### **IWC REPORT 07-11**

# ZLD: New Silica Based Inhibitor Chemistry Permits Cost Effective Water Conservation for HVAC and Industrial Cooling Towers

Dan Duke, Water Conservation Technology International, Temecula, CA

#### **KEY WORDS**

ZLD, Zero Liquid Discharge, High TDS, Reuse Water, Grey Water, Water Conservation, Cooling Towers, HVAC, Silica Chemistry, Corrosion Inhibitor, Scale Inhibitor, Pretreatment Softening, Biostatic Chemistry, "Green Chemistry"

### ABSTRACT

Zero liquid discharge (ZLD) approaches for cooling towers have existed for decades; but capital and operating cost generally made them impractical. New "green" chemistry now makes ZLD operation highly economical for small HVAC to heavy industrial tower systems. This new ZLD enabling process uses pretreatment removal of hardness to eliminate scale formation, and provides silica corrosion inhibitor chemistry to protect metals from corrosion at high total dissolved solids (TDS). Silica chemistry can be used with municipal or other water sources that can be softened by pre-treatment. The patented corrosion and scale inhibitor chemistry is particularly effective for waters that contain high levels of hardness, silica, chloride, TDS and soluble organics. Reuse or reclaim waste waters that contain soluble phosphate, organics and ammonia can also be used without corrosion, and biological proliferation is impeded by natural high pH and TDS chemistry.

Silica corrosion inhibition chemistry protects all metals typically used in cooling water, including carbon steel, galvanized steel, and the various alloys of stainless steel, copper, and aluminum. Use of simple, salt efficient pretreatment equipment design permits even small cooling towers to be treated very cost effectively and reliably. Treatment costs are lowered by elimination of tower water wastage required with existing water treatment technologies, without sacrificing corrosion or scale protection. Corrosion rates are less than 0.1 mpy for all metals. This report presents results of case studies from a number of ongoing applications in HVAC and industrial cooling towers and reviews the respective source water qualities, tower water chemistries and system metallurgy evaluated.

#### **EXISTING ZLD TECHNOLOGY**

Cooling tower water concentrations are limited to a maximum concentration of TDS that is dependent upon the quantity of multivalent metal ions and other ions in the makeup water that cause scale deposition. Generally, these limiting low solubility ions are calcium, magnesium, alkalinity and silica. Other common ions found in source waters, such as sodium, chloride and sulfate are highly soluble in the absence of calcium and magnesium. Various scale inhibitors, pH reduction and pretreatment softening are used to control scaling at higher tower water concentration. However, water corrosiveness increases as a result of rising TDS concentrations and rising chloride and sulfate concentrations. Typically, most cooling tower blowdown (CTBD) is controlled at maximum concentrations from 1000 to 5000 mg/L TDS, and is dependent on the ratio of TDS to the total calcium, alkalinity or silica content of the water.

Normally, to attain ZLD with these lower TDS levels in the CTBD, several stages of water treatment are required to concentrate TDS and recover water before ZLD or dry solids is achieved. Due to the insolubility of salts of multivalent metal ions in the tower water, cooling tower blowdown water must be treated using precipitation softening (PS), ion exchange softening (IES) or inhibitor chemicals to avoid scaling when concentrating blowdown in water recovery systems such as brine concentrators (BC), reverse osmosis (RO) or crystallizers (CR) that ultimately must concentrate the TDS to approved disposable quantities of concentrate or dry salts. Other concentration approaches such as evaporation lagoons or drying beds have also been employed where space, land use cost or environmental restrictions are not prohibitive.

Accordingly, the design and size of each stage will be proportional to the volume of CTBD to be processed and the concentration ratio of TDS to water (% TDS). Typically, the large capital investment, operating and maintenance labor costs, chemical costs and the very significant energy costs have made such ZLD processes only affordable or attractive when there was no option. Accordingly, power producers and co-generation facilities are commonly the only end users that can afford the energy costs. Thus, any technology that can significantly reduce ZLD capital and operating cost, energy consumption, and operating complexity can provide significant incentives for investment in water conservation through expanded ZLD applications.

Excellent discussions of the complexities in selection and design, redundancy for reliability, and operating complexities of such ZLD systems have been presented by others in prior IWC conference reports <sup>1</sup>.

### NEW ZLD TECHNOLOGY

Existing scale and corrosion technology has limited concentration of cooling tower water, and obviously impacts capital and operating costs for ZLD application. New scale and corrosion control technology, applied and developed over the past four years, now permits operation of cooling tower water at significantly higher TDS levels without scale or corrosion limitations.

Prior water treatment methods were generally limited by dependence on calcium concentrations for corrosion control, and management of scale and corrosion indexes such as Langelier Stability Index (LSI) or Ryznar Stability Index (RSI) to avoid scale while also limiting corrosion. These methods were also limited by the solubility of silica in the presence of calcium and other multivalent metal ions. Accordingly, both calcium and silica were controlled by blowdown, which provides relatively low TDS concentrations in cooling tower water. These higher rates of cooling tower blowdown significantly increase the investment in equipment and operating cost required to concentrate and recover CTBD water to achieve ZLD, and at much greater cost than the value of the recovered water. Thus, only those with limited water resources or regulatory mandates would pursue ZLD for water conservation.

In contrast, this new ZLD enabling process has generally eliminated or minimized discharge issues in HVAC and industrial sites. Smaller applications can generally discharge the small volumes of softener regeneration waste to municipal sewers. Some municipalities have given rebates toward payment for the pretreatment equipment and installation in support of water conservation. However, the cost for this equipment is generally recovered in less than 12 months by cost savings from reduced water consumption and sewer discharge fees. Some applications may have access to municipal brine discharge lines or use internal solids waste disposal options for the pretreatment of regeneration waste. The water treatment supplier program service costs for this program are comparable to chemical treatment, but ongoing water cost savings reduce overall treatment cost by as much as 50%.

Most of the ZLD cooling tower applications for this method are operating at TDS concentrations from 10,000 to 60,000 mg/L, although one system has been operated at 146,000 TDS. None of the systems have experienced corrosion of metal surfaces employed in heat transfer or water transport, nor have they experienced scaling or loss of heat transfer at these high TDS concentrations. System metals have included mild steel, copper, 316SS, 304SS and galvanized coatings. White rust on galvanized coatings has also been mitigated. The most commonly used cross flow and counter flow designs for cooling towers have been successfully treated with this ZLD technology. The following two application case histories illustrate water chemistry, corrosion evaluations and equipment inspections typical of treated systems. These applications and other applications which have been in service for over four years are operating without scaling. Corrosion rates in all systems have consistently been less that 0.2 mpy for mild steel and less than 0.1 mpy for copper by weight loss analysis.

### **ZLD APPLICATION CASE HISTORIES**

**STEEL MILL -** This site installed new closed circuit evaporative coolers to provide secondary cooling of closed cooling loops for air compressor equipment. Use of a zero liquid discharge approach for cooling tower water treatment allowed the mill to avert either significant wastewater hauling costs or capital cost investment to install a wastewater discharge collection system.

One location installed a cross flow cooling tower to cool the closed coolant loop supporting three air compressors (two 1250 cfm and one 1600 cfm). The second location installed a counter flow cooling tower to cool the closed coolant loop supporting a single air compressor (1600 cfm). Both towers were constructed with galvanized tube bundles and galvanized housing. The cross flow tower included a 304 SS basin.

The typical operating temperature drop across the tube bundle in the cross flow tower ranged from 5° to 15° F with a 340 GPM evaporative cooling water circulating flow, and a one to two operational air compressor load. The average temperature drop across the tube bundle in the counter flow tower ranged from 24° to 28° F with a 115 GPM evaporative cooling water circulating flow, with the operational load of a single air compressor. Prior to replacement of these two cooling tower systems, elevated temperatures in the primary cooling loop (closed loop) caused air compressors to experience high temperature trip outs and frequent seal failures from overheating. Scaled evaporative condenser tube bundles in the old (same model) cooling towers caused closed loop cooling water temperatures to operate 10° to 20° F higher than design operating conditions. The dissolved mineral content of the source makeup water presented significant scaling potential from both hardness and silica, and

significant corrosion due to total dissolved solids (TDS). Traditional chemical treatment required blowdown of 30 to 40% of makeup water to avoid concentration of hardness toward scale forming water chemistry.

Both of these evaporative cooling systems have operated on ZLD over the last twelve months with TDS concentrations between 25,000 and 146,000 (1 to 5 times that of seawater). Typical soft makeup and cooling tower water chemistry analyses for one of the cooling towers provided in Table I show the chemistry of concentration (COC) of the principal ions produced from 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 silica into higher molecular weight polymeric or colloidal forms not measured by the acid molybdate test which only measures soluble silica monomer. Some excess silica may also be precipitated.

Tower - Concentration of Chemistry (COC) Ratios						
SAMPLE / TESTS Tower Soft MU C						
TDS, mg/L (NaCl Myron L 6P reference)	146,000 251		582			
рН	10.1	7.58				
Copper, mg/L Cu	0.7	0.0015				
Iron, mg/L Fe	ND	ND				
Zinc, mg/L Zn	ND	ND				
Silica, mg/L SiO <sub>2</sub>	1,250	30	42			
Calcium, mg/L CaCO <sub>3</sub>	62	<0.1				
Magnesium, mg/L CaCO <sub>3</sub>	16	<0.1				
Nitrate, mg/L NO <sub>3</sub>	2590	4.5				
Sodium, mg/L Na	145,000	250	580			
Sulfate, mg/L SO <sub>4</sub>	10,260	18	570			
Chloride, mg/L NaCl	22,400 38		589			
Tot. Alkalinity, mg/L CaCO <sub>3</sub> 69,400 120 578						
ND = Not Detected; COC = Concentration of Soft Makeup Chemistry						

Table	I – Steel	Mill Tower	Water	Chemistry	
IUNIC			vvalor		

Calcium hardness was controlled below 62 mg/L in this tower water, even at 582 COC of source water. Soft makeup water quality 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 water quality and reliability. Hardness leakage or upsets in pretreatment necessitate blowdown to lower hardness levels to avert hardness and silica precipitation.

<u>Biological Control</u>: No biological organisms were detected by plate count, and no bio growth was found in either system during the study. Such results have been consistent over four years of testing in other ZLD systems treated with this process when higher levels of pH and TDS were maintained. The following summary of the biostatic effects of pH and TDS on biological organisms was provided in a report prepared by Anderson Engineering <sup>2</sup> (full report available from reference website download).

"Bacteria, Viruses, and Spores have critical portions of their structure made up from polymers of various acids, especially the 20 fundamental amino acids of protein chemistry, or the analogous nucleotide bases in RNA and DNA. These biological species all rely upon a stable evironment of pH and salinity for their healthy existence. Once the pH of a water gets above pH 9.6, it is statistically highly improbable that any organism/spore/virus will have a peptide chain without at least some of the bonds being at sites which will have hydrolyzed. Increasing the pH to 9.7 virtually guarantees this effect, and it is common practice in sterilizing fermentation vessels to use a cleaning solution at pH 10 to ensure the removal of protein residues from the surfaces being cleaned".

"The second aspect of interest is the role of dissolved solids or TDS. Dissolved solids are now ionic species, and can affect the salinity of the water. Where this appears to affect the biological activity of spores and cells is by denaturing various proteins (enzymes) required for reproduction, rendering the water biostatic. Therefore, high TDS waters should be biostatic to animal pathogens. The exact value varies by pathogen species".

"When the pH is greater than 9.7 and TDS values exceed 40,000 ppm, biological activity would be expected to be blocked. Some especially hardy species may survive in a dormant state, and could be brought back to an active state when samples are withdrawn and diluted for laboratory analysis." <u>Scale Control and Heat Transfer</u>; Water temperatures for the closed cooling water loops are now operating at design conditions since startup of the new evaporative condensers on ZLD. Air compressor maintenance requirements on this equipment were reduced to expected levels. After twelve months operation on ZLD, inspection of the galvanized tube bundles in both towers showed no scale deposition. Galvanized tube surface appearance is comparable to their condition when installed, and the galvanized surfaces did not experience white rust (figures I & II). The highest closed loop operating water temperature was of 105°F, with a 28°F temperature drop across the tube bundle. This tower also ran at the highest water concentration (582 COC) at 146,000 TDS.



Figure I – Cross Flow Tower Galvanized Tube Bundle

Figure II - Counter Flow Tower Galvanized Tube Bundle



<u>Corrosion Protection</u>; Carbon steel net corrosion rate of 0.004 mpy was measured by weight loss analysis on 61 day coupon exposure (#1652), showing only slight color variation from an unexposed (control #1664) coupon (Figure III). Both coupons were cleaned and weighed using ASTM Standards G-4-01 and G1-03. A galvanized coupon was also installed, with 60 day exposure for visual inspection only (Figure IV), since the ASTM weight loss procedure would strip the galvanized film from the coupon. Outstanding corrrosion protection of steel with this technology eliminates the need for galvanized surface tube bundles, and provides opportunity for lower equipment cost for this type of cooling service.

Figure III - # 1652 MS exposed 61 days (0.017 mpy), # 1664 MS (control, 0.013 mpy)



Figure IV – Galvanized Coupon # 234 exposed 60 days.



<u>Wastewater Discharge Reduction</u>; Blowdown discharge was eliminated from both tower systems, and now produce less than 9,000 and 5,000 GPY (gallons per year) from respective softener regeneration waste water. This reduction in total tower discharge eliminated potential daily waste haul pickups resulting from the prior 30-40% blowdown (% of total makeup water lost as blowdown) from each tower location's collection point. Currently, waste pickups are less than once per month. Three additional systems have been converted to this ZLD approach since implementation of the first two towers, and the site expects to convert at least 10 systems to ZLD.

**CENTRAL COOLING AND HEATING PLANT** - This college facilty operates adsorbers and high temperature boiler equipment for year round centralized comfort cooling and heating of the campus. The adsorber equipment had an extended history of both scaling and excessive corrosion while treated by various chemical water treatment programs that included pH adjustment. The cooling tower is an atypical design, in that it does not have settling retention (V-bottom basin) to capture suspended solids in the circulating water, and the basin is a concrete structure. It was suspected that use of acid for pH control to prevent scale formation may have contributed to calcium scale deposits in adsorber tubes by removing calcium from the concrete tower basin, and also to excessive corrosion of steel surfaces (5 to 10 mpy by weight loss).

The main objective was to eliminate both scaling and corrosion conditions using the ZLD approach. Water conservation was an additional desired benefit. The facility is also considering use of municipal reclaim wastewater for makeup if the ZLD approach provides desired scale deposition and corrosion protection using current potable water makeup.

Initial results have shown a reduction in mild steel corrosion to 0.109 mpy (figure V) by weight loss coupon analysis #1683 with 83 day exposure. Inspection of two condensers has shown no scale depositon and improved cleanliness of the tubes in less than six months on the ZLD program. Current ZLD water chemistry is concentrating to 40,000 mg/L TDS and pH 9.8, with 5000 mg/L chloride and approximately 70 concentrations (COC) of the softened makeup water.

Figure V – MS #1683, 83 day exposure, 0.019 mpy, slight corrosion at coupon mount.



ZLD WATER SAVINGS AND EQUIPMENT ECONOMICS

**SMALL TOWER ZLD SYSTEMS WITH MUNICIPAL DISCHARGE OPTIONS** – Examples of capital cost, operating cost (for regeneration) and blowdown savings with this ZLD makeup pretreatment approach are provided in Table II for average evaporative makeup water usage from 4 to 140 gpm. The operating cost and water savings examples provided in Table 2 are based on 10 to 15 grains per gallon (170 to 257 mg/L as CaCO<sub>3</sub>) of hardness in the source water, but blowdown rates with traditional chemical inhibitor programs are also dependent on silica and TDS content. Thus, typical blowdown rates at 40%, 33% and 25% of the total makeup water requirement are provided. Reduced regenerate operating costs for the higher flow volume applications assume installation of bulk brine storage silo, with estimated installed cost of \$15,000 in additional capital investment\*.

	Table II Examples of ZED Gapital and Operating Cost, with Net DD Water Gavings							
Peak Flow	Avg.	Estimated	Operating Cost	Example BD Cost Savings				
gpm MU	gpm	Installed Cost	Regeneration	Net \$/Year @ \$3.00/1000 gal				
Unit Size	MU	Dual Unit	\$/1000 gal MU	water use and discharge cost				
				40% BD		25% BD		
7	4	\$3500	\$0.22	\$3100	\$2150	\$1200		
15	10	\$7300	\$0.22	\$7800	\$5400	\$3000		
23	15	\$9500	\$0.22	\$11600	\$8100	\$4500		
38	25	\$13200	\$0.22	\$19000	\$13500	\$7500		
59	40	\$19000	\$0.15	\$34000	\$24000	\$14000		
90	60	\$28000	\$0.15	\$50000	\$36000	\$26250		
115	75	\$36000	\$0.07*	\$66000	\$48000	\$30000		
150	100	\$48000	\$0.07*	\$88000	\$64000	\$40000		
210	140	\$68000	\$0.07*	\$125000	\$90000	\$56000		

Table II - Examples of ZLD Capital and Operating Cost, with Net BD Water Savings

The examples are based on use of high regenerate efficiency design for pretreatment softening which reduces salt use by as much as 50% over traditional equipment designs, while still providing polished water quality (low leakage). The design permits salt usage of 4 pounds per cubic foot (CF) of resin for most water qualities, as compared to 10 to 12 pounds per CF required to attain low leakage with conventional designs. This equipment design also reduces regenerate waste water volume by 70% versus applications with conventional equipment.

Weak acid cation (WAC) resin may be more cost effective than sodium cycle exchange resin for hardness removal with high TDS source water quality, and when use of acid and caustic regenerates are not objectionable. However, two stage regeneration of the WAC to the sodium form or degasification and neutralization are needed before reintroduction as makeup to the tower to avert localized (low pH) silica precipitation. The WAC reduction of carbonate alkalinity is not beneficial since caustic use will be required to control pH in the desired range, and carbonate will reform when caustic is added to carbon dioxide scrubbed from the air during circulation.

**POWER GENERATION TOWER ZLD WITHOUT DISCHARGE OPTIONS** – Application of this technology in larger cooling tower systems such as Power Generation may enable significant benefits in capital and operating cost reduction for ZLD application, where higher tower water TDS operation can be permitted in compliance with drift limits. Depending on source water quality and permitting requirements, the cost for ZLD processes may approach 10% of the total capital cost for a power generation facility and 15% of the operating expense. These higher costs produce significantly higher power rates that are passed on to consumer.

Field experience with one specific forced draft counter flow cooling tower indicates that drift control, and the related impact of TDS salts may be very manageable with existing designs. This system has operated above 145,000 TDS in the cooling water and over 580 concentrations of the TDS content of the makeup water. The TDS material balance (and other ions) demonstrates a maximum of 0.0017 (0.17 %) of the TDS introduced to the tower are lost through drift or precipitation in the tower water. This operating experience demonstrates that high TDS levels are maintainable in cooling towers with this treatment process without precipitation or scale formation. The data also verifies tower manufacturer published drift control rates. Drift discharge concerns related to VOC and organic toxicant emissions may be eliminated because no organic chemical treatment additives are generally used.

Use of staged <sup>3</sup> (cascaded) cooling towers to concentrate tower water to higher TDS has been successfully applied and permitted for attainment of ZLD operation. Retro fitting towers to more efficient drift control or addition of smaller towers with drift efficient design for staged concentration could enable such operations to use auxiliary system waste heat to concentrate tower water to greater TDS concentrations prior to blowdown. Drift discharge permitting is a complex process as reported by Micheletti <sup>4</sup>, but he illustrates that the EPA appears to apply extremely conservative assumptions (10 to 40 times greater drift loss) to set limits for maximum TDS in cooling towers to avert potential PM10 and PM2.5 particle inhalation risks.

A report generated by Anderson Engineering <sup>5</sup> makes the following points relative to cooling tower drift; "It is extremely difficult to produce PM10 or PM2.5 size particles even when using pressurized atomization in commercial processes. It is even less probable that relative low velocity induced air flow that entrains tower water droplets (drift) can produce small enough droplets to form this size of dry particles. Higher saturation of TDS salts in the water also results in formation of larger particles when droplets dry. Since the salts formed in tower water with this softened makeup process will be paired with sodium, they will also be highly soluble in the event of inhalation contact. The silica concentrated by the process in the tower water is in the amorphous form, which is not subject to formation of crystalline forms of silica found in materials like asbestos".

Permitting increased TDS levels with use of this treatment method in cooling towers may provide greater incentive for implementing ZLD applications that conserve water by minimizing unnecessary operating expenses and energy consumption required by current ZLD processes that also indirectly increase emissions to the environment. Modification of existing ZLD approaches can reduce complexity of operation, capital costs, operating costs and provide significant reduction in internal energy consumption used with current ZLD equipment options. For example, brine concentrators typically require 80-100 KWH energy per 1000 gallons of distillate recovery, while crystallizers typically require 250-350 KWH energy per 1000 gallons of distillate recovery. Eliminating or reducing the size of brine concentrators, reverse osmosis concentrators, crystallizers and other energy consuming systems could be accomplished by using cooling towers and existing process waste heat.

The ZLD example below is for a 500 MW power generating unit with evaporative load demand of 2400 GPM makeup. The example makeup quality is 500 TDS with 200 mg/L (as CaCO<sub>3</sub>) calcium hardness, and blow down of 20% of MU (5 COC). Use of acid / pH control or other treatment alternatives could increase COC moderately and reduce BD, but utilities generally want to avoid scale or acid corrosion risk. The following tower water concentration scenarios are presented;

<u>CTBD-A</u> Chemical inhibitor treatment of tower water (current methods), with cooling tower blowdown going to first step chemical precipitation softening, second step either brine concentrator or RO (reverse osmosis) and final step crystallizer or evaporative ponds.

<u>CTBD-B</u> lon exchange pretreatment softening of makeup water (and filtration of suspended solids when using raw surface water), with either sodium cycle or WAC regenerated to sodium form, and use of silica inhibitor technology with tower water TDS limit of 10,000 (20 COC in this example). The cooling tower blowdown would then go directly to a smaller brine concentrator and then to a crystallizer.

<u>CTBD-C</u> Same as above, except 40,000 TDS (80 COC) limit in tower water, but elimination of the brine concentrator with cooling tower blowdown direct to a crystallizer. May require staged cooling towers. <u>CTBD-D</u> Same as above, except 140,000 TDS (280 COC) limit for tower water, with cooling tower blowdown direct to crystallizer. May require staged cooling towers.

Table III provides an example of cooling tower evaporative makeup (EMU), total makeup (TMU) and various cooling tower blowdown (CTBD) flows and TDS levels that would be handled by the respective ZLD system options. Either tower blowdown ion exchange softening or makeup pretreatment ion exchange softening would produce regeneration brine waste (RBW) flow with estimated 60,000 TDS that would need to be processed in the crystallizer.

	TDS	Ca	COC	EMU	CTBD	TMU	RBW	PS/IE/RO	CR
		(CaCO3)		GPM	GPM	GPM	GPM	or BC GPM	GPM
MU	500	200							
CTBD-A	2500	1000	5	2400	600	3000	5	600	20
CTBD-B	10000	<30	20	2400	125	2525	15	125	25
CTBD-C	40000	<50	80	2400	31	2431	15	-	46
CTBD-D	145000	<100	290	2400	8	2408	15	-	23

#### Table III – Makeup and Blowdown TDS and Flow to ZLD Treatment Systems

Table IV provides installed capital and operating cost estimates for respective cooling tower blowdown concentrating systems required. Systems included are precipitation softening (PS), ion exchange softening (IES), reverse osmosis (RO), brine concentrator (BC) and crystallizer (CR). Noted IES\* costs for CTBD-B, CTBD-C and CTBD-D are based on pre-treatment of the example makeup water volume and hardness. These cost figures are approximations from several previous projects and designs, rather than application specific quotes. Operating costs include energy, chemicals, parts, maintenance and consumables.

	TDS	\$(000)	PS	IES	RO	BC	CR	Total (RO* / BC**)
CTBD-A	2,500	Installed Capital Cost	2200	300	2000	14400	5000	9500* - 21600**
		Operating Cost/Yr	750	50	1700	2000	1000	3500* - 3750**
CTBD-B	10,000	Installed Capital Cost	-	800*	-	6000	5000	11800
		Operating Cost/Yr	-	150*	-	900	1000	2050
CTBD-C	40,000	Installed Capital Cost	-	800*	-	-	7000	7800
		Operating Cost/Yr	-	150*	-	-	1300	1450
CTBD-D	145,000	Installed Capital Cost	-	800*	-	-	5000	5800
		Operating Cost/Yr	-	150*	-	-	1000	1150

#### Table IV – ZLD Installed Capital Cost and Operating Cost Estimates

Operating cooling towers at 40,000 mg/I TDS or higher in this example would provide maximum capital and operating cost savings in this power generation ZLD example by eliminating the need for blowdown recovery and concentration equipment (either PS/IE/RO or PS/BC) prior to the crystallizer. More significantly, ZLD operating cost could be reduced by 60% to 70% over existing approaches. Energy usage would be the largest portion of the operating cost reduction.

## SILICA CHEMISTRY / HIGH TEMPERATURE CORROSION STUDIES

A detailed discussion of the scale and corrosion inhibitor chemistry utilized in this ZLD process is beyond the scope of this paper, but prior technical publications and reports at NACE <sup>6</sup> and AIST <sup>7</sup> conferences during 2007 will provide information in this area to those who are interested. Four US published patents <sup>8</sup> also provide details of the inhibition process and mechanisms.

Although operating system results have consistently provided exceptional corrosion results for mild steel and copper over four years in numerous applications, most systems do not provide opportunity to evaluate extremes of temperature or alternative metals that might desirably be used in system heat transfer surface design and construction. Thus, we subjected this chemistry to corrosion inhibition performance studies with multiple metals under high temperature extremes (77° F to 190° F) in high TDS tower water inhibited by silica chemistry.

The lab studies were independently conducted by Lie Yang, Ph.D.<sup>6</sup> using coupled multi array sensors (CMAS) with real time monitoring. Measuring inhibitor efficacy for control of localized (pitting) corrosion is a particular strength of the CMAS corrosion measurement technology. The results of this study indicated excellent

inhibition of all metals (MS, Cu, Al, Zn, 316SS) at high temperature extremes. These results predict that lower cost metals can be used for fabrication in high temperature applications in place of more expensive alloys relative to water side temperature conditions. Study details are covered in the NACE 2007 conference publication <sup>6</sup>.

### **GREY WATER RECLAIM / REUSE APPLICATION STUDY**

A field study is currently being conducted using municipal sewage reclaim water as cooling tower makeup in an industrial manufacturing central cooling and heating facility that operates absorber and centrifugal chiller equipment. The major issues with use of municipal waste water in such applications are the aggressiveness of the ammonia content to copper and its alloys, deposition of calcium phosphate from the high phosphate content and significant biological proliferation resulting from these two nutrients.

The ZLD / silica treatment chemistry presents excellent potential to provide superior corrosion, scale and biostatic control to permit reuse of this lower quality water source where other treatment approaches have had poor performance or proven economically ineffective due to high blowdown rates and excessive chemical treatment cost. Preliminary laboratory studies were conducted with ZLD water containing ammonia, and method results were excellent. Further results of additional lab studies and results in the operating system application are expected to be available within a few months.

### SUMMARY OF ZLD BENEFITS AND LIMITATIONS

This new water treatment technology essentially eliminates the traditional scale, corrosion and biological issues that have limited cooling system operations, and provides new opportunities for water, energy and environmental conservation. Any new approach will have acceptance challenges, especially one that is counter to prior experience or beliefs. We can minimize performance problems and blowdown, but we also have to deal with aesthetics. Towers were designed to operate with low TDS water, and some already experience drift eliminator salt buildup at low concentrations. Drift salt buildup increases as TDS concentrations increase. These sodium salts are easily removed, whereas calcium salts formed with traditional water treatments are difficult to remove. We have successfully applied low volume misting sprays using soft water to intermittently rinse the salts back into the tower water with one problematic tower design.

Tower external wet / dry contact surfaces would also be better suited if made from stainless steel and plastic, to avoid the impact that drift or leaks have on galvanic coatings. ZLD may not be suitable for a roof location directly over a parking lot. However, this technology does not require control of every system at ZLD to get the performance and water conservation benefits. Operating at lower levels of TDS such as 5,000 to 10,000 mg/L (low from our perspective) will still reduce water wastage by 80 to 95% in most applications. With acceptance of performance and conservation benefits, and as water conservation becomes increasingly critical, cooling tower designs and materials of construction will necessarily adapt to what is best for the end user operator and their community. We believe this technology can play an important role for most cooling tower applications, particularly where reducing water usage and discharge are important.

This technology is licensed for application through various water treatment professionals, consultants, engineering contractors and their service organizations to insure proper implementation and performance are maintained. Based on many years of experience in the water treatment industry, it is our conviction that any water treatment technology requires independent assessment and intervention by outside service professionals to ensure success and continued performance. These same professionals also serve related applications in boiler, closed system, process and waste water treatment. Our mission is to focus on continuing research and development to support application of this technology, and dissemination of information through professional organization reports and publications.

### ACKNOWLEDGEMENTS

We appreciate the access to customer application information provided by licensed applicators of this technology to permit presentation of this information to IWC.

### REFERENCES

- 1. ZLD Papers; IWC-05-07, IWC-05-08, IWC-05-08D, IWC-05-09, IWC-06-11, IWC-06-13, IWC-98-27, and Chris Brew, "Ten Years of 'Real Life' Operational Experience of a Zero Discharge Power Plant in Florida", Power Generation, December, 1991.
- Anderson, E., "Project Report PR-WCTI-2007-1: Preliminary Review of the Effects of pH and TDS on Bacteria, Viruses, and Spores in Water", Anderson Engineering, http://www.water-cti.com/publishedpapers.html.
- 3. Staged Cooling / ZLD Papers, CTI TP88-02, CTI TP80-10.
- 4. Michelitti, W. C., "Atmospheric Emissions From Power Plant Cooling Towers", 25th Annual Electric Utility Chemistry Workshop, University of Illinois, 2005.
- Anderson, E., "Project Report PR-WCTI-2007-2: Preliminary Review of Potential for Elevated TDS in Cooling Towers to Form P10 to P2.5 particulates", Anderson Engineering, http://www.water-cti.com/publishedpapers.html.
- Yang, L. & Duke, D., "Laboratory and Field Studies of Localized and General Corrosion Inhibiting Behaviors of Silica in Zero Liquid Discharge (High TDS Cooling Water) Using Real Time Corrosion Monitoring Techniques", NACE CORROSION 2007, Paper No. 07626, March 2007.
- 7. Duke, D., Kubis, J., Reed, J., "Zero Liquid Discharge Cooling Tower treatment at CSI", AIST 2007, May 9, Indianapolis IN.
- 8. Duke, D. et al, U.S. Patents 6,929,749; 6,940,193; 6,998,092; and 7,122,148.