

MEMBRANES

ANTISCALANTS THAT PERMIT OPERATION OF RO SYSTEMS AT HIGH PH LEVELS

The production of high-purity water often begins with a reverse osmosis (RO) system for an initial purification of available water using membranes. The efficient rejection of weakly acidic contaminants in source waters such as carbonic acid (in equilibrium with CO_2), silicic acid, boric acid, phenolic organics, and hydrogen sulfide require ionization at pH values higher than that of natural pH levels. The pKa values (pH values necessary to achieve 50% ionization of the acidic group on a logarithmic scale) of some common contaminants are listed in Table A.

A review of these pKa values shows that at the natural water pH range of 6.0 to 8.5, substantial fractions, if not the entire amounts of these weakly acidic contaminants, are present in RO feedwaters in neutral unionized forms, and hence not rejected by RO membranes. This necessitates expensive post-treatments of the RO permeates. If membrane rejection of these contaminants can be improved by elevation of the feedwater pH, the RO permeate quality can be greatly improved.

Two limitations work against attaining high pH in RO feedwaters. One is that cellulose acetate (CA) membranes are sensitive towards hydrolysis, and have to be operated at a pH of 5-6. This limitation has generally now been overcome by the wide use of polyamide thin-film composite membranes that can withstand an operating pH of 11. Another limitation is scaling by calcium carbon-

ate that requires the acidification of RO feedwaters to prevent conversion of even minute amounts of the ubiquitous relatively soluble calcium bicarbonate to the very insoluble calcium carbonate salt. Most RO systems today are operated with some degree of acidification by continuous injection of concentrated sulfuric or hydrochloric acid, even when antiscalants are used simultaneously.

We have developed and field-tested a large line of proprietary antiscalants that when used singly can control all scaling potential from among the following common inorganic RO foulants: calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, calcium fluoride, iron, aluminum, and reactive silica. The efficiency of many of these antiscalants at inhibiting calcium carbonate crystallization is so high that acid injection in general RO applications are no longer necessary.

For 5 years, we have specified appropriate antiscalant dosages of 1 to 5 parts per million (ppm) in new RO systems without acid injection. With this action, we have found full control of calcium carbonate scaling, even at scaling potentials not previously considered controllable, to be possible. This advance opens up the opportunity to explore operation of RO systems in the pH 8 to 11 range without extensive re-

moval of calcium and bicarbonate ions in pretreatment (1). It also allows for great cost savings in the elimination of acid injection and carbon dioxide and hydrogen sulfide gas scrubbers in existing RO plants (2). Our intension is to inform the readers involved in high-purity water process development of these advances, and to collaborate on applying these antiscalants to elevate RO feedwater pH for better rejection of weakly acidic contaminants.

Overview

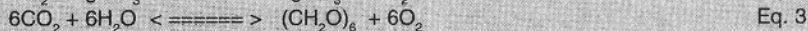
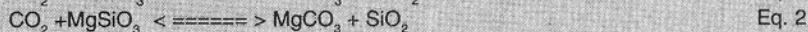
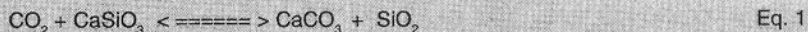
In this article, we will review the chemistry of the main barrier to pH elevation and the basis of the common practice of acidification of RO feedwaters - scaling by calcium carbonate. The mechanisms of calcium carbonate scaling and its avoidance by acidification or with antiscalants are discussed. This understanding is applied to the specific conditions in a major municipal RO plant drawing water from highly alkaline wells.

By suitable selection of an antiscalant, acid elimination was successfully attained with a simultaneous reduction in the antiscalant dosage to 2 to 3 milligrams per liter (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 neu-

By Robert Y. Ning, Ph.D.
King Lee Technologies

ISSN:0747-8291. COPYRIGHT (C) Tall Oaks Publishing, Inc. Reproduction in whole, or in part, including by electronic means, without permission of publisher is prohibited. Those registered with the Copyright Clearance Center (CCC) may photocopy this article for a flat fee of \$1.50 per copy.

Equations



$$\text{LSI} = \text{pH} - \text{pH}_s \quad \text{Eq. 4}$$

$$\text{pH}_s = (9.3 + A + B) - (C + D) \quad \text{Eq. 5}$$

where:

$$A = (\text{Log}_{10} [\text{TDS}] - 1) / 10$$

$$B = -13.12 \times \text{Log}_{10} (^\circ\text{C} + 273) + 34.55$$

$$C = \text{Log}_{10} [\text{Ca}^{+2} \text{ as CaCO}_3] - 0.4$$

$$D = \text{Log}_{10} [\text{alkalinity as CaCO}_3]$$

$$\text{S\&DSI} = \text{pH} - \text{pCa} - \text{pALK} - K \quad \text{Eq. 6}$$

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; and

K is a constant whose value depends on the water temperature and ionic strength.

tralizer 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. Continued application of antiscalants to economically attain high pH levels in RO feedwaters provide opportunities to improve the efficiencies of RO systems to remove weakly acidic contaminants in the production of high-purity water.

Geochemical Carbon Cycle

Calcium carbonate scales experienced in water treatment has its roots in the geochemical carbon cycle (3). About 0.04% of the Earth's atmosphere is composed of carbon dioxide. This level of concentration on the time scale of million 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 (4) in 1952. They are illustrated in Equations 1 and 2 (see Equations table).

The reactions going from left to right represents 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 sub cycle. 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) that returns the carbon dioxide. The overall reaction is represented in Equation 3. 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 esti-

TABLE A
The pKa Values of Some Weakly Acidic Contaminants in RO Feedwaters

Name	Formula	pKa Values*
Carbonic acid (CO ₂ in water)	OC(OH) ₂	6.35 ; 10.33
Silicic acid (reactive silica)	Si(OH) ₄	9.9; 11.8; 12; 12
Boric acid	B(OH) ₃	9.27; >14
Hydrogen sulfide	H ₂ S	7.05; 19
Hypochlorous acid	ClOH	7.40
Phenol	C ₆ H ₅ OH	9.89
Phenolic organics	substituted phenols	9-10

*Taken from CRC Handbook of Chemistry and Physics, 76th edition, CRC Press, New York, N.Y. (1995-1996). Multiple values are for successive ionizations of multi-valent acids.

mate the amount of the three forms in water, it is important to know that carbonic acid (H₂CO₃) is a divalent acid with pK1 = 6.35 and pK2 = 10.33. At pH = 6.35, the unionized acid and the bicarbonate (HCO₃⁻¹) 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 to 8.4 (phenothaline endpoint in alkalinity titrations) is also significant in that above this pH, carbonate (CO₃⁻²) ions begin to appear. At pH = 9.3, about 10% of the bicarbonate ions would have converted to carbonate ion, 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 (5, 6) are usually found in the pH range of 6 to 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 HCO₃⁻¹ ions. Since magnesium carbonate is about 100 times more soluble than calcium carbonate, magnesium ion concentration in seawater is much higher (about 1,310 mg/L), and carbonate scaling potentials in surface waters is mainly focused on calcium carbonate crystallization, since it is the first carbonate scale to form under treatment or use.

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 (5,6). These indices are widely applied for predicting the same in RO systems (7-10). The formulae for the calculation the indices (5-7) are given in Equation 4. The pHs is the pH level at which the water is saturated in calcium carbonate and is calculated in Equation 5.

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 (7). Stiff and Davis modified Langelier's formula for high salinity waters using empirically derived values. The S&D SI is calculated as seen in Equation 6

At an index of less than 0, the water will have a very limited scaling potential. At increasingly positive index values, the 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.

Carbonate Scale Control with Acid versus Antiscalant

Carbonate scale control in large RO systems typically involve 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. 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 B. These recommendations were generally practiced in the field, and are reflected in the operation of the existing RO plants.

TABLE B
Limiting Values of LSI and S&DSI in RO Concentrate
To Avoid Calcium Carbonate Scaling

	Hydranautics (8)	Permasep (9)	Filmtec (10)
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

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 CA membranes are used. Due to hydrolytic instability, the recommended operating pH range is 3 to 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-1) ions are present in the feedwater, acidification would generate the unionized hydrogen sulfide (H₂S) 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 (pKa1= 7.05) would be largely in the ionic HS-1 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 crystals (11). 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. Additionally, SHMP can be 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, the maximum calcium carbonate scaling control possible range from LSI = 2.8 to 3.5 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, silica, iron, aluminum, and heavy metal scales. In each case when used, acidification of feedwater is not necessary.

For all the reasons presented in this article, much effort has focused on the elimination of continuous acid injection in RO plants large and small where thin-film composite membranes are used. New plants are now started without acid injection, and results in our experience are uniformly successful.

Experience at a 5-mgd Municipal RO Plant

A municipal waterworks in South Carolina draws water from highly alkaline wells. There are three RO plants with Hydranautics 8040-LSY-CPA2 membranes producing permeate at approximately 700, 1,050 and 1,800 gallons per minute (gpm), totaling 5 million gallons per day (mgd). The RO systems 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 C. 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 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.

Summary

We have reviewed the geochemical carbon cycle and the organic carbon subcycle that account for the high level of bicarbonate ions in natural waters in equilibrium with insoluble carbonate scales. The LSI and 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, anti-

TABLE C
Chemical Analysis of Typical
Deep Well Water at Mount
Pleasant Waterworks

<i>Analysis</i>	<i>Reading (ppm)</i>
Aluminum	0.424
Arsenic	0.004
Barium	0.014
Cadmium	0.001
Calcium	1.6
Chromium	0.001
Lead	0.004
Magnesium	0.486
Manganese	0.004
Mercury	0.0005
Potassium	3.59
Selenium	0.003
Silver	0.001
Sodium	437
Bicarbonate	893.0
Carbonate	43.0
Chloride	99.0
Fluoride	4.0
Silica	20.0
Sulfate	1.0
TDS	1498.6
pH	8.4

calants 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 the 5-mgd municipal RO plant following a 2-year evaluation is reported in this article 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. In addition, the use of appropriate antiscalants to permit elevation of the pH of RO feedwaters offers the opportunity of improving the efficiencies of RO systems to reject weakly acidic contaminants in the production of high-purity waters.■

References

1. Mukhopadhyay, D.; Whipple, S.S. "RO System that Reduces Membrane Scaling and Fouling Tendencies", *ULTRAPURE WATER* 14(8), pp. 21-30 (October 1997).
2. Ning, R.Y.; Netwig, J.P.; Hill, G.; Burlison, K.; Alexander, P.; Wilder, T.; Phipps, D.; Walker, R. "Elimination of Acid Injection in Reverse Osmosis Plants", Proceedings of Water Quality Technology Conference, American Water Works Association (Nov. 5-9, 2000).
3. Berner, R.A. "A.G. Hoggom and the Development of the Concept of the Geochemical Carbon Cycle", *American Journal of Science*, 295, pp. 491-495 (1995).
4. Urey, H.C. *The Planets: Their Origin and Development*, Yale University Press, New Haven, Conn., p. 242 (1952).
5. *The Nalco Handbook*, 2nd edition, Kemmer, F.N., ed., McGraw Hill, New York, N.Y., pp. 4.10-4.18 and 6.4-6.6 (1988).
6. Betz Handbook of Industrial Water Conditioning, 9th edition, Betz Laboratories, Trevose, Pa., pp. 183-184 and 223-225 (1991).
7. Byrne, W. *Reverse Osmosis: A Practical Guide for Industrial Users*, Tall Oaks Publishing Inc., Littleton, Colo., pp.111-117 (1995).
8. Hydranautics Technical Bulletin, Ocean-side, Calif. (1995).
9. DuPont Permasep Bulletin 4010, Wilmington, Del. (1992).
10. Dow Filmtec Technical Manual, Edina, Minn. (1995).
11. Ning, R.Y. "Operational Characteristics of Reverse Osmosis Process Chemistry" *ULTRAPURE WATER* 16(4), pp. 39-49 (April 1999).

Endnote

*The six antiscalants are available from King Lee Technologies under the Pretreat Plus[™] brand name.

Author Robert Y. Ning, Ph.D., is vice president of science at King Lee Technologies. He holds a Ph.D. in organic chemistry from the University of Illinois, Urbana, Ill. His work has involved research and process development in pharmaceuticals, biotechnology, and water chemistry.

Key words: MEMBRANES, REVERSE OSMOSIS, SCALING