APPLICATION OF OIL FIELD CHEMISTRY TO ENHANCE OIL & GAS PRODUCTION

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Abstract

Many present and future production problems can be identified and predicted with less cost and downtime utilizing oil field chemistry applications. The chemical characteristics of drilling, completion and work-over fluids have immediate and long lasting effects that can enhance or impede production. The temperature and pressure changes that occur during production effect the chemical equilibrium of the formation fluids. The application of oil field chemistry can predict immediate and long-term chemical changes that affect production. The same chemical tests used for problem identification can be applied to maximize production during stimulation and production operations.

This paper presents a review and discussion of readily available oil field chemical testing. A systematic and practical approach to interpretation and application of the results is presented. The oil field chemistry discussed in this paper includes the evaluation of chemical, microbial, and physical components in water, oil, gas, scale, and corrosion products. A water flood case history demonstrates test and results application.

Introduction

Water analysis' can be used to determine if load water has been recovered after acid work, fracturing, remedial treatments and work-over operations. Obtaining a water analysis is the starting point in well problem analysis for determining possible well problems. Some immediate and long-term well problems determined 60m a water analysis include scale, salt block, sludge, emulsions, corrosion, casing leak, cement failure, flood water break-through, formation identification, water compatibility and chemical compatibility.

Bacteria evaluations can be used to determine the sources of hydrogen sulfide, microbial contamination, suspended solids, and to determine best corrosion control methods. Aerobic and anaerobic bacteria populations can result in corrosion and/or plugging. Planktonic bacteria float in the water to live. Sessile bacteria are attached to the surfaces in the well bore. Bacteria populations will increase the suspended solids in a water system. Sessile bacteria will set-up concentration cells on metal surfaces and under deposits that initiate and accelerate corrosion processes. Corrosion induced or influenced by bacteria is termed **MIC** (microbiologically influenced/or induced corrosion).

Oil Analysis can be used to determine if load from hydrocarbon based treating fluids has been recovered after treatments. Information 60m the oil analysis is important to stimulation treatment design, setting optimum treating temperatures, emulsion prevention, sludge prevention, selection of chemicals and solvents for treating paraffin and asphaltene problems. Obtaining an oil analysis is important in well problem analysis to determine well problems. Well problems include sludge, emulsion, paraffin, asphaltene, oil and chemical compatibility.

Gas analyses are run for quality control, contract specification, heating value, composition, specific gravity, compressibility factors, corrosion detection and corrosion control monitoring.

Scale analysis can be used to identify the type of scale present and determine the best scale removal and prevention methods. Scale analysis showing scale components that are not consistent with water analysis often indicate incompatible fluids have been injected into the well or that other problems exist.

Corrosion product analysis can be used to determine major corrosion forces.

Table 1 gives actual analysis results. Samples are from a single water flood operation. Samples from the water flood were chosen since this example covers most of the applications covered in this presentation. The table headings are identified as follows. "WSW represents the water source well. "Produced" represents the produced water from the flood operation. "Injection" represents the mix of water source and produced water being injected. "Formation" represents virgin formation water and oil from the producing zone in the water flood operation. Severe corrosion and equipment failures in injection wells were occurring one year after starting water flood operation even though corrosion inhibitors were being applied. Immediate concern was to identify corrosion forces and establish corrosion control. Test results, descriptions, and interpretations are as follows:

Water Analysis

Physical components of a water analysis are specific gravity, pH and resistivity. Specific gravity and resistivity are a measure of the dissolved salt content in water and can be used as a quick check of analysis accuracy, formation identification and salt saturation. The pH is a measure of the acid or base character. The pH should be tested at time of sampling since it will change as pressure is reduced and dissolved gases escape. The pH is used in scale tendency calculations. Increasing the pH contributes to the formation of iron sulfide, iron and calcium carbonate scales. Decreasing pH increases corrosion.

Water physical properties in Table 1 show injection water to be mostly water source water with some Produced water. The Produced water appears to be mostly-Formation water. This is evident by the comparing the specific gravity and resistivity of the different waters. It is evident Produced and WSW waters are not similar. This indicates waters may not be compatible when mixed. The pH of the WSW water, Injection water and produced water is higher than the pH of the Formation water. These higher pH values will increase calcium carbonate scale tendencies when mixed with formation water in well operations.

Dissolved iron contents can be used to monitor corrosion and corrosion treatment programs. Iron contents may be due to natural iron in the formation water. Iron contents greater than 50 mg/l are usually from corrosion. Increasing dissolved iron in the formation water contributes to the formation of iron carbonate, iron sulfide and iron oxide scales. The iron compounds formed from the reactions with hydrogen sulfide, carbon dioxide and oxygen can be entrained with other types of scales to give unexpected reddish brown to black colors. These compounds can be present as suspended solids and contribute to paraffin, sludge, emulsion and formation plugging problems.

Dissolved iron results in Table 1 show dissolved iron contents are less in Injection water than in WSW, Produced and Formation water analyses. This indicates iron compounds are being formed in system either as suspended solids or scale.

Calcium content can be used to determine the presence of spent acid after acid jobs, compatibility testing when mixing waters, and formation identification. Formation waters with similar chloride contents may differ significantly in calcium contents. Increasing calcium contents contribute to calcium carbonate and calcium sulfate scale formation. Waters containing high calcium contents may not be compatible with waters containing high sulfate contents. Scale inhibitor may be required to prevent calcium sulfate scale when performing acid treatments on formations where waters show high sulfate contents.

Table 1 shows calcium contents are much higher in Produced and Formation water than in WSW or Injection water. The high calcium content in the formation and produced waters indicate they may not be compatible with the WSW and Injection water.

Magnesium content can be used for formation identification. Formation waters with similar chloride and calcium contents may differ significantly in magnesium contents. The ratio of calcium content to magnesium content is usually formation related. A significant change in this ratio indicates presence of foreign water. Increasing magnesium contents decrease calcium sulfate scale formation.

Magnesium contents reported in Table 1 shows magnesium contents to be much lower in WSW and Injection waters than in Produced and Formation waters. Although magnesium contents vary between these waters, the calcium to magnesium ratio in each of the waters is similar.

Barium and strontium are not always present in oilfield brines. These components are most likely found in waters not containing sulfates. Waters containing barium and strontium are not compatible with waters containing sulfate. When barium and strontium are determined to be present, all injection waters used in well work-over and treatment operations should be screened for compatibility.

Analyses results in Table 1 show barium and strontium are not present in these waters.

Sodium is usually the major component of the combined sodium and potassium contents reported. Sodium and potassium contents are formation related and can be used for formation identification. Treatment waters made from actual potassium chloride, KCI, not KCI substitutes, can be identified by testing for potassium content. In formation waters, potassium content is only a minor portion of the sodium and potassium contents reported.

Sodium & potassium contents reported in Table 1 shows sodium & potassium contents to be much higher in WSW and Injection waters than in Produced and Formation waters. Although sodium and potassium contents vary **between** these waters, the sodium and potassium to potassium content ratio in each of the waters is different.

Sulfate ($SO_4^=$) is not always present in oilfield brines. Sulfate content **can** be used for formation identification. Increasing sulfate contents contributes to formation of insoluble sulfate scales. Decreasing sulfate contents with increasing hydrogen sulfide indicates sulfide source may be from sulfate reducing bacteria. Sulfate is a nutrient for sulfate reducing bacteria.

Table 1 shows sulfate contents are much higher in WSW and Injection water than in Produced or Formation water. The high sulfate content in the WSW and Injection waters indicates they may not be compatible with the Formation or Produced waters. These waters should not be used for formation acid treatments or acid flushes unless adequate scale control is present. The increase in calcium content **from** acid jobs will cause calcium sulfate scale to form if WSW or Injection water is used. Load from acid treatments should not be produced back into the flood water system.

Bicarbonate is used in calcium carbonate scale tendency calculations. Increasing bicarbonate contents contribute to calcium and iron carbonate scale formation.

Analysis results reported in Table 1 shows bicarbonate contents are much higher in WSW and Injection water than in Produced or Formation water. The high bicarbonate contents in the WSW water and Injection water will increase calcium carbonate scale tendencies when mixed with Produced *or* Formation water. This indicates the WSW and Injection waters may not be compatible with the Formation or Produced waters.

Chloride content is formation related and can be used for formation identification. The major source of chloride is sodium chloride. Sodium and chloride are nearly always the major components of a water analysis. The chloride content influences the solubility of scales and is used in scale tendency calculations. Increasing chlorides will make corrosion more likely.

Table 1 shows chloride contents are much higher in Produced and Formation water than in WSW or Injection water. This indicates waters may not be compatible.

Total dissolved solids are the total amount of salts dissolved in a given quantity of water and are related to specific gravity and resistivity. Total dissolved solids can be calculated from water analysis results or measured by evaporating a given volume of filtered water to dryness and weighing the residue.

Analysis results in Table 1 shows total dissolved solids much higher in Produced and Formation water than in WSW or Injection water. The high total dissolved solids in the Formation and Produced waters indicate they may not be compatible with the WSW and Injection waters.

Total suspended solids are the total amount of solids that is removed by filtration with a membrane filter and can be used to estimate the plugging tendency of the water. Suspended solids will accelerate corrosion by making the water more abrasive. Sources of suspended solids are formation fines, corrosion products, scale debris, incompatible chemicals, bacteria, foreign water, microbial debris, drilling mud, clay, etc.

Total suspended solids reported in Table 1 are much higher in the injection water than in the other waters. The high total suspended solids in the injection water indicate formation and produced waters may not be compatible with the WSW and Injection waters. The increase in total suspended solids also indicates iron compounds or the presence of bacteria.

Iodine can be used to verify formation identification when found. Iodine is not in all formation waters. It is more informative when iodine is found to be present than when not found.

Analysis results in Table 1 show iodine is not present in these waters.

Hydrogen sulfide will lower the pH and make water more corrosive. The two sources of hydrogen sulfide are non-biological and biological. Non-biological sources are naturally occurring (already present in the producing formation) and chemically induced (chemical reactions). Naturally occurring hydrogen sulfide is usually detected in drilling and completion operations. Biological sources are primarily sulfate reducing bacteria (SRB). Biological hydrogen sulfide is usually not detected in early well production, but occur later in the production life of wells. When hydrogen sulfide is detected, it is important to determine whether its source is non-biological or biological.

Analyses in Table 1 show hydrogen sulfide was not detected in these waters.

Carbon dioxide will lower water pH to make water more corrosive and affect iron and calcium carbonate scale tendencies. As pressure is reduced and carbon dioxide escapes, calcium carbonate scale is more likely to form.

Table 1 shows carbon dioxide is substantially higher in the WSW and Injection waters. The higher carbon dioxide contents in the WSW and Injection water will make these waters more corrosive.

Oxygen is not normally present in formation waters. Major oxygen concern is with injection water for water flood operations. Oxygen sources are surface leaks, open casing valves and treating fluids. Its presence will make the water more corrosive. Hydrogen sulfide and carbon dioxide corrosion will be accelerated substantially when oxygen is present. Oxygen will react with dissolved iron and iron compounds to cause serious plugging problems. Oxygen is a required nutrient for aerobic bacteria.

Oxygen analysis results in Table 1 shows oxygen was detected in the injection water. Oxygen will make the water more corrosive.

Scale Tendencies

In the scale tendencies in table 1, positive calcium carbonate ($CaCO_3$) scale tendencies indicate calcium carbonate is likely. Positive calcium sulfate ($CaSO_4$) differences (Actual – Saturated) indicate calcium sulfate scale is likely.

The scale tendencies reported in Table 1 indicate calcium carbonate scale is more likely than calcium sulfate scale in the individual waters.

Bacteria Populations

Typical bacteria tested for are aerobic, anaerobic acid producing and sulfate reducing bacteria. All equipment, fluids and solids used in drilling, completion and remedial treatments are possible sources of bacteria contamination. Fluids used in well operations should be treated with an effective biocide to prevent the spread of bacteria.

Bacteria test results reported in Table 1 indicate Produced water is the main source of bacteria. The high chlorides of the Produced water will inhibit bacteria growth. Rapid growth of bacteria will result from the mixing of WSW and Produced waters.

Oil Analysis

Typical components of an oil analysis are API gravity, API shakeout, cloud point, pour point, paraffin content and asphaltene content. API gravity is directly related to specific gravity and can be used as a quick check of crude oil quality and formation identification.

API shakeout is used to determine water and sediment content in oil. The API shakeout is mainly used as a quality check before purchasing oil. It can also be used to detect emulsions and presence of suspended solids being produced with oil. Emulsions can be foams, water droplets in oil, oil droplets in water, or combination of the above with solids. Solids may be corrosion products, scale, formation fines, drilling mud, bacteria debris, and iron fines from production equipment.

Cloud point' is the temperature where the heavy hydrocarbon portion of the oil begins to crystallize. It can be used to determine optimum fluid temperatures for stimulation processes. Cloud point depressions can also be used to screen paraffin chemicals and solvents used in treating.

Pour point[3] is the lowest temperature allowing the crude oil to flow (melting point). Pour points can be used as cloud points to determine best storage and treating temperatures. Pour point depressions can be used to screen paraffin chemicals and solvents for treating.

Paraffin waxes[4] are the non-volatile long chain aliphatic liquids in oil that have low to high melting points. Paraffin wax content is a chemical measurement of the heavy aliphatic portion of the oil that contributes to paraffin deposits. Paraffin contents in conjunction with cloud points can be used to predict severity of paraffin problems and determine the types of treating fluids to use in stimulation processes[5].

Asphaltene[6] content is a chemical measurement of the microscopic dispersed heavy organic solids portion of oil that contributes to paraffin and asphaltene deposition. Chemically, asphaltenes are very complex colloidally suspended macromolecules. Asphaltenes can precipitate to compound paraffin problems, reduce formation permeability, alter formation wettability characteristics, affect well injectivity, and cause plugging of producing wells. Asphaltene contents can be used to predict if sludge problems are likely when the well is treated. High asphaltene contents tend to stabilize emulsions and accelerate paraffin deposition.

Oil analysis results in Table 1 show the oil will congeal when wells are treated with cold fluids. All treating fluids should be heated to a minimum of 85 degrees F. before injecting into producing wells. Optimum treating temperature is 120 degrees F. to prevent additional crystallization of the heavy paraffin.

The paraffin and asphaltene content show hydrocarbon stimulation fluids should contain aromatic solvents and asphaltene control chemicals. The asphaltene content is above 1.5%. Addition of aromatic solvents to hot oil and paraffin treatments is recommended. Sludge tendency tests should tie run before treating with hydrochloric acid. If an oil shows sludge tendencies, anti-sludge agents should be tested and recommended in acid jobs.

Gas Analyses

Gas analyses of concern are hydrogen sulfide, carbon dioxide and oxygen content since it is these gases that contribute most to corrosion and well problems. It is important to determine if the sources of these gases are natural or from other sources (microbes, chemical, or leaks). Many chemicals (corrosion inhibitors, scale inhibitors and biocides) used to treat wells are not effective when these gases are present.

Gas analysis results in Table 1 reveal hydrogen sulfide and high carbon dioxide contents in the casing gas from WSW and gas blanket at injection water tanks. The major source of the carbon dioxide and hydrogen sulfide is the WSW water well. Oxygen is not detected until the water levels dropped in the Injection water storage tanks and shows inadequate gas blanket being maintained and opening or leaks at tank for oxygen to penetrate. The combinations of these corrosive gases will result in severe corrosion.

Scale Analyses

The most common oilfield scales are calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, iron sulfide, and iron carbonate. Iron carbonate and sulfide are actually corrosion products, but can also be considered as scales.

Calcium carbonate is usually a hard scale and is acid soluble. Hydrochloric acid is the most common acid used for calcium carbonate removal. Hydrochloric acid strengths usually are from 7½% to 28% in strength. Calcium carbonate scale can be prevented with scale inhibitors.

Scale analysis in Table 1 shows calcium carbonate not detected and is not a problem in system at the time of sampling,

Calcium Sulfate is usually a soft scale and is only slightly acid soluble. Calcium sulfate can be removed by treating with Gyp Converter and allowing 24 hours contact and then following with HCl. Some converters only require a hot-water flush after the contact period. Calcium sulfate scale can be prevented with scale inhibitor.

The scale analysis in Table 1 shows calcium sulfate was not detected and is not a problem in the system at the time of sampling.

Barium and strontium sulfate are hard scales and not acid soluble. The tendency for barium and strontium sulfate scales to form increases as temperature decreases, pressure decreases and total dissolved solids decrease. Barium and strontium sulfate scales, in most cases, can not be removed chemically. The best method of removal is with a hammer and chisel. Barium and strontium sulfate scale can be prevented with scale inhibitor.

Barium and strontium sulfate was not detected.

Iron sulfide is usually a hard scale and is acid soluble. The tendency for iron sulfide scale to form increases as dissolved iron content increases, hydrogen sulfide content increases, pH increases and pressure decreases.

Table 1 shows the major scale to be iron sulfide in the water system and indicates hydrogen sulfide is contributing to corrosion.

Iron carbonate is usually a hard scale and is acid soluble. The tendency for iron carbonate scale to form will increase as the source of iron increases, pH increases and pressure decreases. Iron sulfide and iron carbonate scales can be removed with hydrochloric acid. Higher acid strengths and contact times are required than for calcium carbonate.

Iron carbonate was not detected.

Corrosion Product Analyses

Iron sulfide is the corrosion product of hydrogen sulfide. Iron carbonate is the corrosion product of carbon dioxide. Iron oxides are the corrosion products of oxygen.

Corrosion product analysis results reported in Table I shows oxygen, hydrogen sulfide and bacteria to be primary corrosion forces. Other analysis results indicate carbon dioxide is also contributing to corrosion problems even though iron carbonate was not detected.

Summary

Examination of the chemical properties shows agreement with the physical determinations. Iron content is less in Injection water than in WSW, Produced and Formation water analyses. This indicates iron compounds are being formed in system. The outstanding characteristics of WSW and Injection water are the high sulfate and high bicarbonate contents. Outstanding characteristic of Produced and Formation water is the high calcium content. High calcium content in Formation water and Produced water makes them very close to being incompatible with the WSW and Injection Waters. WSW and Injection waters should not be used for formation acid treatments or acid flushes unless adequate scale control is present. The increase in calcium content from acid jobs will cause calcium sulfate scale to form if WSW or Injection water is used. Load from acid treatments should not be produced back into flood water system. The high bicarbonate contents in the WSW water and Injection water will increase calcium carbonate scale tendencies when mixed with Produced or Formation water.

From the analysis results, the major corrosion factor contributing to system failures was determined to be oxygen. Oxygen was accelerating corrosive forces leading to rapid failure. At the time of tests, changing make-up water source was not feasible. Eliminating sources of oxygen were made. System has been operating for two years since investigation with minimal corrosion failures.

Primary production problems were tubing and flow line plugging due to paraffin accumulations. Large condensate treatments were being used to control paraffin problems and maintain production. It was determined the high gravity condensate being used was contributing to the paraffin problems, even though short-term production increases were observed. Treatments were changed from large condensate dumps to smaller volumes of diesel or hot oiling with diesel and crude oil. The smaller treatments have stabilized production.

Calcium sulfate scale was observed after acid jobs in several wells even though formation water contained low concentrations of sulfate. It was determined using water source well water for acid flush was contributing. Incorporating scale inhibitor into acid jobs or using different water for acid flushes were used to prevent secondary calcium sulfate scale formation.

References

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3. American Standard Test Method D **97:** "Standard Test Method for Pour Point of Petroleum Oils," **1987**
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5. King, S.R and Cotney, C.R.: "Development and Application of Unique Natural Solvents for Treating Paraffin and Asphaltene Related Problems," paper SPE **35265** presented at the **1996** Mid-Continent Gas Symposium, Amarillo, TX, Apr **26-30.**
6. American Standard Test Method D **4055:** " Standard Test Method for Pentane Insolubles by Membrane Filtration," **1987**

Table 1

Analysis Results	WSW	Produced	Injection	Formation
Physical Properties:				
Specific Gravity @ 75 F.	1.034	1.110	1.046	1.110
Resistivity (ohm-meters) @ 75 F	0.141	0.052	0.107	0.052
pH	5.87	6.05	5.89	5.16
Chemical Properties:				
Iron (mg/l Fe^{++} & Fe^{+++})	20	25	12	70
Calcium (mg/l Ca^{++})	2,400	I 1,600	3,840	11,600
Barium (mg/l Ba^{++})	BDL	BDL	BDL	BDL
Strontium (mg/l Sr^{++})	BDL	BDL	BDL	BDL
Magnesium (mg/l Mg^{++})	389	1,895	583	1,993
Sodium & Potassium (mg/l Na^{+})	15,142	48,037	19,388	49,513
Potassium (mg/l K^{+})	430	180	400	180
Bicarbonate (mg/l $HCO3^{-}$)	976	111	832	122
Sulfate (mg/l $SO4^{=}$)	1,700	300	1,475	300
Chlorides (mg/l Cl^{-})	26,904	99,828	36,816	102,660
Total Dissolved Solids (mg/l calc)	47,531	161,796	62,946	166,218
Total Suspended Solids (mg/l)	4.4	5.2	65	15
Hydrogen Sulfide (ppm H_2S)	BDL	BDL	BDL	BDL
Carbon Dioxide (ppm CO_2)	320	80	300	120
Oxygen (ppm O_2)	BDL	BDL	2	BDL
$CaCO_3$ Scale Tendencies:				
77 Degrees F.	-0.540	-0.200	-0.425	-1.009
104 Degrees F.	-0.109	+0.251	+0.006	-0.558
140 Degrees F.	+0.641	+1.001	+0.756	+0.192
$CaSO_4$ Scale Tendencies:				
Actual @ 104 Degrees F.	35.42	6.25	30.73	6.25
Saturated @104 Degrees F.	49.94	20.98	41.76	20.59
Difference (Actual – Saturated)	-14.52	-14.73	-11.00	-14.34
Bacteria Populations:				
SRB Bacteria Population	0	10^1	10^3	10^1
APB Bacteria Population	0	10^2	10^4	10^2
Aerobic Bacteria Population	0	10^2	10^2	10^2
Oil Analysis:				
API Gravity @ 60 F.	N/A	N/A	NIA	36.6
API Shakeout	N/A	N/A	N/A	0% BSW
Pour Point	N/A	N/A	NIA	74 F.
Cloud Point	N/A	N/A	N/A	110 F.

Table 1 (Continued)

Analysis Results	WSW	Produced	Injection	Formation
Paraffin Content (% by Weight)	N/A	N/A	N/A	16.4
Asphaltene Content (% by Wt.)	N/A	N/A	N/A	1.7
Gas Analyses:	Casing	Vapor	Gas	Blanket
Carbon Dioxide (mole %)	84.140	2.000	74.661	N/A
Hydrogen Sulfide (ppm)	150	50	400	N/A
Oxygen (ppm)	BDL	BDL	1000	N/A
Scale Analyses:				
Calcium Carbonate	BDL	BDL	BDL	BDL
Calcium Sulfate	BDL	BDL	BDL	BDL
Iron Sulfide	Major	Major	Major	Major
Iron Carbonate	BDL	BDL	BDL	BDL
Corrosion Product Analyses:				
Iron Sulfide	Major	Major	Minor	Major
Iron Carbonate	BDL	BDL	BDL	BDL
Magnetic Iron Oxide	BDL	BDL	Major	BDL
Iron Oxide (Rust)	BDL	BDL	BDL	BDL

BDL = Below Detection Level