3-3. Prevention of Scale Formation

Scaling of an RO membrane may occur when sparingly soluble salts are concentrated in the RO element beyond their solubility limit. Sparingly soluble salts are listed below in the order of decreasing scaling problem:

$$CaCO_3 > CaSO_4 > Silica > SrCO_3 > BaSO_4 > SrSO_4 > CaF_2 > CaSiO_3 > MgSiO_3 > MgSiO_3 > Ca_3(PO_4)_2 > Fe(OH)_2$$

Calcium sulfate ($CaSO_4$) is more soluble than $BaSO_4$ and $SrSO_4$. However, calcium ion (Ca^{2+}) is present in natural water sources more abundantly than Ba^{2+} and Sr^{2+} and thus $CaSO_4$ will cause more scaling problem than $BaSO_4$ and $SrSO_4$. On the other hand, $BaSO_4$ and $SrSO_4$ are difficult to redissolve once precipitated. Hence, scaling of the two salts should be avoided.

The most frequent scaling problems come from calcium carbonate ($CaCO_3$) because it precipitates fast, once concentrated beyond its solubility limit and also most natural waters are almost saturated with respect to $CaCO_3$. $CaCO_3$ scaling including $SrCO_3$ and $BaCO_3$ can be prevented by acid addition, a scale inhibitor, softening of the feed water, preventive cleaning and low system recovery.

$CaSO_4$ scaling including $BaSO_4$, $SrSO_4$ and CaF_2 is preventable by the same methods as $CaCO_3$ scaling except the acid addition. In fact, using sulfuric acid to lower pH for the prevention of $CaCO_3$ scaling would increase the probability of the sulfate scaling.

3-3-1. Acid Addition

The solubility of CaCO3 depends on the pH as shown in the following equation.

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

The equilibrium can be shifted to the right side to convert $CaCO_3$ to soluble $Ca(HCO_3)_2$ by adding an acid (lowering pH). The acid used should be of food grade quality. Sulfuric acid is commonly employed, but hydrochloric acid is preferred in the case of high scaling potential due to $CaSO_4$, $SrSO_4$ and $BaSO_4$.

In order to avoid calcium carbonate scaling, the pH of the concentrate stream in an RO system should be lower than the pH of saturation (pH_s) where the water of the concentrate stream is in equilibrium with $CaCO_3$. This relationship is expressed by the Langelier Saturation Index (LSI) for brackish waters and Stiff & Davis Saturation Index(S&DSI) for sea waters.

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_S}\ \text{(where TDS} < 10.000\ \text{mg/l)}$$

$$\mathrm{pH_S} = (9.3 + A + B)-(C + D)$$

$$\text{where ; } A = \frac{\log_{10}[\mathrm{TDS}]-1}{10}$$

$$B = -13.12 \times \log_{10}(^{\circ}\mathrm{C} + 273) + 34.55$$

$$C = \log_{10}[\mathrm{Ca^{2+}}\ \text{as}\ \mathrm{CaCO_3}] - 0.4$$

$$D = \log_{10}[\text{Alkalinity as}\ \mathrm{CaCO_3}]$$

Values in brackets are moles/L except TDS which is in mg/L.

Reference ASTM D3739-88 Calculation and Adjustment of the Langelier Saturation Index for Reverse Osmosis

$$\mathrm{S\&DSI} = \mathrm{pH} - \mathrm{pCa} - \mathrm{pAlk} - K$$

Where: pCa is the negative log of the calcium concentration in moles/L.
pAlk is the negative log of the total alkalinity concentration in moles/L.
K is a constant which is a function of water temperature and ionic strength.

Reference ASTM D4582-86 Calculation and Adjustment of the Stiff and Davis Saturation Index for Reverse Osmosis

Concentration factor is used as shown below to calculate the concentration of the constituents in the concentrate stream from that in the feed water.

$$\text{Concentration Factor} = \frac{1}{1-Y}$$

$$\text{where } Y\text{ , recovery} = \frac{\text{Permeate flow}}{\text{Feed flow}}$$

In reality, concentration polarization should be taken into account to get more accurate scaling potential as shown below.

$$\text{Concentration Factor} = \frac{\text{Concentration polarization}}{1 - Y}$$

The concentration polarization depends on the turbulence of the bulk stream in the RO element and varies from 1.13 to 1.2, meaning that the concentration of salts at the membrane surface is 13% to 20% greater than in the bulk stream.

To control calcium carbonate scaling by acid addition alone, the LSI or S&DSI in the concentrate stream must be negative. A rule of thumb is to lower the feed water pH to 6.0. If a high quality scale inhibitor is used, the LSI in the concentrate stream can be as high as 1.8(refer to the inhibitor manufacturer's literature for reference points). This will reduce or eliminate the acid consumption, and also could decrease the potential for corrosion due to the acid.

3-3-2. Scale Inhibitor Addition

Scale inhibitors (anti-scalants) slow the precipitation process of sparingly soluble salts by being absorbed on the forming salt crystals to prevent the attraction of the supersaturated salt to the crystal surfaces. In this situation the crystals never grow to a size or concentration sufficient to fall out of suspension. Furthermore, many scale inhibitors have some dispersive qualities which involve surrounding particles of suspended salt or organic solids with the anionically charged scale inhibitor. Now the anionically charged particles will repel each other to prevent the agglomeration of the particles to larger particles that may precipitate.

Scale inhibitors effective in controlling carbonate scaling, sulfate scaling and calcium fluoride scaling are listed below.

Sodiumhexametaphostphate(SHMP) is most widely used because it offered good inhibition at a low cost. However, care must be taken in order to avoid hydrolysis of SHMP in the dosing feed tank (a fresh solution should be made every 3 days). Hydrolysis would not only decrease the scale inhibition efficiency, but also create a calcium phosphate scaling risk.

SHMP should be dosed to give a concentration in the concentrate stream of 20 mg/L. The dosage into the feed stream can be calculated by the equation:

$$\text{SHMP dosing rate} = 20\text{mg} \times (1 - Y)$$
$$\text{where } Y = \text{a fraction of recovery}$$

Organophosphonates are an improvement over SHMP in that they are more resistant to hydrolysis though more expensive. They offer scale inhibition and dispersion ability similar to SHMP.

Polyacrylic acids (PAA) are good at both scale inhibition and dispersion. The usual molecular weight of PAA is 2000 to 5000. PAA with higher molecular weight distribution in the range of 6000 to 25000 showed the best dispersion ability at the sacrifice of scale inhibition ability. In general, PAA are more effective than SHMP. However, precipitation reactions may occur with cationic polyelectrolytes or *multivalent cations such as aluminum or iron to foul the membrane.*

Blend Inhibitors are a combination of low and high molecular weight of PAA or a blend of low molecular weight PAA and organophosphonates for excellent dispersive and inhibitor performance.

There are many manufacturers of scale inhibitors such as BF Goodrich, Arrowhead, Betz, Grace Dearborn, Calgon, FMC, Degremont, Nalco, King-Lee and Maxwell Chemicals, etc. Please, consult with them for the chemical identity of the scale inhibitor brands and their compatibility with RO membranes. They can usually be considered compatible with PA membranes up to 50 mg/L concentration in the concentrate.

RO permeate should be used when diluting the scale inhibitors, since calcium present in the feed water may form a precipitate with the scale inhibitors at high concentrations. Precautions must also be taken so that there is no microbial growth in the inhibitor dilution tank. Make certain that no significant amounts of cationic polymers are present when adding an anionic scale inhibitor.

3-3-3. Softening with a Strong Acid Cation Exchange Resin

The scale forming cations such as Ca^{2+}, Ba^{2+}, Sr^2+, Mg^{2+}, and Fe^{2+} can be removed by a cation exchange resin which could be a good alternative way to prevent scale formation for small or medium size brackish water RO systems. The resin has to be regenerated with NaCl at the saturation point. A drawback of this process is its relatively high sodium chloride consumption, which might cause an environmental (disposing the brine) or an economic problem. Alternatively, a recent counter current regeneration technique using Dowex Monosphere resins can minimize the NaCl consumption to 110% of the stoichiometrical value.

3-3-4. Softening with a Weak Acid Cation Exchange Resin

The weak acid cation exchange resin can remove only Ca^{2+}, Ba^{2+} and Sr^{2+} linked to bicarbonate and release H^+, thus lowering the pH to a minimum value of 4.2 where the carboxylic acid groups of the resin are no longer dissociated. Therefore, it is only a partial softening and ideal for waters with high bicarbonate content.

The advantages of softening with a weak acid cation exchange resin are :

- Almost stoichiometrical consumption (105%) of acid for regeneration to minimize the operating costs and the environmental impact
- Reduction of the TDS value of the water by the removal of bicarbonate salts to result in the lower permeate TDS.

The disadvantages are :

- Residual hardness due to incomplete softening
- Variable pH of the treated water from 3.5 to 6.5 depending on the degree of exaustion of the resin

At pH < 4.2, the passage of mineral acid may increase the permeate TDS. It is therefore recommended to use more than one resin column in parallel and to regenerate them at different times in order to level out the pH. Other possibilities to avoid extremely low pH values are CO_2 removal or pH adjustment by NaOH.

3-3-5. Lime Softening

Lime [$Ca(OH)_2$] reacts with soluble calcium or magnesium bicarbonate to remove carbonate hardness as shown in the following equations ;

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

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

The non-carbonate calcium hardness can be further reduced by adding sodium carbonate (soda ash) :

$$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3$$

The lime-soda ash process can also reduce the silica concentration. When sodium aluminate and ferric chloride are added as coagulants, the lime-soda ash will precipitate calcium carbonate and a complex consisted of calcium, aluminum and iron silicate. Silica can be reduced to 1mg/L by adding a mixture of lime and porous magnesium oxide. The lime softening can also reduce barium, strontium and organic substances such as humic acid significantly. The effluent from this process needs media filtration and pH adjustment prior to the RO elements. Lime softening should be considered for brackish water plants larger than 200 m^3/h (1.2 million GPD).

3-3-6. Preventive Cleaning

In some applications such as small systems, preventive membrane cleaning allows the system to run without dosage of acids or scale inhibitors or softening. Typically, those systems operate at low recovery in the range of 25% and the membrane elements are replaced after 1-2 years. The simplest way of cleaning is a forward flush at low pressure by opening the concentrate valve. Short cleaning intervals are more effective than long cleaning times, e.g. 30 seconds every 30 minutes. Cleaning can also be performed with cleaning chemicals, which may be done occasionally between the short cleaning intervals.

3-3-7. Adjustment of System Recovery, pH and Temperature

The precipitation of dissolved salts can be avoided by keeping their concentration in the concentrate stream below the solubility limit, which can be achieved by reducing the system recovery, raising temperature, and increasing or decreasing pH.

To be more quantitative for the above operation, solubility product (limit) for each sparingly soluble solute should be calculated under conditions in the concentrate stream as discussed in the following sections. Silica is usually the only reason for adjusting the above three operating variables as a scale control method, since these adjustments have high energy consumption due to low system recovery or other scaling risks such as $CaCO_3$ scaling at high pH. For small systems, a low recovery combined with a preventive cleaning program might be a convenient way to control scaling.