FORMATION CLEANUP AND SQUEEZE TREATMENTS TO REMOVE AND INHIBIT PARAFFIN AND ASPHALTENE DAMAGE FROM OIL AND GAS WELLS

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ABSTRACT

Asphaltenes and/or paraffin, present in all crude oils and condensates, are responsible for damaging a majority of wells in the United States [1,2,3,4,6,10,11,12,13]. Increasing production from these wells can be accomplished by removing the organic damage but the increase may be of short duration unless new damage is prevented. Squeeze treatments using paraffin and asphaltene inhibition chemicals have successfully held oil and gas production increases at elevated levels for greater than six months following stimulation. The extended high levels of production are needed to pay for cost of the sometimes, large treatments required to clean and squeeze the wells[14]. This paper will describe the types of damage possible in flowing wells, pumping wells, CO_2 and NGL floods, water floods, and gas floods. Cleanup and Squeeze treatments will be described and case histories presented of successful treatments.

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[3]. 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[1].

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 ºF**	**Boiling Point ºF @ 1 atm**
Methane	CH_4	-296	-259
Ethane	C_2H_6	-297	-127
Propane	C_3H_8	-305	-44
Butane	C_4H_{10}	-217	31
Pentane	C_5H_{12}	-201	96.8
Hexane	C_6H_{14}	-137	156
Heptane	C_7H_{16}	-131	209
Octane	C_8H_{18}	-70	258
Nonane	C_9H_{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

The longest chain paraffin that has been reported 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[8]. 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 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[6].

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 are 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 are 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 of asphaltenes increases the API gravity tends to go down. Asphaltic crudes (< 20ºAPI) 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 400ºF 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 Problems in Oil and Gas Well Formations

Organic problems in formations do not just happen, they are caused4[,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 of the 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 100 psig downstream of the choke. This 1900 psig pressure drop causes a 95ºF temperature drop in the choke, or 1ºF per 20 psig. In this example the body of the choke is cooled 95ºF, and if the temperature drops below 32ºF, ice forms. The cooling associated with pressure drop takes places wherever a pressure drop occurs; permeability in formation 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 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 100 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 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 $>C_{20}H_{42}$ paraffin 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 70ºF 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 75ºF. If pumped at 50 bbl per minute it will still be 70ºF when it reaches the formation. The situation gets much worse if it is January in Texas and the fluid is only 20ºF in the truck. If the flow paths in a formation are cooled to 20ºF and the cloud point of the oil in the formation is 90º 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_2 or NGL's, can cause cooling at the production well when the gas starts to break out of solution. The 1ºF 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.

CAUSES OF FORMATION ASPHALTENE PROBLEMS

Pressure Drop

High-pressure tests conducted in the lab with formation 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 asphaltenes which leads to oil wetting and asphaltene 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 of asphaltenes. 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 formation 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 from 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 some 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 crude oils. This can cause asphaltene precipitation causing plugging and oil wetting of the major flow paths.

TREATMENTS TO REMOVE ORGANIC DAMAGE

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 limitations.

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 wellbore and tubulars 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 overflushed with oil, water or acid it usually ends up many feet back in the formation in the most open flowpath. It has had only 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 well bore 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 flow paths created can plug with organics from the increased production coming 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 well bore 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 of greater 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 programs may be started. Again, all of this is very expensive and may not be cost effective if the new fractures or wells plug quickly with organic damage.

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. 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 paraffin that plugs 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 well bore. 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.

SQUEEZE TREATMENT TO INHIBIT ORGANIC DAMAGE

Most crude oil production personnel are familiar with Scale Squeezes Treatments used to inhibit scale deposition for long periods of time to maintain production of fluids, unfortunately mostly water from reservoirs in West Texas. It is much less well known that similar Squeeze Treatments are available to inhibit both paraffin and asphaltene deposition in formations and the production system with one treatment.

Squeeze Treatments

Squeeze treatments for organic deposition are done very much like scale treatments for inhibiting scale except they look at the amount of oil produced from a well instead of water. The organic damage inhibitors do not attach to formation minerals so their return may be faster and for shorter duration than scale squeezes. The procedure for a organic inhibition squeeze starts with tests to select the best inhibitor for the paraffin and/or asphaltene deposition being experienced. The treatment is then sized based on the amount of oil and gas being produced by the well to be squeezed. A pill of crude oil and inhibitor is mixed and pumped into the well. This is followed with enough oil or oil/water to displace the pill 6-10 feet into the producing zone. The overflush oil will have a small amount of inhibitor added to it. The well is shut in for a few hours then returned to production. The organic damage inhibitors are oil soluble chemicals so must be applied with oil, usually in large quantities which increases the possible cost of the treatment as oil is much more valuable than the water used for scale treatments. It should be realized however that the organic damage inhibitors are meant to help maintain oil and gas production at much higher levels for extended periods of time following a stimulation treatments. The increased oil and gas levels can quickly pay for the use of oil to squeeze with. It should also be realized that the first squeeze treatment on any well is an experiment to determine how effective and long lasting squeeze treatments will be on that particular well/formation. For a squeeze treatment to be successful it must be produced back slowly and continuously to be effective. The amount of organic inhibitor required to effectively treat an organic problem may be as much 10X as much as for a scale inhibitor.

Squeeze Candidate Well Selection

The increased cost and the fact that organic squeezes may only last 3-6 months make well selection very important as not every well with organic damage problems is a candidate. Only the wells with the most severe organic problems that are occurring constantly or very frequently should be considered for squeeze treatment. It does not make economic sense to treat a $10,000 a year paraffin deposition problem with a twice a year $6,000 squeeze treatment program. Wells that are candidates are experiencing organic problems that occur more than once per month, continuous reduced production levels from formation deposition, viscosity or congealing oil related problems or rapid production decline following stimulation treatments. Examples of these types of problems would include: pump plugging requiring pulling jobs monthly; wells that produce X bopd after initial tests where they produced >2X as much; wells that have high pour condensate or crude oil and have high GOR or constant flowline restrictions and wells that have decline curves of >10% in oil production. Squeeze treatments are for the type of organic problems that cost the producer oil and gas production over long periods of time not to solve tubing deposition problems that are hot oiled once a month. The value of the increased production must be many times greater than the cost of the squeeze or the squeeze treatment is more trouble than it is worth.

CASE HISTORIES

Case History #1

A well producing 105 bopd of 33˚API black crude oil was fractured to increase production. The frac job increased oil production from 105 to 440 bopd. The well then experienced a 50% annualized decline rate as production dropped from 440 to 290 bopd in the next 6 months. Paraffin deposition in the formation was suspected as the oil had a cloud point of 108˚F and the formation temperature was 115˚F before the cold water frac and gas production increase following the frac. It was decided to do an organic stimulation treatment using aromatic solvent and crystal modifier to see if damage removal would increase production. The oil / solvent / crystal modifier treatment increased production from 290 to 350 bopd. The well then experienced a 7% decline curve over the next few months when it was decided to try a larger treatment and a squeeze inhibitor treatment. The well responded by going from 330 to 440 bopd average for two months before going on >30% decline rate. It was decided to stimulate and squeeze the well a second time when oil production had fallen to 400 bopd. The second treatments were more effective than the first as oil production went from 400 to 490 bopd average for two months before starting to decline rapidly. It was apparent at this point that production decline was directly related to paraffin deposition in the formation around the wellbore. A series of cleanup and squeeze treatments took place over the next 12 months that held oil production levels above 400 bopd average for 17 months by cleaning the well and inhibiting paraffin deposition. See graph 1 at end of paper.

Case History #2

An oilfield in the Texas Panhandle producing from the Marmonton Formation had never experienced any paraffin problems. The 40˚API gravity, orange oil had a 50˚F pour point but experienced no problems due to the high formation and wellhead temperatures. It was decided to start CO_2 injection to increase oil production from the field. The cooling caused by CO_2 breakthrough into the producing wells created a congealing oil problem which required 70 barrel hot oil jobs every three days to maintain production. A well producing 365 bopd experienced a 12-16 hour production loss following each hot oil treatment. The cost of hot oiling the well was $1,410 per month and $21,000 per month reduced production. A $7,400 squeeze treatment was done using 4 drums of crystal modifier pushed 3 feet outside of the wellbore was done. The well produced without hot oiling for 7 months at a hot oil savings of $9,870 and stabilized production worth $214,000.

Case History #3

A field in Canada was started on Natural Gas Liquids WAG injection as an IOR project, they had not experienced any asphaltene problems prior to this. Four years after start of WAG injection 80 of 144 wells had experienced NGL breakthrough. The 80 wells required: 34 aromatic solvents washes a month (>$100,00), 3 workovers for stuck rods a month($240,000), eight days lost production per month per well per problem and the field averaged 63,000 barrels lost production per month because of these asphaltene problems. One well in particular experienced pump plugging every three days and waited an average of 10 days for a workover rig to pull pump. The well was producing 24.5 m3/d (154 bopd) when it was producing. Organic removal solvent treatments would clean up the problem but required large volumes costing $26,000 a month to help pull pumps. The first squeeze treatment was tried using 275 gallons of asphaltene inhibitor placed 10 feet deep into the formation with oil treated with 1000 ppm of inhibitor. This first squeeze treatment lasted 19 days before the next pump plugged. This response was 6 times the normal production interval giving additional 2000 barrels of production for the month. A second squeeze sized for 16 foot radial penetration gave a 42 day problem free pump life or 6 months worth of the pre-squeeze production interval.

Case History#4

A field in Midland County, TX was producing from a number of deep formations and experiencing severe paraffin deposition/congealing oil problems through the system in 39 wells. Hot Water/chemical batch treatments were being done on 29 wells at a cost of >$240,000 a year and a cleanup/squeeze program was started on the other ten wells. The majority of the crude was from the Wolfcamp, Devonian and Atoka formations and a cold finger test was used to select the best crystal modifier for the oil. Each of the test wells was squeezed with two to three drums of product and overflushed to give 6 feet radial penetration. The 10 wells were squeezed every six months and paraffin related problems were almost eliminated on these wells at a cost of <$50,000 a year.

CONCLUSIONS

1. Paraffin and/or Asphaltenes can cause organic damage in formations.
2. Normal organic removal programs may be more expensive than squeeze inhibition treatments.
3. Organic formation damage can reduce oil and gas production, significantly and quickly.
4. Organic cleanup treatments can restore higher production rates by cleaning the near wellbore formation.
5. Laboratory testing is needed to pick the most effective organic inhibitor.
6. Squeeze treatments to inhibit organic damage can solve deposition problems over extended periods of time.
7. Most problems with organic deposition in the well, flowline and surface equipment can be treated with more cost effective batch treatments.
8. Organic deposition and congealing oil problems that occur continuously, frequently and reduce the production levels of oil and gas are most cost effectively solved by squeeze treatments.
9. Sizing treatments to the individual well and using sufficient overflush fluid to push treatment > 6 feet from the wellbore will increase the length of successful inhibition.
10. The first squeeze treatment on any well is an experiment to see how long the treatment will last.

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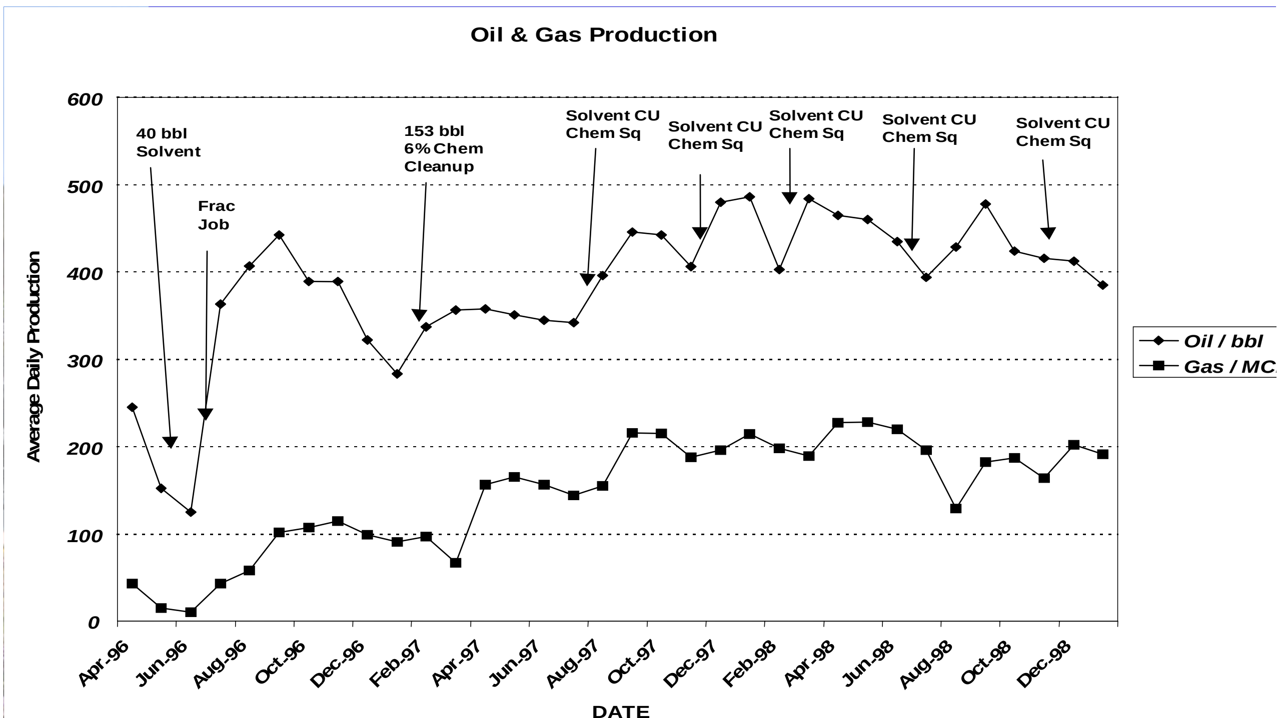

Case #1 Production Graph