PRODUCTION STIMULATION BY REMOVAL OF PARAFFIN AND ASPHALTENE DEPOSITION

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ABSTRACT

Paraffin and/or asphaltenes are part of the oil that is produced from all the formations in West Texas. They are stable in the untouched reservoir. but once production begins, natural and maintenance caused deposition of these oil components can occur. The deposits can reduce permeability. plug pore throats or cause changes in wettability that can drastically reduce production. This paper will cover the chemistry of the deposits, causes of deposition and removal methods. Case histories oftreatments of West Texas wells will be included.

INTRODUCTION

Natural gas. gas liquids and crude oils are the products upon which the petroleum industry is built. The petroleum industry is plagued by a number of problems that originate from these hydrocarbon liquids [1]. The problems are generally identified as either paraffinic or asphaltic in nature. Since the education received by most petroleum industry personnel does not include a study of the chemistry of crude oil. few are prepared to deal with or understand these problems that can plug the formation and reduce the amount of oil recovered from a formation'.

CHEMISTRY OF CRUDE OIL

No two crude oils are ever exactly the same. Just as oilfield waters vary from well to well. so do crude oils. Crude oils are made up of various organic components (compounds of carbon and hydrogen) that can be divided into two general classes of compounds — aliphatic (paraffinic) and aromatic (asphaltic).

Paraffinic Hydrocarbons

The aliphatic paraffin series of compounds or 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_nH_{2n-2}. This means that for every carbon atom we will have twice as many hydrogen atoms plus two.

PHYSICAL CHARACTERISTICS OF SOME N-ALKANES IN CRUDE PETROLEUM

Compound	**Formula**	**Melting Point "F**	**Boiling Point "F @ 1 atm**
Methane	CH	-296	-259
Ethane	$C\ H^4$	-297	-127
Propane	C^2H^6	-305	-44
Butane	C^3H^8	-217	31
Pentane	C^4H^{10}	-201	96.8
Hexane	C^5H^{12}	-137	156
Heptane	C^6H^{14}	-131	209
Octane	C^7H^{16}	-70	258
Nonane	C^8H^{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	$C^{70}\ H^{142}$ 100 202	239	NA

The longest chain paraffin that has been rcportcd in crude petroleum products is $C_{103}H_{208}$ The shorter chain length n-alkanes are the solvents for the longer chain length n-alkanes. Paraffin deposits in the system are mixtures of n-alkanes ($>C_{20}H_{42}$) and crude oil'. Paraffin deposits may contain percentages of water and solids. The cloud point of an oil 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 fortnation or equipment surface reaches the cloud point temperature ofthe oil. paraffin deposition will start even though the bulk oil is still above the cloud point".

Asphaltenes

The asphaltenes are aromatic hydrocarbons that contain oxygen (0.3-4.9%), nitrogen (0.6-3.3%) and sulfur (0.3-10.3%) in their benzene ring structure. They are defined by their insolubility **in** n-pentane or n-heptane when one volume of crude oil is blended with 40 volumes or more of either of these solvents. All other organic components of crude are soluble in n-pentane or n-heptane.

The asphaltenes arc amorphous solids that are colloidally dispersed by asphaltic resins. The asphaltenes and resins give crude oils their color. Asphaltenes are those deposits in the oilfield that will dissolve (disperse) in xylene at room temperature, but will not go back into solution in the oil with heat. They arc usually hard. coal like deposits. but can also be a tar like deposit as an interface or bottom in a flowline or vessel.
Asphaltenes are the most-dense component in crude oil. As the amount ofasphaltenes increases the API gravity tends to go down. Asphaltic crudes (< 20°API) contain more than 20% asphaltenes and asphaltic resins. The lower the API gravity the larger the % asphaltic components. Asphaltenes do not have a melting point. They soften and flow a little faster, but do not melt. They are described as an amorphous solid, a solid that will cold flow. At temperatures above 400°F asphaltenes start to decompose and will turn into coke if heated to a high enough temperature. Once coked the asphaltene is not soluble in any solvent. Asphaltenes are very polar and will combine with metal ions in acid to produce a rigid film emulsion. The metal is usually ferric and ferrous iron from the tubulars in the well being acidized, but can also be from the truck the acid is delivered in. The electrical charge in the asphaltene molecule causes the oil wetting of solids in the oilfield production system. As oil is produced the flow of fluids causes a static charge to build up on solids of all kinds. the formation, fines. pumps, tubulars and surface equipment. The asphaltenes are responsible for the oil wetting of the near wellbore flow paths in the formation called permeability. Oil wet formations restrict the flow of oil to the well and increases the flow of water.

Asphaltic Resins

Asphaltic resins have the same benzene ring structure as asphaltene, contain lesser amounts of oxygen, nitrogen and sulfur. and have more methyl side chains attached. The resins are also soluble in n-pentane or n-heptane. The resins are the dispersing agents in crude oil that colloidally disperses the asphaltenes in the crude oil. Resins are the component in oil that will adsorb on Fuller's Earth, but will be removed by a xylene wash.

CAUSES OF ORGANIC FORMATION PROBLEMS

Organic formation problems do not just happen, they are caused [4,5,6,7,10,11]. They are predictable if we understand the causes. **All** paraffin formation problems occur because of cooling in the formation and the loss of solubility ofthe paraffin. Asphaltene formation problems are caused by the flow of crude through the formation. by the pressure drop and the mixing of incompatible fluids with the oil in the formation. We cannot eliminate the causes. so we must learn to reduce the problems to a manageable level to control costs or production loss.

CAUSES OF FORMATION PARAFFIN PROBLEMS

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 I00 psig downstream of the choke. This I900 psig pressure drop causes a 95°F temperature drop in the choke, or 1"F per 20 psig. In this example the body ofthe 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 fortnation rock [6,13], perforations. across pumps. chokes and separators.

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 ofthe 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 I00 barrels 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 wariner the oil will reach the surface. This will reduce downhole problems, but inay 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 cornpared to the rest ofthe 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 ofthe 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. Ifa 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 ofthe 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 ofthe paraffin can be high enough to permanently dainage 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 l°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 ofthe highest melting paraftin 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 inakes little sense if the formation is eventually plugged causing the abandonment ofthe well. Hot oiling is cheaper than many other paraffin treatments. but is not worth what it costs.

CAUSES OF FORMATION ASPHALTENE PROBLEMS

Pressure Drop

High-pressure tests conducted in the lab with fortnation bomb samples of oil have shown that asphaltenes start to destabilize at up to 5.000 psi above the bubble point of the crude. Most dark crudes in older fields have unstable asphaltenes. As the crude approaches the wellbore. gases and gas liquids can precipitate asphaltenes as they come out of solution. Precipitated asphaltenes can plug pore throats and oil wet flowpaths.

High Flow Rates

The higher the flow rates in the flow paths leading to the wellbore. the higher the electrical charge that can build up on formation minerals. Charged surfaces attract asplialtenes, which leads to oil wetting and asplialtene and/or paraffin buildup.

Formation Minerals

Some types of formation minerals are more susceptible to asphaltene buildup. Clays are used as absorbents for asphaltenes and resins in laboratory testing. Natural clays and drilling muds lost into the formation can adsorb large quantities ofasphaltenes. Dolamite is a strong attractant of asphaltenes because of the metals present. Sand will also attract unstable asphaltenes if sufficient flow is present to set up a charge.

Temperature

If a low API gravity crude reservoir is cooled by injected fluids the crude oil viscosity may increase enough to restrict production. Huff and puff operations with high temperature steam may precipitate asphaltenes and coke them leading to fines plugging.

Acid Jobs

Acid (hydrochloric or acetic) containing ferrous and ferric irons can cause the formation of rigid film emulsions that can plug a well immediately or months later can reduce the production dramatically. Acid sludge can also lead to oil wetting of the near wellbore forination causing a major increase in water production.

Condensate Treatments

Condensate (n-butane. pentane. hexane and heptane) can precipitate asphaltenes from most crudes <40° API. Use of barrels of condensate to remove paraffin can lead to plugging of the formation with asphaltenes. As the condensate dilutes the crude in the formation the asphaltene micelle is destabilized and solid asphaltenes are precipitated. If >10 barrels of condensate is used damage can be done deep into a formation depending upon the formation pressure.

CO_2 Floods

Most CO_2 flooded fields in West Texas have experienced asphaltene problems somewhere froin the formation to surface equipment. Unrecognized formation problems are reducing production in many of these fields. CO_2 does a very good job of-increasing production by re-pressuring old formations and mobilizing oil. In sonic: fields. however. the reestablishment of a bubble point from injector to producer causes propane. butane and pentane to destabilize the asphaltene micelle as they bubble out of the oil with the CO_2 near the producer.

NGL Floods

Injection of propane and butane liquids into the formation can precipitate asphaltenes as they mix with some crudes. This can cause asphaltene precipitation causing plugging and oil wetting of the major flow paths.

TREATMENTS TO CONTROL ORGANIC FORMATION PROBLEMS

Many types of treatments are used to stimulate production of fluids and gas from reservoirs in West Texas'. In the above "causes" of organic problems we have seen that many of these stimulation/production techniques can lead to new (sometimes. unrecognized) organic damage. Discussion of these practices as stimulation techniques is worth while to recognize their liinitations.

Solvent

Down hole solvent treatments have been used to remove paraffin and asphaltenes as long as hot oiling has been done. Solvents of various types are used in volumes ranging from 1 gallon to 100's of barrels per treatment. Most of this solvent is removing paraffin from the casing and tubing rather than the formation. Most solvent treatments are too small and the contact time *too* short to remove the higher melting paraffins that are plugging the formation. If a solvent treatment is over flushed with oil, water or acid it usually ends up many feet back in the formation in the most open flowpath. It has only had minutes to contact paraffin in the near wellbore area. so very little is removed. A barrel of solvent will hold very few pounds of $>C_{50}H_{102}$ paraffin at temperatures of less than 110°F, the temperature of many West Texas formations [12]. Xylene alone will not remove asphaltenes from formation minerals and so cannot change an oil-wet formation.

Acidizing

Hydrochloric acid does not dissolve any paraffin or asphaltenes. The best acid can do is open up flowpaths around the organic damage. not remove it. Solvents placed in front of acid jobs usually are not given any time to dissolve the organic deposits present and cannot remove asphaltenes from the rock. Any new flowpaths opened can be plugged by asphaltenes or sludge caused by the acid [14].

Thermal

Getting heat to the formation is very difficult [2,9,10]. Hot oil jobs at 1.5 bbl per minute rates at 200-300°F only heat the wellbore to 500 feet (160°F) and don't remove any paraffin at the formation. **All** hot oil reaches the formation at or below the formation temperature. Exothermic treatments that can heat at deeper depths by delaying the chemical reaction can melt paraffin. but may not get it out before it re-solidifies causing worse plugging. Heat does nothing to asphaltenes since they do not have a melting point.

Perforating

Re-perforation through "the damage" (organic damage) is possible in some cases, but the new flowpaths created can plug with organics from the increased production coining through the new flow paths. Increased production may be short-lived and not pay for the cost of the job.

Fracturing

Re-fracturing a formation to penetrate through "the damage" around the wellbore is the most expensive stimulation treatment used. In many cases the gas/oil and/or water production is increased. The new flowpaths allow larger quantities of gas and oil to be produced. but again this production is carrying the same components that originally plugged the formation. Decline rates ofgreater than 50% a year are not unusual. Over the life of a field some wells may be re-fractured a number of times. and infield-drilling prograins may be started. Again, all of this is very expensive and may not be cost effective.

Chemical

Over the last 20 years combination chemical/solvent stimulation treatments have been developed to address organic formation damage problems. New chemicals in combination with improved solvents have been used with new application techniques to do a superior job of removing damage and keeping it from reoccurring. New chemicals developed include; patented surfactants that remove asphaltenes from formation minerals including clay, new inhibitors to stop paraffin/asphaltene deposition in the formation and new patented solvents that will dissolve much larger quantities of long chain paraftins that plug formations. New application techniques take into account the need for large volumes and long soak times to get to the organic damage, slowly removing it to open up the original permeability that has been plugged around the wellbore. The new treatments can do a better job at a lower cost to stimulate oil and/or gas production and can pay out much quicker that many of the normally used stimulation techniques mentioned above. Success depends upon doing a good job of looking at well history. oil chemistry. chemical selection and application technique in each field. Case histories follow that demonstrate how organic damage is responsible for much more formation damage than suspected by the industry and how it can be successfully treated.

CASE HISTORY #1

A well in the Upton County, TX area was recompleted into the Clearfork Formation at a depth of 6200 feet. To keep the two formations froin co-mingling a packer was set at 6,000 feet. The well started producing in September making 23 HOPD and no water. Paraffin problems developed in the tubing after two months and the well was hot oiled down the tubing every six weeks as a maintenance program. After four hot oil treatments the production had dropped to 10-11 HOPD. The fifth hot oil job was completed in April and this treatment killed the well. The paraffin was carried from the tubing back into the formation where it plugged off the permeability leading to the wellbore. In less than 8 months this recompleted well was totally plugged froin hot oiling. **A** recommendation was made to chemically stimulate the well using 550 gallons of chemical flushed with one tubing volume of oil. The well was shut in for a week to give the chemical time to dissolve paraffin back in the formation and open up plugged permeability around the wellbore. Upon restart of production the well produced 60 BOPD. after two weeks 21 BOPD. after 6 weeks 18 BOPD and after 3 months I5 BOPD. The treatment cost $2,854.50 and in the first three days incremental oil above 11 BOPD paid for the treatment. The chemical treatment was able to clean up and stimulate a dead well and allow the production of I600 barrels in the three months after the treatment.

CASE HISTORY #2

A pumping well in the Goldsmith, TX area completed at 4200 feet was producing 60 BOPD of 36°API crude and 8 BWPD. Production had been dropping from 130 BOPD since the well was first completed over 2 years before. Hot oiling down the casing was started after six months of production due to downhole paraffin deposition on the rods and tubing. **A** chemical treatment of 110 gallons mised with 20 barrels of clean lease crude was pumped down the casing and allowed to soak for 8 hours. Production was increased from 60 BOPD/8 BWPD to 100 BOPD/15 BWPD where it held for a total of 3 months before the decline began again. At that time the treatment was repeated using a new combination solvent/dispersant chemical. This treatment produced 100BOPD for 5 months. The treatments paid for themselves in 2-3 days and the additional oil amounted to over 9600 barrels during these eight months.

CASE HISTORY #3

A well producing from 30 feet of the Atoka Bend Conglomerate formation in West Texas was making 70 BOPD and 89MCF of gas. Possible paraffin formation damage from gas expansion cooling was suspected and a 500-gallon chemical treatment was recommended. The chemical was applied down the casing and the well was shut in for 24 hours. Total cost of the chemical. trucking and shut in time lost production was ~$6.000. The well was restarted and production increased to 95BOPD and 103 MCF of gas. Over the nest 100 days the incremental oil and gas revenue paid for the treatment in 22 days and generated an additional $22,000 incremental oil and gas.

CASE HISTORY #4

Three rod pumped wells drilled into a limestone formation in West Texas were experiencing severe paraffin deposition in the tubing. resulting in frequent failures. Fortnation paraffin damage was also suspected. The limestone formation was 8.460 feet deep. had a porosity of 12.5%, permeability of 57 md, 640psi BHP, 121°F BHT and produced 44" API crude. Using a computer program, treatments were designed for all three wells costing a total of $20.873 for chemical, trucking and delayed production. The wells were treated and shut in for 24 hours to give the chemical time to soak; then returned to production. **All** three wells were treated a second time and a third treatment was preformed on one of the wells in conjunction with a crystal modifier squeeze treatment. All three wells experienced a significant increase in oil and gas production and a I00 BPD decrease in water production. After 197 days of production the return on investment was 2236%. and the net production increase was 21%. The well receiving the third treatment and crystal modifier squeeze experienced a significant increase in run time between problems.

CASE HISTORY #5

A mature CO_2 flood in West Texas was completed in the San Andres Formation. The dolamite reservoir was at 5100 feet with 135 feet of net pay. It had 13% porosity. a bottom hole temperature of 157°F and produced a 35°API crude oil. The crude contained ~ 2.50% paraffin, 0.2% asphaltenes and 7.0% asphaltic resins. Asphaltene damage was suspected, but thought to be minor because of the low percentage ofasphaltenes. Acid jobs were employed. but were not thought to cause any problems. Problems with asphaltene deposition and acid sludging of the resins were determined to be possible damaging agents. A well was selected and a 1720-gallon solvent/dispersant treatment was pumped into the well followed by 55 barrels of oil containing dispersant. The well was shut in for 72 hours and when returned to production made an additional 33 BOPD. The chemical costs. trucking costs and lost production costs were paid out in <15 days. The increased production has been maintained for over 60 days at this time.

CASE HISTORY #6

A second mature CO_2 flood in West Texas was experiencing asphaltene deposition in the tubing and electric submersible pumps. Batch treatments of solvent and dispersant were being done to keep the equipment operating in a cost-effective manor. Formation damage was a possibility, but the high BHP of 3I50 psi made it hard to treat these wells. The dolomite formation was 6300 feet deep and had 80 feet of net pay with a porosity of 11%. The 39° API crude contained both paraffin and asphaltenes, but asphaltene deposition was the predominate problem. Treatments consisted of 2200 gallons of solvent/chemical followed by 4I65 gallons of a solvent/chemical /oil mixture flushed with produced water. The wells were shut in for 48 hours. Five wells were treated at a cost of ~$35,000. The average oil production increase over the nest 63 days for the five wells was 193 BOPD. This gave a $6 return for every dollar spent, or > $200,000 of incremental oil above the cost of the jobs.

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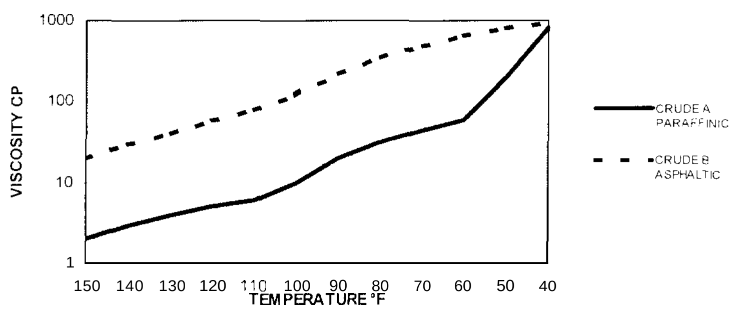

Figure 1 - Viscosity VS Temperature

Figure 2 - Asphaltenes from Tubing

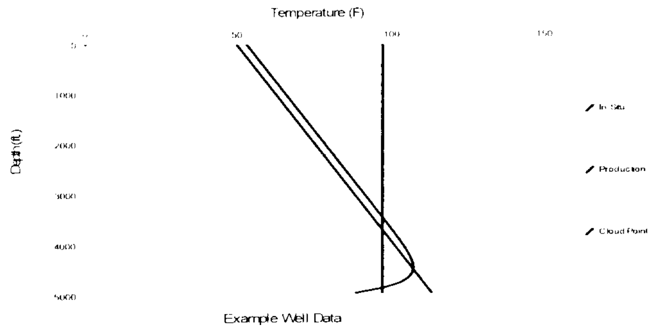

Figure 3 - Sandia Lab Joule-Thompson Cooling Program

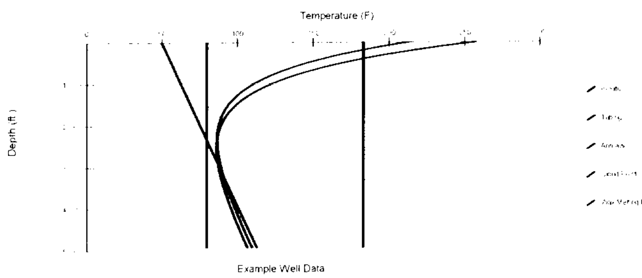

Figure 4 - Sandia Lab Heat Transfer Computer Program