A Brief Review of Natural Water's Influence on Scale Formation in Heat Exchangers

Brad Buecker

ABSTRACT

Calcium carbonate scaling ($CaCO_3$) is a persistent challenge that has plagued water heating and industrial heat exchange systems since ancient times. This paper reviews the fundamental chemical interactions between natural water sources and carbonate minerals that lead to scale formation and shows how environmental conditions, temperature effects, and operational factors influence saturation and deposition. Historical and modern approaches to scale control including acid feed, phosphate/phosphonate programs, synthetic polymer inhibitors, and lime softening are evaluated for their mechanisms and practical performance. A case study highlights the importance of comprehensive raw-water characterization in designing treatment systems, particularly for high-recovery applications such as zero liquid discharge.

INTRODUCTION

Since humans began heating water for hygiene, cooking, comfort, and so forth, we have been plagued by "lime scale" formation. ("Lime scale" is somewhat of a misnomer, as the compound is actually calcium carbonate ($CaCO_3$).) To this day, calcium carbonate scaling still occurs in industrial heat exchangers and steam generators around the globe, especially those with inadequate water treatment programs. "Lime scale" also continues to appear in the hot water lines, showerheads, etc., of many home plumbing networks. This article examines some of the foundations of this issue.

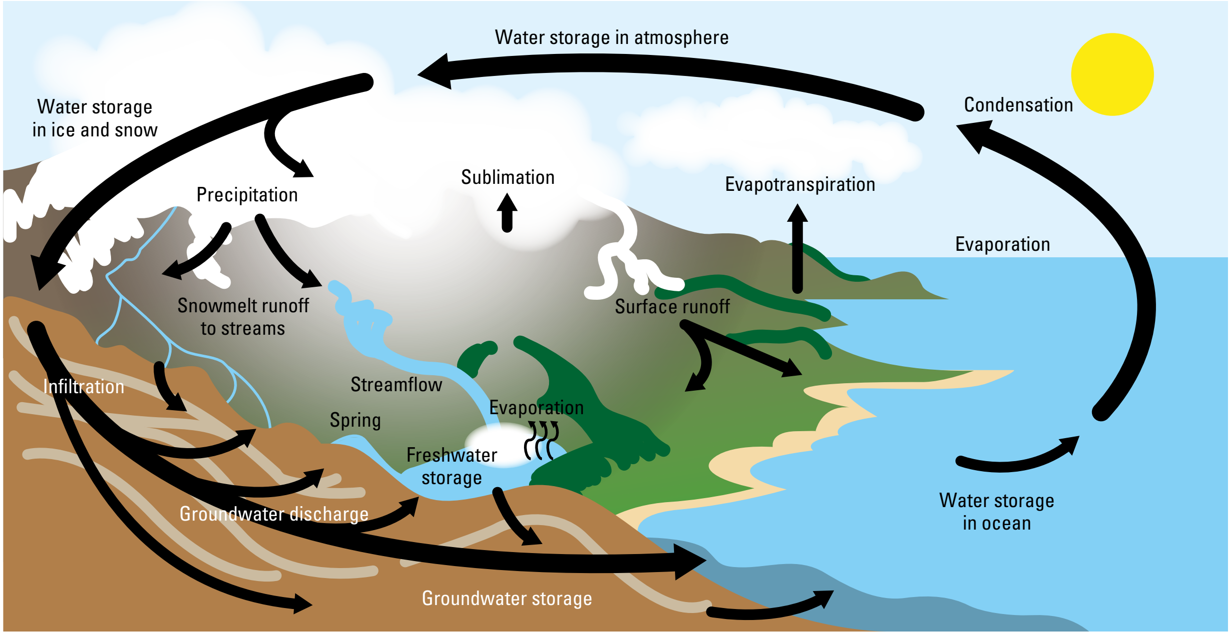


Figure 1:
Schematic of the hydrologic cycle (adapted from [1]).

NATURAL WATER CHEMISTRY

Many factors influence the chemistry of global water supplies, as is visually summarized in Figure 1. Moisture of course can pick up compounds from the atmosphere, most notably carbon dioxide, but most dissolved and suspended solids accumulate when water flows along the ground or percolates through soil into underground aquifers. Table 1 illustrates the ten most common elements in the earth's crust [2].

Silicon does not exist on its own and is typically bonded with oxygen and light metals such as aluminum, magnesium, potassium, and sodium in mineral deposits that are only slightly soluble in normal surface waters. However, a common deposit in many locations is limestone, whose principal component is calcium carbonate ($CaCO_3$) with lesser concentrations of magnesium carbonate ($MgCO_3$). This versatile mineral serves as a raw material for numerous important industrial and infrastructure applications including concrete, water treatment chemicals, flue gas scrubbing reagent, and simply for gravel roads.

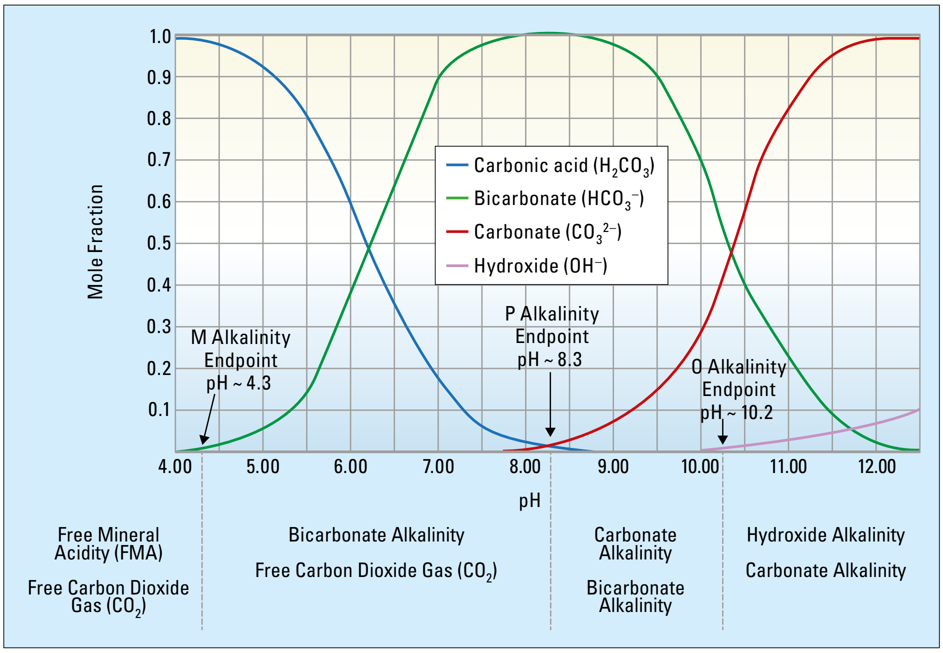


Figure 2:
The relationship between carbonate species in water [4]. For waters that pass along or through limestone deposits, the reactions are driven towards the maximum HCO_3^- alkalinity.

Many surface waters come in contact with limestone, and groundwaters often percolate through limestone deposits and accumulate in aquifers that are contained by rock formations. Calcium carbonate has a strong crystal lattice, and thus $CaCO_3$ is only slightly soluble in water [3].

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad (1)$$

$$K_{SP} = [Ca^{2+}][CO_3^{2-}] = 4.6 \cdot 10^{-9} mol^2 \cdot L^{-2} \quad (2)$$

Per this solubility product (K_{SP}), the molar concentrations of calcium and carbonate in neutral water would be $6.8 \cdot 10^{-5} mol \cdot L^{-1}$, which is indeed very slight. But an additional factor must be considered. CO_3^{2-} is a fairly strong base and will hydrolyze water to some extent.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad (3)$$

Combining Eqs. (1) and (3) illustrates the overall reaction of $CaCO_3$ in neutral water.

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \quad (4)$$

Element	%
Oxygen	46.1
Silicon	28.2
Aluminum	8.23
Iron	5.63
Calcium	4.15
Sodium	2.36
Magnesium	2.33
Potassium	2.09
Titanium	0.565
Hydrogen	0.140
Total	**99.8**

Table 1:
Ten most common elements in the earth's crust [2].

Calculations indicate that CO_3^{2-} hydrolysis of water increases the limestone solubility from $6.8 \cdot 10^{-5} mol \cdot L^{-1}$ to $9.9 \cdot 10^{-5} mol \cdot L^{-1}$ at 25 °C [3]. An important point to keep in mind is that these reactions produce hydroxide alkalinity (OH^-), even if only in slight concentrations.

Now, let's examine other factors that influence surface water chemistry.

ATMOSPHERIC INFLUENCES

Atmospheric moisture and surface water absorb carbon dioxide. While it is often argued that CO_2 exists as hydrated molecules, the following equations sufficiently represent the chemistry.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (5)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (6)$$

The lowest pH that can be achieved in natural surface waters by these reactions (excluding acid rain influences) is around 5.6, but the solution is still acidic, which is very important. Consider again Eq. (4). When the acidity generated by CO_2 absorption interacts with the alkalinity produced by the fractional $CaCO_3$ dissolution, the hydrogen and hydroxyl ions combine to form water, and per Le Chatelier's Principle, the reactions in Eqs. (4) and (6) are both driven to the right. This synergistic effect can produce water with a HCO_3^- concentration of $1 \cdot 10^{-3}$ mol·L^{-1} (equivalent to about 60 parts-per-million as the species), and "a pH of about 8.3" ([3], p. 448). The relationship of the carbonate species is illustrated in Figure 2.

Similar acid–base synergy is what makes high-purity limestone (high $CaCO_3$ content) quite reactive and economical as a scrubbing agent (when ground to very fine particles) in wet flue gas desulfurization systems. Aqueous sulfur dioxide (SO_2) is a stronger acid than CO_2, and analytical data has shown nearly complete $CaCO_3$ reactivity in well-designed scrubbers [5].

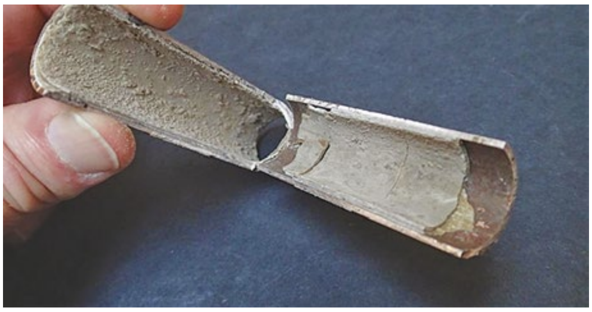


Figure 3:
$CaCO_3$ scale in an extracted and bisected heat exchanger tube [4].

A quite practical example of this chemistry is illustrated in Table 2 below. It is an analysis from a lake in the midwestern United States that was built for power plant cooling (for a plant at which the author worked for 5.5 years) and for recreational purposes. The two units at the plant have once-through condensers.

In accordance with Eq. (2) above, if the concentrations of calcium and alkalinity exceed the solubility product, deposition is possible (Figure 3).

$$Ca^{2+}_{(aq)} + 2HCO^{-}_{3(aq)} \rightarrow CaCO_3 \downarrow + CO_2 + H_2O \qquad (7)$$

From Table 2, the 60 mg·L^{-1} calcium concentration equates to $6 \cdot 10^{-4}$ mol·L^{-1} and the 163 mg·L^{-1} bicarbonate alkalinity concentration equates to $2.67 \cdot 10^{-3}$ mol·L^{-1}. Multiplying these two concentrations gives a value of $1.60 \cdot 10^{-6}$ mol^2·L^{-2}, which considerably exceeds the K_{SP} value shown in Eq. (2). When I began working at the plant, I found a chemical feed system that injected a polymeric scale inhibitor upstream of the steam condensers. At some point, either in the design stage or after the plant began operation, someone became aware of the $CaCO_3$ scaling potential in the once-through condensers. The need for the scale inhibitor at this plant was accentuated, as it is in many cases, by the inverse solubility of calcium carbonate with temperature (see Figure 4).

$$Ca^{2+} + 2HCO_3^- + \text{heat} \rightarrow CaCO_3 \downarrow + CO_2 + H_2O \qquad (8)$$

So, water which might be below the $CaCO_3$ saturation limit at ambient conditions could exceed the limit in heat exchangers. And, of course, solubility issues can be greatly magnified when makeup is cycled up in a cooling tower. Consider if the benign water outlined in Table 2 was cycled up four, five, or six times. Similar difficulties may arise with some groundwater supplies as the makeup source. "Once rainwater penetrates soil, it is exposed to CO_2 gas levels much greater than in the atmosphere, cre-

Cations [mg·L^{-1} as species]		Anions [mg·L^{-1} as species]		Others	
Calcium	60	Bicarbonate Alkalinity	163	pH	8.0
Magnesium	12	Chloride	32	Turbidity	5 NTU
Potassium	7	Nitrate	0.5	Iron	0.1 mg·L^{-1}
Sodium	32	Sulfate	77	Manganese	0.1 mg·L^{-1}
				Silica	2 mg·L^{-1}

Table 2:
Snapshot analysis of the major ions in a midwestern USA lake.
NTU nephelometric turbidity unit

ated by respiration of soil organisms as they convert organic food into energy and CO_2" ([7], p. 434). The elevated CO_2 can dissolve calcium and magnesium carbonate to generate high hardness concentrations. Other impurities may include silica, iron, and manganese.

A BRIEF REVIEW OF $CaCO_3$ SCALE CONTROL METHODS

In the middle of the last century, a very popular and straightforward cooling tower corrosion/scale control treatment program consisted of sodium dichromate ($Na_2Cr_2O_7$) and sulfuric acid feed to the cooling water. Dichromate establishes a chromium oxide film on carbon steel for corrosion protection, while sulfuric acid removes bicarbonate alkalinity, which in turn reduces the $CaCO_3$ scaling potential. A representative reaction is shown in Eq. (9):

$$H_2SO_4 + NaHCO_3 \rightarrow NaHSO_4 + CO_2\uparrow + H_2O \qquad (9)$$

Operation within a pH range of 6.5 to 7.0 is often adequate for $CaCO_3$ scale inhibition.

Beginning in the 1980s, chromate programs were banned due to health issues related to the formation of toxic hexavalent chromium (Cr^{6+}). However, acid feed is still utilized in some applications to reduce bicarbonate alkalinity.

Phosphate/phosphonate chemistry replaced acid/chromate, but many modern programs now utilize synthetic polymers to inhibit scale formation via such mechanisms as crystal modification and ion sequestration. These polymers may have one or more of several active groups to inhibit not only $CaCO_3$ but other scale formers including sulfates, phosphates, etc.; see Figure 5.

Monitoring programs have become quite sophisticated. A prime example is French Creek Software, which, with comprehensive data input, can calculate the scaling potential of a wide variety of dissolved minerals [8]. The program includes an expansive database of treatment chemicals that a user can select to evaluate scale control while accounting for the influence of such parameters as cooling water pH, temperature, and cycles of concentration. Figure 6 outlines several data display screens. The screens will adjust to show scaling or non-scaling conditions

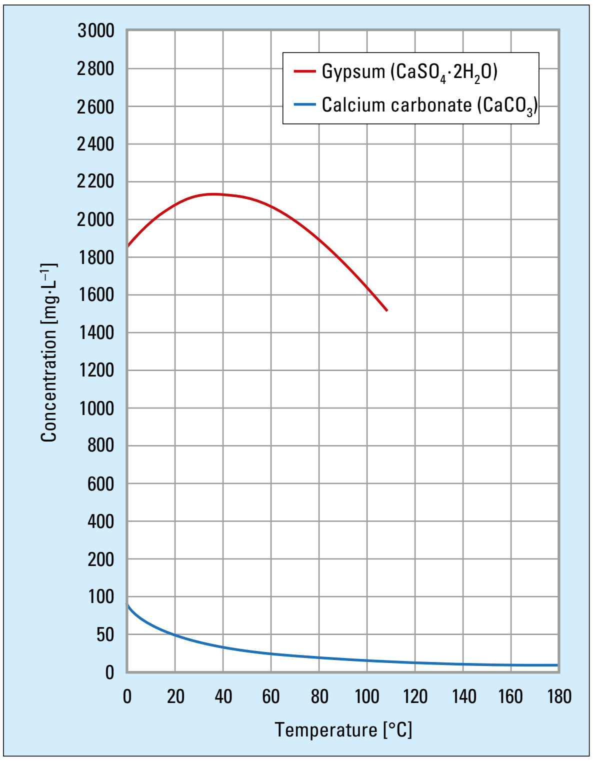
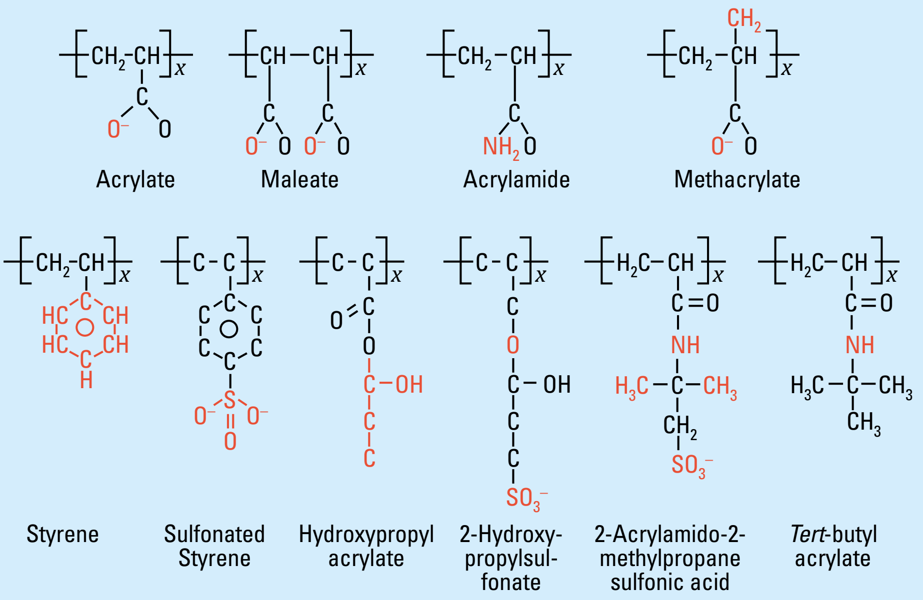


Figure 4:
The inverse solubility of two of the most common potential deposits in natural waters [4].



- Generally, carboxylic acid performs best on carbonates and sulfates.
- Generally, sulfonic acid functionality performs best on phosphates, Zn, Mn, Fe

Figure 5:
Monomeric structures and active groups of common polymers for cooling water scale inhibition [4].

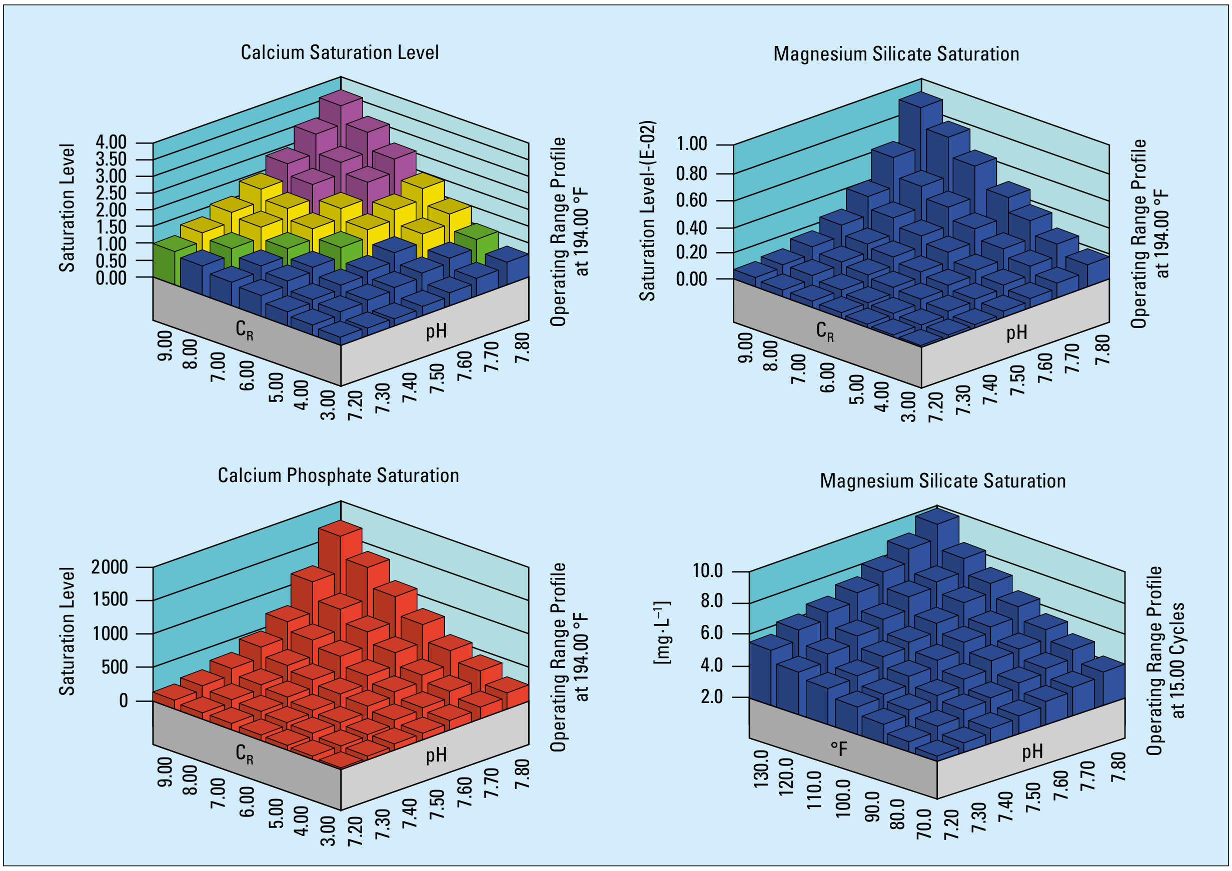


Figure 6:
Examples of scaling potential visualized in 3D graphs based on important cooling water parameters [4]. The user can adjust any of the parameters and immediately observe changes in the predicted scaling potential.

per user inputs, including chemical formulations. A comprehensive collection of treatment chemicals is included in the program database.

Lime Softening

For applications with large makeup requirements or with makeup that has high hardness concentrations, lime softening clarification remains a practical technology [9].

Using Table 2 as a guide, hardness that associates with bicarbonate alkalinity or related species is known as "carbonate" or "temporary" hardness. Hardness associated with chloride or sulfate is "permanent" hardness.

Temporary hardness can be lowered by the addition of lime ($Ca(OH)_2$). The principal reactions are shown below.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O \qquad (10)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O \qquad (11)$$

Lime alone does not reduce permanent hardness but only exchanges magnesium for calcium.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2 \qquad (12)$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4 \qquad (13)$$

Removal of permanent hardness from the raw water, and that which remains from the reactions shown in Eqs. (12) and (13), requires supplemental soda ash (Na_2CO_3) feed.

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl \qquad (14)$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4 \qquad (15)$$

Silica to some extent will co-precipitate with magnesium hydroxide, which is an added benefit. The reactions shown in Eqs. (10) to (15) and SiO_2–$Mg(OH)_2$ co-precipitation are all enhanced by higher temperatures, and hot lime softeners can produce effluent with greatly reduced hardness and silica concentrations. However, hot lime softening requires more specialized equipment plus a steam source for heating.

Lime and lime/soda ash softening generate significant quantities of sludge, and this must be taken into account during system design. Common is a filter press to convert the sludge to a cake-like material for easier disposal.

Lime Softening, Practical Example

The author once assisted with a project in which zero liquid discharge (ZLD) was a requirement at a combined cycle power plant in a semi-arid location in the US. The plant has a steady source of makeup water from a large river. All plant wastewater streams are routed to the cooling tower basin, such that the tower blowdown serves as the sole stream for ZLD treatment. The ZLD network includes microfilters, sodium softening, and a high-recovery reverse osmosis (RO) unit, as shown in Figure 7.

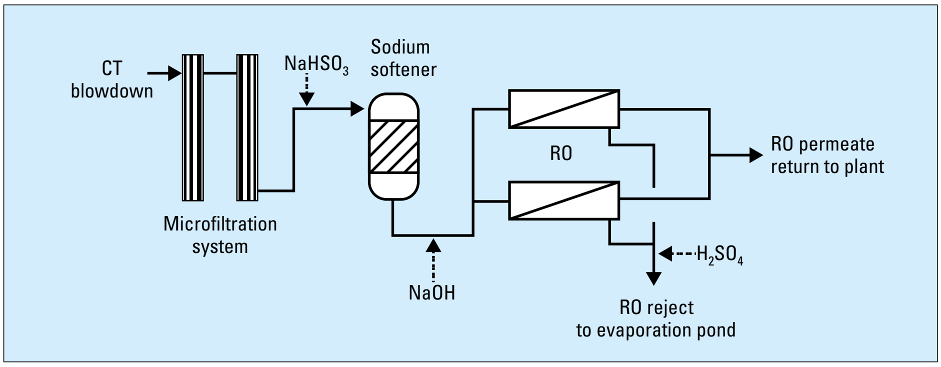


Figure 7:
Schematic of the combined cycle power plant ZLD system. RO reject is delivered to an evaporation pond.

CT	cooling tower
RO	reverse osmosis

A key parameter in the plant water balance is minimizing flow to the evaporation pond; therefore, the cooling tower must operate at reasonably high cycles of concentration. This requirement necessitated a cold lime softening clarifier to lower hardness and silica concentrations in the plant makeup. Plant commissioning revealed an issue that arises too often for makeup treatment systems of varying arrangements: the clarifier was designed based on just a few water analyses early in the project, and the water chemistry had changed significantly by the time of commissioning. Startup managers and plant personnel had to make numerous clarifier chemical feed adjustments to produce the quality of makeup needed to achieve acceptable cycles of concentration. This was yet another example showing that comprehensive raw-water sampling over time is necessary at project inception to accurately design the makeup treatment system and evaluate seasonal variations in water chemistry

CONCLUSION

Calcium carbonate scaling remains a persistent operational issue in heat exchangers, cooling systems, and steam generators due to the natural interplay of atmospheric CO_2, mineral dissolution, and temperature-dependent solubility. Even modest concentrations of calcium and bicarbonate can exceed solubility limits under heated conditions, driving $CaCO_3$ deposition unless appropriate mitigation strategies are applied. While early acid/chromate programs effectively controlled scaling, modern treatment approaches rely on more environmentally acceptable technologies, including synthetic polymers and optimized softening processes. The choice of treatment must be informed by a thorough understanding of local water chemistry, which can vary significantly due to geological, seasonal, and biological influences. Case experience further demonstrates that accurate and comprehensive raw-water analyses are essential for designing reliable treatment systems, particularly for high-pressure or high-recovery applications.

REFERENCES

[1] Perlman, H., Evans, J., *The Water Cycle*, **2019**. U.S. Geological Survey, Reston, VA, USA.
Available from https://www.usgs.gov/.

[2] Price, C., *The Most Abundant Elements in the Earth's Crust*, **2023**. Reunion Technology Inc., St. Laurent, QC, Canada.
Available from https://www.worldatlas.com/.

[3] Baird, C., *Environmental Chemistry*, **1999**. W. H. Freeman and Company, New York, NY, USA, 2nd Edition.

[4] Post, R., Buecker, B., Shulder, S., "Power Plant Cooling Water Fundamentals", *presented at the pre-conference seminar of the 37th Annual Electric Utility Chemistry Workshop*, **2017** (Champaign, IL, USA). University of Illinois at Urbana-Champaign, Champaign, IL, USA.

[5] Buecker, B., "Wet Limestone FGD Solids Analysis by Thermogravimetry", *presented at the 24th Annual Electric Utility Chemistry Workshop*, **2004** (Champaign, IL, USA). University of Illinois at Urbana-Champaign, Champaign, IL, USA.

[6] Buecker, B., Kalakodimi, P., "Current Concepts in Cooling Water Chemistry", *pre-*

sented at the pre-workshop seminar of the 41st Annual Electric Utility Chemistry Workshop, **2023** (Champaign, IL, USA). University of Illinois at Urbana-Champaign, Champaign, IL, USA.

[7] Flynn, D. J., *The Nalco Water Handbook*, **2009**. The McGraw-Hill Companies, Inc., New York, NY, USA, 3rd Edition.

[8] French Creek Software, Inc., Valley Forge, PA, USA: https://www.frenchcreeksoftware.com/.

[9] *Five Common Problems with Raw Water and How You Can Treat Them*, **2016**. Samco Technologies, Inc., Buffalo, NY, USA. Available from https://samcotech.com/.

THE AUTHOR

Brad Buecker (B.S., Chemistry, Iowa State University, Ames, IA, USA) is a senior technical consultant with SAMCO Technologies (Buffalo, NY, USA). He is also president of Buecker & Associates, LLC, consulting and technical writing/marketing. Buecker has over four decades of experience in or supporting the power industry, much of it in steam generation chemistry, water treatment, air quality control, and results engineering positions with City Water, Light & Power (Springfield, IL, USA) and Kansas City Power & Light Company's (now Evergy) La Cygne, KS, USA, station. His work has also included eleven years with two engineering firms, Burns & McDonnell and Kiewit, and he spent two years as acting water/wastewater supervisor at a chemical plant. Buecker has a B.S. in chemistry from Iowa State University with additional course work in fluid mechanics, energy and materials balances, and advanced inorganic chemistry. He has authored or co-authored over 250 articles for various technical trade magazines and has written three books on power plant chemistry and air pollution control. He is a member of the ACS, AIChE, AIST, ASME, AWT, and the Electric Utility & Cogeneration Chemistry Workshop planning committee (now co-located with the Power-Gen International conference), and he is active with the International Water Conference. He is also a member of the International Advisory Board of the PPCHEM journal.

CONTACT

Brad Buecker
Buecker & Associates, LLC
2816 Harrison Ave
Lawrence, KS 66047
USA

E-mail: beakertoo@aol.com