



## Precipitation Prevention by SCALE INHIBITORS

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### INTRODUCTION

Without some means of scale inhibition, reverse osmosis (RO) membranes and flow passages within membrane elements will scale due to the precipitation of sparingly soluble salts. Some common examples of scale are calcium carbonate, calcium sulphate, barium sulphate, and strontium sulphate. Less commonly seen are silica and calcium fluoride scales.

The effect of scale on the permeation rate of RO systems is illustrated in Figure 1. Following an induction period, plant flow decreases rapidly. The length of the induction period varies with the type of scale and the degree of supersaturation of the sparingly soluble salt.

The induction period for calcium carbonate is much shorter than that for sulphate scales such as calcium sulphate. While there are effective cleaners for scale, economics strongly favour preventing scale formation. Scale often plugs RO element feed passages, making cleaning difficult and very time consuming. There is also the risk that scaling will damage membrane surfaces.

### SCALE CONTROL METHODS

There are three methods of scale control commonly employed:

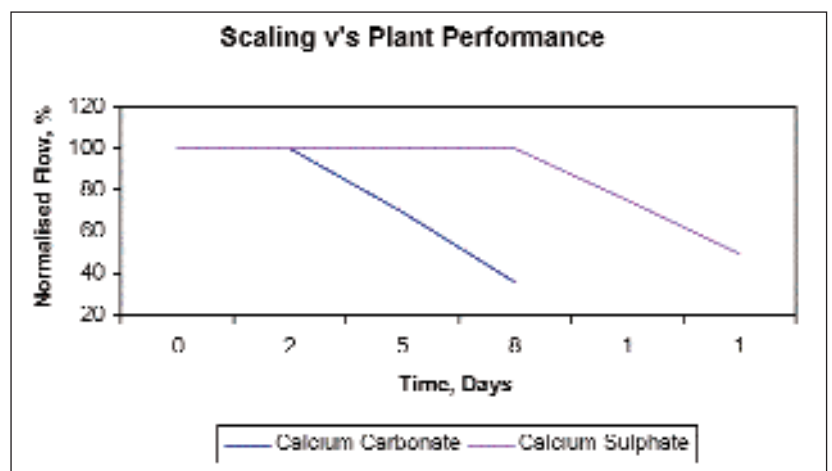
- Acidification
- Ion Exchange softening, and
- Antiscalant addition.

#### Acid Addition:

Acid addition destroys carbonate ions. This removes one of the reactants necessary for calcium carbonate precipitation. While extremely effective in preventing the precipitation of calcium carbonate, acid addition is ineffective in preventing other types of scale such as calcium sulphate. The use of sulphuric acid may even make sulphate scale occurrence more likely since sulphuric acid contributes sulphate ion. The use of hydrochloric acid avoids this problem but is more costly.

Additional disadvantages include the corrosivity of the acid, the cost of tanks and monitoring equipment, and the fact that acid lowers the pH of the RO permeate. Unless removed by degasification, excess carbon dioxide contained in the permeate of acid-fed systems increases the cost of ion exchange regeneration.

Figure 1 Effect of Scale on Permeation



*Ion Exchange Softening:*

Ion Exchange softening utilizes the sodium form of strong acid cation exchange resin. Sodium contained in the resin is exchanged for magnesium and calcium ions that are contained in the RO feedwater. These reactions are demonstrated by the following chemical equations. NaZ represents the sodium exchange resin. Ca and Mg are calcium and magnesium, respectively.



When all of the sodium ions have been replaced by calcium and magnesium, the resin must be regenerated with a brine (sodium chloride) solution. Ion exchange softening eliminates the need for a continuous feed of either acid or antiscalant. Some advocate softening as a means of removing trace organics from RO feedstreams as well as making colloidal contaminants less likely to foul membrane surfaces.

It is true that softening resin adsorbs many different organic molecules, and softening increases the negative electrostatic charge of colloidal solids. However, there is no persuasive evidence that either of these functions significantly improves the performance of RO systems.

When compared to either acid or antiscalant addition, the main disadvantage to softening is cost. Table 1 gives a cost comparison between softening and antiscalant treatment options for different levels of hardness. The basis for this example is an RO system designed to produce 75 gpm (17 m3/hr) of permeate at 75 % recovery.

This comparison does not include disposal costs for the spent softener regenerate, which are significant in some areas. Factoring in equipment costs through a present worth analysis, there is no level of hardness in which softening competes economically with antiscalant addition.

*Antiscalants:*

Antiscalants are surface-active materials that interfere with precipitation reactions in three primary ways:

- Threshold inhibition
- Crystal modification
- Dispersion

Threshold inhibition is the ability of an antiscalant to keep supersaturated solutions of sparingly soluble salts in solution.

As crystals begin to form at the

submicroscopic level, negative groups located on the antiscalant molecule attack the positive charges on scale nuclei interrupting the electronic balance that is necessary to propagate growth of the crystal.

Figure 2 illustrates the threshold mechanism for calcium carbonate. In the figure, antiscalant (R) terminates crystal growth by attaching to the positively charged calcium ions located at the corners of the crystal.

Crystal modification is the property of an antiscalant to distort crystal shapes, resulting in soft, non-

*... when compared to either acid or antiscalant addition, the main disadvantage to softening is cost.*

SOFTENING			
Hardness, ppm	Equipment Cost	Salt , Costs per year	Present Worth
10	\$20,000	\$1,906	\$27,566
20	\$20,000	\$3,812	\$35,133
50	\$40,000	\$9,530	\$77,834
100	\$40,000	\$23,825	\$134,585
250	\$40,000	\$47,600	\$198,972
ANTISCALANT ADDITION			
Hardness, ppm	Equipment Cost	Antiscalant, Cost per year	Present Worth
10	\$2,000	\$1,300	\$7,161
20	\$2,000	\$1,300	\$7,161
50	\$2,000	\$1,300	\$7,161
100	\$2,000	\$1,300	\$7,161
250	\$2,000	\$1,600	\$8,352

Footnote:

- Skid mounted softeners, containing 40 ft3 (1.2 m3) of resin each. 50 ppm of hardness and above employ two softeners with one as standby.
- Kiln-dried rock salt for softener regeneration costs \$0.17 per pound.
- Antiscalant equipment consists of feed tank and pump.
- Antiscalant dosages range from 2 to 5 ppm
- Amortization period for the present worth calculations is 5 years at 8% interest.

Table 1 Cost Analysis of Softening vs. Antiscalant Addition

adherent scale. When treated with crystal modifiers, scale crystals appear distorted, generally more oval in shape, and less compact.

Dispersancy is the ability of some antiscalants to adsorb on crystals or colloidal particles and impart a high anionic charge. The high charge tends to keep crystals separated. In addition, adsorption of dispersants occurs in loops, thus adding a steric barrier to crystal growth. Figure 3 illustrates these mechanisms. The high anionic charge also separates particles from fixed anionic charges present on the membrane surface. (In Figure 3, membrane is denoted by a line from which fixed anionic charges originate.)

The modern formulator combines different antiscalant components to accentuate one or more of these mechanisms in order to meet the demands of specific water treatment processes. Avista tailors its antiscalant products to meet the multiple needs of membrane separation systems. In this process, concerns regarding membrane compatibility with the antiscalant, antiscalant interactions with other treatment chemicals, and the antiscalant efficacy itself must all be addressed.

### PREDICTING SCALE FORMATION

Precipitation of sparingly soluble salts leads to scale formation. As scale-forming ions concentrate within the flow passages of RO systems, a point may be reached in which the solubility of one or more of these salts is exceeded.

Fortunately for designers and operators of RO systems, calculation procedures exist for predicting the likelihood of scale formation.

Use of these predictors depends upon an up-to-date water analysis and a knowledge of system design parameters. At a minimum, the water analysis must include the following parameters:

Aluminum	Barium
Calcium	Chloride
Fluoride	Iron
Magnesium	Manganese
Phosphate	Potassium
pH	P and Mo alkalinity
Silica	Sodium
Strontium	Sulphate
Temperature	Nitrate

While the monovalent ions listed do not enter directly into precipitation reactions, they do contribute to the total ionic strength of the feedwater, and the solubility of virtually all of

the scale formers is a function of ionic strength.

Since the ions contained in the feedwater concentrate through the RO system, the point of maximum scale potential is the concentrate stream. Antiscalant dosage is therefore based upon the mineral analysis at this point, which is calculated from the feedwater analysis and the system recovery factor.

In general, the concentrate value for any individual ion is calculated by the following equation:

$$C_{bi} = \frac{(C_{fi} - SP * C_{fi})}{(1 - R)}$$

Where,  
 $C_{fi}$  = Concentration of ion in the

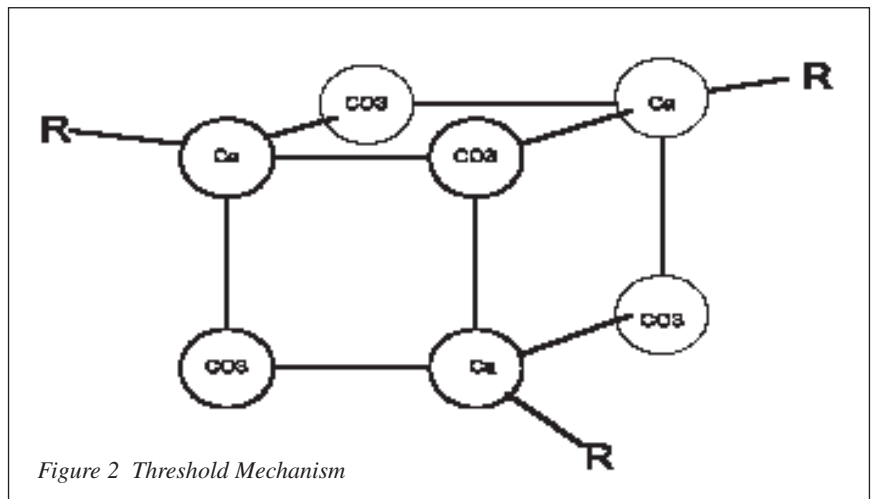


Figure 2 Threshold Mechanism

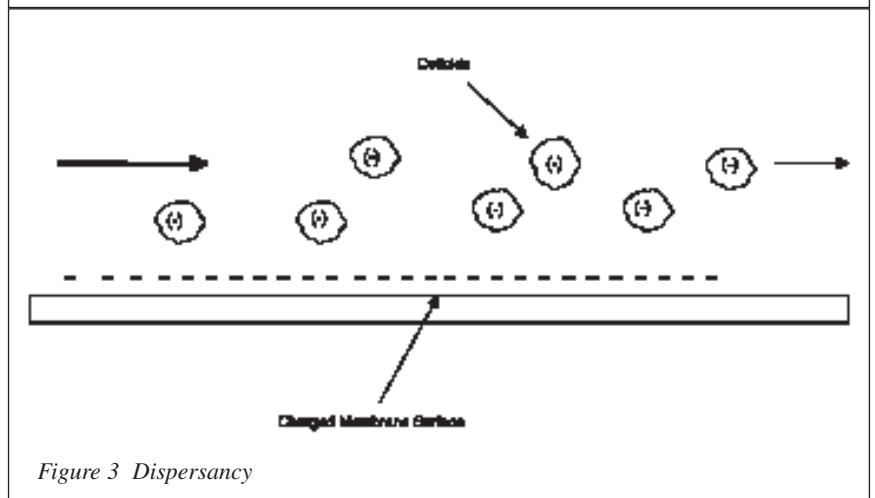


Figure 3 Dispersancy

feedstream.

*Cbi* = Concentration of ion in the concentrate stream.

*SP* = Salt passage through the membrane of ion as a decimal.

*R* = System recovery as a decimal.

*Calcium carbonate scale potential:*

Calcium carbonate scale potential is generally based upon the Langelier Saturation Index (LSI) when the TDS of the concentrate stream is below about 6000 ppm. Above 6000 ppm an extension of the LSI known as the Stiff Davis Index is generally applied.

It is beyond the scope of this technical bulletin to give details on how these indices are calculated, but both depend upon the calculation of a saturation pH (pH<sub>s</sub>). For given values of temperature, TDS, calcium, and alkalinity, saturation pH is defined as that pH in which calcium carbonate just becomes saturated. LSI or Stiff Davis index is LSI or Stiff Davis Index = Actual pH - pH<sub>s</sub>.

When the LSI or Stiff Davis Index is positive, it indicates a tendency for calcium carbonate to precipitate. A negative value indicates a scale dissolving tendency. A zero value indicates that calcium carbonate will neither precipitate nor dissolve. When concentrate LSI or Stiff Davis indices are positive, some form of scale control must be applied.

These indices are used to calculate if calcium carbonate will form in your system.

To calculate how much antiscalant you require to prevent this scaling a separate index called the CCPP (Calcium Carbonate Precipitation Potential) is used. This measure uses an iterative procedure to calculate the actual quantity of scale which would precipitate up to the saturation level of the water (pH<sub>s</sub>).

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The Avista Advisor software calculations are based on this index to give an accurate antiscalant dose rate.

*Sulphate scales:*

For specific conditions of temperature and ionic strength, there is a specific solubility value for each of the sulphate scales. This value is the solubility product, abbreviated K<sub>sp</sub>.

The degree of saturation is expressed as the mole product of sulphate times the balancing cation (calcium, barium, or strontium) divided by the K<sub>sp</sub>. Multiplying by 100 converts this expression to percent saturation.

$$\frac{(\text{Cation}) (\text{Sulphate}) * 100}{K'_{sp}}$$

Values greater than 100 percent indicate a tendency for precipitation. Values less than 100 percent indicate that the solution is undersaturated with the sulphate salt.

*Silica:*

Silica forms an amorphous precipitate unlike that of calcium carbonate or the sulphate scales. Silica solubility is a function of both temperature and pH (See figure 4).

At pH of 7 and 25 degrees Centigrade, silica solubility is 125 ppm. At pH 5 and 9, solubility increases to 150 and 238 ppm, respectively.

With an increase in temperature from 25 to 35 degrees Centigrade, silica solubility increases from 125 to 145 ppm. Silica saturation is generally expressed as the ratio of silica actually present in the concentrate stream to the theoretical solubility at the actual concentrate pH and temperature.

**ANTISCALANT SELECTION**

Avista offers a choice of antiscalant formulations which are detailed on the anti-scalant selection bulletin.

The selection of the best antiscalant for your particular application can be made by Avista. Alternatively our, easy to use, projection software 'Avista Advisor' is available to guide you to the best anti-scalant and optimum dose rate.

*The picture on page 1 shows two thin film membranes, one irreversibly fouled with calcium carbonate scale and the second permanently damaged by silica scale.*

