Pretreatment
Carbonate Scale

The following are general recommendations for controlling carbonate scale in systems using reverse osmosis (RO) and nanofiltration (NF) elements. For additional information on pretreatment or cleaning elements, please see MANN+HUMMEL Water & Fluid Solutions' Pretreatment and Cleaning Guides or contact MANN+HUMMEL Water & Fluid Solutions Technical Service.

INTRODUCTION

Due to water's ability to dissolve calcium carbonate ($CaCO_3$) from the ground, most natural surface and ground waters contain, among other ions, calcium and carbonate ions. As these waters are concentrated in an RO/NF system, calcium carbonate becomes one of the first salts to precipitate and scale the membrane surface.

Scaling is when sparingly soluble salts precipitate and deposit on the surface of a membrane element. Scaling typically first affects the elements in the last stage and then gradually affects the stages upstream.

Calcium carbonate scale tends to occur on the membrane surface where the salts are most concentrated. It often results as a loss in normalized permeate flow and a slight decline in salt rejection. The increased salt passage is the result of calcium carbonate's ability to form an equilibrium reaction with the water. Some of the calcium carbonate continuously passes into and out of solution, and because of this, it appears that there is a large concentration of calcium and carbonate ions present at the membrane surface. Due to the higher concentration of ions at the surface, the membrane tends to pass a greater concentration of the ions.

In order to control calcium carbonate scale in RO/NF systems, it is highly recommended to determine the scaling potential for calcium carbonate of the particular feed water and design a pretreatment and cleaning regime.

DETERMINING SCALING POTENTIAL

For brackish waters, the Langelier Saturation Index (LSI) is used to express the scaling potential for calcium carbonate. In most natural waters, the LSI of the concentrate is a positive value without pretreatment. For seawaters, the Stiff & Davis Stability Index (S&DSI) is used to determine calcium carbonate scaling potential. To control calcium carbonate scaling, the LSI and S&DSI values of the concentrate have to be adjusted to a negative value, except if adding a scale inhibitor or antiscalant.

The definitions of LSI and S&DSI are:

$$\text{LSI} = \text{pH} - \text{pH}_s \qquad (\text{TDS} < 10{,}000\ \text{mg/L})$$
$$\text{S\&DSI} = \text{pH} - \text{pH}_s \qquad (\text{TDS} > 10{,}000\ \text{mg/L})$$

Where pH_s is the pH of saturation; when water is in equilibrium with calcium carbonate. The methods for predicting pH_s are different for LSI and S&DSI.

A recommended target LSI in the RO concentrate for brackish waters is -0.2 (which indicates that the concentrate is 0.2 units below the point of calcium carbonate saturation in terms of pH). A -0.2 LSI allows for small fluctuations in pH during plant operation.

When using a scale inhibitor or antiscalant, the LSI is recommended to be around 1.8.

If the scaling potential for calcium carbonate is high, the most common methods to help control scaling potential include:

- The use of a scale inhibitor or antiscalant.
- Decreasing the calcium and alkalinity concentrations in the feed solution by means of lime or lime-soda ash softening to lower pH_s (the pH of saturation).
- Adjusting operational parameters including pH, system recovery, temperature and incorporating a permeate flush.

PRETREATMENT

Scale Inhibitor or Antiscalant

A high quality scale inhibitor or antiscalant for carbonate scale may be helpful to use in the feed stream prior to the membrane system. For extremely high calcium or magnesium carbonate applications, the dosage rate may be predetermined by the chemical manufacturer.

MANN+HUMMEL Water & Fluid Solutions offers several antiscalants that battle carbonate species and helps protect and enhance the operation of RO and NF systems by controlling carbonate scale as well as other mineral scale. These antiscalants may significantly increase the allowable system recovery. For more information, please see product spec sheets at www.microdyn-nadir.com/trisep or contact MANN+HUMMEL Water & Fluid Solutions Technical Service.

Lime Softening

In most raw water sources, hardness is present as calcium and magnesium bicarbonate (sometimes referred to as carbonate hardness or temporary hardness). Lime softening can be used to remove carbonate hardness by adding hydrated lime, $Ca(OH)_2$:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 + 2\ H_2O$$
$$Mg(HCO_3)_2 + 2\ Ca(OH)_2 \rightarrow Mg(OH)_2 + 2\ CaCO_3 + 2\ H_2O$$

Noncarbonate calcium hardness (hardness that is present as a sulfate or chloride salt, referred to as noncarbonated or permanent hardness), on the other hand, may be reduced by a combination of lime and sodium carbonate (soda ash), along with coagulant and flocculent chemicals to promote a precipitation reaction. The lime-soda ash process can also be used to reduce high silica concentrations. When sodium aluminate and ferric chloride are added, the precipitate includes calcium carbonate and a complex with silica acid, aluminum oxide and iron.

Lime softening may be performed at different temperature ranges to increase the solubilities of calcium, magnesium and silica. Cold lime softening is performed at ambient temperatures, warm lime softening is performed in the temperature range of 49 – 60°C (120 – 140°F) and hot process softening is performed at temperatures of 108 – 116°C (227 – 240°F).

OPERATIONAL CONSIDERATIONS

pH

The solubility of calcium carbonate depends on the pH:

$$Ca^{2+} + HCO_3^- \leftrightarrow H^+ + CaCO_3$$

By adding H^+ as acid, the equilibrium can be shifted to the left side to keep calcium carbonate dissolved. Adding acid (H_2SO_4 or HCl) to the feed stream will decrease the pH as well as the LSI (as explained in *Determining Scaling Potential* above). Acid may be added either with or without lime or lime-soda ash softening.

Sulfuric acid (H_2SO_4) is easier to handle and in many countries more readily available than hydrochloric acid (HCl). However, when using sulfuric acid, additional sulfate is added to the feed stream and may potentially cause sulfate scaling. It is recommended to use food-grade quality acid.

Recovery

The system's recovery may be lowered. At a lower operating recovery, the concentration of calcium carbonate in the concentrate decreases and lowers scaling potential.

Temperature

Calcium carbonate solubility decreases as temperature increases. Typically, when water is saturated with carbon dioxide, calcium carbonate solubility increases due to the formation of more soluble calcium bicarbonate. However, due to the fact that the solubility of carbon dioxide decreases with increasing temperature, the solubility of calcium carbonate also decreases.

Permeate Flush

The membrane elements should be flushed for a minimum of 3 minutes with permeate water each time that the membrane system shuts down. This will flush out the highly concentrated water in the tail-end of the system which will prohibit precipitation during this stagnant flow period.

CLEANING PROCEDURE

A customized cleaning procedure may be implemented on a scheduled maintenance basis. This will ensure complete removal of any precipitated carbonate.

If calcium carbonate is present in a cellulose acetate (CA) system, it is recommended to clean the system as soon as possible as calcium carbonate scale may hydrolyze the membrane. An acidic cleaning solution (and the presence of a surfactant in the cleaning solution) should be able to remove the scale from both a thin-film composite as well as a CA membrane surface.

Please refer to MANN+HUMMEL Water & Fluid Solutions' **Membrane Cleaning Guide – Water Application Elements** (TSG-C-001) for cleaning recommendations using low pH cleaners TriClean™ 210 or TriClean™ 310 to battle carbonate.

Contact

Europe
Germany: +49 611 962 6001
Italy: +39 0721 1796201
info@microdyn-nadir.com

Americas
USA: +1 805 964 8003
sales.mnus@microdyn-nadir.com

Asia
Singapore: +65 6457 7533
China: +86 10 8413 9860
waterchina@mann-hummel.com

MANN+
HUMMEL