FIELD ANALYSIS OF OIL FIELD DEPOSITS TO DETERMINE THE TYPE OF PROBLEM BEING EXPERIENCED

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ABSTRACT

In many cases fast identification of the type of problem occurring in oil, gas, injection or gas storage well is needed before remediation of the problem can start. The longer it takes to identify the problem the more expensive the problem becomes in lost production. 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]. Misidentification of the problem can lead to mistreatment which at best does nothing to help the well and could cause additional damage further complicating the well problems. What is needed is a set of simple tests that can be done in the field to tell the difference between organic and inorganic type problems. Is it a paraffin, asphaltene, emulsion, reverse emulsion, bacterial slime, scale, or solids problem? What type of treatment is needed? A set of simple tests will be presented that can determine the type of problem being experienced and what type treatment is needed.

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 liquids and water[3]. The problems are generally identified as either organic (paraffinic or asphaltic in nature) or inorganic (solids, fines, scales or baterial slime). Since the education received by most petroleum industry personnel does not include a study of the chemistry of crude oil and water, few are prepared to deal with or understand these problems that can plug the formation, pumping equipment, tubulars, flowlines, separators, dehydrators, heater treaters and tanks. In this paper a series of simple tests will be presented that can help anyone identify the type of solid problem that is plugging a well or equipment.

CHEMISTRY OF CRUDE OIL AND POSSIBLE PLUGGING DEPOSITS

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 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[7]. 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[5,6]. If an oil contains >10% by volume $C_{20}H_{42}$ to $C_{36}H_{74}$ paraffins it can have a high congealing or pour point. The oils with these high pour points > 75˚F can have formation, tubing, flowlines or surface equipment plugged by the oil itself.

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 of crude is, the larger the percent asphaltic components are. 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.

Asphaltenes can deposit as pure solid asphaltenes, oil wet inorganic solids that can plug the system, or in low gravity crudes they make the crude so heavy and viscous that it can appear to be a deposit at low temperatures.

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. The Resins when separated from the crude are reddish in color. In CO_2 Floods Resins have been seen to deposit as a semi-solid when carried with recycled CO_2 back into the injection system.

Chemistry of Oilfield Water and Possible Plugging Deposits

No two produced waters are the same. Water produced from oil, gas and coal seam methane wells can be fresh (<5,000 TDS) to brine (>250,000 TDS). Produced waters can vary across this range and can cause numerous scale problems in various locations based on temperatures, pressures and mixing of waters from various sources. In addition to the scales water can harbor bacteria, salt and become part of the emulsions in many systems.

OILFIELD SCALES

The following table lists a number of common oilfield scales and lists information about them. All of the scales can be plugging materials from the formation to the batteries in systems depending upon system conditions and mineralogy of the water produced or mixed.

Type	Name	Synonym	Formula	Color When Pure
Barium	Barium sulfate	Barite	$BaSO_4$	White
Calcium	Calcium carbonate Calcium sulfate	Aragonite, calcite Anhydrite, gypsum	$CaCO_3$ $CaSO_4$	Colorless to white Colorless to white
Iron	Iron carbonate Iron (II) oxide Iron (III) oxide Iron oxide Iron (II) sulfide Iron (III) sulfide	siderite wuestite hematite magnetite troilite --	$FeCO_3$ FeO Fe_2O_3 Fe_3O_4 FeS Fe_2S_3	Gray Black Red brown to black Black Black-Brown Yellow-Green
Lead	Lead sulfide	galena	PbS	Black
Strontium	Strontium sulfate	celestite	$SrSO_4$	Colorless to white
Sulfur	Colloidal sulfur	--	S_8	Yellow

BACTERIA

Bacteria live in water and can become plugging or interface problems. Bacteria that attach to pipe surfaces surround themselves with a slime like membrane to keep the colony from being washed off the pipe. In many systems this bacteria, that corrodes metal, produces iron sulfide, listed in the table above. The iron sulfide produced by bacteria is part of the colony but can be dispersed into the water if the bacteria is killed or displaced by a work over or other treatment to the well. The bacteria can collect in equipment and show up as interfaces or floating on oil.

EMULSIONS

It is not uncommon that with all the possible variations in both oil and water that sometimes the wrong ratios are present with sufficient mixing to cause emulsions. Some emulsions can be very stable and have very high viscosity. Some are so viscous that they appear to be solids that do not melt with heat.

Possible Plugging Deposits

Based on the chemistries of oil, water, mixtures of them and things that live in water we have a list of the following possible types of deposits: paraffin, asphaltenes, asphaltic resins, Asphaltene or oil wet solids/fines, congealing paraffinic oil, viscous low gravity oil, barium sulfate, calcium carbonate, calcium sulfate, iron carbonate, iron II oxide, iron III oxide, iron oxide, iron II sulfide, iron III sulfide, lead sulfide, strontium sulfate, colloidal sulfur, calcium chloride (salt), hydrates, sand, formation fines, bacteria bodies, bacterial slime containing iron sulfides, emulsions, and manmade introduced emulsions, chemicals and solids. Manmade materials can range from fish scales to packing material; red rags to rubber boots, plastic, drilling chemical, completion fluids, pipe dope, grease, lube oil and dead birds.

Identifying Plugging Deposits

Crude oil and gas production can be hampered by any of these various types of plugging materials depositing in production equipment. Often deposits are identified visually or by feel as paraffin, solids or scale and a hot oil treatment program[9] was started based on this casual identification. In many cases the compound chosen failed, not because it wasn't a good compound, but because it was being used on the wrong type of problem. This problem of identification is often complicated by the fact that a given deposit is not just one type of material but a combination of many different materials.

The following test information is meant to help anyone identify the type of deposit causing a plugging problem anywhere in a system:

1) In a short period of time.
2) On site, at the well or local lab.
3) Using simple equipment usually available locally.
4) Without sending samples to a distant lab with associated delay in treatment.

Getting a Sample

To identify a deposit a sample must be obtained from the system. The sample can usually be obtained when the problem is discovered or recognized for the first time or during a workover. Sufficient quantity of deposit is needed for testing, usually 4 ounces is sufficient. The container that the deposit is placed in should have a lid that can be removed repeatedly and the container should be able to hold a small amount of pressure, in case a volatile sample is carried into a heated room. All safety considerations should be observed with containers that hold oil as it is volatile and flammable. Do not heat up a closed container above room temperature. If upon trying to get a sample of deposit from the location the problem occurred one cannot be found, it is possible that a viscosity problem with a congealing oil or low gravity crude, ice or gas locked pump is being experienced.

<u>WATER TEST</u>

One of the easiest tests that can be done is to take a cup or glass (don’t drink of it later) and fill it with fresh water. It is best if it is a glass container so you can see through the sides to determine what happens when the deposit is dropped into the water. Use a pea size sample of hard deposit or teaspoon of soft deposit, drop it into the water. One of four things will be observed. The deposit sinks, sinks and dissolves, disperses into the water or floats.

Deposit sinks in water – A deposit that sinks is one of the solids listed above: oil wet solids/fines, barium sulfate, calcium carbonate, calcium sulfate, iron carbonate, iron II oxide, iron III oxide, iron oxide, iron II sulfide, iron III sulfide, lead sulfide, strontium sulfate, colloidal sulfur, calcium chloride (salt), sand, formation fines, solids.

Deposit sinks and dissolves – If the deposit sinks and then dissolves it is probably salt. Heating of the water will help this occur. If the salt has oil coating it may not dissolve. Addition of a soap or surfactant to the water will help (but may not) remove oil coating from any of the above scales.

Deposit disperses into the water- If the deposit disperses into the water, discoloration of all the water. The deposit was a bacterial slime (if black it probably contains one of iron sulfides), a reverse emulsion (water external) or a chemical residue.

Deposit floats – If the deposit floats on the water it is one of the following: Hard Deposit: paraffin, asphaltenes, Soft Deposits: asphaltic resins, congealing oil, viscous low gravity oil, emulsions, manmade introduced emulsions, chemicals, packing material; plastic, drilling chemical, completion fluids, pipe dope, grease, lube oil.

The results of the water test have basically separated the deposits into oil (organic) based deposits that float on water and solid (inorganic) deposits that sink in water.

MELTING TEST ROOM TEMPERATURE UP TO 300˚F

The Melting Test will help separate inorganic deposits from organic deposits and help determine if a deposit will melt (turn totally liquid when melted, such as ice and water, go through a phase change). The apparatus to melt a sample can be as simple as a hot plate, a coffee warmer, a hot water bath or the radiator cap of a car or truck. It is recommended that the surface being used to heat the deposit be covered with aluminum foil (to make cleanup easy). If a hot water bath is used you will need containers to hold the deposit and this may take longer as water heats slowly. Heating to quickly on a hot plate should be avoided as observations are needed as deposits heat up.

Soft Deposits such as emulsions, bacterial slime and bug bodies may give problems with this test as they will not melt but when heated above 212˚F may splatter as the water boils. Safety procedures should be observed so that eyes and hands are protected. These deposits will eventually dry out and leave either dried oil or power like residue on the hot surface.

Inorganic Deposits

The Melting Test shows that inorganic will not melt. Some oil may spread out on hot surface but physical shape of deposit will not change. No melting of deposit indicates you are dealing with oil wet solids/fines, barium sulfate, calcium carbonate, calcium sulfate, iron carbonate, iron II oxide, iron III oxide, iron oxide, iron II sulfide, iron III sulfide, lead sulfide, strontium sulfate, colloidal sulfur, calcium chloride (salt), sand, formation fines, solids.

Organic Deposits

A hard deposit that floats on water is most likely paraffin, congealing oil or asphaltenes. As a organic deposit is heated up from room temperature congealing oil will melt first, usually below 125˚F. Paraffin deposits will melt between 125˚F and 250˚F. Asphaltene deposits will soften and look like road tar or heavy oil but will not turn to a low viscosity liquid. If a pointed instrument is used to touch the softened asphaltene deposit a string of plastic type material will be pulled up from the surface of the hot plate. If asphaltenes are heated above 400˚F they will start to decompose into coke. Congealing oil is mostly a winter time problem when ambient temperatures are low or if the congealing point is very high. Congealing oil problems can sometimes be suspected if repeated frequent hot oiling is needed to keep the system operating. Hard paraffin deposits are the most common type of organic problem encountered in the oilfield. Hard asphaltene deposits are most often found in systems producing >38˚ API gravity oil or condensate. The lighter crude and condensate precipitates the asphaltene particles which deposit due to electrostatic charge on the equipment caused by the high fluid or gas velocity. Asphaltene deposits have plugged the injection side of gas lift systems due to the gas being wet with condensate which carried the asphaltenes with it.

SOLVENT TESTING

Follow all safety requirements as solvent are volatile, hazardous to breathe and flammable. Solvent testing should be done in a bottle (that holds pressure) in a hot water bath with temperature control in a hood or well ventilated room. Fill 100 ml bottles with 50 ml of solvent to be tested and drop pea size piece of deposit into solvent. Allow it to heat to at least 160˚ F, preferably 180˚F before determining if a deposit is soluble in the solvent tested.
Solvents that should be used are kerosene and xylene.

Inorganic Deposits

Barium sulfate, calcium carbonate, calcium sulfate, iron carbonate, iron II oxide, iron III oxide, iron oxide, iron II sulfide, iron III sulfide, lead sulfide, strontium sulfate, colloidal sulfur, calcium chloride (salt), sand, formation fines, solids are insoluble in kerosene, xylene, toluene, gasoline, diesel, n-pentane, n-heptane or condensate. If any of these solids is coated with oil the solvent will remove the oil but the solid deposit will remain on the bottom of the bottle.

Organic Deposits

Deposits including paraffin, asphaltenes, asphaltic resins, congealing paraffinic oil, viscous low gravity oil, grease and lube oil are soluble in xylene or toluene. If solids are present in the deposits the solids will be left on the bottom of the bottle.

Deposits including paraffin, asphaltic resins, congealing oil, low gravity oil some grease and lube oil are soluble in kerosene. Asphaltenes are not soluble in kerosene, diesel, condensate, n-pentene, n-heptane or gasoline. If solids are present they will be found on the bottom of the bottle after solvating the deposit.

If a determination of the percent solids present is needed a sample will need to be solvated in a centrifuge tube.

<u>HYDROCHLORIC ACID SOLUBILITY</u>

Deposits including paraffin, asphaltenes, asphaltic resins, congealing paraffinic oil, viscous low gravity oil, grease, lube oil and any solids coated with oil, condensate, solvent, corrosion inhibitor will not be soluble in HCl. A solvent treatment is needed to remove any of these organics off of scales before they can be removed by HCl.

Scale Deposits

Deposits should be cleaned of oil, grease or oil soluble chemical before placing in HCl. Observe safety requirements when working with acid including safety glasses/goggles and/or face shield and rubber gloves.

1) Carefully fill bottle half full of hydrochloric acid;

    a)if acid bubbles or effervesces <u>without</u> sour odor and
        i)remains colorless - probably calcium carbonate
        ii)turns yellow - probably iron carbonate or iron oxide (rust). In pure form iron carbonate is gray in color and iron oxide is red-brown to black.
    b) if acid bubbles or effervesces <u>with</u> sour odor and
        i)remains colorless - probably lead sulfide
        ii)turns yellow - probably iron sulfide
    c) no reaction - go to step 3

2) Repeat steps 1; fill tube half full scale converter.

    a) If the sample swells and becomes fluffy, probably calcium sulfate (fluffy material should dissolve in 15% HCl).
    b) No reaction - go to step 3

3) Repeat steps 1 and 2; fill the tube with fresh water and heat.

    a) If deposit dissolves, it is probably salt.
    b) If sample is brown and disperses in water, it is probably mud, clay or dirt.
    c) If neither of above, sample is probably:
        i)Sand - tell by granular consistency glass like appearance.
        ii)Barium sulfate - white - send to lab for positive identification.
        iii)Strontium sulfate - color less to white - send to lab.
        iv)Colloidal sulfur - yellow - will dissolve in carbon tetrachloride.
        v)Coke - black powder like - asphaltene residue caused by heating at fire tube surfaces.

Type	Name	Synonym	Formula	Color When Pure
Barium	Barium sulfate	Barite	$BaSO_4$	White
Calcium	Calcium carbonate Calcium sulfate	Aragonite, calcite Anhydrite, gypsum	$CaCO_3$ $CaSO_4$	Colorless to white Colorless to white
Iron	Iron carbonate Iron (II) oxide Iron (III) oxide Iron oxide Iron (II) sulfide Iron (III) sulfide	siderite wuestite hematite magnetite troilite --	$FeCO_3$ FeO Fe_2O_3 Fe_3O_4 FeS Fe_2S_3	Gray Black Red brown to black Black Black-Brown Yellow-Green
Lead	Lead sulfide	galena	PbS	Black
Strontium	Strontium sulfate	celestite	$SrSO_4$	Colorless to white
Sulfur	Colloidal sulfur	--	S_8	Yellow

BACTERIAL SLIME

Bacterial slime sometimes appears at interfaces in treaters or floating on top of oil tanks and is often misidentified as paraffin, but it can be identified if it:

1) **Disperses in Water**

   Bacterial slime will be water external so that when it is placed in fresh water it will break up into small particles.

2) **Will Not Dissolve in Xylene**

   Bacterial slime will not dissolve in xylene, it will stick to the sides of the bottle.

3) **Slimy - Jelly Like Appearance**

   Unless dried out, normally will be slimy.

4) **Sewage (decay) Type Odor**

   Distinctive once recognized.

Bacterial slime can be removed with batch water treatments with surfactants added, but the system should be looked at to discover source of bacteria and the use of bactericides be started.

Remember that plugging deposits are almost always composed of a mixture of these materials. The more closely you identify the type of plugging material that is present, the more successful your treatment will be. By finding out that a paraffin deposit contains iron sulfide, you know that it may be necessary to treat with both a paraffin compound and HCL to dissolve iron sulfide. This type of treatment can make the difference between partial success and complete success.

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