Desalination Post-Treatment Considerations

Dr. Steven J. Duranceau

The use of synthetic membrane processes for desalination and production of drinking water has increased over the past five decades, primarily in coastal areas with limited freshwater sources. Desalting techniques primarily intended primarily to remove total dissolved salts (TDS) that generally cannot be removed by conventional treatment processes.

Initially, water desalination had been used to produce or augment drinking water supplies through the use of evaporative or distillation methods. Beginning in the 1970s, the water industry began to focus on commercially viable desalination applications using synthetic membranes.

Today, reverse osmosis (RO), nanofiltration (NF), and electrodialysis reversal (EDR) are the most commonly used desalting processes for potable water treatment in the United States, typically treating brackish or impaired water supplies. Globally, many seawater RO water treatment plants (WTPs) have been operating successfully for more than 30 years (Redondo 2001. Busch and Mickols 2004), but synthetic membrane processes produce permeate water depleted in minerals and often is aggressive toward distribution system components.

Moreover, the water produced by membrane processes typically is incompatible with existing water distribution system infrastructure. Post-treatment is thus needed for municipal water treatment before the membrane-treated water is delivered to the distribution system as finished water.

Studies regarding the application and effectiveness of brackish and seawater desalination to augment drinking water supplies have focused primarily on pretreatment challenges, process optimization, energy efficiency, and concentrate management; however, less has been documented with regard to post-treatment requirements, water quality, and secondary impacts.

The behavior of desalinated water in the distribution system remains largely non-documented, and potential issues that may arise after introducing desalinated water into existing distribution systems include impacts on internal corrosion control, disinfectants and disinfection byproducts, hydraulics, infrastructure maintenance, water quality, aesthetics, and customer acceptance. This article discusses the post-treatment of synthetic membrane processes used for desalting drinking water supplies.

Membrane Systems

Figure 1 presents a general flow diagram of a membrane system with an example post-treatment chemical feed sequence. Typical RO, NF, and EDR membrane systems consist of pretreatment and post-treatment processes in addition to the membrane process. Many municipal plants have multiple process trains installed in parallel, allowing flexibility in the production of permeate (product water) and ease of expansion.

In some instances it is possible to bypass a portion of the raw or pretreated water around the membrane system and blend that flow with the permeate stream to reduce the capacity of the membrane system, improve finished water stability, and minimize capital

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and operating costs (Bergman and Elarde 1995). The maximum allowable blend ratio is determined from an analysis of bypassed and permeate qualities.

Post-treatment processes typically include disinfection and corrosion control, and they can include degasification and/or air stripping processes if carbon dioxide and hydrogen sulfide gases are present in the permeate water. Post-treatment is needed for municipal water treatment before the membrane-treated water is delivered to the distribution system as finished water.

A recent overview of the current state of 62 full-scale RO/NF plants was conducted by Burbano and others (2007) for plants greater than 1 million gallons per day of capacity, used for either seawater desalination, brackish water desalination (including ground water, surface water and agricultural runoff), or wastewater reclamation. This overview provides an insight into post-treatment practices.

All the surveyed facilities reported using at least one post-treatment method for permeate conditioning and corrosion control.
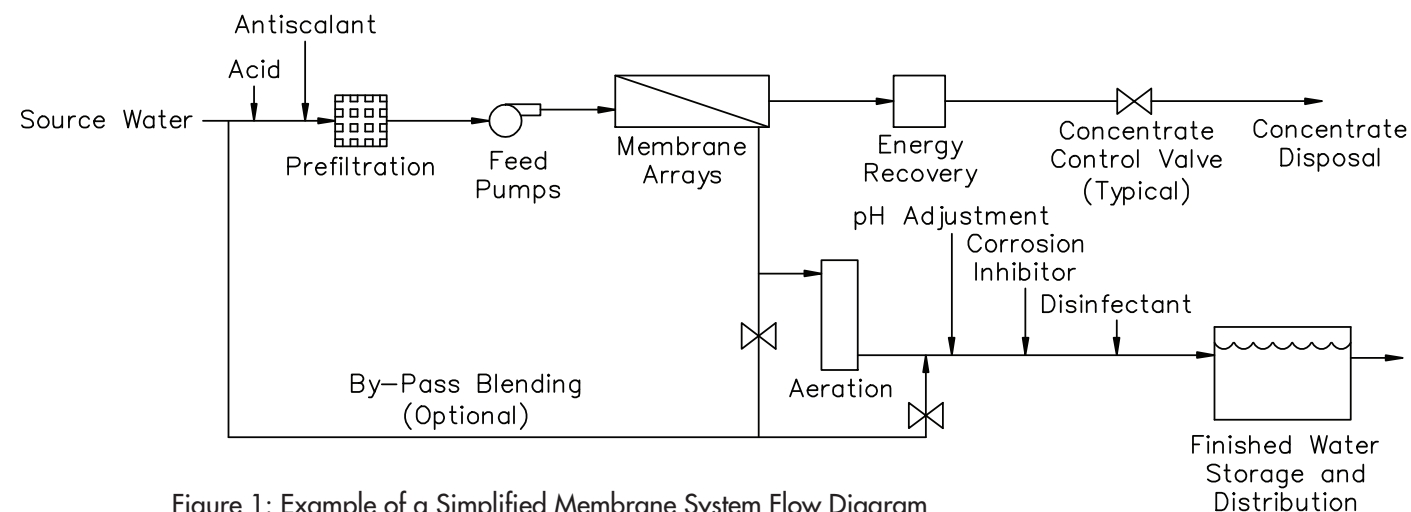
Figure 1: Example of a Simplified Membrane System Flow Diagram
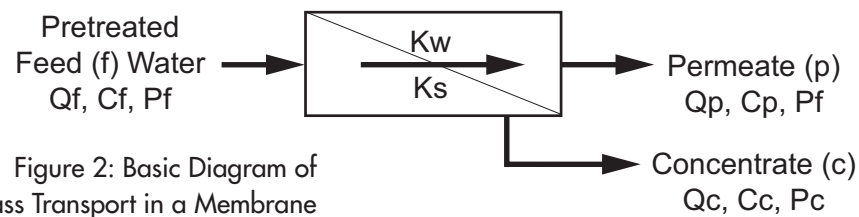
Figure 2: Basic Diagram of Mass Transport in a Membrane

Continued from page 4

These included such methods as caustic addition (31 percent); blending with raw, semitreated, or finished water (29 percent); degasification/decarbonation (25 percent); and addition of corrosion inhibitor (14 percent).

Most of the brackish water RO plants responding to the survey reported using degasification/decarbonation and caustic addition, with the majority blending permeate with groundwater. Permeate disinfection was reported to be used by 85 percent of the surveyed facilities that responded, most of which used chlorine. Other reported disinfection methods included the use of chloramine (24 percent) and ultraviolet irradiation (4 percent).

Permeate Concentration Mathematics

The permeate concentration of a membrane process can be predicted using several key mass transfer and membrane parameters, and is useful for determining post-treatment requirements. A basic element flow and mass balance diagram is shown in Figure 2. There are many different theories and models describing mass transfer in diffusion controlled membrane processes; however, a few basic principles or theories are used to develop most of these models.

The basic equations used to develop these models are shown in equations 2.1 through 2.5 with reference to the membrane element shown in Figure 2.

$$J = k_w(\Delta P - \Delta \Pi) = \frac{Q_p}{A} \qquad (1)$$

$$J_i = ki\,\Delta C = \frac{Q_p C_p}{A} \qquad (2)$$

$$r = \frac{Q_p}{Q_f} \qquad (3)$$

$$Q_f = Q_c + Q_p \qquad (4)$$

$$Q_f C_f = Q_c C_c + Q_p C_p \qquad (5)$$

Where:
J = Water flux (L^3/L^{2}t)
J_i = Solute flux (M/L^{2}t)
k_w = Solvent mass transfer coefficient (L^{2}t/M)
ki = Solute mass transfer coefficient (L/t)
ΔP = Pressure gradient (L), ((P$_f$+P$_c$)/2-P$_p$)
$\Delta \Pi$ = Osmotic pressure (L) ((Π$_f$+Π$_c$)/2-Π$_p$)
ΔC = Concentration gradient (M/L^3),((C$_f$+C$_c$)/2-C$_p$)
Q_f = Feed stream flow (L3/t)
Q_c = Concentrate stream flow (L^3/t)
Q_p = Permeate stream flow (L^3/t)
C_f = Feed stream solute concentration (M/L^3)
C_c = Concentrate stream solute concentration (M/L^3)
C_p = Permeate stream solute concentration (M/L^3)
r = Recovery
A = Membrane area (L^2)
Z = Combined mass transfer term

If ΔC is defined as the difference of the average feed and brine stream concentrations and the permeate stream concentration, then equation 6 can be derived from equations 1 and 5 (Duranceau, Mulford and Taylor 1992). This model can be described as a linear homogenous solution diffusion model in that it predicts solute flow is diffusion controlled and solvent flow is pressure (convection) controlled. Equation 6 is simplified by including a Z term that incorporates effects of the mass transfer coefficients, pressure and recovery into a single term.

$$C_p = \frac{k_i C_f}{k_w(\Delta P - \Delta \Pi)\left(\frac{2-2r}{2-r}\right) + k_i} = Z_i C_f \qquad (2.6)$$

Although this is a simple model, it does allow the effect of five independent variables on permeate water quality to be considered. If pressure is increased and all other variables are held constant then permeate concentration will decrease. If recovery is increased and all other variables are held constant, then permeate concentration will increase.

These effects may be difficult to implement if an existing membrane array is considered, for it is not possible to increase recovery without increasing recovery in such an environment; however, it is possible to increase pressure without varying recovery when arrays are designed.

Different membranes may have different mass transfer characteristics. Using a membrane with a lower molecular weight cutoff would decrease the permeate concentration, and the solvent and solute MTCs would need to be considered before such a result could be obtained.

Post-Treatment Process Overview

Treatment processes downstream of RO, NF, or EDR facilities are referred to as post-treatment processes. The water produced from the RO and NF membranes used to desalt water supplies in most cases requires some form of post-treatment; desalted and purified water, processed by a membrane process, will require additional treatment before it is suitable for potable water use and may consist of several different unit operations (Taylor et al, 1989; Byrne, 1995; Duranceau, 2001).

Typically the choice and sequence of post-treatment operations are determined by regulatory requirements, the design of the system, and finished water quality criteria. The need for post-treatment generally depends on several factors, which can be grouped into several categories, all of which are related to water quality:
✓ Chemical Stability
✓ Microbiological Stability
✓ Palatability and Customer Acceptability
✓ Secondary Impacts on Wastewater Influent Quality

Desalinated waters are commonly blended with small volumes of more mineral-rich waters to improve their acceptability and particularly to reduce their aggressive attack on materials (WHO, 2004). Blending water should be fully potable; where seawater is used for this purpose, the major ions added are sodium and chloride. This does not contribute to improving hardness or ion balance, and only small amount, no more than 3 percent, can be added without leading to problems of acceptability.

Blended waters from coastal and estuarine areas may be more susceptible to contamination with petroleum hydrocarbons or algal toxins, which could give rise to taste and odor. Some groundwaters or surface waters, after suitable treatment, may be employed for blending and may improve hardness and ion balance.

Selection of post-treatment processes may not completely consider the impacts on the distribution system, particularly when blending multiple varying supplies (Lovins 2004; Duranceau, 2005). This subject is of great importance for many water purveyors. Blending of variable and differing water supplies where desalted water serves as one of the supplies is increasingly become more frequent.

Recently concern has also been expressed about the impact of extremes of major ion composition or ratios on human health. There is lim-

Supply Type	Process	Examples of Applicable Post-Treatment Processes
Seawater	RO	1. Recarbonation. 2. Lime addition. 3. Calcite bed filtration. 4. pH and/or alkalinity adjustment. 5. Addition of corrosion inhibitors. 6. Primary and secondary disinfection. 7. Blending with fresh water supplies.
Brackish Water (Surface)	RO, NF, EDR	1. pH and/or alkalinity adjustment. 2. Addition of corrosion inhibitors. 3. Primary and secondary disinfection. 4. Blending with fresh water supplies.
Brackish Water (Ground)	RO, NF, EDR	1. Decarbonation (degasification) 2. Hydrogen sulfide stripping. 3. pH and/or alkalinity adjustment. 4. Addition of corrosion inhibitors. 5. Primary and secondary disinfection. 6. Blending with fresh water supplies. 7. Bypass blending with raw water supply.
Fresh Water (Ground)	NF, EDR	1. Decarbonation 2. Hydrogen sulfide stripping. 3. pH and/or alkalinity adjustment. 4. Addition of corrosion inhibitors. 5. Primary and secondary disinfection. 6. Blending with fresh water supplies. 7. Bypass blending with raw water supply.

Table 1: Typical Post-Treatment Processes Based on Supply Type

ited evidence to describe the health risk associated with long-term consumption of such water, although mineral content may be augmented by stabilization processes typically used by utilities practicing desalination (WHO, 2003a).

Table 1 presents the typical categorization of permeate post-treatment depending on source water type. There are four primary issues concerning the post-treatment water. These relate to blending, remineralization, disinfection, and the materials used for storage and transport of the water to the tap.

Desalinated water is often blended with other sources that contribute minerals to the final blended water. Seawater as a source for blending is limited because of issues related to corrosivity and taste if the blending levels exceed about 1 percent.

Blending of permeate water with seawater results in the addition of sodium, potassium, calcium, and magnesium to drinking water but also will contribute bromide and iodide, which are DBP precursors, and is limited in quantity due to the significant concentrations of these constituents. Consideration should be given to the natural minerals present and whether these will result in finished water having unacceptable water qualities in addition to unacceptable taste and odor.

Water Quality

The chemical composition of permeate water produced by RO or NF when blended with other source water can cause water quality and infrastructure problems when distributed. Many facilities pump desalinated water directly into the distribution system without being mixed or blended with other finished water supplies that cause concern with regard to distribution system water quality (Fayad, 1993; Imran et al 2005).

Consequently, evaluation of water quality parameters for use in determining appropriate post-treatment actions is required for desalination membrane treatment applications. Factors that should be included when referring to the quality of desalinated waters include the chemical and biological stability of water and its interaction with the distribution system (Lahav and Birnhack 2007; Taylor et. al. 1989).

Corrosion control strategies can be divided into two general approaches. The difference between these two approaches is the mechanism by which a protective film is formed.

The first approach includes precipitate formation of protective coatings for corrosion control. Water chemistry is adjusted to cause the precipitation of a compound onto the pipe wall and form the protective film. The success of this approach depends on the ability to form precipitant and the characteristics of deposits that result on the pipe walls.

The second approach involves the interaction of the potable water supply and the pipe material to form metal compounds that create a protective film of insoluble material for corrosion control. Passivation is the mechanism of this second approach. Adherence of the insoluble metal compound on the pipe wall determines the success of this approach.

Permeate streams from seawater and brackish water desalting processes are primarily a dilute solution of sodium chloride. To provide stability to water and to prevent corrosion (metal release) of piping systems and domestic plumbing, post-treatment is necessary to return some calcium hardness and bicarbonate alkalinity to the water.

In many situations, post-treatment also includes the removal of carbon dioxide to raise the pH, hydrogen sulfide removal when required, and the addition of fluoride which is removed during the desalting process. Corrosion control is a priority when either directly pumping desalted finished waters into the distribution system or when blending different water sources from membrane process.

The constituents of concern when establishing a post-treatment process include the pH which will be dependant upon the buffering capacity and bicarbonate alkalinity, calcium, sulfate and chloride, dissolved oxygen, boron, total dissolved solids concentration, and corrosion indices. These parameters are interrelated in the final treatment process selected for post-treatment, depending on application and source water (i.e., ocean surface versus brackish ground water supplies).

Alkalinity, Scale and Red Water
Alkalinity in water is a measure of the

general buffering capacity or stability of the water. Increasing the alkalinity generally leads to lower and corrosion rate and results in fewer changes in pH of distributed water, but excess alkalinity can cause excessive scale deposition where calcium may be present. Alkalinity is thus directly related to the buffering capacity of water and is considered an important parameter affecting the pH.

Alkalinity depends on the concentration of bicarbonate, carbonate, and hydroxide ions in water. According to Lahav and Birnhack (2007) for a given pH value, the higher the alkalinity value, the higher the ability of the water to withstand a change in pH due to release of H^+ and OH^- ions to the water. A higher alkalinity at a given pH translates into a higher dissolved inorganic carbon (DIC) concentration of the carbonate species (CO_3^{2-}), but too high an alkalinity at higher pH levels may accelerate lead and copper metal release (Duranceau et al, 2004).

It is also known that red water can be prevented by maintaining the alkalinity in the system when considering a subsequent pH shift if treatment were to be employed. A non-stabilized finished water can experience fluctuations in pH in the distribution system as scale is deposited (scale) or dissolved (corrosion). It is desirable to maintain the alkalinity concentration in distributed water above one millequivalent of alkalinity, or 60 mg/L (as calcium carbonate).

Dissolved Oxygen

The oxygen concentration can have varying effects on iron corrosion. The corrosion rate increases with increasing dissolved oxygen. Dissolved oxygen also is responsible for the ability of buffering ions, including phosphates, to inhibit corrosion (McNeill and Edwards 2001).

pH

Various studies have been done to correlate the effect of pH on corrosion in pipes. The pH in a system is related directly to the alkalinity, Ca^{2+}, and CCPP in the system. In Lahav and Brinhack (2007) it is stated that the pH deter-

mines the buffer capacity of the water sources.

When different water sources are blended, the chemical stability of the blend is determined significantly by the buffering capacity of the original waters. A higher pH will usually result in a lower buffer capacity, which also can be noted to be associated with low corrosion rates and prevention of red water episodes, although most studies has show pH to be an isolated single parameter.

Boron

Boron removal becomes more costly and difficult to process, especially when dealing with seawater, because seawater is not drinkable or useable for irrigation. Treatment must be taken into consideration in order to decrease boron and to correct any other corrosive minerals that may be in the water.

Gabelich (2005) and others demonstrated post-biofilters and ultraviolet light disinfection. It was concluded that in order to maintain low bacterial levels, residual disinfectants must be applied. With this process, it is also recommended that free chlorine be added to keep bacterial from re-growing.

Pervov (2003) discusses that boron depends on pH values. This theory was found in many reviews, demonstrations and articles. In Pervov's experiment, he based it on the fact that boron rejection depends on the temperature. In his experiment, there was an 80-percent rejection rate when at room temperature. This percentage will increase as we decrease the temperature, as with seawater, which will have a temperature below 10°C.

Bonnelye (2006) stated that boron has a pH of approximately 8.2 in Curacao seawater and is mostly boric acid. Boron rejections depend on temperature, pH and salt rejections.

Because of low boron levels required, a two-stage reverse osmosis treatment was proposed. The first stage will entail antiscalants being used on both passes to avoid risk of salt precipitation. The second stage will use caustic soda to transform boric acid to borate, which is much easier to remove.

Residual boron is related to the pH levels in this stage. The post-treatment of this plant was based on re-mineralization through limestone filters, UV disinfection and GAC filtration.

Treatment Strategies

The primary options for corrosion control include (USEPA, 2003):
- pH adjustment
- Bicarbonate stabilization (alkalinity adjustment)
- Calcium adjustment
- Inhibitor addition

pH Adjustment

Adjustment of pH is used to induce the formation of insoluble compounds on the exposed pipe walls. Passivation is the operating mechanism for this corrosion control strategy. pH adjustment is accomplished with the addition of chemicals, such as lime, soda ash, sodium hydroxide, potassium hydroxide, and carbon dioxide.

pH adjustment is most suitable for source waters with low to moderate hardness and alkalinity levels (between 80 and 150 mg/L as $CaCO_3$). Frequently this treatment technique is used in lieu of calcium carbonate precipitation.

Some concerns with pH adjustment include higher trihalomethane formation potentials at pH values greater than 8.1, increased formation of other disinfection byproducts at pH levels above 7.8, decreasing chloramines disinfection efficiency with pHs below 7.8, and a higher potential for calcium carbonate scaling in the distribution system pipe at pHs above 7.9.

Alkalinity Adjustment

Alkalinity adjustment frequently is used to induce the formation of insoluble compounds on the pipe walls of the distribution system. Passivation is the operating mechanism for this corrosion control strategy.

Carbonate passivation is achieved by incorporation of pipe materials into a metal hydroxide/carbonate protective film. This corrosion control strategy is most suitable for source waters with minimum alkalinity, and it is frequently used in lieu of calcium carbonate precipitation.

Alkalinity adjustment alters the concentration of dissolved inorganic carbonate (DIC) in the source water. Alkalinity adjustment can be accomplished with lime, soda ash, sodium bicarbonate, sodium hydroxide, potassium hydroxide and carbon dioxide.

Sodium bicarbonate addition is preferable for alkalinity adjustment. Sodium hydroxide contributes little alkalinity to the water, but can cause dramatic increases in pH.

The primary disadvantages of alkalinity adjustment include capital, operation, and

maintenance cost and increased carbonate scaling on pipe walls. The primary benefit of alkalinity adjustment is increasing the buffering capacity for the source water, which helps to prevent wide fluctuations in pH throughout the distribution system.

A buffer intensity greater than 0.5 milliequivalents per pH unit is indicative of a balanced, stabilized source water. The regional water appears to have adequate alkalinity and buffer intensity as long as the alkalinity is maintained 1 and 3 meq/L of bicarbonate alkalinity.

Calcium Carbonate Adjustment

The mechanism for this corrosion control strategy is the adjustment of the equilibrium for the calcium carbonate system for the source water. The objective for this treatment technique is the precipitation of a protective film of calcium carbonate onto the pipe walls.

Calcium addition or removal is not necessary for the precipitation of calcium carbonate; instead, this is accomplished with pH and alkalinity adjustment of the source water. The key to this treatment technique is to provide the conditions necessary for achieving calcium carbonate saturation.

Adjustment of the pH/alkalinity is done to create conditions necessary for the calcium and carbonate ions to exceed their solubility limits in water. Alkalinity or pH adjustment can be done with lime, soda ash, sodium bicarbonate, or carbon dioxide. These chemical additives directly contribute calcium or carbonate ions to the water.

The concerns with using calcium carbonate adjustment include precipitating a uniform protective film throughout the distribution system, reduction in the hydraulic capacity of the water lines, and scaling in mechanical systems such as boilers and water heaters. Scaling is of particular concern for those water systems with high levels of non-carbonate hardness and sulfate.

Adjustment of the pH is necessary for the precipitation of calcium carbonate and iron stability. For lower-alkaline waters, sulfate can also precipitate calcium and cause scale.

Use of Corrosion Inhibitors

Inhibitors have found wide spread use as a method of corrosion control. The most prominent forms of inhibitors used are polyphosphates, zinc phosphates, and silicates (AWWARF 1985).

The inhibitors control corrosion by several mechanisms, including sequestering the corrosion byproducts, specifically lead and copper; inhibiting scale; developing a coating film on the pipe walls; and buffering the water at the desired pH. Operating data indicate that the choice of inhibitor depends upon pH, alkalinity, calcium and total hardness, chloride,
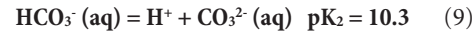
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sulfide, iron concentrations, and dissolved oxygen levels of the source water.

Brackish Groundwater Post-Treatment Considerations

The primary desalination water plant post-treatment unit operations for potable water supplies reliant upon brackish ground waters are (Duranceau, 1993):
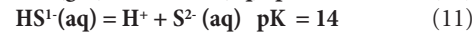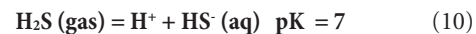
1. Carbon dioxide removal (degasification or decarbonation)
2. Hydrogen sulfide removal (stripping) and odor control treatment (scrubbing)
3. Alkalinity recovery, pH adjustment, stabilization and corrosion control
4. Disinfection

Carbon dioxide is removed from brackish permeate water easily with the use of aeration (degasification or decarbonation). Carbon dioxide exists in equilibrium with other carbonate species as defined by equations 7, 8 and 9. The pH of the permeate water will determine the amount of carbon dioxide available to be removed from the water.

$$CO_2 \text{ (gas)} + H_2O = H_2CO_3 \text{ (gas)} \quad pK_1 = 2.8 \quad (7)$$
$$H_2CO_3 \text{ (gas)} = H^+ + HCO_3^- \text{ (aq)} \quad pK_1 = 6.3 \quad (8)$$
$$HCO_3^- \text{ (aq)} = H^+ + CO_3^{2-} \text{ (aq)} \quad pK_2 = 10.3 \quad (9)$$

Many of the brackish groundwaters used as feed streams to RO or NF plants contain hydrogen sulfide. Conventional pretreatment (acid addition, scale inhibitors, cartridge filtration) will not remove hydrogen sulfide, nor will the membrane process, and hydrogen sulfide will permeate the membrane as a gas.

Aeration and oxidation are the two primary means for removing hydrogen sulfide; incomplete chemical reactions in the process often are responsible for formation of polysulfide complexes and elemental sulfur, which manifest themselves as turbidity in the finished water. Hydrogen sulfide dissociates in water according to equations 10 and 11:

$$H_2S \text{ (gas)} = H^+ + HS^- \text{ (aq)} \quad pK = 7 \quad (10)$$
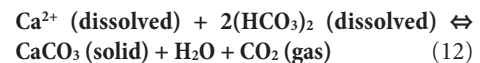$$HS^{1-} \text{ (aq)} = H^+ + S^{2-} \text{ (aq)} \quad pK = 14 \quad (11)$$

As shown in equation (10), since at pH of 7 only 50 percent of hydrogen sulfide exists in the gas form and is available for stripping, pH adjustment normally is used to improve removal efficiency. Since the pK for hydrogen sulfide is 7, half of the sulfide speciation is present as a gas and strippable. Hence, hydrogen sulfide gas can be removed effectively at pH levels of 6.0 or less without the formation of turbidity (elemental sulfur), but all of the carbon dioxide in the permeate water will also be removed. If stripping of sulfide occurs at pH 6.3, the pK of the carbonate system, some buffering capacity will remain in the aerated water.

Unless carbonate is added or a significant amount of alkalinity passes the membrane, there will be no carbonate (alkalinity) buffering in permeate, a possible problem with respect to stabilization and corrosion control, even if pH is adjusted with sodium hydroxide.

Better methods are required to resolve this common post-treatment issue; an increase in the pH entering the tower prior to air stripping to recover 1 to 2 meq/L of alkalinity would be beneficial. The use of carbonic acid pH adjustment prior to air stripping of hydrogen sulfide has proven beneficial with regard to buffering loss of finished water (Duranceau, 1999; Lovins, 2004).

The alkalinity of water is a measure of its capacity to neutralize acids. Bicarbonates represent the major form of alkalinity in water, since they are formed in considerable amounts from the action of carbon dioxide upon basic materials in the soil. Temperature, pH, and the concentration of bicarbonate are important in the formation of $CaCO_3$ feed water (equation 12):

$$Ca^{2+} \text{ (dissolved)} + 2(HCO_3)_2 \text{ (dissolved)} \Leftrightarrow$$
$$CaCO_3 \text{ (solid)} + H_2O + CO_2 \text{ (gas)} \quad (12)$$

Stabilization

The need to stabilize water so that it would not enhance metal corrosion and concrete dissociation has been recognized for decades. In order to prevent corrosion in the distribution system, the water purveyor distributing the water for blending with other water sources will have to include post-treatment in order to stabilize the water.

Permeate from RO and NF processes are specific to the plant, and usually pilot studies should be done before blending waters in order to determine the parameters in permeate and the needed adjustment to stabilize the water so that "red water" does not occur.

As noted by Fritzmann (2007), untreated permeate from seawater or brackish water reverse osmosis plants does not conform to the drinking water standards such as WHO or the GDWQS. Because of the low TDS values, RO permeate water can be unpalatable, corrosive, and unhealthy. Permeate must be re-hardened in order to prevent corrosion of pipes in the distribution network, pH value and CO_2 content need to be adjusted for scaling prevention, and permeate water needs further disinfection.

Three main groups of post-treatment processes currently exist for stabilizing reverse osmosis effluents: (1) Processes based on dosage of chemicals such as $Ca(OH)_2$ followed by CO_2; (2) Processes that are based on mixing the desalinated water with other water sources, with or without further adjustment of water quality parameter; and (3) Processes that center around
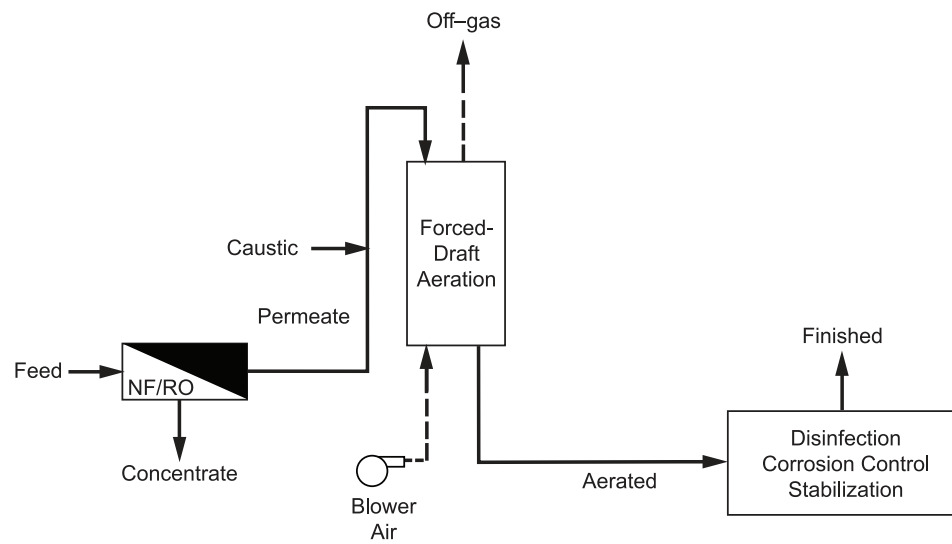
Figure 3: Permeate Alkalinity Recovery Process Flow Diagram

Continued from page 12

dissolving $CaCO_3$ for alkalinity and Ca^{2+} supply followed by pH and CCPP adjustment using NaOH according to Lahav and Birnhack (2007).

As stated by Lahav and Birnhack (2007), the first two groups are less commonly practiced because a) direct dosage of chemicals is usually expensive and b) desalinated water is diluted with other water sources further chemical dosage is usually unavoidable. The third process is the more cost effective of the two, particularly where $CaCO_3$ is available.

Permeate Akalinity Recovery

For groundwater treatment using RO and NF, the membrane can be considered as a closed system and the carbon dioxide will remain under pressure until exposed to an open system. Consequently, if acid addition is used for scaling control, the alkalinity in the raw water will be destroyed but not lost. Alkalinity recovery needs to be considered when selecting scaling control options, and depends on how much carbon dioxide and bicarbonate is in the raw water.

Normally, finished waters with 1 to 3 meq/L of bicarbonate alkalinity are considered highly desirable for corrosion control. Since carbon dioxide will pass unhindered through the membrane, the desired amount of alkalinity can be recovered in the permeate by acidifying the desired amount, passing it through the membrane, and adding the desired amount of base to convert the carbon dioxide back to its original bicarbonate form. Figure 3 depicts a permeate alkalinity recovery process flow diagram that illustrates this concept.

Carbon dioxide that is converted from bicarbonate ion during pretreatment or post-treatment will be available in a closed system. Consequently, the desired carbonate alkalinity in the finished water can be attained by car-

bon dioxide conversion before aeration, given presence of adequate CO_2. Normally, 1 to 3 meq/L of bicarbonate alkalinity is considered desirable for corrosion control.

Since CO_2 passes unhindered through a membrane, the desired amount of alkalinity can be recovered in the permeate by acidifying the desired amount of bicarbonate ion, passing it through the membrane, and adding the desired amount of base to convert the carbon dioxide back to its original bicarbonate form. The reactions are shown as (13) and (14).

$$H^+ + CO_3^{2-} \textbf{ (aq)} = HCO_3^- \qquad (13)$$
$$H_2CO_3 + OH^- = HCO_3^- + H_2O \qquad (14)$$
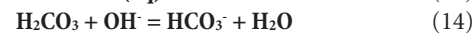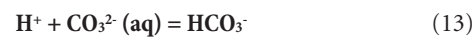
If the pH before alkalinity recovery is past the point of alkalinity neutralization, then additional base must be added to reach the point of alkalinity neutralization before alkalinity recovery can begin.

Disinfection

Normally, post-treatment disinfection is accomplished with chlorine. As in conventional treatment, disinfection is required, but the chlorine demand is reduced greatly by the desalting process, resulting in minimal formation of disinfection byproducts (Taylor et. al. 1989). If the desalting process allows the blending or bypass of water that contains disinfection byproduct (DBP) precursors, then chloramines, or some additional post-treatment of the blended water (or a reduction in the quantity bypassed or blended) may be required to comply with DBP drinking-water quality standards.
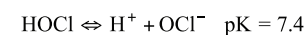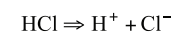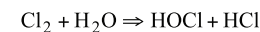
Desalinated waters constitute a relatively easy disinfection challenge because of their low TOC and particle content, low microbial loads, and minimal oxidant demand after desalination treatments. Turbidity is not likely to affect chem-

ical disinfectant performance, since turbidity values of desalinated water are relatively low.

Post-treatment with lime can cause an increase of inorganic turbidity that would not interfere with disinfection; use of food-grade lime aids to limit the amount of inorganic turbidity imparted to the water. The target levels of inactivation for pathogens remaining in desalinated waters can be achieved readily by appropriate disinfection processes.

Chlorine and the corresponding base can be applied simultaneously to the permeate stream following alkalinity recovery. If chlorine has been used for sulfide removal and excess chlorine has been used, some disinfection may have been accomplished; however, chlorine will react preferentially with sulfides and will not form any free chlorine until the sulfide demand has been exceeded. If chlorine and a base are added to the process stream before aeration, disinfection, oxygen addition, and stabilization will occur.

Almost no chlorine demand will remain following a reverse osmosis or nanofiltration process. The chlorine will convert some of the recovered alkalinity to carbon dioxide, which will be lost during aeration; however, the pH should return to the stabilization pH as carbon dioxide will tend to be at equilibrium with the atmospheric carbon dioxide. The pH will closely approach pHs with respect to calcium carbonate. The basic equations are:

$$Cl_2 + H_2O \Rightarrow HOCl + HCl$$
$$HCl \Rightarrow H^+ + Cl^-$$
$$HOCl \Leftrightarrow H^+ + OCl^- \quad pK = 7.4$$
$$pH = pK_{H_2CO_3} + Log\left|\frac{HCO_3^- - \left(1 + \alpha_{OCl^-}\right)C_{T_{Cl_2}}}{H_2CO_3 + \left(1 + \alpha_{OCl^-}\right)C_{T_{Cl_2}}}\right|$$
$$OH^- addition = OH^- \frac{mg}{meq}\left|\frac{meq}{mmol}\right|C_{T_{Cl_2}}\left|1 + \alpha_{OCl^-}\right|$$

Chlorine addition to water will produce equal moles of hypochlorous acid and hydrochloric acid. The hypochlorous acid will partially ionize to hypochlorite ions and protons. The hydrochloric acid will completely ionize producing protons and chloride ions.

One mole of protons will be produced for every mole of hydrochloric acid and every mole of hypochlorite ion produced. Consequently, the complete proton production during chlorination would be canceled by the addition of OH- as shown. Typical chlorine doses following a reverse osmosis or nanofiltration process range from 5 to 10 mg/L.

Inhibitors

Inhibitors are especially formulated chemicals that are characterized by their abil-

ity to form metal complexes which reduce the potential for corrosion. The treatment mechanism is passivation of the metal pipe surface.

Inhibitors commonly form inorganic scales with the pipe material. The scale acts as a diffusion barrier to both reactants and products of the corrosion half reactions. The electrical potential increases at the interface between the scale and the pipe wall.

There are a diverse range of corrosion inhibitor formulations that are offered commercially by manufacturers/vendors. The two major types are phosphates and silicates. Inhibitors for use in potable water must comply with the standards established by the American National Standards Institute (ANSI) and the National Sanita¬tion Foundation (NSF) Health Effect Standard 60 for Direct Additives to Drinking Water Supplies.

The type of inhibitor that may be used for corrosion control is determined by the calcium, alkalinity, pH, and temperature of the source water. Other constituents that may affect the selection of an inhibitor and the effective dose include iron, manganese, total hardness, sulfate, chloride, sodium, and TDS.

The use of inhibitors for corrosion control is analogous to the maintenance of chlorine residual within the distribution system. The elevated initial dose is reduced after the distribution system becomes stabilized. A typical maintenance dose is 0.5 to 1.25 mg/L.

Consideration should be given to the secondary impacts of using an inhibitor, particularly if the product is a pollutant of concern or interferes with reuse of treated effluent from the wastewater treatment facility. It is important to maintain the pH range throughout the distribution system, as well as to utilize an inhibitor that is not subject to rapid hydrolysis effects. This requires that the source water be well buffered to the targeted pH range to prevent variations in the distribution system. Fluctuations in pH result primarily from low carbonate alkalinity.

Blending Considerations

The process of generating freshwater from brackish or saltwater using a reverse osmosis system yields a (permeate) product water that is low in both pH and alkalinity. If the pH and alkalinity of this water is not adjusted, it will create a corrosion problem in the existing water distribution system. These problems include but are not limited to issues with the taste and odor of the water, discoloration of the water (turbidity), and corrosion of distribution components.

Adding or blending pretreated source water into the (permeate) product water can help stabilize the product water, thereby reducing the impact of the before-mentioned issues, but the pretreated water must be disinfected prior to or after blending. Blending can improve the stability of the product water by increasing the alkalinity and calcium in the permeate and reduce the corrosiveness of the water (Hendricks. 2006), (Binnie, Kimber, & Smethurst. 2002). The water that is to be used for blending may be the source water used for the reverse osmosis process or from another source (Bergman & Elarde 2005).

When integrating into an existing system, control over corrosion inhibitors and pH adjustment should be optimized for maximum efficiency (Duranceau. 2006). It is necessary to model the affects of different blends to prevent the release of red water in the distribution system (Imran, Dietz, Mutoti, Taylor, Randell & Cooper. 2005).

Unfortunately, blending will not stabilize the product water completely. The permeate must still be infused with calcium, which can be accomplished by employing either lime or limestone treatment. If the water to be blended with the product water from the reverse osmosis system is from a ground source from a limestone or chalk geological formation, the amount of lime treatment will be reduced substantially (Withers 2005).

Tampa Bay Water and the American Water Works Association Research Foundation commissioned a study on corrosion problems in water distribution systems that historically have relied on groundwater and are now being required to get water from other sources. A pilot plant was constructed using pipes from the existing distribution system. These pipes consisted of polyvinyl chloride (PVC), unlined iron, lined iron, and galvanized iron pipes.

The pilot plant blended water from three sources: groundwater (GW), surface water (SW), and desalted water (RO). This plant was operated for two years and detailed sampling was taken of the various water blends and piping combinations. That data was then used to create a mathematical model that would be used to calculate the corrosiveness of different water blends.

The input variables for the corrosiveness model are pH Alkalinity, Calcium, Magnesium, Sodium, Chlorides, Sulfates, UV254, Iron, Turbidity, Dissolved Oxygen, Apparent color, Chlorine, and Conductivity. The mathematical formula is $\Delta C = [10^{\beta_0} * (DO)^{\beta_1} *(Cond)^{\beta_2} * (SO_4^{2-})^{\beta_3} * (Cl^-)^{\beta_4} * (Na)^{\beta_5} * (T)^{\beta_6} * (HRT)^{\beta_7}]/[(Alk)^{\beta_8} * (Ca^{2+})^{\beta_9} * (SiO_2)^{\beta_{10}} * (UV)^{\beta_{11}} * (pH)^{\beta_{12}}]$.

Models were created to predict the release of copper, the release of lead, the release of iron, and the dissipation of monochloramine's in the distribution system. The input variables for the copper release model are temperature, alkalinity, pH, SO_4, and SiO_2. The mathematical formula is $Cu = (T)^{0.72} * (Alk)^{0.73} * (pH)^{-2.726} * (SO_4^{2-})^{0.1} * (SiO_2)^{-0..22}$.

The input variables for the lead release model are temperature, alkalinity, pH, SO_4, and Cl. The mathematical formula is $Pb = (1.027)^{(T-25)} * (Alk)^{0.677} * (pH)^{-2.86} * (SO_4^{2-})^{-0.228} * (Cl)^{1.462}$.

The input variables for the iron release model are temperature, alkalinity, Cl, Na, SO_4, DO, and HRT. The mathematical formula is $\Delta C = (Cl)^{0.485} * (Na)^{0.561} * (SO_4^2)^{0.118} * (DO)^{0.967} * (T)^{0.813} * (HRT)^{0.836} / 10^{1.321} * (Alk)^{0.912}$.

The input variables for the Monochloramine dissipation model are NH_2Cl, : Initial

monochloramine concentration, K_B : Bulk Decay Constant, UV, K_W : Wall Decay constant, A: Temperature correction Coeffient, T: Temperature in °C, and t: time. The mathematical formula is $NH_2Cl = NH_2Cl, * exp [-(K_B * UV_{254} + K_W) * A^{(T-20)} * t(5)$.

Blends that contained more than 60 percent groundwater created unacceptably high releases of copper into the distribution system, while blends with less than 20 percent increased corrosion because of the low alkalinity of the water. Blends with desalted water allowed this ratio to increase.

Blends with high ratios of desalted and surface waters should be avoided, as they result in corrosive blends. Limitations on the amount of groundwater available for blending may require the use of inhibitors in the blend. These results were for low-flow conditions. High-flow distribution systems will need to calibrate the models.

Blending will reduce the stress on the membrane system as it reduces the amount of water that needs to be treated and thereby reduce the operating costs of the system (Bergman & Elarde 2005); however, the utility most likely will need to develop a unidirectional flushing program prior to the incorporation of a desalting process into existing infrastructure. The utility also may need to increase storage reservoir size and maintenance. The utility should expect to see an increase in its operational and maintenance expenses (Duranceau. 2006).

Acknowledgements

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