

## OIL & GAS INDUSTRY - PRODUCED WATER CHEMICAL TREATMENT 101

### **Introduction**

Produced water is defined as the water brought up from the hydrocarbon bearing strata during the extraction of oil and/or gas and can include formation water, injection water, condensed water and trace amounts of treatment chemicals. The production stream containing the oil/gas/water mixture is passed through separation equipment to separate oil, gas, and water followed by treatment of the produced water for discharge or re-use.

Produced water is the highest volume waste generated in association with oil and gas production operations. This waste stream is characterized as a high volume - low toxicity waste. Over the life of a typical oil field, as much or more water than oil is likely to be produced. For gas fields, the volumes of produced water are significantly lower.

### **CHEMICAL TREATMENTS**

The most common types of problems encountered in oil and gas production operations and types of treatment chemicals include the following:

<b>Problem</b>	<b>Treatment Chemical</b>
Hydrate Formation	Hydrate Inhibitor
Water Vapor	Dehydrator
Mineral Deposits	Scale Inhibitor
Chemical Corrosion	Corrosion Inhibitor
Bacterial Corrosion	Bactericide
Emulsions (Normal or Reverse)	Emulsion Breakers, Coagulants, Flocculants
Foaming	Defoamer
Paraffin	Paraffin inhibitor, solvent

Use of chemical and biological corrosion treatment chemicals is common to both oil and gas production operations where their use is necessary. Hydrate inhibitor and dehydration chemicals are almost exclusively used in gas production. Emulsion breakers, coagulants, flocculants, defoamers, paraffin inhibitors and solvents are most commonly used in liquid (crude oil, condensate, water) production.

### **Chemical Feed Considerations**

An often-overlooked fact is that a produced water treatment program usually represents a small percentage of the overall costs of an entire operation. However, poor treatment or equipment performance can create domino effects increasing operating and maintenance costs.

For best results, well designed equipment coupled with a sound chemical treatment program can reduce chemical consumption variation by as much as 90% while significantly improving the operational safety and longevity of a facility. That in turn reduces the risk of a catastrophic failure that can result in a loss of resources (oil and gas), human injury, or spills.

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**Hayward Gordon** offers a wide range of custom designed chemical feed systems. These systems are built to customer specification. Our chemical metering and control systems ensure process specifications and industry standards are met. We pride ourselves on our services: 3-D computer aided design (CAD) drawings, which include process & instrumentation drawings, system layout & design and operation & maintenance instructions. Each system is assembled and thoroughly tested at our factory to assure your satisfaction.

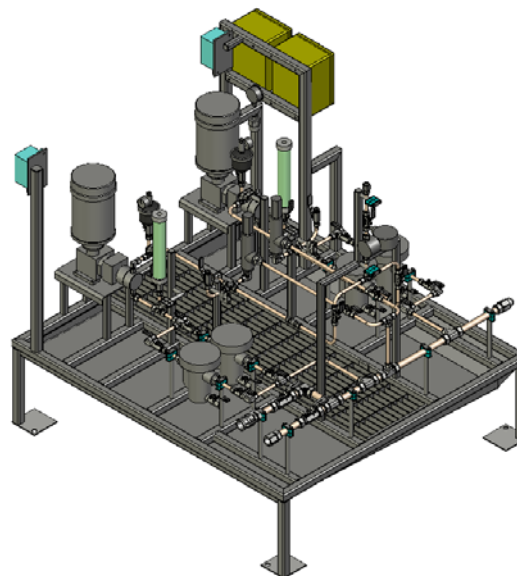
### **Typical Feed Equipment Requirements**

In general, the following basic equipment is needed:

- Skid Mounted Dual API Metering Pumps (Duty/Stand-By) With Stainless Steel Wet End/Trim
- Pulsation Dampener
- Stainless Steel Relief Valve
- Stainless Steel Check Valve
- Stainless Steel Y-Strainer
- Stainless Steel Tubing, Valves, And Fittings
- Flowmeter
- Calibration Cylinder
- Pressure Gauge With Diaphragm Seals
- Electrical Junction Boxes (CSA)
- Dilution Water Line C/W Static Mixer (Optional)
- Drip Pan (Optional)
- CRN's for all fittings

*In all cases, an injection quill is recommended.*

Storage tanks must be selected according to chemical resistance requirements. Materials typically include stainless steel, fiberglass, or polyethylene. Lines may be PVC or 316 stainless steel.



### **Computerized Chemical Feed Systems**

Computerized chemical feed systems are being used to improve program results and cut operating costs. These systems can be used to feed most treatment chemicals. A typical system incorporates a metering pump, feed verification equipment, and a microprocessor-based controller. These systems are often linked to personal computers, which are used to monitor program results, feed rates, system status, and plant operating conditions. Trend graphs and management reports can then be produced to provide documentation of program results and help in troubleshooting.

In many cases, these systems can be programmed to feed treatment chemicals according to complex customized algorithms. For example, chelant feed can be adjusted automatically, based on analyzer or operator hardness test results, feedwater flow, and minimum/maximum allowable product feed rates. Thus, chemical feed precisely matches system demand, virtually eliminating the possibility of underfeed or overfeed.

Feed verification is another important facet of some computerized feed systems. The actual output of the pump is continuously measured and compared to a computer-calculated setpoint. If the output doesn't match the set point, the speed or stroke length is automatically adjusted. The benefits of this technology include the elimination of time-consuming drawdown measurements, the ability to feed most chemicals directly from bulk tanks, precise chemical residual control, and minimal manpower requirements.

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## COMMON TREATMENT PROGRAMS

### ***Chemical Corrosion Control***

The chemical corrosivity of produced fluids is most commonly associated with the presence of hydrogen sulfide, carbon dioxide, or oxygen. Chemical corrosion is one area where the application of technology, through the use of corrosion resistant metallurgy, can reduce the use, hence the potential discharge, of chemicals.

Carbon dioxide is the most common corrodent, while hydrogen sulfide poses the most significant risk to human health and the environment. Oxygen is not typically found in unaltered produced fluids. Oxygen is usually introduced as the produced fluids are treated. Most corrosion inhibitors work by adsorbing onto exposed metal surfaces. Corrosion inhibitors are very complex compounds that can be sorted into four generic groups: amine imidazolines, amines and amine salts, quaternary ammonium salts, and nitrogen heterocyclics.

Oil soluble corrosion inhibitors are most commonly used since they are usually the most effective at providing a stable, durable film. The concentration of active ingredient in bulk corrosion inhibitors is usually 30 - 40%. The remaining material (inert ingredients) is usually a hydrocarbon based solvent like heavy aromatic naphtha. When improved water solubility is required, dispersants or surfactants may be added, or water soluble corrosion inhibitors such as quaternary amines can be used. Oil soluble inhibitors will follow the oil stream to the refinery and water-soluble inhibitors will stay with the water phase.

Selection of a particular corrosion inhibitor is usually made based on the type of corrodent, the type of production, prior experience, and laboratory or field testing.

Corrosion caused by oxygen is controlled by chemical reaction rather than adsorption. Oxygen inhibitors (scavengers) are usually some form of sulfite, with ammonium bisulfite the most common form being used. These compounds and their reaction products (sulfates) are highly water soluble and will be discharged with the produced water. Oxygen scavengers are typically used at concentrations of less than 100 ppm. The use of oxygen scavengers in discharged produced water is not common. Far more frequently, oxygen scavengers are used to treat injection water.

There are three standard treatment methods used for corrosion inhibition, continuous treatment, displacement treatment, and squeeze treatment. Continuous treatment involves continuous injection of corrosion inhibitor into the production stream. Treatment concentrations normally range between 5 - 15 ppm for liquid production depending on the concentration of the corrodent. The treatment concentration for gas production may be as high as 100 ppm.

Displacement treatments involve filling the production tubing with corrosion inhibitor, allowing it to stay in contact with the tubing for a period of time (up to several hours) and then producing the inhibitor back through the production equipment. Squeeze treatments are similar to displacement treatments except that the corrosion inhibitor is pumped into the formation. These two treatment methods are usually used in wells with lower production rates.

### ***Bactericides***

Sulfate reducing bacteria (SRB) are the most common biological problem found in oil and gas production facilities. SRB reduce the sulfate ion to hydrogen sulfide, which causes chemical corrosion, steel embrittlement, and fouling of equipment by formation of iron sulfide. There are three common chemical types used as bactericides in production operations, quaternary amine salt, amine acetate, and gluteraldehyde.

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Each of these bactericides are highly water soluble and are sold as aqueous solutions with bulk concentrations ranging from 10% - 50%. Application of bactericides is either through slug treatments or continuous treatment. For a slug treatment typical concentrations will be between 100 – 200 ppm for 2 –6 hours, once or twice a week, depending on the type of production, volume of produced water and size and complexity of the production system being treated. Continuous treatment concentrations usually range between 5 – 20 ppm and will vary based on the same factors just mentioned.

### ***Hydrate Inhibition***

Natural gas hydrate is an ice-like solid that can form in natural gas in the presence of water under certain thermodynamic conditions (usually high pressure and low temperature). Hydrates can plug piping, stopping fluid flow, or pieces of hydrate moving through pipes or equipment can cause catastrophic failures.

Hydrates can be controlled mechanically and with treatment chemicals. Thermal insulation and heat tracing is often used to maintain fluid temperatures above that of hydrate formation. Chemical hydrate inhibitors work the same way antifreeze works in a car, by chemically altering the freezing point of the fluid. Mechanical and chemical methods are commonly used together where there is a continuous risk of hydrate formation or where the consequences of hydrate formation are severe, i.e. plugging of a wellhead or a flowline.

Ethylene glycol and methanol are the two chemicals used for hydrate inhibition, with methanol use being the most common due to cost. Treatment concentrations depend on the specific thermodynamic situation but usually range between 5 – 15 gallons per million cubic feet of produced gas for either methanol or ethylene glycol. The volume of ethylene glycol required for an equivalent level of protection is less than ½ that required for methanol. Risks from hydrates are one of the main reasons gas wells are usually shut in at the onset of significant water production. About 50% of the methanol used for hydrate inhibition will stay in the discharged water stream; the rest vaporizes into the gas. Essentially all of the ethylene glycol will stay with the produced water waste stream. However, when ethylene glycol is used, glycol recovery equipment is used due to the cost of ethylene glycol. Most of the glycol is recovered prior to discharge. The exact amounts remaining may vary.

### ***Dehydration***

Removal of water vapor from natural gas to meet sales specifications, dehydration, is commonly done in gas processing plants. Triethylene glycol (TEG) is almost exclusively used for this purpose. TEG absorbs water from the gas. To remove the water from the TEG, the TEG is heated to above the boiling point of water causing the water vapor to separate from the TEG. The condensed water removed by dehydration is discharged, however because the process of separating the water from the TEG is essentially a distillation process, unless there is an upset situation, there will not be any significant concentration of TEG in the discharged water. The discharged water from this process is essentially distilled water with small amounts of TEG.

### ***Mineral Deposits***

Inorganic mineral compounds in produced water can be deposited on the metal surfaces of production equipment with severe consequences. Deposits at perforations or in production tubing can reduce or stop production. Deposits in surface equipment can increase operating pressures and reduce efficiency.

Deposits in heater tubes can increase fuel use and operating temperatures resulting in increased air emissions. The most common of the mineral scales is calcium carbonate. This is essentially the same

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material that is formed as a mineral deposit on a water faucet. Other common mineral deposits include calcium sulfate (gypsum), strontium sulfate, and barium sulfate.

Control of mineral scales is through chemical treatment alone. All of the chemicals used for control of mineral scales work by interfering with crystal growth. There are three common types of chemical compounds used for this purpose, phosphate esters, phosphonates, and acid polymers. All scale inhibitors are highly water-soluble and will stay with the produced water to discharge.

Typical treatment concentrations are 3 - 5 ppm. Scale inhibitors are used either in squeeze treatments into the producing formation or by continuous injection.

### ***Emulsion Breakers***

There are two types of emulsions, normal and reverse, and both exist in oil production. In a normal emulsion, water droplets are dispersed in the continuous oil phase. In a reverse emulsion, oil droplets are suspended in the continuous water phase. Produced water treatment to discharge standards is simply treatment of a reverse emulsion. The stability of an emulsion can be increased by the presence of naturally occurring materials such as solids, resins, asphaltenes, and organic acids in the produced fluids. Additionally, introduced materials such as corrosion inhibitors, bactericides, and corrosion inhibitors can also increase emulsion stability.

Both technology and chemical treatment are used to treat (break) emulsions. Technological solutions include increased residence time, gravity enhancement, increased temperatures and use of electric fields. The performance of each of these technological solutions can be improved using chemical additives. Chemical emulsion breakers work by attacking the droplet interface to either cause dispersed droplets to aggregate intact or to rupture and coalesce into larger droplets. As the droplet size increases, the separation force between the oil and water increases and gravity separation is enhanced.

At least three types of chemical compounds are commonly used as normal emulsion breakers, oxyalkylated resins, polyglycol esters, and alkyl aryl sulfonates. Within these groups there are a wide variety of individual compounds and blends of compounds marketed. Operators often use more than one type of emulsion breaker at a single facility. Most emulsion breakers are offered in bulk concentrations of 30 - 50% with the remainder of the material being a heavy aromatic naphtha or similar material. From this it can be seen that these compounds will be highly oil soluble. Very little of the treatment doses of these compounds (<10% of the dosage concentration) will remain in the produced water stream and be discharged. Normal emulsion breakers are added continuously to the production system at concentrations ranging from 10 - 200 ppm (typically < 30 ppm) depending on the severity of the emulsion problem.

Reverse emulsion treatment is more problematic since the concentration of oil is much lower. Treatment of reverse emulsions is also done with a combination of technology and chemical treatment. The technological solutions are what are commonly recognized as produced water treatment equipment and includes parallel plate interceptors, flotation cells, hydrocyclones and other equipment.

This equipment can be used individually or as part of a system. The performance of this equipment can be significantly improved through the use of treatment chemicals. The most common compounds used for reverse emulsion treatment are polyamines, polyamine quaternary compounds polyacrylates and thiocarbamates. These compounds are generally soluble in water, however the oil solubility of polyamines will increase as pH increases. Reverse emulsion breakers are continuously added to the production stream at concentrations between 5 – 15 ppm (based on water).

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### ***Solids Removal***

Excessive solids in production systems can increase the stability of both normal and reverse emulsions. Compounds used for solids removal (coagulants and flocculants) are very similar to those used as reverse emulsion breakers; polyamines or quaternary polyamines that may be augmented with inorganic iron, zinc, or aluminum salts. As with the reverse emulsion breakers, these materials are water soluble. In their application as a solids remover however, they will stay with the removed solids, which are not normally discharged.

Typical treatment concentrations are between 5 - 10 ppm. Essentially all the compounds used in solids treatment are discharged in only trace amounts.

### ***Defoamers***

Foaming during treatment of produced fluids can cause excessive liquid carry over and reduce separation or treatment efficiency. In produced water treatment, foaming can either be a problem or a benefit, depending on the amount of foam. For example, a certain amount of foam is beneficial in gas flotation cells, however excessive foam makes subsequent handling of the recovered waste stream more difficult.

Two types of compounds are commonly used for controlling foam, silicones and polyglycol esters. These compounds work by disrupting the gas/liquid interface thus breaking down the foam. These compounds have low solubility in both oil and water. Treatment concentrations are 5 -25 ppm. In produced water treatment applications, these compounds stay with the recovered oil froth, which is returned to the produced oil stream. Therefore only small amounts of the defoamers are discharged in the produced water.

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