot Water-200F	85% Water 10% Oil - est. 5% Paraffin- NC
1:48PM	Hot Water-225F	80% Water 10% Oil - est. 10% Paraffin-NC
1:55PM	225F	75% Water 10% Oil - est. 15% Paraffin-NC
2:00PM	225F	85% Water 10% Oil - est. 5% Paraffin-NC
2:05PM	125F End Hot Water	90% Water 10% Oil - No Paraffin-NC
2:18PM	125F	90% Water 10% Oil - No Paraffin-NC
2:45PM	125F	90/10 No Paraffin- No chemical
3:30PM	125F	100% Water- No Paraffin- Chemical with Foam
3:45PM	125F	100% Water- No Paraffin- Chemical with Foam
4:05PM	125F	100% Water- No Paraffin- Chemical with Foam
4:25PM	125F	100% Water- No Paraffin- Chemical with Foam
4:50PM	125F	100% Water- No Paraffin- Chemical with Foam
5:25PM	125F	100% Water- < 0.1% Paraffin- Chemical with Foam
5:55PM	125F	100% Water- No Paraffin- Chemical with Foam
6:25PM	125F	100% Water- No Paraffin- Chemical with Foam
6:55PM	125F	100% Water- No Paraffin- Chemical with Foam
7:25PM	125F	100% Water- No Paraffin- Chemical with Foam

At 7:25PM the test was ended with the heat having removed some paraffin during first few minutes of heat application, chemical was seen in the water for 4 hours but no paraffin was being removed. It was decided that this indicated that the chemical as applied, did not work or that the heat had removed all the paraffin from the well.

A way to determine if the well still contained paraffin after the hot water/chemical treatment was done was needed. The Heat Transfer Program showed that paraffin deposited down to $\approx 2,500$ feet in the test well. We could try to pull the well but that could be a problem if the well was restricted with paraffin and the rods stuck. Suggestions were made to try another type of treatment on the same well to see if any more paraffin could be removed from an already treated well. If paraffin was removed we would clean the well, prove that heat alone did not remove the paraffin and possible find a new, unique to this field treatment for paraffin problems that had never been solved economically.

CURRENT CHEMICAL TREATMENT PROGRAM

To determine which of these statements was true it was decided to treat well C-2 again, the next day with 20 gallons of paraffin dispersant was slipstreamed into 20 barrels of a green dyed mixture of 50/50 cold produced/fresh water (accident) using the vendor's chemical truck in place of a hot oiler. The higher concentration of chemical in 120,000 TDS water was found to work much better at removing paraffin.

The success of slipstreaming chemical into the fresher water was shown by catching samples of well fluids, from the tubing, as the treated water was being produced out of the well. On 7-18-02 at 9:00AM the treatment was started. The well was put on manual, water was started and chemical was pumped into water stream going into the casing. No heat was applied.

9:00AM	Start Pumping	90%Water 10%Oil- No Paraffin-No Chemical
9:30AM	End Pumping	90%Water 10%Oil- No Paraffin-No Chemical
10:00AM	Producing	90%Water 10%Oil- Foam-No Paraffin
10:30AM	Producing	90%Water 10%Oil- Foam-No Paraffin
10:45AM	Producing	100%water- Foam- >10% Paraffin
11:00AM	Producing	100%water- Foam- > 30% Paraffin
11:10AM	Producing	100%water- Foam- > 20% Paraffin
11:20AM	Producing	100%water- Foam- > 50% Paraffin
11:40AM	Producing	100%water- Foam- > 10% Paraffin
12NOON	Well Pumped Off	100%water- Foam- > 10% Paraffin
2:10PM	Producing	90%Water 10% Oil-No Paraffin-Foam

The treatment showed that large amounts of paraffin were still present after the hot water treatment, that cold slipstreamed chemical treatments would remove large amounts of paraffin. The resulting oil production increase in the two weeks following the successful paraffin removal treatment indicated that paraffin was restricting oil production either by plugging formation or back pressure on formation by plugging the tubing.

RESULTS AND DISCUSSIONS

The paraffin program being used in the Texas panhandle field tried to use a hot oil truck that was unable to slip-stream chemical into the water being batch treated into the well. The chemical was not compatible with ~240,000 TDS produced water when sucked into the 70 bbl tank that already contained varying quantities of oil and water. Surfactant was being used to try and overcome this by mixing 10-25 gallons of surfactant/dispersant mixed with 70 bbl of produced water. The mixed chemicals were more compatible but problems with gelling and emulsions were still being experienced.

The mixed chemicals (10/10) were found not to be effective at removing paraffin from deep in well C-2 during a 70 bbl, 225°F treatment. Samples caught from the flowline during the hot water treatment showed paraffin being melted from the tubing but when the treated water returned up the tubing no further paraffin was removed from below the area that heat could reach.

A second cold, fresher water treatment was done on well C-2. A truck capable of slip-streaming 20 gallons of chemical dispersant into 20 barrels of cold produced was used to treat the well. Samples taken during and following this treatment showed large quantities of paraffin being removed as this 2.4% chemical solution was produced back from a well already treated with the larger, hot 0.7% solution of mixed chemical. The slip-streamed paraffin dispersant gave a very foamy paraffin water mixture when sampled from the flowline with high gas pressure.

In the next two months the paraffin treatments were changed from the hot water treatments to cold water treatments. The chemical was slipstreamed into the mixed water. The treatments were sized to give 4 hours of chemical/water treatment contact with the paraffin in the tubing based on the latest production tests.

In the first six months of the cold truck treating paraffin program Paraffin Related Failures dropped from 0.4 to 0.2 failures / well / year. (See Graph 2 & 3) The number of paraffin treatments done on some wells was starting to be reduced. The quantity of water pumped down the wells was reduced from thousands of barrels a month to hundreds. The smaller treatments allowed the use of the vendor's truck which saved 83% of the trucking costs. See Graph 3

The program has been in use for over a year and a half. Some wells were found that did not respond to the cold treatments but had congealing oil / emulsion problems that were thought to be paraffin deposition problems. Some wells were also found that produced so little fluids that they had trouble producing all the paraffin that was being removed before they pumped off. Corrosion has increased on some of the wells that are now clean of paraffin for the first time in years. Tubing in contact with 240,000 TDS water will corrode so wells have to be added to corrosion treating program. The cold treatment of slipstreamed chemical into compatible water at a higher concentration than used for hot treatments has been found to be much more cost effective and its use has been started in many other West Texas Fields. The cold program is a constantly changing program that can be changed as more in learned about each, individual well.

CONCLUSIONS

- 1. High TDS water may be incompatible for use in paraffin treatment programs.
- 2. Hot water treatment programs will not remove paraffin from deep in the tubing unless enough chemical is used to remove the paraffin as the hot treatment is produced cold up the tubing.
- 3. Smaller cold treatments with higher chemical concentrations can be more cost effective than larger hot treatments that are not removing all the paraffin.
- 4. Smaller chemical trucks made to slipstream chemical into water can be much more cost effective at applying chemical than hot water trucks.
- 5. Gathering of samples during treatments is a valuable method to see if the treatment is removing paraffin.
- 6. Failures rates will be reduced almost immediately when a successful paraffin treating program is found for a field.
- 7. Problems can be encountered with wells that produce <10 bbl a day when cold batch treating if the wells pump off too quickly.
- 8. Congealing oil problems may not respond to cold water treatments. Crystal modifier or continuous treatments may be needed on some wells.
- 9. Sizing treatments to the individual well can reduce amount of chemical and truck charges while increasing the effectiveness of a program.

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Graph 1- Heat Transfer of Hot Water Treatment-Paraffin Melted down to 400-600 feet deep in tubing



Graph 2 - Failure Rate Trend Since Cold Treating Started July 2002



Graph 3 - Reduction in Well Service Cost per Boe since Cold Treating Started July 2002



Graph 4 - Reduction in Truck Annual Charges Hot Treatments vs Cold