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Demineralized water system design: Considerations for the petrochemical industry—Part 1

Site utility leads, engineers and other professionals in the hydrocarbon/chemical processing industries (HPI/CPI) are facing a perfect storm of increasing demineralized water demand, end of life of existing demineralized water plant equipment, changing source water quality, corporate directives to diversify water sources, and pressure from regulators and community stakeholders to minimize the volume of waste generated from water treatment. The last decade has seen large-scale investment in ethane crackers, and a second wave of crackers are being designed and engineered that will begin service in the next few years. These investments have resulted in a keen focus on raw water treatment and demineralization for steam production, which, along with ethane, is a basic input to the cracking process. Many refineries, especially those along the U.S. Gulf Coast, have also seen increased demineralized water demands as they upgrade their operations to produce higher-value products. The main steam uses in refineries include steam cracking, stripping, steam distillation and vacuum distillation. Steam is also used for process heating, pumping and electric power generation.

Over the last 10 yr to 15 yr, these developments have coincided with increased water stress from both droughts and floods in various watersheds tapped by HPI/CPI for their source water. Key design considerations and approaches utilized in demineralized water treatment system design for HPI/CPI are presented in this article. Alternatives for demineralization systems are compared and analyzed, and key decision-making criteria are discussed to introduce utility engineers and professionals to the thought process behind demineralized system design. The choice of demineralized water treatment technology boils down to several factors, including the type of raw water, temperature and associated chemistry, nature of demineralized water demand and quality of steam required (mainly the pressure). Constraints related to the footprint (especially in brownfield developments) and any wastewater volume limitations at the site should also be considered in the design process.

Source water.

The following are types of source water that can be used in processing plants.

Surface water. Surface water sources for demineralized water treatment include rivers, lakes and oceans. Overall, 72% of all water used by refineries in the U.S. is drawn from rivers and lakes.[1] Surface water is most often pumped directly from a water body or drawn through a canal by a quasi-state body, which then supplies the water to several industrial customers. However, the total volume allocated to users might be regulated by state or local authorities to ensure that supply is available for all users. Seawater is also used for once-through cooling in some coastal refineries. The use of seawater is limited to coastal refineries and chemical facilities due to high conveyance cost and associated corrosion-resistance material requirements. In addition, high ionic strength, compositional variability in estuarine locations, high suspended solids and macrofouling organisms all contribute to high maintenance cost and operational complexity in seawater systems.

Groundwater. It has been reported that 10% of the water used by refineries is drawn from groundwater.[2] Groundwater can be very hard, with high mineral content, making it more expensive than lake water to treat into demineralized water. Some brackish groundwater is also available as a water source, but its high cost of treatment limits its use by most refineries. Furthermore, there are concerns related to the settlement of ground due to long-term groundwater extraction. Groundwater also typically has higher concentrations of reduced ions—such as iron and manganese—which, when brought to the surface, will oxidize and require specialized pretreatment prior to handling in a demineralized system. Combined, these factors mean that groundwater rarely provides a significant portion of the demineralized water supply at most industrial facilities—although there are some exceptions in the absence of alternate water sources.

Municipal wastewater reuse. Municipal wastewater generally consists of grey water and black water. Grey water includes water from bathing, hand washing and clothes washing, while black water includes water from kitchens, sinks and toilets. The combination of grey water, black water and storm water is treated in a municipal treatment plant and the effluent could be used in a refinery for boiler feedwater with further polishing, particularly for trace organics. The cost of conveyance from municipal wastewater treatment plants (WWTPs) into the refinery, along with extensive pretreatment to remove soluble organic carbon, should be taken into consideration and will result in increased treatment complexity and higher capital and operating costs than in instances when a typical city water supply is used. A more common strategy is to reuse treated municipal wastewater for cooling, which, in turn, frees up surface water for use as feed for demineralized water treatment.

Industrial wastewater reuse. Wastewater generated from oil refinery and petrochemical plants could potentially be reused after further treatment, as cooling water offers the prospect of freeing up higher-quality raw water for demineralized water usage. Cooling system blowdown water is also a potential candidate for demineralized system source water, after further treatment. However, in contemplating cooling water for use as demineralized supply, the water chemistry and process design must be thoroughly reviewed, with special consideration given to the capability of the demineralized plant to handle condenser leak events in the cooling system. The benefits of reusing refinery wastewater include consistent water quantity and quality; reduced demand on other water sources; and reduced discharge to water bodies. Total dissolved solids (TDS) concentration is the primary concern of industrial wastewater reuse. A TDS concentration of 1,000 mg/l or less is generally considered acceptable for reuse as cooling water, fire water and wash water. Typically, reusing any type of wastewater, including from industry, requires evaluation on a site-specific basis regarding wastewater availability, reliability, quality, energy consumption and process design.

Reusing all industrial wastewater with no liquid waste stream discharged into the environment is termed *zero liquid discharge* (ZLD). This water reuse concept has the potential to produce a portion of its recovered water as a high-quality distillate, which is very suitable for supplementing demineralized water production. It should be noted that ZLD usually entails a high treatment energy requirement, high capital cost (due to the need for exotic metallurgy) and high operational complexity. A decision to pursue a ZLD outcome is typically driven by either severe water scarcity and/or regulations and is rarely considered as part of site demineralized water strategy.

Water quality characterization. It is critical that appropriate water quality characterization studies are undertaken at the outset of any demineralized plant design project. For a relatively small sum of money (low thousands of dollars vs. hundreds of millions of dollars required for the demineralized plant construction and the billions of dollars for the overall facility), a good water quality data set can be collected to characterize and select source water and decide treatment process configuration. Often, data is not collected or inadequately detailed (e.g., some parameters are not collected, or no data is collected during times when the river is in flood or at minimum flow). To prepare a robust system design, data covering all typical quality and flow scenarios giving a complete picture of the anticipated water quality in the watershed is required. Understanding trends in suspended and colloidal solids, including colloidal silica, can be very valuable in the design of the treatment system. Assessing the potential for algal blooms and any anecdotal data related to past bloom events (e.g., duration and frequency) is also helpful in designing an effective pretreatment process. At a minimum, seasonal data over a period of 5 yr–10 yr is typically used as a starting point for a water chemistry basis of design. If available, longer periods of data—from site records or publicly available databases—can also be helpful to understand longer-term trends.

Pre-treatment. Prior to demineralized water treatment, most raw water sources must first undergo pretreatment to remove suspended solids and reduce scale forming hardness and/or compounds that have a propensity to generate corrosion. Depending on the source of raw water, water chemistry varies significantly. Relative ranges for key parameters are shown in TABLE 1. Main contaminants of concern for boiler feedwater include:

- **Suspended solids.** Suspended solids will settle out on equipment surfaces and cause deposition.
- **Total hardness.** In most waters, nearly all hardness is due to calcium and magnesium. Hardness can cause scale in heat exchangers, pipe and vessel surfaces, resulting in unnecessary downtime and reduced process performance (e.g., in heat exchangers).
- **Silica.** Hard scales resulting from silica are called silica-based deposits. These result from either amorphous silica and/or magnesium silicate. Silica entering a boiler can also be carried with the saturated steam as silicic acid, which can cause precipitates on metal surfaces. Hence, silica is considered one of the most critical parameters in any demineralized water treatment system and it is essential to closely monitor and control silica in the demineralized water makeup supply and, in turn, the demineralized water.
- **Iron.** Soluble and insoluble iron will combine with phosphates and hydroxides to form scale and cause corrosion and overheating problems.
- **Dissolved solids.** High ranges of dissolved solids can cause process interference and foaming in the boiler.
- **Total organic carbon.** Under high temperature and pressure, organic compounds can break down and form carbonic acid in the steam and condensate. This results in an increase in the conductivity of the steam and reduced pH in the condensate, increasing the propensity for corrosion around the steam system.
- **Sodium.** Sodium can build up on critical components as steam condenses and causes embrittlement, leaks and cracks.

TABLE 1. Typical ranges of main contaminants from different source water[3,4,5,6]

	Suspended solids, mg/l	Total hardness as $CaCO_3$, mg/l	Silica, mg/l	Iron, mg/l	Dissolved solids, mg/l
Surface water, river/lake	60–2,000	10–180	5–30	0.5–1	100–2,000
Surface water, seawater	< 500	< 6,000	> 10	1–3	> 35,000
Groundwater	10–50	< 1,000	1–30	< 20	100–30,000
Municipal WWTP effluent	< 30	< 200	5–20	< 0.5	600–1,000
Industrial WWTP effluent	Site-specific data				

In demineralized treatment processes, it is critical that adequate pretreatment is used to remove colloidal materials and suspended solids. Otherwise, it can lead to the failure of the demineralized treatment system. The degree and complexity of the pretreatment equipment are determined by the raw water quality. In a small flow facility, a low level of suspended solids (< 30 mg/l) might be managed with just cartridge filtration. However, it is more common in the case of surface water for pretreatment to include disinfection, solids clarification and filtration. Two common pretreatment systems for suspended solids removal are media filtration and membrane filtration. The following will introduce these systems, along with their advantages and limitations.

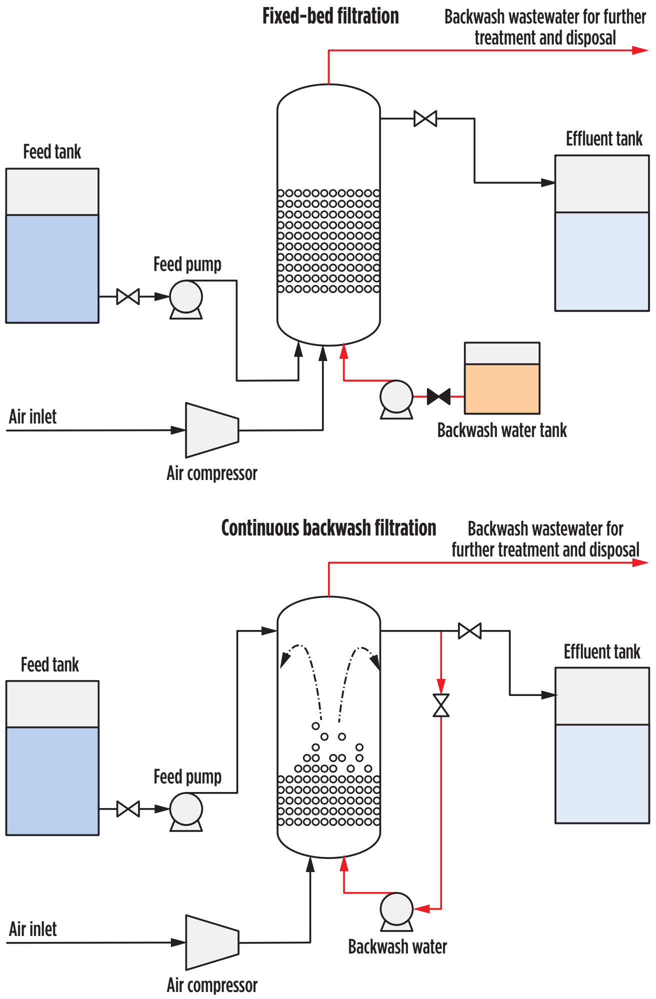

FIG. 1. Comparison between fixed-bed filtration and continuous backwash filtration.

Media filtration captures pollutants through physical filtration and adsorption. Typical media-based filtration systems are composed of sand, anthracite and other media. Media filtration can be utilized in either a fixed-bed or moving-bed configuration (**FIG. 1**). After a period in service (typically once per day or when differential pressure setpoint is triggered), fixed beds of sand and anthracite and/or other media combinations (housed in either pressure vessels or in concrete basins) are taken offline for backwashing (cleaning) to remove accumulated solids. This requires additional infrastructure (backwash tanks, associated pumps, sludge treatment, solids handling, etc.) and footprint. In a moving-bed (or continuous backwash sand filtration) configuration, the media is continuously backwashed and a separate backwash tank is not required. The backwash wastewater from both continuous backwash filtration and fixed-bed filtration are handled in similar fashion before disposal.

Sometimes, media filters are used to treat soluble components in the water, usually following the primary particle filtration step. The most commonly used media to remove soluble components include activated carbon (for organics) and zeolite (for removing hardness). A comparison of three types of media commonly used in media filtration is shown in **TABLE 2.**

Membrane-based filtration, using ultrafiltration (UF) membranes that have a pore size of around 0.05 µm, is another way to remove suspended solids. The thin, permeable, hollow-fiber membrane layer physically excludes particles in the water, allowing only soluble components (and the water itself) to pass through into the ultrafiltrate. Two main formats of membrane filtration systems exist: pressure and vacuum-driven. Pressure-driven membrane systems use membrane elements installed in pressure vessels, and the membrane separation process is driven at 20 kPa–250 kPa (3 psi–36 psi). Vacuum-driven systems immerse the membrane modules in a tank, and the filtrate is drawn through the membranes via suction. A comparison of media filtration and UF is provided in **TABLE 3.**

The selection and performance of pretreatment technologies largely depends on feedwater quality. UF usually shows better removal efficiency for total organic carbon (TOC) and turbidity as compared with media filters for river water.[7] UF is

TABLE 2. Common media used for filtration

Filtration media	Advantages	Limitations
Sand and other mixed-media formats	• Removal of suspended solids to less than 5 mg/l • Simple cleaning and inexpensive backwashing systems	• Water temperature should be less than 65°C (120°F) to avoid pickup of silica • Does not remove dissolved solids
Activated carbon	• Removal of organics and chlorine residual to protect downstream unit operations, such as ion exchange and/or membranes • Can accommodate influent fluctuation in the concentration of chlorine or organics	• High cost of bed replacement • Can suffer attrition loss during backwashing
Zeolite	• Removal of hardness, iron and manganese • Not as commonly used as carbon and sand	• Stringent operating conditions: o pH: 6.6–8.8 o Maximum water temperature: 38°C (100°F)

also less susceptible to particle breakthrough and offers a more reliable barrier than media filtration. However, UF is more sensitive to algae blooms, high natural organic loading, reactive species such as manganese, certain types of colloidal contaminants and water temperature variation. Increased biofouling has been observed on UF, compared to media filters for seawater pretreatment, in some instances.[8] The selection and deployment of the most effective filtration solution should be based on site-specific water quality parameters. Other factors, such as footprint, construction cost and lifecycle costs, should also be considered in the final selection. If the filtered water is used as cooling tower makeup, the value of performance benefits from better-quality water (e.g., increased cycling of cooling towers and reduction in fouling of heat exchanger surfaces) should also be considered in the selection of filtration technology.

After pretreatment, the feedwater—free of suspended solids—passes through the demineralized process to remove undesirable ions. These include heavy metals and, in most refineries, the entire dissolved solids content of the water. The target quality of demineralized water treatment depends on the pressure at which the boiler is operated. The general principle is that the higher the pressure, the higher the quality of water required. A low-pressure boiler can usually tolerate some feedwater hardness, while almost all impurities must be removed from water used for high-pressure boilers. Boiler feedwater quality requirements issued by the American Society of Mechanical Engineers (ASME) are shown in **FIG. 2.**

To ensure the purity of boiler feedwater, key parameters, such as TDS and silica, must be monitored. Conductivity is one of the most commonly used methods to obtain a rapid and reasonably accurate measurement of water/steam purity. However, some gases (especially carbon dioxide) can ionize in water solution and interfere with measurement of dissolved solids by increasing conductivity. The measurement of silica can use a colorimetric technique, while the reliability of this method is low under high temperature/pressure (form of silica can change from non-reactive colloidal form into reactive ionic form). Online measurement of sodium using specialized glass electrodes can provide a very sensitive indication of contaminants in water and/or steam condensates. Sodium measurement can give reliable measurements down to a concentration of 0.1 µg/l, which is well below the purity at which electrical conductivity can be measured reliably. However, sodium electrodes can be prone to drift and must be regularly calibrated. Each of these three methods can provide an indication of boiler feedwater purity, and the combination of any two generally provides reliable confirmation of boiler feedwater purity.

The common demineralizing technologies include ion exchange, reverse osmosis and electro-deionization. Frequently, a

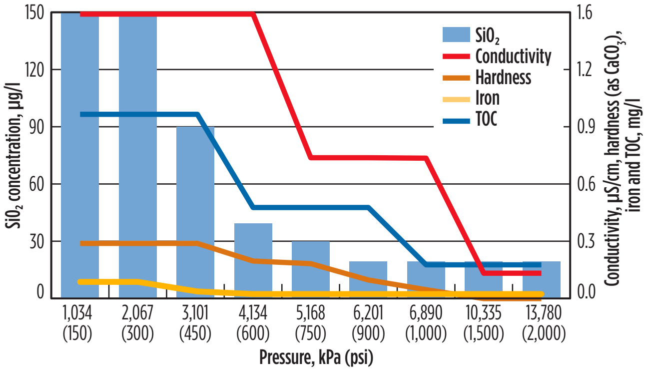

FIG. 2. Boiler feedwater quality requirements at various pressures. The actual target silicon dioxide (SiO_2) values in the demineralized water are set based on the site-specific considerations, including boiler cycles and types of metallurgy involved. Usually, the concentration will be in the range of 10 µg/l–20 µg/l for greater than 6,000 kPa (approximately 900-psi) steam.

TABLE 3. Selection guidance for media vs. membrane filtration

Criteria	Media filtration	Membrane filtration (UF)	Notes
Filtered water quality	–	+	Membrane filtration has a wider spectrum of particle removal capability than media filtration, as it represents a direct barrier to entry of contaminants. It generates higher-quality water (non-detect TSS and turbidity) on a consistent basis. It can remove colloidal silica.
Source water quality variation	–	+	Membrane filtration is better able to handle water quality variations, especially when combined with pre-clarification to keep gross solid loadings low.
Source water temperature	+	–	Throughput of membrane filtration is reduced at low temperatures.
Waste stream generation	+	–	Media filter backwash is 5%–7% of total feedwater, while membrane filtration backwash can be around 10%. Membranes may require additional cleanings and associated handling of cleaning waste.
Energy cost	+	–	Media filtration energy requirement is less than 0.05 kWh/m^3 and membrane filtration is 0.2 kWh/m^3–0.4 kWh/m^3.
Media replacement cost	+	+	Depending on how well either system is managed—can be comparable.
Capital cost	–	+	For large flowrates, UF may have a lower capital expenditure than media filtration. UF also tends to have lower installation costs, as UF is skid-mounted equipment that can be installed at a site quickly.
Footprint	–	+	UF has a lower footprint (typically 20%–30%) for the same flowrate.
Expandability	–	+	Modular design can permit easier staged expansion.

Note: (-) represents the less preferred option, while (+) stands for the preferred option[7] combination of these technologies is used to achieve the target water quality specification. Thermal methods to demineralize water, once quite common, especially in the Middle East, are now usually only considered in instances where a low-cost source of thermal energy is available.

Part 2. Part 2 of this article, to be published in the April issue, will discuss the common technologies and approaches considered for water demineralization and introduce the reader to demineralized water treatment design variables that must be considered for an effective design. HP

ACKNOWLEDGEMENTS

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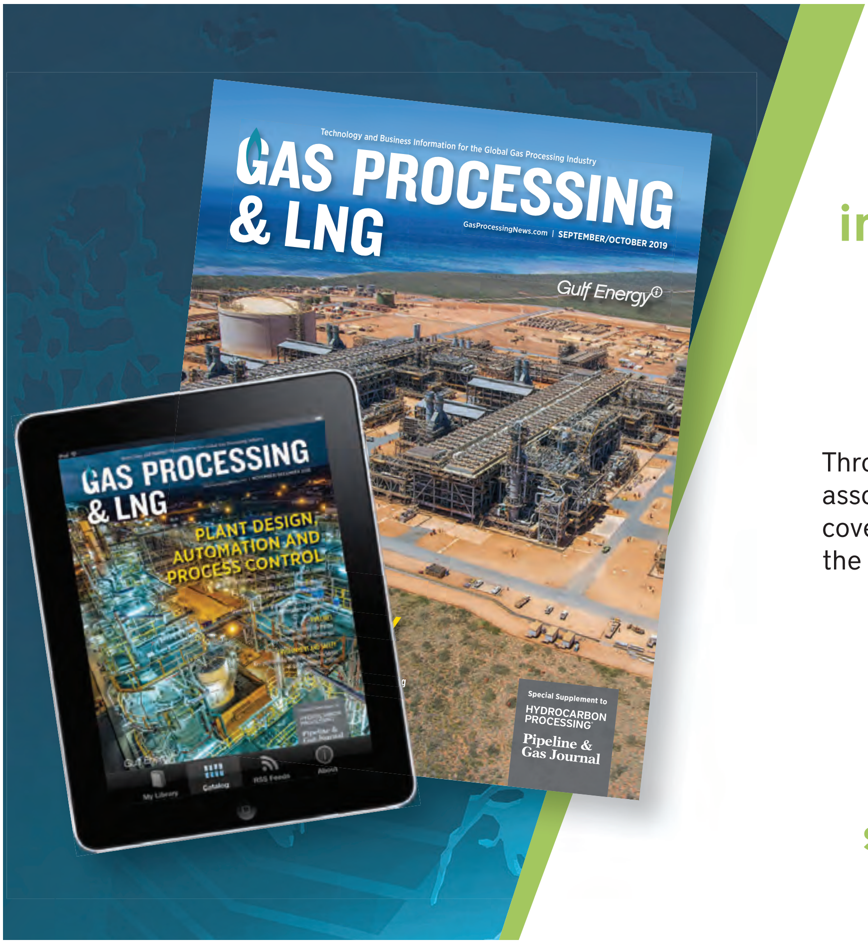

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Demineralized water system design: Considerations for the petrochemical industry—Part 2

Demineralized water treatment systems play an important role in the petrochemical industry. The ability to consistently supply demineralized water that is subsequently used for steam generation is essential for all types of steam cracking processes. During the conceptual design of demineralized water treatment plants, special attention must be paid to raw water source identification and the associated quality and reliability of the demineralized water desired. Other considerations include the nature of demineralized water demand, condensate return rates and amount of storage. As mentioned in Part 1 of this article (published in the March issue of *Hydrocarbon Processing*), a typical design decision matrix should consider raw water source selection, the type of pretreatment for suspended solids removal and the quality desired by other users (utility and cooling water makeup). Part 2 discusses common technologies considered for water demineralization, along with some considerations for demineralized water treatment plant design optimization.

Ion exchange (IX) process. In the IX process, ions of a given species are displaced from an insoluble exchange material—usually an organic resin. IX resins consist of an organic or network structure with attached functional groups. The exchange capacity is determined by the number of functional groups per unit mass of resin. Once the exchange capacity of the resin is depleted, the resin will begin to cease exchanging dissolved ions and must be regenerated prior to reuse.

Four major classes of resins in water treatment exist: strong acid cation (SAC), weak acid cation (WAC), strong base anion (SBA) and weak base anion (WBA). The type of resin selected is based on source water chemistry and constituents that must be removed. SAC resins are the most common resins used for softening and demineralization applications. SAC resin removes the non-carbonate hardness, and WAC resin removes hardness associated with alkalinity. Hence, weak acid resins are more suitable for high alkalinity water and for when the hardness-to-alkalinity ratio in the feedwater is greater than 1. SBA resins are used for dealkalization, de-silicization and organic trap applications, while WBA resin removes only the anions of the strong mineral acids such as sulfate, chloride and nitrate. Carbonate/bicarbonate and silica ions will pass through a WBA resin.

Typically, the selectivity of SAC is best for calcium and magnesium, and SBA resin is ideal for sulfate and nitrate. On a cation resin, the most weakly held ion is sodium, and silica is often the most weakly held by anion resins. Therefore, sodium and silica are usually the first to break through on bed exhaustion, and monitoring these offers a good means of confirming demineralized water purity.

WBA has a higher working capacity than SBA and offers good resistance to organic fouling—such as from the polymer carryover downstream of a clarifier and from total organic carbon (TOC). However, these resins do not remove silica and bicarbonate. SBA offers the lowest silica leakage, so WBA is typically paired with an SBA.

Degasifiers are commonly used to reduce alkalinity in decationized water by stripping CO_2, using air. This removes the loading of carbonate to the anion resin and results in lowered operating cost by reducing the frequency and associated cost of regeneration. However, the additional capital cost for a degasifier must be justified with a payback analysis and will depend on the raw water quality.

Mixed-bed systems. With both cation and anion exchanges, due to the acid base equilibria driving the exchange processes, there is a limit to how perfectly the ions can be removed. Thus, to obtain very-high-purity water, a mixed-bed deionizer—in which SBA and SAC are intimately mixed and contained in a single pressure vessel—is used. The combination of SAC and SBA resins allows for very low silica and low sodium leakage. A gel resin combination is most commonly used to allow for physical separation during regeneration. The two resins are mixed by agitation with compressed air so the mixed bed can be considered as an almost infinite number of anion and cation exchangers in series. In general, a mixed-bed IX step (**FIG. 3**) can lower the conductivity to result in demineralized water with less than 0.1 μS/cm and with an ionic silica content of less than 10 μg/l.

Waste stream management. IX resins must be removed from service and regenerated when the maximum allowable effluent concentration is reached. Ideally, this removal from service will take place slightly before sodium or silica breakthrough. The higher the total dissolved solids (TDS) in the water, the more frequently the resins must be regenerated. During regeneration, regenerant agents contact active exchange sites on the cation and anion resins, and replace the adsorbed ions by H^+ or hydroxide (OH^-), respectively. The common regenerant agents for cation and anion resins are mineral acid and caustic soda, respectively. The mineral acid used is often sulfuric acid due to lower cost, although hydrochloric acid is often preferred for superior regeneration performance.

The two main regeneration processes are: co-flow regeneration and counter-flow regeneration. For co-flow regeneration, regenerant flow is in the same direction as feed flow, while regenerant flow is in the opposite direction to feed flow for reverse flow regeneration. Hence, for reverse flow regeneration, the most highly regenerated resin is located at the point where, during normal operation, the deionized water leaves the resin vessel, which, in turn, leads to a better contaminant removal performance. In addition, counter-flow regeneration is more efficient in the use of water as compared with co-flow regeneration, since fast rinse and backwash are combined into one stage. Due to higher purity in the treated water, higher water efficiency, low leakage and less required regenerant, a reverse flow arrangement with uniform-particle-size resin offers the best regeneration performance. Co-flow regeneration systems are a little simpler in terms of valving and piping complexity.

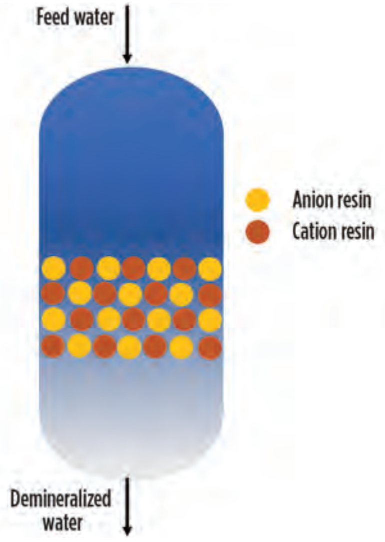

FIG. 3. Illustration of mixed-bed IX.

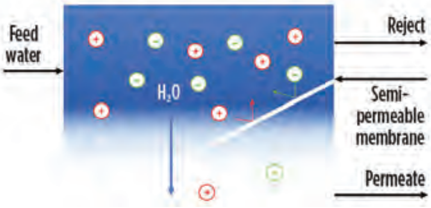

FIG. 4. Illustration of RO.

Regeneration can take place onsite or offsite. Onsite regeneration is typically utilized for large-volume users with more than 45 m^3/hr (20 gpm).[9] After onsite regeneration, the resin will be rinsed with treated water—a consumption that must be allowed for in system design. The regenerant waste must be treated before disposal. The common treatments for regenerant waste include pH neutralization and commingling with other waste streams for final disposal. For smaller systems [< 45 m^3/hr (20 gpm)], regeneration can be conducted offsite by a service contractor. The contractor will remove the exhausted IX exchange vessels and swap them out with pressure vessels containing regenerated resin. Offsite regeneration systems are much lower in capital cost than onsite regeneration due to the elimination of chemical handling equipment and storage facilities. However, offsite regeneration incurs higher operating costs and associated logistical issues that may hinder operational stability.

Advantages and limitations. Mixed-bed IX removes most impurities, except colloidal silica and nonionic organics. The system can be regenerated based on conductivity or silica concentration. However, mixed-bed systems normally have a lower resin capacity and a more complicated operating procedure because of the separation and remixing steps during the regeneration process. In addition, a separate acid or caustic regeneration system requires regenerant waste neutralization.

TABLE 4. Comparison of different RO membranes[10–12]

	PA	CA	PS
Sodium chloride (NaCl) rejection, %	> 98	90	95
Permeate flux	22 l/m^2/hr (lmh)–34 lmh or 13 gal/ft^2/d (gfd)–20 gfd	27 lmh–30 lmh or 16 gfd–18 gfd	75 lmh–94 lmh or 44 gfd–55 gfd
Chlorine tolerant	No	Yes	Yes
Cost	Medium	Low	High

Reverse osmosis (RO). RO is a membrane separation process capable of removing molecules with a molecular weight higher than approximately 200 daltons (Da), such as most colloids, naturally occurring organics, bacteria and pathogens from water (**FIG. 4**). RO is also able to remove both cations and anions. In the RO process, water is forced through a semi-permeable membrane at a pressure greater than the osmotic pressure characteristic of that water to produce a low-salinity permeate. The dissolved salts are retained on the reject side of the membrane, while water with minimal dissolved salts passes to the permeate side of the membrane. A continuous waste bleed stream, or reject, is maintained that sweeps salts from the membrane surface. This prevents the salt concentration from accumulating so much that the osmotic pressure exceeds the applied hydrostatic pressure, and permeation ceases.

Types of RO membranes include cellulose acetate (CA), polyamide (PA) and polysulfone (PS). **TABLE 4** compares the performance of these types. The most common choice for demineralization is PA. Pretreatments for RO include suspended solids removal, softening, ultrafiltration and disinfection to prevent scaling and biofouling.

The common configurations for RO systems are a one-pass RO or a two-pass RO. In a one-pass RO, the permeate has passed through an RO membrane just once. In a two-pass RO, the permeate from the first pass is treated a second time to produce a higher-quality permeate. With a two-pass RO, more than 99% of salt removal is usually achieved.

Waste stream management. RO recovery and reject stream flowrates vary by water source, and are primarily dictated by the solubility limits of sparingly soluble salts like calcium, strontium and barium salts. For a surface water system, a typical design for RO will have recoveries between 70% and 85%. Recovery from seawater will be lower at around 45%. Generally, reject quantities increase (i.e., recovery ratio decreases) with higher dissolved salt concentration in the water because the higher TDS tends to include more sparingly soluble salts. Higher salinity is not necessarily a cause of low recovery, but it will require higher operating pressures. The RO reject stream is often blended with other wastewater at the site for final disposal. Unless mandated by disposal requirements, it is uncommon to see the use of additional volume reduction processes, such as evaporation and/or crystallization on the reject stream, as these processes are typically very expensive to install and operate.

Advantages and limitations. A key advantage of RO systems, compared to IX processes, is that they have a relatively low chemical consumption and tend to have a more continuous operation—although they do require periodic shutdowns for cleaning. This is particularly advantageous when the influent TDS is higher than a few hundred mg/l. RO permeate can sometimes be suitable for boiler feedwater without further treatment, but it is often paired with a mixed-bed IX system for final permeate polishing. RO also removes colloids, including silica and a wide range of nonionic organics.

Even though RO produces high-purity water, the overall purity is usually not comparable with IX treatment unless the feedwater is already of good quality or a two-pass system is used. RO systems do not achieve as much removal of reactive silica as IX systems, but are much better at removing colloidal silica.

IX systems are a little more tolerant of poor pretreatment than RO, for which a robust pretreatment is essential to prevent membrane scaling and fouling. Several ions must be reduced before feedwater enters RO due to their scaling and fouling propensity. In general, the iron or manganese should be treated to less than 0.05 mg/l, barium to less than 0.01 mg/l, strontium to less than 0.01 mg/l, aluminum to a minimum, and silica to less than 20 mg/l.

In addition, RO operation is more sensitive to temperature. The rate of water permeation through the RO membrane increases as the feedwater temperature increases, since the viscosity of the solution is reduced and a higher diffusion rate of water through the membrane is obtained. Additionally, temperature more significantly impacts salt rejection performance in RO than in IX. Although the absolute operating range for RO is around 2°C–38°C, it has been reported that the optimum RO operation temperature is 25°C (77°F) and the upper temperature limit is around 35°C (95°F) to avoid membrane damage.[13] Conversely, IX can operate over a wider temperature range, including, if necessary, down to 0°C (32°F). Hence, preheating of the water may be required to achieve consistent RO performance when low water temperature is experienced.

Feedwater TDS concentration will also impact the RO performance, with higher feedwater TDS concentration decreasing permeate flow for the same feed pressure because the osmotic pressure increases, giving less net driving force to sustain permeation. A comparison of permeate flow under different TDS concentrations is shown in **FIG. 5.**

Another membrane-based technology called forward osmosis (FO) has attracted attention in both academic research and industrial development in the past 5 yr. Unlike RO, which uses pressure to drive flow through the membrane against the osmotic pressure gradient, FO utilizes a concentrated solution with a higher osmotic pressure than the feedwater to draw water from the feedwater into a "draw solution." The draw solution, diluted by the perme-

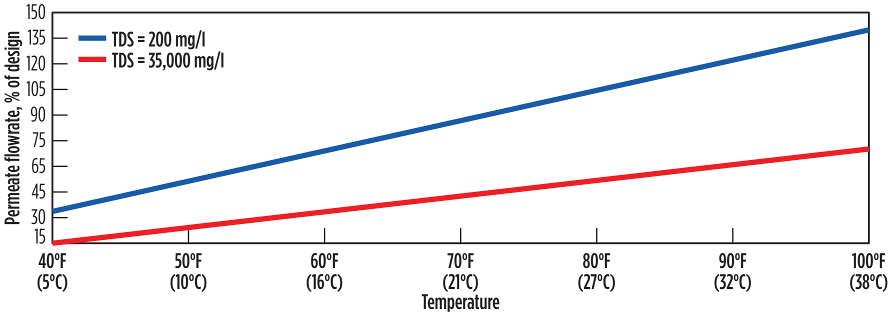

FIG. 5. Effect of temperature and TDS on permeate flowrate at constant pressure.

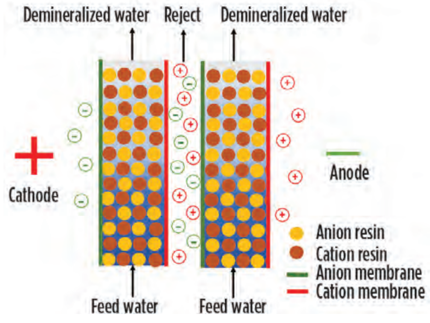

FIG. 6. Illustration of EDI.

ate drawn through the membrane from the feed stream, is reconcentrated to produce purified water and to recover the draw solutes. FO is reported to have several advantages over RO; however, the feasibility and reliability of FO systems on a large scale have not yet been widely demonstrated.

Electrodeionization (EDI). EDI utilizes electricity, IX membranes and resins to deionize water and separate dissolved ions from water. Each EDI module consists of five primary components: IX resin, two IX membranes (cation and anion exchange) and two electrodes (cathode and anode). When flow enters the EDI module, strong ions are scavenged out of the feed stream by mixed-bed resins. Under influence of a strong direct current field applied across the stack of components, charged ions are pulled off the resin and drawn toward the respective, oppositely charged electrodes. In this way, these charged strong-ion species are continuously removed and transferred into adjacent concentrating compartments (**FIG. 6**).

As strong ions are removed from the process stream, conductivity of the stream is reduced. The strong applied electrical potential splits water at the surface of the resin beads to produce hydrogen and hydroxyl ions. These act as continuous regenerating agents of the IX resin. Like IX, EDI can remove more than 99% of dissolved solids, except for colloidal silica.

Waste stream management. An EDI system typically converts 80%–95% of feedwater into product water, and the waste stream contains the same contaminants as in the feed, with 5–20 times higher concentration.

Advantages and limitations. The design of EDI provides continuous regeneration of IX resin without acid or caustic handling. EDI will also provide more consistent water quality in a compact space with low operating costs, provided power is available and its costs are acceptable.

However, EDI can be used only for water with hardness less than 1.5 mg/l to prevent calcium carbonate precipitation. Other drawbacks for EDI include a relatively high capital cost, high EDI stack replacement costs (a typical EDI stack lifetime is 5 yr) and difficulty in removing weakly ionized contaminants, such as silica, CO_2 and organics. Tanaka has compared the lifetime cost between EDI and IX and reported that, with an increase of TDS in the feedwater, EDI becomes increasingly cost-effective,[14] up to the previously mentioned water quality constraints.

However, detailed site-specific comparisons must be conducted. In addition, EDI is susceptible to fouling by colloidal silica or organic material typically found in the surface water, such as humic, fulvic or tannic acids.[15] Any ionic species formed from CO_2 gas will lower outlet resistivity of water produced by EDI, leading to decreased treatment efficiency. Hence, CO_2 management is required for an EDI system. At present, EDI systems are available only with plastic piping due to the danger of accelerated corrosion from stray currents.

For these reasons, EDI can be a good alternative to mixed-bed IX treatment, especially if paired with a two-pass RO, with which it can provide a demineralized water production system with low chemical consumption.

Electrodialysis reversal is another variation on EDI, where the polarity of the stack is reversed at a predetermined frequency. This technology is mostly suited for high-silica water (> 50 mg/l). It has lower capital cost, a larger footprint and higher operation and maintenance cost requirements when compared with RO, which is typically preferred when silica concentration is lower.

Thermal distillation (evaporation/condensation). The thermal distillation process requires thermal energy to form pure water vapor by heating the raw water source. This water vapor is then condensed on a cooling surface to collect as freshwater. Three thermal distillation technologies have emerged and are used commercially: multiple-stage flash (MSF) distillation, multiple-effect distillation (MED) and vapor compression (VC).

MED consists of several consecutive stages that are maintained at a decreasing level of pressure or temperature. In each stage, feedwater is heated by steam in tubes, causing evaporation of water. This newly generated steam flows into the tubes of the next stage (effect), heating and evaporating more water. Each stage essentially reuses energy from the previous stage, with successively lower temperatures and pressures after each one. Each stage mainly contains a multiphase heat exchanger.

In the MSF process, freshwater is produced in an evaporator of each stage by flashing some hot feed saline water due to low pressure. The produced water vapor passes through a demister to remove the entrained brine droplets and condenses on the external surface of the heat exchanger. The heat released from condensation is transferred to the flowing feed seawater through successive stages, resulting in increasing its temperature.

The VC distillation process is based on the principle of reducing boiling-point temperature by reducing the pressure over the liquid. Two methods are used to create the low pressure to evaporate incoming seawater: a mechanical vapor compressor (MVC), which is electrically driven; and a steam jet [thermal vapor compression (TVC)], which is driven by low-temperature heat. The

TABLE 5. Demineralized water technology summary

	IX	RO	EDI	MED-TVC
Typical recovery,[1] %	95	70–80	80–95	30–40
TDS removal efficiency, %	> 99	90–99	> 99	> 99
Colloidal SiO$_2$ removal	No	Yes	No	Yes
Pretreatment complexity	High	High	High	Low
Operation temperature	< 85°C (< 185°F)	18°C–35°C (65°F–95°F)	10°C–38°C (50°F–100°F)	49°C–71°C (120°F–160°F)
Waste stream treatment	Yes	Yes	No	No (but might be subject to temperature restrictions)
Energy consumption, kWh/m^3	1–1.5	3.3–5[2]	0.7–3.7	1–1.4[2,3]
Total electrical energy equivalent,[19] kWh/m^3	1–1.5	3.3–5	0.7–3.7	11–28
CO$_2$ generation,[4] kg CO$_2$/m^3	1–2	2–6	0.7–4	25–30

[1] Fraction of feed converted to demineralized water

[2] Range shown for seawater; brackish water is approximately 0.5 kWh/m^3–1.5 kWh/m^3 for an RO system

[3] GOR of greater than 12

[4] CO$_2$ intensity of each process depends greatly on the CO$_2$ intensity of the inputs

VC could be combined with MED designs to improve the energy efficiency of MED plants by taking advantage of exhaust steam from a steam turbine [usually 250 kPa–300 kPa (36 psi–43 psi)].[16] However, the higher the steam extraction pressure, the higher the electrical equivalent that is sacrificed to drive the desalination process.

The performance of distillation processes is measured by a dimensionless parameter known as gain output ratio (GOR), which is defined as the mass of distilled water per mass of input steam. Typically, higher GOR systems cost more, but consume less energy; therefore, they have lower operating costs. The GOR of MSF plants range from 8–12, 10–14 for MED, and 14–17 for TVC-MED.[17] Thermal distillation technologies are mostly used in regions where cheap energy is available, and they are often coupled with electricity production. The TDS in thermal distillation effluent is less than 5 mg/l.

Waste stream management. Like EDI, no additional chemicals are added into the thermal distillation process. Hence, the waste stream can often be discharged directly to an ocean outfall via a high-dilution diffuser.

Advantages and limitations. Due to high energy consumption and high capital cost, MSF is generally the process of choice for dual-purpose facilities (i.e., electric power and water production) and for applications that cannot be performed by other means, such as hypersaline groundwater. MSF has proved to be more economically favored than RO when energy costs are low, or when a waste heat source is available. MED combined with TVC has lowered capital cost and reduced power consumption. It has been reported that MED and MED-TVC require less electricity (1 kWh/m^3–1.4 kWh/m^3) as compared with RO (3.3 kWh/m^3–5 kWh/m^3), while MSF energy consumption is estimated around 4 kWh/m^3–6 kWh/m^3.[17] The lower energy consumption rate can make MED-TVC more economically comparable with RO, if there is no lost electrical generation.

In terms of pretreatment, the distillation process only requires simple pretreatment to avoid scaling and foaming by adding acid or advanced scale-inhibiting chemicals and anti-foaming reagents. In addition, the thermal distillation process is more tolerant to operational upsets and water quality variations.

However, the intensive combustion process for thermal distillation might pose environmental concerns associated with greenhouse gases. The CO$_2$ emissions for MED, MSF and RO are calculated to be 26.9 kg CO$_2$/m^3, 34.7 kg CO$_2$/m^3 and 4.3 kg CO$_2$/m^3, respectively.[18] Hence, for areas subject to a carbon tax or where CO$_2$ emissions are constrained, RO likely remains the more favorable process.

TABLE 5 summarizes the different demineralized water technologies.

Optimized design for demineralization. In general, relability and cost considerations must be evaluated during a demineralized water treatment plant design optimization. In this article, we have focused on design reliability, since it is an important consideration for the petrochemical industry, where demineralized water is a critical input to maintain operations. For demineralized water system design, both inherent reliability and mechanical reliability must be taken into consideration. Inherent reliability is the probability that the treatment plant can supply the demineralized water specification under all likely feed and demand conditions, while the mechanical reliabilty is related to the key pieces of equipment in the plant where failure may impact the demineralized water production rate.

Good data collection and a design appropriate to incorporate variabilities in demineralized water demand will improve the inherent reliability. For example, it is prudent to have a demand characterization workshop with all the demineralized water users. This allows for demand development to consider abnormal conditions such as plant outages; condensate dump (due to contamination); rate of condensate return during freezes; startups; and plans for more frequent occurrences, such as furnace decoking. Based on the workshop for demineralized water, demand rate curves can be developed. The demand curve can then be utilized to develop the design flowrate for the demineralized plant.

To achieve better mechanical reliability, a flexible equipment arrangement might be considered. Common configurations for demineralized water treatment include 2 × 100%, 2 × 75% and 3 × 50%; other configurations, such as 7 × 20%, have also been used. In general, a demineralized system should be adequate to accommodate sudden variations in water demand and allow isolation of an entire treatment train without impacting production, for maintenance flexibility. For example, in a 3 × 50% configuration, all major unit processes have three identical units, such that any two units operating at 100% capacity can meet the overall water demand.

Temporary and mobile water treatment systems also might be considered to handle short-term demineralized water demand. For example, using a third-party provider that supplies demineralized water treatment equipment in a mobile or a semi-permanent trailer format is an approach that many sites are considering for managing demand shortfalls during sustained peak events. It may make sense during the project planning stages to include a site footprint for trailers and tie-ins as part of a larger strategy to optimize the demineralized plant capacity. Some buffer treatment capacity can be built into the pretreatment processes (clarification and filtration) to allow for feeding of the third-party trailers during campaign events.

Providing adequate storage of demineralized water is another item that should be considered as part of the plant design discussion. Storing 12 hr–24 hr (or more, depending on site-specific needs) of demineralized supply, along with sufficient redundancy in the design, can allow for a guaranteed shutdown period, over which maintenance or retrofits can be made. This storage can also be used as a buffer capacity to fulfill instantaneous peak demand without incurring significant operating costs. The right amount of storage usually boils down to economics, available footprint and criticality of operations supported by the demineralized plant, and this is usually derived by reliability modeling.

Demineralized water system reliability analysis must consider critical factors such as the impact of water quality variations (both temperature and chemistry) on the type of demineralized technology selected, along with fluctuations in demineralized water demand and plant redundancy. In addition, if a demineralized treatment system is coupled with other facilities within the chemical complex—such as waste heat generated from cogeneration or a power plant—by using exhaust steam to preheat feedwater or to drive thermal desalination, then additional reliability analysis must be conducted to eliminate potential single points of failure.

In the authors' experience, an optimum configuration for demineralized water treatment employs both RO and IX processes. IX is typically preferred where there is a constraint on the volume of wastewater generated, where feedwater temperature is less than 18°C (65°F) year-round, where power costs are high (> \$0.10/kWh), or where feedwater TDS is substantially less than 500 mg/l. At temperatures below 18°C (65°F), it is unlikely that RO without feedwater preheating (which typically is cost-prohibitive if there is no waste heat available) will be economical. RO tends to be more economical as feed salinity increases. Variations in water quality resulting from prolonged drought might result in an increase of TDS by 20%–30% in some watersheds. RO tends to be more suitable for handling these swings in TDS, provided there is adequate reserve capacity. Other site-specific factors—such as available footprint, expandability of the plant, operability, and availability of skilled water treatment operators—must be considered in the selection of a demineralized technology.

In many cases, a combination of RO with IX resins (in mixed-bed configuration) provides a robust water quality and offers the potential for lower lifecycle costs than either IX or RO alone. This is primarily driven by decreased TDS loading on IX resins and reduced chemical demand due to performing the main work of TDS removal using RO. RO typically reduces TDS to less than a few tens of mg/l, resulting in a higher IX resin efficiency. Decreased TDS loading on an IX system decreases the frequency of regeneration and reduces waste, leading to lower overall operational cost of demineralized water.

Takeaways. Demineralized water treatment design is critical to ensure high-purity steam generation. Proper pretreatment for suspended solids removal must be evaluated based on various raw water sources. No one formula exists for choosing a demineralization technology. As demonstrated throughout this article, a wide range of factors should be considered, and data should be gathered and assessed on a case-by-case basis. A methodical consideration of the issues outlined in this article will lead to a demineralized plant design that reliably supports refinery operation. HP

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Meeting strict government standards for wastewater reuse and improved water quality

China's recent three Five-Year Plans have put clean water in the forefront. For example, new central government requirements for reducing chemical oxidation demand (COD) in refining and petrochemical wastewater effluents and controlling their use of freshwater sources have gotten increasingly strict. As a result, China has driven greater wastewater reuse of these industries and the need for more sophisticated treatment technology to achieve the new effluent and wastewater reuse standards.

The Chinese government's 13th Five-Year Plan (2016–2020) presented the latest in a series of increasingly stringent discharge standards for China's petrochemical industry, including China Petroleum and Chemical Corp.'s (Sinopec's) Anqing refinery.

The standards set out in the current plan require maximum COD concentration in discharged water to be limited to 40 mg/l. By comparison, in the U.S., where discharge standards are measured as biochemical oxygen demand (BOD), the equivalent COD discharge limit would be 150 mg/l–200 mg/l, which are levels much higher and far less stringent than China's new standard.

The current plan also reduces total nitrogen (TN) discharge levels to less than 40 mg/l, requiring an additional biological treatment step to achieve compliance.

Coupled with these technical challenges, another factor that made the new discharge standards particularly pressing for the Sinopec Anqing refinery is the high visibility of its location on the north bank of the Yangtze River in Anhui Province. This location is approximately 500 mi west of Shanghai, where the river flows into the East China Sea. Not only is the Yangtze River China's longest—and the world's third-longest river—but it is also the world's longest river contained completely in one country. This means China has virtually complete control over its water quality.

How important is the water quality of the Yangtze? The Yangtze Basin accounts for more than one-third of both China's total surface water resources and its total population—a population responsible for more than 40% of the country's GDP.[1]

To meet the new wastewater effluent standards in the 13th Five-Year Plan, the Anqing refinery decided to build on the existing design and in-place process equipment of its wastewater treatment plant built to meet the standards of the earlier 12th Five-Year Plan.

How the Anqing refinery met the new, stricter water treatment standards. For the Chinese petroleum and chemical industries, these new standards present challenges such as:

- Defining the appropriate and cost-effective technology that will consistently produce water quality that meets the new effluent standards.
- Maximizing the use of existing infrastructure in the revamp plan that must work in concert with the newly added technology.

A successful approach to adhering to the new standards would involve reconfiguring existing equipment and process units, as well as adding new process treatment trains to achieve the required high levels of treatment efficiency.

The Anqing refinery had just completed construction of a new water treatment plant, so to undertake a complete rebuild of this system was not necessary nor economical. That is why the technical strategy for meeting the government's new, stricter water treatment standards was to repurpose or adapt as much of the existing equipment as possible to a new design and treatment

FIG. 1. The refinery's wastewater treatment process units include PACT biological treatment systems and a wet air regeneration (WAR) hydrothermal treatment unit.

strategy, installing new equipment only where necessary.

This approach solved the challenge of the new Five-Year Plan standards, while making both technical and financial sense. For help, the refinery turned to its water treatment solutions partner[a], which supplied the existing equipment and systems.

The existing treatment facilities consisted of powdered activated carbon treatment (PACT) systems (FIG. 1), one for each of two separate plants:

- **Oily plant operations,** where the treated wastewater is used for cooling water make-up. This system cost-effectively treats low-salt wastewater from petrochemical, steam stripping and oily wastewater refinery operations.
- **Salty plant operations,** from which the treated water is discharged to the Yangtze River. This system cost-effectively treats high-salt wastewater from the refinery production process, including highly toxic and malodorous spent caustic, as well as alkaline wastewater from petrochemical spinning (acrylic fiber) and polymerization operations.

As previously mentioned, the challenges for the new treatment facilities included the need to meet new, more stringent effluent discharge standards for COD and TN content for both treatment facilities (< 50 mg/l and < 40 mg/l, respectively). In addition, the facility had to handle a 25% increase in designed COD load from the oily plant compared to its original design capacity.

The existing wastewater treatment process units for the original design of each of the oily and salty facilities included PACT biological treatment systems and sand filtration systems, along with a shared common wet air regeneration (WAR) hydrothermal unit and a common sludge thickening system.

The required performance limits for the PACT system/sand filter effluent PACT for the oily and salty facilities are shown in TABLE 1.

Effluent COD: Test runs demonstrate good news. The refinery's water solutions partner[a] used bench-scale laboratory test results to formulate carbon isotherms that defined the process configuration and changes required to meet the new effluent COD standards.

The PACT biological treatment system relies on powdered activated carbon dosing into the biological system and regeneration of that carbon using the WAR technology. The Anqing refinery's existing WAR system features a defined carbon regeneration capacity, so maximizing its carbon dosing capability was an especially important design criterion in the upgrade plan.

As part of the refinery's upgrade design and engineering phase, its water solutions partner's field services personnel conducted a bench-scale, proof-of-concept study using final effluent samples from the wastewater treatment plant. In addition, samples of the Anqing oily and

TABLE 1. The required performance limits for the PACT system/sand filter effluent PACT for the oily and salty facilities

Oil PACT system/sand filter effluent PACT

Item	Unit	Process performance guarantee value
pH	–	6–9
Oil	mg/l	≤ 2
TSS	mg/l	≤ 10
COD_{cr}	mg/l	≤ 40
BOD_5	mg/l	≤ 10
NH_3-N	mg/l	≤ 5
TN	mg/l	≤ 35 (max); ≤ 30 (average)
Sulfide	mg/l	≤ 0.1
Phenol	mg/l	≤ 0.1
Phosphorous	mg/l	≤ 0.5
Salty PACT system/sand filter effluent PACT		
pH	–	6–9
Oil	mg/l	≤ 3
TSS	mg/l	≤ 10
COD_{cr}	mg/l	≤ 50
BOD_5	mg/l	≤ 20
NH_3-N	mg/l	≤ 5
TN	mg/l	≤ 35 (max); ≤ 30 (average)
Sulfide	mg/l	0.5
Volatile phenol	mg/l	≤ 0.1
Phosphorous	mg/l	≤ 0.5

FIG. 2. The refinery's WAR is used to reactivate spent powdered activated carbon from its PACT system.

salty wastewaters and treated effluents were shipped to the partner's headquarters to validate the work performed in the field and confirm the upgrade plan.

The evaluations were performed in a 1,000-m^2 pilot testing plant supported by more than 500 m^2 of analytical testing laboratories—one of the world's best-equipped facilities for analyzing industrial, municipal and hazardous wastewaters, waters and sludges.

The validation work consisted of bench-scale PACT system treatability testing and laboratory analyses to screen powdered activated carbon types and dose, as well as process modeling to determine the optimum configuration of process trains needed to achieve the required treatment at the lowest possible cost.

> Typically operating at a regenerated carbon recovery rate of up to 95%, high-quality effluents can be produced at a powdered activated carbon cost of 97%–98% lower than the typical cost for granular activated carbon producing the same quality effluent.

Effluent TN: Denitrification process units added. The effluent discharge specification for TN introduced a new challenge to the current wastewater treatment process. Much of the nitrate nitrogen (NO_3-N) created during nitrification would need to be converted to nitrogen gas by a biological process known as *denitrification.*

This new process step required the addition of anoxic (oxygen-limited) biological process units immediately upstream of the PACT aeration tanks. The addition of a readily biodegradable substrate, such as acetate, is normally required to promote high-efficiency TN removal. However, the need for this nutrient was controlled and kept to a minimum by routing the filtrate from regenerated carbon to the anoxic reactors. The regenerated carbon filtrate contains an abundant source of soluble, biodegradable substrates, thereby optimizing the use and cost of this essential nutrient.

Salty wastewater treatment system. Because of its greater COD loading design, the salty PACT system was converted to a true two-stage PACT process to meet the new effluent quality standards. New, larger first-stage PACT system anoxic and aerobic bioreactors and clarifiers were constructed. The first-stage effluent could then be routed to a second-stage PACT system bioreactor, consisting of an existing, but repurposed, oily PACT system bioreactor. The second-stage PACT system effluent is then run through the sand filter and discharged to the Yangtze River.

Oily wastewater treatment system. To meet the new effluent standards, the oily PACT system bioreactor needed to be larger, and the existing salty PACT system bioreactor provided the right volume for this need. The oily PACT system upgrade was accommodated by rerouting oily wastewater flow to a new anoxic tank for TN control and to the existing salty PACT system bioreactor to meet the new effluent COD requirement.

PACT system technology: Synergistic cleaning efficacy. The refinery's PACT system combines powdered activated carbon adsorption and biological treatment synergistically to maximize the cleaning efficacy of each. PACT system treatment also provides the refinery with three key advantages for high-quality effluent water when compared with granular activated carbon column treatments. These advantages include:

1. Powdered activated carbon costs far less than granular carbon used in filtration columns
2. Because powdered activated carbon is powdered instead of granulated, it offers more active surface area per equivalent mass than granular carbon
3. Powdered carbon interacts more efficiently and thoroughly with treated water inside the bioreactor, and the required dose can be tailored to the precise discharge requirement.

WAR to reactivate spent powered activated carbon. Pairing the refinery's WAR system with its PACT biological treatment system enables it to reactivate spent powdered activated carbon (**FIG. 2**). This significantly reduces the amount of fresh carbon required in the PACT system, while destroying the excess biomass and eliminating the need for costly sludge dewatering and disposal. Typically operating at a regenerated carbon recovery rate of up to 95%, high-quality effluents can be produced at a powdered activated carbon cost of 97%–98% lower than the typical cost for granular activated carbon producing the same quality effluent.

Takeaway. China's system of Five-Year plans has guided the nation's development and modernization. With each Five-Year Plan, the government has shown an increasing focus on the reclamation and preservation of the country's natural resources with ever-stricter environmental regulations. In doing its part, Sinopec has stepped up its water treatment capabilities to help minimize the impact its oil and gas refining operations have on the environment, while also maximizing the cost-efficiency of those operations. HP

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Advanced cooling tower water treatment—Part 1

Refineries, petrochemical plants and similar facilities rely on a significant number of heat exchangers for process control and product formulation throughout the plant. Distillation, cracking and reforming, polymerization, steam generation, etc., require heat addition and heat removal.

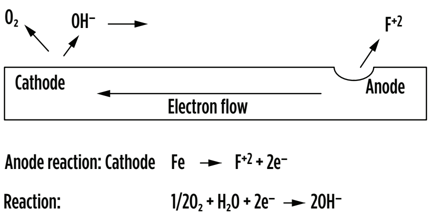
While many heat exchangers may supply closed-loop circuits, their cooling water supply comes from cooling towers. Others, such as steam surface condensers, are directly supplied by raw cooling water. Thus, it is not unusual to see many cooling towers dotted over the vast landscape of a refinery or chemical plant. Because the towers often sit in somewhat isolated locations, it is easy to overlook cooling water treatment until a problem occurs that forces a shutdown. For example, microbiological fouling of cooling tower film fill has, in some cases, caused partial or full tower collapse. Thus, establishing and maintaining the proper chemistry in these cooling systems is of paramount importance.

In Part 1 of this series, the authors examine the evolution of scale and corrosion control chemistry for cooling tower systems. Part 2, which will be published in the July issue, will focus on control of microbiological fouling. Continuing improvements to treatment programs allow for enhanced performance of cooling systems and better protection of the environment.

The good old days. To understand the evolution of cooling water chemistry, a brief review of the most common cooling water corrosion mechanisms is appropriate. All corrosion mechanisms are electrochemical in nature, although some—such as erosion corrosion—are also influenced by mechanical factors. **FIG. 1** provides a schematic of the primary corrosion mechanism of carbon steel—the most common cooling system piping material—in aerated water.

Iron (Fe) is oxidized at the anode and enters the solution as ferrous ion (Fe^{+2}). The process releases electrons that flow through the metal to the cathode, where the electrons reduce dissolved oxygen to hydroxyl ions (OH^-). Hydroxyl ions then react with the Fe ions to complete the electrical circuit and form an initial product of $Fe(OH)_2$, which continues to oxidize to form rust—with a basic formula of $Fe_2O_3.xH_2O$. Uncontrolled oxygen attack can cause severe damage in piping networks, and can also generate deposits that may partially or completely restrict flow (**FIG. 2**).

Corrosion inhibitors function by slowing down reactions at either the anode, the cathode or sometimes both. For a long time during the middle of the last century, chromate (CrO_4^{-2}) was very popular for corrosion control in many cooling systems—both open-recirculating and closed. While CrO_4^{-2} is considered an anodic inhibitor, with enough dosage, it will form a complete surface layer of Fe chromate (pseudo-stainless steel), which can be quite protective. CrO_4^{-2} programs were often coupled with acid feed to react with bicarbonate ion (HCO_3^-) and convert it to carbon dioxide (CO_2) that escapes. Removal of alkalinity greatly reduces the potential for calcium carbonate ($CaCO_3$) scaling, which is typically the first mineral deposit that would otherwise precipitate without treatment. CrO_4^{-2}/acid chemistry is very straightforward and effective; however, environmental issues regarding chromium discharge, particularly in relation to the toxicity of hexavalent chromium (Cr^{+6}), essentially led to the abandonment of this treatment method.



Anode reaction: Cathode Fe $\rightarrow F^{+2} + 2e^-$

Reaction: $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

FIG. 1. Fundamental carbon steel corrosion cell in aerated waters.

FIG. 2. A pipe nearly blocked by corrosion products.

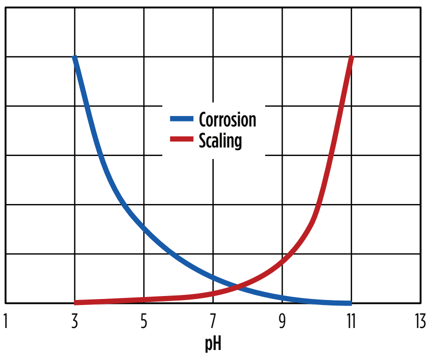


FIG. 3. Outline of corrosion and scaling tendencies as a function of pH.

Phosphorus chemistry to the rescue?

With the phase-out of CrO_4^{2-}, alternative treatment methods became a priority. For 40 yr, the most common treatment programs for large industrial cooling tower-based systems have relied on a combination of inorganic and organic phosphate (i.e., phosphonate) chemistry for both scale and corrosion control. These programs typically function at a mildly alkaline pH, which minimizes general corrosion, but at the cost, without proper protection, of increased scaling potential (**FIG. 3**).

The chemistry also provides more specific corrosion protection, as phosphate will react with Fe^{+2} produced at anodic sites to form a reaction-limiting deposit, while calcium phosphate [$Ca_3(PO_4)_2$] precipitates in the local alkaline environment at cathodic sites to inhibit electron transfer. However, even small upsets in phosphate programs can cause severe $Ca_3(PO_4)_2$ fouling, and, at one time, excess $Ca_3(PO_4)_2$ deposition became almost as great a problem as calcium carbonate scaling had been before. Accordingly, treatment methods evolved to more forgiving methodologies, where in many cases, the backbone of these programs are organic phosphates (phosphonates), with a supplemental polymer to control $Ca_3(PO_4)_2$ deposition. Phosphonates attach to crystal nuclei in solution and limit deposition by disrupting crystal growth and lattice strength (**FIG. 4**).

A common phosphate/phosphonate treatment program might include one or two of the phosphonate compounds in low mg/l dosages for primary scale control, 5 mg/l–15 mg/l of orthophosphate and some polyphosphate for additional scale control and corrosion protection. Phosphate programs are sometimes supplemented with 0.5 mg/l–2.5 mg/l of zinc (Zn) for improved corrosion control. Zn reacts with the hydroxyl ions generated at cathodes to form a precipitate [$Zn(OH)_2$], which provides additional cathodic protection. However, Zn solubility is also a strong function of temperature and pH, further increasing deposition on hotter heat exchangers. Moreover, Zn discharge is also tightly regulated due to its effects on aquatic life. It is included on the U.S. Environmental Protection Agency (EPA) list of 129 priority pollutants and 65 toxic pollutants. Typically included in these formulations is 5 mg/l–10 mg/l of dispersant polymer to control $Ca_3(PO_4)_2$ and zinc hydroxide deposition.

Phosphate/zinc programs are far from simple, and under- or over-feed can result in either corrosion or scale formation. Even with seemingly proper chemistry, the corrosion-inhibiting deposits are porous, and may wash away. Beyond those issues, two important factors are driving an evolution away from phosphate-based chemistry towards polymer treatment methods. One is the increasingly problematic issue of phosphorus discharge and its effects on the generation of toxic algae blooms in receiving bodies of water. The second is the growing evidence that well-

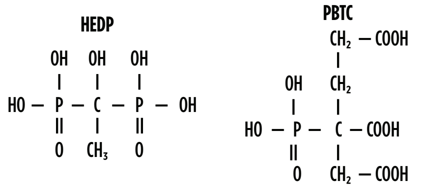


FIG. 4. Two common phosphonates: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) and 2-phosphono-butane-1,2,4-tricarboxylic acid (PBTC).

FIG. 5. Blue-green algae bloom in Lake Erie. Source: U.S. National Aeronautics and Space Administration (NASA).

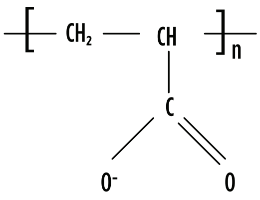


FIG. 6. Carboxylate functional group.

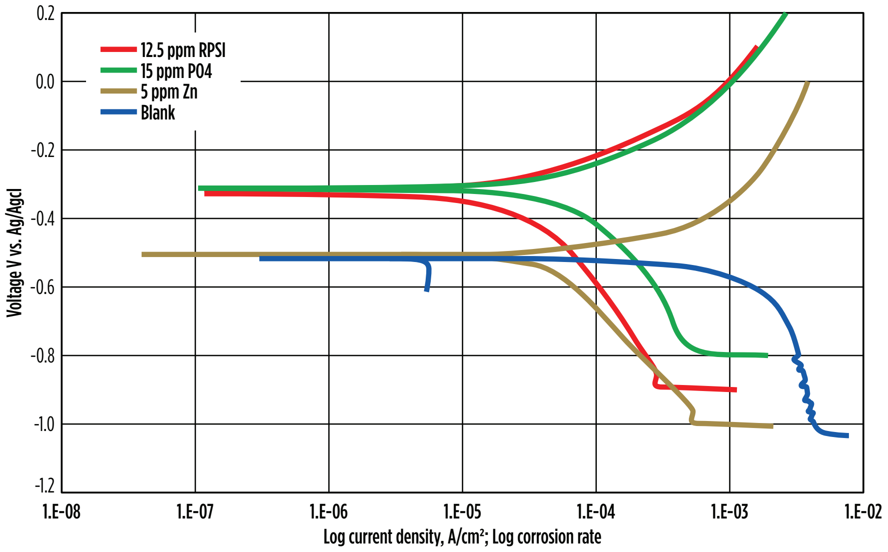


FIG. 7. Cyclic polarization evaluation of RPSI, ortho-phosphate and Zn corrosion inhibitors on mild carbon steel.

FIG. 8. Mild-steel coupons placed at the hot exit temperature of heat exchangers. The average corrosion rate was 0.25 mpy, one-tenth of industry corrosion standards.

formulated polymer programs are more effective—from both a performance and economic standpoint—than phosphate/phosphonate chemistry for scale prevention *and* corrosion protection.

Influence of phosphate in the natural environment. Phosphorus, along with nitrogen and carbon, is a macronutrient that is essential for all life forms. Algae derive their carbon requirements from inorganic bicarbonate and carbonate, utilizing energy from sunlight to convert the inorganic carbon into organic carbon for cellular tissue growth. Some species of algae are also capable of "fixing" atmospheric nitrogen gas, using the nitrogenase enzyme to convert N_2 into ammonia and other compounds required for the biosynthesis of nucleic acids and proteins. Common among the photosynthetic nitrogen fixing species are cyanobacteria, commonly referred to as "blue-green algae." Phosphorus is often the limiting nutrient for growth in aquatic systems because it is present in very low concentrations relative to that required by plants and microorganisms.

Cyanobacteria are known for their extensive and highly visible green blooms. **FIG. 5** shows an aerial photograph of a cyanobacteria bloom in the shallow western basin of Lake Erie in 2011. The unpleasant and unsightly algae growth resulted in fouled beaches, sharply reduced tourism and a decline in fish populations. Apart from their noxious sensory impact, cyanobacteria also produce microcystins and other cyanotoxins that are toxic to fish, birds and mammals. Many lakes closed in 2019 to recreational activities due to concern over the health effects of harmful algal blooms (HAB).

The presence of phosphorus in aquatic systems is also problematic because it ultimately leads to a reduction in dissolved oxygen, which is required by fish and other aquatic life forms. Dissolved oxygen is consumed rapidly by bacteria associated with the decay of algae, resulting in hypoxic conditions (< 2 mg/l dissolved oxygen) that do not support aquatic life. A notable example is the hypoxic or "dead" zone in the Gulf of Mexico, influenced by nutrient loading from the Mississippi River and other nutrient-laden streams that enter the Gulf. In the summer of 2017, the hypoxic area reached 22,730 km^2 in size, and stretched from the Louisiana-Alabama coast westward to the Texas border.

The emergence of polymer and other non-phosphorous chemistry. Polymer formulations containing the carboxylate group (**FIG. 6**) have been successfully utilized for decades to control $CaCO_3$ scale in cooling water.

However, many other scaling compounds are possible, including calcium and magnesium silicates, calcium sulfate, calcium fluoride and manganese dioxide. The need to combat these and other scale-formers has generated development of co- and ter-polymers, containing more than one functional group. These compounds act as crystal modifiers and sequestering agents, and, when tailored properly, each application can be quite effective at low concentrations.

Corrosion protection with non-phosphorous chemistry. The chemistry outlined has proven very effective for scale inhibition, but what about corrosion control? Significant development has occurred in that area, as well. Particularly effective is a chemical formulation that can be described generically as a reactive polyhydroxy starch inhibitor (RPSI).[a] In this chemistry, the compounds, by virtue of many active sites on

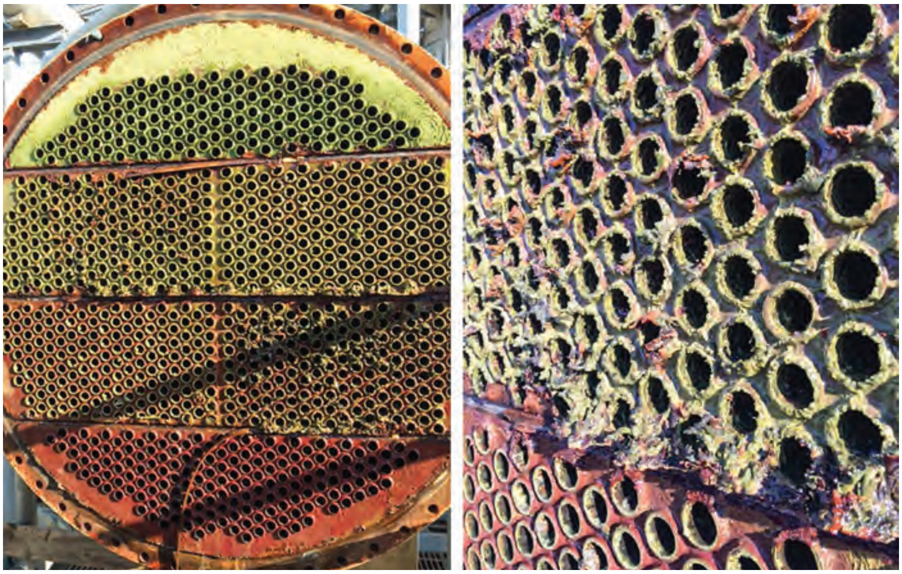


FIG. 9. Multi-pass heat exchanger on the phosphate program at the 2015 turnaround. Note: Corrosion in the colder inlet at the bottom and deposition at the hotter outlet at the top.

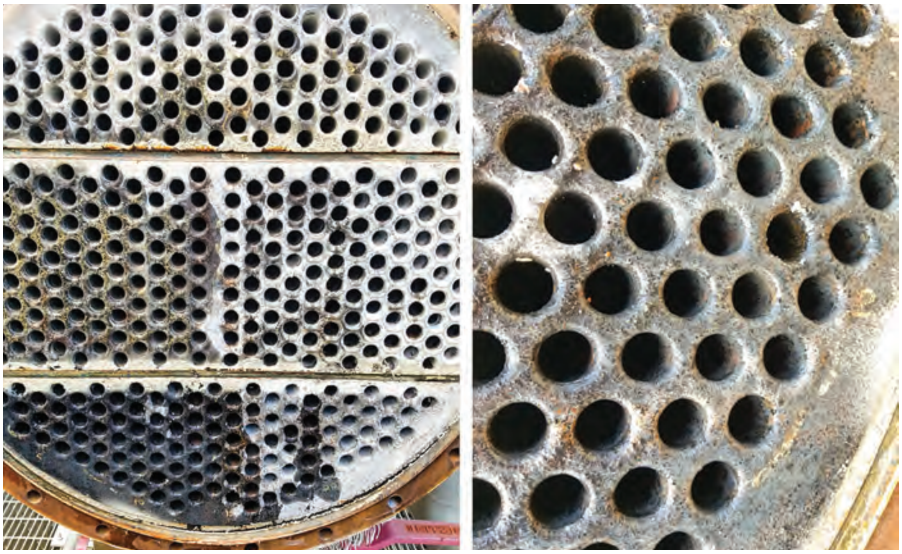


FIG. 10. Heat exchanger on non-P, non-Zn program at the 2018 turnaround. Tubes are nearly free of corrosion and deposition.

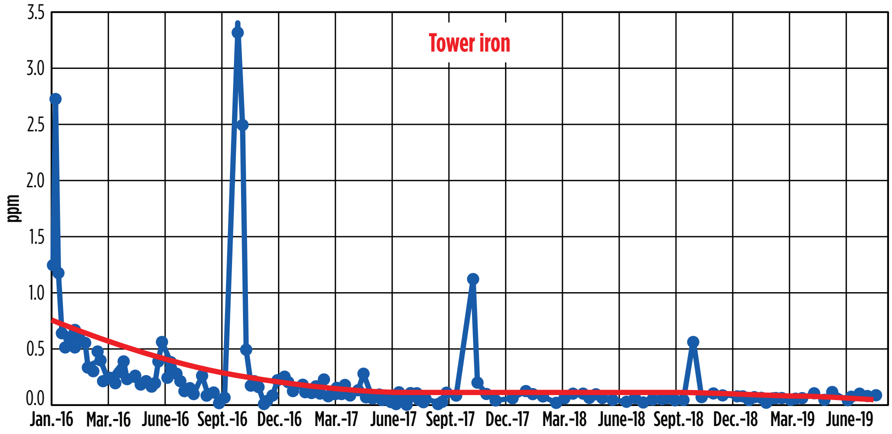


FIG. 11. Cooling tower Fe concentrations declined steadily since conversion from the stabilized phosphate treatment program to the non-phosphorous, non-Zn program.

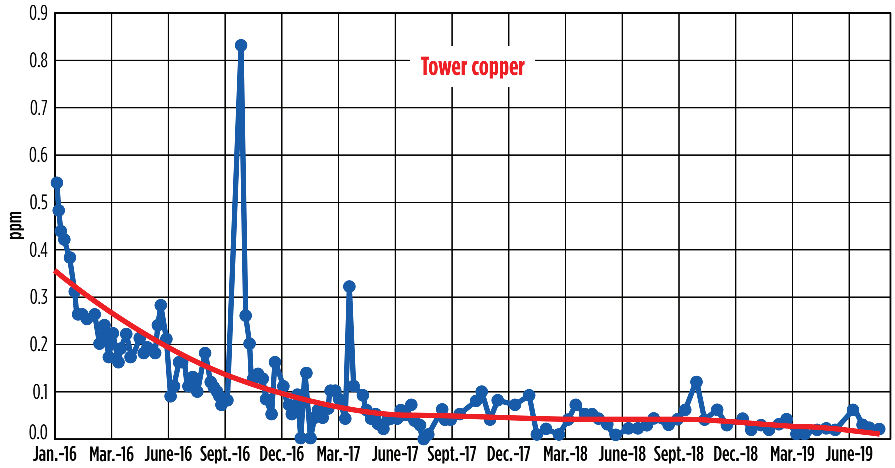


FIG. 12. Cooling tower copper concentrations declined steadily since converting from the stabilized phosphate program to the non-phosphorous, non-Zn program, with halogen stable triazole.

the molecules, attach to the base metal and form a protective layer.

Initial laboratory tests of RPSI illustrated the effectiveness of the chemistry in providing a synergistic combination of anodic and cathodic corrosion inhibition. **FIG. 7** is a cyclic polarization evaluation of the compound as compared to the cathodic inhibitor, Zn and the anodic inhibitor (ortho-phosphate).

As indicated in **FIG. 7,** 12.5 mg/l of the nonphosphorus RPSI is shown to inhibit the cathodic corrosion reaction as effectively as 5 mg/l Zn and inhibit the anodic reaction as effectively as 15 mg/l of ortho-phosphate. The figure clearly illustrates the dual cathodic and anodic inhibition, indicative of RPSI's film-forming nature.

Full-scale application of the chemistry has proven to be more effective than phosphate chemistry. During late 2015, a phosphate-based program at a large U.S. Gulf Coast chemical plant was replaced by a non-phosphate and non-Zn technology to mitigate the corrosion and scaling issues on the high-temperature (71°C/160°F) heat exchangers. After a year of using the improved chemistry, the equipment inspection during the turnaround cycle showed much cleaner heat exchangers. The Fe and copper (Cu) in the tower also decreased, consistent with the improved corrosion performance. Further improvements to the non-phosphorous, non-Zn chemistry were implemented after the 2017 turnaround, including the addition of a halogen stable triazole for Cu inhibition. This resulted in a dramatic improvement in both mild steel and Cu corrosion rates and heat transfer efficiency, as well as maintaining Fe and Cu levels in the water at historically low levels.

Corrosion is an electrochemical reaction, and the corrosion rate will roughly double with every 10°C increase in temperature, similarly to most chemical reactions. Placing the corrosion coupons at the outlet of the hottest heat exchangers provides a severe, but realistic, indication of the corrosion at the exchanger outlet. **FIG. 8** shows the mild-steel corrosion coupons that were placed at the exit of the hottest heat exchangers.

The heat exchanger results on the phosphate program from the 2015 turnaround (**FIG. 9**) can be contrasted with the results of the non-phosphorous, non-Zn program in **FIG. 10.** Conditions under the phosphate program exhibited significant corrosion in the lower part of the bundle where there is insufficient phosphate to form a barrier film. The upper part of the bundle is hotter and induced substantial phosphate deposition. With the non-phosphorous, non-Zn program (**FIG. 10**), the heat exchanger shows minimal deposition in the hot upper part of the bundle and little to no corrosion in the colder zone at the bottom.

Tower Fe and Cu levels. When corrosion occurs in a recirculating cooling system, corrosion products, primarily Fe and Cu, are released to the cooling water. The concentration of corrosion products in the cooling water is often a more accurate indicator of actual equipment corrosion than corrosion coupon results, especially in the chemical and hydrocarbon processing applications where the heat exchanger surfaces are frequently much hotter than the cooling water in a coupon rack. Cooling tower Fe and Cu concentrations declined steadily, to vanishingly low levels, after transition to the non-phosphorous, non-Zn program in late 2015, confirming that cooling system assets are effectively protected (**FIGS. 11** and **12**).

Since implementing the non-phosphorous technology, the large chemical plant has been able to extend its turnaround schedule from 1 yr to 2 yr., resulting in significant production increases and reduced cleaning costs associated with removing phosphate deposits in high-temperature bundles.

Potential application for stainless-steel (SS) protection. SS is the material of choice for heat exchanger tubes in many applications. However, austenitic stainless steels, such as common grades 304 and 316, are susceptible to stress corrosion cracking (SCC) at seemingly low-chloride concentrations with increasing temperature.[2]

The ability of RPSI to potentially protect 304 SS from SCC has been demonstrated in laboratory tests, in which U-bend stressed specimens were placed for 15 d in a bath of 105°C tap water spiked with 1,000 mg/l of chloride. **FIG. 13** shows the condition of the samples following the test.

The untreated specimen is clearly tarnished and pitted. The specimen exposed to the same solution containing the RPSI corrosion inhibitor shows no evidence of tarnish or pitting. Under magnification, cracking is evident at the bend of the untreated specimen, while the treated specimen shows no indication of cracking.

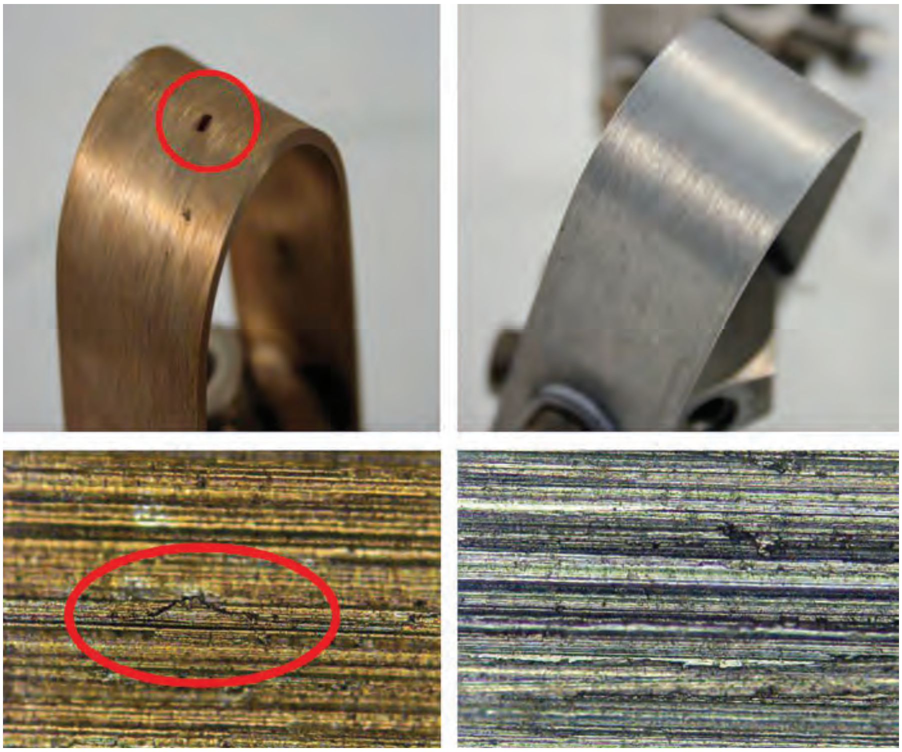


FIG. 13. Type 304 stainless steel U-bend coupons exposed to 1,000 mg/l chloride at 105°C for 15 d. Untreated coupon (left) shows tarnish, pitting and SCG. Coupon treated with RPSI (right) has no evidence of tarnish or cracking.

Environmental sustainability. The original goal behind the development of non-phosphorus and non-Zn chemistry was to provide a more environmentally sustainable alternative to phosphates in cooling systems. The RPSI corrosion inhibitor chemistry is formulated into several finished products, typically applied at a dosage of 100 mg/l, which have an LC_{50} per common U.S. EPA aquatic marker organisms in the range of 1,000 mg/l–10,000 mg/l. In most cases, the products can be formulated at mild pH ranges, making them less hazardous to handle than many products that must be prepared at extreme pH values.

Takeaway. Scale and corrosion control in refinery and petrochemical cooling water systems are of primary importance in maintaining reliability. Corrosion and fouling can directly affect the bottom line, and, most importantly, sometimes present safety issues. Technologies that have emerged and continue to be enhanced to improve cooling water chemistry have been outlined here. This article offers only a general overview. Any facility that decides to adopt a treatment program should conduct due diligence and consult with water treatment experts. These enhanced chemistries, like their predecessors, may be quite ineffective without proper microbiological control of the cooling water. Formation of bacterial colonies and accompanying protective slime layers, or accumulation of other microorganisms, can wreak havoc in cooling systems. Part 2 will focus on improved methods to control microbiological fouling. HP

NOTES

[a] Refers to ChemTreat's FlexPro technology

ACKNOWLEDGEMENT

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Cooling water microbiological control

The authors' previous article, "Advanced cooling tower water treatment," published in the June issue of *Hydrocarbon Processing*, outlined modern chemical treatment methods for scale and corrosion control in cooling towers and associated cooling systems, which are integral components of refineries, petrochemical plants and similar facilities. However, an issue that can sometimes dwarf other problems is microbiological fouling.

Cooling systems provide an ideal environment—warm and wet—for microbes to proliferate and form colonies. Bacteria will grow in condensers and cooling tower fill, while fungi will grow on and in cooling tower wood, and algae will appear on wetted cooling tower components exposed to sunlight. A major problem with microbes, particularly many bacteria, is that once they settle on a surface, the organisms secrete a polysaccharide layer (slime) for protection. By itself, this film can severely inhibit heat transfer, but it also collects silt from the water and grows thicker, further degrading heat exchange (**FIG. 1**).

FIG. 1. Heat exchanger tubes fouled with microbes and slime.

FIG. 2. A large under-deposit corrosion pit (with deposit removed) in a stainless-steel heat exchanger tube.

However, this is just part of the problem. Even though the bacteria near the surface might be aerobic, the slime layer allows the anaerobic bacteria underneath to flourish. These organisms generate acids and other harmful compounds that can directly attack metals. Microbial deposits also establish concentration cells, where the lack of oxygen underneath the deposit causes the locations to become anodic to other areas of exposed metal. Metal loss occurs at anodes, resulting in pitting (**FIG. 2**).

FIG. 3. Fouled cooling tower film fill.

Fouling is not limited to heat exchangers; cooling towers can also be very susceptible to fouling (**FIGS. 3** and **4**). Numerous cases of a partial or complete cooling tower collapse have been recorded over the years due to weight gain in tower fill from fouling. Treatment programs must be carefully planned and implemented to proactively prevent fouling and to maintain cooling systems in proper condition.

The first compound: Chlorine gas.

Around 200 yr ago, chlorine was first used as a disinfectant in water. Although microbiology was still in its infancy, scientists began to recognize that waterborne diseases were greatly reduced when water consumed by humans was treated with chlorine. As understanding of microbiology continued to grow, chlorine's benefits for cooling water chemistry also emerged.

Chlorine gas was the workhorse for cooling water treatment for many years. When the chemical is added to water, the following reaction occurs (Eq. 1):

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl \quad (1)$$

Hypochlorous acid (HOCl) is the killing agent. It functions by penetrating cell walls and then oxidizing internal cell components. The efficacy and killing power of this compound are greatly affected by pH due to the equilibrium nature of HOCl in water, as shown in Eq. 2.

$$HOCl \leftrightarrow H^+ + OCl^- \quad (2)$$

OCl^- is a much weaker biocide than HOCl, probably because the charge on the OCl^- ion does not allow it to effectively penetrate cell walls. The dissociation of HOCl dramatically increases as the pH goes above 7.5. Since most cooling tower scale/corrosion treatment programs operate at an alkaline pH, chlorine chemistry may not be the best choice in some applications. Chlorine efficiency is further influenced by ammonia and organics in the water that react irreversibly with the chemical and increase chlorine demand.

Due to safety concerns, liquid bleach (NaOCl) feed, although more expensive, has replaced gaseous chlorine at many facilities. Bleach often contains a small amount of sodium hydroxide. When it is injected into the cooling water stream, it raises the pH, perhaps only slightly, but, if the water is alkaline to begin with, most of the reactant will exist as the OCl^- ion. An alternative is onsite generation of hypochlorite, which has proven to be effective in several applications.

Several factors influence the performance of chlorine or bleach-generated chlorine, and have led to the evolution of more advanced technologies. First, oxidizing biocides, such as chlorine, are very effective on free-floating organisms (e.g., planktonic bacteria). However, if gaps in the treatment, or problems with the treatment program, allow organisms to settle, some of these sessile bacteria will quickly begin to form a protective glycocalyx (slime) layer for protection (**FIG. 5**). The colonies may contain a variety of organisms, including aerobic, anaerobic and facultative bacteria. The slime layer can be very protective, and powerful oxidizers, such as chlorine, are consumed by the slime and do not reach the organisms underneath.

Accordingly, it is quite important, regardless of the oxidizing biocide chosen for the application, to be proactive in preventing deposition and buildup of microbiological colonies. If these colonies become established, it can be difficult to remove them. For example, one of the authors participated in a shock chlorine treatment of a steam surface condenser at a former power plant. The condenser had become microbiologically fouled due to an upset in the biocide feed system, and condenser heat transfer had noticeably declined. The shock treatment killed the microbes, but the slime layer was so adherent that only a portion of it detached during the cleaning and subsequent rinse, such that condenser performance[1] did not fully recover from the upset. A mechanical tube scraping was required shortly after to remove the remaining slime.

A serious issue that has increasingly come to the public's attention (and certainly to the water technology community's attention) in the last 40 yr is that of airborne pathogens—most notably *Legionella,* which was responsible for the original Legionnaires' Disease outbreak in 1976, and causes infection via inhalation of water droplets or mist (< 5 micron diameter) containing the organisms. Such small droplets may come from many sources, including cooling towers, decorative fountains, potable hot water systems and shower heads, humidifiers, and whirlpools and spas, among others.[2] These organisms do not grow independently, but proliferate within sessile colonies of other microbes. This makes it quite imperative to keep cooling systems clean, with an oxidizing biocide as a core treatment method. It is also important to eliminate "dead legs" in any system, where low flow conditions can keep biocides from contacting and killing microorganisms.

Another issue that has caused concern from chlorine treatment is the potential for the chemical to react with organic compounds in the water to form halogenated organics. Some of these compounds are suspected carcinogens, and guidelines have been formulated that restrict the concentration of these substances. This issue has only grown in importance, given the diminishing availability of freshwater supplies for new industrial plants, including those for power production. Common in some areas of the U.S. (California is a notable example) are mandates for the use of treated mu-

FIG. 4. Severe algae growth in a cooling tower.

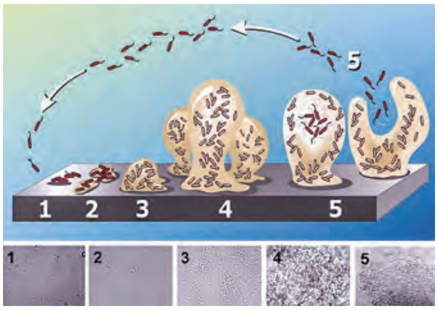

FIG. 5. Development of sessile bacteria colonies, which release organisms that can then establish colonies elsewhere in the cooling system. Photo is by an unknown author licensed under CC BY-NC.

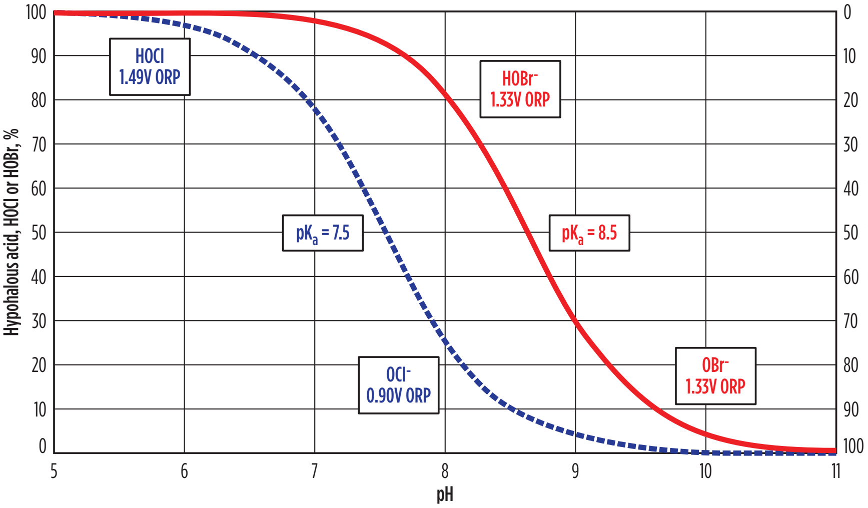

FIG. 6. Dissociation of HOCl and HOBr vs. pH. Note: At a pH of 8, approximately 80% of the HOBr remains undissociated, while only about 25% of the HOCl is still intact.

TABLE 1. Non-oxidizing biocides

Chemical	Advantages	Disadvantages
Isothiazoline	Effective against bacteria, particularly nitrifiers and fungi. Works well with oxidizing biocides. Active over a wide pH range.	Skin sensitizer. Degraded by sulfide, sulfite and reducing conditions.
2,2-dibromo-3-nitrilopropionamide (DBNPA)	Fast acting and effective against bacteria. Degrades quickly into non-hazardous byproducts.	Degrades quickly above pH 9, and is not very effective against fungi and algae. Degraded by reducing conditions.
Quaternary amines	Effective against most microorganisms, particularly algae. Active over a wide pH range.	Can cause foaming. Efficacy is reduced by hardness. Interacts with anionic dispersants and fluorescent tracers.
Glutaraldehyde	Effective against sulfate-reducing bacteria.	Incompatible with ammonia and some amines. Weak on algae.

nicipal wastewater plant effluent as industrial facility makeup. These supplies can introduce a variety of impurities to the cooling water, including ammonia, organics and phosphorus, among others.[3]

Chlorine alternatives. As previously mentioned, the killing power of chlorine falls off with a rise in pH, which is problematic, given that most scale/corrosion inhibitor programs operate in a mildly basic pH range. A popular answer to this challenge has been bromine chemistry, where a chlorine oxidizer (bleach is the common choice) and sodium bromide (NaBr) are blended in a makeup water stream and injected into the cooling water. The chemistry produces hypobromous acid (HOBr), which has similar killing powers to HOCl, but functions more effectively at an alkaline pH level. **FIG. 6** compares the dissociation of HOCl and HOBr as a function of pH.

Another strong oxidizer that has seen some success is chlorine dioxide (ClO_2). Unlike chlorine, ClO_2 is not consumed by ammonia or organics in the water—thus, it is free to attack organisms. However, ClO_2 must be generated onsite, which adds to the expense of this chemical.

Some promising alternatives include monochloramine (NH_2Cl) and monobromamine (NH_4Br). While these compounds are weaker oxidizers than the compounds previously outlined, they appear to be more effective at penetrating the protective slime layer that is produced by bacteria, which enables them to then directly attack these organisms.

Recently developed is a new halogen stabilizer/biodetergent that is applicable for bleach-only oxidizing treatments. This product has no biocidal properties and, therefore, does not fall under regulatory guidelines, but it is effective in stabilizing chlorine and reducing losses from irreversible reactions. The critical portion of the formulation is the biodetergent, which disperses the biofilm formed by the organisms and allows the biocide to contact the microbes directly.

In many cases, oxidizer feed is limited to 2 hr/d, which gives microbes time to settle and form colonies during off times. Accordingly, a supplemental feed of a non-oxidizing biocide on a once-per-week basis can be quite successful in controlling biological growth. These non-oxidizers, in conjunction with biodetergents, reduce overall chlorine usage and do not produce halogenated organic byproducts. **TABLE 1** lists properties of some of the most common non-oxidizers.

Careful evaluation of the microbial species in the cooling water is necessary to determine the most effective biocides. Antimicrobial compounds should not be used or even tested without approval from the appropriate regulatory agency. They must be incorporated into the plant's National Pollutant Discharge Elimination System (NPDES) permit. In addition, as with all chemicals, safety is a critical issue with biocides. Safety data sheet guidelines should be followed when handling these products.

Takeaway. This article provides an overview of some of the most important concerns and treatment methods for microbiological fouling control in industrial cooling water systems. It is not designed to be an absolute reference, but rather to give plant personnel a starting point for further inquiry into ideas for establishing the best program at their plant.

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Chemical treatment program for closed-loop cooling system

Closed-loop cooling water (CLCW) systems are utilized in areas where cooling is critical. In such areas, a high level of chemical treatment is required to maintain good corrosion and scale control. This article discusses various treatment methods and the frequently encountered chemistry problems of such systems, as experienced at the Tüpraş İzmit refinery.

CLCW systems are frequently used in the cooling of reciprocating compressors, which handle light hydrocarbons or hydrogen—specifically, the jackets where the tube metal temperature (TMT) exceeds 100°C. High TMT eliminates open-loop (evaporative) cooling water as a cooling medium due to its high scale-forming potential.

A series of CLCW system failures induced by poorly handled water chemistry is presented in this article. It also discusses the actions taken to diagnose the root cause and address the chemistry problem to ensure that all CLCW systems are stable.

Closed-loop cooling system design.

Closed-loop circulation cooling systems are specifically developed for engine applications, and use high-quality water. These engines may include diesel or other internal combustion machines, or jacket cooling systems for compressors.

Closed-cooling systems are used instead of open systems for several reasons. Among these, most cases include hot processes where scale formation on heat transfer surfaces must be eliminated. The products to be cooled impose a limit on the film temperature in the coolers; therefore, cooling water must be kept above a certain temperature. If this temperature is high, then the closed system must be filled with treated water or condensate to prevent solids precipitation.

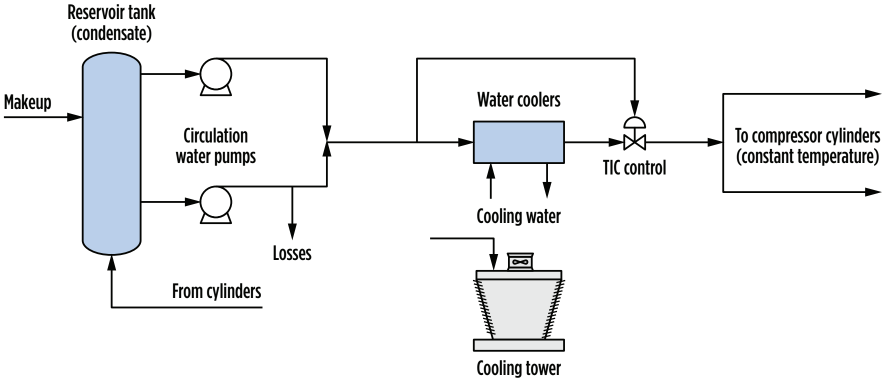

FIG. 1. Typical closed-loop cooling system.

High-quality water is often used, and the heat absorbed by the cooling water is removed in a heat exchanger without direct contact. Heat absorbed by cooling water in a closed-system exchanger is transferred to atmosphere via a cooling tower, thereby accommodating the evaporation process. Temperatures in these systems vary from 0°C–116°C, and system volumes range from 0.04 m^3–26,500 m^3, according to literature.

Typical cooling console skids comprise a centrifugal water circulation pump with an outlet pressure of 4 kg/cm^2g–5 kg/cm^2g, a reservoir or expansion water tank with a level indicator, a filling connection to this tank, a vent nozzle to ambient, an electric heater stab into the tank, a circulating water cooler, and a shell-and-tube exchanger with compressor connection lines and cooling water at the tube side. **FIG. 1** illustrates a typical closed-cooling system.

Since evaporative coolers are not used in closed circulation systems, there is very little loss of water from such systems. It is generally easy to maintain, at reasonable cost, the necessary concentrations of treatment chemicals in the water to prevent corrosion. Closed-loop systems are simple in these circumstances; however, these systems can become problematic to maintain when problems begin occurring.

High-purity water can be used for filling the system and for makeup; this minimizes the risk of mechanical failure throughout the system. A scale control problem is managed in this way, if condensate is available. Hard water should be avoided, even in small amounts. The use of dissimilar metals and a coolant ethylene glycol water-antifreeze mixture can become a source for corrosion. Any treatment chemicals used should not react with the antifreeze mixture. The ethylene glycol mixture may be oxidized to give acidic decomposition products in the case of high-temperature zones. Glycol breakdown products are acidic and contribute to a drop in pH. Other issues are water leakage and microbial growth, which can result in performance-related problems.

These systems may contain mixed metallurgy of cast iron, steel, copper, copper alloys and aluminum. Mild steel

FIG. 2. Pump internals.

FIG. 3. Closed-loop heat exchanger with dirt.

TABLE 1. İzmit refinery closed-loop circulation systems list

Compressor	Process	Volume, l
47K-2A/B/C	Hydrocracker	2,200
36K-110A/B	Platformer	1,700
36K-201A/B		
36K-203		
63K-1A/B	Unifiner	1,000
63K-101A/B/C	Platformer	1,000
63K-202A/B	Desulfurizer	1,000
63K-203		
74K-1A/B	Hydrodesulfurizer	1,000
147K-2A/B/C	Hydrocracker	5,800
Plant-9 G5 Cogen	Cogen	1,250

and copper require a pH of 8.5–9.5. Aluminum requires a lower pH range of 7–7.5. Closed-loop corrosion control programs may contain compounds like nitrite, molybdate, phosphonate, azoles, borate, carbonate and caustic. Among these compounds, nitrite and molybdate are the most common. They are often combined with Borax (disodium tetraborate decahydrate) for buffering capacity.

Molybdate requires oxidizing agents to prevent corrosion. Generally speaking, system pH must be controlled at 7–9 for effective treatment. Molybdate dosage can be increased to 200 ppm–1,000 ppm at a pH of 9–11 in some problematic systems. The challenge with molybdate programs is that the role of air is not clear. Molybdate systems that work well in saturated air situations (cooling towers) may not work in air-free (closed cooling water) situations.

Phosphonate-minimizing conductivity is successfully used as a corrosion inhibitor for environmental and economic reasons. Refiners can choose a nitrate program over molybdate when nitrite is more economic, reliable and easier to control. The major disadvantage of nitrate programs is the fact that nitrates are oxidized by microorganisms. The program may require nonoxidizing antimicrobial agents to maintain microbial control.

Borax allows operators to keep pH above 7–8 if there is a potential for pH-lowering ions. The buffering action of Borax maintains the pH above 7 and inhibits corrosion by minimizing the rate of oxidation. Solution pH becomes difficult to change since any addition of H+ ions only bonds with a borate conjugate base to form boric acid/weak acid. Borax neutralizes the acidic residue resulting from the decomposition of ethylene glycol and minimizes the rate of oxidation at the surface of the metal.

Managing closed systems may require a different approach to understanding and problem-solving. Testing of parameters like pH, conductivity, alkalinity, total hardness, dip slide, iron, copper, turbidity, corrosion inhibitor and molybdate in makeup water and closed-loop water is required for diagnosis and good monitoring. In a refinery environment, a process engineer must optimize the frequency and type of analysis to optimize the monitoring treatment program. Iron analysis is useful for corrosion monitoring, and it is advised to keep iron content below 0.5 mg/l in a weekly analysis.

Monitoring the pH level of the system is essential to maintaining the correct operating range. It is also important to regularly check the makeup water. Water loss from the system can be detected via laboratory analysis through the corrosion inhibitor, iron and conductivity figures. Loss of water means loss of chemicals; if water is added to the system to control the level, then chemicals must be added. If water levels drop regularly, then the reason must be investigated. Better control of the water and chemicals levels will reduce operational costs.

Root cause analysis of corrosion in cooling system. The Tüpraş İzmit refinery has been suffering from low pH and high corrosion rates for a long period of time. Nine closed-circulation systems cool reciprocating compressors and piston cylinders. These reciprocating compressors pressurize hydrogen-rich (> 90 mol%) makeup gases in the Platformer, gasoline treatment and hydrocracker units.

These streams may include impurities such as chloride, hydrogen sulfite, CO and CO_2 and have concentrations of less than 4 ppm (mostly 1 ppm or lower). Observed system temperatures are 90°C–110°C in the compressor and 35°C–40°C in the water circulation side. **TABLE 1** shows a list of closed-loop systems. The types of metallurgy used in circulation pumps are ASTM A48 Class 30 cast iron or ASTM A216 WCB carbon steel.

According to SAP records, there were more than 20 mechanical failures from 2015–2018. High corrosion rates damaged the impellers of the condensate circulation pumps and nearly blocked heat exchangers with viscous chemical sludge. **FIG. 2** shows the damaged pump internals. **FIG. 3** shows the heat exchanger to be cleaned in the closed-loop system.

An analytical approach was taken in 2018 to solve the various problems observed in these closed cooling systems. Meanwhile, the Tüpraş maintenance group decided to implement an emergency solution to prevent systems from reaching total failure. An expert chemical company applied a special coating of ceramic-reinforced epoxy to the surfaces of the internals after a sandblast enabled SA 2.5 quality. This coating helped the circulation pumps, but other parts of the system were still experiencing trouble.

To address the additional problems, it was necessary to first understand which chemicals were being used in these systems. Molybdate-based corrosion inhibitor and glycol antifreeze were used in the reservoir tanks and expansion tanks. Plans were made to strengthen the role of the cooling systems. An analysis revealed the results shown in **TABLE 2.**

TABLE 2. Test analysis results

Equipment	36K-110	47K-2	63K-1	63K-101	63K-201	74K-1
pH	7	7.3	8.6	7.6	9.5	5.4
Total iron, ppm	9.57	8.9	8.63	7.98	9.23	6.78
Molybdate, ppm	7	36	350	41	169	14

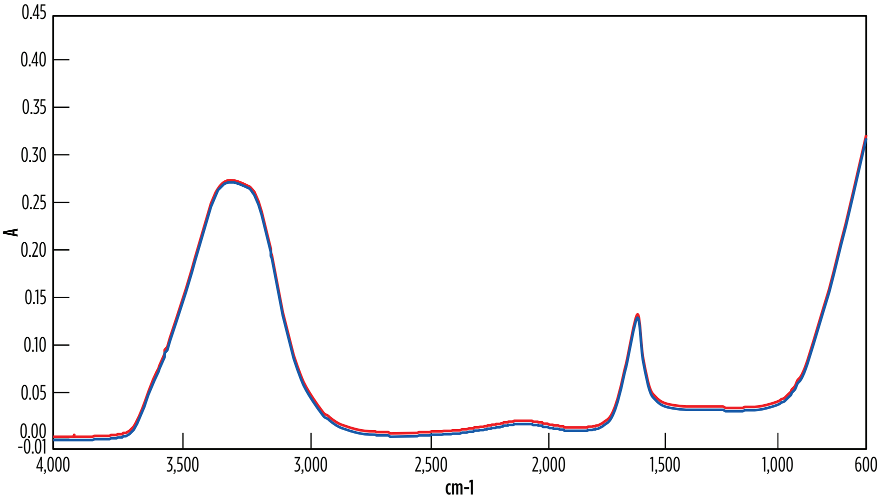

FIG. 4. The FTIR results of makeup condensate and circulating water filled in closed-loop systems.

The damages shown in **FIGS. 2** and **3** were due to inconsistency in the molybdate concentration, along with very high iron levels. The only passivated result was in the 63K-202 system, where the molybdate figure was around 160 ppm. At this point, a solution of 200 ppm–1,000 ppm of molybdate and a pH of 9–11 was advised; however, the desired pH level was not achieved.

A root cause analysis for understanding the source of the problem was immediately undertaken. Laboratory test analyses were performed for makeup water and filled water for all loops to detect potential human error during daily operations. Makeup water samples had pH figures above 9 and conductivities of less than 4 µs/cm. Circulation water samples showed unexpected levels of different compounds and a low pH of around 5–7. Among these compounds, M alkalinity, total organic carbon, chemical oxygen demand and Fourier transform infrared (FTIR) spectroscopy oil figures were high.

No gas leaks were detected, and a nonvolatile component was suspected for reacting as acidic and decreasing the pH. A further analysis was performed to understand how organic components could have resulted in these test figures. Meanwhile, a CO_2 test showed an increase in CO_2 levels from 0 ppm in makeup water to 5 ppm–10 ppm in circulation water. **FIG. 4** shows the FTIR analysis from one of the most severe loops. Repetition of the same analysis in other systems showed similar results.

The topologies of the results were similar in the makeup water and circulating water. Boiler treatment amine components were suspected for the issue, since no differences were observed in any other hydrocarbon component between the two samples. Systems with dip sides were also checked for microbiological reproduction.

During the root cause analysis, the hydrocracker makeup gas compressor closed-loop system (which was started up during the recent refinery resid upgrading expansion project) was also checked. The system, which contained only antifreeze solution, tested at a poor pH level of less than 6. As a part of the analysis, a corrosion inhibitor with organics and sodium hydroxide was added to the system. The result was the same soft, brown-colored sludge seen in existing systems (**FIG. 3**). The decision was made to remove antifreeze from all of the refinery's systems, since there was no freezing risk.

The chemical supplier advised refinery personnel to first elevate the pH level to enable the corrosion inhibitor to work properly. To this end, a caustic solution was used. After flashing the systems and filling them with condensate, the addition of a low-percentage caustic solution (20 Be) temporarily altered the pH

FIG. 5. Reservoir tank of hydrodesulfurization unit before and after maintenance.

TABLE 3. Test values before and after implementation of chemical blend without antifreeze

Compressor	Process	Test figures before	Test figures after
36K-110A/B 36K-201A/B 36K-203	Platformer	pH: 6.84 conductivity: 114 Fe: 0.01	pH: 9.01–7.91 conductivity: 49 Fe: 0.01
63K-1A/B	Unifiner	pH: 7.88 conductivity: 208 Fe: 2.04	pH: 9.1 conductivity: 98 Fe: 0.07
63K-202A/B 63K-203	Desulfurizer	pH: 6.55 conductivity: 44 Fe: 5.75	pH: 8.23 conductivity: 32 Fe levels stable
74K-1A/B	Hydrodesulfurizer	pH: 6.51 conductivity: 25 Fe: 5.58	pH: 8.1 conductivity: 48 Fe: 1.04
147K-2A/B/C	Hydrocracker	pH: 5,65 conductivity: 55 Fe: 5.94	pH: 8.95 conductivity: 44 Fe: 0.02
Plant-9 G5 Cogen	Cogen	pH: 6.11 conductivity: 44 Fe: 5.36	pH: 8.97 conductivity: 356 Fe levels stable

figures; however, caustic was ultimately found not to be a beneficial compound to stabilize pH figures. It is difficult to completely purge antifreeze from a system, and the cleaning rate affected the success of the caustic pH treatment.

The hydrodesulfurization unit's closed-loop system was used for analysis during the unit shutdown. The reservoir tank surface was cleaned of surface finishing dye, and a new lining and topcoat surface finishing material containing phenolic epoxy without solvent were implemented. **FIG. 5** shows the reservoir tank before and after maintenance. The new lining and topcoat were expected to help reduce interference from treatment chemicals in the future.

During the root cause analysis, frequent CO_2 measurements were performed and showed a stable increase from 0 ppm to 8 ppm–10 ppm. It is known that in pure condensate at 65°C, 1 ppm of dissolved CO_2 will reduce pH from 6.5 to 5.5 (**FIG. 6**).

Since caustic addition brought no benefit to the existing systems despite cleaning, a new mix of treatment chemicals was injected into the system. Clean condensate was flashed and refilled several times to remove the existing chemicals. A blend of organics, inhibitors, neutralizing amines and Borax was injected into the reservoir tanks filled with the clean condensate stream. In the absence of antifreeze, the pH values stabilized at 8–8.5, and iron levels showed almost no increase. The same results were observed in all other systems. Test results remained satisfactory as long as the system was free of the previous antifreeze inhibitor mix (**TABLE 3**).

The cooperation of refinery personnel and the chemical treatment supplier was necessary to find a solution to the corrosion issues in the closed-loop cooling systems. Thorough analysis of properties and components also helped achieve this success. HP

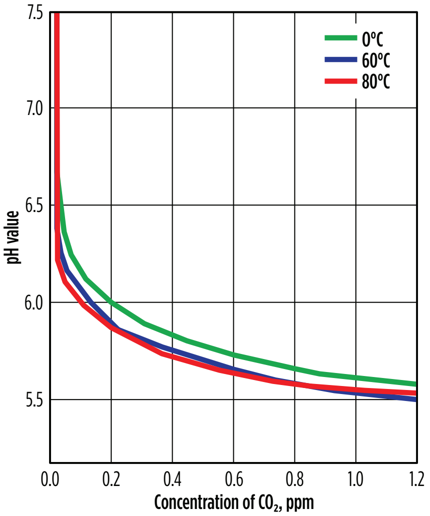

FIG. 6. pH values of CO_2 solutions in pure water.

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Protect your assets and our environment

Process cooling usually comprises the largest part of the water footprint of a refinery or petrochemical plant. Typically, most treatment programs contain phosphate (PO_4) and zinc (Zn) as key components in corrosion control to protect assets. These inorganic phosphates-based programs raise concerns of eutrophication in sensitive water bodies receiving the cooling water blowdown. Although surface run-off and sewage disposal are the main sources of eutrophication,[1] legislation on discharge of nutrients is tightening. Similarly, the use of zinc is restricted in some regions, and industrial producers have begun to seek more environmentally friendly treatment solutions to comply with the changing legislations.

This article describes a series of innovations tailored to regionally specific water qualities and discharge limits developed by the author's company to deliver on both the environmental and performance goals. Examples in industrial cooling systems are given to highlight that environmental protection and cost control are not necessarily mutually exclusive.

Traditional Zn- and PO_4-based cooling water treatment. Common examples of Zn- and phosphate-containing chemistries in cooling treatment have become the industry standard after chromates were phased out due to their toxicity. These standards include:

- Zn as cationic corrosion inhibitor component
- Ortho-phosphates, or poly-phosphates as key anodic corrosion inhibition actives
- Phosphonates in all-organic programs, degrading to phosphate.

Global legislation has tightened significantly to protect sensitive water bodies and drinking water resources. The main challenges associated with phosphate are not only eutrophication and associated algal blooms, but (tricalcium) phosphate scaling potential at high heat flux and control issues from variable background in the makeup. The high variability is sometimes seasonal or can come from recycled wastewater.

Traditional, organic-based, non-phosphorous (P)/low-P treatment programs have limitations, particularly if process control is not stringent.[2] Mild steel corrosion protection is challenging in high-stress water containing high chlorides and sulfates, and soft water with low hardness to aid inhibition mechanisms and low buffering. The long holding time index (HTI) at high cycles can increase the risk of tricalcium phosphate scaling.

Low-P, low-Zn (< 1 ppm limit each) cooling treatment of RO desalinated seawater. Reverse osmosis (RO) desalinated seawater is extremely corrosive due to a lack of buffer capacity and protective calcium ions, while the concentration of the aggressive chloride ion is relatively high. Localized corrosion can lead to process leaks and elevated maintenance costs if the water chemistry is not controlled carefully in the operating window.

A large petrochemical complex in Saudi Arabia suffered from severe localized corrosion and fouling due to lime deposition in the cooling system running on desalinated water (**FIG. 1**). This led to frequent shutdowns for re-tubing and reduced heat exchanger lifespan. The annualized cost of corrosion is estimated at $2.6 MM in maintenance alone. These systems were being treated by a competitor using calcium re-mineralization through lime addition and a Zn phosphate program. This treatment was not meeting the effluent limits on zinc and total phosphorous.

The author's company has established the optimal treatment window for RO desalinated water via bench-top and pilot cooling tower testing,[3] using dual cathodic inhibition utilizing the synergies between low levels of Zn and a proprietary, phosphorous-based inhibitor (phosphoric oligomer).[a] Additional research was conducted to arrive at the required low-P, low-Zn solution for this specific customer. Corrosion inhibition chemistry, as well as the operating window, is controlled to permit limit through a proprietary and advanced water performance system.[b]

The synergistic effects of low Zn and PSO dual-cathodic inhibitor (DCI), combined with best-in-class dispersancy under tag polymer control, ensured maximal availability of the inhibitor chemistry (**TABLE 1**). It provided excellent protection against general and pitting corrosion in desalinated water without the need for calcium re-mineralization. Target (general) mild steel (MS) corrosion rates of 4 mpy (mils/yr) were achieved throughout (**FIG. 2**), while in full-scale optimization

FIG. 1. Fouling and under-deposit corrosion leading to premature bundle replacement.

the average corrosion rate was below 2 mpy.

Suspended solids and turbidity values have dropped dramatically, as lime slurry was no longer dosed. The improved pH control and resulting drop in turbidity (15 ppm TTS down to below 2 ppm) voids the need to invest in side-stream filtration ($400,000).

The total Zn limit in the blowdown was consistently < 1 ppm. However, the tagged polymer, designed to maintain phosphate in solution, was re-dissolving the calcium phosphate deposits that had been built up in the system. The program was adjusted accordingly so that the effluent limit was reached over time.

The benefits of moving away from breaching effluent limits without achieving corrosion targets are significantly reduced maintenance cost, less production loss due to maintenance, and lower compliance costs, as shown in **TABLE 2.** The frequency of re-tubing and re-bundling was excessively high, with heat exchanger lifespan being much lower than the benchmark, incurring $1.7 MM in excessive maintenance costs.[4]

No-P, low-Zn in soft cooling water. A major petrochemical and refining corporation in China sought to improve its cooling water treatment both to comply with the Total P legislation (< 0.5 ppm P as total phosphate) and achieve better corrosion results. With the makeup source alternating between river water and soft ground water with high chlorides, the corrosion rates were causing lower lifespan of assets and high maintenance costs (**TABLE 3**). A low-P treatment program had been used since the plant commenced operation. The high chlorides and high HTI compromised the robustness of this treatment program. The novel non-P program addresses these challenges through:[5]

TABLE 1. Before and after: Competitor treatment vs. DCI program

KPI	Before	Target/limit	Author's company
pH control	Poor	Tight	Tight
TSS	15 mg/l	15 mg/l	< 1.5 mg/l
MS corrosion	6.6 mpy	4 mpy	1.8 mpy
Pitting corrosion	Severe	Low	Low
Free chlorine	0 mg/l	0.2 mg/l	0.2 mg/l
Bacterial counts	10^5 TVC/ml	10^3 TVC/ml	10^3 TVC/ml
Chloride	60 mg/l	40 mg/l	40 mg/l
Dissolved iron	2 mg/l	3.5 mg/l	0.1 mg/l
Effluent P	2.6 mg/l	1.0 mg/l	< 1 mg/l
Effluent Zn	1.8 mg/l	1.0 mg/l	< 1 mg/l

TABLE 2. Benefits of tailored treatment

Result	Impact
Pitting stopped, corrosion halved	$1.7 MM/yr maintenance cost savings
pH control lowering TSS discharge	Avoided $400,000 investment in side-stream filtration
Meet Zn and P limits, reduce analyticals	Avoided $500,000 in fines and analytical costs

TABLE 3. Water characteristics

Cooling water	Value
Effluent P-limit	< 0.5 ppm P
Chlorides	300 ppm Cl
MU Ca hardness	20–25 ppm $CaCO_3$
Low alkalinity in MU	30–35 ppm $CaCO_3$
Silica scaling risk	115 ppm SiO_2
Holding time index	> 200 hr
Alternating source	Fluctuations

TABLE 4. Novel no-PO_4, no-zinc treatment results

Characteristics	Remarks/results
Makeup source	City water, dissolved Al
Inorganic phosphate	84% reduction
MS coupon corrosion	70% reduction; ~1 mpy
Tower fill and tube replacement	Back to normal intervals (5 yr–7 yr)
Asset protection	Improved heat transfer and production security

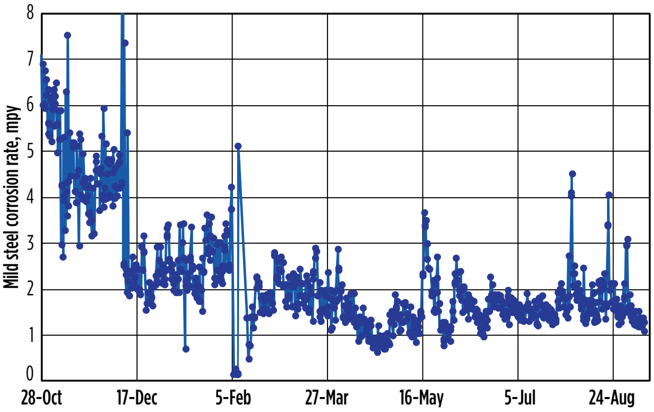

FIG. 2. Mild steel corrosion rate improvement with new program, with a target of < 4 mpy.

FIG. 3. MS coupons before (top) and after.

- Scale inhibition and dispersion
- Corrosion protection and inhibitor stabilization.

The synergistic effect incorporates improved corrosion control, extending the application window to more corrosive water matrices, such as soft water and high-chloride/high-sulfate water. Since beginning the new non-P program, the mild steel corrosion rates have been much improved in corrosion coupons (**FIG. 3**). Online probe readings on the controller fell from 1.9 mpy to 0.6 mpy.

With the new, non-phosphorus treatment program, the plant:

- Lowered maintenance costs and extended asset life
- Reduced wastewater treatment cost by $480,000
- Complied fully with the total phosphorus discharge limits.

No PO$_4$, no Zn in city water cooling tower. Cooling systems running on city water experienced severe scaling due to high dissolved aluminum from algae control. Aluminium phosphate was formed, depleting the corrosion inhibitor and causing high mild steel corrosion rates of > 3 mpy. With Zn prohibited onsite, removing the ortho-phosphate from the treatment program required an alternative cathodic corrosion inhibitor. Pilot cooling tower testing was conducted to tailor a treatment program without inorganic phosphate to the challenging water chemistry. The resulting innovative, no-PO4, no-Zn cooling water treatment program significantly reduced scaling and discharge of phosphate, lowering corrosion and protecting both the operating assets and the environment, as shown in **TABLE 4.**

Takeaway. Innovations tailoring the corrosion control treatment to local regulatory requirements have led to a large improvement in both corrosion control and effluent quality, showing that protecting the environment can coincide with reductions in total cost of operation. Besides chemical innovation, control and data management are key to deliver these results. HP

NOTES

[a] Nalco Water Research's PSO
[b] 3D TRASAR™ technology

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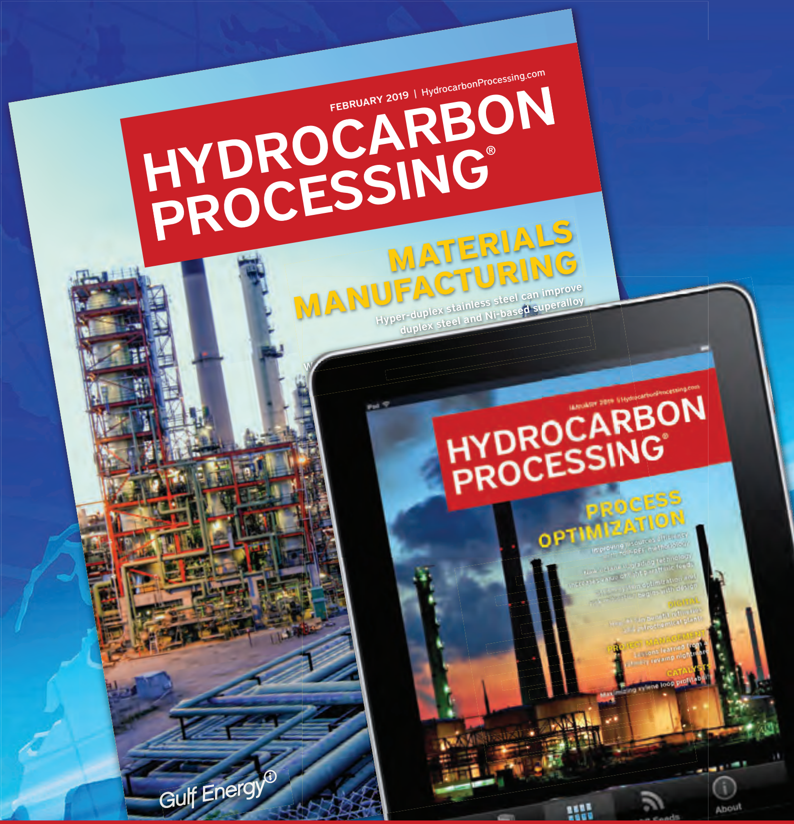

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Selection of cooling water system for gas, petroleum and petrochemical plants located on coastline—Part 1

Cooling water systems play an important role in today's industry. In the selection of a proper cooling water system, conceptual studies are usually carried out by chemical and process engineers, if different choices are available. Conceptual designs and relevant discussions are time-consuming and difficult in the early stages of projects; consequently, quick decision-making methods are of interest.

The main options for the cooling water systems of gas, petroleum and petrochemical plants located on coastlines are studied here, and alternatives are compared with the consideration of several technical and economic parameters, including loss in cooling water loop, cooling water capacity, project payback period, required investment, operation costs, discount rate, etc.

Many calculations have been carried out for numerous cases. The results of these calculations are provided as user-friendly graphs to help managers, engineers and researchers quickly select the proper cooling water system in a project's early stages.

The performance data shown in the graphs have been checked against several existing industrial projects. The results of the graphs are in good agreement with the decisions made for actual projects. Since relative costs have been used to compare different options, the results of this research are not location-sensitive and can be used by researchers, managers and engineers around the world.

Design of cooling water system. Heat exchanger networks are designed to maximize heat recovery at the lowest possible cost. Below the pinch point, excess heat that cannot be transferred to cold process streams is removed from the process via utility coolants (including air, cooling water, chilled water and refrigerant).

The selection of proper coolant depends on the process-side required temperature. Usually, air coolers are used to cool hot process streams as much as possible and as economically feasibly (depending on ambient conditions and target temperature), and then water coolers are used to further cool a hot process stream. Chilled water and refrigerants (e.g., propane) are used in lower-temperature processes.[1,2]

The cooling water system is one of the most important utility units that can be found within every gas, petroleum, chemical and petrochemical plant. Researchers have investigated a number of subjects related to this system. Kim and Smith[3] and Panjeshahi *et al.*[4] have studied the interactions of water cooler networks and cooling towers. Ortega *et al.*[5] and Castro *et al.*[6] have utilized nonlinear programming methods to optimize open-loop cooling water systems and to select components.

A mathematical model has been developed by Gololo and Mojazi[7] for the optimization of pressure drop in open-loop cooling water systems. Sun *et al.*[8] have evaluated pump networks for cooling water systems and proposed an auxiliary pump network to optimize yearly costs.

A dual-circuit cooling water system has been modeled by Muller and Craig[9] and optimized from control and energy consumptions points of view. Georgescu *et al.*[10] have used numerical methods to model a hydropower plant for different operating scenarios. The application of a precooling water spray system in dry cooling towers has been investigated by Xia *et al.*,[11] and computational fluid dynamic (CFD) approaches have been used to analyze the system performance. Rahmani *et al.*[12] have evaluated corrosion, scaling and fouling in cooling water systems and the effects of inhibitors and biocides on cooling system elements.

The Monte Carlo simulation method has been applied by Cheng *et al.*[13] to develop an optimal design method, and a proposed method has been checked for a local building. Zhou *et al.*[14] have experimentally investigated the performance of water spray systems and have studied the effects of several design parameters. Decreasing the water makeup demand by increasing the cycles of concentration has been studied by Rahmani,[15] along with corrosion and scaling in cooling water systems.

Bucur *et al.*[16] have evaluated the operating condition of cooling water systems in a power plant via EPANET software. An economic hybrid nonlinear model predictive model (HNMPC) has been used by Muller and Craig[17] to reduce cost and energy consumption in a cooling water system. The effect of wind on the performance of an open-loop cooling water system has been studied by Wang *et al.*[18] Ma *et al.*[19] noted several disadvantages of separately optimizing water cooler networks and pump networks, and proposed how coolers and pump networks can be simultaneously optimized. In another study,[20] Ma *et al.* have shown how the addition of air coolers to a cooling water system can improve its efficiency. Simulation, modeling and hydraulic debottlenecking of a cooling water system have been discussed by Souza *et al.*[21,22]

As is evident, several topics related to cooling water systems have been studied by scientists, engineers and researchers. However, the selection of a proper cooling water system based on technical and economic points has not been widely discussed.

Different types of cooling water systems are selected in projects depending on accessible water sources, environmental conditions, technical requirements and economic parameters. If several options are available, process engineers will usually perform conceptual studies to select the best option for a cooling water system.[23] However, conceptual studies are time-consuming and difficult in the early stages of project execution, when sufficient data are not available. This article discusses the proper evaluation and selection of a cooling water system based on technical and economic viewpoints for gas, petroleum and petrochemical plants located along coastlines.

Cooling water system. Three major types of cooling water systems are open loop, closed loop and once through. Other types may be generated by a combination of the aforementioned categories. In cases where a reliable source of water is unavailable or water is extremely expensive, the designer may decide to use dry cooling towers or air coolers to cool the cooling water return (CWR) stream.

Most petroleum refineries, gas refineries and petrochemical complexes are constructed near reliable source(s) of water (mostly near seas and rivers) and, as a result, dry cooling towers and air coolers are generally not the best choices for a cooling water system, especially at high capacities.

Brief descriptions of commonly used cooling water systems are provided in the following section. The details of cooling water system operation can be found in engineering procedures and textbooks.[24,25]

Desalinated open-loop cooling water system. The schematic for a desalinated open-loop cooling water system is shown in **FIG. 1.** The CWR header gathers warm cooling water from water coolers and delivers cooling water to the top of the cooling tower(s). Water is cooled, mostly due to vaporization, and accumulated in the cooling tower sump. Cooled cooling water is pumped through the cooling water pump to the cooling water supply (CWS) header and is delivered to users (i.e., water coolers).

TABLE 1. CAPEX and OPEX of cooling water systems

	Cooling water system		
	Desalinated open loop	Closed loop	Seawater once through
CAPEX			
Cooling tower	✓		
Water coolers	✓	✓	✓
Cooling water pumps	✓	✓	
Seawater pumps		✓	✓
Intake system		✓	✓
Chlorination package		✓	✓
Plate-and-frame exchangers			
Other	✓	✓	✓
OPEX			
Desalinated water	✓	✓	
Electrical power	✓	✓	✓
Maintenance	✓	✓	✓
Spare parts	✓	✓	✓
Other	✓	✓	✓

To compensate cooling water losses due to wind, evaporation and blowdown stream (which avoids chemicals accumulation in the cooling water loop), a makeup water stream should be considered for the cooling water loop. Usually, desalinated water (with required additives) is circulated in open-loop systems; however, in specific cases where using a once-through seawater system is justified after conceptual design, a designer may decide to use a seawater open-loop system because of considerable distance from the sea, high pumping costs and/or environmental regulations.

Closed-loop cooling water system. The schematic for a closed-loop cooling water system is shown in **FIG. 2.** To avoid cooling water loss due to evaporation and wind, as discussed in the preceding section, a designer may decide to use cooling water in a closed loop. Warm cooling water is gathered from wa-

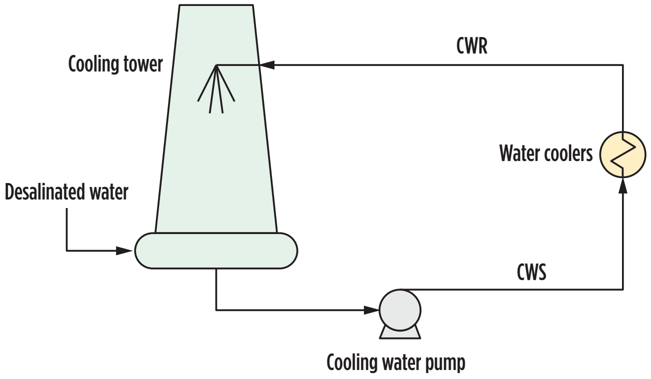

FIG. 1. Schematic drawing for a desalinated open-loop cooling water system.

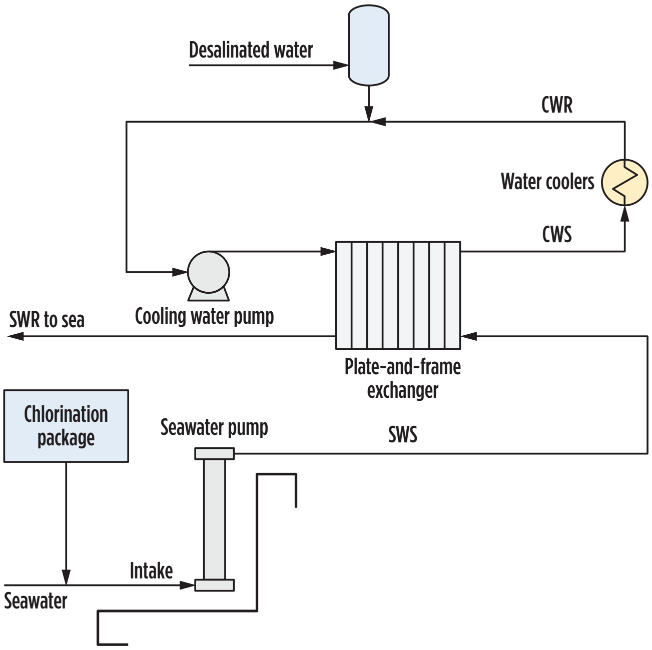

FIG. 2. Schematic drawing for a closed-loop cooling water system.

ter coolers via the CWR header and pumped by cooling water pump to the plate and frame heat exchanger(s), where cooling water is cooled to the required supply temperature by seawater. Cooled cooling water is pumped to the CWS header and delivered to users (i.e., water coolers).

Seawater is pumped through a seawater pump from seawater intake facilities to the seawater supply (SWS) header and delivered to plate-and-frame heat exchanger(s). Warm seawater leaves the plate-and-frame exchanger(s) and is discharged to the sea via the seawater return (SWR) pipeline. Cooling water losses in a closed-loop system are significantly lower than in an open loop; consequently, less desalinated makeup water is needed.

Once-through cooling water system. The schematic for a once-through cooling water system is shown in **FIG. 3.** Seawater is pumped from seawater intake facilities to the SWS header by a seawater pump and delivered to water coolers. Warm seawater is gathered by the SWR header from water coolers and is discharged to sea. Due to the direct application of seawater in water coolers, more severe corrosion is anticipated; consequently, better materials (e.g., titanium, special alloys, etc.) should be used in water coolers, which makes them more expensive than carbon steel water coolers.

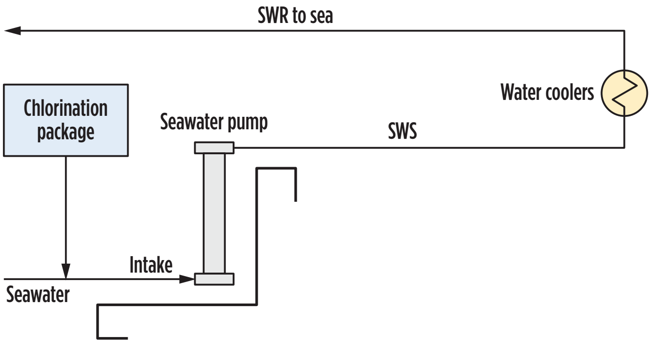

FIG. 3. Schematic drawing for a once-through cooling water system.

Calculation methods. In this section, a summary of applied assumptions and a calculation method are described. The details of this calculation method can be found in textbooks.[1,2,3]

Like other utility units, a cooling water system does not directly make money for the owner(s), excluding centralized utility projects. The role of a cooling water system is to support the main process and other facilities; consequently, income cannot be clearly defined for such units. Expenses imposed by a system (e.g., a cooling water unit) for the plant can be used as a parameter to evaluate different options.

Yearly costs. Yearly costs, also known as total yearly costs, are used to evaluate and compare different systems in short periods after the first plant startup (usually based on expected payback period). To consider capital expenditures (CAPEX) and operating expenditures (OPEX) as a single parameter, yearly costs are defined as shown in Eq. 1:

$$\text{Yearly costs} = \frac{\text{CAPEX}}{\text{Investment return period}} + \text{OPEX} \qquad (1)$$

The investment return period (i.e., payback period) can be replaced by any other time span important to a specific project.

TABLE 1 shows CAPEX and OPEX that have been considered for evaluation and comparison of cooling water systems. Other CAPEX represent minor equipment (if any), piping, instrument items, civil works, etc., that cannot be accurately estimated during conceptual design. Equipment prices are estimated based on actual project data and updated via escalation and cost indices. Where required, exponent factors are used to modify costs for new capacities.

TABLE 2. Applied technical assumptions

Parameter	Value	Remark
Cooling water loss		
Desalinated open loop	2%	Usually 1%–3%, depending on environmental conditions and cycle of concentration (COC)
Closed loop	0.5%	
Temperature change		
Desalinated water	10°C	Typical average value
Seawater	8°C	Usually SWR temperature will be restricted as per local regulations; average typical value has been selected
Pumps differential pressure		
Cooling water pump	4 bar–7 bar	Average value; depends on site dimensions
Seawater pump (closed loop)	3.5 bar–5.5 bar	Average value; depends on site dimensions
Seawater pump (once through)	6 bar–10 bar	Average value; depends on site dimensions
Pumps efficiency		
Mechanical efficiency	70%	Typical value
Electrical efficiency	90%	Typical value
Heat capacity		
C_p for desalinated water	4.19 kJ/kg°C (Average value)	
C_p for seawater	3.85 kJ/kg°C (Average value; depends on salt content)	

Total costs. Yearly costs are a well-known and important economic parameter for quick decision-making; however, it covers a limited time span of a plant's lifetime. "Total costs" is used to evaluate all imposed costs by a system during a plant lifetime (Eq. 2):

$$\text{Total costs} = \text{CAPEX} + \text{Plant lifetime} \times \text{OPEX} \qquad (2)$$

To consider the time-value of money, OPEX can be discounted to the present value by applying the owner's discount rate. In this case, the second term of Eq. 2 is replaced by a sigma term (Eq. 3):

$$\text{Total costs} = \text{CAPEX} + \sum_{i=1}^{N} \frac{\text{OPEX}}{(1+DR)^i} \qquad (3)$$

where N, DR and i are plant lifetime (usually 20 yr in gas, petroleum and petrochemical industries), discount rate and year number, respectively.

Assumptions. Major technical assumptions applied in this study are shown in **TABLE 2.** Obviously, all projects do not have the same conditions, and actual technical data for each project is used for conceptual design. Used assumptions are average

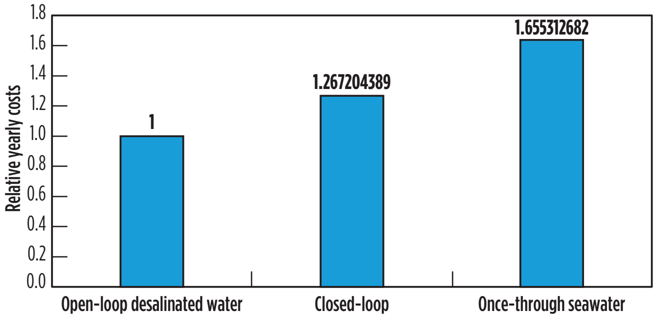

FIG. 4. Relative yearly costs for sample calculations 1.

TABLE 3. Applied economic assumptions

Parameter	Value	Remark
Desalinated water	$2.1/m^3	Average Middle East price for 2017
Electrical power	$57.66/MWh	Average Middle East price for 2017
Maintenance	2.5% of CAPEX	Typical value
Spare parts	1.5% of CAPEX	Typical value

TABLE 4. Calculation summaries

Specification	Measurement	Unit (remark)
Summary of main technical calculations for desalinated open-loop cooling water system		
Circulating cooling water	2,500	m^3/hr
Required desalinated water for cooling water loss	50	m^3/hr
Cooling water pump brake horsepower (BHP)	596	kW
Required electrical power for cooling water pump	663	kW
No. of required cooling water pumps	2	(1 working + 1 standby)
No. of cooling towers	1	
Required electrical power for cooling tower	292	kW
Total estimated required electrical power	955	kW
Summary of main technical calculations for closed-loop cooling water system		
Required sea cooling water	3,290	m^3/hr
No. of seawater pumps	2	(1 working + 1 standby)
Required electrical power for seawater pump	581	kW
Circulating cooling water	2,500	m^3/hr
Cooling water pump BHP	596	kW
No. of cooling water pumps	2	(1 working + 1 standby)
Required electrical power for cooling water pump	663	kW
Total required electrical power for pumps	1,244	kW
Required desalinated water for cooling water loss	13	m^3/hr
Summary of main technical calculations for once-through seawater system		
Required sea cooling water	3,290	m^3/hr
No. of seawater pumps	2	(1 working + 1 standby)
Required electrical power for seawater pump	1,161	kW

values and sufficiently precise for the purposes of this article and for conceptual designs.

TABLE 3 indicates applied economic assumptions. These assumptions are average values gathered from the Middle East. The location factor of the Middle East has been used (if required) to unify all economic calculations. Since the purpose of this study is comparison of different options, absolute values of calculation results are not prominent.

For each comparison, the option with the lowest cost (yearly costs or total costs, see Eqs. 1–3), is used as the reference case with a relative cost of 1, and relative costs of other options are compared with this value. Since relative values have been used for the comparison of available options, results are not location-sensitive and location factors have few effects on outcomes.

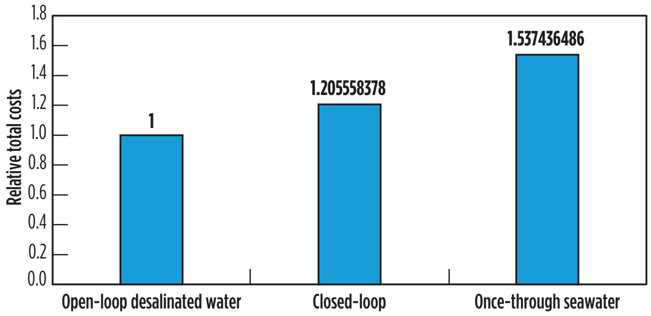

FIG. 5. Relative total costs for sample calculations 1 (plant lifetime = 20 yr).

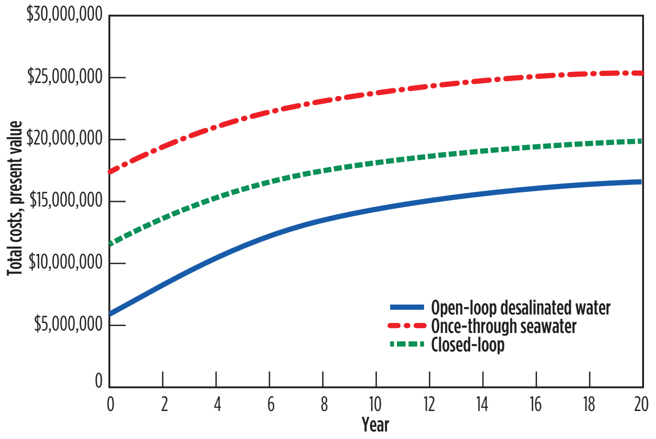

FIG. 6. Total costs for sample calculations 1.

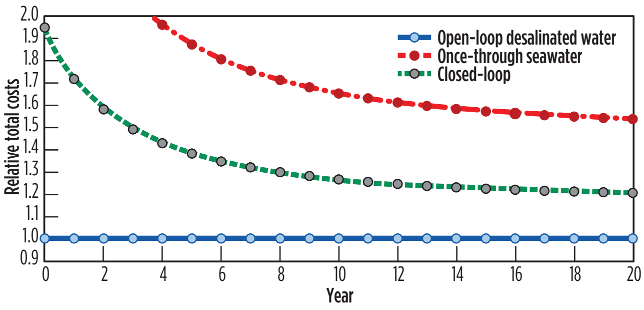

FIG. 7. Relative total costs curve for sample calculations 1.

Sample studies. Summaries of two sample calculations have been provided in this section to show how the aforementioned methods and assumptions have been used.

Sample calculations 1. The following specifications have been assumed for a project:

- Design cooling water capacity: 29.17 MW
- Expected project payback period: 5 yr
- Owner discount rate: 15%.

TABLE 4 shows calculation summaries. Based on these technical calculations, a summary of economic results is presented in **TABLE 5.** Yearly costs can be calculated for all options based on estimates presented in **TABLE 5,** and **FIG. 4** shows calculated relative yearly costs for all options. **FIG. 4** shows that open-loop desalinated water is the best option in this case, from a short-term viewpoint.

Also, total costs can be calculated based on estimates presented in **TABLE 5. FIG. 5** represents relative total cost, considering a plant lifetime of 20 yr (a typical plant lifetime in gas, petroleum and petrochemical industries). From a long-term

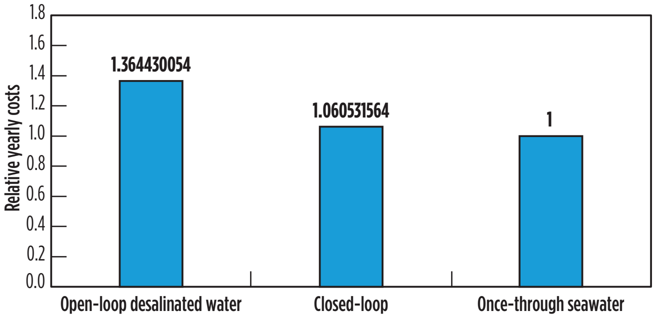

FIG. 8. Relative yearly costs for sample calculations 2.

TABLE 5. Details of estimated costs for sample calculations 1

	Open-loop desalinated water	Closed loop	Once-through seawater
Capital costs	**$5,897,200**	**$11,504,600**	**$17,470,800**
Cooling towers	$978,000	$0	$0
Water coolers	$3,388,000	$3,388,000	$12,037,000
Cooling water pumps	$762,000	$762,000	$0
Seawater pumps	$0	$984,000	$1,616,000
Intake system	$0	$833,000	$833,000
Chlorination package	$0	$706,000	$706,000
Plate-and-frame exchangers	$0	$3,331,000	$0
Other	$769,200	$1,500,600	$2,278,800
Yearly operating costs	**$1,689,450**	**$1,334,550**	**$1,254,750**
Desalinated water	$920,000	$240,000	$0
Electrical power	$483,000	$629,000	$587,000
Maintenance	$129,000	$251,000	$380,000
Spare parts	$77,000	$151,000	$228,000
Other	$80,450	$63,550	$59,750

viewpoint, open-loop desalinated water is the best option.

FIG. 6 represents total costs during a plant lifetime, and **FIG. 7** shows relative total cost for different plant lifetimes. Based on these figures, for all plant lifetimes open-loop desalinated water is the best choice.

Sample calculations 2. The following specifications have been assumed for a project:

- Design cooling water capacity: 2,333.33 MW
- Expected project payback period: 6 yr
- Owner discount rate: 10%.

Applied assumptions are those represented previously, and details of calculations are similar to the previous sample.

Yearly costs can be calculated for all options based on the estimates presented in **TABLE 6. FIG. 8** shows calculated relative yearly costs for all options. From a short-term viewpoint, once-through seawater is the best option in this case.

Also, total costs can be calculated based on the estimates presented in **TABLE 6. FIG. 9** represents relative total cost, considering a typical plant lifetime of 20 yr. From a long-term viewpoint, once-through seawater is the best option.

Calculations can be carried out for other plant lifetimes, depending on project nature. **FIG. 10** represents total costs during a plant's lifetime, and **FIG. 11** shows relative total costs for different plant lifetimes. Based on these figures, plant lifetime may affect the cooling water system selection.

Part 2 will discuss the results of case studies presented in Part 1. HP

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TABLE 6. Details of estimated costs for sample calculations 2

	Open-loop desalinated water	Closed loop	Once-through seawater
Capital costs	**$81,725,900**	**$159,445,200**	**$242,147,450**
Cooling towers	$13,552,000	$0	$0
Water coolers	$46,964,000	$46,964,000	$166,846,000
Cooling water pumps	$10,550,000	$10,550,000	$0
Seawater pumps	$0	$13,634,000	$22,390,000
Intake system	$0	$11,541,000	$11,541,000
Chlorination package	$0	$9,786,000	$9,786,000
Plate-and-frame exchangers	$0	$46,173,000	$0
Other	$10,659,900	$20,797,200	$31,584,450
Yearly operating costs	**$120,685,950**	**$77,818,650**	**$58,076,550**
Desalinated water	$73,584,000	$18,396,000	$0
Electrical power	$38,512,000	$50,170,000	$46,887,000
Maintenance	$1,777,000	$3,467,000	$5,265,000
Spare parts	$1,066,000	$2,080,000	$3,159,000
Other	$5,746,950	$3,705,650	$2,765,550

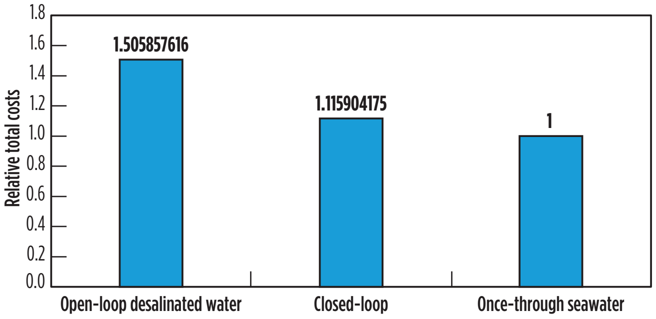

FIG. 9. Relative total costs for sample calculations 2 (plant lifetime = 20 yr).

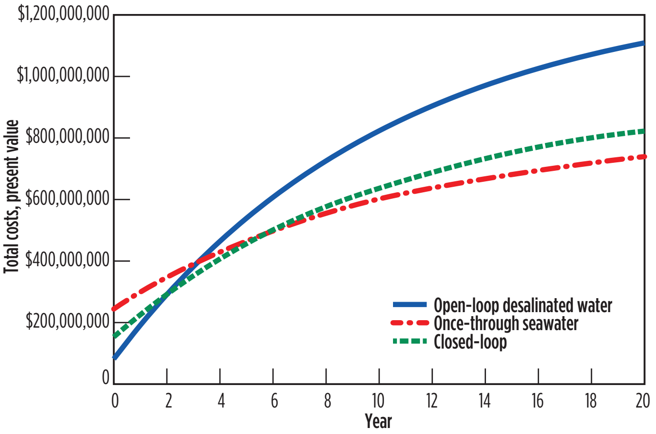

FIG. 10. Total costs for sample calculations 2.

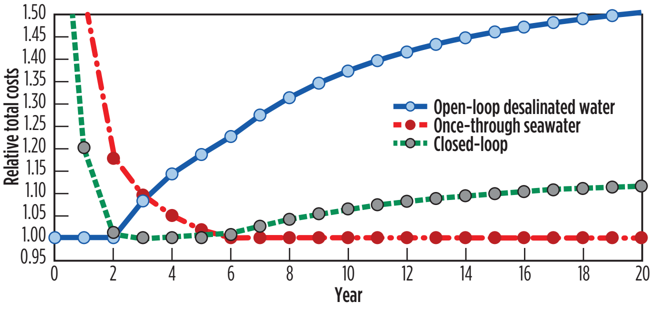

FIG. 11. Relative total costs curve for sample calculations 2.

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Selection of cooling water system for gas, petroleum and petrochemical plants located on coastline—Part 2

The main options for the cooling water systems of gas, petroleum and petrochemical plants located on coastlines are studied here, and alternatives are compared with the consideration of several technical and economic parameters.

Many calculations have been carried out for numerous cases. The results of these calculations are provided as user-friendly graphs to help managers, engineers and researchers quickly select the proper cooling water system at the early stage of a project.

The performance data shown in the graphs have been checked against several existing industrial projects and are in good agreement. Since relative costs have been used to compare different options, the results of this research are not location-sensitive and can be used by researchers, managers and engineers around the world.

Part 1 of this article, which appeared in the April issue, covered the different types and designs of cooling water systems, as well as calculation methods for design choices and performance costs for sample studies. Part 2 discusses the results of the case studies presented in Part 1.

Results and discussion. Based on the methods and assumptions explained in Part 1, a total of 216 case studies have been carried out to compare the three main cooling water system options at different conditions. **TABLE 6** shows the parameter ranges for the studies, based on actual ranges for gas, petroleum and petrochemical plants.

Yearly costs and payback period (short-term study). Yearly costs (Eq. 1,

TABLE 6. Range of case study parameters

Parameter	Value	Remark
Capacity of cooling water system	0.12 MW–11,667 MW	Depends on type and size of project
Project payback period	1 yr–8 yr	Usually 4 yr–7 yr
Discount rate	0%–15%	

TABLE 7. Examples of calculation results for relative yearly costs of cooling water systems

Cooling water capacity, MW	Payback period = 4 yr			Payback period = 5 yr			Payback period = 6 yr		
	Open loop	Closed loop	Once through	Open loop	Closed loop	Once through	Open loop	Closed loop	Once through
0.12	1	1.7	2.17	1	1.67	2.06	1	1.63	1.97
0.58	1	1.81	2.54	1	1.78	2.47	1	1.76	2.4
1.17	1	1.72	2.46	1	1.68	2.38	1	1.65	2.31
2.33	1	1.63	2.34	1	1.58	2.25	1	1.54	2.17
5.83	1	1.54	2.16	1	1.49	2.05	1	1.44	1.96
11.67	1	1.45	2	1	1.38	1.88	1	1.33	1.79
29.17	1	1.33	1.78	1	1.27	1.66	1	1.22	1.56
58.33	1	1.23	1.6	1	1.17	1.48	1	1.12	1.39
116.67	1	1.14	1.43	1	1.08	1.32	1	1.04	1.23
233.33	1	1.06	1.27	1	1	1.16	1.04	1	1.13
291.67	1	1.03	1.22	1.02	1	1.14	1.06	1	1.11
583.33	1.05	1	1.12	1.1	1	1.08	1.14	1	1.05
875	1.09	1	1.09	1.14	1	1.05	1.19	1	1.02
1,166.67	1.12	1	1.06	1.18	1	1.03	1.22	1.01	1
1,750	1.17	1	1.03	1.23	1.01	1	1.31	1.04	1
2,333.33	1.2	1	1.01	1.29	1.03	1	1.36	1.06	1
5,833.33	1.38	1.07	1	1.47	1.1	1	1.55	1.13	1
11,666.67	1.52	1.12	1	1.61	1.16	1	1.68	1.19	1

see Part 1) and payback period were used to select an optimum cooling water system at different capacities. For each case study, the option with the lowest yearly costs was used as the reference case, with a relative cost of 1. Relative costs of other options have been compared with this value. **TABLE 7** shows some of the obtained results. For each capacity, conceptual design was carried out for all options, and final results were reported. Complementary calculations were carried out to find the borders between available options. **FIG. 12** shows a decision-making graph with the final results.

It should be noted that available borders are not solid lines and should not be considered as completely precise borders. Near the borders, **FIG. 12** should be used with caution, as a change in applied assumptions may slightly change a border. **FIG. 12** was developed based on performed calculations for the payback period time span; consequently, it can be more suitable for short-term studies (entire plant lifetime is not covered by this graph).

Total costs and discount rate (long-term study). Total costs (Eq. 3, see Part 1) and owner's discount rate have been used to select the best cooling water system. For each case study, the option with the lowest total cost has been used as the reference case, with relative total costs of 1. Relative total costs of other options have been compared with this value. **TABLE 8** shows some of the obtained results.

As with the short-term study, complementary calculations have been carried out to find the borders between available options. **FIG. 13** shows a decision-making graph with the final results of all performed calculations in this section. **FIG. 13** was developed based on total costs during a normal plant lifetime of 20 yr, and is more suitable for long-term studies. Since change in applied assumptions may slightly alter the borders in **FIG. 13,** this graph should be used with caution near the borders.

Verification of developed graphs. Both graphs (**FIG. 12** and **FIG. 13**) were developed based on scientific and engineering methods and reasonable assumptions. However, they should be verified and their performance in actual projects should be checked. In this regard, actual data from real projects have been extracted to test the performance of the graphs.

TABLE 9 represents actual data from real projects and selected cooling water systems during engineering design, based on conceptual studies. **TABLE 10** shows the performance of the graphs.

The graphs can be used for the selection of a suitable cooling water system without spending time and money on conceptual

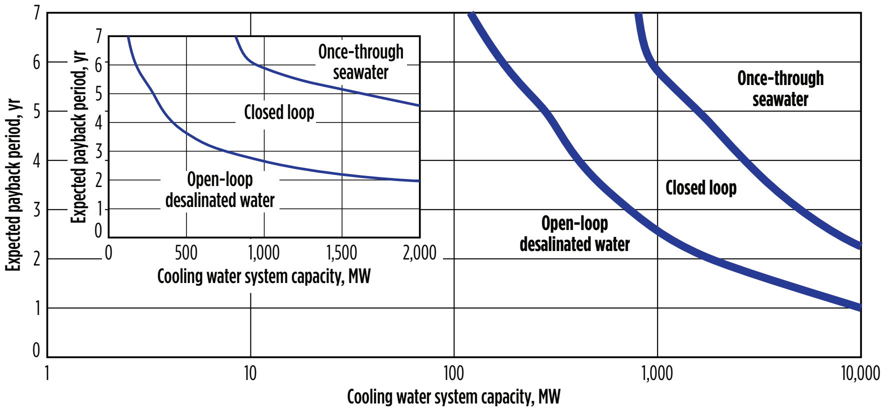

FIG. 12. Cooling water system decision-making graph based on system capacity and payback period; suitable for short-term studies.

TABLE 8. Examples of calculation results for relative total costs of cooling water systems

Cooling water capacity, MW	Discount rate = 5%			Discount rate = 10%			Discount rate = 15%		
	Open loop	Closed loop	Once through	Open loop	Closed loop	Once through	Open loop	Closed loop	Once through
0.12	1	1.51	1.6	1	1.57	1.79	1	1.63	1.95
0.58	1	1.67	2.13	1	1.72	2.27	1	1.76	2.39
1.17	1	1.51	2.01	1	1.58	2.16	1	1.64	2.29
2.33	1	1.37	1.84	1	1.46	2.01	1	1.53	2.15
5.83	1	1.26	1.61	1	1.35	1.79	1	1.43	1.94
11.67	1	1.15	1.44	1	1.24	1.61	1	1.32	1.77
29.17	1	1.04	1.23	1	1.13	1.39	1	1.21	1.54
58.33	1.04	1	1.13	1	1.04	1.23	1	1.11	1.37
116.67	1.12	1	1.07	1.04	1	1.13	1	1.03	1.21
233.33	1.19	1	1.01	1.12	1	1.07	1.05	1	1.12
291.67	1.22	1.01	1	1.14	1	1.05	1.07	1	1.1
583.33	1.36	1.06	1	1.22	1.01	1	1.15	1	1.04
875	1.45	1.09	1	1.31	1.04	1	1.2	1	1.01
1,166.67	1.51	1.12	1	1.36	1.06	1	1.24	1.01	1
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2,333.33	1.64	1.17	1	1.51	1.12	1	1.38	1.07	1
5,833.33	1.81	1.23	1	1.68	1.19	1	1.57	1.14	1
11,666.67	1.91	1.28	1	1.81	1.23	1	1.7	1.19	1

studies. This capability is very important, especially at the early stages of a project, when some technical data are not available. If applied assumptions in this article deviate significantly from the basis of a project, then the graphs should be used with caution and for preliminary studies only.

In specific cases where a once-through seawater system is selected and plant distance from the shore is considerable, a designer should perform complementary studies to find the optimum selection (i.e., once-through seawater or open-loop seawater). Case 5 in **TABLE 9** is an example of such a situation (see Note "c" in **TABLE 9**). In this article, it is assumed that the source of water (e.g., sea, river, etc.) is near the plant, which is correct for most gas, petroleum and petrochemical plants. Comparison of actual project data (**TABLE 9**) with the results of the graphs (**TABLE 10**) confirm the accuracy of the graphs.

Recommendations. The selection of a proper cooling water system is important from both technical and economic viewpoints. Usually, the selection of a proper cooling water system for a plant or a complex is based on conceptual studies, which should be carried out by engineering teams. Conceptual studies are time-consuming and usually difficult at the early stages of a project.

This article provides the results of several case studies in two simple, user-friendly graphs that enable researchers, managers and engineers to select the proper cooling water system for petroleum, petrochemical and gas plants without performing lengthy or complicated calculations.

For each capacity, a conceptual design has been carried out for all options, and final results have been provided. Since relative costs have been used here, the graphs are not location-sensitive and can be used at locations around the world. The performances of the graphs have been checked against actual project data, and the precision of the results have been confirmed.

End of series. Part 1 appeared in April. HP

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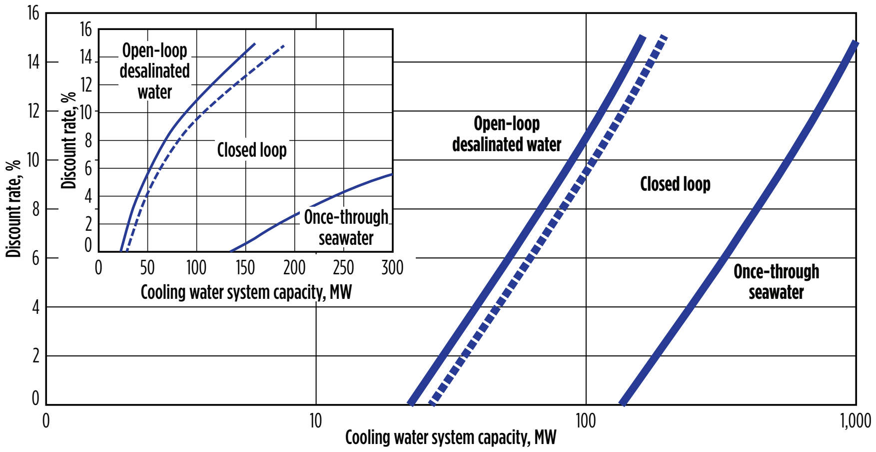

FIG. 13. Cooling water system decision-making graph based on a plant lifetime of 20 yr, system capacity and owner's discount rate; suitable for long-term studies.

TABLE 9. Cooling water system selection in real projects

Case	Project	Cooling capacity, MW	Discount rate[a]	Payback period[b]	Selected system in project
1	60,000-bpd condensate refinery with low complexity	30	14%	6 yr	Open-loop desalinated water
2	150,000-tpy propane dehydrogenation plant	105	18%	5 yr	Open-loop desalinated water
3	5,000-tpd methanol plant	250	15%	5.5 yr	Closed loop
4	3 × 120,000-bpd refinery with high complexity	950	12%	7 yr	Once-through seawater
5	Large petrochemical complex	1,400	14%	6 yr	Once-through seawater[c]

[a] Owner's discount rate [b] Expected payback period

[c] Selected system in basic design when plant is assumed to be on seashore; for Case 5, the designer finally selected a seawater open loop due to the new location of the complex and its considerable distance from the sea

TABLE 10. Selection of proper cooling water system via **FIG. 12** and **FIG. 13** for real projects[d]

	Selection via total cost graph (FIG. 13)			Selection via yearly cost graph (FIG. 12)		
Case	Open-loop desalinated water	Closed loop	Once-through seawater	Open-loop desalinated water	Closed loop	Once-through seawater
1	✓			✓		
2	✓			✓		
3		✓		(Can be an option, based on short-term studies)	✓	
4			✓			✓
5			✓			✓

[d] See Table 9

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Minimize energy consumption in water treatment with forward osmosis technology—Part 1

Heavy industries like refining, petrochemicals and mining have concerns about the availability of fresh water, as these are affected by local water scarcities and stringent water discharge regulations. The oil and gas industry needs relatively huge volumes of water, as the water/oil ratio averages 8:1.

The preferred conventional water treatment technology, reverse osmosis (RO), is still energy-intensive even after an upgrade of RO process technology. Industries are examining alternative water sources and treatment technologies, and implementing water recycling or reuse practices.

Forward osmosis (FO) technology, an emerging method, can be used to mitigate the aforementioned problems. FO uses the natural osmotic pressure difference between two solutions of different concentrations as a driving force to permeate freshwater through the semi-permeable barrier. Due to freely available renewable osmotic energy, projected energy savings from the FO systems compared with conventional technologies has been realized in the range of 30%–70%, depending on the product (freshwater) recovery.

FO can energetically outperform conventional technologies with much lower fouling propensity. This article provides information on this state-of-the-art process and the physical principles and applications of FO, as well as their strengths, limitations, economics, pilot/commercial-scale status and major challenges. Two different types of FO approaches—direct and indirect FO desalination—are discussed.

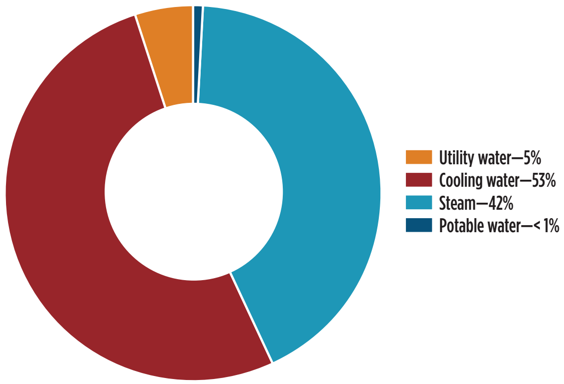

FIG. 1. Percentage distribution of water use in refinery.

Introduction. Industrial water demand has been growing with the pace of industrial development.[1–5] The World Bank has projected that approximately $700 B[1] will be needed worldwide in the next decade to meet freshwater demand. Progress in some water-intensive industries has been significant, placing further pressure on industrial demand for water.[2]

Crude oil refining is also a water-intensive industry; around 1.5 bbl of freshwater is essential to process 1 bbl of crude oil. Poor-quality, "price-advantaged" crude needs relatively higher volumes of water to remove salt and impurities from crude, adding heat to the processes (as steam), removing heat from the processes (as cooling water), and equipment cleaning and maintenance purposes. **FIG. 1** illustrates the percentage distribution of water use in a refinery.[2,3]

Seawater desalination and wastewater reuse are the most feasible means for the world's biggest industries to mitigate scarcity of freshwater. RO is the preferred technology.[6] RO is a process in which water permeates through the membrane from high- to low-solute concentrated solution due to applying higher hydraulic pressure (P) than osmotic pressure (π) on the high-solute concentrated solution, as shown in **FIG. 2A.** The osmotic pressure of the solution is the minimum pressure required to permeate water in a solution through a semi-permeable membrane.

After many developments, RO is still an energy-intensive technology.[5,6] Therefore, the need exists to utilize alternate energy-efficient technology to meet freshwater demand. FO is emerging as an energy-efficient membrane technology for seawater desalination and wastewater reuse.[6]

The main difference between the FO and RO processes is the direction of water permeation, as shown in **FIG. 2.** In FO, the water (solvent) permeates, in the opposite direction of RO, from low- to high-solute concentrated solution due to the higher osmotic pressure difference ($\pi_2 - \pi_1$) than the hydraulic pressure difference ($P_2 - P_1$). The low concentrated solution is usually considered as feed solution, while the high concentrated solution is considered a draw solution. Recent developments of FO are mostly focused on seawater desalination and wastewater treatment.

FO has a range of potential benefits compared to RO, as shown in **FIG. 3.** In seawater desalination, a hydraulic pressure in the range of 60 bar–90 bar is required in RO to overcome the osmotic pressure of seawater and obtain sufficient recovery; in FO, negligible hydraulic pressure in the range of 1 bar–2 bar is needed to enter the feed into the system. Due to the lower hydraulic pressure requirement, the fouling tendency (deposition of natural organic matter and polymerized silica on the membrane surface) is relatively less in FO. Fouling is reversible in FO, but irreversible in RO. In other words, the deposition of foulants on the membrane in FO is temporary and, therefore, the reduced flux can be completely recovered after simple cleaning processes that improve the total average water flux, quality of product and membrane life.[6,7]

Water flux and recovery in FO can be easily increased by raising the osmotic pressure difference across the membrane.[8] These aforementioned benefits reduce OPEX against RO. Apart from low OPEX, additional advantages of using FO systems compared to RO include:

1. Chemical storage and feed systems may be compact for capital, operational and maintenance costs
2. Lesser process piping
3. More flexible treatment units
4. Greater total sustainability of the desalination process.[5,6,7]

Many scientists and economists are attracted to idea of driving desalination units using solar or wind energy. However, these technologies are restricted to small scales and may be practical only for "off-the-grid" locations.[4] The main disadvantage of these technologies is that energy sources are not available 24 hr/d.

Several advances have been seen in graphene membrane, a thin layer of sp^2 hybridized carbon, due to its peculiar mechanical, thermal and electrical properties. In such a membrane, water or selected solutes passes through straight pores; at present, however, the pores cannot be made small enough to reject salt.[4,9] Furthermore, graphene-based RO membrane would be expensive compared with commercially available membranes.[9]

Two ways of FO desalination exist: direct and indirect FO desalination.[5] The former takes seawater as a feed solution and a solution of relatively higher osmotic pressure as a draw solution, which is again treated to reuse. The latter uses impaired water, like municipal or industrial wastewaters, to dilute seawater through FO; the diluted seawater is then treated by the low-pressure RO process to produce freshwater. Both ways of FO desalination are discussed in detail in the following sections.

Direct FO desalination systems. In a direct FO desalination system (**FIG. 4**), saline water (like seawater) as feed solution and an osmotic reagent solution of relatively higher osmotic pressure as draw solution are taken on either side of a semipermeable membrane. Freshwater is extracted through the membrane from the feed solution into the draw solution due to the osmotic pressure difference across the membrane. Diluted draw solution is then sent to an additional stage to recover freshwater and regenerate the draw solution. Osmotic reagent in the draw solution can be a volatile or non-volatile salt.[5]

The most widely studied direct FO desalination process is with ammonium bicarbonate osmotic reagent due to its easily separable and regenerable characteristics.[6] Ammonium bicarbonate converts into ammonia, carbon dioxide and water at very low temperature (around 40°C) in an endothermic process, and again can be recovered in a crystalline structure at 30°C.

It has been reported that energy savings of around 70% may be realized with the use of this osmotic reagent, compared with conventional technologies. However, challenges to making the process commercial include the reduction of loss of ammonium bicarbonate due to its flow into the feed solution and complete transformation of ammonia, carbon dioxide and water into ammonium bicarbonate for regenerating the draw solution.

The studies are being directed toward developing a novel osmotic reagent, which has favorable abilities like high solubility,

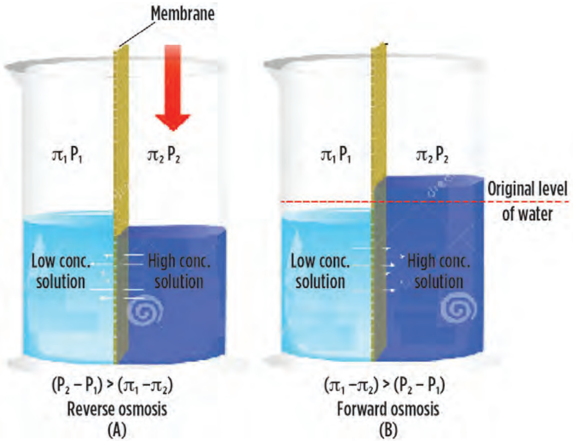

FIG. 2. Illustration of reverse osmosis (RO) and forward osmosis (FO).

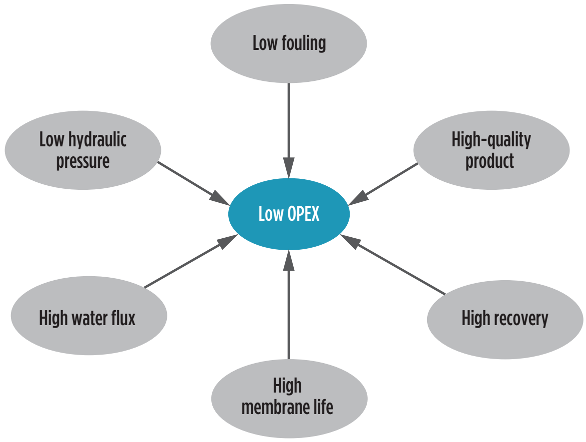

FIG. 3. Potential benefits of FO as compared to the more preferable conventional RO technology.

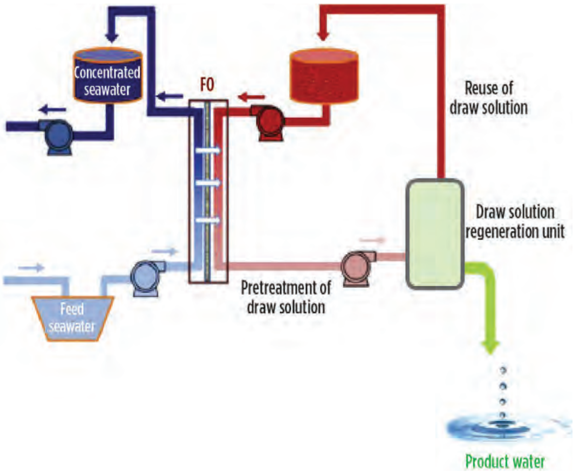

FIG. 4. Direct FO desalination system.[5]

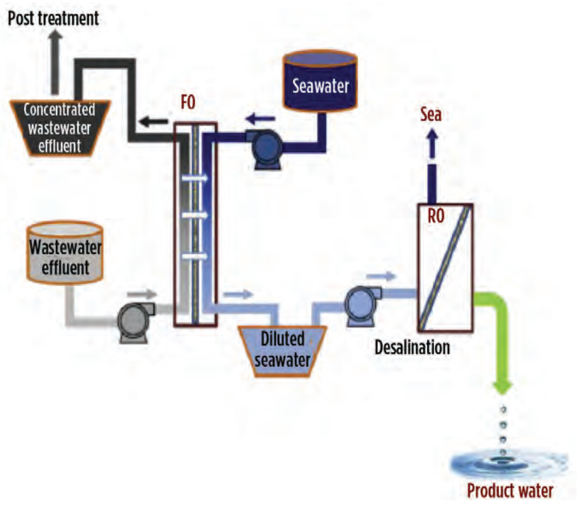

FIG. 5. Indirect FO desalination system.[5]

high osmotic pressure, low cost, nontoxicity, easy separation, reusability and eco-friendliness.[5,6] Hydrophilic nanoparticles have also been considered as an osmotic reagent solution, with synthetic seawater as a feed solution.

Ultrafiltration membrane-based processes have been used for the regeneration of draw solutions. Lower recovery of hydrophilic nanoparticles and poorer water flux are the main concerns with this osmotic reagent draw solution. Another study on divalent salts, such as Na_2SO_4, used an osmotic reagent draw solution for the FO process. The study showed adequate fluxes when desalinating brackish water; the draw solution regeneration process was nanofiltration.[9] Most of the draw solutes studied so far are less realistic due to their high cost, poorer water flux and inefficient regeneration.[6,7]

Indirect FO desalination systems. In indirect FO desalination, FO is not directly involved in the desalination process, but rather used as pretreatment for the conventional desalination unit,[7] as shown in **FIG. 5.**

Unlike direct desalination, an additional regeneration step is not required in this type of desalination. Seawater as the draw solution and any impaired water source, such as industrial or municipal wastewater, is taken as the feed solution. The freshwater is permeated through the FO membrane into seawater from impaired water using the free osmotic energy, leading to partially desalinated water. This water is then sent to a relatively low-pressure RO unit for further desalination.

The coupling of seawater desalination and simultaneous wastewater treatment by integrating FO and RO lessen overall energy consumption, offering a viable solution for the water-energy nexus for coastal locations. The supplementary benefits of this integration are providing cost-effective wastewater treatment and mitigating expensive treatment management.

The concentrated wastewater has further worth, which can be used to produce biogas or other valuable compounds. Furthermore, freshwater in wastewater permeates through both FO and RO membranes. Due to these double barriers, the rejection of most of the micro-pollutant impurities in wastewaters is relatively high[7] in such a desalination system vs. traditional wastewater treatment systems.

Like traditional RO technologies, fouling on the surface of the FO membrane is also seen in indirect desalination. The various methods of FO membrane cleaning, like chemical cleaning, air scouring and osmotic backwashing (which reverses the permeate flow by generating the opposite osmotic pressure gradient across the membrane) have been extensively investigated. It is reported that osmotic backwashing does not help recover flux, but air scouring and chemical cleaning using commercial chemical agents can increase the flux recovery to 90%–95%.[5,7,10,11]

This offset of flux restore of 5%–10% may be ascribed to the permanent deposition of biopolymers on the surface of the membrane. However, it can also be noted that the percentage of flux recovery depends on the type of foulants present in wastewater. The spacers (mesh-like structures) in membrane modules generally mitigate the fouling rate in membrane processes.

Part 2 of this article, to be published in the August issue, will look at membrane development and manufacture, as well as the integration of FO with an existing multi-stage-flash-distillation unit. HP

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Minimize energy consumption in water treatment with forward osmosis technology—Part 2

Heavy industries like refining, petrochemicals and mining face concerns about the availability of freshwater, as these are affected by local water scarcities and stringent water discharge regulations. The oil and gas industry needs relatively huge volumes of water, as the water/oil ratio averages 8:1.

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Forward osmosis (FO) technology, an emerging method, can be used to mitigate the aforementioned problems. FO uses the natural osmotic pressure difference between two solutions of different concentrations as a driving force to permeate freshwater through the semi-permeable barrier. Due to freely available renewable osmotic energy, projected energy savings from the FO systems compared with conventional technologies have been realized in the range of 30%–70%, depending on the product (freshwater) recovery.

FO can energetically outperform conventional technologies with much lower fouling propensity. Part 2 of this article examines membrane development and manufacture, as well as the integration of FO with an existing multi-stage-flash-distillation unit.

Membrane development and manufacture. The influence of feed spacer thickness on the fouling rate and permeation rate in the FO process was investigated.[12] The amount of foulants did not alter the thickness of the spacers, but the flux decreased with higher thickness. These remarks are in good agreement with earlier fouling studies for RO technologies. The flux reduction due to fouling was also explored at different feed and draw solution velocities. Higher velocities also mitigate fouling rate and improve FO performance.

FO membranes are generally asymmetric in nature, comprising two layers: an active layer and a support layer. The water flux in FO depends primarily on the membrane mass transport parameters, which include the pure water permeability (A) and solute permeability (B) of the active layer, as well as the structural parameter of the support layer (S).[13]

The ideal FO membrane has high A value, and low B and S values with sufficient mechanical strength to sustain moderate pressure. Most work on FO membrane behavior and efficiency has been carried out using small-sized membrane test cells.[5,9] Largely, the membranes made of thin film composite (TFC) polyamide and cellulose triacetate (CTA) (with the support of polysulfone/polyethersulfone/polyester) have been tested for the FO process in literature. These membranes were either self-made or purchased for testing purpose. More recently, researchers have fabricated novel TFC FO hollow-fiber membranes to boost the membrane surface area-volume ratio.[8]

For an industrial-scale purpose, membrane modules having a large surface area of membrane per unit volume are used in the membrane-based processes.[13,14] As in the RO process, four kinds of module geometries (spiral-wound, hollow-fiber, tubular and plate-and-frame) may be used in the FO process.

The spiral-wound and hollow fiber-modules have received much attention over the past five decades for RO since they offer definite advantages over tubular and plate-and-frame modules. Due to the unique characteristics of high membrane surface areas per unit volume, these modules yield the highest water flux. This higher productivity per unit volume represents more efficient operation through better space utilization, high-percentage water conversion and reduced water cost.

The flexibility of the TFC polyamide membranes is greater than that of the CTA membranes in choosing active and support layers. As such, TFC polyamide membranes with greater hydraulic permeability and reduced support resistance were made, allowing for higher water fluxes. The support-layer FO membrane containing nanofibers to limit support resistance is also a novel way to improve TFC polyamide membranes.

Another strategy to achieve novel FO membranes involves adapting RO membranes. These membranes have high permeability and high salt rejection, but they also have the drawback of a thick, porous hydrophobic support layer that is insufficient for FO owing to the severe support resistance.

The data obtained from literature are being used in the development and commercialization of numerous FO membranes—tabulated in **TABLE 1.**[5,8,9] It has been seen that most commercial membranes are TFC flat sheet membranes;

development of hollow fiber (HF) membranes is still in progress. Most companies have developed FO membrane with water flux around 30 l/m^2hr and reverse solute diffusion of less than 1 g/l. It seems that these new membranes will help further grow FO applications.

Pilot/commercial-scale status. Yale University in New Haven, Connecticut, US has built a pilot plant to demonstrate direct FO desalination plant. The aqueous solution of ammonia and carbon dioxide (CO_2) is used as draw solution. As per the research group at Yale University, the estimated energy savings is in the range of 25%–45% of conventional desalination technology.[15]

One more pilot plant of 500 l/d was constructed at the Korea Institute of Machinery and Materials using the same type of aqueous draw solution of ammonia and CO_2.[16] The model seawater solution of 0.55 M NaCl as feed, and ammonia/CO_2 solutions of 1 M, 1.5 M and 2 M as draw solutions, were used for the study. A packed-column distillation system was used to recover the draw solution. The results indicate 60% recovery of the draw solution and difficulty in regaining CO_2 in the solution as carbonate.

Direct FO desalination technology was commercialized at a plant (**FIG. 6A**) in 2012 in Al Najdah, Oman.[5, 17] Reverse osmosis was used to regenerate the draw solution. The installation proved the potential of FO for direct desalination in terms of OPEX and CAPEX; reduced chemical consumption; robust, fouling-resistant membranes; and a lower carbon footprint than competing technologies, such as conventional, high-pressure RO membrane systems. These benefits are realized only because of lower fouling problems in FO-RO hybrid systems. No chemical cleaning was required over several years of operation, yet the conventional process required cleaning every few weeks, with several membrane changes. The type of osmotic reagent/draw solution used in the plant has not been disclosed.

An FO-based, zero-liquid-discharge technology was recently developed.[18] This direct desalination technology was commercialized in China at the Changxing power plant (**FIG. 6B**) for wastewater reuse in the boiler feedwater loop and reducing both the intake of local surface water and the outflow of industrial wastewater. The capacity of this plant is 650 m^3/d and uses an aqueous draw solution of ammonia and CO_2. The FO unit is combined with a two-stage crystallizer for simultaneously producing mixed salt crystals of > 95% NaCl and Na_2SO_4. The plant's FO system functions at greater than 90% recovery, and the entire system gives 100% water recovery at lower CAPEX and OPEX than evaporator-based offerings.

FIG. 6. The world's first FO-based plant for seawater desalination (A) and the world's first FO-based, zero-liquid-discharge plant for industrial wastewater treatment (B).

The pilot plant for the FO nanofiltration hybrid system was operated for almost 6 mos using $(NH_4)_2SO_4$ fertilizer draw solution for the desalination of saline groundwater from coal mining activities; the water was reused for fertigation.[19] Results showed that the hydraulic cleaning was satisfactory to restore almost complete water flux in FO. No fouling or scaling issues were seen with the NF post-treatment process. Although this hybrid FO-NF system is technically feasible for fertigation purpose, an economic analysis and a full lifecycle analysis are needed. Furthermore, it was found that low rejection of both feed and draw salts is a concern and, therefore, the FO feed brine does not agree with the effluent discharge standard.

The FO and RO were also integrated at pilot scale in South Korea for indirect desalination using the wastewater treatment in a coal-fired power plant.[20] The water flux in summer and winter, fouling rate, reverse permeation of solutes and energy requirement in both FO and RO subsystems were estimated during 5 mos of pilot operation.

TABLE 1. Development and performance of commercial FO membranes [performance as seen in the literature with deionized water (DI) as feed and active layer facing feed solution (AL-FS) used as membrane orientation]

				FO performance		
Company	**Type of module**	**Commercial name**	**Status**	**Draw solution**	**Water flux, l/m^2hr**	**Solute to water flux ratio, g/l**
HTI	Spiral-wound	CTA-NW	Commercial	2M NaCl	8.5	0.1
HTI	Spiral-wound	CTA-ES	Commercial	1M NaCl	10.1	0.5
HTI	Spiral-wound	TFC	Commercial	1M NaCl	10	0.8
Oasys	Spiral-wound	TFC	Commercial	1M NaCl	30	0.7
Woongjin Chemicals	Spiral-wound	TFC	Development	1M KCl	16	1.3
Woongjin Chemicals	Spiral-wound	TFC	Development	1M KCl	27.9	0.4
Aquaporin	Spiral-wound	AqP	Commercial	1M NaCl	9.5	–
CSM-Toray	Spiral-wound	FO membrane	Commerical	1M NaCl	35	< 0.5
Porifera	Plate-and-frame	PFO elements	Commerical	1M NaCl	33	0.2–0.6
Samsung	Hollow-fiber	HFFO lumens	Development	1M KCl	9.3	0.6
Toyobo	Hollow-fiber	–	Commercial	–	–	–
Mattershift	Hollow-fiber	CNT membrane	Commercial	–	–	–

The energy savings from this hybrid system (as compared to the conventional RO system) were 15%. This percentage can be further improved by optimization of system parameters such as operating condition, membrane module arrangement, etc.

The water flux mitigated with time in the FO subsystem owing to organic fouling was easily restored by simply increasing crossflow velocity. The data obtained from the plant demonstrated that the FO-RO hybrid system is technically and economically feasible due to easy fouling control, low energy consumption and superior final water quality.

Another indirect desalination FO-RO hybrid system was built at pilot scale for simultaneous treatment of seawater and wastewater from the steel industry in Egypt.[21] The hybrid system was evaluated in terms of water flux, fouling behaviors and solute rejection. The concentration of seawater was found to have decreased from 3.5 wt% to 1.3 wt% after 180 min, using the FO system, while after 360 min it reached 1 wt%. No impurity was noticed in RO permeate during the complete duration.

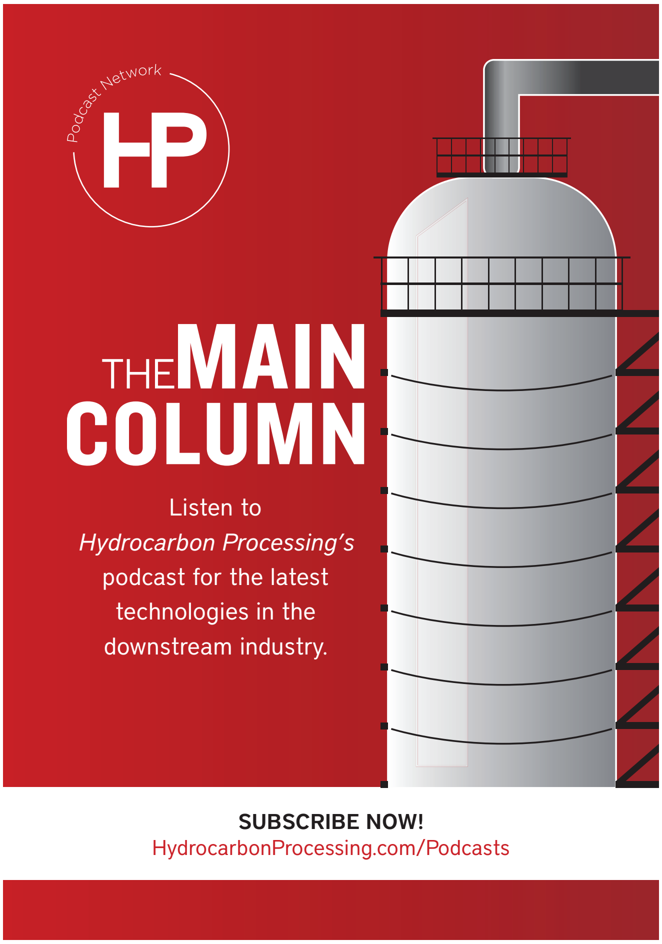
For treating secondary and tertiary effluent from a domestic wastewater treatment plant, the indirect FO-RO hybrid desalination system was also investigated at pilot scale in the Denver Water Recycling Plant in Denver, Colorado, US.[22] The hybrid system was claimed to be economically and technically viable across a wide scope of operating conditions.

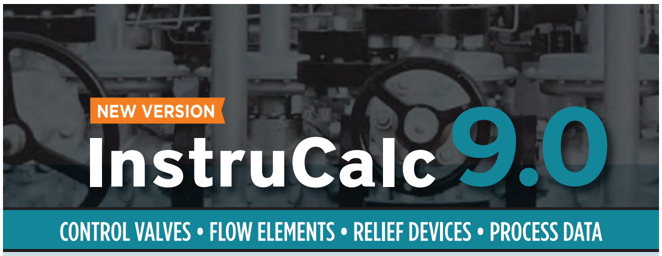
One company is trying to develop the integration of FO with existing and under-development multistage-flash-distillation (MSF) desalination units to increase plant efficiency.[23] MSF is a widely preferred seawater desalination technology in large industries (e.g., crude oil refining) where waste heat is used to heat seawater and produce vapor, which is then condensed to yield freshwater. As shown in **FIG. 7,** FO can be fit into an MSF unit. Brine can be recirculated as a draw solution, and seawater can act as feed solution.

During the process, freshwater in seawater permeates through the semipermeable membrane into the recirculating brine and, simultaneously, scaling precursors like Ca^{2+}, CO^{3-}, Mg^{2+} and SO_4^{2-} in seawater are rejected. Due to the addition of freshwater into the recirculating brine solution, the capacity of the recirculation stream pump is the same as the original unit. The top brine temperature is also sufficiently increased due to the removal of scalants, thereby significantly improving the overall efficiency of the MSF process.

As mentioned earlier, few FO schemes have been commercialized; although other, more efficient FO-based schemes are still in the research stage. The major challenges for these schemes for seawater desalination and wastewater reuse are:[8,9]

1. Developing an efficient membrane with an elevated salt rejection and reduced membrane/support-related resistance
2. Finding an appropriate draw solution that can easily regenerate (in direct desalination)
3. Better understanding of fouling and biofouling
4. Ensuring the high quality of produced water
5. Availability of a low-cost FO module.





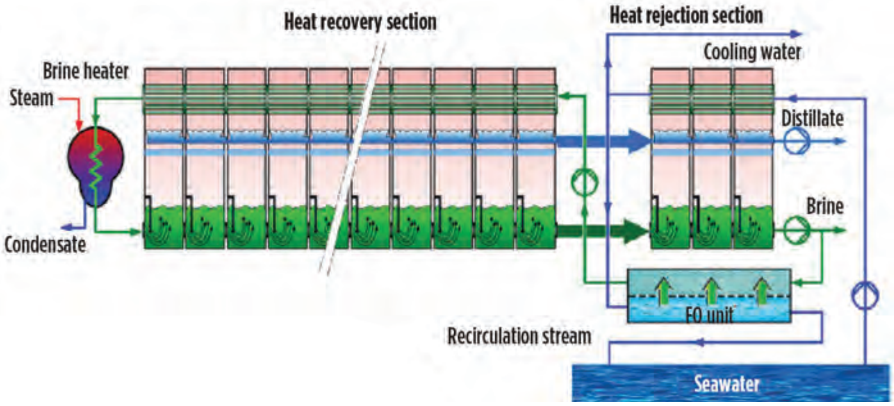


FIG. 7. Integration of FO with an existing MSF unit.

TABLE 2. Comparison of energy requirements for seawater desalination technologies to the ammonia-carbon dioxide FO technology[12]

Technology	Total energy required, KWh/m³	Percent energy savings using low-temperature FO
MSFD	5.66	85%
MED	4.05	79%
RO	3.02	72%
FO	0.84	–

Some excellent review papers have been recently published describing the status of FO membrane development, different types of membrane materials and fabrication techniques to improve membrane flux.[8,9] The minimum water flux needed to compete with conventional water reuse technologies is 10.5 l/m^2hr, and a water flux of 5.5 l/m^2hr is needed for desalinated water to compete with conventional RO systems at a lesser cost.[24] Several recently commercialized FO membranes have improved water flux of about 10 l/m^2hr up to 30 l/m^2hr–40 l/m^2hr, but their long-term sustainability and economic feasibility must be verified.

Energy and economics of an FO system. As conventional technologies for desalination and/or wastewater reuse are energy-intensive, a comparison between FO systems and conventional technologies in terms of specific energy consumption is essential. TABLE 2[12] shows predicted specific energy consumption in various conventional technologies and direct ammonia-CO_2 FO desalination technology. Due to the use of a direct FO desalination system, the percent reduction in specific energy consumption may be realized at around 80% as compared to thermal desalination technologies, such as multistage flash distillation (MSFD) and multi-effect distillation (MED), and around 70% as compared to the most preferred RO technology.

For an indirect FO desalination system, the predicted specific energy consumption is in the range of 1.3 KWh/m^3–1.5 KWh/m^3, using a secondary wastewater effluent as feed and seawater as a draw solution.[5] These energy savings are due only to the decrease in the osmotic pressure of the feed seawater and the hydraulic pressure required in a low-pressure RO system, compared to a conventional RO system.

The capital cost of the FO hybrid system may be higher than that of conventional technologies because of the additional FO membrane unit. Nevertheless, the lower operational cost, payback time and unit cost of each m^3 of freshwater produced would far outweigh the concern of higher capital cost.[9,24] According to a recently developed mathematical model,[23] a cost savings of $0.1/$m^3$ can be realized from the indirect FO desalination. Further improvement in FO membrane modules, packing density and water permeability may again boost the cost savings figure. HP

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Chemistry system—A key to increased steam system reliability

Oil refineries and petrochemical plants rely on steam systems to maintain utility and process unit operations. Consequently, operational reliability of the steam system is essential to maintain efficient, profitable plant performance.

Water treatment chemicals and controls designed specifically for individual plant operating conditions help provide the desired steam system reliability. A proprietary chemistry modeling system[a] (CMS) helps optimize the selection of chemical treatments, their application points and the water treatment chemistry controls.

FIG. 1 illustrates the typical $pH_{25°C}$ variation found in a simple industrial steam system with 5 ppm of carbon dioxide (CO_2) in the steam and a single neutralizing amine feedpoint. If enough amine is fed to the feedwater to achieve a fully condensed steam sample pH of 8, then the pH of the condensate leaving the steam turbine surface condenser will normally be close to 9. This is because the surface condenser vent will remove most of the CO_2 in this condensate stream but leave much of the neutralizing amine.

By contrast, the condensate formed by steam flow through the two process heat exchangers will have a pH of 8—the same as condensed samples of steam leaving the boiler. However, when hot condensate from these exchangers goes to a flash tank, the CO_2 concentrates in the flashed steam. In this example, a pH of 8.9 is produced in the flash tank bottoms and a pH of 6.4 is produced in the condensate from the process heat exchanger that uses the flashed steam.

When the three condensate streams—turbine surface condenser, flash tank bottoms and condensate from the exchanger using flashed steam—are blended together, the pH of the blended streams will be approximately 8.2. If it is relatively hot condensate, then it will lose some CO_2 in the vented storage tank and return to the deaerator with a pH of approximately 8.5.

Oil refineries. While these same basic principles apply in oil refinery steam condensate systems, their configurations are not this simple. Consequently, the refinery system complexity often makes the selection of chemical treatment, treatment application points and monitoring locations difficult to ensure effective protection of the entire system. The CMS can eliminate the "guesswork."

Building a digital twin of a refinery steam condensate system with the CMS enables a company to evaluate the potential performance of various products, feedrates and feedpoints throughout the system. In operation, the CMS combines conventional system analysis with pH and temperature-dependent distribution ratios, using advanced algorithms that enable the development of a balance of flows and chemistries throughout the system.

The program parameters required to build a digital twin of a refinery steam condensate system with a CMS typically consist of system configuration, flowrates, operating temperatures and pressures, contaminants and applied chemistry. Wherever the water and steam are in thermodynamic equilibrium, such as boilers, flash tanks, deaerators and condensers, these phase separation units are linked together in a system flow diagram using the CMS graphical interface.

Using the input flows and temperatures, the program calculates the flows around the rest of the units, such as flash tanks, and then calculates the vapor liquid distribution constant (*Kd*) and acid dissociation constant (*Ka*) for each chemical or combination of chemicals in each unit operation at that unit's operating pressure and temperature. After the required flows and constants are derived, the program calculates the coupled series of equations for each phase separation unit. Each form of the ionic species for each chemical in both liquid and steam phases is accounted for, and the interaction between them determines the pH at each location.

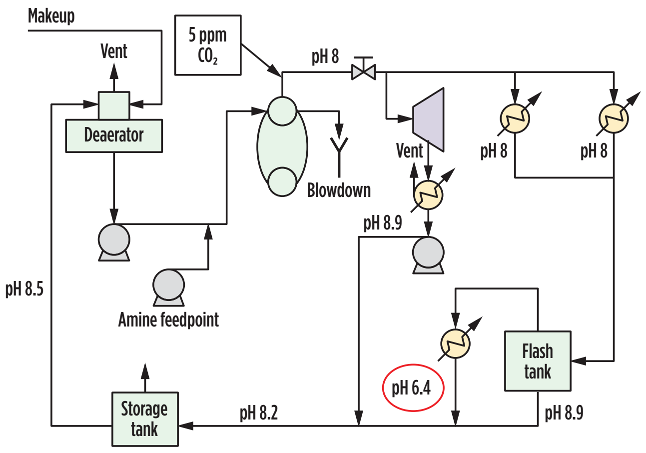


FIG. 1. $pH_{25°C}$ varies substantially throughout most industrial steam systems.

The program outputs include system flows, chemical concentrations (amine, CO_2, organic acids, etc.), pH at 25°C, pH at operating temperature (pH@T), conductivity and ionic species for a given chemistry throughout the system.

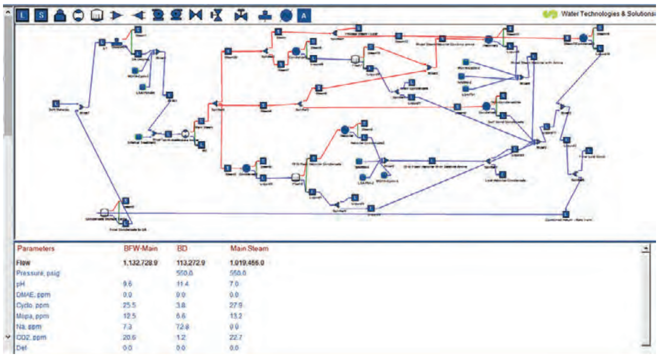
If looking for a simple analogy, the CMS program lets the user take various water treatment chemistry options for a "test drive."

Customer application. An oil refinery with sodium zeolite softened makeup water was experiencing significant reboiler corrosion problems, despite high neutralizing amine feed and costs.

A model of the boiler-steam-condensate system at the refinery was constructed to simulate the behavior of the treatment chemistries and contaminants throughout the plant. The model incorporates several key components of the system, including feedwater and steam flows from multiple pressure boilers, condensate return, surface condensers, flash tanks, reboilers using steam from flashed condensate and vented receivers. This model enables evaluation of the impacts of variation in makeup water purity, chemical treatments and chemical feedpoints.

The CMS digital twin (FIG. 2) represents a simplified version of the refinery steam system. This was used to evaluate a total of seven different treatment options. The evaluations included different neutralizing amine chemistries, various satellite feed points, reverse osmosis to reduce alkalinity in the makeup and CO_2 in the steam, and a combination neutralizer-polyamine filmer treatment.

A neutralizing amine and polyamine filmer blend was recommended as it offered an economical approach to controlling reboiler corrosion with reduced total amine usage, thereby reducing the potential for amine-chloride salt fouling in the crude unit atmospheric tower.



Parameters	BFW-Main	BD	Main Steam
Flow	1,132,728.9	113,272.9	1,019,456.0
Pressure, psig		550.0	550.0
pH	9.6	11.4	7.0
DMAE, ppm	0.0	0.0	0.0
Cyclo, ppm	25.5	3.8	27.9
Mopa, ppm	12.5	6.6	13.2
Na, ppm	7.3	72.8	0.0
CO2, ppm	20.6	1.2	22.7
Det	0.0	0.0	0.0

FIG. 2. A model of a simplified representation of the refinery steam and condensate system, which has more than five flash tanks and 15 reboilers. Despite this complexity, the CMS was able to identify an economical treatment plan to control reboiler corrosion.

The refinery implemented the prescribed treatment program several years ago. The treatment program has been able to maintain excellent plantwide corrosion protection. Most importantly, the refinery has not suffered any reboiler failures, and the opportunity for recent inspections revealed good reboiler protection from the new treatment program.

Petrochemical plants. In petrochemical plants, transfer line exchangers (TLEs) cool the pyrolysis coil effluent gases, while producing high-pressure steam. The design of these systems, the heat flux, the water circulation rates and the temperature require high-purity boiler feedwater.

At first thought, it might seem that with high-purity boiler feedwater the potential for problems would be minimal. However, since high-purity feedwater is unbuffered, very small levels of contamination—either acidic or caustic—can produce large pH changes, making the water potentially corrosive to the system metal. Complicating the issue further, neutralizing amines, commonly used to boost the pH of feedwater and condensate systems to protect them from corrosion, also raise the pH of cooled boiler water samples, but have very little effect on the "at" temperature pH of the water in a 1,500-psig (104-barg) TLE/boiler, potentially providing the operator with confusing or misleading information.

TABLE 1 shows the effect of temperature on the pH of pure water and otherwise pure water treated with four commonly used amines in a 1,500-psig (104-barg) steam generating system. When the amines are fed to produce a feedwater pH of 9, cooled boiler water sample pH levels are near 9 as well, varying slightly as a function of amine distribution between the water and steam phases. However, due to a lack of amine ionization at high temperatures, the effect on the pH of the water in the operating boiler varies from only 0.1 pH–0.4 pH units above 5.8, the pH of pure untreated water in the boiler.

The lack of correlation between the pH of water in the operating boiler and the pH in cooled boiler water samples can lead to confusion concerning the potential for problems. For example, when there is no feedwater contamination, TLEs treated with all volatile treatment (AVT) using a 50/50 mixture of cyclohexylamine and morpholine will have a pH profile like that shown in line A of TABLE 2.

By contrast, when there is 5 ppb of acidic chloride contamination in the feedwater, with the same amine treatment, line B of TABLE 2 shows that the cooled boiler water sample pH (8.2) is somewhat lower, but still alkaline, while the pH of the water in the boiler is 5.2, well below 5.8, the pH of pure (neutral) water in the boiler. This acidic boiler water pH at operating conditions creates a potential for corrosion, which becomes even

TABLE 1. The lack of amine ionization in high-temperature boiler feedwater significantly reduces the effect of amines on the pH of water in an operating boiler, compared to their effect on the pH of cooled boiler water samples

Amine	Feedwater pH at 25°C (77°F)	Boiler water pH at 25°C (77°F)	1,500-psig boiler water pH at 314°C (597.6°F)
Pure water	7	7	5.8
Morpholine	9	9	6
Cyclohexylamine	9	8.6	5.9
Methoxypropylamine (MOPA)	9	9	6
Monoethanolamine (MEA)	9	9.4	6.2

more pronounced if the water is locally concentrated beneath deposits or in areas of marginal circulation. For example, 10 concentrations of this boiler water will decrease the local boiler water pH to a very corrosive 4.3.

Can this low level of chloride contamination be neutralized with increased amine feed? Yes, but to increase the pH to that of pure water in the operating boiler, the amine feed must be increased to boost the cooled boiler water sample pH to 9.4. As noted in line C of **TABLE 2,** this will require a feedwater pH of 9.8.

Whatever the level and type of contamination, the CMS can help identify the extent of potential risks and evaluate the potential options to mitigate them.

Phosphate treatment. To protect against low-level feedwater contamination, the boiler water is often treated with sodium phosphate. Slightly different controls are used depending on whether coordinated phosphate-pH, congruent phosphate-pH, equilibrium phosphate treatment or other similar controls are chosen.

Each of these programs are based on maintaining sodium hydroxide-to-phosphoric acid mole ratios within specified control ranges. These are often referred to as sodium-to-phosphate mole ratios discounting the presence of neutral sodium salts, such as sodium chloride, that may also be present in small quantities. In practice, the control is normally accomplished by utilizing a phosphate vs. pH control chart that is based on the desired sodium hydroxide-to-phosphoric acid mole ratios in otherwise pure water.

A typical control chart for the commonly used congruent phosphate-pH treatment control program is shown in **FIG. 3.** The usual control chart is based on the solid chemistry in the boiler water without consideration of the effect of amine on the pH of the cooled boiler water samples and the corresponding lack thereof in the boiler itself. This practice is normally acceptable when cyclohexylamine and morpholine are the amines being used, because cyclohexylamine is very volatile and little of it stays in the boiler water; and morpholine (more of which stays in the boiler) is a weak base. Consequently, in normal use, morpholine and cyclohexylamine have little effect on the pH of cooled boiler water samples in the presence of 5 ppm or 6 ppm of sodium phosphate.

However, other neutralizing amines, such as methoxypropylamine (MOPA) and monoethanolamine (MEA), are pro-

TABLE 2. pH profile in 1,500-psig boiler water with no feedwater contamination and with 5 ppb of acidic chloride feedwater contamination when operating with AVT and blowing down 1% of the boiler feedwater

	Feedwater additives and contaminants	Feedwater pH (25°C)	Boiler water pH (25°C)	Boiler water pH (314°C)
A	Cyclo/morph	9	8.8	5.9
B	Cyclo/morph + 5 ppb chloride	9	8.2	5.2
C	Increased cyclo/morph + 5 ppb chloride in feedwater	9.8	9.4	5.8

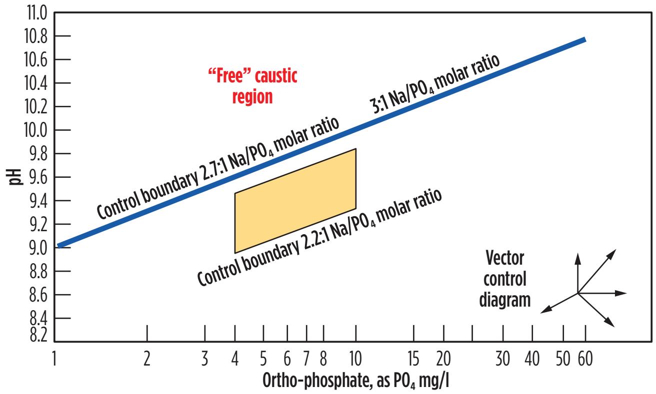


FIG. 3. Typical control chart for congruent phosphate-pH control treatment based on sodium hydroxide-to-phosphoric acid mole ratios of between 2.2:1 and 2.7:1.

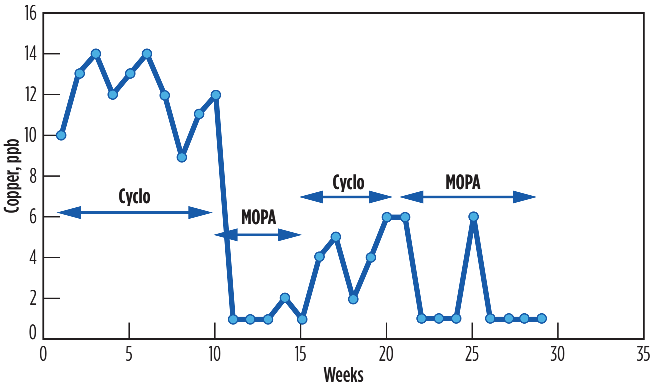


FIG. 4. Copper levels in charge gas compressor condensate were reduced by changing from cyclohexylamine (cyclo) to MOPA in the amine blend used for feedwater and condensate system protection.

viding benefits in some systems not achievable with morpholine and cyclohexyamine.

For example, MOPA has demonstrated the ability to improve corrosion protection of copper alloy surface condensers compared to the use of cyclohexylamine. Due to its high volatility and strong base properties, cyclohexylamine often concentrates in the air removal section of surface condensers boosting localized pH levels and increasing corrosion of the copper alloys. **FIG. 4** shows the reduction in copper in the condensate from a charge gas compressor surface condenser when a plant changed from using cyclohexylamine to MOPA in its treatment program.

The lower distribution ratio of MOPA, which keeps it from concentrating as much in the air removal section of the surface condenser, also keeps more of it in the boiler water. Consequently, it can have a significant effect on the pH of cooled boiler water samples. Since the goal of the phosphate-pH charts is to maintain the sodium hydroxide to phosphoric acid ratio within a certain range, the control chart for plants using MOPA should be adjusted for the effect of MOPA on the pH of cooled boiler water samples.

FIG. 5 shows the effect that feeding only MOPA to achieve a boiler feedwater pH of 9 will have on the minimum boiler water pH level required in a 1,500-psig steam generating system to maintain the minimum 2.2:1 sodium hydroxide-to-phosphoric acid mole ratio in the boiler water.

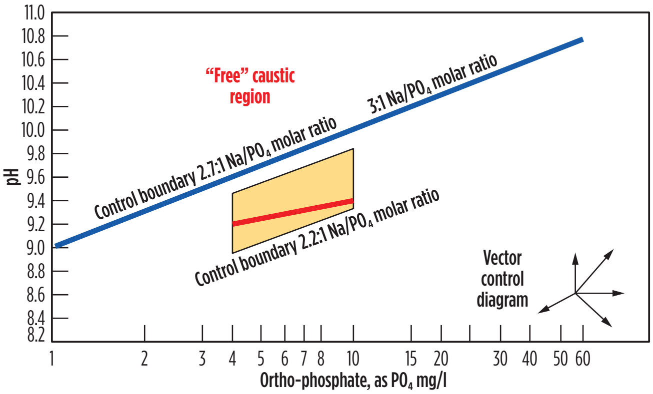


FIG. 5. The red line shows the effect that feeding only MOPA to achieve a feedwater pH of 9 will have on the 1,500-psig boiler water phosphate-pH relationship required to maintain the minimum sodium hydroxide-to-phosphoric acid mole ratio of 2.2:1.

Significantly greater changes in the phosphate-pH control charts are needed whenever a product contains a low distribution ratio and a strong base amine (such as MEA) is being used. The CMS can be used to provide amine-corrected phosphate-pH control charts for the chemistry that will best benefit a system.

Takeaways. The proprietary CMS is helping customers maintain reliable operations throughout their steam generation and condensate systems. This is accomplished by enabling the evaluations of different chemistries and contaminants throughout complex steam condensate systems and assessing the chemistry, not only of cooled water samples but also in the operating equipment, such as high-pressure boilers (e.g., TLEs).

This valuable utility modeling program has been used in numerous refinery/petrochemical applications for assisting in performance predictions, developing proper chemistry programs and control parameters, optimizing condensate return, managing contamination, economic evaluations of pretreatment and chemistry options, minimizing flow-accelerated corrosion and even product development. Combining the CMS with process-side modeling tools can also enhance the refinery's ability to manage process-side corrosion when steam is used in the process. HP

NOTES

[a] SUEZ's Chemical Modeling System

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HP | Water Management

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Are produced water emissions factors accurate?

Rules of thumb are often required to estimate hydrocarbon emissions from produced water storage tanks due to a lack of sampling or inadequacies of sample analysis—the "1% rule" being the most common. The premise behind the 1% rule is that entrainment from upstream separation introduces hydrocarbon liquids into the produced water tank. This entrained material forms a layer of hydrocarbons that float on top of the water in the tank and should be expected to increase total emissions. As it is difficult to measure the entrained oil content in the water fed to the tank, there is uncertainty in how much of this entrained oil is lost to emissions. Therefore, the 1% rule is applied as an estimate.

If 1% entrainment is assumed, a problem arises as to how this should be incorporated into typical emissions calculations. In discussions with industry colleagues, the author has found at least four different definitions for the 1% rule and how it should be applied. As each method produces significantly different estimates, questions arise: Do any of these methods provide accurate estimates of produced water tank emissions? Which of these methods makes the most sense?

Storage tank emissions are commonly divided into four categories: flashing, working, breathing and loading. Flashing losses occur from vaporization of components in the tank inlet due to a pressure decrease and/or temperature increase of the material. These losses occur when the material is introduced to the tank. Working, breathing and loading (WB&L) losses occur as the material in the tank weathers or as it is removed. They are all caused by a changing vapor space in the tank. For working losses, this is by liquid level changes in the tank. Working losses increase as tank throughput and hydrocarbon vapor pressure increase. Breathing losses are the result of daily ambient temperature changes as the changing temperature causes the vapor space in the tank to expand and contract. Breathing losses increase with vapor pressure and are not directly influenced by tank throughput. Loading losses occur as vapors in a cargo transport vessel are displaced by liquid being loaded into the vessel. These losses increase as tank throughput and vapor pressure increase.

Before evaluating the various methods of applying the 1% rule, it makes sense to discuss a few items: How do hydrocarbons make their way to the produced water storage tank? Is there a logical method that would provide a more rigorous estimate of emissions than methods being used?

A diagram of a typical wellsite configuration is shown in **FIG. 1.** After exiting the wellhead choke, the well stream is commonly a three-phase mixture of gas, hydrocarbon liquid and aqueous liquid. The gas is first separated from the liquid mixture in a high-pressure separator (HPS). After leaving the HPS, liquids will flow to a heater treater (HT), where more gas is removed, and the two liquid phases are separated at an elevated temperature and reduced pressure (typically 20 psig–50 psig). The produced water leaving the HT then flows to the produced water storage tank, and the hydrocarbon stream flows to the hydrocarbon storage tank. These streams are stored until loaded and transported away from the wellsite.

Hydrocarbons can make their way to the produced water storage tank in two ways—either by dissolving in the water or by mechanical carryunder, known as entrainment. While it is often said that "oil and water do not mix," hydrocarbons are slightly soluble in water, with lighter hydrocarbons and aromatic components being the most soluble. This solubility increases somewhat proportionally with pressure, and it is dependent on the concentration of salts in the produced water. The solubility is highest in pure water and declines with increasing salt concentration. An estimation of dissolved hydrocarbons on a "salt-free" basis would produce a conservative estimate if using a process simulator. Analytical techniques exist that mimic the pressure reduction from upstream separator conditions to stor-

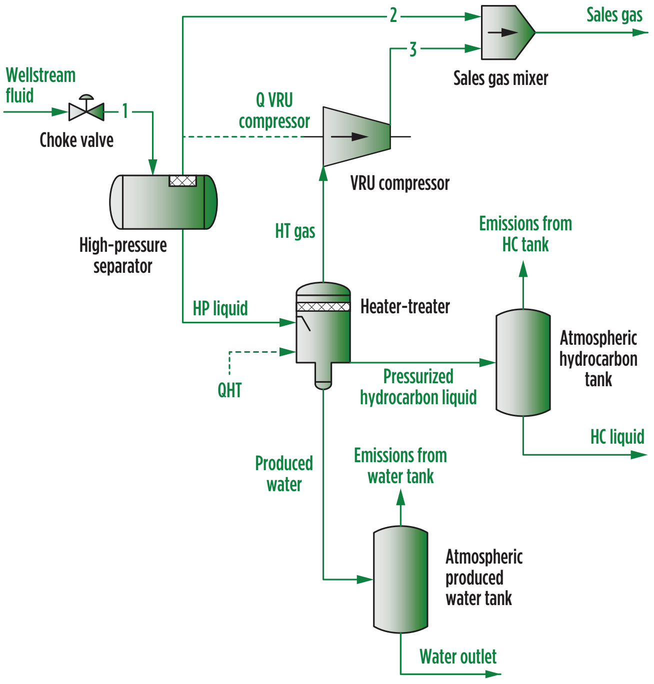

FIG. 1. Typical wellsite configuration.

TABLE 1. Sample conditions and composition of hydrocarbon mixtures from wellsite facilities

Sample	**1**	**2**		**3**	**4**
Temperature, °F	120	66		146	130
Pressure, psia	56.7	56.7		45.7	29.7
			Composition, mol%		
Methane	0.41	0.89	**H_2S**	0	0
Ethane	2.07	2.56	**N_2**	0.01	0.01
Propane	5.12	5.45	**CO_2**	0.03	0.01
i-Butane	1.31	1.33	**Methane**	0.15	0.05
n-Butane	6.17	6.22	**Ethane**	1.18	0.61
Isopentane	2.32	2.3	**Propane**	4.69	3.68
n-Pentane	4.19	4.15	**i-Butane**	1.11	0.96
2-Methylpentane	2.2	2.17	**n-Butane**	5.51	5.26
n-Hexane	2.3	2.26	**2,2-Dimethylpropane**	0.12	0.03
2,2,4-Trimethylpentane	0.12	0.12	**i-Pentane**	2.64	2.57
n-Heptane	10.21	10.05	**n-Pentane**	3.75	3.46
n-Octane	9.08	8.93	**2,2-Dimethylbutane**	0.02	0.02
n-Nonane	3.78	3.71	**Cyclopentane**	0	0
Benzene	0.28	0.28	**2,3-Dimethylbutane**	0.63	0.52
Toluene	0.93	0.92	**2-Methylpentane**	1.61	1.44
Ethylbenzene	0.34	0.33	**3-Methylpentane**	1	0.89
p-Xylene	1.44	1.41	**n-Hexane**	2.64	2.25
C_{10}+*	47.72	46.9	**Methylcyclopentane**	2.37	2.15
			Benzene	0.24	0.24
			Cyclohexane	1.36	1.18
			2-Methylhexane	0.93	0.81
			3-Methylhexane	0.86	0.78
			2,2,4-Trimethylpentane	0	0
			2-4-Dimethylpentane	2.8	2.54
			n-Heptane	2.06	1.76
			Methylcyclohexane	2.97	2.56
			Toluene	0.81	0.69
			2,3,3-Trimethylpentane	5.65	5.11
			n-Octane	1.8	1.57
			Ethylbenzene	0.91	0.17
			m-Xylene	0.79	0.56
			o-Xylene	0.4	0.51
			Hexane, 2,3,4-Trimethyl-	5.49	4.58
			n-Nonane	1.5	1.17
			2-Methylnonane	5.12	4.65
			n-Decane	1.04	0.94
			Nonane, 2,3-Dimethyl-	5.05	4.46
			C_{12}	3.82	3.73
			C_{13}	3.81	3.93
			C_{14}	3.18	3.26
			C_{15}	2.44	2.76

TABLE 1. Sample conditions and composition of hydrocarbon mixtures from wellsite facilities (cont.)

C_{16}	1.95	2.46
C_{17}	1.65	1.99
C_{18}	1.53	1.86
C_{19}	1.45	1.91
C_{20}	1.03	1.39
C_{21}	0.87	1.39
C_{22}	0.86	1.28
C_{23}	0.69	1.18
C_{24}	0.59	1.13
C_{25}	0.62	1.03
C_{26}	0.39	0.72
C_{27}	0.43	0.92
C_{28}	0.35	0.8
C_{29}	0.29	0.76
C_{30}	6.82	9.28

Note: C_{10}+ molecular weight = 282.7, specific gravity = 0.88

age conditions, providing an additional estimate of the flashing emissions from dissolved hydrocarbons in the produced water.

The results of these estimation techniques will confirm the expected low solubility of hydrocarbons in the water, and, therefore, a low contribution of overall emissions by the dissolved hydrocarbons. **TABLE 1** provides the separator conditions and compositions for four samples of pressurized liquids leaving the HTs. For Sample 1, the equilibrium dissolved hydrocarbon solubility in pure water—predicted by a proprietary simulation software[a]—is below 100 ppm, indicating a low contribution to overall emissions from dissolved hydrocarbons.[1]

The second way that hydrocarbons enter the produced water storage tank is as an entrained second phase. This second phase is a significantly greater contributor to emissions than the dissolved hydrocarbons. To estimate emissions from the entrained liquid, the composition and volume of the material must be known. The entrained hydrocarbon droplets are the same material as the hydrocarbon liquid stream leaving the HT, a material of which the composition is typically known. However, what is usually unknown is the size or total volume of the droplets that are entrained.

Separators are designed to remove droplets of a certain diameter. Typical minimum droplet diameters are 100 microns–150 microns. A fraction of the droplets smaller than this threshold will be entrained due to inadequate residence time in the separator. Directly measuring these droplets—either in terms of size or total volume—is difficult. Therefore, the amount of entrainment is typically assumed or estimated. Some individuals assume that approximately 200 parts per million (ppm) of hydrocarbon leave the HT with the produced water. A separator manufacturer questioned for this article stated that their typical design point is 0.5% (5,000 ppm). Meanwhile, companies reclaiming hydrocarbons from produced water estimate that 1%–2% of the material entering the tank is entrained hydrocarbons.

With such widely varying estimates of entrainment and no reliable or cost-effective way to measure the hydrocarbon content, it is helpful to look for alternative ways to estimate entrainment. Fortunately, one can look at what is *leaving* the tank to estimate what is *entering*. As the produced water with the entrained hydrocarbon droplets enters the storage tank, a portion of the hydrocarbons will flash due to the lower pressure and enter the vapor space. The remaining liquid hydrocarbons will eventually coalesce as a separate layer on top of the water. Care is taken to avoid removing material from the hydrocarbon layer when unloading the water. The hydrocarbon layer itself is removed periodically by the operator in known quantities. As the hydrocarbon layer is removed only intentionally, the rate at which entrained hydrocarbons enter the tank can be estimated by monitoring the rate at which they are removed.

AP 42 correlations for estimating WB&L. The US Environmental Protection Agency (EPA) has recommended that Chapter 7 of AP 42[2] be followed for estimating tank WB&L emissions for *organic liquid* storage vessels. All the rules of thumb discussed in this article rely on AP 42 in some manner.

Two basic components comprise AP 42 methodology: Conditions and throughput (C&T) and vapor pressure (VP). The C&T component is a set of equations for estimating emissions based on tank geometry, tank throughput, daily temperature changes in the vapor headspace and hydrocarbon VP at the liquid surface.

For estimating the VP of pure components, AP 42 recommends Antoine's equation and provides Antoine's coefficients for several organic liquids, although many of the common oil and gas components are not included. AP 42 also includes nomographs and equations for estimating the VP of crude oil and refined petroleum stocks as a function of Reid Vapor Pressure and temperature.

For the VP of a mixture of components, AP 42 states that the *total vapor pressure* is simply the sum of the individual component partial pressures. AP 42 recommends that Raoult's law be used to calculate individual component partial pressures for hydrocarbon-only mixtures. Raoult's law states that the individual component partial pressure, p_i, can be calculated as shown in Eq. 1:

$$p_i = x_i P_i \tag{1}$$

where:

x_i and P_i = the mole fraction and pure component partial pressure for component *i*, respectively.

For *hydrocarbon mixtures* encountered in the oil and gas industry, the Raoult's law assumption is typically not problematic and will result in reasonable VP estimations. The US EPA recently compared emissions data from organic liquid storage tanks vs. estimates provided by AP 42 methods and found the predictions satisfactory.[3] Thus, it appears that the C&T component of AP 42 is sound *when teamed with reasonably good vapor pressure estimates.* This validates the C&T portion of the method in general.

If 1% entrainment is assumed, then the overall liquid would be 99 parts water and 1 part of the hydrocarbon. This would no longer be considered an organic liquid, and the application of Raoult's law would be problematic. Raoult's law applied to this mixture will greatly underestimate the VP and lead to severe underprediction of emissions.

TABLE 2. AP 42-required parameters used in this comparison

Working and breathing parameters			
Tank geometry	Vertical cylinder	Maximum average temperature, °F	75.9
Tank height, ft	25	Minimum average temperature, °F	53.9
Tank diameter, ft	12	Average ambient pressure, psia	14.66
Number of tanks	1	Daily solar insolation, Btu/(ft²d)	1,388
Throughput, bpd	100	Tank and roof color	Medium gray
Maximum fill	90%	Roof type	Cone
Average fill	50%	Roof slope (rise/run)	0.05
Loading loss parameters			
Land-based mode of operation		Submerged loading of a clean cargo tank	
Overall reduction efficiency		70%	

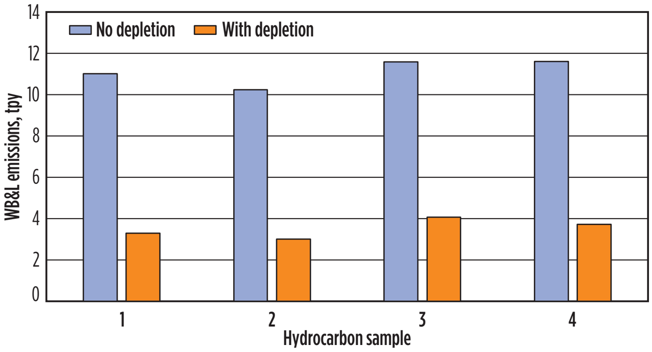

FIG. 2. Comparison of estimated emissions rates when depletion of material in the tank is considered, assuming 1% entrainment.

For dilute aqueous solutions of hydrocarbons, AP 42 specifies that Henry's law be used to calculate hydrocarbon partial pressures. However, if a second liquid phase is present, the use of Henry's law can be problematic. Henry's law extrapolates the volatility of a component at *infinite dilution,* which can lead to significant error (higher volatility than actual) when the hydrocarbon content is high enough to form a second phase. Furthermore, the use of Henry's law requires knowing the Henry's constant for each component at the temperature of interest. AP 42 does provide Henry's constants at a single temperature (25°C) for several organic components in water. However, as with Antoine's coefficients, many of the common oil and gas components are not included.

When a hydrocarbon layer floats on top of an aqueous layer, the hydrocarbon VP is dependent on the temperature and composition of the hydrocarbon layer alone. The thickness of the layer is inconsequential. The practical effect of this is that WB&L losses will not vary linearly with the amount of hydrocarbon entering the tank. However, the hydrocarbon layer's composition in the tank does change over time due to depletion of the lighter components (e.g., heavy components remain while light components are removed as emissions). As the entrained fraction decreases, the hydrocarbon losses consume a larger fraction of the lighter components entering the tank. The net result is that the composition of the hydrocarbon layer may not be the same as the hydrocarbons entering the tank and, in fact, may be heavier. This reduces the hydrocarbon layer VP, leading to decreased emissions.

This paper introduces a method that uses a process simulator to better estimate the VP of the floating hydrocarbon layer and consider the depletion of lighter components from that layer. It then presents and compares produced water tank emissions estimates for various definitions of the 1% rule.

A better way to estimate produced water emissions.

Modern process simulators can provide accurate estimates of VP for hydrocarbon/water mixtures over a wide range of compositions and temperatures, regardless of the number of phases present. Therefore, it is logical to replace Raoult's law or Antoine's estimates of the VP with those from the simulator, while using the C&T component of AP 42 to estimate emissions.

A tool was developed within proprietary simulation soft-

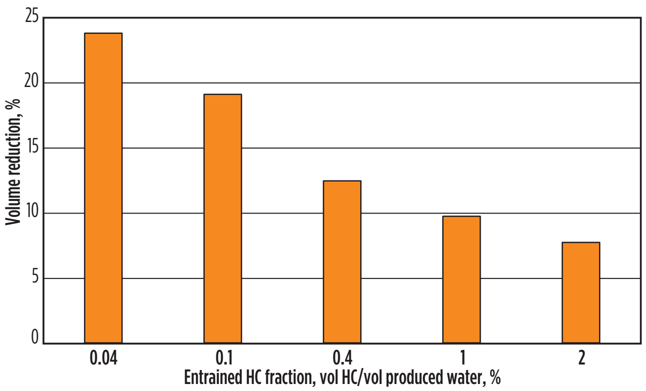

FIG. 3. Reduction in total hydrocarbons remaining in the produced water tank when considering depletion due to vapor emissions.

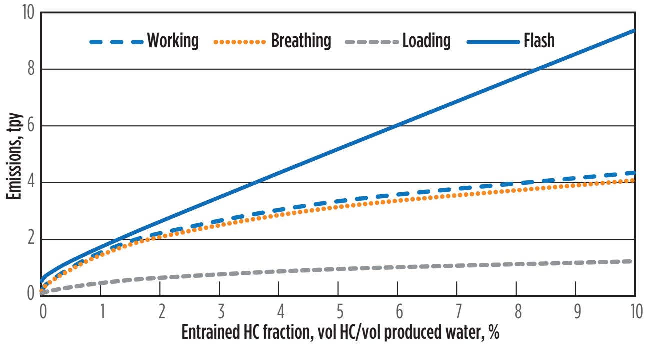

FIG. 4A. Sample 1 emissions vs. entrained HC fraction.

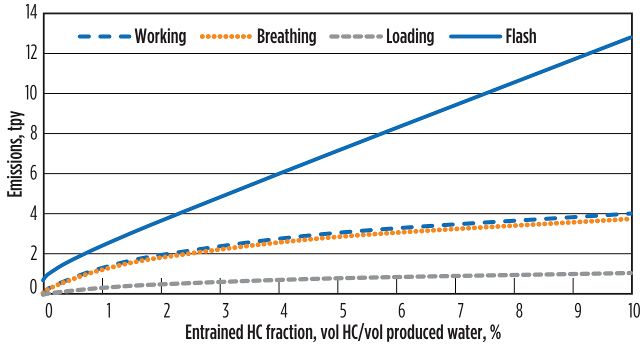

FIG. 4B. Sample 2 emissions vs. entrained HC fraction.

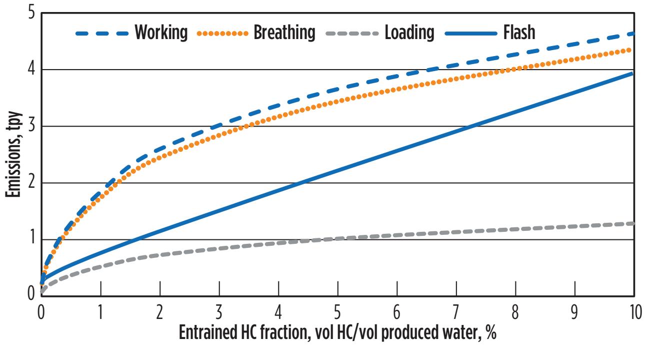

FIG. 4C. Sample 3 emissions vs. entrained HC fraction.

ware[a] to automate the use of the AP 42 C&T equations with hydrocarbon-water VP predictions. For brevity, this new tool will be referred to as the proposed produced water (PPW) method.

The AP 42 C&T equations assume the use of a constant composition. The composition that is typically used is the incoming feed composition, with possibly some conditioning to account for the initial flashing of the feed as it enters the tank. The AP 42 methodology was originally developed for *hydrocarbon storage tanks,* where the amount of material lost to emissions is very small compared to the throughput of material in the tank. The overall composition in the tank is assumed to be like the composition of the material entering the tank.

In *produced water tanks,* only a small fraction of the incoming feed is hydrocarbons. Since the hydrocarbon emissions do not change proportionally to the amount of incoming hydrocarbons, the hydrocarbons in the tank can become significantly depleted of the more volatile components when the entrainment is low. As the AP 42 equations are typically based on the incoming composition, *the predicted emissions of the lighter components can be greater than the feed rate of those components into the tank.*

To avoid this unrealistic result, one could develop a set of equations that attempts to determine the steady-state concentration of each component in the storage tank. However, for the sake of simplicity and clarity, the tool used here bases individual component emissions rates on the VP calculated from the incoming composition, capping the emissions for a given component at that component's inlet rate (e.g., ensuring that more of a component is not leaving a tank than entering). This should give conservative but reasonable WB&L estimates.

The PPW tool uses water that has been saturated with the known pressurized liquid composition at the temperature and pressure of the HT. This ensures that a reasonably conservative estimate of dissolved hydrocarbon emissions is attained and prevents solubilizing more hydrocarbons when the entrained hydrocarbons are added. The entrained pressurized liquid is used in the appropriate amount based on assumed entrainment, and the speciated emissions are predicted using AP 42 C&T correlations with ProMax VP predictions. The speciated emissions are capped at the incoming species flowrate.

PPW method predictions. Emissions estimations with the PPW methodology for a 500-bbl tank (vertical, fixed roof) were made and discussed below. Some AP 42 parameters that were used are shown in **TABLE 2.**

Using the information in **TABLE 2,** WB&L emissions were estimated for the four representative samples. **FIG. 2** shows how the total emissions estimates for the four samples are affected by the difference in composition of incoming hydrocarbons and the composition of the layer in the tank that has been depleted of lighter components. In the case of 1% entrainment, neglecting to account for component depletion would yield a threefold higher emissions estimate.

The depletion of lighter components does not just affect the composition of the layer in the tank, it also affects the volume of hydrocarbon remaining in the tank. Since the composition of this layer has changed due to material being removed, depletion should be considered when estimating entrainment rates from the amount of hydrocarbon removed from the tank. **FIG. 3** shows that there is a noticeable loss of hydrocarbons due to depletion, especially at lower entrainment fractions. This should be considered when estimating incoming flow based on outgoing flow.

FIGS. 4A–4D show the flash and WB&L predictions of this PPW methodology for each of the samples. The flash emissions increase linearly with entrained hydrocarbon fraction, while the WB&L emissions increase rapidly and then begin to level off. For these four samples, the WB&L emissions at 1% entrainment averaged *one quarter* of the WB&L emissions of a tank with a pure hydrocarbon feed, even though the hydrocarbon flow is 100 times lower. Likewise, emissions estimated for 0.1% entrainment are around *one-tenth* the emissions of a similar, pure hydrocarbon feed, even though the hydrocarbon flow into the tank is 1,000 times lower.

FIG. 4E shows the same information as **FIG. 4A,** but at very low entrainment fractions. When entrainment is assumed to be zero, the emissions are not zero. This is due to the dissolved hydrocarbons in the water. As mentioned previously, the estimates used here represent emissions from hydrocarbons in salt-free water, which should be an upper bound on actual dissolved emissions.

Comparison of PPW method to common rules for estimating produced water emissions. The PPW method for calculating produced water storage tank emissions can now be compared to the various definitions of the 1% rule. A basic premise of the 1% rule is that at the upstream separator, the water and hydrocarbons were at thermodynamic equilibrium. It is assumed that the composition of the hydrocarbon stream leaving the separator is the same as the composition of any entrained hydrocarbons in the water, and that hydrocarbon composition may be used in estimating emissions from the produced water tank. In discussions with oil and gas industry professionals and in Texas Commission on Environmental Quality (TCEQ) documentation, four different definitions of the 1% rule were discovered. These are presented here, with the order from most common to least common in the author's informal survey. These all assume some method is available for calculating flashing losses, and that WB&L losses will be calculated with AP 42 methods for hydrocarbon storage tanks.

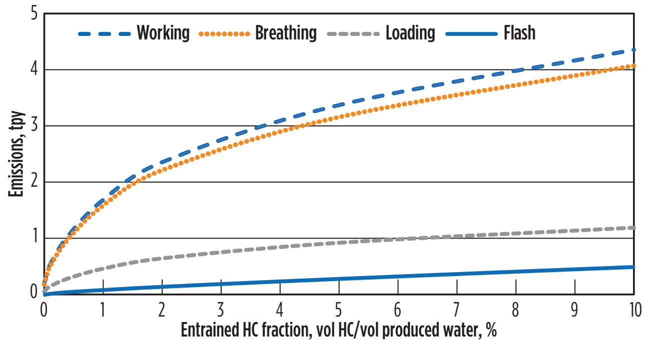

FIG. 4D. Sample 4 emissions vs. entrained HC fraction.

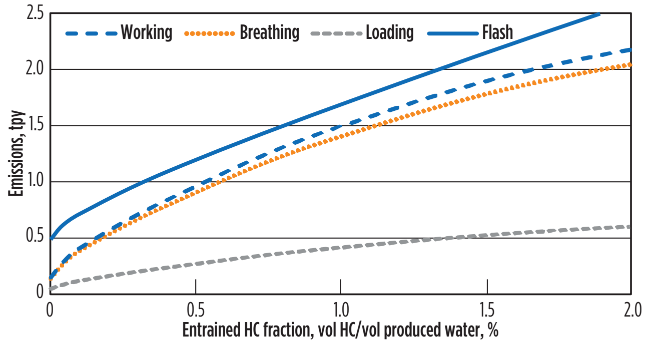

FIG. 4E. Sample 1 emissions vs. entrained HC fraction (low entrained fractions).

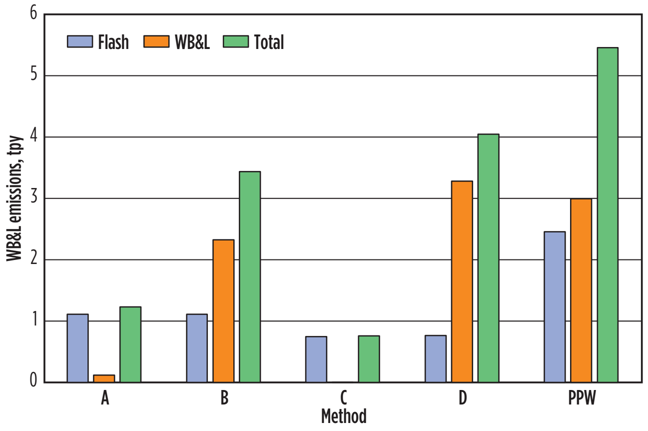

FIG. 5. Emissions estimates using the various methods for hydrocarbon Sample 2, assuming 1% entrainment.

Method A—Use the produced water flowrate and the composition of the hydrocarbon streams when performing the calculations. Calculate flash, working, breathing and loading per AP 42, then multiply results by 1%.

This method will give reasonably accurate flash emissions from the entrained hydrocarbons since these emissions are proportional to the entrained hydrocarbon flowrate. However, this method will not account for the flash emissions from dissolved hydrocarbons in water. Furthermore, this method will substantially underestimate WB&L losses as these losses do not decrease proportionally with incoming hydrocarbon flow.

Method B—Use the produced water flowrate, multiplied by 1%, and the composition of the hydrocarbon stream when performing the calculations. Calculate flash, working, breathing and loading without further modification using AP 42.

This method will yield the same flash estimates as Method A, and it will provide reasonable breathing losses. However, since the throughput of the tank is reduced to 1% of actual, changing tank levels are not appropriately considered, and the working/loading losses are underestimated.

Method C—Use the produced water flowrate and a composition of 99% water and 1% hydrocarbon stream when performing the calculations. Calculate flash emissions with a process simulator. Calculate working, breathing and loading without further modification, using AP 42.

This is the method published in a guideline from the TCEQ.[4] The guideline indicates that this method should be used in conjunction with the software program TANKS 4.09d,[5] which uses Raoult's law to calculate VP. TANKS 4.09d is a software program developed and distributed by the US EPA, which implements the methods specified in AP 42 Chapter 7.

The problem with this method is the use of Raoult's law in TANKS 4.09d to calculate the VP of the water/hydrocarbon mixture after the initial flash. Raoult's law will drastically under-predict VP, resulting in significant under-prediction of WB&L losses.

The flash predictions of this method will also be underestimated. When mixing one part hydrocarbon with 99 parts water, there is enough absorption of light hydrocarbon to significantly affect the VP of the remaining liquid hydrocarbons, thereby affecting emissions. In reality, the water is already saturated with the hydrocarbon components, and little to no additional absorption should take place.

Method D—Use the produced water flowrate and a composition comprised of 99% water and 1% hydrocarbons when performing flash calculations. Use the produced water flowrate and the hydrocarbon composition when performing WB&L calculations with AP 42.

This is another TCEQ guideline.[6] For flashing emissions, the results are identical to Method C and are underestimated due to absorption of hydrocarbons into the water. The WB&L emissions are very similar to that of the PPW method. This is logical since the VP used in the PPW method is essentially hydrocarbon VP. The slightly higher WB&L losses for Method D are because there is less hydrocarbon depletion from the Method D flash, which leaves more material available for WB&L losses.

FIG. 5 shows the flashing, WB&L losses of these four methods compared against the predictions of the PPW method. One percent by volume of hydrocarbons was assumed to be entrained, and the composition of Sample 2 was used. For all methods, the emissions of any component were capped at the incoming feed rate for that component.

Takeaway. The AP 42 methodology is widely accepted for estimating hydrocarbon storage tank emissions and has been shown to give reasonable results for hydrocarbon tanks. A desire exists to apply a similar methodology for estimating produced water storage tank emissions, but typically the produced water composition or levels of hydrocarbon entrainment are unknown. The four methods presented that rely on the use of AP 42 and the pressurized hydrocarbon liquid composition show deficiencies in some way and can produce significantly different emissions estimates.

A process simulator-based methodology, which can be easily automated, is presented here for calculating produced water emissions. This methodology uses the C&T component of AP 42, which is known to provide reasonable results, and replaces faulty VP predictions with rigorous process simulator predictions. Further, it captures the fact that with low entrainment fractions, there can be significant depletion of lighter hydrocarbon components. Neglecting this can cause substantial overprediction of emissions.

A next step would be to compare the predictions of this new method against tank emissions measurements. The AP 42 C&T methods appear to be qualitatively correct. The trends predicted by the methods do track in the correct direction, but whether they should be modified for use with produced water emissions remains an open question. HP

NOTES

[a] Refers to Bryan Research and Engineering's ProMax simulation software

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Sustainability and the water management company's role

Water is key to the hydrocarbon processing and chemical processing industries. Yet, it is not an infinite resource, which creates operational, financial and regulatory risks. The true cost of water can include insurance and litigation costs and disposal costs, plus the capital expenditures (CAPEX) and operating expenses (OPEX) of water infrastructure.

Sustainability is top of mind, especially in the areas of raw water availability, freshwater minimization and wastewater recycle and recovery. A major global hydrocarbon and chemical processing company stated the importance of water management on its 2018 corporate sustainability report. This company is seeking to continuously improve its development and implementation of water management strategies, taking into consideration local factors such as quality and availability at each plant.

Understanding the mass balance of a facility's water consumption is a critical first step in creating water management strategies. This global HPI/CPI company understands how water sustainability is a major component of resource management. It continuously works to improve its understanding of water consumption, including when and how much at each area of the facility. Using a water tool developed by IPIECA, the global oil and gas industry association for environmental and social issues, the company identified that 37% of its major operating sites are in potentially water-scarce areas.

FIG. 1. Wastewater recycle and reuse at HPI/CPI facilities is becoming a trend. Treated wastewater can be recycled for use onsite or in other beneficial areas such as cooling tower makeup, service water, boiler feedwater and, in some cases, irrigation.

Water management companies can play a valuable role in helping the HPI/CPI industry with water sustainability in the areas of recycle and reuse, zero liquid discharge, consulting services and system design. Operators will benefit by mitigating operational, regulatory and reputation risks.

This article discusses the ways in which one water management company is helping the HPI/CPI industry, including a particular global partner, with water management.

Benefits from water management services. By reducing their demand for freshwater and also more efficiently managing wastewater, HPI/CPI operators can significantly reduce their water footprint. Water management companies can provide site-specific recommendations based on water needs assessments, treatability studies, audits, piloting and lab testing. They offer technologies and services, such as primary and secondary oil/water separation, biological treatment, clarification, recycle and reuse, sludge handling and treatment, and zero liquid discharge.

Wastewater recycle/reuse minimizes freshwater intake and is becoming a trend in drought-stricken areas, and as wastewater discharge costs increase. The treated wastewater can be recycled for use onsite or for cooling tower makeup, service water, boiler feedwater and, in some cases, irrigation (**FIG. 1**).

Water management strategies for hydrocarbon processing can be adopted from upstream oil and gas operations. In the upstream market, for instance, the oil and gas industry is incorporating non-potable water sources as alternatives to freshwater for completions. Historically, produced water has been regulated as a waste for disposal. Stakeholders now recognize that produced water can be reconditioned as a source of supply for oil and gas activities.

Regulators, the industry, and the public and private sectors all support treatment innovation for this emerging reuse trend. Technologies such as water softening can stabilize frac supply water for recycle. Other technologies combine a high-rate softening process with ceramic membrane technology to treat frac flowback and produced water for reuse as frac water. These types of technologies can also be used to treat produced water for injection to achieve enhanced oil recovery and to treat produced water for steam generation.

Benefits of water reuse technologies include:

- Reduced freshwater demand, disposal costs, truck traffic and emissions

- Removal of hardness, silica, iron, barium and strontium, which can scale equipment
- Removal of particulates (oil, solids, bacteria) and creation of an absolute barrier, minimizing downstream carryover
- High system recovery rates of greater than 98%.

Industrial client support. One water management company is working with large hydrocarbon and chemical companies to identify solutions to economically reduce water usage. Global HPI/CPI companies should consider water reduction efforts early in project planning. The driver is different for each project, depending on location and water availability (**FIG. 2**). Rarely is a "standard" solution available. Companies understand that optimal water reduction solutions will vary significantly based on water chemistry.

Water technology management companies ask the client's project coordinators about potential water reduction configurations during the screening stage, often before details are known about water quality in the regions where the work is being done. They leverage previous installation configurations and costs to highlight the different technology options.

By developing and implementing local water management strategies, the referenced company is working with businesses to lower freshwater consumption during operations. Since 2011, some oil and gas companies actually report having lowered freshwater use by 20%. As previously mentioned, major oil and gas companies are recognizing that 30%–40% of major operating sites are in areas with water scarcity potential. They are pursuing site-specific management strategies, such as deploying water conservation technologies, using alternative water sources, recycling industrial wastewater and using lower-quality water sources. For example, the use of secondary or tertiary municipal wastewater will have constituents of concern that other feedwater sources may not (e.g., nitrates, chlorine or chloramine).

Oil and gas companies are continuously investigating wastewater mitigation strategies for "typical" wastewater types originating from a number of industrial processes. Most companies have the goal of developing a strategy to implement treatment methods for each wastewater type, based on the best technology available.

The author's company routinely investigates zero liquid discharge (ZLD) options globally to eliminate liquid discharge and recover virtually all the water in wastewater streams for reuse. The company also provides water audits/consulting services that include investigating multiple wastewater streams and suggesting system designs. Audits and recommendations consider project scope, availability of labor, electrical transmission capacity and capital cost estimates for budgetary purposes. A number of different water recovery options exist, including membrane (reverse osmosis) concentration (**FIG. 3**), falling film evaporation and forced-circulation evaporation. Recommendations are made based on operating cost projections, performance and the feasibility of electrically driven evaporation.

Industrial plants often receive makeup water that does not meet normal requirements for cooling tower purposes. This can increase cooling tower operation and maintenance costs, and negatively impact system components. Water management and technology companies can help these plants meet future

FIG. 2. Global HPI/CPI companies should consider water reduction efforts early in project planning. The driver is different for each project, depending on location and water availability.

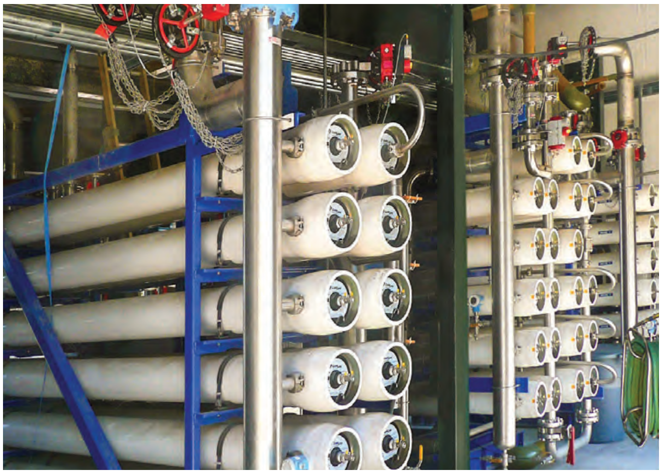

FIG. 3. Membranes (reverse osmosis concentration) can be a water recovery option for HPI/CPI companies. Recommendations are made by water management companies after analysis of operating cost projections, performance needs and feasibility.

FIG. 4. Cooling tower operation and maintenance costs can be high. Water management companies can recommend strategies for facilitating delivery of consistent, high-quality makeup water, and can develop cooling tower blowdown discharge and reuse solutions.

high-quality water demands. These include strategies for facilitating delivery of consistent high-quality makeup water, and treatment strategies to meet future requirements. Water technology companies can also help develop cooling tower blowdown discharge and reuse solutions that are both environmentally compliant and economical (**FIG. 4**).

For example, high-rate clarification for raw water, and cooling tower blowdown treatment for reuse, are other areas of consideration. A proprietary, high-rate softening technology lowers the raw water footprint. The system (**FIG. 5**) combines microsand-ballasted coagulation, flocculation and lamella settling to treat raw water and wastewater. The system then sends water to reverse osmosis (RO) pretreatment (membrane or multimedia filters) and then RO/demineralization systems, and finally to the reuse point.

FIG. 5. A proprietary, high-rate softening technology lowers the raw water footprint. The system combines microsand-ballasted coagulation, flocculation and lamella settling to treat raw water and wastewater.

Meeting sustainability challenges. Water technology companies help HPI/CPI clients better manage their freshwater usage, as well as wastewater recycle and recovery. As a result, these clients not only become more sustainable, but also improve operations and the bottom line.

As water becomes scarcer and more expensive, and as environmental regulations change, water technology companies can help clients choose the best and most cost-effective solutions. HP

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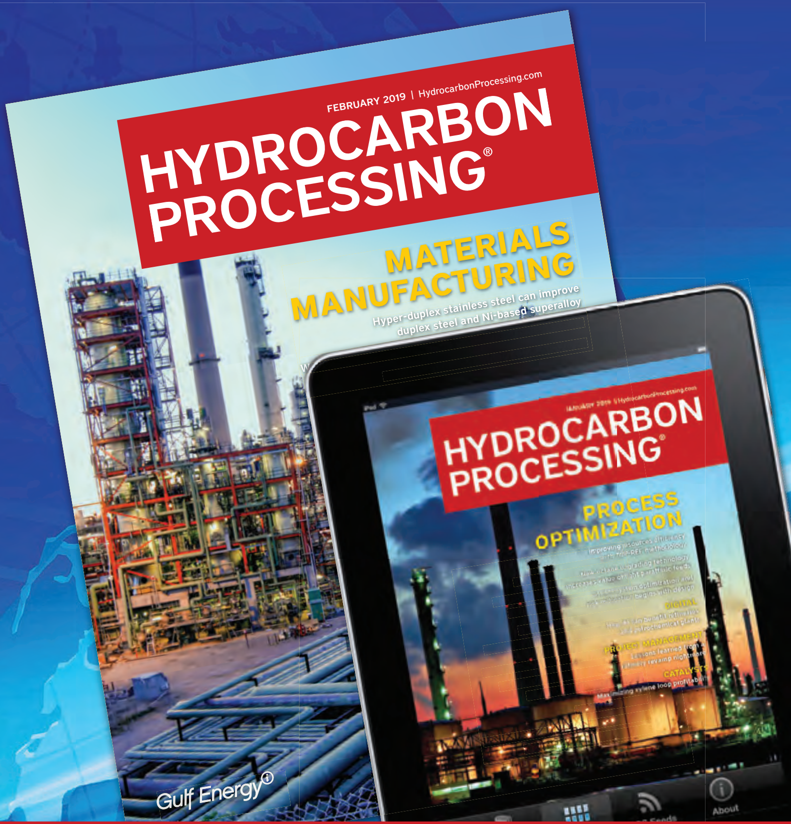

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Improved cooling system performance begins with data

Refineries consume large amounts of energy and water to refine crude oil into products. Up to 10% of crude oil's energy content is consumed during processing, and it takes 1.5 bbl of water to process one barrel of crude oil. Refining processes also generate large quantities of excess thermal energy that needs to be expelled into the environment using a once-through or recirculating cooling system. A once-through system draws water from a raw water source and pumps it through process heat exchangers where it absorbs heat and is then sent back to the source. These systems are cheaper to construct and consume significantly less water than recirculating systems, but they may also require more water treatment chemicals and pose environmental risks.

Unless a raw water source is abundant and readily available, recirculating cooling water as much as possible is critical not only to reduce the cost of water treatment, but also to conserve the water supply. Unlike once-through systems, recirculating systems reuse the cooling water and employ evaporative cooling towers (**FIG. 1**) to transfer heat from the process to the atmosphere. Evaporative cooling towers have high construction, operational and maintenance costs, while consuming large quantities of water, often as much as 90% of the total water consumption in a refinery.

FIG. 1. Cooling towers are often used to transfer heat from processes to the atmosphere, but they have high construction, operational and maintenance costs.

Cooling water availability is critical for refining operations. It is highly dependent on maintaining cooling towers and the rest of the cooling water system at peak performance. Equipment failures within a cooling tower can be costly to fix, can potentially lead to unplanned downtime, and may create an unsafe environment for plant personnel. As shown in **FIG. 2,** there are many things that can go wrong with a cooling tower. To those responsible for maintaining them, there are two main areas of concern:

- Problems with mechanical components, such as fans, pumps and valves
- Cooling water quality and integrity of the distribution system.

Problems with mechanical components. Cooling towers incorporate a variety of mechanical equipment—most notably pumps and fans—that are susceptible to problems common to rotating equipment, but with a unique set of challenges. These challenges include:

- Cooling tower fans operate under variable load conditions with differing stresses over a prolonged period, putting them at higher risk of structural failure.
- Bearings and gears can fail due to misaligned drive shafts, and high vibration is common.
- Vibration data from a cooling tower's gearbox is difficult and dangerous to collect without permanently installed sensors.
- Mechanical components are often difficult to access, and thus are undermaintained.
- Failure of a fan requires a crane to remove and fix or replace, which costs time and money and is a potential safety hazard.

By installing wireless sensors on cooling tower pumps, fans and gear boxes to monitor vibration and temperature, a facility can automate data collection for asset health evaluation—increasing worker safety, saving time and freeing technicians for performing repairs prior to failure and other higher-level tasks. Furthermore, continuous monitoring can enable condition-based maintenance, which is more effective than time-based maintenance or reactive maintenance that addresses a failure after the fact.

Cooling water quality. The measure of cooling water recirculation is defined as cycles of concentration (COC), which is the ratio of dissolved minerals in the recirculating water to dissolved minerals in the makeup water. It can be calculated using Eq. 1:

$$COC = \frac{\text{Total dissolved minerals in blowdown water}}{\text{Total dissolved minerals in makeup water}} = \frac{\text{Evaporation rate} + \text{blowdown rate}}{\text{Blowdown rate}} \quad (1)$$

Increasing COC introduces several problems that can impact cooling system performance, such as corrosion, scale deposition, fouling from airborne contaminants, microbiological growth and degradation of a cooling tower's structural integrity. The severity of these problems depends on multiple parameters, such as chemical composition of the makeup water, cooling tower location, cooling system materials of construction and operating conditions. In addition, these problems are interrelated, and addressing one may exacerbate the other. For example, lowering pH of the cooling water by adding acid can help control scale deposition, but may intensify corrosion and make controlling certain types of microbiological growth more difficult.

It is critical to establish and maintain a program of corrective measures to maintain optimal cooling system performance. Concentration of dissolved minerals and pH of cooling water must be carefully monitored and controlled to avoid excessive scale deposition while maintaining acceptable corrosion rates. Organic and inorganic contaminants must be removed through side-stream filtration and prevented from depositing on heat-transfer surfaces. Finally, microbiological growth must be controlled with biocides. Some of these microbiological contaminants may include harmful bacteria such as *Legionella,* which causes Legionnaires' disease.

Preventing scale while controlling corrosion. As COC increases, more water evaporates, and additional minerals enter the system via makeup water. The recirculating water becomes supersaturated with dissolved minerals and precipitation begins to occur, resulting in formation of scale deposits, such as calcium carbonate and magnesium silicate, on heat-exchange surfaces. While small amounts of scale can be beneficial for corrosion protection, if left unchecked, scale deposits will start to impede heat

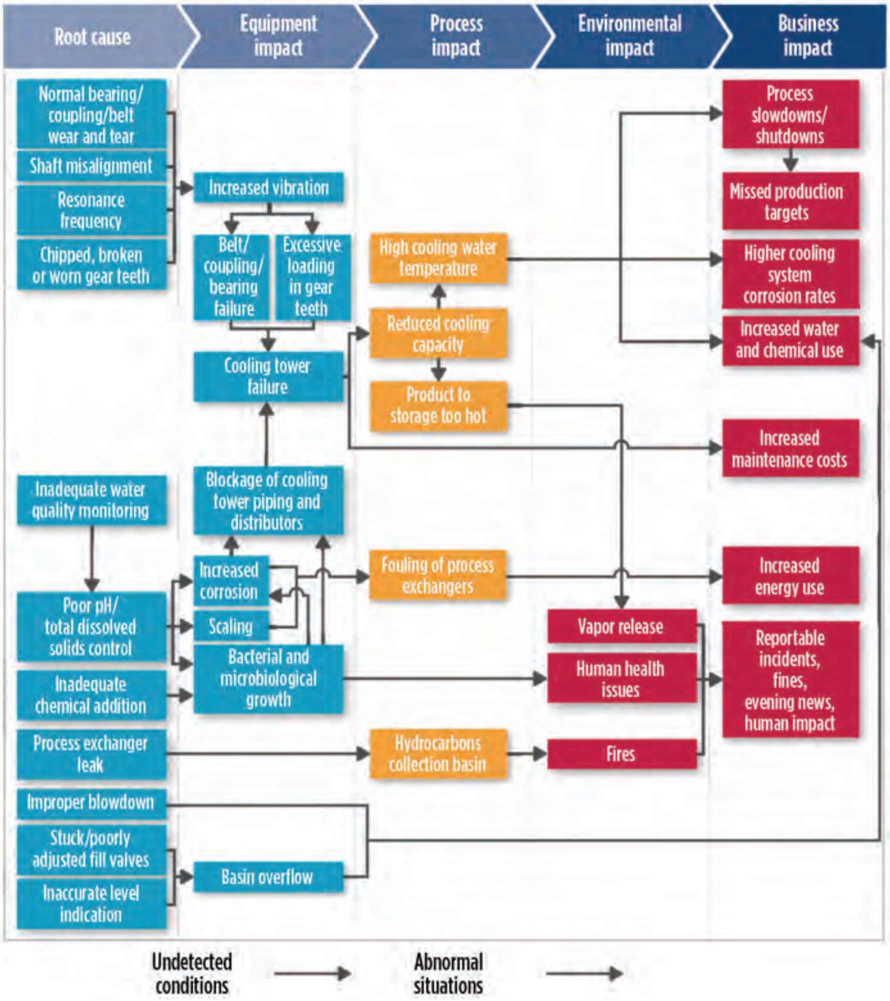

FIG. 2. Following the chain of effects of a problem shows how a small issue can escalate if not addressed quickly.

FIG. 3. A general-purpose pH sensor[a] is an appropriate choice for this type of application.

FIG. 4. A conductivity sensor[b] can control blowdown cycles when conductivity becomes too high.

transfer and significantly increase the risk of localized corrosion.

In addition, some carbonate deposits may accelerate delignification of cooling tower lumber and undermine structural integrity. Scaling is typically controlled by blowing down (bleeding off) some of the recirculated water from the system to reduce concentration of dissolved minerals. This may be sufficient for operation at low COC, however; at high COC, reducing alkalinity by adding sulfuric or hydrochloric acid and dosing chemical scale inhibitors may be required to control scale deposition.

Corrosion in a cooling system is a factor of temperature, pH, concentration of dissolved minerals, water flow velocity and extent of microbiological fouling. Three main types of corrosion exist: general, localized and galvanic. Localized corrosion is the major concern with these systems because it may lead to a rapid metal failure and is often hidden from sight under deposits.

Corrosion effects are widespread and often result in unscheduled downtime and costly repairs. These include:

- Fouling of heat exchangers and distribution piping by corrosion products (e.g., rust)
- Leaks in heat exchangers resulting in contamination of the process fluid by cooling water or vice versa
- Decrease in heat transfer efficiency.

pH control, along with chemical anodic and cathodic corrosion inhibitors such as chromates, nitrites, polyphosphates and bicarbonates, are commonly used to maintain corrosion within acceptable limits. Corrosion inhibitors must be carefully chosen for the specific metallurgy of the cooling system.

Controlling fouling and microbiological growth. During normal operations, cooling water becomes contaminated by organic and inorganic matter. Dosing of dispersants may be necessary to prevent coagulation or flocculation of suspended solids, which are drawn in with the outside air. Warm water also produces an ideal environment for algae, slime and bacterial growth. If left untreated, microorganisms form a gel-like substance called biofilm that allows them to attach to heat-transfer surfaces and protects them from biocides. Biofilm also prevents corrosion inhibitors from reaching the metal surfaces and may accelerate corrosion.

To control microbiological growth, non-oxidizing and oxidizing biocides, such as chlorine, bromine or ozone, are typically added on timed intervals. Some of these are highly toxic and pose a significant safety risk. Ozone is an effective alternative to traditional chemical biocides and has the following advantages:

- More effective than chlorine or ultraviolet light at destroying bacteria and viruses
- Does not produce harmful residuals that need to be removed from effluent water
- Reacts with iron, manganese and sulfur in the water to form insoluble metal oxides or elemental sulfur
- Can be generated onsite, eliminating the risks of storing and handling toxic chemicals
- Does not increase corrosion.

Cooling water monitoring. Effective control of COC and chemical treatment to maintain water quality requires continuous online measurement of water quality. Nonetheless, many facilities operate based on daily or even weekly analysis of their cooling water. Online monitoring of cooling water quality can help optimize cooling system performance and lower water and chemical usage.

At a minimum, plants should continuously monitor their cooling water pH and conductivity, using temperature-compensated pH sensors (**FIG. 3**) to monitor the alkalinity of the cooling water, along with conductivity sensors (**FIG. 4**) to monitor the concentration of dissolved minerals to maintain an optimal COC. General-purpose pH sensors and contacting conductivity sensors are suitable for most cooling water systems; however, for systems with a high degree of fouling, pH sensors resistant to fouling (**FIG. 5**) and toroidal conductivity sensors (**FIG. 6**) are recommended.

Measuring free chlorine in cooling water provides feedback to the chlorination system on biocidal efficacy to control and optimize dosing. To obtain accurate measurement of chlorine concentration in the cooling water, a free chlorine measurement (**FIG. 7**) compensated by a pH sensor should be used.

FIG. 5. Conventional pH sensors[c] can be fouled when suspended solids levels are high, so a fouling-resistant sensor can be used to reduce maintenance requirements.

FIG. 6. Where suspended solids levels are high, a toroidal conductivity sensor[d] may be necessary to make the measurements used to reduce the level.

FIG. 7. Chlorine necessary to suppress biological growth can be monitored using a sensor[e].

FIG. 8. Ozone treatment to reduce biological growth is growing in popularity but requires a specific sensor[f] to monitor concentration.

When utilization of a free chlorine measurement system is cost prohibitive, an oxidation reduction potential (ORP) measurement may serve as an alternative. The effectiveness of chlorine depends on its ability to oxidize water to produce hypochlorous acid, a strong oxidizing agent. ORP measurement—also compensated by a pH sensor—may be correlated to the amount of hypochlorous acid and may be used as a proxy to a free chlorine measurement for controlling the chlorination. If ozone is used to control biological growth, a dissolved-ozone sensor (**FIG. 8**) may be used to provide a continuous measurement of ozone concentration to control and optimize dosing.

FIG. 9. Measuring total suspended solids requires a sensor[g]. Data from this can be used for regulatory compliance reporting.

A blowdown stream turbidity measurement (**FIG. 9**) provides a way to monitor suspended solids and can be used to control sidestream filtration and for reporting of effluent total suspended solids levels to government regulators.

Cooling water return temperature is a good indicator of cooling performance and can be monitored easily with the temperature sensor incorporated into most pH or conductivity sensors, eliminating the cost of an additional temperature measurement point.

Cooling water treatment control. Since chemical water treatment is one of the largest variable cost components in cooling tower operations, automated control of blowdown and chemical dosing is important for cost-efficient operation.

In addition to monitoring and communicating various cooling water parameters, some liquid analytical transmitters may offer alarm relays, as well as proportional integral derivative (PID) and time proportional control (TPC) functions. These functions allow the transmitter to direct control of the cooling tower's makeup and blowdown valves, heaters and chemical treatment dosing pumps.

PID control can be applied to any of the sensor measurements connected to the transmitter, as well as to external analog and digital signal inputs. The output signal of a PID controller can vary its output from 0%–100% in response to the measured variable.

TPC is more commonly known as duty cycle or pulse-width modulation. It applies PID control to a relay, rather than using an analog current output. The TPC output is defined as the percent of time that a relay is activated.

The following alarm relay functions are common for cooling towers:

- **High/low concentration:** Primary and secondary measured variables (such as pH, conductivity and temperature) can be used to drive outputs to control concentrations. These outputs have an adjustable dead band and perform on/off control of pumps and valves. A typical application is control of blowdown.
- **Delay timer:** A delay timer can be used in a concentration control scheme to delay measurement following dosing of treatment chemicals. This ensures enough mixing time in a cooling water recirculation loop before performing a measurement, preventing unmixed readings that might cause overshooting. This function can be utilized when adding acid or inhibitors.
- **Bleed and feed:** This approach is typically used to replace chemicals lost during blowdown and involves two or more relays. Once the bleed relay deactivates, one or more feed relays activate for a percentage of the time the bleed relay was on. Bleed and feed support continuous monitoring of blowdown water conductivity to determine the point of excessive conductivity. At a programmable maximum concentration value,

FIG. 10. Where it is not practical to add a permanent temperature measurement point, a transmitter[h] can infer the water temperature without a process penetration.

bleeding of blowdown water is triggered. Subsequently, pumping to feed additional makeup water chemicals is enabled to account for lost blowdown water. Through level control, makeup water is added in proportion to the volume of water lost through blowdown and evaporation.

- **Totalizer-based relay activation:** This approach feeds chemicals for a preset period every time a programmed volume of liquid has been added or removed. The relay energizes when the volume has been reached and remains energized for a fixed time. The process repeats once the volume has been reached again. The scheme uses pulse inputs from a flow meter or 4-20 mA current input from a flow transmitter to calculate a volumetric total flow. A typical application is chemical dosing control.
- **Interval timer:** When a sensor needs to be cleaned or the process requires adjustment, an interval timer turns on to begin the cycle. When the interval time has expired, the analyzer deactivates the "hold" mode on the assigned measurement and the relay is energized for the on-time period.
- **Date and time activation:** This relay feature allows programming of relays to activate on an assigned day of the week and time of day or night for an assigned interval, functioning like a sprinkler timer. The programmable timeframe cycle is typically two weeks. A typical application example is daily biocide dosing.

Evaluating condition and performance. In addition to liquid analytical measurements used for monitoring and control of cooling water quality and COC, continuous measurements of other parameters—such as flow, temperature, level and pressure—at various points throughout the cooling system work together to monitor performance and further optimize efficiency. Typical points of measurement include:

- A cooling tower's exhaust air temperature
- Ambient air dry-bulb and wet-bulb temperatures
- Cooling water supply and return temperatures
- Level measurements in water and chemical storage tanks
- Water flowrates
- Pressure differential across heat exchangers.

The data generated by these instruments can be recorded and analyzed by preconfigured applications to continuously monitor the cooling tower and its related equipment health. This can enable:

- Tracking and optimizing cooling tower efficiency
- Monitoring and optimizing water and chemical usage
- Monitoring heat exchanger performance
- Monitoring rotating equipment for condition-based maintenance to mitigate asset failures
- Alerting operators when something abnormal is detected
- Training operators to act on this new information and to update procedures as needed.

Wireless products are supported by, and are fully compliant with, the IEC 62591 standard, making this kind of monitoring much easier and less expensive than with wired instruments. All the types of instruments necessary for monitoring a cooling tower are available with either native *Wireless*HART transmitters or with adapters to connect to *Wireless*HART networks. This makes installation easier, and, if added to existing networks, the cost is especially low. Some things to consider:

- Surface-mounted temperature sensors do not require thermowells, and are able to accurately measure water temperature through the pipe wall (**FIG. 10**).
- If it is practical to use conventional temperature sensors, a single transmitter (**FIG. 11**) can send data from up to four sensors on one wireless signal.
- Vibration and bearing temperature sensors can be added to fan and pump motors and gear boxes to warn of developing mechanical problems.
- Wireless pressure sensors may be installed on the inlet and outlet of a heat exchanger to measure differential pressure and to monitor fouling.
- Liquid analytical transmitters can connect to a *Wireless*HART network with an adapter.

All these elements working together, guided by data gathering and analytical apps, can improve cooling tower performance and plant profitability.


FIG. 11. Some temperature transmitters[i] can send data from up to four sensors on one channel.

NOTES

[a] Refers to the Emerson Rosemount 3900 general-purpose pH/ORP sensor

[b] Refers to the Emerson Rosemount 400 contacting conductivity sensor

[c] Refers to the Emerson Rosemount 396P/396PVP pH/ORP sensor

[d] Refers to the Emerson Rosemount 228 toroidal conductivity sensor

[e] Refers to the Emerson Rosemount 499ACL free chlorine sensor

[f] Refers to the Emerson Rosemount 499AOZ amperometric ozone sensor

[g] Refers to the Emerson Rosemount T1056 Clarity II turbidimeter

[h] Refers to the Emerson Rosemount X-well technology

[i] Refers to the Emerson Rosemount 848T wireless temperature transmitter


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Impact of opportunity crudes on refinery desalter and wastewater treatment performance—Part 1

Refiners are becoming increasingly dependent on opportunity crudes to stay competitive and enhance margins in the industry's present uncertain state. *Opportunity crude* is a term to describe newer types of crudes that have not been traditionally processed in the past.

Although these crudes offer refiners an opportunity to buy at much lower than West Texas Intermediate (WTI) and Brent benchmark prices, their abundance has created major challenges to global refining operations due to the special characteristics that make such crudes difficult to process. Refiners are compelled to take special measures to overcome these difficulties, including blending these crudes with traditional ones to balance the properties. In many cases, such crudes are incompatible and lead to the formation of solid or semi-solid asphalt-like materials that tend to precipitate in the process equipment, particularly desalters. A brief introduction of the operating principle of desalters is presented here for a clear understanding of the types of challenges and their remedies.

Desalter operating principle. Crudes contain numerous impurities that can impede refining processes. Desalters are the first equipment to handle and process crudes in a refinery, and are designed to encounter and mitigate the deleterious effects of such impurities. The primary function of a desalter is to make intimate contact between crude and water by thorough mixing to transfer inorganic salts and other contaminants contained in the crude to the water, and then remove it as a brine stream. The salt is primarily sodium chloride, with other salts containing sodium, calcium and magnesium cations, and chloride and sulfate anions.

Inside the desalter, crude is thoroughly mixed with water (4% v/v–6% v/v) at 105°C–150°C (221°F–302°F), which facilitates the transfer of salt and other water-soluble materials to the aqueous phase. Bulk segregation of oil and water phases occurs by gravity as the oil phase separates in the top layer and water gravitates in the bottom layer. Oil-water separation is enhanced under an electrostatic field applied inside the desalter vessel with the help of two parallel electrode plates with opposite electrical charges. Water droplets, which are negatively charged, coalesce together, migrate toward the positive electrode and accumulate in the water layer. The separated aqueous phase leaves the desalter as a brine stream and leads to the wastewater treatment plant. Desalted oil is fed to the atmospheric distilling column after preheating. A schematic representation of a desalter is shown in **FIG. 1.**

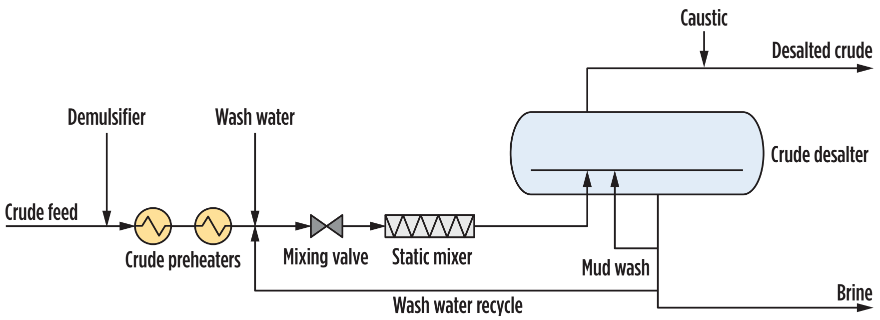

FIG. 1. Schematic of a desalter in a petroleum refinery.

Typically, the oil-water separation is not ideal: rather than a sharp interface, the two layers are separated by an emulsion layer, also called a "rag layer," which consists of oil-water emulsion made up of fine droplets of water dispersed into oil and entrained solids. A thick emulsion layer indicates poor oil-water separation in the desalter and results in the escape of large concentrations of water in the oil phase and oil in the water phase. High desalter performance is essential to ensure minimum entrainment of oil in the effluent brine stream and water in the desalted crude. Carryover of excessive oil in the effluent brine leads to excessive oil and grease and large chemical oxygen demand (COD) loads to the wastewater treatment system. On the other hand, the escape of excessive water in desalted crude increases the thermal load in the atmospheric distilling column. Additionally, dissolved constituents in carryover water with desalted crude can cause corrosion in column internals.

Solids contained in crude settle at the bottom of the desalter vessel and accumulate with time. These solids are routinely removed by applying a water jet through a set of mud wash lines inside the vessel from an external header. Mud washing effluent leaves the desalter with the brine stream leading to the wastewater treatment plant. The frequency of mud washing is based on the solids content in the crude.

Proprietary demulsifiers from chemical vendors are introduced into the desalter feed to break emulsion and improve desalter performance. The right type and dosage of these chemicals are determined by pilot and/or field scale tests.

Crudes contain dissolved chloride salts of sodium, calcium and magnesium. Both magnesium and calcium chloride hydrolyze under the prevailing temperatures in the atmospheric column, according to the following reactions in Eqs. 1 and 2:

$$MgCl_2 + 2\,H_2O \rightarrow 2\,HCl + Mg(OH)_2 \quad (1)$$

$$CaCl_2 + 2\,H_2O \rightarrow 2\,HCl + Ca(OH)_2 \quad (2)$$

However, sodium chloride is a stable salt and does not hydrolyze under the column operating conditions. Therefore, caustic soda solution is typically dosed into the desalted crude to convert dissolved calcium and magnesium chloride into sodium chloride, and to prevent hydrochloric acid (HCl) formation by hydrolysis inside the crude distilling column, which can cause corrosion in the column internals.

Several manufacturers offer desalters of proprietary design. The designs vary based upon arrangement of the electrode, oil-water interface control, mechanical internal details, etc. However, the operating principle is the same.

Wastewater treatment. The process train of a typical refinery wastewater treatment plant is shown in **FIG. 2.** Desalter brine blends in an equalization tank with other process wastewater streams, contaminated storm water from refinery process areas and water from the tank farm. Other sources of wastewater are blowdown streams from cooling towers, boiler drums and backwash streams from filters and demineralizers. Wastewater from equalization tanks is fed sequentially into American Petroleum Institute (API) or corrugated plate interceptor (CPI) separators for primary oil-water separation and suspended solids removal, and dissolved (or induced) air or gas separators for oil for secondary separation. This is followed by biological treatment to remove residual oil and grease, and COD in the wastewater.

Most commonly, activated sludge process is used for biological treatment of wastewater in petroleum refineries, although some facilities use attached growth processes, especially trickling filters, for upfront roughing purposes. As regulations are becoming increasingly stringent, many refineries are required to remove ammonia by nitrification. Additionally, some refiners may have to control the total nitrogen in their discharge by adding a denitrification step in the treatment train. The mix from the aeration basin is then separated in a clarifier by gravity settling.

Clarifier effluent typically fulfills the discharge regulatory requirements in most cases. However, exceeding total suspended solids (TSS) and COD limits is not uncommon among refineries, particularly when processing opportunity crudes.

OPPORTUNITY CRUDES AND THEIR IMPACTS

The introduction of opportunity crudes disturbs the operation of desalters, which were not designed to handle the widely fluctuating constituents that were not originally intended to be processed by the refinery. These include crudes from a wide range of sources: heavy crudes from the Canadian Rockies; Doba crude from West Africa; and light tight oil (LTO) from various shale plays in North America. These crudes with undesirable properties present unique challenges: low API gravity, high viscosity, high acidity as expressed by the total acid number (TAN), high metals concentration, high filterable solids (FS) and high amines content. Impacts of the various properties are discussed here.

Western Canada crudes. Crudes from western Canada are heavy, typically with an API gravity of 19°–22°. These crudes are produced by traditional exploration, or by steam addition to solid bitumen, e.g., from oil sands. These crudes have high viscosity, which causes the following challenges to refiners:

- High energy demand in piping transportation
- Poor mixing, leading to reduced salt removal from crude
- Emulsion formation in the desalter, which is enhanced by the presence of asphaltenes, leading to poor oil-water separation.

Additional challenges in desalter operation arise from high levels of filterable solids (FS) in these types of crudes. The reported values of 90 lb/Mbbl–100 lb/Mbbl (pounds per thousand barrels)[1] of crude as compared with a normal value of ~50 lb/Mbbl FS. These solids are difficult to separate in desalters due to their fine size and transfer to the desalter brine. The solids in this stream deposit into all process equipment in the wastewater treatment plant. As a result, the active volume and hydraulic retention times of all equipment decrease drastically, affecting their performance. Moreover, high FS in crudes help the growth of the rag layer inside the desalter, promoting emulsion formation, which is detrimental to good oil-water separation.

These crudes contain high concentrations of reduced sulfur compounds [hydrogen sulfide (H_2S), mercaptans, etc.] to the extent of ~3 wt%–5 wt%. Sour crudes pose health and safety risks, and are corrosive to metals. Typically, amines are added to tie up H_2S, and are used in the crude production process (also called tramp amines) that become associated with crude, a part of which partitions into the water phase in the desalter and leads to the wastewater treatment plant with the brine stream. This leads to very large COD and nitrification loads, as well as dissolved oxygen demand in the biotreater. If the aeration system is inadequate to handle excess loads arising from tramp amines, then the possibility exists that part of the COD is leaving the wastewater plant untreated.

Canadian heavy crudes are also known to have a high TAN, which is a

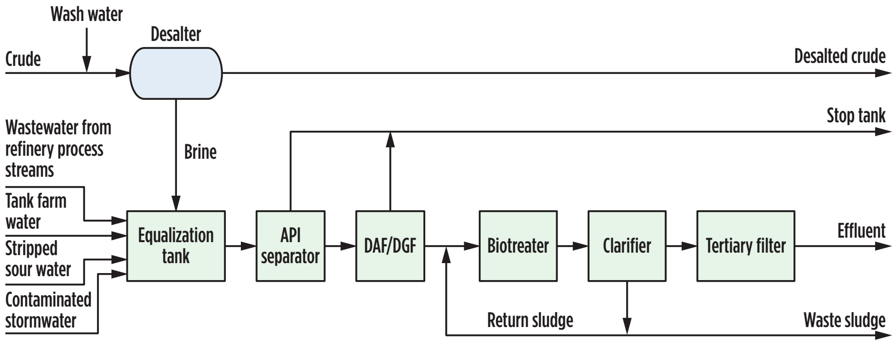

FIG. 2. Typical refinery wastewater treatment process train.

measure to quantify the acidity of crudes. High-molecular-weight naphthenic acids contribute significantly to the TAN of a crude. Typically, the TAN value of crudes ranges from 0.3–0.5. However, TAN values as high as 4.3 have been reported for California crudes.[2]

Naphthenic acids are complex, organic acids occurring naturally in crudes, bitumen and their products. They are both acyclic and cyclic in structure, with molecular weights in the range of 140–500. The general structure of a simple acyclic, and a cyclic naphthenic acid with a single ring, are shown in **FIGS. 3A** and **3B.**

High concentrations of naphthenic acids cause corrosion of metals, as exhibited by pitting and metal impingement. In the desalter, naphthenic acids partition into both oil and water phases. The part transferring into the aqueous phase leaves with the brine stream. These long chain organic acids are highly toxic to aquatic life, as they are not sufficiently broken down by biological treatment and they accompany the treated effluent as un-degraded COD.

West African crudes. The Doba oil fields in the West African nation of Chad are among the major sources of crude in West Africa. This heavy crude has an API gravity of 21°. One of the main attractive features is that it is a low-sulfur, sweet crude. However, it presents two major challenges in the form of high TAN and very high metals content, particularly calcium concentrations and, to a lesser extent, iron. Up to 250 mg/l of calcium in the form of naphthenate salts have been reported in literature.[3]

A large excess of calcium presents scaling concerns. Moreover, if it carries over with desalted crude, it can poison fluid catalytic cracking (FCC) catalysts. The presence of calcium as an impurity in coke diminishes its product value.

Additionally, high metals concentrations contribute to the high conductivity of crudes, which leads to the lowering of grid voltage and the electrostatic field between the electrode plates. This results in poor separation of oil and water in the desalter. Beyond these individual effects, their simultaneous presence has a negative effect on desalter operation as it stabilizes the emulsion layer in desalter, thus preventing oil and water trapped in the emulsion layer to break loose.

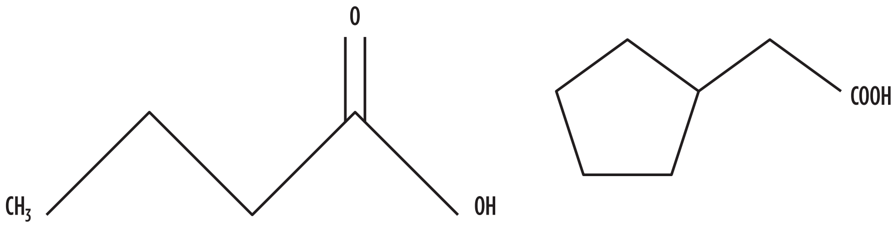

FIG. 3A AND 3B. Structures of simple acyclic (left) and a single-ring cyclic naphthenic acid.

TABLE 1. Desalter performance targets

Target	Light crudes	Heavy crudes
Salt removal efficiency, %	> 90 in a single-stage desalter > 95 in a double-stage desalter	> 90 in a single-stage desalter > 95 in a double-stage desalter
Salt in desalted crude, lb/Mbbl	< 2	< 2
Water carryover in desalted crude, % v/v	< 0.3	< 0.7
Oil under carry in brine, ppm	< 200	< 1,000

TABLE 2. Analytical methods for crude oil characterization

Crude property	Analytical technique	Method number
Density	API gravity by hydrometer	ASTM Method D 1298
Filterable solids (FS)	Membrane filtration 0.45 μm media	ASTM Method D 4807
Water in oil	Colorimetric titration by Karl Fischer method	ASTM Method D 4928
Salt in water	Potentiometric titration	ASTM Method D 6470
Chloride in water	Ion specific electrode	ASTM Method D 512
Oil in water	Extraction by cyclohexane followed by IR spectroscopy	ASTM Method 3921
Total acid number (TAN)	Potentiometric titration	ASTM Method D 664

Light tight oils. LTOs are crudes derived from hydrofracturing operations of shale formations. Hydrofracturing and horizontal drilling were game-changing technologies that completely altered the global oil supply and demand scenario, and impacted the market very significantly over the last few years. Based on a projection by the US Energy Information Administration (EIA),[4] LTO is increasingly poised to become the major source of crude in the US in the foreseeable future. The US is the second largest among the top 10 countries, with more than 75% of recoverable reserves.[5] The country is by far the largest producer of LTO-grade crudes from shale formations, such as the Bakken in North Dakota, and the Permian and Eagle Ford basins in Texas.

LTOs are light crudes with high API gravity (≥ 42°), so they do not pose any hydrodynamic challenges and are fairly easy to handle. Although readily and inexpensively available in abundance, US Gulf Coast refineries had initial difficulties adjusting to the new reality after they had modified the equipment to process heavy crudes prior to the advent of shale oil. This requires blending LTO crudes with heavy crudes to balance the properties for ease of processing. However, in some cases, they are incompatible. Specific challenges of LTO crudes include:

- Incompatibility with certain heavy crudes, resulting in asphaltene precipitation in desalters and downstream processes
- High filterable solids
- Entrained H_2S that requires the addition of amines for handling and transportation
- High concentrations of paraffin wax, leading to the fouling of equipment at low temperatures.

Effects of opportunity crudes. The following section is a summary of the impacts of various contaminants associated with the opportunity crudes presented here, as they relate to the performance goals of desalters listed in **TABLE 1.**

- **Low API gravity** creates difficulty in handling, processing and transportation due to high viscosity and specific gravities.
- **High acidity** imposes high COD load and affects the microbiological population in biological treatment, as discussed in the following sections.
- **High metals concentrations,** of which the primary metals of concern, calcium and iron, are present both in particulate and dissolved forms.
- **High sulfur,** present as H_2S and various organic sulfur compounds (mercaptans, disulfides, etc.), can cause a wide range of problems in handling and processing due to corrosion potential, and health and safety risks.
- **High filterable solids** (FS) are present in certain types of crudes. A number of challenges are posed by FS: the clogging of equipment and pipes, and the reduction in active-volume desalters, promoting the stabilization of rag layers and affecting the desalter.
- **High amine concentrations** resulting from addition during the production of crude to mitigate H_2S problems. In desalters, part of the amines partition with the water phase and leave with brine to wastewater treatment, creating high COD and nitrification loads. Moreover, amines cause an increase of pH in desalters, which promotes stabilization of the rag layer and impedes desalter operation.

Process monitoring and control. Several case studies are presented of refinery wastewater treatment plants that have been affected by the constituents present in opportunity crudes processed by those refineries. Characterization of crudes and wastewater samples at these refineries were conducted following standard tests and analytical protocols, as listed in **TABLE 2.**

Additional tests were performed using portable electric desalters (PEDs) to evaluate the performance of full-scale desalters handling new crudes and crude slates. PEDs are instruments widely used in the industry that simulate the operation of a desalter in bench scale (**FIG. 4**).

In a laboratory setting, PED tests demonstrated the salt removal potential, oil-water separation and emulsion formation potential from a new crude under the operating conditions of a desalter, before being used by a refinery as a feed. The results of these tests help optimize the operating parameters of the desalter to achieve the desired performance.

A PED test is conducted in multiple steps. First, about 5%–7% of wash water and a volume of preselected demulsifier (both the volume and type of demulsifier are recommended by a chemical vendor) are added to a preheated crude sample (80 ml–90 ml) in a graduated glass tube with a conical bottom. The mixture is blended thoroughly with the help of a blender for a specified length of time. This well-mixed liquid is then placed in the test setup, where the mixture is heated to a typical operating temperature of a de-

FIG. 4. Portable electric desalter in a laboratory. Photo courtesy of Dorf Ketal, USA.

FIG. 5. Tubes containing crude and demulsifying chemical for PED tests. Photo courtesy of Dorf Ketal, USA.

salter [105°C–150°C (221°F–302°F)], in an electrical field under quiescent conditions. The conical bottom of the glass tube facilitates oil-water separation into layers. The thickness of each layer is recorded with time for approximately 1 hr, which is typically the time it takes for the layers to stabilize. The appearance of a thick rag layer indicates poor oil-water separation and the potential for emulsion formation. Salt concentrations in the separated oil and water layers, when compared to the crude, indicate the desalting efficiency. The variables in these tests include:

- Mixing intensity (mixer rpm)
- Amount (% v/v) of wash water
- Type and amount of demulsifier
- Test temperature
- Applied voltage.

The three tubes in **FIG. 5** are examples of crude mixed with 6% water. The mixture was emulsified in a blender, heated and then exposed to the electrostatic field, as described above. The tube on the left was a test blank that had no demulsifying chemical added to it. The other tubes compared the effectiveness of two different demulsifiers to assist in breaking the emulsion. The tubes were allowed to sit for 20 min before the photograph (**FIG. 5**) was taken. It is evident that the PED is effective at screening for differences in the chemical programs, as the tube on the right shows significant improvement. Every major chemical vendor that markets their products and services to support desalter operations in refineries are equipped with their own design of PED equipment, and they select the ranges of operating variables.

For wastewater treatment, the parameters monitored are inlet and outlet oil and grease, and TSS of the API separator and the dissolved air flotation (DAF) separator. For biotreatment, the typical parameters are inlet and outlet oil and grease, TSS, biochemical oxygen demand (BOD), chemical oxygen demand (COD), reactor basin mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). Refineries requiring nutrient removal also monitor influent ammonia-N, total Kjeldahl nitrogen (TKN) and effluent total nitrogen (TN). All of these parameters are measured by relevant Hach methods at the in-house laboratory for process control. The regulated parameters in the effluent are measured by third-party, certified laboratories by standard methods [American Public Health Association (APHA), 2012][6] for reporting purposes.

Oil-water separation by a DAF separator is enhanced by the addition of suitable flocculation agents. The selection of the correct type of chemical and its dosage is performed by chemical vendors onsite by conducting jar tests (American Society for Testing and Materials, 2013).[7] Also, the optimum operating parameters for a DAF separator (air-to-solids ratio, gas saturation pressure, overflow rate) must be determined by laboratory-scale DAF prototype units.

In certain cases, as reported in Part 2 in the September issue, the aeration basins of wastewater treatment plants were severely affected by foaming and floating solids. It is essential to identify the types of microorganisms causing such problems, and the operating environment responsible for their growth and proliferation.

Part 2 of this article will explore, through three case studies, the effects of the contaminants resulting from processing opportunity crudes. These three case studies will cover a wide range of refinery locations, as well as their crude sources and types.

ABBREVIATIONS

COD	Chemical oxygen demand
API	American Petroleum Institute
CPI	Corrugated plate interceptor
TAN	Total acid number
TN	Total nitrogen
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
FS	Filterable solids
LTO	Light tight oil
DO	Dissolved oxygen
EIA	Energy Information Administration
PED	Portable electric desalter
DAF	Dissolved air flotation separator
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
ASTM	American Society for Testing and Materials
MBBR	Moving bed bioreactor

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Water Management

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Impact of opportunity crudes on refinery desalter and wastewater treatment performance—Part 2

Refiners are becoming increasingly dependent on opportunity crudes to stay competitive and support margins in the industry's present uncertain state. *Opportunity crude* is a term to describe newer types of crudes that have not been traditionally processed in the past.

Although these crudes offer refiners an opportunity to purchase feedstock at much lower costs than West Texas Intermediate (WTI) and Brent benchmark prices, their abundance has created major challenges to global refining operations due to the special characteristics that make such crudes difficult to process. Refiners are compelled to take special measures to overcome these difficulties, including blending these crudes with traditional ones to balance the properties.

In many cases, such crudes are incompatible and lead to the formation of solid or semisolid asphalt-like materials that tend to precipitate in the process equipment, particularly desalters. A brief introduction of the operating principle of desalters was presented in Part 1 of this article, which appeared in the August issue of *Hydrocarbon Processing.*

Part 2 of this article explores, through three case studies, the effects of the contaminants resulting from processing opportunity crudes. These three case studies cover a wide range of refinery locations, as well as their crude sources and types.

EFFECTS OF PROCESSING OPPORTUNITY CRUDES ON WASTEWATER TREATMENT

Case 1. A US Gulf Coast refinery has been processing a crude blend predominantly containing Maya crude, which is a heavy sour crude with an API gravity of 21.5 and a sulfur content of 3.4%. The well-operated refinery routinely meets the effluent requirements. The refinery wastewater treatment plant effluent total suspended solids (TSS) are sometimes higher than the effluent limit, but multimedia tertiary filters have been effective in containing the final effluent within limits. Sometimes, incidents of aeration basin foaming occur. On one occasion, the aeration basin foaming was severe. The reactors became covered with thick foam that spilled over the top, making the outside areas slippery to walk around, and the clarifiers became non-functional due to foaming.

Microscopic analysis of mixed liquor and foam samples from the reactor basin indicated the presence of high populations of the filamentous nocardioform organism *Skermania pineformis (S. pineformis).* This type of microorganism is readily observed due to its filamentous, pine-tree-like growth (**FIG. 6**) and its Gram. This microorganism possesses hydrophobic cell walls that cause it to float in an aerated reactor basin, thereby creating a stable, thick layer of foam on the water surface. The foam can pass into the secondary clarifier, where it can seriously interfere with clarification and solids-liquid separation. An analysis of the operating data concluded

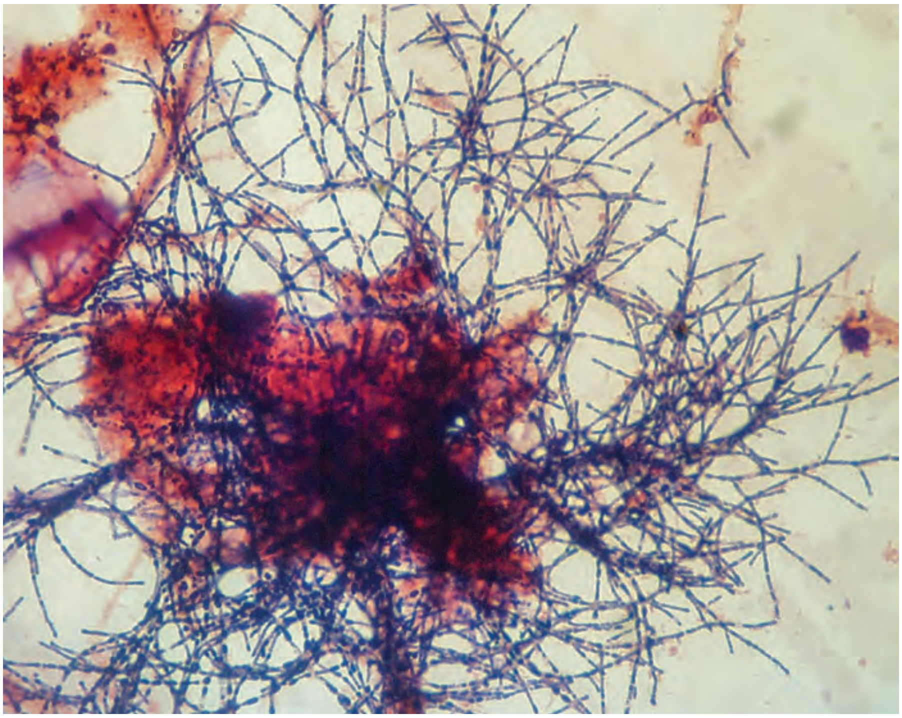

FIG. 6. *S. pinformis* Nocardia Foam on secondary clarifier surface at a refinery effluent treatment plant, visible under 1000 × direct illumination Gram staining. Source: David Jenkins & Associates.[6]

The abundance of opportunity crudes has created major challenges to global refining operations due to the special characteristics that make such crudes difficult to process.

two possible reasons for the growth of this nocardioform organism: slippage of high concentrations of oil due to poor oil-water separation, and excessively high solids retention time (SRT) in the aeration basins (bioreactors). Indeed, it has been observed that in other activated sludge systems, *S. pineformis* does not occur unless the SRT is close to 20 d or more.[6]

Once a nuisance-level growth of nocardioform organisms appears, it must be completely removed to restore normal operation. In most cases, this can be accomplished by applying a fine spray of bleach solution on the top water surface of the reactor and clarifier tanks to kill the undesirable population. However, in this instance, the problem was so severe that the foam had to be mechanically removed by deploying vacuum trucks.

Case 2. A North American refinery began experiencing operational difficulties at the wastewater treatment plant after the introduction of light tight oil (LTO) sourced from North Dakota into the crude slate. A review of the operating data indicated excessive oil carryover with brine after this change, as the desalter was failing to effectively separate oil from water. This was compounded by a simultaneous high concentration of filterable solids (FS) in the LTO that was settling in all the equipment of the treatment plant, leading to reduced volume and retention times. Under an extreme situation, this caused an incident of oil escaping with treated effluent that appeared as a sheen on the surface of the receiving water at the discharge point. To overcome the recurrence of this situation, a new desalter system that was designed to better handle such crudes had to be installed at the refinery.

Case 3. A refinery in the Far East had been using Arab Light Sweet crude. For a short period, Al Shaheen crude from Qatar (medium heavy sour crude of API gravity 28 and a sulfur content of approximately 2.4%) was blended. Consequently, the desalter salt removal dipped from an average of 80% down to 50%. Within a short time, the heavy crude was removed from the blend, which restored the original salt removal efficiency.

REMEDIAL MEASURES

Poor performance of a wastewater treatment system can cause permit violations and even lead to refinery shutdown for environmental noncompliance. Several measures can be taken in both desalters and wastewater treatment to ensure that the challenges posed by opportunity crudes do not become a bottleneck to the overall refinery operation.

For trouble-free operation of the crude distillation columns and downstream catalytic reactors, it is essential to remove the contaminants to the maximum extent possible and transfer those to the brine stream. This can largely be accomplished by controlling the formation of emulsion and growth of the resulting rag layer. Steps taken to achieve this goal include:

- Characterize the crude to evaluate its potential for emulsion formation due to the presence of certain components
- Select the right type and dosage of demulsifying chemical(s) that can break emulsion and help effective oil-water separation
- Follow a standard operating procedure for the desalter based on the close monitoring of its operation.

Information on crude characteristics and their broad range of properties are generally available based on their source. Refiners can also conduct their own assays using in-house or third-party laboratories. Demulsifying agents play a critical role in treating the crude to minimize emulsion formation tendencies. No single demulsifier can fulfill the needs of all types of crudes. The selection and dosing rates of these chemicals are determined by refiners in collaboration with chemical vendors in their own laboratories with the help of bench-top portable electric desalters (PED) instruments. After the laboratory tests, full-scale tests are performed onsite to examine the suitability of a demulsifier before finalizing its application on a routine basis.

Treatments. Desalter performance is significantly impacted by certain metals in the crude. The presence of calcium and iron in high concentrations in several types of opportunity crudes is a concern, as discussed in Part 1 of this article. Calcium and iron concentrations are present in crudes in both particulate and soluble forms. The particulate matter separates as filterable solids in the desalter and is removed by a mud-washing operation. In the soluble form, metals are present as organometallic compounds—e.g., calcium exists in the crude in complex forms with naphthenic acids as calcium naphthenates. The addition of organic acids in the desalter (acetic acid, glycolic acid, etc.) helps remove calcium from such complexes by forming water-soluble salts that are removed from the crude to the brine.

Acids are also effective in treating amines, which contribute to an increase in pH and promote the propensity for emulsion formation and stabilization of rag layers. From this viewpoint, the addition of organic acids offers the double benefit of treating both metals and amines. However, the downside is that acids create a corrosive environment in the desalter and downstream process equipment. As an alternative, refiners also use other types of non-acidic, simple organic molecules as chelating agents to sequester metals and amines from crudes and transfer those into the brine stream. This includes various aldehydes and ketones that incorporate calcium and iron ions from naphthenates to form soluble complexes and free up naphthenic acid, according to the reaction:

Ca^{2+} naphthenate + aldehyde →
Ca-aldehyde complex +
Naphthenic acid

Amines are also removed by aldehydes and ketones as they form imines. Therefore, the potential corrosive effect of acid addition can be avoided by replacing acids with aldehydes and ketones. On the other hand, the deleterious effect of amines on the oil-water phase separation in desalters can be mitigated by removing those as imines.

Demulsifier and chemical additives, however, cannot guarantee best performance of a desalter if proper operating procedures are not followed. These include mud washing; monitoring of rag layer; the proper control of oil-water interface; maintaining temperature, pH and grid voltage; etc. These procedures are even more important when processing opportunity crudes containing impurities that adversely impact the desalter operation. Routine laboratory analyses of the crude slate properties and efficacy of the chemical addition program must be strictly followed to adjust process parameters, dosing chemicals and their rates, for the success of desalter operation. Details of desalter internals, oil-water interface control, mudwashing operation, etc., are not discussed here and are available in literature.[7]

For the wastewater treatment plant, it is essential to monitor the TSS and oil and grease solids concentration of the influent and effluent streams of primary and secondary separation steps [API separator and dissolved air flotation (DAF)]. For high-solids crudes, the solids accumulation at the bottom diminishes the active volumes and hydraulic residence times of the equalization tank, API separator, DAF and aeration basins, and compromises treatment performance at every step. Routine monitoring of solids thickness by ultrasound or other measurement techniques, and routine removal during turnaround periods, are essential to ensure that the influent to the aeration basin is free from excessive (> 50 mg/l) oil and grease carryover.

Biological treatment. As discussed here, carryover of oil into the aeration basin is among the causes of bulking and foaming of sludge in the reactor. In addition to filaments, certain non-filamentous microorganisms cause bulking. A recent study demonstrated bulking due to amorphous Zoogloea promoted by the presence of organic acids. Heavy Canadian crudes have been observed to be the cause of this type of bulking. From this perspective, the addition of organic acids in the desalter for amines and metals treatment could be detrimental to the health of the microbiological population in the treatment reactor. Replacing acids by other types of organic chelating agents will provide a better overall solution in such cases.

Maintaining a pH within 6.5–8, a dissolved oxygen (DO) concentration of 2 mg/l–3 mg/l, and a solids retention time (SRT) of 20 d–30 d is critical to the success of biological treatment. Some refineries operate biotreatment reactors at a very high SRT, exceeding 40 d, by minimizing wasting of the sludge. This is motivated by two reasons:

- Minimizing the sludge disposal cost
- Breaking down some of the non-biodegradable chemical oxygen demand (COD).

However, a long SRT contributes to bulking and foaming.

Some crudes contain large amounts of naphthenic acids, a part of which leaves unaffected by biological treatment as refractory COD. These are some of the most toxic compounds to fish and other forms of aquatic life. A laboratory study on the biodegradation potential of naphthenic acids by an enriched culture of aerobic microorganisms indicated that

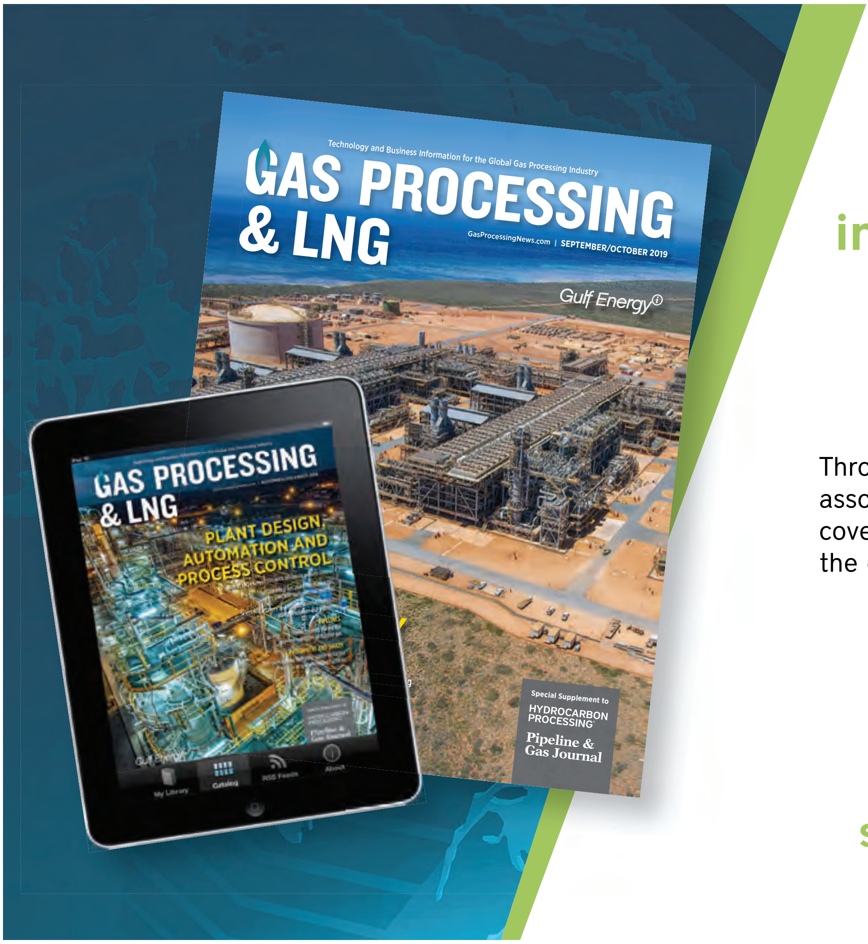

FIG. 7. Attached growth on MBBR media surfaces.

these compounds are partially mineralized, with a portion remaining as various oxidized breakdown products.[8]

Residual COD in the treated effluent from a refinery wastewater treatment plant contributes to the aquatic toxicity in the receiving stream. If a regulatory requirement exists on the discharge COD, a moving bed bioreactor (MBBR) process may provide a better solution than a conventional activated sludge process. While on an equivalent basis—the biofilm in an MBBR reactor corresponds approximately to 1,000 mg/l–5,000 mg/l of suspended solids in an activated sludge reactor—the performance of an MBBR in terms of biochemical oxygen demand (BOD) and COD removal rates is superior to an activated sludge reactor of identical volume.[9] Some of the advantages relevant to wastewater treatment at refineries processing opportunity crudes include:

- An MBBR is resilient to peak flows and shock loads.
- The attached growth biomass in an MBBR is resistant to toxic and shock loads.
- An MBBR is more effective in degrading refractory COD than can be obtained by traditional biological treatment processes.
- Biomass in attached growth in MBBR reactors are less vulnerable to bulking and foaming compared to suspended growth in an activated sludge reactor. Incidents of foaming have been reported only during startup, which can be handled by temporarily adding a defoamer.

The attached growth of biomass on the media surface is shown in **FIG. 7.**

In cases of stringent COD limits in the treated effluent, biological treatment may require further supplementation by advanced oxidation processes (AOPs), e.g., UV-peroxide and UV-ozone. Even AOPs do not ensure a complete removal of toxicity from treated effluent, as oxidation byproducts in certain instances have been reported to be more toxic than the parent compounds themselves.[10] The selection of such a process should be made on a case-by-case basis by conducting bench-scale or pilot test programs.

Findings. Opportunity crudes present difficult operating challenges for desalters and wastewater treatment. The desalter plays the vital role of ensuring that contaminants in such crudes are effectively removed and transferred to the aqueous phase so that the quality of refined products are not compromised, catalyst lives are maintained, and process equipment are not affected by corrosion or scaling.

Good performance by desalters means an increased burden to the wastewater treatment process due to the transfer of undesirable and difficult-to-degrade components unique to opportunity crudes. These include larger-than-normal concentrations of TSS, amines, naphthenic acids and other refractory organic compounds. Moreover, certain contaminants of these crudes promote oil-water emulsion formation. However, their abundance and discounted prices are very attractive to refiners. Challenges of opportunity crudes can be overcome by careful design and operation of the desalter. Understanding water chemistry and implementing a suitable chemical treatment program is critical to the successful operation of desalters.

A wastewater treatment system is susceptible to the carryover of large quantities of suspended solids and emulsified oil in the brine streams from desalters. Common problems are escape of untreated oil in the discharge, and microbiological bulking and foaming. Naphthenic acids are not readily degradable, and their breakdown can be enhanced by an MBBR. At locations that require the achievement of low-effluent COD (< 50 mg/l), additional treatment by advanced oxidation processes may be required.

Opportunity crudes will remain important constituents in the overall crude diet of refineries around the globe in the foreseeable future. Close monitoring and control of desalters, aided by routine sampling and analytics, and chemical dosing programs are essential in achieving operating success with these crudes. Further details of desalting of opportunity crudes are discussed in literature.[11]

ABBREVIATIONS

COD	Chemical oxygen demand
API	American Petroleum Institute
CPI	Corrugated plate interceptor
TAN	Total acid number
TN	Total nitrogen
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
FS	Filterable solids
LTO	Light tight oil
DO	Dissolved oxygen
EIA	Energy Information Administration
PED	Portable electric desalter
DAF	Dissolved air flotation separator
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
ASTM	American Society for Testing and Materials
MBBR	Moving bed bioreactor

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Options for meeting wastewater effluent selenium limits

Wastewater treatment units (WWTUs) in petroleum refineries are designed to meet effluent limitations incorporated into National Pollutant Discharge Elimination System (NPDES) permits for "conventional pollutants." These pollutants include oil and grease, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), chromium, sulfide, phenolic compounds, pH, ammonia and total suspended solids (TSS). The technology-based effluent limitations were originally promulgated by the US Environmental Protection Agency (EPA) for the Petroleum Refining Point Source Category [40 Code of Federal Regulations (CFR) Part 419] in 1974, with amendments in 1975, 1977, 1982 and 1985. Technology is well established for treating these contaminants, and refineries generally meet these limits.

Increasingly, refineries are also receiving water quality-based effluent limitations (WQBELs) in their wastewater discharge permits for trace elements. Selenium is one such trace element in refinery permits, because it is a component of crude oil that finds its way through refineries to the effluent. Limits of single-digit micrograms/liter (µg/l) are becoming more common. Furthermore, the EPA released a new selenium water quality criterion in 2016 that will lead to limits in discharge permits over the next 3 yr–5 yr for many refineries that presently have no WQBELs.[1] The 2016 national recommended aquatic life criteria for water concentrations in lentic and lotic water columns are 1.5 µg/l and 3.1 µg/l, respectively. Some refineries that discharge to publicly owned treatment works (POTWs) follow selenium limits that are derived from the POTWs' biosolids standards.

Meeting these low selenium limits is challenging, as a target of single-digit µg/l is at or near the limits of technology. Having the ability to remove selenium from wastewater may allow a refinery more flexibility in processing opportunity crudes, as the selenium content of crudes varies from < 0.01 ppmw–0.96 ppmw.[2] However, no single selenium removal technology is appropriate for all refineries. The process engineer must consider the distribution of selenium in the refinery to decide what streams to treat, and then select the technology to meet the limit at the compliance point, which is typically at the point of discharge.

Selenium in refinery streams. Some selenium enters a refinery in its raw water source. The selenium maximum contaminant level (MCL) for drinking water in the US is 50 µg/l, an order of magnitude higher than some refineries' discharge limits; however, generally the largest source of selenium in a refinery is crude. As selenium is directly beneath sulfur on the periodic table, it follows sulfur through a refinery and is released from hydrocarbons in cracking and coking processes. It then dissolves in the sour water condensing in these units. Sour water is typically the most concentrated source of selenium in a refinery.

Sulfur and selenium part ways in the sour water stripper. Sulfur goes overhead; selenium stays in the bottoms. This separation occurs because sulfur is largely present in these streams as hydrogen sulfide (H_2S), while selenium exists primarily as selenocyanate ($SeCN^-$), a reduced anion.

How sour water and the stripper bottoms (i.e., stripped sour water) are managed has a large impact on how best to control the refinery's effluent selenium:

- At some refineries, care is taken to route all sour water to the stripper. At others, some is lost to the process sewer during parts of the delayed coking cycle or via the slop oil system, when the sour water tank is skimmed.
- When stripped sour water is reused for desalting, selenium can go to the process sewer either directly or via a brine treatment unit. Once in the process sewer, it combines not only with wastewater from other units but also with stormwater, thereby increasing the volume of water requiring treatment.
- At other locations, stripped sour water is kept segregated and routed directly to the WWTU. Some facilities have dedicated biological treatment for stripped sour water due to its high COD and phenolic content.

In the aerobic biological section of a WWTU, selenocyanate is oxidized primarily to selenite (SeO_3^{2-}), with small amounts being oxidized further to selenate (SeO_4^{2-}). This oxidation can also be done chemically, as discussed in the following section. Fortunately, selenite is one of the easiest selenium species to remove.

What stream to treat? The ideal wastewater stream to treat is small in volume, contains all of the refinery's selenium (i.e., is high in concentration) and is not oily. The stream that most often meets these criteria is the stripped sour water. With these characteristics, the selenium present as $SeCN^-$ can be either removed directly or oxidized to SeO_3^{2-} and then removed. Aside from the capital cost savings in treating a small stream, the target is not as low, because the treated water will be blended with the remaining refinery wastewater before discharge.

Several reasons exist for why these ideal conditions are not always available:

- Enough selenium may be present in the remaining refinery wastewater due to incomplete segregation of selenium-containing sources, so that blending will not achieve the effluent limit
- The refinery may have multiple sour water strippers that are geographically separated
- The sour water strippers may not consistently produce non-oily stripped sour water.

In these cases, it may be necessary to treat the final effluent.

Treatment technologies. Virtually all refineries treat wastewater with oil/water separation and sometimes other physical and chemical processes. That may be the extent of wastewater treatment if the water is discharged to a POTW or injection well. Other refineries, particularly those that discharge directly to receiving water, follow this initial treatment with biological treatment to remove COD, ammonia and other contaminants.

These treatment processes were never intended to remove trace elements, such as selenium. Sampling studies have shown that some selenium is removed in biological treatment, as discussed in the following sections, but many conventional refinery WWTUs generally cannot meet the selenium WQBELs. Additional treatment steps—either physical/chemical or biological—are needed.

Physical/chemical technologies. The selenium in the effluent of refinery biological treatment systems (i.e., biotreaters) exists primarily as SeO_3^{2-}, which can be removed by adsorption onto iron oxides and hydroxide, a ferrihydrite complex. Iron coprecipitation is a process in which an iron salt, typically ferric chloride ($FeCl_3$) or ferric sulfate, is mixed with wastewater at a controlled pH, precipitated and removed by sedimentation. The precipitated sludge contains trace elements that have been "coprecipitated"—a generic term for removal by chemical adsorption, precipitation and/or entrainment. The pH determines the charge on the iron oxide surface and which trace elements are adsorbed. At high pH, cationic metals such as copper and zinc are removed, while at slightly acidic pH, anions such as SeO_3^{2-} and arsenate are adsorbed. For SeO_3^{2-}, the optimum pH is 5–6.5.

Two refineries in Northern California installed iron coprecipitation systems on their biotreater effluents in the 1990s. Their effluent limit was 50 μg/l, owing to a dilution credit afforded by their deep-water diffusers. One uses a circular clarifier for solids separation, while the other utilizes parallel plate separators.

Iron coprecipitation is effective on biotreated refinery wastewater because bacteria in the biotreater oxidize $SeCN^-$ (the predominant species in stripped sour water) to SeO_3^{2-}, which adsorbs onto iron oxide. Other anionic forms of selenium, including $SeCN^-$ and SeO_4^{2-} (the most oxidized form of selenium) do not adsorb well onto iron oxide. Some refineries do have a significant amount of SeO_4^{2-} in their effluents, and as a result cannot achieve very low selenium limits with this process.

If the water to be treated has not been biologically treated, then $SeCN^-$ must be chemically oxidized before iron coprecipitation. This has been done with hydrogen peroxide, sodium hypochlorite[3] and potassium permanganate.[4] Reportedly, potassium permanganate provides the benefit of additional oxide surfaces for SeO_3^{2-} adsorption, as it is reduced to manganese dioxide solids.

Other chemical processes used at full scale are variants of iron coprecipitation. Typically, these involve specialty chemicals that include iron-based coagulants and sulfur-based metal scavengers. The sludge formed can be removed by sedimentation or flotation.

All iron-based technologies produce large amounts of sludge. Tests for the Western States Petroleum Association showed sludge generation at 2.6 g–3.2 g of dry solids per g of iron added.[5] Treatment of a 3,500-gal/min refinery effluent using 40 mg/l of iron would produce 2 tpd–3 tpd of iron solids on a dry weight basis. At least one refinery transfers this sludge to its coker; others dewater it using centrifuges and ship it to landfills offsite. The dewatered sludge may be a characteristic hazardous waste in California, depending on the concentration and leachability.

Effective solid/liquid separation is important in an end-of-pipe iron coprecipitation. Excessive solids in the effluent can result in exceedance of limits for TSS and selenium. In addition, inland refineries discharging to fresh surface waters may have an effluent limit for iron, as the National Recommended Aquatic Life Criterion for iron in freshwater is 1,000 μg/l, and the TSS is primarily iron oxide solids.

Ion exchange[6] and adsorption[7] have also been tested extensively and implemented in at least one US refinery. As with many packed-bed wastewater treatment processes, ion exchange and adsorption media are fouled by oil and plugged by TSS, so these technologies cannot be used on streams with even occasional slugs of oil that have not been filtered of TSS. Other disadvantages of ion exchange include competition by other anions (e.g., sulfate and thiosulfate) and the fact that it produces a liquid waste that must be further treated.

One US refinery uses a unique system that precipitates $SeCN^-$ directly using a copper salt.[8,9] The process was originally developed to remove selenium from the regenerated solution of an ion exchange that was being pilot tested on stripped sour water, but it was then applied directly to the stripped sour water stream. It is very effective on selenium removal but adds copper to the wastewater, which then requires additional process steps to remove.

Biological technologies. Two mechanisms exist for biological selenium reduction: assimilative and dissimilative. The first, assimilative reduction, occurs in all refinery biotreaters, since not all of the selenium that enters the biotreaters is found in the effluent. A portion is removed, largely to the biosolids. This removal has been attributed to assimilative reduction, a mechanism by which selenium is taken up in place of sulfur in amino acids (e.g., forming selenomethionine instead of methionine) and other organic compounds to become part of the bacterial cells. This process alone is generally insufficient to meet effluent limits.

Oxidized forms of selenium (e.g., SeO_3^{2-} and SeO_4^{2-}) can also be used by some heterotrophic bacteria as an electron acceptor under anoxic conditions in dissimilative reduction. This process is analogous to denitrification, in which bacteria metabolize organics for growth and synthesis, using nitrate as an electron acceptor and reducing it to nitrogen gas.

Similarly, certain bacteria reduce SeO_3^{2-} and SeO_4^{2-} to elemental selenium, which is an insoluble solid. These solids exist as nanospheres (1 nm–100 nm) that are loosely held in the extracellular polymer of the heterotrophs. The reduction occurs at a lower redox potential than nitrate reduction, so all nitrate must first be removed before selenium can be reduced. In both cases, an oxidizable organic (i.e., electron donor), such as acetate or glycerin, is needed. Other oxyanions, such as arsenate and vanadate, may also be reduced and compete for an electron donor.

Dissimilative selenium reduction cannot be used on $SeCN^-$ or other reduced species. Therefore, at a refinery, it would be considered only for treatment of aerobic biotreater effluent, which contains oxidized selenium species. That stream is not ideal, however, because all readily oxidizable organics have already been removed, so supplemental organics would need to be added. To drive the reaction to a low residual selenium concentration, the supplement must be added in excess. However, the refinery cannot simultaneously discharge this excess and meet its effluent COD limit, so there must be an aerobic biological organics polishing step, along with exceptional solid/liquid separation, to remove the elemental selenium particles. To add to these complications, biotreater effluent contains nitrate (formed by nitrification of ammonia), which increases the amount of supplemental organics that must be applied.

Some refineries will face effluent limits on total nitrogen in the coming years, as regulatory authorities address potential eutrophication of receiving waters, and effluent denitrification will be needed. The removal of nitrate will make biological reduction a more attractive candidate for selenium removal. To that end, refineries that must reduce total nitrogen discharge should consider how selenium removal could be incorporated into that process, so that a single process could be used to remove both nitrate and selenium. Data collected at a full-scale municipal treatment plant with biological nitrogen removal showed a 93% reduction of selenium in the anoxic tank, but re-oxidation to SeO_3^{2-} and SeO_4^{2-} in the aerobic section.[10]

The anoxic process of biological reduction of selenium has been exploited in commercial systems to remove selenium from mine waters and power plant wet flue gas desulfurization (WFGD) scrubber waste. Selenate is the predominant form of selenium in many mining discharges; WFGD scrubber waste contains a mixture of SeO_3^{2-} and SeO_4^{2-}. Since SeO_4^{2-} cannot be removed by most of the physical-chemical processes, biological reduction is used instead. Packed-bed and fluidized-bed systems are commercially available. On refinery biotreater effluent, biological reduction in tanks has been tested but not implemented at full scale. It occurs naturally in pond-based refinery wastewater systems.

Case study 1: End-of-pipe iron coprecipitation. One US refinery installed an iron coprecipitation system (**FIG. 1**) in the mid-1990s, immediately downstream of its existing activated sludge system, which consists of aeration tanks, clarifiers and induced air flotation (IAF) for additional suspended solids removal. The activated sludge effluent

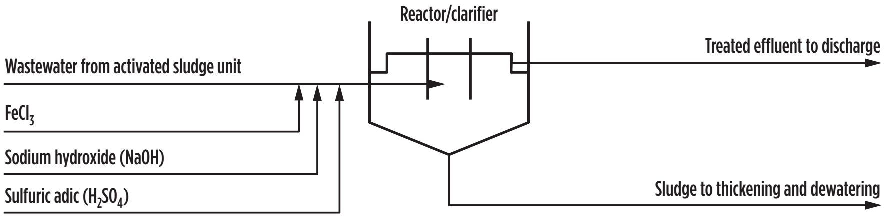

FIG. 1. Process flow diagram of a refinery iron coprecipitation system removing selenium from biotreater effluent.

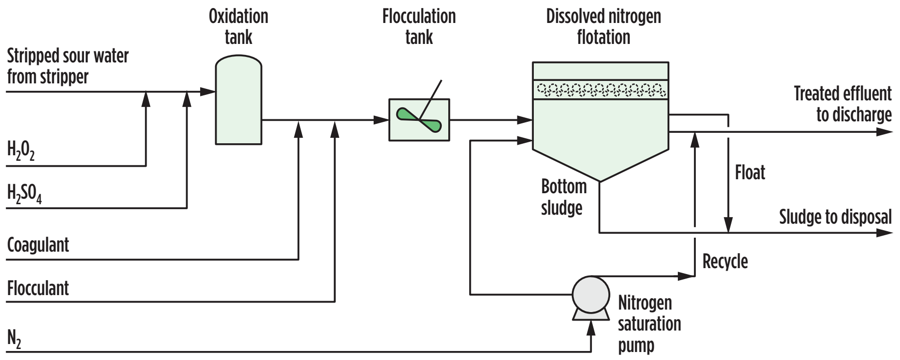

FIG. 2. Process flow diagram of a refinery oxidation, precipitation and flotation system removing selenium from stripped sour water.

contains selenium, primarily in the form of SeO_3^{2-}. In the selenium treatment unit, IAF effluent is dosed with ferric chloride, acid or base as needed, and a polymeric flocculant and is then introduced into the center well of a flocculating clarifier. Clarifier sludge, which contains the removed selenium, is centrifuged by a contractor and disposed offsite.

Prior to implementation, the refinery effluent contained approximately 60 µg/l–80 µg/l of selenium. At present, the median effluent selenium concentration is approximately 20 µg/l, well below the refinery's monthly average effluent limit of 42 µg/l.

Case study 2: Chemical oxidation and precipitation in stripped sour water. Another US refinery installed a chemical oxidation and precipitation system (**FIG. 2**) in the mid-2010s to treat stripped sour water only. The water is first acidified and then treated with hydrogen peroxide (H_2O_2) to oxidize $SeCN^-$ to SeO_3^{2-}. Controls are in place to prevent the addition of acid without H_2O_2, since acidifying $SeCN^-$ can potentially form hydrogen cyanide (HCN). After oxidation, proprietary coagulant and flocculant are added. The coagulant is iron based, so the chemistry is similar to iron coprecipitation. The flocculant includes a sulfur-containing organic molecule developed for metals removal.

In this system, flotation is used instead of settling to remove the selenium-containing solids. The flocculant particles are very light, and bench-scale testing during process development showed that flotation was an effective solid/liquid separation process that left a clean effluent. At full scale, this system was designed with a flocculating tank followed by dissolved nitrogen flotation (DNF). The DNF has a special pump that saturates recycled effluent with nitrogen under pressure. As this fluid is returned to the DNF, fine bubbles form and adhere to the flocculant particles, lifting them to the surface of the DNF tank, where they are skimmed for separation. Some solids settle instead. The bottom sludge and float, which contain the removed selenium, are combined and disposed. The DNF is covered and vapor-controlled due to the possibility of odors or volatile organic compounds (VOCs) emissions.

During commissioning, it was found that in-line pH control was problematic. Stripped sour water is formed from condensates, so it has little buffering capacity, and the titration curve has a sharp drop from highly basic to highly acidic pH. At times, too much acid was being added, resulting in excessive corrosion rates. This problem was reduced by a combination of modifying the acid pumps and upgrading the acid injection quill.

This refinery has a high effluent limit—approximately 200 µg/l—because it discharges to a POTW rather than to surface water. Therefore, operators are able to treat as much stripped sour water as needed to meet the effluent limit treating without having to treat the entire refinery effluent flow. Stripped sour water that is used for desalting is not treated for selenium. This system allows the refinery to process opportunity crudes with higher selenium.

Recommendations. The choices of which streams to treat for selenium and what technology to use are site-specific. They depend on the amount of selenium entering the refinery, the effluent limits, and how well stripped sour water is kept segregated from other process wastewaters. Iron-based technologies are the most common; however, room exists for technological progress in reducing the mass of residuals produced, in separating biological and selenium solids, and in tertiary treating of trace constituents resulting from application of selenium treatment technology. HP

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Advanced biological treatment removes benzene, phenol from refinery wastewater

Historically, US regulators have not required benzene and phenol monitoring for wastewater from oil refining, petrochemical processing, coking or coal gasification operations. However, a new dynamic has come into play. In the Marcellus shale, lower-priced natural gas at just under $3/MMBtu is prompting industry to construct ethane cracker plants that refine natural gas for usable products, such as polyethylene. The thinking, according to industry sources, is that proximity to the natural gas source is a better business model compared with the Texas Gulf Coast, especially after Hurricane Harvey shut down refineries in late summer of 2017.

With the development of the Marcellus shale came requests for proposals for wastewater treatment at newly constructed ethane crackers in the region that have very low benzene and phenol limits. Going forward, other new projects along the Ohio River watershed are expected to have similar requirements. In time, these new, stricter benzene and phenol effluent regulations for greenfield facilities could potentially spread throughout the US.

This insight provided the impetus to launch a study to monitor the capability of moving bed biofilm reactor (MBBR) technology to achieve very low limits for benzene and phenol under normal design conditions for complete chemical oxygen demand (COD) removal.

New capabilities in proven technology. MBBR technology has been proven as an effective biological treatment in a variety of applications since its invention in the mid-1980s. The technology utilizes polyethylene carriers (or media) to create a large, protected surface on which biofilm can attach. Bacteria required for treatment of a variety of organics develop on the carriers. The continuous motion of the carriers optimizes diffusion in and out of the biofilm, enhancing process kinetics. It also ensures continuous sloughing of excess biomass, facilitating process operation, and it can achieve the results of more conventional biological processes in a much smaller footprint.

The company that invented MBBR continues to conduct research and development to discover new ways to apply the technology to meet the water treatment needs of industry and municipalities. The company also monitors the performance of existing facilities to evaluate the ability of the process to meet more stringent discharge limits. In response to new demand in the marketplace for technology to achieve low benzene and phenol limits, a study was initiated to determine the effectiveness of MBBR technology to remove these constituents from refinery wastewater.

Benzene and phenol removal in full-scale MBBRs. Samples were collected at three refineries where MBBR wastewater treatment systems are in operation. Two were US refineries, while the other is in Lund, Sweden. The plants have been in operation for many years. Grab samples were collected at these facilities to evaluate the removal efficiency of benzene and phenol under normal operating conditions, even though these parameters are not regulated at those sites. In addition, laboratory studies were conducted at the R&D facility with spiked samples to learn the upper limit for the influent benzene and phenol concentrations while still achieving an effluent concentration of 10 μg/l.

Refinery 1. One US refinery wastewater treatment plant has two MBBRs operating in parallel, with a total reactor volume of 4,554 m^3. The reactors have a fill rate of 26% of carrier media,[1] with a surface area of 500 m^2/m^3, as shown in **FIG. 1.**

The MBBRs, installed downstream of a nonmechanized deoiling tank, can achieve combined removal of COD and nitrification in a single stage. The applied surface area loading rate (SALR) is 1.5 g–9.8 g total COD (TCOD)/m^2/d.

Feed and effluent samples were collected 10 times over 5 mos. A third-party laboratory analyzed the samples for benzene and phenol, COD and hexane-extractable material (HEM), and the TSS concentration was analyzed in-house. Samples for soluble chemical oxygen demand (SCOD) were filtered using 0.45-μm paper.

Despite exposure to fluctuating levels of HEM (oil and grease), the MBBR performed well. HEM in the MBBR effluent

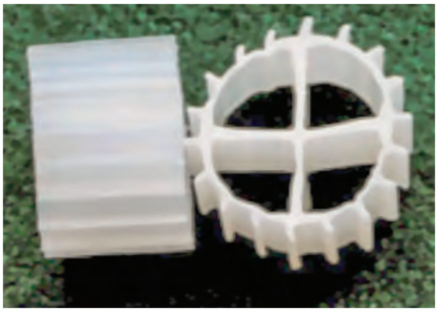

FIG. 1. This proprietary MBBR carrier removed benzene from influent concentrations to below the detection limit of 4.4 μg/L, while reducing pure phenol to below 10 μg/L on most of the samples from a US refinery wastewater treatment plant.

was consistently below 10 mg HEM/l with an influent concentration ranging from 7 mg/l up to 270 mg/l. The MBBR reduced SCOD to between 4 mg/l and 66 mg/l (average 56 mg/l) from influent concentrations of 168 mg/l–567 mg/l (average 369 mg/l). The MBBR removed benzene to below the detection limit of 4.4 µg/l from influent concentrations of 4,700 µg/l–14,000 µg/l, while reducing total recoverable phenols to 10 µg/l–30 µg/l from influent concentrations of 540 µg/l–4,900 µg/l. Pure phenol was reduced below 10 µg/l in samples containing 540 µg/l–1,500 µg/l.

Refinery 2. The second US refinery also has two MBBRs operating in parallel. The pretreatment system at this facility consists of gravity separation and dissolved air flotation for oil and grease removal. The pretreated effluent is pumped through a cooling tower and then discharged to an equalization tank. The equalized effluent is then pumped to the MBBR. The MBBR system is designed for partial COD removal as pretreatment to an activated sludge system. The MBBRs have an operating volume of 2,006 m^3 with 50% fill of proprietary media carriers. The average applied loading rate of 32 gSCOD/m^2/d is significantly higher than that applied in reactors designed for complete COD removal, since only 60% SCOD removal is required. With considerably more readily biodegradable COD available, it is not surprising that total phenols are reduced only from 3 mg/L to 0.6 mg/l.

FIG. 2. This proprietary MBBR carrier reduced influent distillable phenols to 40 µg/L–48 µg/L, while benzene could be detected only in the third sample, with a reduction to 24 µg/L in samples from a refinery wastewater treatment plant in Sweden.

FIG. 3. This proprietary MBBR carrier reduced phenols to 19 µg/L–79 µg/L. Benzene removal was below the detection limit of 0.5 µg/L on all samples collected from the effluent of the second reactor. Measured benzene concentration was above the detection limit twice in a laboratory test.

Refinery 3. The MBBR at the Swedish refinery is applied as pretreatment to remove organic material prior to nitrification in a downstream process. To allow nitrification to occur in a trickling filter, complete removal of degradable COD is required in the MBBR. With a flow ranging from 2,830 m^3/d–4,190 m^3/d, the MBBR hydraulic retention time is 30 min–50 min, which is relatively short for such an application. The single MBBR, which has a volume of 95 m^3, is filled with 55% of proprietary media carriers with a protected surface area of 500 m^2/m^3 (FIG. 2).

The wastewater, pretreated with gravity oil separation followed by sand filtration, is cooled to a range of 86°F–95°F (30°C–35°C) before entering the MBBR.[1] The applied surface area loading rate (SALR) is 18 g–22 g total COD (TCOD)/m^2/d.

Influent and effluent samples were collected on three occasions. The MBBR reduced influent distillable phenols to 40 µg/l–48 µg/l from 1,300 µg/l–2,000 µg/l. Benzene could be detected only in the third sample, with a reduction to 24 µg/l from 3,900 µg/l. SCOD was reduced to 50 mg/l–70 mg/l from 114 mg/l–177 mg/l.

Determining maximum organic loading rates. In addition to full-scale testing, a laboratory test was conducted to determine the maximum organic loading rates at which effluent benzene and phenol concentrations below 10 µg/L could be obtained at standard design loading rates for complete COD removal. The laboratory test was conducted in two parallel bench-scale models of two-stage MBBR processes, using a proprietary media carrier (FIG. 3).

The first trial was conducted with synthetic wastewater at an overall SALR between 4 g SCOD/m^2/d and 14 g SCOD/m^2/d, corresponding to volumetric loads between 1.5 kg SCOD/m^3/d and 5 kg SCOD/m^3/d. Distillable phenols were removed from 11,000 µg/l–28,000 µg/l, to below 10 µg/l. Benzene was removed to below the detection limit of 0.5 µg/l from an influent concentration of 240 µg/l–7,500 µg/l.

The second laboratory setup was operated using a refinery wastewater. The applied SALRs ranged from 3 gSCOD/m^2/d–11 gSCOD/m^2/d, corresponding to volumetric loads of 1 kgSCOD/m^3/d–3 kgSCOD/m^3/d. Phenols were reduced to 19 µg/l–79 µg/l from 5,800 µg/l–14,000 µg/l. Benzene removal was below the detection limit of 0.5 µg/l on all samples collected from the effluent of the second reactor.

The laboratory-scale trials and the data collected from the full-scale plants demonstrate that the MBBR process can consistently achieve total phenols and benzene concentrations lower than 10 µg/l under normal design conditions for complete COD removal. As refineries look to meet more stringent discharge limits, the MBBR process can offer the reliability that is required of an industrial process.

The capital cost of an MBBR system typically would be about 30% less than a conventional activated sludge system.

The study has allowed for the development of design guidelines for the removal of benzene and phenol as an optimal technological solution. HP

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