Zero Liquid Discharge (ZLD) Cooling Tower Treatment at CSI

In 1984, California Steel Industries (CSI) reopened operation of the prior Kaiser Steel facility that was commissioned in the 1940s. CSI installed additional wastewater recovery and reuse systems in 1992, and has continued to optimize systems to conserve water and avert wastewater discharge issues. The site currently reuses its own treated sewage as makeup to cooling water systems. The local southern California community still lacks abundant water resources or wastewater discharge infrastructure to serve this operation, and CSI has continued to explore and develop alternatives to manage its own water use and wastewater discharge requirements in coordination with area municipalities and regulatory authorities.

CSI installed new closed-circuit evaporative coolers at two different site locations in 2006 to provide secondary cooling of closed cooling loops for air compressor equipment. No wastewater discharge collection lines were in place for tower blowdown, and previous tower blowdown had to be collected in wastewater collection pits or tanks, from which CSI's tank truck could haul this water to CSI's in-plant waste processing system. Use of a zero liquid discharge (ZLD) approach for cooling tower water treatment allowed CSI to avert either significant wastewater hauling cost or capital cost investment to install a wastewater discharge collection system.

The EC West location installed an EVAPCO ATW 64-4H cross-flow closed-circuit cooler tower to support three air compressors (two Quincy 1,250 cfm and one Ingersol Rand XLE 1,600 cfm). The EC 10 location installed one BAC VF1-027-42J counterflow closed-circuit cooling tower to support a single air compressor (Ingersol Rand XLE 1,600 cfm). Both coolers were constructed with galvanized tube bundles and galvanized housing. The EVAPCO unit included a 304 SS basin.

The typical operating temperature drop across the EVAPCO tube bundle ranges from 5 to 15°F with a 340 gpm evaporative cooling water circulating flow, and 1-to-2 operational air compressor load. The average temperature drop across the BAC tube bundle is 24–28°F with a 115 gpm evaporative cooling water circulating flow, and the operational load of the single air compressor. Prior to replacement of these two systems, loss of adequate primary water (closed-loop) cooling caused air compressors to experience high-temperature trip-outs, with frequent seal failures and oil changeouts from overheating. Scaled evaporative condenser tube bundles in the old cooler towers caused closed-loop cooling water temperatures to run 10–20°F higher than design operating conditions.

Two new cooling towers were started up using zero liquid discharge water chemistry. The new technology permits operation at high total dissolved solids without scale or corrosion, and costs less than chemical treatment.

Evaporative makeup water to the cooling towers is provided from both municipal and well sources using the same aquifer, and with equivalent water quality. The dissolved mineral content of this source water presented significant scaling potential from both hardness and silica, and corrosion potential from total dissolved solids (TDS). Providing reliable chemical treatment control for these systems to prevent scale, corrosion and biological fouling was difficult with varying operational loads and required discharge (blowdown) of 30–40% of makeup water to aviod concentration of hardness toward scale-forming water chemistry.

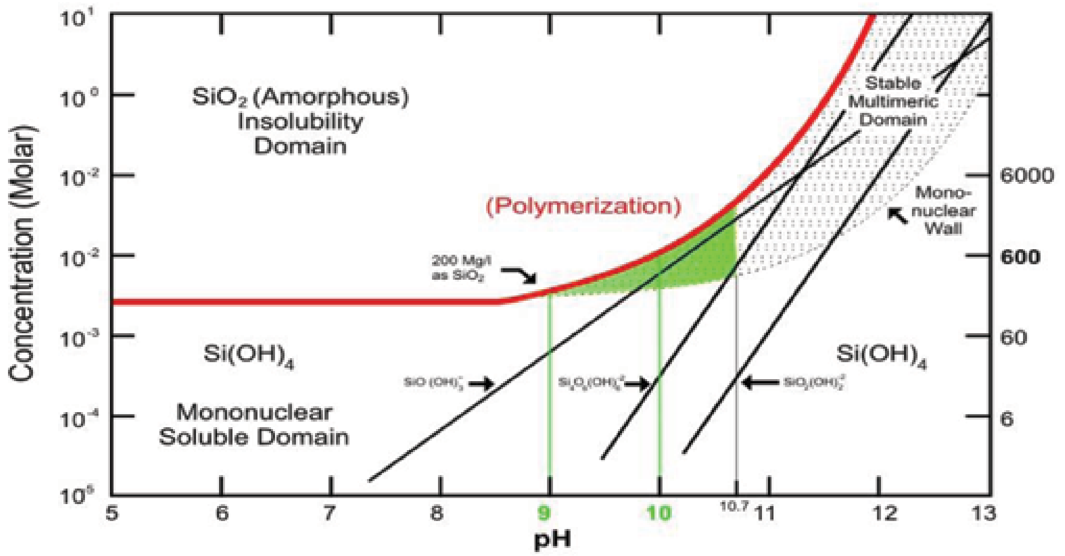
ZLD/Silica Chemistry

Application of a new patented corrosion and scale inhibition technology was well-suited for this situation, because it permitted ZLD

Authors

Dan Duke, chief financial officer, and **John Kubis,** chief executive officer, Water & Enviro Tech Co. Inc. (WETCO), Mission Viejo, Calif. (jack@wetco.biz); and **Jeff Reed,** site maintenance planner, California Steel Industries Inc., Fontana, Calif. (jreed@californiasteel.com)

Figure 1



Relationship between soluble, insoluble and polymerized silica species at varying pH and concentration.

operation of the cooling towers.[1] The technology is licensed by Water Conservation Technology International to U.S. and international water treatment companies.[2] The process eliminates scaling potential by removing hardness with ion exchange pretreatment (softening). Silica in the source water, which is normally associated with scale deposition, is modified by the silica chemistry control process to non-scaling forms of silica. This modified silica chemistry also provides outstanding corrosion protection to system metals. The silica corrosion inhibition mechanism is so effective that cooling water can now be concentrated to TDS levels that would not have been possible with traditional chemical inhibitors.

This technology also provides the opportunity to implement "green chemistry," since use and discharge of environmentally restricted organic, phosphate and heavy metal–containing chemicals used in traditional water treatment are eliminated. With higher tower water concentration, even the use of biocidal agents may be eliminated or reduced due to impeded biological proliferation of freshwater organisms by high TDS concentration in tower water. With ZLD operation, discharge issues may be totally averted.

Highly efficient salt softening equipment that produces polished quality soft water was designed and installed prior to start-up of the new evaporative condensers at both locations. The design of this softening equipment reduced consumption and handling of salt by more than 50%, as regeneration used only 4 pounds of salt per cubic foot of resin (versus the normal 8–12 pounds per cubic foot). This equipment design also produced only 35% of the regeneration water waste of normal softening equipment — also important since the brine waste has to be collected and hauled by an in-plant tank truck to in-plant waste processing.

Dicussion of the origins of this new silica chemistry and the mechanisms of scale inhibition and corrosion inhibition are beyond the scope of this paper. However, a substantial list of references has been provided in this paper for information on silica chemistry

Table 1

EC West Tower Water Chemistry

Sample/Tests	Tower	Makeup	COC
TDS	44,000	250	176
pH	9.90	7.5	
Copper (mg/l Cu)	ND	ND	
Zinc (mg/l)	ND	ND	
Silica (mg/l SiO_2)	474	27.6	17
Calcium (mg/l $CaCO_3$)	14.5	< 0.1	
Magnesium (mg/l $CaCO_3$)	3.3	< 0.1	
Iron (mg/l Fe)	ND	ND	
Aluminum (mg/l Al)	ND	ND	
Sulfate (mg/l SO_4)	3,375	19	178
Chloride (mg/l)	954	3.8	251
Total alkalinity (mg/l $CaCO_3$)	21,160	140	151

ND = Not detected, COC = Concentration of soft makeup chemistry.

behavior and development of the currrently applied technology.[1,6,9–22] It is, however, interesting to note that much was known about the corrosion-inhibiting properties of silica in other applications outside of high-TDS cooling water treatment, and in the steel industry in particular. Amorphous silica coatings have been studied as an alternative means to protect galvanized steel from white rust in sheet production and shipping, and is used to coat and protect the inside of stainless tubing used for hydrochloric acid dispensing from chloride attack.[3–4] It is also used to coat and provide additional corrosion protection for galvanized steel parts used in automotive parts manufacture.[18] Though water treatment specialists recognized that removing scale-forming minerals (softening) from cooling water was the only practical approach to protect some critical applications, they continued to rely on traditional treatment chemicals, and did not recognize the opportunity to change silica from a threat to a resource in corrosion protection and water conservation.[5] None visualized a reliable and cost-effective process that could easily be employed to control the concentration and equilibrium of amorphous silica (Figure 1) in cooling towers, or that it would provide outstanding scale and corrosion inhibition. This technology is now available to those water treatment professionals and their customer applications.

CSI/ZLD Results

Both CSI evaporative cooling systems have been operating on ZLD over the last nine months with TDS between 25,000 and 50,000 (1X to 2X seawater). Typical soft makeup and system water chemistry analyses are provided in Tables 1 and 2, and show chemistry of concentration (COC) of the principal ions produced in the softened source water. Notably, silica does not show the equivalent level of concentrations (COC) as other soluble ions due to the modification of the majority of the source water chemistry into higher-molecular-weight polymeric or colloidal forms not measured by the acid molybdate test, which measures only soluble silica monomer.

Hardness levels were controlled below 50 mg/l in the tower water, even at 125–250 COC of source water, as enabled by the polished quality of the pretreatment system. Soft makeup is the only important control requirement for plant operators with ZLD operation, since there are no chemical feed or blowdown control adjustments. Hardness in the tower water must be controlled below levels that would precipitate silica and interfere with the corrosion-inhibiting film formation on metals. Thus, for high-COC operation, hardness removal equipment must provide excellent quality and reliability. Pretreatment hardness leakage or upsets necessitate blowdown (or system water disposal) to lower hardness levels to avoid hardness and silica precipitation. No hardness leakage occurred with the two CSI pretreatment systems. No biological organisms were detected by plate count, and no bio growth was found in either system during the study.

Scale Control and Heat Transfer — Water temperatures for the closed cooling water

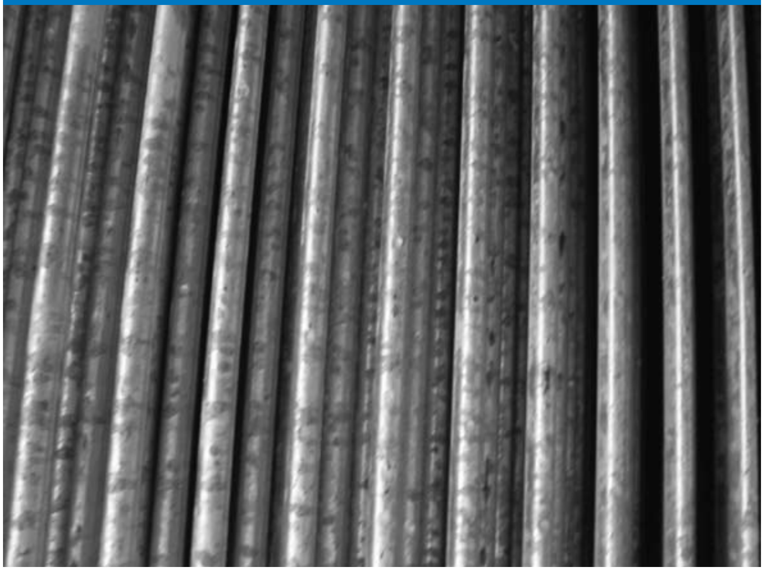
Table 2

EC 10 Tower Water Chemistry

Sample/Tests	Tower	Soft makeup	COC
TDS	62,500	250	250
pH	10.00	7.58	
Copper (mg/l Cu)	ND	ND	
Zinc (mg/l)	ND	ND	
Silica (mg/l SiO_2)	640	27.6	23
Calcium (mg/l $CaCO_3$)	19.3	< 0.1	
Magnesium (mg/l $CaCO_3$)	12.5	< 0.1	
Iron (mg/l Fe)	ND	ND	
Aluminum (mg/l Al)	ND	ND	
Sodium (mg/l Na)	27,840	120	232
Sulfate (mg/l SO_4)	4,375	19	230
Chloride (mg/l)	903	3.8	238
Total alkalinity (mg/l $CaCO_3$)	32,500	140	232

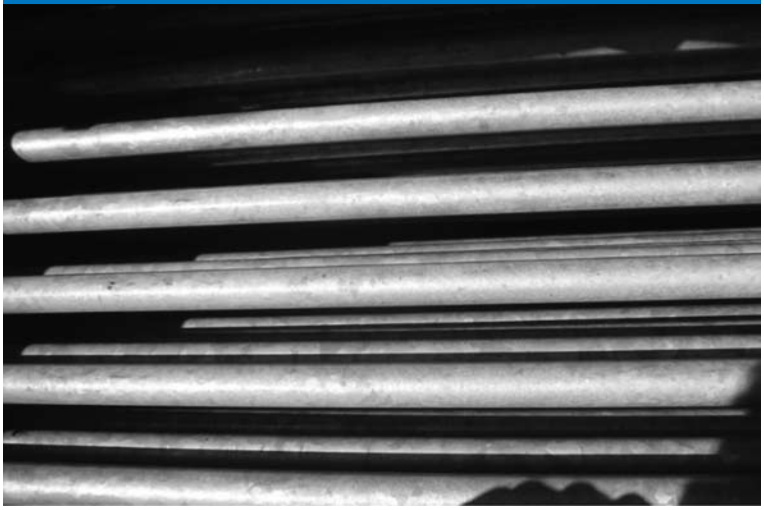
ND = Not detected, COC = Concentration of soft makeup chemistry.

Figure 2



EC West galvanized tubes.

Figure 3



EC 10 galvanized tubes.

Figure 4

#1652 CS exposed 61 days (0.017 mpy), #1664 CS (control, 0.013 mpy).

Figure 5

#283 GS exposed 60 days (bottom), and #282 GS (control) (top).

loops have operated at design conditions since start-up of the new evaporative condensers, and air compressor maintenance requirements on this equipment have been reduced to expected levels. Inspection of the galvanized tube bundles on both the EC West and EC 10 towers after six months of operation on ZLD showed no scale deposition. Galvanized tube surface appearance was comparable to their condition when installed, and had experienced no white rust (Figures 2–3). The EC 10 unit ran at the highest closed-loop operating water temperature of 105°F, with a 28°F temperature drop across the tube bundle. It also ran at the highest chemical concentration (250 COC) at 62,500 TDS.

Corrosion Protection — Carbon steel corrosion rates of < 0.020 mpy were measured by weight loss analysis on 61-day coupon exposure, showing only slight color variation from an unexposed (control) coupon (Figure 4). Both coupons were cleaned and weighed using ASTM standards G-4-01 and G1-03. Galvanized coupons were also installed, with 60-day exposed and unexposed coupons for visual comparison only (Figure 5), since the acid cleaning procedure for weight loss measurement strips the galvanized film from the coupon. With outstanding corrrosion protection of steel with this technology, use of galvanized surface tube bundles is not necessary, and provides opportunity for lower equipment cost for this type of cooling service.

Wastewater Discharge Reduction — The EC West and EC 10 systems were able to reduce (eliminate) blowdown discharge by 534,000 and 330,000 gpy, respectively, and now produce less than 9,000 and 5,000 gpy from respective softener regeneration wastewater. This reduces the necessity for daily waste haul pickups from each tower location's collection point to less than once per month from this source. CSI owns and operates its own 1,250 gallon waste haul truck, so the internal cost benefit will not be disclosed.

TDS Buildup on Drift Eliminators — Evaporative TDS (dissolved salts) buildup on drift eliminators is normal for most towers, but is accelerated by the higher TDS concentration in the tower water with ZLD. However, these ZLD salts are highly soluble, since hardness has been removed from the source water, and they are easily washed back into the tower system. This buildup may be insignificant in some tower designs, as it was with the BAC counterflow tower, while aesthetically undesirable in others. Significant buildup was experienced with the Evapco cross-flow tower due to the tendency for tower basin water to splash onto the side eliminators. This was intially manged with periodic pressure wash with soft water supply, but later with installation of low-volume soft water misting sprays outside the eliminators. The mister operation was tied to fan operation and a timer to maximize spray water capture in the tower basin and to limit makeup contribution.

ROI from water conservation, wastewater discharge reduction and improved system performance is provided by control of scale, corrosion and biological issues with this technology. It presents new solutions for corrosion, scale and biological limitations that impact cooling water equipment energy efficiency mangement, maintenance, replacement costs, and process operational reliability.

Other Corrosion Studies

Electrochemical corrosion studies were performed to evaluate how silica inhibitor chemistry would perform at elevated temperatures with various metals.[6] Testing was performed at temperatures of 77, 130, 160 and 190°F (25–88°C) with tower water test chemistry of 50,000 TDS, 9,000 chloride, 450 silica and pH 10. The independent study was conducted by Corr Instruments using real-time coupled multi-electrode array corrosion probes which also accurately measure localized (pitting) as well as general corrosion rates.[7–8] The metals tested were carbon steel 1008, 316L SS, aluminum 1100, copper 1100 and zinc. Control testing was conducted with a 0.5 normal solution of sea salt (25,000 TDS) without silica chemistry.

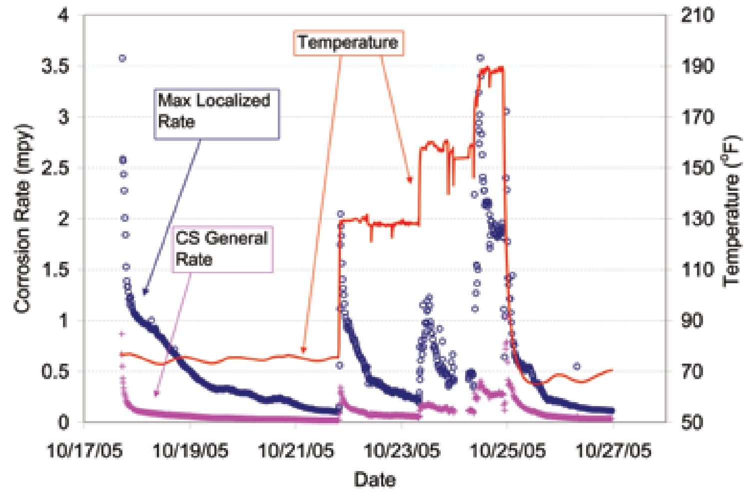
Figures 6 and 7 show the results of the evaluations with carbon steel and aluminum. Corrosion was mitigated to very low levels at each of the temperatures in the study for all metals. Carbon steel corrosion rates are comparable to those expected for stainless steel. Aluminum, which is amphoteric and soluble at pH 10, showed very low corrosion at all temperatures. The localized (pitting) corrosion was equally mitigated with all metals (pitting is normally 10–40X general corrosion rates). Table 3 summarizes results for all metals tested with silica inhibitor chemistry and non-inhibited control results.

The study results in Table 3 indicate that all these metal types and their various alloys commonly utilized in cooling water contact applications are well-protected by silica chemistry at higher water temperatures and high TDS. Thus, lower-cost alternatives for heat transfer metal selection are available with use of this corrosion inhibitor chemistry.

Summary

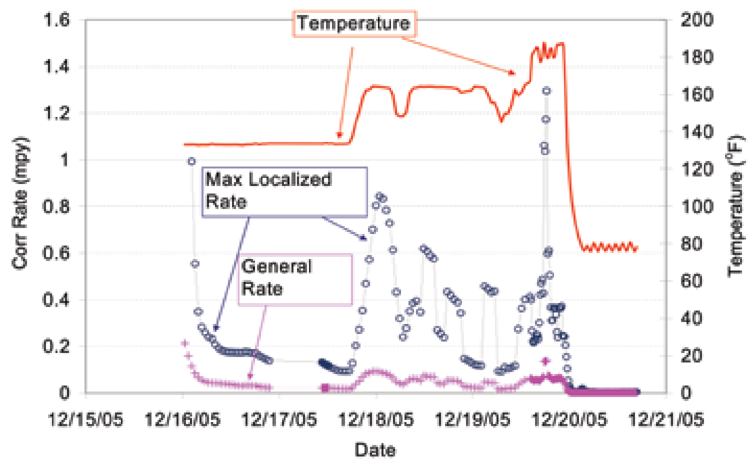
Averting the discharge handling costs for cooling tower blowdown was CSI's principal justification for implementing ZLD in these systems. However, other benefits included improved performance and reliability of the air compressor equipment, reduced tower fan operation (from improved heat transfer), and reduced operator maintenance. Eliminating chemical storage, handling and discharge was also beneficial from the environmental and safety perspective. Most significant is that the cost savings and system performance from this new approach did not have to be at the expense of water conservation or environmental protection. The ZLD approach will facilitate additional opportunities to manage water use and wastewater challenges, while also addressing scale and corrosion performance issues. Three additional cooling tower systems have been converted to ZLD at CSI since this study was undertaken.

Figure 6



Localized and general corrosion rates of carbon steel 1008 in high-TDS/high-silica water.

Figure 7



Localized and general corrosion rates of aluminum 1100 in high-silica/high-TDS water.

Table 3

The Effect of Silica and Temperature on Corrosion Rates in High-TDS Waters

Metals	Inhibitor/solution	Temp (°F)	Temp (°C)	General (mpy)	Max. loc. (mpy)
CS 1008	Sea salt	77	25	—	60
CS 1008	Silica	77	25	0.02	0.1
CS 1008	Silica	130	55	0.1	0.2
CS 1008	Silica	160	71	0.2	0.4
CS 1008	Silica	190	88	0.2	1.9
SS 316 L	Sea salt	77	25	—	0.04
SS 316 L	Silica	77	25	< 0.0015	< 0.005
SS 316 L	Silica	130	55	< 0.01	< 0.01
SS 316 L	Silica	160	71	< 0.01	< 0.01
SS 316 L	Silica	190	88	< 0.01	0.013
AL 1100	Sea salt	77	25	—	20
AL 1100	Silica	77	25	< 0.05	< 0.1
AL 1100	Silica	130	55	0.002	0.009
AL 1100	Silica	160	71	< 0.05	0.2
AL 1100	Silica	190	88	< 0.060	0.37
Zn	Sea salt	77	25	8	80
Zn	Silica	77	25	< 0.05	< 0.01
Zn	Silica	130	55	< 0.2	0.4
Zn	Silica	160	71	—	2.0
CU 110	Sea salt	77	25	—	0.4
CU 110	Silica	77	25	< 0.05	< 0.2
CU 110	Silica	130	55	< 1.0	3.0
CU 110	Silica	160	71	—	4.0

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