CHEMICAL PROCESSING

<u>DESIGN EXPERTISE</u> | IN Wastewater eHandbook

Maintain Your **Wastewater** Systems

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WATER & PROCESS SOLUTIONS

Make the Most of RO Membranes

Proactive steps can maximize life and performance for water purification

By Gregg Poppe, Dow Water & Process Solutions

MANY PROCESSORS striving to lower operating costs are missing an opportunity for savings in their reverse osmosis (RO) water treatment systems. Proactive steps to optimize both the cleaning frequency and cleaning method can extend the life of the installed membranes. Proper tracking of system performance combined with this optimized cleaning can reduce chemical, electrical and membranereplacement costs. Additionally, a wise choice when it's time to replace membranes that operate in a fouling-prone environment can pay dividends.

MAINTAIN OPTIMAL OPERATION

Proper maintenance is the key to protect the investment in your current membranes. So, here, we'll look at some guidelines that can help you extend the productive life of the membranes and reduce overall operating costs of the RO plant.

The loss of permeate flow during operation is normal for a membrane system, so the first question is: "When to clean?" The frequency depends on the feed water source, operating parameters such as flux, and pretreatment. Commonly, systems are cleaned two-to-three times/year with well water, three-to-four times/year with city water, and fourto-six times/year with surface water. But it really depends on the specific situation. So, it's important to vigilantly look for signs of fouling. Any of the following observations should trigger a cleaning:

• Normalized permeate flow declines by 10–15%.

- Normalized feed pressure increases by 10–15%.
- Pressure drop rises by 10–15%.
- Normalized salt passage increases by 5–10%.

To make proper judgments, it's essential to normalize the permeate flow, feed pressure and salt passage to a standard reference point. Otherwise, fluctuations in feed temperature, salinity or pressure will either mask or accentuate the trends, leading to inaccurate conclusions about when to clean. Membrane suppliers can help provide software tools to normalize the data.

Foulants usually can be cleaned from the membrane surface with the right cleaning chemicals and good technique. Waiting too long to clean can permanently reduce RO performance (Figure 1).

Figure 1. Waiting too long to clean can lead to permanent performance loss.

ACHIEVE EFFECTIVE CLEANING

Before cleaning, it's very important to determine the type and location of the fouling:

- Colloidal and particle fouling (Figure 2) is specific to the first RO stage. (Its feed screen tends to catch these foulants.)
- Scaling (Figure 3) appears in the second stage. (Recovery of product water in this stage boosts the concentration of salts in the remaining water, possibly exceeding the solubility limit of certain salts.)
- Organic and microbiological fouling (Figure 4) can occur in either the first or second stage of the system.

Before starting to clean, find out the cleaning pH and temperature limits set by the membrane manufacturer and make sure the cleaning chemicals are compatible with the membranes.

Clean with alkaline cleaners first and then, if necessary, with acid. High-pH cleaners are more likely to break down fouling layers. Acid may react with organics, silica and biofouling, possibly leading to irreversible performance decline — that's why you should remove these foulants first with an alkaline cleaner.

Clean at the appropriate pH and temperature to remove the foulants:

- To remove biofouling, cleaning at pH 12 is much more effective than pH 11— about an order of magnitude better at restoring permeate flow. It's important to know the temperature range permissible for the membrane type at the high pH.
- To remove calcium carbonate scale, cleaning at lower pH and higher temperature restores permeate flow more fully (Figure 5). Some plants use citric acid (Cleaner A in the figure) to remove scale but it's usually not very effective compared to HCl at pH 1 (Cleaners D and E).

Figure 2. Such fouling occurs in the first RO stage, particularly on its feed screen.

Figure 3. This appears in the second stage when salts exceed their solubility limits.

More extreme pH is more effective at removing foulants — but not all membrane manufacturers allow cleaning at a pH as high as 12 or as low as 1.

Different foulants require different cleaning protocols to achieve effective results. Consider the following guidelines (if the membrane can handle these conditions):

- Inorganic salts (such as $CaCO₃$): 0.2 wt.% HCl, 25–40°C and pH 1–2.
- Metal oxide (such as iron): 1.0 wt.% sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), 25°C and pH 5.
- Inorganic colloids (silt), silica, biofilms and organic compounds: 0.1 wt.% NaOH, 35°C max and pH 12 or 0.1 wt.% NaOH and 0.025 wt.% Na-DSS [sodium salt of dodecylsulfate], 35°C max and pH 12.

USE THE PROPER PROTOCOL

The cleaning procedure is important. When mixing the cleaning solution, ensure all chemicals are dissolved and well mixed before circulating it through the membrane elements. When first introducing the cleaning solution into the RO system, use a low flow rate while the water in the system is displaced. Also, to avoid driving foulants into the membrane surface, apply only enough pressure to compensate for the pressure drop. Dump the concentrate stream at first for as long as necessary to prevent diluting the cleaning solution upon recycle.

Once cleaning chemicals have displaced water, recycle concentrate and permeate to the cleaning tank. Measure the pH and adjust as needed to maintain the desired value. Monitor the color of the cleaning solution — a color change indicates removal of foulants. Then dispose of the heavily contaminated cleaning solution and mix fresh solution. Continue this for as long as it appears new foulants are being removed. However, with an

Figure 4. Both the first and second stages of a system can suffer from such fouling.

Figure 5. Temperature and pH impact the performance of acid cleaners.

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acid cleaning, recirculating for longer than 20–30 minutes increases the risk of any heavy metals falling out of suspension and becoming permanently embedded on the surface of the membrane, making it more difficult to clean.

Prepare fresh cleaning solution for the soaking step. The length of the soak varies. While alkaline cleanings may require an overnight soak, acid cleanings typically only need 30 minutes. To maintain the desired elevated temperature during an extended soak, use a low recirculation rate through the elements. As before, monitor the color of the cleaning solution and dispose or refresh the solution when you observe a change in color.

After the soak, recirculate the cleaning solution at a high flow rate for 30–60 minutes to flush out foulants removed from the membrane surface. Finally, flush out the cleaning solution using RO permeate or deionized water. During the flush, the minimum temperature should be 20°C.

RETHINK MEMBRANE CHOICE

When it's finally time to replace RO membrane elements that handle fouling-prone water, check into technological developments introduced by membrane manufacturers to help mitigate fouling. For example, there's been a growing acceptance that elements with 34-mil spacers foul less quickly and are easier to clean than those with thinner spacers.

Membrane manufacturers continue to innovate in their quest to optimize spacer geometry and thus flush the membrane surface more effectively. Work also is advancing to improve the fouling-

resistant properties of the spacer material and membrane surface.

All these development efforts aim to extend the time between cleanings, improve the effectiveness of cleaning, and lengthen the overall lifetime of the membranes. Plants benefit from lower operating costs via: 1) decreased consumption of cleaning chemicals due to less frequent cleanings, 2) less electricity use due to slower increases in feed pressure, and 3) reduced membrane replacement costs due to longer life.

CUT COSTS

As this article has stressed, timely and proper membrane maintenance is necessary to ultimately achieve the lowest operating costs.

Monitor the condition of the plant, normalize and assess the data, and use the results to decide when to clean so membrane performance isn't irreversibly reduced.

Before starting to clean, determine the type of fouling and its location so you can use the proper cleaning chemical. Cleaning at more extreme pH is much more effective — but first always check the membrane manufacturer's literature for information about pH (and temperature) limits for cleaning.

Waiting too long to clean will shorten membrane life and cost far more than appropriate cleaning to keep membranes healthy.

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Prevent Rust Formation in Pipes

Electronic water treatment transforms existing red rust and speeds scale removal

By Jan De Baat Doelman, Scalewatcher North America

MOST PROCESS plants use substantial amounts of water. The water comes from a range of sources such as rivers, lakes, wells and oceans and contains dissolved and suspended solids. To reduce consumption, most plants reuse water; this, in turn, causes it to be highly concentrated in silicate, iron and calcium carbonate that prompt limescale build-up and rust.

Limescale deposition results in the need for regular shutdown to remove the build-up. Sometimes, this removal can take place as part of a planned maintenance program but, on other occasions, severe or even complete blockage by limescale can force unscheduled equipment outages until the blockage is cleared. In addition, scale deposits can increase corrosion due to entrapped oxygen and the scale itself sometimes can corrode the surface it contacts. Also, scale will interfere with the action of inhibitors in the system, keeping them from reacting with the surface below the scale. If the scale is patchy, the differential aeration between the clean surface and the scale surface may cause a corrosion cell to set up.

Iron reacts with oxygen to form red rust (Fe₂O₃). Dissolved oxygen in water causes growth of such rust inside a ferrous pipe that accelerates scale deposition (see photo). Electronic water treatment (EWT) devices such as Scalewatcher change that red rust into black rust $(Fe₃O₄)$ called magnetite. This conversion makes it possible to extend the lifespan of pipe material by forming a film on the inside of the pipe wall that prevents rust growth. The transformation into black rust by EWT not only removes the red rust but also allows the ongoing flow of water to remove scale.

To explain the effect of electronic scale removal, it is important to first understand the major factors that cause scale. While scale can be a complex of many minerals, calcium carbonate is the most prevalent in industrial processes.

Aqueous solutions can become supersaturated, which means they contain higher concentrations of dissolved solute than their equilibrium concentration. Such solutions are not stable and are easily triggered into dropping back to saturation level, forcing the dissolved compound to precipitate. Even when a bulk solution is less than fully saturated, scale formation can occur spontaneously due to localized supersaturation — for example, a drop in calcium carbonate solubility on a surface can lead to the formation of deposits.

THE TECHNOLOGY

EWT is a non-invasive system that involves wrapping a solenoid coil or coils around the pipework to be treated. A signal generator that produces a continuously changing frequency within a specified range supplies current to the coils. The pulse-shaped current creates an induced electric field, concentric around the axis inside the pipe. As a consequence of this arrangement, any charged particle or ion moving within the field experiences a so-called Lorentz force generated by the interaction between charged particles and magnetic and electric fields.

The treatment influences the initial nucleation, resulting in idiomorphic, scattered crystals that do not stick together or form matted structures — in contrast to the matted structures that continuously grow in untreated water. The crystals' large volume relative to their surface area makes them sensitive to water currents; they are easily flushed out of the pipeline. Because no new scale layers are formed, the shear force of the water flow gradually will remove existing layers of scale. The ability to adjust power, frequency and coil configurations on site enables optimizing performance without downtime and pipe replacement.

The treatment requires flowing water to be effective. In addition, to ensure the best possible results, the coils should be located 39 ft from the equipment to be protected — and not installed immediately before or after a pump.

Payback on EWT normally is less than two years. In some cases, the return on investment can be as little as three months.

SUCCESSES

EWT has proven effective in treating rust problems in a variety of applications. Here are two examples:

River water used in a compressor cooling-water line. The pipe work was clogged with scale, resulting in a safety device automatically stopping the compressor when the temperature of cooling water exceeded 194°F. The main components of the scale were calcium carbonate and iron.

The river water, gathered in a water pond, passes through a strainer, cools the compressor, and then goes to a sump from which it is returned to the water pond by a circulation pump. It was difficult to pull up the screen of the strainer because 0.2 inch of rust adhered to the screen case. A Scalewatcher was installed on the discharge side of the pump. After about three weeks, red rust inside the screen case of the strainer disappeared and remaining rust had changed into a black color. Then it became easy to pull up the screen. In the compressor, the temperature of the cooling water did not surpass 176°F, making it possible to operate the compressor safely without interruption.

Iron scale caused by chlorine at a power plant. Seawater was used in a pipeline supplying analyzing equipment. The line was clogged with micro-organisms and iron scale. The strainer had to be cleaned every week. A Scalewatcher was installed on the line between the water pump and the strainer to see if it could prevent corrosion by dissolved chlorine. After a month, the rust and hard scale inside the pipeline had softened. After a further three months, the red rust had changed to black rust, the strainer was not clogged and the microorganisms had disappeared.

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Activated Carbon Gets New Use

Several "new, but old" activated carbon applications are gaining ground in water treatment

By Steven Ragan and Holger Fuchs, Jacobi Carbons

In 1971, when accepting the Skakel Award at the 10th Biennial Carbon Conference of the American Carbon Society, Professor Philip Walker of Penn State University made his famous quote "carbon, an old but new material" and predicted that "… the development of new carbon materials and the improvement of old carbon material will continue." [1] In the four decades since Professor Walker gave those comments, his words have proven prophetic. The award of two Nobel prizes to "old but new" carbon materials in recent years (Chemistry 1996 — Curl, Kroto and Smalley for Fullerenes and Physics 2010 — Geim and Novoselev for Graphene) attests to the fact that carbon, so abundant and commonplace an element, remains a material full of new possibilities.

Activated carbon, like other forms of carbon, possesses both old and new characteristics. Examples can be readily found of new applications for old forms of carbon, as well as new forms of carbon for old applications. This article will focus on one example of each.

Old Process Gets New Life

The presence of active pharmaceutical ingredients, radio-opaque substances and endocrine-disrupting chemicals in wastewater is a relatively new issue in relation to water quality. Evidence of the potential toxicology of these difficult-to-treat pollutants is relatively recent but the links to the emotive and headline-grabbing health issues of carcinogenicity and effects on human population fertility is emerging. To remove these substances from wastewater or sewage, the "old" contact treatment process with powdered activated carbon (PAC) has found ready application.

Studies for the removal of these micro-pollutants

by PAC has recently been completed by the Biberach University of Applied Science, at a full-scale sewage treatment plant in Southern Germany. [2,3] Activated carbon grades with pore structure well suited to adsorption of medicinal residues were applied that met the treatment objectives.

For the 15 key pharmaceuticals detectable in water, the removal rate after PAC application was >50% and >90% for target substances, i.e., carbamazepine and diclofenac, and hence application of PAC was shown very effective in reduction of these medical residues (Figure 2a).

Furthermore, the study also investigated the possibility to remove radio-opaque substances, commonly termed x-ray dyes, often used in medical investigations and industrial processes. Although the

Figure 1. The contact treatment process with powdered activated carbon has found ready application in the removal of active pharmaceuticals in wastewater.

REMOVAL OF DRUG RESIDUES

Figure 2a. Powdered actuated carbon helped remove four pharmaceuticals from wastewater at rates of 50% or higher.

investigation was limited to iodine-containing substances, this provides a representative study, as these compounds are the most present and most persistent members of this substance group in water. Radio-opaque substances are highly polar molecules in comparison to the pharmaceuticals investigated within this study and therefore they show significantly lower removal rates (Figure 2b). Nevertheless, activated carbon has a significant impact on the residual levels of radio-opaque substances after treatment and is proven effective in the removal of these compounds.

New Forms of Carbon for Old Applications

Being a powerful oxidant effective against almost all bacteria and virus particles, dissolved chlorine gas or hypochlorous acid released by chemicals such as calcium hypochlorite or sodium hypochlorite has proven the most effective and widespread disinfection process applied to water. However, this very oxidative and reactive property of available or "free" chlorine requires its careful control in process water to prevent its interaction with specific process chemicals. The undesirable nature of chlorinated by-products in brewing or beverage preparation, e.g. cola drinks, is obvious. The removal of this free chlorine, i.e., dechlorination, by flow in contact with activated carbon is one of the oldest process

applications of carbon. However, it is important to realize that dechlorination by activated carbon does not remove reactive "free" chlorine by adsorption but results in its transformation to the less reactive and tasteless chloride (Cl-) ion. The dechlorination capability of granular activated carbons (GAC) are typically measured using the half-value length (the method of which was first published in DIN 19603). This test measures the bed depth of carbon that halves a free chlorine concentration of 5 mgL⁻¹. For typical activated carbons, the half-value length is typically 3–5 cm.

However, the dechlorination performance of GAC is very sensitive to external surface-area-tomass ratio and is known to be favored by small particle sizes. New fibrous forms of activated carbon, including cloths or felts, offer very high external surface area/mass ratios. The structure of one such punched fabric product is shown opposite and its dechlorination performance is shown in Figure 3. Although the felt layer was only 4mm thick and weighed 2.5 g, it was shown to dechlorinate or "transform" a concentration of 2 mgL $^{-1}$ chlorine at >75% removal efficiency for over 200 liters. This was achieved at flow velocity of 12.5 cms-1, considerably quicker than the 1 cms-1 velocity used in the DIN 19603 half-value test method. Such fibrous forms clearly offer improved dechlorination performance

REMOVAL OF RADIO-OPAQUE SUBSTANCES

Figure 2b. Activated carbon has a significant impact on the residual levels of radio-opaque substances after treatment.

in comparison to traditional GACs and illustrate a "new" form of activated carbon offering enhanced performance for "old" treatment processes and wastewater applications.

Figure 3. New fibrous forms of activated carbon are being used successfully in dechlorination processes.

Reinventing Activated Carbon

As the activated carbon application performance data here shows, activated carbon fully exemplifies its description as "an old but new material" in application to water treatment. "Old" carbon applications, such as contact treatment with PAC, have been shown effective in removing "new"

emerging contaminants from medical residues. The "new" fibrous activated carbon forms have been shown especially effective in the "old" application of dechlorination using activated carbon. The continuous "re-invention" of activated carbon as a material or in process will ensure its continued application by scientists and treatment engineers to traditional and novel water treatment processes.

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