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Complete elimination of acid injection in reverse osmosis plants

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Abstract

Antiscalants with broad activity spectra are available today. When properly chosen, a single antiscalant can efficiently and simultaneously control calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate and calcium fluoride scales as well as inorganic foulants resulting from iron, aluminum and reactive silica present in any given water or wastewater. The effectiveness of many antiscalants towards controlling calcium carbonate scaling in reverse osmosis (RO) plants has allowed us, in the past five years, to successfully help eliminate the continuous injection of acid in all RO systems operating with polyamide membranes. A minority of systems with cellulose acetate membranes however still require acidification due to hydrolytic sensitivity of cellulose acetate towards feedwater pH higher than 6. The chemistry behind the main reason for acidification — the prevention of scaling by calcium carbonate — is reviewed. The mechanisms of calcium carbonate scaling and its avoidance by acidification or with antiscalants are discussed. Major seawater and brackish water RO plants around the world are designed and operated with the continuous injection of concentrated sulfuric or hydrochloric acid for scale control, sometimes simultaneously with an antiscalant. We present a case study in southeastern USA of a 5 million gallons permeate per day plant as a typical example among many for the conversion of major municipal RO plants. By suitable selection of an antiscalant, acid elimination was successfully attained with a simultaneous reduction in the antiscalant dosage, in this case to 2–3 mg/l in the feedwater. While process optimization continues in the plant, current chemical cost savings due to the deletion of 93% sulfuric acid and the associated caustic soda neutralizer alone amounts to 67% of the annual cost of all chemicals used. This does not include savings through benefits accrued in equipment, operation, maintenance and safety in the plant.

Keywords: Reverse osmosis (RO); Antiscalant; Calcium carbonate scaling; Scale control; Acidification; Acid injection; Seawater; Brackish water; Plant safety; Cost reduction; Sulfuric acid; Hydrochloric acid

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1. Introduction

Major seawater [1–3] and brackish water [3–7] RO plants around the world are designed and operated with the continuous injection of concentrated sulfuric or hydrochloric acid for scale control, sometimes simultaneously with an antiscalant. Demand for RO plants for municipal and industrial water supplies is rapidly increasing. The associated consumption of acid, typically 93% sulfuric acid or concentrated hydrochloric acid, and worker and equipment exposure to this corrosive and potentially hazardous chemical, have become very significant economic, safety and environmental issues.

Antiscalants with broad activity spectra are available today. When properly chosen, a single antiscalant can efficiently and simultaneously control calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate and calcium fluoride scales as well as inorganic foulants resulting from iron, aluminum and reactive silica present in any given water or wastewater. The effectiveness of many antiscalants towards controlling calcium carbonate scaling in RO plants has allowed us in the past five years to successfully help eliminate the continuous injection of acid in all RO systems operating with polyamide membranes. A minority of systems with cellulose acetate membranes however still require acidification due to hydrolytic sensitivity of cellulose acetate towards feedwater pH higher than 6.

The chemistry behind the main reason for acidification — the prevention of scaling by calcium carbonate — is reviewed here. The mechanisms of calcium carbonate scaling and its avoidance by acidification or with anticalants are discussed. We present a case study in southeastern USA of a 5 million gallons RO permeate per day plant as a typical example among many for the conversion of major municipal RO plants. By suitable selection of an antiscalant, acid elimination was successfully attained with a simultaneous reduction in the antiscalant dosage, in this case to 2–3 mg/l in the feedwater. While process optimization continues in this plant, current chemical cost savings due to the deletion of 93% sulfuric acid and the associated caustic soda neutralizer alone amounts to 67% of the annual cost of all chemicals used. This does not include savings through benefits accrued in equipment, operation, maintenance and safety in the plant.

2. Geochemical carbon cycle

Calcium carbonate scales experienced in water treatment has its roots in the geochemical carbon cycle [8]. Natural waters are heavily buffered with relatively soluble calcium and magnesium bicarbonate. About 0.04% of the Earth's atmosphere is composed of carbon dioxide. This level of concentration on the time scale of millions of years is controlled mainly by a combination of degassing from the Earth's interior balanced by the uptake of carbon dioxide via the weathering of calcium and magnesium silicate minerals. The carbon dioxide in water as carbonic acid is converted to dissolved calcium and magnesium bicarbonate on land during weathering. This carbon form is stored in lakes and aquifers or carried to the sea by rivers, and precipitated there as calcium and magnesium carbonate minerals. The overall reactions shown here were first formulated by Urey [9] in 1952.

$$CO_2 + CaSiO_3 \Leftrightarrow CaCO_3 + SiO_2$$
$$CO_2 + MgSiO_3 \Leftrightarrow MgCO_3 + SiO_2$$
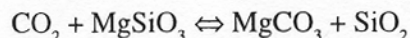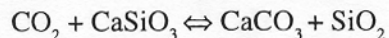
The reactions going from left to right represent carbon dioxide absorption via weathering. The reactions going from right to left represent degassing due to the thermal decarbonation of the carbonates after burial to sufficient depths in the Earth's crust. Added to the Urey reactions should also be the Organic Carbon Subcycle. It exerts an important additional control on atmospheric carbon dioxide level. This involves the removal of carbon dioxide from the atmosphere through photosynthesis by organisms, the burial

of organic matter in sediments, and the weathering of organic matter (or its thermal decomposition) which returns the carbon dioxide. The overall reaction is represented as:

$$6CO_2 + 6H_2O \Leftrightarrow (CH_2O)_6 + 6O_2$$
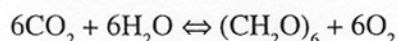
Together these reactions regulate carbon dioxide on a geologic time scale.

Relevant to water treatment then is the fact that natural waters contain high concentrations of soluble bicarbonate salts in dynamic equilibrium with carbonic acid (dissolved carbon dioxide) and insoluble carbonate salts. To estimate the amount of the three forms in water, it is important to know that carbonic acid (H_2CO_3) is a divalent acid with $pK_1 = 6.35$ and $pK_2 = 10.33$. At pH = 6.35, the unionized acid and the bicarbonate (HCO_3^-) ion exist in equal concentrations. Since pH is a logarithmic scale, at pH = 7.35 (one unit higher) the solution would contain 90% bicarbonate and 10% carbonic acid, and at pH=8.35, the solution would contain 99% bicarbonate and 1% carbonic acid. The pH of 8.2–8.4 (phenothaline endpoint in alkalinity titrations) is also significant in that above this pH, carbonate (CO_3^{2-}) ions begin to appear. At pH = 9.3, about 10% of the bicarbonate ions would have converted to carbonate ions, while at pH = 10.33, carbonate and bicarbonate ion concentrations would be equal. Since calcium carbonate is quite insoluble (14 mg/l water at 25°C), natural waters [10,11] are usually found in the pH range of 6–8, with bicarbonate ions ranging between 6 to 600 mg/l and calcium ranging between 2 to 200 mg/l. Seawater representing 98% of blended natural waters on the surface of the Earth typically contains 410 mg/l of Ca^{2+} ions and 143 mg/l of HCO_3^- ions. Since magnesium carbonate is about 100 times more soluble than calcium carbonate, magnesium ion concentration in seawater is much higher (about 1310 mg/l), and carbonate scaling potential in surface waters is mainly focused on calcium carbonate crystallization, since it is the first carbonate scale to form under concentration or basification.

3. Calcium carbonate scaling indices

Langelier Saturation Index (LSI) and the form modified for high salinity water called Stiff and Davis Stability Index (S&DSI) are widely used for predicting calcium carbonate scaling potentials in cooling systems and boiler waters [10,11]. These indices are widely applied for predicting the same in RO systems [12–15]. The formulae for the calculation of the indices [10–12] are given below:

$$LSI = pH - pH_s$$

where pH_s is the pH at which the water is saturated in calcium carbonate, and is calculated by the following:

$$pH_s = (9.3 + A + B) - (C + D)$$

where:

$$A = (\log_{10}[TDS] - 1) / 10$$
$$B = -13.12 \times \log_{10} (°C + 273) + 34.55$$
$$C = \log_{10} [Ca^{2+} \text{ as } CaCO_3] - 0.4$$
$$D = \log_{10} [\text{alkalinity as } CaCO_3]$$

In this model, we see that calcium carbonate saturation is affected by salinity (Total Dissolved Solids, TDS) and temperature along with calcium and bicarbonate ion concentrations. The Langelier index loses its accuracy in predicting the solubility of calcium carbonate for water with salt concentrations exceeding 4,000 mg/l [12]. Stiff and Davis modified Langelier's formula for high salinity waters using empirically derived values. The Stiff and Davis Stability Index (S&DSI) is calculated as follows:

$$S\&DSI = pH - pCa - pALK - K$$

where pCa is the negative log of the calcium concentration expressed as molarity; pALK is the negative log of the total alkalinity concentration expressed as molarity; K is a constant whose value depends on the water temperature and ionic strength.

At an index of less than 0, the water will have no calcium carbonate scaling potential. At increasingly positive index values, the calcium carbonate scaling potential increases. By projecting the pH, TDS, calcium and alkalinity concentrations in RO concentrates, the calcium carbonate scaling indices can be calculated, and feedwater pretreatment appropriately designed.

4. Carbonate scale control with acid vs. antiscalant

Carbonate scale control in large RO systems typically involves the use of either acid to reduce pH and bicarbonate concentration, or antiscalant to inhibit the growth of calcium carbonate crystals, or a combination of the two depending on the water chemistry. Due to the cost of pure water produced, the alternative of reducing recovery to lower the degree of supernaturation in the RO reject is seldom practiced. It may be noted that acidification only lowers the scaling potential of calcium carbonate, and not that of calcium fluoride, calcium, strontium and barium sulfate, and reactive silica.

The LSI and S&DSI are used by some leading RO membrane manufacturers to guide the use of feedwater treatment chemicals as shown in Table 1. These recommendations were generally practiced in the field, and are reflected in the operation of the existing RO plants.

Sulfuric acid (93%) is by far the most commonly used acid for feedwater acidification due to its availability and low price. Concentrated hydrochloric acid is sometimes used to avoid the introduction of additional sulfate ions that aggravate scaling by barium, strontium and calcium sulfate scales. However, it is very expensive, and corrosive to all plant equipment due to its fumes. Acid injection is necessary when cellulose acetate (CA) membranes are used. Due to hydrolytic instability, the recommended operating pH range is 3–6. With the advent of pH-tolerant low-pressure polyamide thin-film composite membranes that most new plants use today, acidification is no longer necessary. Since natural waters are heavily buffered by bicarbonate ions, large amounts of acid are needed to lower the pH and the related LSI and S&DSI through conversion of bicarbonate ions to carbonic acid and carbon dioxide. The non-ionic carbon dioxide that is formed causes an additional complication in that it is not rejected by the RO membrane, and passes into the product water where it has to be neutralized with caustic soda or lime before distribution in water supply systems. If sulfide (S^{2-}, and HS^-) ions are present in the feedwater, acidification would generate the unionized hydrogen sulfide (H_2S) gas. Since hydrogen sulfide like carbon dioxide, would not be rejected by the RO membrane, it has to be thoroughly degassed from the acidified feedwater and scrubbed. In contrast if feedwater is used without acidification, hydrogen sulfide (pKa = 7.05) would be largely in the ionic HS^- form, and would be rejected by the membrane.

Sodium hexametaphosphate (SHMP) is a generic antiscalant widely used due to its low cost. It acts, as do the newer organic antiscalants, by inhibiting the growth of calcium carbonate seed

Table 1
Limiting values of LSI and S&DSI in RO concentrate to avoid calcium carbonate scaling

	Hydranautics [6]	Permasep [7]	FilmTec [8]
LSI and S&DSI without scale inhibitor	<−0.2	<0.0	<0.0
LSI and S&DSI with SHMP* scale inhibitor	≤0.5	<1.0	<1.0
LSI and S&DSI with organic scale inhibitors	≤1.8	<2.3	<1.8

*SHMP = Sodium hexametaphosphate

crystals [16]. The limitations of SHMP are that it is stable only in the anhydrous solid form. It is difficult to dissolve in the plant, and that once dissolved in water, it slowly hydrolyzes to phosphate ions which precipitates calcium, magnesium, aluminum, iron and other ions as insoluble phosphate salts, in addition to being a stimulant for microbial growth. As an antiscalant for simultaneous control of other types of scales, it is much less effective than the newer types of organic antiscalants.

Great advances have been made in the development and use of organic antiscalants. In a line of six distinctly differentiated organic antiscalants all classified under ANSI-NSF Standard 60 for drinking water production [17], the maximum calcium carbonate scaling control possible range from LSI = 2.8 to 3.2 and S&DSI = 3.9 to 4.5. With these high limits for calcium carbonate control, the differentiated antiscalants are selected more on the basis of simultaneous control of calcium, strontium, and barium sulfate, calcium fluoride, reactive silica, iron, aluminum and heavy metal scales. In each case when used, acidification of feedwater is not necessary.

For all the reasons presented above, many efforts have been focused on the elimination of continuous acid injection in RO plants large and small where thin-film composite membranes are used. More and more new plants are now started without acid injection, and results in our experience are uniformly successful. Due to the large volume of acid consumed in many municipal RO systems, it is especially important that the demonstrated advances in antiscalant chemistry are implemented at these locations, and operations and engineering staff and consultants associated with these systems, be alerted and informed.

5. Successful implementation of acid elimination at a major municipal RO plant

At a municipal waterworks in southeastern USA, there are three RO plants with Hydranautics 8040-LSY-CPA2 membranes producing permeate at approximately 700, 1050 and 1800 GPM totaling 5 MGD. The ROs are fed from several deep wells with no pretreatment except cartridge filters, acid and antiscalant injection. Recoveries are between 80 and 85%. A typical well water analysis is given in Table 2. Consistently since startup in 1991, the plant ran with continuous injection of 93% sulfuric acid to reduce feedwater pH from about 8.6 to 6.8, simultaneously with an antiscalant. The acidic pH (about 5.7) of the product water is raised with 50% sodium hydroxide to minimize corrosivity. With careful monitoring of trend charts, work on acid elimination was started in 1997. With RO trains in the plants, side-by-side comparisons of the performance of antiscalants from different chemical suppliers were performed, with and without acidification, or with partial acidification. Outstanding results obtained with a chosen antiscalant have now allowed for complete elimination of acid injection, and simultaneous reduction in the dosage of the antiscalant used to 2–3 mg/l in

Table 2
Chemical analysis of typical deep well water at 5MGD RO waterworks

Aluminum, ppm	0.424
Arsenic, ppm	0.004
Barium, ppm	0.014
Cadmium, ppm	0.001
Calcium, ppm	1.6
Chromium, ppm	0.001
Lead, ppm	0.004
Magnesium, ppm	0.486
Manganese, ppm	0.004
Mercury, ppm	0.0005
Potassium, ppm	3.59
Selenium, ppm	0.003
Silver, ppm	0.001
Sodium, ppm	437.0
Bicarbonate, ppm	893.0
Carbonate, ppm	43.0
Chloride, ppm	99.0
Fluoride, ppm	4.0
Silica, ppm	20.0
Sulfate, ppm	1.0
TDS, ppm	1498.6
pH	8.4

the feedwater. The LSI in the RO concentrate under control without acidification is about 2.1. While process optimization will not stop, current savings due to the deletion of sulfuric acid and associated caustic soda alone amounts to 67% of the annual cost of all chemicals used. This does not include savings through benefits accrued in equipment, operation, maintenance and safety of the plant.

6. Conclusions

The Geochemical Carbon Cycle and the Organic Carbon Subcycle account for the high levels of calcium and magnesium bicarbonate in natural waters in equilibrium with insoluble carbonate scales. Langelier Saturation Index (LSI) and Stiff and Davis Stability Index (S&DSI) are two calcium carbonate scaling indices used in designing RO feedwater pretreatment to avoid carbonate scaling on the membranes. Continuous acid injection to lower pH and the associated LSI and S&DSI is commonly used to control carbonate scales. Bicarbonate ions in waters are converted to carbon dioxide with acid, requiring the consumption of large amounts of acids in RO plants. Simultaneously or alternatively, antiscalants are used to control not only calcium carbonate scale, but all the other common scales as well. The availability of superior organic antiscalants today makes possible its singular use at low dosages to simultaneously control all scales including calcium carbonate. Continuous injection of acid can now be safely eliminated in RO plants not using cellulose acetate membranes.

Successful implementation of acid elimination at a 5 MGD municipal RO waterworks following a two-year evaluation is reported here with major savings and improvements in operation. We wish to alert and inform operations and engineering staff and consultants associated with other major RO plants currently using acid, especially those

designing the future generation of huge municipal RO systems. The avoidance of acid injection will have major beneficial impacts on economics, safety and the environment.

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