Avoid Problems in Process Water Systems

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Prevent corrosion, emulsification and fouling by implementing these operational and chemical measures.

In the production of petrochemicals, water is often used to control various chemical reactions or is a reaction byproduct. Because it is in intimate contact with the process streams, this water is commonly referred to as process water. Examples of processes that generate process water include ethylene, styrene and acrylonitrile production.

In olefins production, steam is used to control the pyrolysis cracking process by lowering the partial pressure of the feedstock and improving the efficiency. The steam is recovered as water in the quench system and is cleaned up and reused in the cracking process. Steam is used in the production of styrene monomer from ethylbenzene to increase conversion and protect the catalyst.

In the production of acrylonitrile, water is used to remove unreacted feedstock rather than moderate the process. Acidified water removes unreacted ammonia in a quench column. Then water is used to selectively absorb the acrylonitrile product and separate it from other process contaminants.

Those are just three of the many petrochemical processes that utilize water or steam, and the purpose of the water is different for each process. However, in all processes, it is economically and environmentally desirable to recover the water and reuse it in the process.

Significant quantities of hydrocarbons and various other contaminants can concentrate in the process water. These contaminants must be removed or controlled to minimize problems throughout the process water system. If unchecked, the contaminants can lead to fouling, foaming, corrosion and product quality issues.

This is particularly common in olefins production, where the process water system typically consists of a quench tower, a water strippper to remove hydrocarbons, and a waste-heat recovery system. Steam from the latter is sent to the pyrolysis furnace and is recovered as water in the quench tower. This complex water loop can experience a variety of problems due to contaminants in the process water.

This article discusses some of the most typical problems seen in the olefins plant, but the concepts are applicable to process water systems in other petrochemical processes.

Process description

Within an olefins plant, cracked hydrocarbon exits the pyrolysis section and enters the water quench section, which may also serve as a primary collection point for other process water generated within the plant (*e.g.,* compressor knockouts, etc.). A common quench system is shown in Figure 1, although the exact configuration varies depending on the process and unit design.

The quench water tower (QWT) cools the cracked hydrocarbon and recovers residual heat through absorption in the hot water. This is commonly followed by a process water stripper (PWS) and possibly a dilution steam generator (DSG).

Typical quench water has a temperature in the 80–91°C (175–195°F) range, and is used for low-level heating throughout the plant. The various heat-recovery steps cool the quench water to approximately 35–40°C (95–105°F) and return it to the quench water tower. As the hot cracked hydrocarbon mixes with the cooler quench water, the heavier hydrocarbon components are condensed. The lighter components and water vapor go overhead from the

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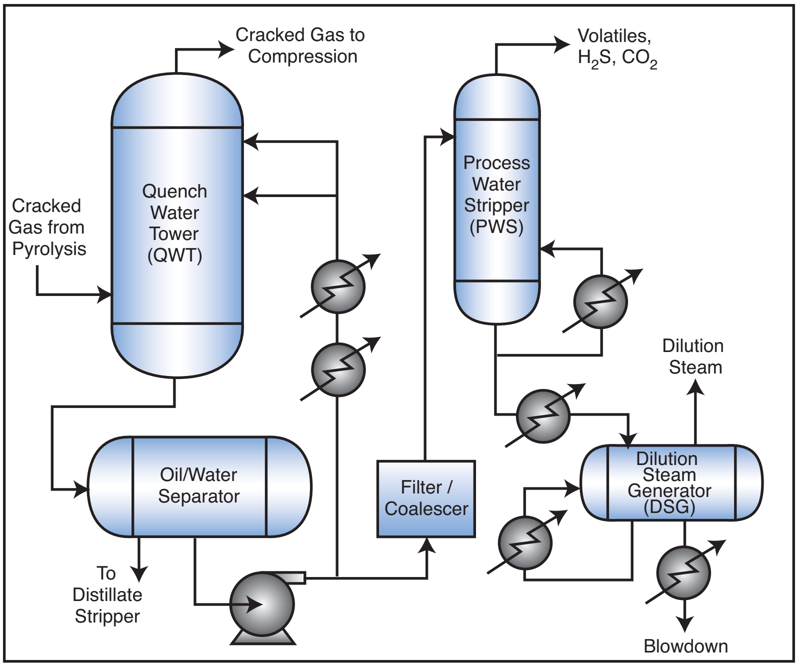
tower to the next process section.

The bottom draw from the QWT typically enters an oil/water separator. (In some designs, this separation may take place in the bottom of the QWT itself.) Three phases are generally present in the oil/water separator. Heavy hydrocarbons settle to the bottom, where there is a collection and/or removal system. The lighter liquid hydrocarbons rise to the top, where they are drawn off via a weir system and typically become part of a recycle stream or byproduct stream for export or further processing. The bulk phase is water containing both emulsified and dissolved light liquid hydrocarbons. This bulk water phase is circulated throughout the plant for heat recovery and then the cooled stream is returned to the QWT. From there, the water is distributed through the tower to quench additional cracked hydrocarbon, thus being termed "quench water." A sizeable volume is commonly blown down from the oil/water separator.



■ Figure 1. A typical ethylene plant quench-water system includes a quench water tower (QWT), process water stripper (PWS) and dilution steam generator (DSG).

It is common for a plant to have additional separation and/or filtration units downstream of the oil/water separator (*e.g.,* a liquid/liquid coalescer to further reduce the oil content of the water). However, coalescers and filters are often plagued with maintenance and/or operational problems.

The PWS then removes additional light contaminants (*e.g.,* CO_2, H_2S, additional light hydrocarbons, etc.). The bottom draw from the stripper serves as the DSG feed.

The "processed" quench water is then fed directly to the DSG. The heating medium for the DSG is often a hot process stream (*e.g.,* quench oil), or may be medium-pressure (12–14 kg/cm^2 [175–200 psia]) or low-pressure (4.5–5.6 kg/cm^2 [65–80 psia]) steam. The quench water blowdown (to wastewater) from the DSG is minimal, usually 2–5% of the DSG feed rate.

Problem areas

The quench water is contaminated with a variety of hydrocarbons, acid gases, organic acids and dissolved solids. Before the water can be reused for dilution steam, it must be cleaned of hydrocarbon and solids, and corrosive species must be appropriately mitigated.

The most common problems in the quench system are emulsification, corrosion and fouling — which are typically interrelated. Foaming can also occur, and is often a symptom of one or more of the primary problems.

The performance throughout the quench system depends very much on the performance of the upstream sections. To ensure good performance of the DSG, the PWS must be operating relatively problem-free. Likewise, problems in the QWT are likely to be compounded in the PWS and again at the DSG.

Corrosion

Three fundamental requirements for corrosion exist in abundance within the quench system:

- a reactive metal — most quench systems are constructed of carbon steel
- an electrolyte — water is the most common
- a corrodent — acids are the most common corrodents in quench systems.

Acids in the cracked hydrocarbon will condense in the quench water. The acids typically found in quench systems are organic acids — for example, acetic, formic, propionic and butyric (table). These acids are all highly soluble in water. The quench water pH is buffered in the 4.5–5.0 range because the pKa of the organic acids average around 4.75.

Table. Common organic acids found in quench systems.

Acid	Formula	Boiling Point	Solubility in Water	pKa
Formic	HCOOH	100°C (212°F)	100%	3.8
Acetic	CH_3COOH	118°C (244°F)	100%	4.8
Propionic	CH_3CH_2COOH	141°C (286°F)	100%	4.9
Butyric	$CH_3(CH_2)_2COOH$	165°C (330°F)	100%	4.8

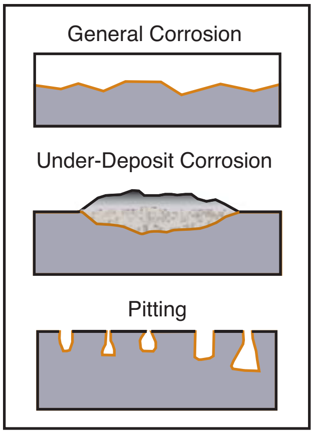


Figure 2. Common corrosion morphologies.

Hydrogen sulfide, sulfuric acid and thiosulfate can be found as a result of sulfiding chemicals being used for coke inhibition in the cracking furnaces. This can cause large fluctuations in the pH of the quench water. Quench water pH values as low as 3.0 have been seen when furnaces are being brought online and are being pre-sulfided. Although chlorides are typically not a problem in the quench system, they are occasionally seen. System pH can vary due to changes in feedstock and unit operation.

Low pH conditions can cause general corrosion throughout the system. General corrosion refers to a uniform corrosion across a metal surface due to acid attack (Figure 2).

Also common in these systems, and often more serious, is under-deposit corrosion, which can occur as a result of either organic or inorganic fouling. Under-deposit attack is a localized attack resulting from deposits on a metal surface that produce concentration cells. Water trapped inside these cells can concentrate corrosive species that cannot be neutralized by the bulk fluid's neutralization chemistry, and very aggressive localized corrosion can result. This corrosion can occur while the bulk fluid pH is adequately controlled and corrosion is believed to be under control. The rate of under-deposit corrosion can be 10–100 times the general corrosion rate.

Additional localized pitting corrosion within the quench system is often an indication of oxygen-related corrosion.

Indications of corrosion in the quench circuit include:

- low pH conditions. Every system is different. Some quench towers can operate with little or no corrosion at pH levels as low as 5.0, and other systems will require a pH of 7.0–7.5 to minimize corrosion. Most strippers require a pH in the 6.5–7.5 range. Many DSGs are operated with a blowdown pH of 8.0–8.5, but those with a history of corrosion problems typically perform best with blowdown pH in the 9.0–10.0 range.
- high iron concentrations in the water. Due to the high volume of water, even iron levels of 1–2 ppm can indicate a very severe corrosion problem
- wall thinning. Piping and column wall thinning is a result of corrosion.
- equipment failures. Tube leaks are often caused by under-deposit corrosion. However, equipment failures can also be caused by oxygen attack and generalized corrosion. Pump impeller failures can occur due to generalized attack or oxygen attack.
- high oxygen levels in the DSG blowdown. Typically, oxygen levels greater than 0.1 ppm can be of concern.
- inorganic fouling. This is generally due to the deposition of corrosion products.

Operational solutions to corrosion

Changing feedstocks can reduce or eliminate quench water corrosion problems. However, the plant's flexibility to crack different feedstocks may be limited by design or the availability of certain feeds. This could result in lost revenues if the plant has to switch to more expensive feedstocks.

Controlling the quench water pH can minimize corrosion problems. This can be accomplished in several ways, although each has its own drawbacks that must be considered:

- recycling waste streams from downstream amine or caustic gas scrubbers. These streams may contain polymers and solids that can deposit in equipment in the quench water circuit to cause fouling. Thus, this method of pH control could contribute to additional problems.
- routing compressor knockout-pot liquids back to the quench system. Knockout water can contain reactive polymers and hydrocarbons that can increase or stabilize emulsions and/or contribute to additional fouling potential.
- adding tramp amines. In some cases, there are already tramp ammonia and/or amines present as a result of neutralizers being added to the boilers (makeup steam) or from ammonia present in the feedstocks. Amine-based neutralizers added to the boiler are extremely volatile and can be vaporized back into the dilution steam going to the cracking furnaces, where they can be cracked to ammonia.

Identifying and reducing or eliminating oxygen intrusion can control oxygen pitting. Identification can be difficult because intrusion may not be continuous. Elimination of the intrusion source(s) may require capital investment.

Chemical solutions to corrosion

Corrosion can be controlled by adding a neutralizer to the quench water, PWS feed, and/or DSG feed to raise the pH. Performance can be optimized with multiple injection locations and different pH targets for the different sections of the system. Various neutralizers may be used:

- ammonia. It is often difficult to control the pH within the desired ranges using ammonia. Some producers have experienced product specification problems.
- caustic. It can also be difficult to control the pH within the desired ranges using caustic. Foaming in the DSG and/or operational upsets can cause sodium carryover into the dilution steam, which can lead to undesirable sodium levels in the cracking furnaces and result in an increased coking rate.

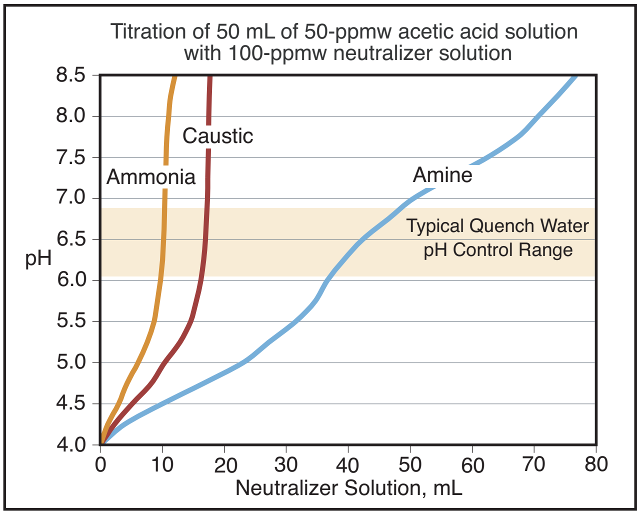
- neutralizing amines. Organic amines are more expensive than ammonia or caustic, but they have many advantages. Organic amines can be carefully selected to provide buffering in the desired pH region for tight pH control (Figure 3). Water-soluble organic neutralizing amines can be selected specifically for the acids present in the system. The amines should have an appropriate amine vapor/liquid distribution ratio to minimize volatilization into the dilution steam going to the cracking furnaces. However, if there are any corrosion issues in the steam condensate, then a volatile amine may need to be added to protect that area. The neutralizer salt properties should be such that they will form non-adherent, liquid-dispersible salts that will not lay down in equipment to cause under-deposit corrosion or fouling.
- combination programs. Amine neutralizer costs may be reduced by feeding a baseline level of caustic or ammonia and trimming with an amine neutralizer for pH control.
- coordinated phosphate. To protect the DSG reboilers from corrosion due to surface boiling phenomena at the water/steam interface, it may be necessary to add some coordinated phosphate chemistries to aid buffering at the higher pHs required to protect this area.

A water-dispersible organic filming inhibitor can be used in conjunction with the neutralizing amine. The filming inhibitor will form a monomolecular film on the metal surface to form a protective barrier against corrodents.

An oxygen scavenger chemistry can be applied to address oxygen pitting corrosion. Minimizing oxygen can also reduce potential polymerization of various polymer precursor contaminants (*e.g.,* styrene, isoprene, indene, etc.) often found in DSG foulant deposits. The polymerization reactions may be catalyzed by oxygen, so this approach can also aid fouling control and reduce under-deposit corrosion potential. Certain oxygen scavengers are volatile and can aid passivation of the steam system as well.

The corrosion control program should include monitoring of some or all of the following:

- pH in the PWS feed, DSG feed and DSG blowdown
- iron in the PWS feed, DSG feed and DSG blowdown
- dissolved oxygen in the DSG feed and DSG blowdown
- organic acids (*e.g.,* formic, acetic, propionic, butyric) in the QWT
- inorganic acids (*e.g.,* sulfuric, hydrogen sulfide, sulfurous, thiosulfate) in the QWT
- process parameters — water and process stream flowrates, temperatures, feedstock changes and furnace-decoking cycles
- corrosion probes or corrosion coupons at strategic locations throughout the system
- failed portions of process equipment to confirm the specific corrosion mechanism.



■ Figure 3. Neutralizing amines provide tighter pH control than strong bases (*e.g.,* ammonia, caustic, etc.).

Emulsification and fouling

The emulsification of water and hydrocarbons in the quench water can make the normal separation of these two phases in the oil/water separator difficult. The degree of fouling throughout the system is typically directly related to the severity of the emulsion. Although inorganic fouling can and does occur in these systems, organic fouling is more common and more serious. The best way to control fouling in the DSG is to eliminate the emulsion in the quench water effluent.

Emulsion problems are aggravated by:

- fluctuations in the quench water pH below 4.0 and above 8.0
- liquid feedstocks and heavier liquefied petroleum gas (LPG) feedstocks such as butane
- high throughput rates and increased turbulence
- bringing a furnace online or taking it offline (*e.g.,* during decoke cycles).

Quench water contains high levels of both soluble and insoluble oils. The water-insoluble oils can be removed in the oil/water separation equipment. The water-soluble oils are removed via distillation/stripping. The efficiency of both of these steps is key to eliminating or reducing problems in the DSG. The degree of emulsification typically impacts the efficiency of separation and distillation/stripping.

Analyses of QWT effluent streams, PWS reboiler deposits, and DSG deposits commonly indicate the presence of aromatic oils containing indene, benzene, naphthalenes or acenaphthalenes. It is also common to find styrene and other polymer precursors present. These materials are carried via the QWT effluent into the PWS reboiler, DSG and DSG exchangers, and are the principal foulants in the PWS and DSG. The higher-molecularweight organics will drop out of solution and degrade, and to a lesser extent they will polymerize and foul reboilers, preheat exchangers and generator tubes. The deposits will continue to dehydrogenate over time until they form a carbonaceous material. When heat transfer is limited, the tubes must be mechanically cleaned.

Emulsification problems in the quench water can be recognized upon visual inspection. The appearance of emulsified quench water will vary from slightly hazy to milky, with or without free oil, depending on the severity of the problem.

The consequences of emulsion problems may be seen throughout the quench system:

- difficulty controlling the level in the oil/water separator
- fouling and/or corrosion in the DSG
- fouling and/or corrosion in the heat exchangers
- fouling and/or corrosion in the PWS
- high levels of oil and grease (O&G) and/or total organic carbon (TOC) in the DSG feed
- high benzene concentration in the wastewater
- compressor fouling — in rare cases, where significant amounts of quench water are carried over into the compressor, the hydrocarbon emulsified in the water can cause fouling.

Sensitivity to and degree of fouling varies tremendously from plant to plant. Some facilities operate with O&G levels of several hundred ppm in the DSG feed with no significant fouling problems. For others, fouling can be a problem when the O&G levels exceed 50 ppm. Some plants even desire to control levels at less than 20 ppm.

Fouling will result in reduced heat transfer in system exchangers and an increase in the makeup steam rate due to reduced DSG capacity. Additionally, fouling contributes to under-deposit corrosion.

Operational solutions to emulsification and fouling

Installing additional hydrocarbon/water separation equipment or liquid/liquid coalescers, if this equipment is not currently in place, can reduce quench water problems. However, this will increase the plant's capital and operating costs.

Changing feedstocks can also reduce or eliminate emulsion problems. But as previously noted, plant flexibility for cracking different feedstocks could be limited due to design or the availability of certain feeds, potentially resulting in lost revenues if the plant has to switch to more expensive feedstocks.

Controlling the quench water pH can lessen emulsion problems. In general, a slightly acidic pH will aid emulsion resolution more effectively than a basic pH. However, the system's sensitivity to corrosion will limit the permissible pH range.

Modification of the DSG blowdown system can facilitate improved removal of heavy hydrocarbons, solids and inorganics that can accumulate and contribute to fouling.

Chemical solutions to emulsification and fouling

Most hydrocarbon-in-water emulsions can be resolved through the use of emulsion-breaking chemicals. Since water is the continuous phase, reverse breakers are preferred to separate hydrocarbon from the water. Water-soluble demulsifiers of positively charged solution polymers are added to neutralize the negative surface charge on the particles, thereby destabilizing the particles. This increases droplet size so that the once-emulsified oil droplets rise back to the oil phase in the settlers, resulting in improved separation of the hydrocarbon and quench water.

Quench water emulsions cannot be accurately simulated in the laboratory. On-site emulsion-breaker screening tests using fresh quench water samples is the best way to determine the appropriate chemistry for the system. An emulsion breaker that works in one system will not necessarily work in another because quench water systems and emulsions vary significantly from plant to plant.

Determining an effective dosage range is important. These additives can easily be overfed. When that happens, the excessive chemical can stabilize the emulsion rather than break it.

In some cases, emulsion breakers alone cannot control all of the fouling in the PWS and DSG. A dispersant antifoulant additive can be beneficial, even necessary, because there can be a large amount of soluble oils in the water that cannot be removed in the oil/water separators or the PWS. The dispersant prevents the agglomeration and deposition of both organics and inorganics. Therefore, it becomes crucial to maintaining clean metal surfaces and preventing agglomeration and deposition of foulant. Dispersants provide protection against fouling during periods of variable operation that may impact emulsion-breaker efficiency. The dispersant itself should not contain any hydrocarbons that contribute to fouling and/or emulsification.

As mentioned earlier, it is common to have various monomer species present in the quench water feed to the DSG. These monomers can polymerize in the DSG and the DSG reboiler and cause fouling. In addition to depositing directly, they serve as a bonding component to increase deposition of straight-chain hydrocarbons, contributing to additional fouling. The presence of oxygen can catalyze the polymerization reaction. Even if measurements indicate that oxygen should not be a problem, some oxygen scavenger chemistries can also function as polymerization inhibitors, and their use can be beneficial in reducing free-radical polymerization.

The benefits of resolving emulsion problems through the use of a water-soluble reverse emulsion breaker and the use of a dispersant antifoulant are many and diverse, including:

- reduced fouling and/or corrosion in downstream equipment
- improved unit operation
- increased steam production
- reduced unit downtime
- lower maintenance costs
- lower energy costs due to improved heat transfer in heat exchangers
- increased production capability.

The chemical and service costs associated with emulsion breaker and dispersant antifoulant programs are typically quite low relative to the savings generated by such programs.

Many factors affect water quality. To ensure adequate-quality water, the following parameters should be monitored:

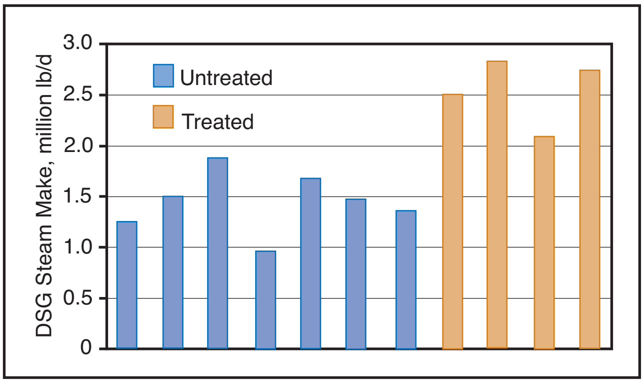
- O&G — the soluble and insoluble organic content in the sample that can be extracted into a solvent. Freon has historically been the most common solvent, but due to environmental concerns hexane is becoming more popular. The analysis is run on the entire sample, which would include an insoluble oil phase floating on top of the sample as well as the emulsified water phase on the bottom. This information can be used to optimize the emulsion breaker dosage, confirm proper emulsion-breaker chemistry, and quantify the benefits of treatment.
- TOC — the soluble oil in the sample as ppm carbon. This information should be compared to the O&G analysis to calculate the amount of free oil available for removal with the emulsion breaker and the separation equipment.
- transmittance (turbidity). The physical appearance of the water should be thoroughly documented. The turbidity of the process water should be visually checked often to obtain a qualitative judgment of the water quality. The turbidity reading in terms of percent transmittance of the water sample should be recorded and used as an aid in making adjustments in chemical feed rate. Turbidity, TOC and O&G can be reasonably well correlated.
- pH. Process water pH levels should be monitored routinely, with the goal being to maintain as stable a pH range as possible. Wide swings in pH make it difficult to control the emulsion. The corrosion experience and monitoring will dictate the system's acceptable pH range.
- process parameters. Water and process stream flowrates, temperatures, feedstock changes, furnace decoking cycles, etc., should be measured and recorded. These data will aid troubleshooting and optimization.

Example. Emulsion breaker and dispersant antifoulant reduces DSG fouling

Problem. The dilution steam generator at one plant was fouling due to residual hydrocarbon emulsified in the quench water feed. Analysis of the quench water feed showed an oil and grease content of 100–200 ppm. The high temperatures reached in the dilution steam generator essentially cooked the hydrocarbon onto the process equipment. Fouling of the equipment reduced steam generation and necessitated supplementing the dilution steam with plant steam. Excess quench water that could not be sent to the DSG was blown down to the sewer, incurring wastewater disposal costs. The costs associated with DSG fouling included cleaning costs, increased energy usage and increased wastewater disposal costs.

Solution. This problem required a two-pronged approach. Initially, an emulsion breaker was fed to the system, but variations in operation limited the emulsion breaker's effectiveness. Therefore, the program was supplemented with the addition of a dispersant to the PWS feed, which is just upstream of the DSG. This location was chosen to ensure good mixing of the dispersant prior to the DSG as well as to protect the line and the preheat exchanger between the PWS and the DSG.

Results and benefits. The most significant improvement provided by the dispersant treatment was an increase in the DSG efficiency, which resulted in major improvements in the steam production. The DSG run lengths also increased, by an average of 50%. More importantly, though, the steam production increased to over 60% more than before treatment (Figure 4). This increased steam production provides cost-savings over imported plant steam and reduces the volume of wastewater generated.



■ Figure 4. A program of an emulsion breaker and a dispersant antifoulant improved dilution steam production.

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Conclusion

A variety of chemical additive treatments can be applied to address fouling and corrosion problems. No two systems perform exactly the same, and solutions are very specific to the unit and the problem. Among the chemical additive programs that may be needed are (Figure 5):

- neutralizers — ammonia, caustic, amines or combinations
- water soluble corrosion inhibitors
- dispersant antifoulants — for organics and/or inorganics
- emulsion breakers
- oxygen scavengers
- coordinated phosphates.

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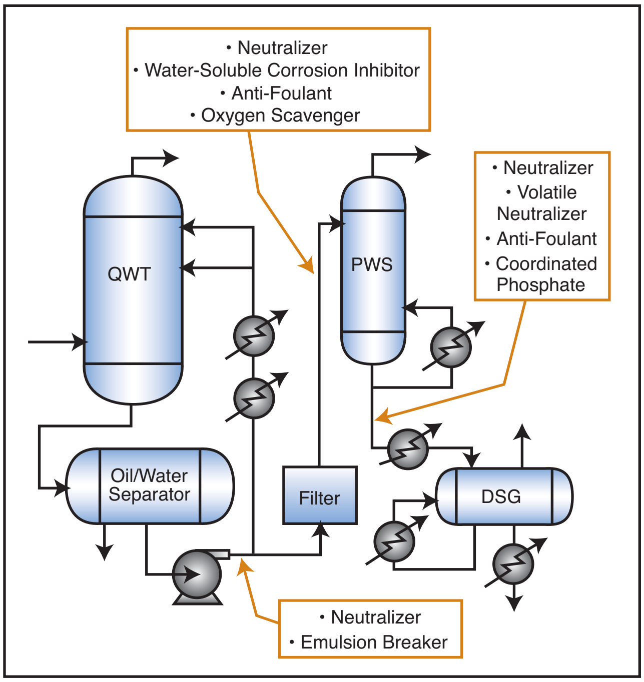

■ Figure 5. Various treatment options are available to address corrosion and fouling problems.