WATER TECHNOLOGY: UNDERSTANDING, INTERPRETING AND UTILIZING WATER ANALYSIS DATA

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ABSTRACT

The significance and importance of water to the Oil and Gas Industry cannot be overstated. While water is often an unwanted by-product of production, water is utilized in many production scenarios and is often times the primary driver for the production of oil. Water, by its inherent nature, will dissolve and carry many impurities within it. These impurities will remain in equilibrium with each other until acted upon by some outside force. These impurities can result in accelerated corrosion, mineral scale depositions, stress corrosion cracking of metals, plugging problems and erosion/corrosion of metallic equipment. It is vital to gain an understanding of the dissolved and suspended constituents of produced, or injected, water and to identify relevant changes in these compositions. This paper will discuss the importance of an accurate water analysis and will discuss the practical uses of this information.

Key words: total dissolved solids, dissolved gases, total suspended solids, mineral scales, corrosion, sampling, reporting

INTRODUCTION

Water is often referred to as the universal solvent. Water will dissolve and carry many impurities within it. These impurities can be trouble-some in many industries, including the oil and gas industry. While water, to the oil and gas industry, is viewed as a by-product of production, it can yield vital information on the reservoir characteristics, corrosiveness within a well, the tendency for the deposition of mineral scales, and influences many other factors pertaining to oil and gas production. Without water, many of the production challenges experienced within the oil and gas industry would be substantially minimized.

A water analysis is one of the basic analytical tests performed within the oil and gas industry; however, its accuracy and interpretation are often left to chance. This paper will discuss the challenges associated with water production and the importance of an accurately sampled and interpreted water analysis.

THE IMPORTANCE OF WATER

Water is one of the most abundant and important substances on earth. Water can exist as a solid, liquid or a gas over a very narrow range of temperatures. It has the ability to act as an acid or a base in chemical reactions and is utilized for many different uses, ranging from drinking water to industrial uses. Its role in supporting life cannot be understated. It is critical to life. Understanding its impurities is also critical to life. A water analysis is a tool that can be used to determine these impurities, and it can range from simple, to very complex, depending on the application and criticality of the results.

Within the oil and gas industry, water is produced as a by-product of the production of oil and gas. The presence of water can result in many production challenges, including the formation of mineral scales, increased corrosion of metallic equipment, gas well loading, emulsions, and bacterial activity. An accurate water analysis can indicate the tendency for many of these production problems.

In addition to the challenges water can cause, it can also be beneficial. It can be utilized for reaction cooling, steam generation, and secondary and tertiary recovery installations (waterflood and polymer injections). The quality of the water utilized for projects varies based on the tolerances of each project requirement. Again, the water analysis is a critical tool in the success of these projects. The project engineer, or quality control engineer, must have confidence in the data generated within the water analysis report. In the case of a water analysis, bad data can be worse than no data at all!

THE WATER ANALYSIS

Because water will dissolve most inorganic substances to some degree, it is rarely found in nature in its pure form. While rain water is probably the purest water form, it is still subject to atmospheric contaminations from gases, dust and other pollutants. Surface waters, such as stream and lake waters, contain silts, minerals, organic matter, and other pollutants of human and animal origin. The materials (specifically, ions) dissolved within water are known as the total dissolved solids, or TDS. Any material suspended within the water, such as silts or sands are known as total suspended solids, or TSS. The analyses of these dissolved ions and suspended materials will indicate the substances to which the water has been exposed, whether the water source is rain water, stream/lake water, or ground water. Each source can have impurities characteristic to its origin.

In the case of water produced as a by-product of oil and gas production, the water can indicate many aspects of the downhole production zone. The water analysis can indicate the potential for corrosivity, for mineral scale deposition, can identify the production zone, can assist in the identification of casing leaks and is critical when selecting production chemicals or corrosion resistant alloys. While the water analysis is probably the most common test performed within the oil and gas industry, it is often times the most misunderstood and misapplied piece of information gathered. Unless sampled and performed correctly, the water analysis can result in the absence of vital information, or the presentation of incorrect information that can prove costly to the production or quality control engineer.

The constituents normally analyzed within oil-field water are shown in Table 1. Understanding these components is vital to understanding what an analysis is communicating to the reader. The significance of these constituents is detailed below.

Cations – Positively charged ions

Sodium (Na)

Most sodium salts are soluble in water; therefore, sodium is a major constituent of oil-field and drinking waters. Generally, sodium does not result in any specific problems. The exception would be the precipitation of sodium chloride (NaCl) from extremely salty brines.

Calcium (Ca)

The calcium ion is a major constituent of oilfield brines and can range in concentration up to 30,000 mg/L, although it is generally much lower. This ion is of major importance due to its ability to combine with bicarbonate, carbonate or sulfate ions and precipitate mineral scales, adherent and/or suspended.

Magnesium (Mg)

The magnesium ion concentration is generally much lower than the calcium ion concentration. The primary importance of the magnesium ion is also its ability to form scales with the carbonate ions; however, these magnesium scales are 50 times more soluble in water than the $CaCO_3$. Most other magnesium salts, such as $MgSO_4$ are quite soluble in water and cause few problems in the oil-field environment.
*It should be noted that for the application of boiler feed water quality, both the calcium and the magnesium are monitored and controlled for the prevention of scales/deposits under boiler temperatures and services.

Iron (Fe)

Natural iron content in most oil-field waters varies. Many times, its presence signifies active corrosion. Iron counts are often utilized in “sweet” systems (systems not containing hydrogen sulfide) to monitor and semi-quantify corrosion rates. In “sour” systems, the iron will be present as a form of iron sulfide and is often responsible for plugging issues downhole or within surface equipment. Iron sulfide is almost always an indicator of corrosion, bacterial activity, or incompatible mixtures of water.

Manganese (Mn)

As a general rule, manganese is not naturally occurring in formation waters (exception, Barnett Shale formation). Manganese is an alloying material utilized in the steel milling process; therefore, its presence can be an indicator of active corrosion of metallic components. When analyzed, trends can be developed to enable the engineer to evaluate active corrosion, or evaluate the effectiveness of a corrosion inhibitor program. The manganese levels are generally analyzed in conjunction with total iron counts and are usually 1/100th of the iron level when originating from the metallic materials. A target level of manganese, based on “rules of thumb”, is at, or below 0.2 mg/L.

Barium (Ba)

Barium is important because of its ability to combine with the sulfate ion and precipitate barium sulfate. This compound is extremely insoluble in water and most acids. The formation of barium sulfate will result in serious plugging problems. Furthermore, the radioactive isotopes of radium often co-precipitate with the barium and form Naturally Occurring Radioactive Material, or NORM, scale.

Strontium (Sr)

Like the barium and calcium ions, strontium can combine with the sulfate ion to form insoluble strontium sulfate. Although more soluble than the barium sulfate, it is very likely to co-precipitate with the barium sulfate.

Anions – Negatively Charged Ions

Chloride (Cl)

The chloride is almost always the major anion produced in oil-field brines. It is also a major constituent of fresh waters. Although salt deposition in high saline brines can be a problem, usually the concern with chlorides is that with increasing chlorides comes increasing conductivity and thus, increased corrosion. Furthermore, chlorides are utilized to assist in determining the identity of a producing formation. The chloride levels can assist in monitoring wells for casing or packer leaks as well as flood-water break-through in water flood applications.

Carbonate and Bicarbonate (CO_3 and HCO_3)

These ions are important because they are the natural buffer for the water. These ions will influence the pH of a water, and the pH of the water will define which ion, or if both ions, are present in a water sample. Bicarbonates are present in waters with pH's ranging from 4.5 – 8.2. Above 8.2, carbonates can also be present. These ions can combine with cations to form insoluble mineral scales. Most carbonate scales are soluble in hydrochloric acid.

Sulfate (SO_4)

The sulfate ion is important because of its ability to react with calcium, barium and/or strontium to form acid insoluble scales. This also serves as a nutrient for sulfate reducing bacteria (SRB's).

In a completed water analysis, the milli-equivalents of cations must balance to the milli-equivalents of anions. In other words, all anions are matched up with cations. How these cations and anions "pair-up" is related to their reactivity, solubility, and availability within the water.

Other Water Properties

pH

One of the most important properties of a water is its pH. The pH is a measurement of the acidity, or alkalinity, of a water. It is extremely important in a water analysis for several reasons. The solubility of calcium carbonate ($CaCO_3$) and iron compounds is highly dependant of the pH of the water. Generally, oil-field waters have a pH ranging from 5.0 – 8.0. If a water's pH is below 7.0, it is said to be acidic, and corrosion rates can increase. If a water's pH is above 7.0, it is said to be alkaline in nature, and calcium carbonate and iron compounds are less soluble.

With increasing amounts of acid gases (hydrogen sulfide and carbon dioxide) the pH of the water will decrease. Understanding their effect on pH will help us to understand and predict their impact on the corrosivity of the water.

The constituents affecting the pH are very unstable upon a pressure release (ie, H_2S, CO_2, HCO_3), therefore, the pH of water will rapidly change when removed from a pressurized system. It is imperative that the pH be measured immediately upon sampling. The pH can also be measured in-vitro with an in-line pH meter.

Suspended Solids Content

Also known as "filterable solids" this test is determined by filtering a given volume of water through a membrane filter (usually 0.45 micron pore size). This is helpful in determining how much of what type of solids are currently dispersed in the water. Determining the total amount of solids, as well as the composition and particle sizes, will help in designing field or well-head filtering systems. This test will also indicate if scale particles or corrosion by-products are present in the water stream. This test is very useful in water-flood and water injection applications in estimating plugging tendencies in the reservoir.

Resistivity

The resistance to electrical flow (resistivity) is a function of the number of ions dissolved in the water. Lower resistivity (higher conductivity) results in the potential for higher corrosion rates. The lower the resistivity, the higher the conductivity, and the higher the concentration of ions; the higher the resistivity, the lower the conductivity, and the lower the concentration of ions. This property aids in predicting the corrosivity of the water and is an important property in the identification of water sources. It is directly related to the total dissolved solids and serves as a good checks/balances test for the water analysis' accuracy.

Dissolved Oxygen

Dissolved oxygen contributes significantly to the corrosivity of a water. It acts as a catalyst in the corrosion reaction of hydrogen sulfide and/or carbon dioxide on metallic equipment. Furthermore, dissolved oxygen can react with hydrogen sulfide and result in the formation of elemental sulfur. Oxygen can react with soluble iron present in sweet production systems and result in the formation of iron oxide. Any of these solids can result in plugging problems. Oxygen also facilitates the growth of aerobic bacteria.

Dissolved Carbon Dioxide

Dissolved carbon dioxide influences the pH, the corrosivity and the calcium carbonate scaling tendencies of a water.

Sulfide as H_2S

Hydrogen sulfide will also affect the pH and the corrosivity of a water. Hydrogen sulfide may be naturally occurring or may be the result of sulfate reducing bacterial activity. The corrosion product of hydrogen sulfide corrosion of ferrous materials is iron sulfide – which is a very efficient plugging agent and acts as a stabilizer for oil-field emulsions. Furthermore, depending on the concentration of the H_2S and the pressure of the system, hydrogen sulfide can also crack certain metallic substances. The cracking phenomenon is addressed in the NACE/ISO published standard MR 0175/ISO 15156. Care will need to be taken to examine all potential effects of hydrogen sulfide in the design phases of a project.

Bacterial Population

The presence of bacteria can result in accelerated corrosion and/or plugging problems in filters. Many techniques are available for enumeration. However, it should be noted that bacteria can result in souring an otherwise sweet system, can produce organic acids and can exist in "microenvironments" under deposits present in systems.

Oil Content

The oil content is most relevant in a water-flood or water-injection scenario. The oil can reduce the injectivity in several ways. It can form "emulsion blocks" in the formation thereby reducing the effectiveness of a water-flood and it can serve as an excellent "glue" for many types of suspended solids. Additionally, oil content in water can be recovered through the use of chemicals and can then be sold if economics support its recovery.

SAMPLING FOR THE WATER ANALYSIS

It must be noted that unless waters are sampled correctly and sampled to represent the water production stream, the results of the analysis may be in question. Proper sampling, preserving and labeling must occur to ensure the data is relevant. Additionally, unstable ions should be determined on-site at the time of sampling. Failure to conduct these critical analyses on-site can substantially affect the final interpretation of the water analysis.

Critical In-Field Analyses

Within the water sample are unstable ions/gases. The concentration of these ions can quickly change once removed from a pressurized system. Therefore, it is pertinent that these ions/gases be determined on-site for the most accurate results. These include the following: pH, bicarbonate ion, carbonate ion, dissolved carbon dioxide, hydrogen sulfide, and oxygen. If the water sample is allowed to age, the concentrations of these unstable ions/gases will change and thus can affect the interpretation of the waters from the aspect of predicting corrosivity and prediction of scaling tendencies.

If special environmental tests are to be conducted (total petroleum hydrocarbons, BTEX, heavy metals and/or other EPA tests), a sample of the water must be captured according to the procedures set forth by EPA and must be preserved with the appropriate preservative as outlined in the procedure. Additionally, water samples for many environmental tests must be kept at cool temperatures (often below 40^0 F) to ensure the accuracy and compliance of the results.

Proper Sampling

There are many publications available that recommend sampling, labeling and analytical testing procedures. The most common of these are the National Association of Corrosion Engineers International (NACE), American Petroleum Institute (API), and American Society for Testing and Materials (ASTM). These organizations prepare recommended practices and standards that are utilized in all aspects of industrial analyses. Understanding and adhering to the procedures contained within these publications can ensure accuracy in the analytical data gathered and will assist in making sound and profitable decisions based on these analyses.

National Association of Corrosion Engineers International (NACE)

NACE has multiple recommended practices, test methods and material standards to assist various industries, including the oil and gas industry. These procedures range from coating/painting procedures to cathodic protection to field application and laboratory analysis of corrosion coupons and membrane filter testing. The NACE publications can be obtained through the NACE web-site at www.nace.org. These publications are reviewed at least every five years and some are renewed and reissued annually. NACE has committees comprised of volunteer industry professionals that review and develop these publications. Each is scrutinized in great detail prior to its publication. They are, therefore, written by our peers for the benefit of our industry. By utilizing standard approaches to sampling, testing and reporting, we can have confidence in past, present and future data.

American Petroleum Institute (API)

API was developed by and for the petroleum industry. They offer a wide range of standards and recommended practices that apply to all aspects of our industry, upstream and downstream. The recommended practice pertaining to water analyses is API-RP-45: Recommended Practice for Analysis of Oilfield Waters. API publications are also reviewed at least every 5 years and are reissued with updated information. Much of the analytical work (field and laboratory) required for upstream petroleum production is based on this recommended practice.

American Society for Testing and Materials (ASTM)

ASTM publishes many reference books containing detailed and precise analytical testing procedures. These procedures may be utilized in all industries and are often referenced for environmental testing. Therefore, it is important to be aware that these procedures exist and need to know when it is appropriate to utilize them.

INTERPRETATION OF THE WATER ANALYSIS

When proper sampling, preservation and analytical procedures have been utilized, the analyst or engineer can then interpret the water analysis with confidence. The analysis should, at a minimum, contain the constituents noted within Table 1, designated by the (*). By analyzing for these constituents, several conclusions can be ascertained.

Identification of Production Zone

Production zones have distinct water properties characteristic to the location within a given County, or geographic area. These records have been gathered, cataloged and utilized for over 50 years by Independent laboratories to aid in the identification of production zones, or contamination within a production zone. The characteristics are highly dependant on chlorides, calcium, magnesium, sulfate, barium, and the ratios of these cations and anions to each other. It is recommended to conduct a water analysis as soon as possible after a well has stabilized following its initial completion, recompletion, or when new zones are opened for production. When suspect production trends are noted, a repeat water sample can be captured and analyzed. An accurate water analysis can be compared to existing historical records on that specific well, or on offset well records within the geographic area to determine if this produced water is characteristic to the water produced from that formation, or if possible casing leaks, foreign water entry, or contamination has occurred. An accurate water analysis is vitally important in this situation, for costly well workovers could be scheduled based on their results. It is recommended to conduct a repeat water analysis prior to rigging-up on a well to verify suspect water constituents.

Predicting Corrosivity

The water analysis can also indicate whether corrosion is likely to occur, based on several factors. The water analysis identifies the acid gases in the produced water as well as the dissolved minerals, gases and metals that could contribute to the corrosion process. As stated earlier, the acid gases tested on location immediately after the sample is obtained are CO_2 and H_2S. The acid gas content determines the dominate type of corrosion and greatly influences the corrosion rate of a system. Corrosion rates are directly related to the amount of these gases dissolved in the produced water in combination with the dissolved chlorides. CO_2 corrosion is directly related to its concentration and the system pressure and can result in various forms of metal loss and pitting. H_2S can result in a severe pitting attack and can often create high pitting/failure rates. In systems where CO_2 and H_2S are both produced, the ratio of the CO_2 to the H_2S will determine which species is dominant in the corrosion of the system.

As CO_2 and H_2S dissolve in water, they form acids. As the levels of dissolved CO_2 and H_2S increase in the water, the pH of the produced fluids will continue to decline. This creates a corrosive environment. Dissolved carbon dioxide acid gas or dissolved hydrogen sulfide gas present in the water, when combined with the low pH and high chloride content, would indicate the water is potentially corrosive in nature.

In addition to reviewing the acid gases, chloride levels and pH, it is also advantageous to review the levels of iron and manganese contained within the water sample. Since these are analyzed on acidized samples, these measurements are reflective of both dissolved and any suspended compounds that were solubilized by the acid. Therefore, the term is known as “total iron and total manganese”. High iron and manganese levels can be indicative of active corrosion occurring downhole or in surface equipment. Additional monitoring of equipment integrity, reviews of failure records and visual inspection of any removed metallic components is recommended to verify active corrosion. Depending on their history, older waterfloods will some times recirculate iron and manganese, making the monitoring process difficult. In situations such as this, it is recommended to review trend analyses on the iron/manganese and attempt to relate these trends to actual field corrosion failure data.

Additionally, the water analyses may include a determination for oxygen. This is commonly included on water injection or water disposal systems. Levels of oxygen should not exceed 50 ppb (0.050 ppm) when H_2S and/or CO_2 are present. Not only is oxygen a severely corrosive species, but acid gas corrosion is accelerated in the presence of oxygen. In the absence of H_2S and/or CO_2, it is recommended for oxygen levels to be maintained below 100 ppb (0.10 ppm). Ideally, oxygen should be excluded or scavenged from production facilities. However, metallic surface and downhole equipment should be protected through the use of material selection or through the application of a corrosion inhibitor if oxygen is present.

Using the water analysis to understand the potential for corrosion and relating this information to actual failure records within a field or area, the engineer can design an appropriate corrosion mitigation program. This program can consist of engineering solutions to remove the corrosive species, selection of corrosion resistant alloys, the application of protective coatings, or the application of corrosion inhibitors.

Predicting Scaling Tendencies

Mineral scales are defined as a mineral deposition that results from an oversaturation of a given compound within a solution under a certain set of conditions. Scales can result in plugging problems within the producing formation, within the downhole equipment, and/or within the surface piping/equipment. Additionally, under-deposit corrosion can occur beneath scale depositions, resulting in high corrosion rates and pre-mature failure of production equipment. The prediction of the water’s tendency for scale deposition is derived from the analysis and arithmetical combination of the cations, anions, pH and temperature of the water using the downhole conditions. This model of temperature/pressure is then compared to surface conditions (usually cooler, yet lower in pressure). The indication of a pressure drop can signal the potential for the formation of calcium carbonate scales. Increased temperatures (ie, submersible pumps or surface pumps) result in a potential for the formation of calcium sulfate. Barium sulfate, very insoluble in water, will form upon mixing of incompatible waters.

These calculated tendencies are only indicators of possible deposition, which may occur, given the operating conditions of the system, including pressure drops and temperature of the produced fluids. It should be noted that calcium carbonate and calcium sulfate mineral scales have an inverse solubility in water as the temperature increases: ie, they become less soluble with increasing temperatures. Therefore, as temperatures increase, the likelihood of deposition increases. An example of the calculated scaling tendencies is illustrated in Figure 1. These results reflect the testing of the acid gases, pH and the bicarbonates in the water on location. It is imperative that these tests are performed immediately upon obtaining the water samples or the calculated tendencies will be incorrect.

There are typically three (3) types of mineral scales that are present in production and injection systems; Calcium carbonate ($CaCO_3$), Calcium sulfate ($CaSO_4$) and Barium sulfate ($BaSO_4$). Table 2 shows the solubilities of these scales in water (Calcium sulfate > calcium carbonate > barium sulfate). Table 3 shows the primary variables that can result in the deposition of these mineral scales.

Calcium Carbonate scale is an acid soluble mineral scale that forms easily and is most common in low-pressure systems and injection wells. This scale deposition can be removed with the application of acid. However, acids will not typically penetrate an oil-wet solid and therefore it is necessary to utilize a mutual solvent to assist in removing the hydrocarbons from the scale. This will allow the acid to effectively dissolve the mineral scale and clean the equipment. This scale can be prevented and controlled at very low concentrations of scale inhibitor. An illustration of calcium carbonate is shown in Figure 2.

Calcium Sulfate scale is the second most common scale found in production/water systems and is formed through pressure and temperature variances. This scale is not acid soluble and must first be converted to an acid soluble salt chemically with a sulfate converter. The removal of this type of mineral scale requires a two-phase clean up where a converter is applied and allowed to convert the calcium sulfate scale into a calcium salt. This usually takes a period of 8-12 hours to effectively convert as much of the scale as possible. Once the sulfate scale has been converted to a calcium salt, acid can be applied to remove the converted mineral deposition.

It is possible to use a calcium sulfate dissolver in some applications to reduce the two-phase cleanup to a single application. The “dissolver” is designed to dissolve the calcium sulfate molecule in a single procedure. It is not necessary to apply acid in conjunction with this application. However, it is recommended to allow at least 12-24 hours for the process to completely dissolve the scale present. An illustration of calcium sulfate is shown in Figure 3.

Barium Sulfate is the third mineral scale that can be found in production/water systems. This scale is neither acid soluble nor is it converted economically. Once this scale is formed, it is usually only removed by mechanical means. Barium sulfate scale will form before calcium sulfate scale if there is any barium present in the produced water with any amount of sulfates. This type of mineral scale can be inhibited, but usually requires a higher concentration of chemical to work effectively. An illustration of barium sulfate is shown in Figure 4.

Other types of depositions can occur; however, many are the by-products of bacterial activity, acid gas corrosion of metallic components, or the result of mixing incompatible waters. Reviewing the water analysis, field failure history and monitoring for biological activity can help to determine the origin of deposits. Iron carbonate and iron sulfide are two deposits that can originate from either corrosion or biological activity. They should not be categorized as scales, but should be categorized as “deposits” and are most effectively controlled with corrosion inhibitors, biocides, or controlling the quality of make-up water for injection systems (ie, mixture of incompatible waters).

Understanding Solubilities of Chemicals

A water analysis is also helpful when designing a production chemical program. Knowledge of the chloride level is critical in the selection of gas enhancement products (ie, foam assisted lift products). The TDS and calcium levels are also critical in the solubility of scale and corrosion inhibitors. Again, an accurate water analysis is the beginning for screening these products and is necessary to design an effective program to address production challenges.

TOTAL SUSPENDED SOLIDS, (TSS)

In addition to the total dissolved solids, understanding the total suspended solids can be beneficial, especially in a water injection or water disposal system. Total suspended solids are generally measured, examined and analyzed through the use of the membrane filter. The NACE standard test procedure TM 0173-2005, Methods for Determining Quality of Subsurface Injection Water Using Membrane Filters, utilizes a pre-weighed 0.45 micron pore size filter pad. The water is filtered at 20 psig for up to 10 minutes, or until a set volume of water has been filtered. The filter pad is then dried, re-weighed and the TSS can be determined. Further analyses can be conducted on the solids captured on the filter pad to yield useful information: hydrocarbon content, acid solubles, acid insolubles, and deposited particle sizes. TSS can be naturally occurring (silicates, sands) or can be formed as a result of corrosion by-products or mineral scale deposition. In injection systems, a target of 50 mg/L or less of TSS is desirable; however, if the matrix into which the water is to be injected is tight, ie, low porosity and/or low permeability, knowing the particle sizes may be as important as the quantity of particles present. Both size and quantity of particles can be determined on the membrane filter.

TSS can result in solids depositions throughout a reservoir, on downhole equipment or within surface equipment. TSS can also result in erosional damage of equipment, erosion/corrosion damage (especially with stainless steels), plugging of the reservoir or production equipment, loss or reduction in injectivity of injection wells, and TSS can be involved in the development of oil-field emulsions (normal and reverse emulsions).

Suspended solids can be addressed chemically and/or mechanically. Chemicals can aid in water wetting solids and can be utilized in conjunction with mechanical solids removal equipment such as WEMCO Units, up-flow or down-flow filtration units, hydrocyclones, and simple cartridge filtration. The removal of the solids will aid in increasing the life expectancy of projects and equipment and can increase profitability on such projects.

Again, understanding the water analysis can assist in predicting the types and possible location for the formation of suspended solids throughout a production facility.

Table 4 illustrates the common suspended solids and their probable origins. It should be noted that 1 mg/L of suspended solids equates to 0.00035 lbs/Bbl of potential deposition. On a 10,000 BWPD injection system at 50 mg/L, if all of the TSS were deposited, would calculate to 175 lbs/day, or 32 tons, of deposition per year.

CONCLUSIONS

A water analysis can be an extremely informative piece of analytical information. The water analysis can assist in identifying the production zone, contamination to the production zone, the tendency for corrosion and/or scale deposition, plays an integral role in production chemical selection, and can aid in the design and development of secondary and tertiary recovery systems for the oil and gas industry. However, the water analysis must be sampled correctly, analyzed correctly, and interpreted correctly. Furthermore, it must be representative of the system being tested. Regular testing of produced waters (annually unless conditions warrant a retest) can indicate whether corrective actions are necessary, and will also assist in confirming the success, or failure, of past actions. Within waterflood systems, quarterly monitoring of injection water is recommended (TDS, TSS and bacteria). However, any frequency of sampling should be modified if changes are implemented to a system, or if conditions within a system deteriorate.

REFERENCES

1. Ostroff, A.G.: *Introduction to Oilfield Water Technology*, National Association of Corrosion Engineers, Houston, Texas (1979)

2. API RP-45: *API Recommended Practice for Analysis of Oil-Field Waters Third Edition*, American Petroleum Institute, API Publishing Services, 1220 L St., N.W., Washington, D.C., 20005 (1998)

3. NACE International Standard TM-0173-2005: *Test Method for Determining Water Quality for Surface Injection Using Membrane Filters*
4. Patton, C.C. Dr.: *Applied Water Technology*, Campbell Petroleum Series, Norman, Oklahoma (1986)

5. Van Delinder, L. S., Editor, *Corrosion Basics, An Introduction*, National Association of Corrosion Engineers, Houston, Texas, 77084 (1984)

6. Oddo, J. E. and Tomson, M.B. : *Why Scale Forms and How to Predict It*, SPE Production and Facilities, February, 1994

7. Kemmer, F. N., Editor, *The NALCO Water Handbook, Second Edition*, McGraw-Hill Book Company (1979)

8. Patton, C. C. Dr.: *Injection-Water Quality,* Journal of Petroleum Technology, October 1990

9. Martin, W. C.: *Waterflood Waters – Problems and Practices,* AIChE Symposium, Midland, Texas, (1965)

10. Martin, W.C.: *Water Quality and Control*, Panel Discussion for Southwestern Short Course, (April 1964)

Table 1
Primary Constituents of Oilfield Waters

Cations	**Anions**	**Other Properties**
*Calcium (Ca) *Magnesium (Mg) *Sodium (Na) *Iron (Fe) *Barium (Ba) Strontium (Sr) Manganese (Mn)	*Chloride (Cl) *Carbonate (CO_3) *Bicarbonate (HCO_3) *Sulfate (SO_4)	*pH *Temperature *Specific Gravity *Dissolved Carbon Dioxide *Sulfide as H_2S Resistivity Dissolved Oxygen Bacterial Population Oil Content Turbidity Suspended Solids – amount, size, shape, chemical composition

The components marked with an (*) are essential to obtaining a thorough and meaningful water analysis.

Table 2
Relative Solubilities of Mineral Scales in Water

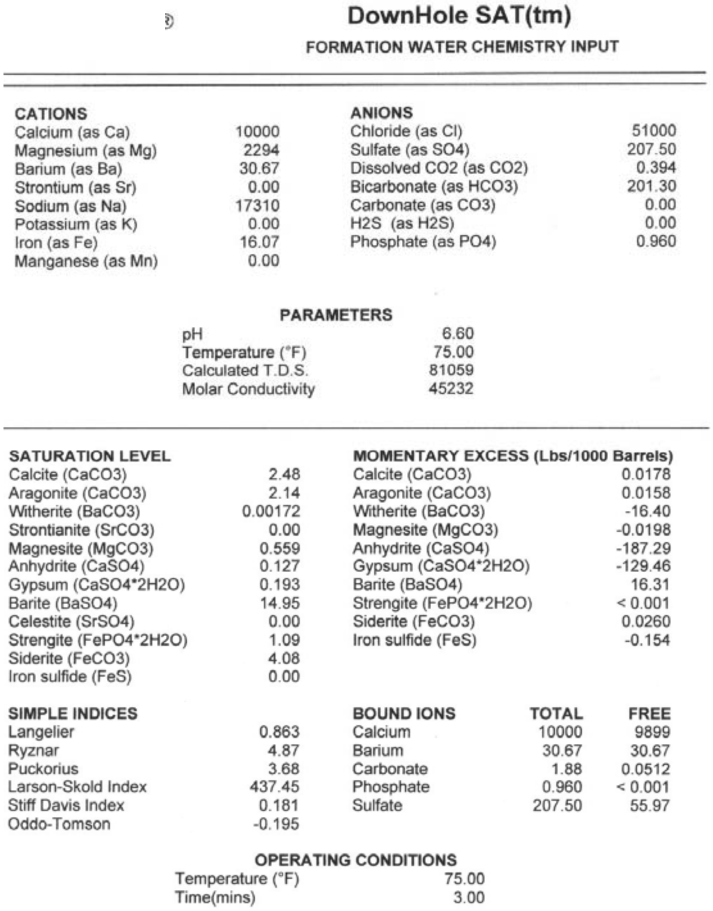
Mineral Scale	**Solubility (mg/L) in Water**
Calcium Sulfate (Gypsum) - $CaSO_4 . 2H_2O$	2080 mg
Calcium carbonate - $CaCO_3$	53 mg
Barium Sulfate - $BaSO_4$	2.3 mg

Table 3
Primary Variables in the Formation of Mineral Scales

Scale, or Deposit	**Chemical Formula**	**Primary Variables**
Calcium Carbonate	$CaCO_3$	-Partial pressure of CO_2 (scale increases as CO_2 decreases) -Less Soluble with Increasing temperature -Pressure Drops -More soluble as TDS increases
Calcium Sulfate	$CaSO_4 . 2H_20$ (dehydrate) $CaSO_4$ (anhydrite)	-Less Soluble with Increasing temperature -Pressure drops -More soluble as TDS increases
Barium Sulfate Strontium Sulfate	$BaSO_4$ $SrSO_4$	-More soluble as Temperatures increase -More soluble as TDS increases
Iron Compounds: Iron Carbonate Iron Sulfide Iron (II) Hydroxide Iron (III) Hydroxide Iron Oxide	 $FeCO_3$ FeS $Fe(OH)_2$ $Fe(OH)_3$ Fe_2O_3	-Corrosion by-products -Bacterial activity -Dissolved gases -Depositions increase as pH increases (especially true after an acid job with spent acids)

Table 4
Common Suspended Solids and their Probable Origins

Type	**Hydrocarbons**	**Iron Compounds**	**Carbonates**	**Sulfates**	**Insolubles/organics**
Detail	-Oil Carry Over -Paraffin Deposition	-Iron sulfide -Iron oxide -Iron carbonate	-Calcium carbonate -Iron carbonate -Magnesium carbonate	-Calcium sulfate -Magnesium sulfate -Barium sulfate	-Formation fines -Sand -Microbes -Asphaltenes
Probable Origin	-Separator malfunction -Truck treating schedules -Surface tank damages -Improper equipment sizing	-Corrosion -Incompatible waters -Oxygen introduction -Stimulation by-products	-Scaling waters -Corrosion -Pressure drops -Fluid property changes	-Scaling water -High temperature -Pump outlets/shrouds -Incompatible waters	-Inadequate wellbore cleanouts -Pump intakes set low -Bacterial activity -Natural, or induced, formation of asphaltenes (CO_2 flood)



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                  FORMATION WATER CHEMISTRY INPUT

CATIONS                                ANIONS
Calcium (as Ca)            10000       Chloride (as Cl)               51000
Magnesium (as Mg)           2294       Sulfate (as SO4)              207.50
Barium (as Ba)             30.67       Dissolved CO2 (as CO2)         0.394
Strontium (as Sr)           0.00       Bicarbonate (as HCO3)         201.30
Sodium (as Na)             17310       Carbonate (as CO3)              0.00
Potassium (as K)            0.00       H2S  (as H2S)                   0.00
Iron (as Fe)               16.07       Phosphate (as PO4)             0.960
Manganese (as Mn)           0.00

                          PARAMETERS
              pH                            6.60
              Temperature (°F)             75.00
              Calculated T.D.S.            81059
              Molar Conductivity           45232

SATURATION LEVEL                         MOMENTARY EXCESS (Lbs/1000 Barrels)
Calcite (CaCO3)                 2.48     Calcite (CaCO3)                 0.0178
Aragonite (CaCO3)               2.14     Aragonite (CaCO3)               0.0158
Witherite (BaCO3)            0.00172     Witherite (BaCO3)               -16.40
Strontianite (SrCO3)            0.00     Magnesite (MgCO3)              -0.0198
Magnesite (MgCO3)              0.559     Anhydrite (CaSO4)              -187.29
Anhydrite (CaSO4)              0.127     Gypsum (CaSO4*2H2O)            -129.46
Gypsum (CaSO4*2H2O)            0.193     Barite (BaSO4)                   16.31
Barite (BaSO4)                 14.95     Strengite (FePO4*2H2O)         < 0.001
Celestite (SrSO4)               0.00     Siderite (FeCO3)                0.0260
Strengite (FePO4*2H2O)          1.09     Iron sulfide (FeS)              -0.154
Siderite (FeCO3)                4.08
Iron sulfide (FeS)              0.00

SIMPLE INDICES                           BOUND IONS          TOTAL       FREE
Langelier                      0.863     Calcium             10000       9899
Ryznar                          4.87     Barium              30.67      30.67
Puckorius                       3.68     Carbonate            1.88     0.0512
Larson-Skold Index            437.45     Phosphate           0.960    < 0.001
Stiff Davis Index              0.181     Sulfate            207.50      55.97
Oddo-Tomson                   -0.195

                       OPERATING CONDITIONS
             Temperature (°F)                75.00
             Time(mins)                       3.00
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Figure 1 - Representative Water Analysis Indicating Scaling Tendencies

Figure 2 - Calcium Carbonate Scale

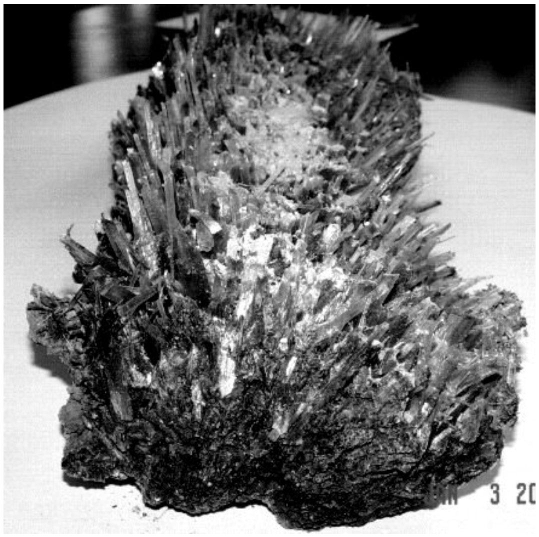

Figure 3 - Calcium Sulfate Scale

Figure 4 - Barium Sulfate Scale