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**INTRODUCTION**

As water concentrates within a reverse osmosis (RO) system salt concentration increases in the feed direction. In most systems that operate at 50 percent recovery and above, sparingly soluble salts will precipitate, starting at the concentrate end of the systems and working forward. Over time, hard scale deposits will form on membrane surfaces and within the feed channel spacers. Scaling within RO systems is a serious matter. Not only does scaling drastically reduce system performance, but the abrasive scale deposits may also cause irreversible damage to the rejecting membrane surfaces. Examples of some common sparingly soluble salts are calcium carbonate and the sulfates of calcium, barium, and strontium. Less common salts include calcium phosphate and calcium fluoride.

**SCALE CONTROL METHODS**

Over the years, the RO industry has developed methods of scale prevention which fall into three categories:

- **Acidification**
- **Ion exchange softening**
- **Scale inhibitor addition**

*Acidification.* Acidification destroys bicarbonate and carbonate alkalinity needed to produce calcium carbonate scale as illustrated by the following equations:



While acidification prevents calcium carbonate scaling from occurring, it is not effective against the sulfate scales of calcium, barium, and strontium. Additional disadvantages of acidification include corrosivity of the acid, the cost of storage tanks, and the monitoring equipment required to properly dose the acid. Acidification also lowers permeate pH, requiring the use of degasifiers to remove excess carbon dioxide that would increase ion exchange regeneration costs.

For waters with high barium and sulfate concentrations, sulfuric acid, the least costly acid, will increase barium sulfate

saturation. For this reason, in lieu of sulfuric acid, plant operators sometimes use hydrochloric acid, but its more costly and difficult to handle.

**ION EXCHANGE SOFTENING**

Ion exchange softening utilizes the sodium form of strong acid cation resin. In this process, hardness ions in the water are exchanged for sodium contained in the resin. The following equations illustrate these softening reactions. NaZ represents the sodium resin.



Regeneration of the resin is required following the replacement of all the sodium ions by calcium and magnesium.

There are anecdotal accounts of ion exchange softening reducing colloidal and particulate fouling of RO systems by increasing the electrostatic charge on the colloidal and particulate solids. However, to date there is no convincing evidence to support this claim. When compared to either acid or scale inhibitor addition, the main disadvantage of ion exchange softening is cost.

**CORPORATE OFFICES**
**Avista Technologies, Inc.**
**Global Headquarters**

140 Bosstick Boulevard  
 San Marcos, California 92069  
 United States

Tel. | +1.760.744.0536

**Avista Technologies (UK) Ltd**

13 Nasmyth Square, Houstoun Industrial Estate  
 Livingston, EH54 5GG  
 United Kingdom

Tel. | +44 (0) 131 449 6677

Table 1 gives a cost comparison between softening and scale inhibitor treatment for different levels of hardness. The basis for this example is an RO system designed to produce 75 gpm of permeate at 75 percent recovery. Using a present worth analysis, there is no level of hardness in which ion exchange softening competes economically with scale inhibitor addition.

The comparison does not include disposal costs for spent softener regenerate, which is significant in some areas.

### SCALE INHIBITOR ADDITION

Scale inhibitors are surface-active substances that prevent precipitation of sparingly soluble salts by three different mechanisms.

- **Threshold inhibition**
- **Crystal modification**
- **Dispersion**

*Threshold Inhibition.* Threshold inhibition is the delaying of crystal formation by scale inhibitors at very low concentrations. Physical chemists call this delay an induction period. Prior to crystallization, crystal nuclei begin to assemble on a sub-microscopic scale. Scale inhibitors act as structure breakers, associating with cations present in the assembling nuclei. Eventually crystal nuclei greatly outnumber inhibitor molecules and crystallization of the sparingly soluble salt begins.

**TABLE 1. Cost Analysis of Softening vs. Antiscalant Addition**

#### SOFTENING

HARDNESS, ppm	EQUIPMENT COST	SALT, cost 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

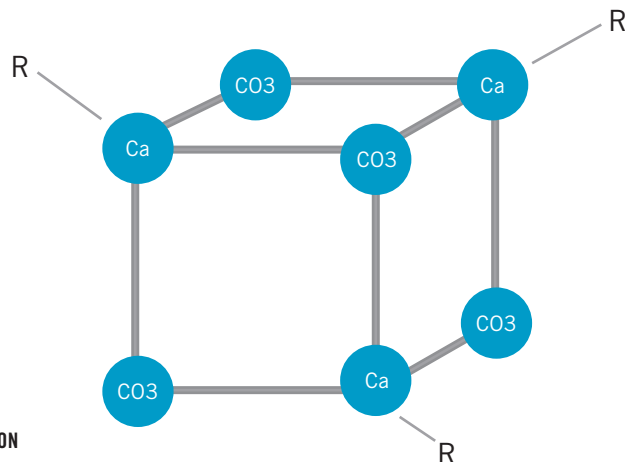
#### ANTISCALANT ADDITION

HARDNESS, ppm	EQUIPMENT COST	ANTISCALANT, cost per year	PRESENT WORTH
10	\$2,000	\$1,300	\$1,300
20	\$2,000	\$1,300	\$1,300
50	\$2,000	\$1,300	\$1,300
100	\$2,000	\$1,300	\$1,300
250	\$2,000	\$1,600	\$1,600

**NOTES:**

- Assumes skid-mounted softeners containing 40 ft<sup>3</sup> of resin each. For 50 ppm of hardness and above, two softeners are employed, with one as a standby.
- Kiln-dried rock salt for softener regeneration costs \$0.17 per pound.
- Antiscalant equipment consists of feed and pump.
- Antiscalant dosages range from 2 to 5 ppm.
- Amortization period for present worth calculations is 5 years at 8% interest.

*Crystal Modification.* Scale inhibitors incorporate into growing crystal structures and distort their shape. Thus modified, crystals are slower to grow on membrane surfaces. Figure 1 illustrates the incorporation of inhibitor molecules into the crystal structure by association of the crystal cations with negative functional groups present on the inhibitor. R represents the inhibitor molecule.



**FIG. 1**  
**CRYSTAL MODIFICATION**

**Dispersion.** Due to negative functional groups present on scale inhibitor molecules, they are able to increase the negative electrostatic charge already present on colloids and particulates. The greater negative electrostatic charge coupled with steric hindrance created by the adsorbed inhibitor increases the repulsion between the colloids and particulates, again delaying crystal growth on membrane surfaces.

Figure 2 illustrates the delay in crystallization caused by the addition of 2.4 mg/l of a neat scale inhibitor to supersaturated solutions of calcium carbonate. Sudden increases in turbidity signal the onset of crystallization. Arrows show the times at which incrustations first appeared on the flask walls. The delay in time between the onset of crystallization and the occurrence of incrustations is due to the combined effects of dispersion and crystal modification.

## SCALE INHIBITOR TYPES

Phosphonates and polymers are the two types of organic scale inhibitors in use today.

**Phosphonates.** Phosphonates contain phosphorous and have the following general structure:



*R represents an organic group or groups.*

Compared to polymeric scale inhibitors, phosphonates are relatively small molecules having molecular weights ranging from about 200 to 600. Examples are 1-hydroxyethane 1, 1-diphosphonic acid (HEDP) and nitrilotris (methylene phosphonic acid) (ATMP). Phosphonates are most effective against crystalline sparingly soluble salts such as calcium carbonate and the sulfate salts of barium, calcium, and strontium. A significant advantage of phosphonates is that at normal use levels, they are compatible with quaternary amine coagulants used in upstream filters.

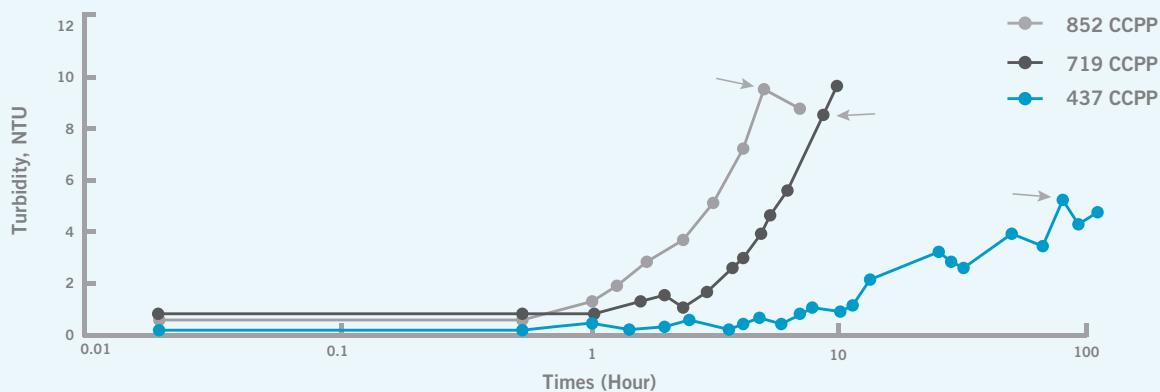
**Polymers.** Polymeric scale inhibitors include polyacrylic acid, polymaleic acid, and numerous copolymers and terpolymers constructed from acrylic acid, maleic acid, AMPS and other monomer types. All scale inhibitors contained in this category contain carboxylate (-COOH) functional groups. Polymeric scale inhibitors have molecular weights ranging from about 1000 to 4500. A disadvantage of these inhibitors is that they are not compatible with quaternary amine coagulants. Polymeric inhibitors are most effective against the following sparingly soluble substances:

- Silica
- Calcium phosphate
- In-vitro synthesized clays
- Minerals such as magnesium silicate

In-vitro synthesized clays form within RO systems from their constituent elements (silica, aluminum, and various metals).

Combining phosphonates and polymers results in formulations that are effective against most types of scale formers, and the combinations often produce unexpected synergies.

**FIG. 2** Time-Turbidity Plots for Saturated Calcium Carbonate Solutions with 2.4 ppm Added Scale Inhibitor



Note: CCPP is calcium precipitation potential, mg/l CaCO<sub>3</sub>

## PROJECTION SOFTWARE

Avista® Advisor is a projection software program that selects the most appropriate inhibitor and calculates its dosage based upon specific feed water mineral analysis and system design and operating parameters for RO membranes. Advisor bases its calculations on both laboratory and field data and requires the following information as input:

### Feed Water Analysis

#### Cations

Sodium (Na)  
Potassium (K)  
Calcium (Ca)  
Magnesium (Mg)  
Iron (Fe)  
Manganese (Mn)  
Barium (Ba)  
Strontium (Sr)  
Aluminum (Al)

#### Anions

Chloride (Cl)  
Sulfate (SO4)  
Dissolved CO2 (CO2)  
Bicarbonate (HCO3)  
Carbonate (CO3)  
Boron (B)  
Nitrate (NO3)  
Fluoride (F)  
Silica (SiO2)  
Phosphate (PO4)

\*Laboratories often express alkalinity as P and Mo alkalinity, where P and Mo refer to the titrimetric endpoints (ref.). With this information, one can calculate bicarbonate and carbonate concentrations. Other laboratories may do the calculations internally, simply reporting alkalinity as bicarbonate and carbonate, either as the ions or as calcium carbonate.

It is very important to analyze for all of the elements listed above. Especially important are barium and aluminum, for even at very low concentrations, these metals form very insoluble precipitates.

#### NOTES:

Concentrate (brine) analysis are required for Advisor to allow calculation of antiscalant for a nanofiltration membrane system.

*System parameters.* Required system and operating parameters are:

- **Element manufacturer and model**
- **System recovery**
- **Feed water temperature**
- **Use of a quaternary amine coagulant upstream**
- **For well waters, does the water contain air**

## REFERENCE

Permutit water and waste treatment book