Aegis Tech Line

Aegis Chemical Solutions

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BASICS OF OILFIELD WATER CHEMISTRY

Dissolved Solids – Cations and Anions

The dissolved solids in water are virtually always associated pairs of cations and anions. These associated pairs are called "salts". Cations are positively charged and anions are negatively charged. There are equal numbers of positive and negative ions, so water solutions are electrically neutral. Dissolved salts increase the electrical conductivity of water, and thereby increase the corrosion potential of water to steel. Under certain conditions the solubility of some cation/anion pairs are exceeded. When this occurs, scale usually results. The individual cations and anions and their concentration can have a dramatic impact on emulsions, scale potential, corrosivity, bacteria growth and the solubility of treating chemicals. High concentrations of dissolved solids are major limitations to using produced water for fracturing wells. Fracturing chemicals such as friction reducers, cross linkers and guar gels are all impacted by dissolved solids. The sum of the cations and anions in mg/liter is commonly called total dissolved solids or TDS.

Primary Constituents & Properties of Oilfield Waters

Cations (chemical symbol)	Units	Anions (chemical symbol)	Units	Other Properties and Components	Units
Sodium (Na)	mgs/l	Chloride (Cl)	mgs/l	pH	
Calcium (Ca)	mgs/l	Carbonate (CO_3)	mgs/l	Suspended Solids	mgs/l
Magnesium (Mg)	mgs/l	Bicarbonate (HCO_3)	mgs/l	Chemical Residual	PPM
Iron (Fe)	mgs/l	Sulfate (SO_4)	mgs/l	Temperature	^oF
Barium (Ba)	mgs/l	Nitrate (NO_3) - rare	mgs/l	Specific Gravity (or density)	g/ml
Strontium (Sr)	mgs/l	Organic Acids -rare	mgs/l	Dissolved Oxygen (O_2)	PPM
Zinc (Zn) – rare	mgs/l	Hydroxide (OH) – rare	mgs/l	Dissolved Carbon Dioxide (CO_2)	PPM
Lead (Pb) – rare	mgs/l	Silica (SiO_2)	mgs/l	Dissolved Hydrogen Sulfide (H_2S)	PPM
Potassium (K)	mgs/l			Bacteria Population	Cells/ml
Manganese (Mn)	mgs/l			Oil Content	PPM

Cations – Na, K, Ca, Mg, Ba, Sr, Fe, and Mn (positively charged)

Sodium (Na) is usually the largest concentration of cation in produced water. Sodium is normally associated with chloride (Cl) ions. Sodium chloride (NaCl) in crystal form is common table salt. In rare cases, the concentration of NaCl can be so high that it precipitates and causes problems in the formation, wells or surface equipment. The mineral form of NaCl is called halite. Halite precipitation is usually most common in drilling operations especially when drilling through salt zones. Halite scale also forms in producing wells that are very hot and evaporation of water occurs to concentrate NaCl above its solubility.

Potassium (K) is a minor component of oilfield brines, but is widely used in fracturing and stimulation. Potassium chloride (KCl) is an excellent stabilizer of clay in formations. It prevents clay swelling and migration. If K levels are significant, it is likely that a well or system has been fractured or worked over.

Calcium (Ca), Magnesium (Mg), Barium (Ba) and Strontium (Sr) are the cations that make up the "hardness" of water, particularly Ca and Mg. The carbonate (CO_3) and sulfate (SO_4)

salts of these 4 cations are sparingly soluble in water and often form scales that deposit and plug pipes, valves, meters, etc. They also contribute to under-deposit corrosion. These are often called “mineral” scales. Calcium carbonate ($CaCO_3$) is by far the most common scale. In order of occurrence the other common scales are calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$) and strontium sulfate ($SrSO_4$). Computer models are available to predict the potential for each of these mineral scales to form under varying conditions of temperature, pressure, CO_2 in the gas and total dissolved solids. Combinations of these scales are often found in oilfield equipment. Mineral sulfate or carbonate scale is prevented using a scale inhibitor. High levels of Ca and Mg are often incompatible with scale inhibitors and compatibility tests are recommended.

Iron (Fe) and Manganese (Mn) are usually byproducts from corrosion of steel and their concentrations in water are directly proportional to corrosion rate. Both ions are often measured as part of a corrosion monitoring program. Iron (Fe) scales which are due to corrosion of steel may also be found in combination with mineral scales. In some cases Fe will be found in producing formations. A prominent example is the Sadlerochit formation in Prudhoe Bay Alaska; which contains the mineral siderite ($FeCO_3$). In this case Fe analysis cannot be used for corrosion monitoring since some of the Fe in water is from naturally occurring siderite. Iron sulfide (FeS) is a corrosion byproduct of H_2S corrosion of steel. Iron oxide (Fe_2O_3 or Fe_3O_4) is a corrosion byproduct of O_2 corrosion of steel. Both of these often deposit as a “scale” on pipe walls restricting flow and increasing the potential for under-deposit corrosion. Although iron sulfide and iron oxide are often called scales, they are corrosion byproducts that are prevented by using a corrosion inhibitor.

Anions – Cl, CO_3, HCO_3, SO_4, and Organic Acids

Chloride (Cl) is normally associated with Na as sodium chloride. At certain temperatures chloride can cause stress cracking of high strength, highly alloyed steels.

Sulfate (SO_4) is usually a minor component in produced water. It is much more concentrated in sea water. When sea water is used for water flooding – the sulfate scales of Ba, Sr, and Ca are of major concern, especially when the injected sea water breaks through to producing wells. SO_4 is also necessary for growth of sulfate reducing bacteria (SRB). Very low levels (<5 mg/liter) of sulfate may be all that is required.

Carbonate (CO_3) is very rare in produced water, but it can be found in certain caustic floods and alkaline / surfactant / polymer floods. $CaCO_3$ scale is major problem in these floods.

Bicarbonate (HCO_3) is usually present at low concentrations in produced water. HCO_3 is key to determining scaling and corrosion potential of water. HCO_3 is formed when carbon dioxide (CO_2) in the formation dissolves in water. In rare cases such as coal seam wells, HCO_3 is found as the sodium salt and can be at a very high concentration.

Organic acids are rare and usually present at low concentrations. Organic acids are usually formic, acetic, propionic, and butyric acid. Organic acids can contribute to corrosion. Organic acids can also increase the apparent amount of oil in water, which is critical for offshore operations where water is dumped overboard. Organic acids can impact scaling and scale modeling.

Water pH and its impact

pH is a measure of the acidity of water and ranges from 0 to 14. pH is a log scale. Therefore, a pH of 6.0 has 10 times as much acid as a pH of 7.0 (see the chart below). As pH decreases, corrosion potential increases. As pH increases scaling potential of calcium carbonate ($CaCO_3$) increases. Iron oxides and hydroxides precipitate at higher pH values. pH should be measured in the field immediately after catching water sample, ideally with a flow through sampler. Most produced oilfield water has a pH between 4 and 8.

pH as a Function of H^+ Ion Concentration

Concentration of Hydrogen ions compared to distilled water		Examples of solutions at this pH
10,000,000	pH= 0	Battery acid, Strong Hydrofluoric Acid
1,000,000	pH = 1	Hydrochloric acid secreted by stomach lining
100,000	pH = 2	Lemon Juice, Gastric Acid Vineger
10,000	pH = 3	Grapefruit, Orange Juice, Soda
1,000	pH = 4	Acid rain Tomato Juice
100	pH = 5	Soft drinking water Black Coffee
10	pH = 6	Urine Saliva
1	pH = 7	"Pure" water
1/10	pH = 8	Sea water
1/100	pH = 9	Baking soda
1/1,000	pH = 10	Great Salt Lake Milk of Magnesia
1/10,000	pH = 11	Ammonia solution
1/100,000	pH = 12	Soapy water
1/1,000,000	pH =13	Bleaches Oven cleaner
1/10,000,000	pH = 14	Liquid drain cleaner

Other Properties/Components – Dissolved Gases – O_2, CO_2 and H_2S

Oxygen (O_2) is rarely ever found in reservoirs. O_2 is almost always introduced from the atmosphere as a contaminant. O_2 is extremely corrosive to steel. Care must be taken when analyzing for oxygen due to potential contamination. O_2 is commonly found in water floods, water supply wells, and downstream of compressors or pumps due to leaking seals or open hatches/vents. O_2 is found in seawater floods and is usually removed by vacuum dearation.

Carbon dioxide (CO_2) is found in most oil and gas producing reservoirs. CO_2 is corrosive to steel, especially at high velocities. CO_2 dissolves in water to form carbonic acid which reduces the pH and increases the corrosion rate.

Hydrogen sulfide (H_2S) is commonly found in producing formations. H_2S is extremely hazardous to health and very corrosive to steel. At high enough concentrations H_2S will cause certain steels to crack or rupture. H_2S is also a byproduct of sulfate reducing bacteria.

Other Properties/Components – Total Suspended Solids

Suspended solids are materials that are insoluble in water, but may be suspended in water or carried along with flowing water. Suspended solids are usually iron corrosion products, mineral scales, and/or formation sand or clay.
Insoluble materials can cause plugging of valves, meters or any orifice; and most importantly, injection wells.
Measurement and control / removal of solids is important in water flood injection wells, or waste water disposal wells.

Chemical analysis of solids collected on a 0.45 micron filter is often used to determine the specific plugging materials, so that appropriate prevention or removal of solids can be implemented. Oil in the water will also be collected on a filter.

Other Properties/Components – Chemical Residual

In waters being treated with a production chemical, part of the monitoring program may be testing for residual chemical usually to ensure there is sufficient concentration in the system.

Scale inhibitor residuals are commonly monitored on produced water from wells that have been "squeezed", to ensure an adequate amount of scale inhibitor is being returned. When the scale inhibitor drops below a certain level, the well is typically scheduled for another formation "squeeze". The concentration of scale inhibitor injected down the back side of a well may be tracked in the produced water to ensure an adequate concentration.

Corrosion inhibitor residuals are commonly run on water taken from pipelines that are being treated with corrosion inhibitor. Many gas pipelines have varying amounts of water. The corrosion inhibitor residual is used to fine tune the corrosion inhibitor injection rate.

Biocide residuals are analyzed on occasion to ensure treatment is adequate.

Other Properties/Components – Total Dissolved Solids

Total dissolved solids (TDS) is the total amount of dissolved material in a given volume of water. TDS is usually calculated by taking the sum of all cations and anions in the water. It may also be measured by evaporating a sample to dryness and weighing the residue, but this is rare.

Other Properties/Components – Bacteria Population

Bacteria are usually determined by a technique called serial dilution (see NACE Standard TM0194-94, Item No. 21224). Various bacteria can be determined by using this technique although the media in the serial bottles is different to detect different types of bacteria. Sulfate-reducing bacteria (SRB) are the most common type of bacteria that is evaluated. Acid-producing bacteria (APB) are also of concern. Bacteria are a serious cause of corrosion and plugging problems. In stagnant areas, SRB can proliferate and cause severe under-deposit corrosion. Prime stagnant areas are bottom of tanks, separators, heater treaters etc. especially if sand or other solids are present. Low spots in pipelines that are low velocity are a major source of corrosion failures due to SRB causing under-deposit, pitting corrosion.

During drilling and stimulation of wells, contamination of the entire producing reservoir is possible. This can make the entire field “sour” due to H_2S produced by SRB. Drilling muds and fracturing fluids should ALWAYS be treated with biocide or some other technique to sanitize the water.

Other Properties/Components – Oil Content

The presence of free or dispersed oil is of primary concern when injecting produced water, or pumping water overboard in offshore production. Oil in water can cause decreased injectivity by acting as a “glue” to bind solids together in a large mass. Iron sulfide is particularly prone to this problem. Oil can also change formation rock from water-wet to oil-wet, which will reduce injectivity of water. Most countries have regulatory limits on the amount of oil that can be in water dumped overboard into bodies of water. Oil causes slicks or sheens on the water, and can be deadly to sea life.

Field Water Analysis

Certain water properties change rapidly after sampling. The following determinations should be done on site for maximum accuracy:

- pH
- pH can also be calculated using the % CO_2 in the gas phase, total pressure of system, and HCO_3 content or from dissolved CO_2
- Carbonate
- Bicarbonate
- Dissolved Oxygen
- Dissolved Carbon Dioxide
- Dissolved Hydrogen Sulfide
- Temperature
- Suspended Solids Concentration
- Bacteria Counts

Technical Service Laboratories perform tests for the other constituents in the water analysis. Samples should be collected in the field that represent the water being processed through the system. Stagnant fluids should not be used as a sample. Three (3) 100ml samples should be collected and submitted to the laboratory for testing. Two of the samples are submitted as collected with one of these samples being the backup should something happen to the other. The third sample is acidized with hydrochloric acid to determine the presence of iron, barium, strontium and/or phosphate (scale inhibitor residual). Refer to field testing manual for more details.