IWC 07-11

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

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Presentation Outline

- Prior VS New ZLD Technology
- Small ZLD Installation
- Power / Industrial ZLD
- Case Histories
- High Temperature Studies
- Other ZLD Benefits / Current Studies

Prior ZLD Limitations

- Only feasible for large systems
- Combinations of pre-treat and side stream treatment to remove TDS and precipitates
- Extensive capital and operational costs
- Corrosion, deposition and biological control still difficult / limited
- Increased solids disposal, chemical treatment, discharge issues

New ZLD Technology

- Tower evaporation provides water recovery
- ZLD operation (High TDS) is very cost viable for either small or large systems
- “State of Art” corrosion & scale inhibition
- Effective from 2,500 to 150,000 mg/L TDS
- Reduces water use without risk of scale, corrosion, bio fouling and pathogens
- Ideal for high silica and reclaim MU sources

ZLD / Silica Chemistry

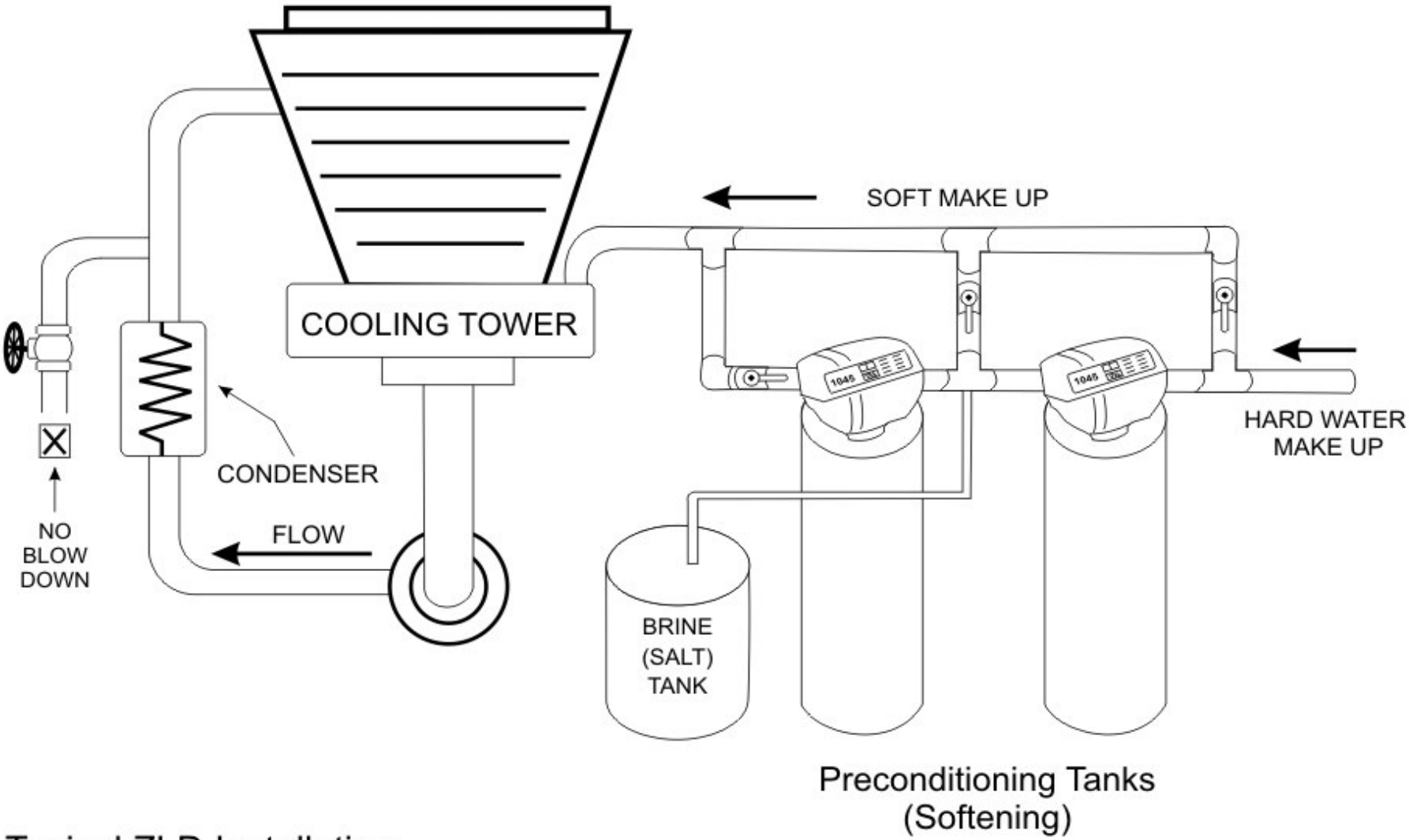
- Pre-treatment removes low solubility ions
- Scale limitations eliminated in tower water
- Permits unlimited water concentrations (600X)
- Soluble silica concentrates to > 200 mg/L
- Polymerized silica protects metals from TDS
- Excess silica polymerized / amorphous colloids
- High TDS/pH prohibits bio & pathogen growth
- US Patents # 6,929,749; # 6,949,193; # 6,998,092; and # 7,122,148

Natural Biostatic Chemistry

- Elevated pH and TDS are naturally biostatic to bacteria, spores and viruses
- Hydrolysis of peptide chains as water pH is increased (used in waste treatment)
- Denaturing of proteins or enzymes by elevated TDS
- Report by Anderson Engineering

Small ZLD Systems

Discharge of Regenerate
to Municipal Sewer



Typical ZLD Installation

ZLD Equipment Economy and ROI

- Low salt use design @ 4# / CF resin
- Typical salt usage cost of $0.22 to $0.07 per 1000 gallons tower make up
- Typical make up / blow down discharge costs of $2.00 to $3.00 /1000 are saved
- Equipment cost recovery < 12 months
- Some municipalities rebate costs for water conservation equipment and installation

Small ZLD Example Cost

- Low salt use design equipment cost approximately $3000 for 10 GPM flow
- Applicable for 50 to 400 ton tower load
- Program service and testing cost is comparable / less than chemical program
- Simple / automated / low maintenance

Power / Industrial ZLD

(Site Discharge Processing)

Prior Power ZLD Approaches

- Required combination of chemical precipitation, reverse osmosis, evaporator and crystallizer stages to recover water and produce dry solids
- Capital cost can be 10% of power plant facility
- Operational cost 15% of power plant facility
- Complex operation, control and maintenance
- Still use organic chemicals and biocides
- Costs passed on in higher rates to consumers

Option A — Conventional Average Cycles of Concentration

Raw Water

Distillate

Cooling Tower

Blowdown

Evaporator

Blowdown (High TDS)

Crystallizer

Solids

Landfill

Option B — Pre-Treated Make-up with Silica Inhibition Program

Softened Water

Other Anions Present

Distillate

Cooling Tower

Blowdown (High TDS)

Crystallizer

Solids

Landfill

Option C — Raw Water Option with Evaporation Pond

Raw Water

Other Anions Present

Cooling Tower

Blowdown (High TDS)

Evaporation Pond

Example 500 MW Power / ZLD Comparison

(Final Dry Solids Produced by Crystallizer)

Prior ZLD; CTBD to LS/IE/HERO or LS/BC	New ZLD; Tower /waste heat concentrates TDS
Concentration of CTBD to 40-150,000 TDS	CTBD to crystallizer at 40-150,000 TDS
Capital Cost $10-22 million	Capital Cost $6-8 million
Operating Cost $3.6 million	Operating Cost $1.3 million
Added energy use $1.8 million	Added energy use $0.6 million

Case Histories

Steel Mill Tower - ZLD Chemistry

Tower / Makeup - Concentration of Chemistry (COC) Ratios			
SAMPLE / TESTS	Tower	Makeup	COC
TDS, mg/L	146,000	251	582
pH	10.05	7.58	
Copper, mg/L Cu	0.7	0.0015	
Iron, mg/L Fe	ND	ND	
Zinc, mg/L	ND	ND	
Silica, mg/L SiO_2	1,250	30	42
Calcium, mg/L $CaCO_3$	62	< 0.1	
Magnesium, mg/L $CaCO_3$	16	< 0.1	
Nitrate, mg/L NO_3	2590	4.5	
Sodium, mg/L NaCl	145,000	250	580
Sulphate, mg/L SO_4	10,260	18	570
Chloride, mg/L NaCl	22,400	38	589
Tot. Alkalinity, mg/L $CaCO_3$	69,400	120	578
ND = Not Detected; COC = Concentration of Makeup Chemistry			

Steel Mill Tower #1 (24 months ZLD)
Galvanized Tube Bundle / No White Rust

Steel Mill Tower
Galvanized Coated Steel Coupon
60 Day Exposure

Mild Steel Coupons
60 Day Exposure VS Non-exposed

0.017 mpy #1652 VS 0.013 mpy #1664 (control)

Steel Mill Tower #2 (20 months ZLD)
Galvanized Tube Bundle / No White Rust

(146,000 TDS; 582 COC; 110° F / 82° F)

Steel Mill Effluent Control Impact

- Averted cost of discharge waste system
- 98% reduction in waste volume
- 30% reduction in tower makeup water
- No chemical or biocide used
- Eliminated chemical storage / handling
- Design heat transfer efficiency maintained
- New galvanized bundles protected

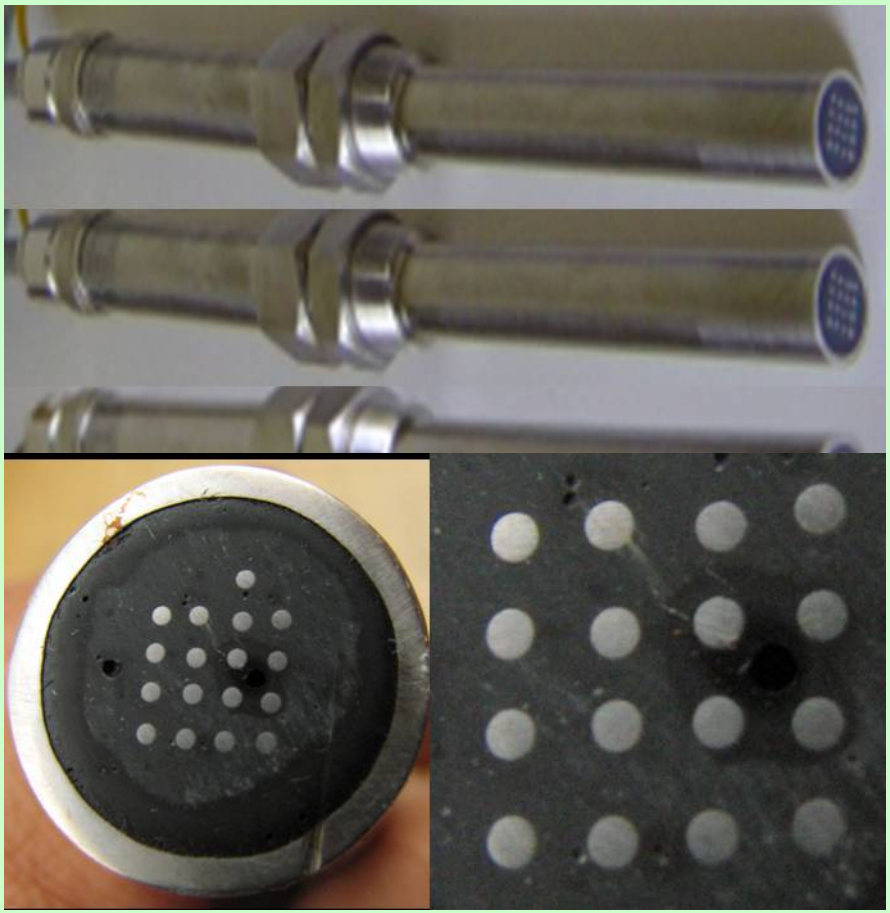
Central Absorber Plant - ZLD Chemistry

Concentration of Chemistry (COC) Ratios			
SAMPLE / TESTS	Tower	Makeup	COC
TDS, mg/L	68,500	593	115
pH	10.0	8.1	-
Silica, mg/L SiO2	360	12	30
Hardness, mg/L CaCO3	29	< 0.3	-

Central Absorber Plant Carbon Steel Corrosion (0.11 mpy @ 83 days)

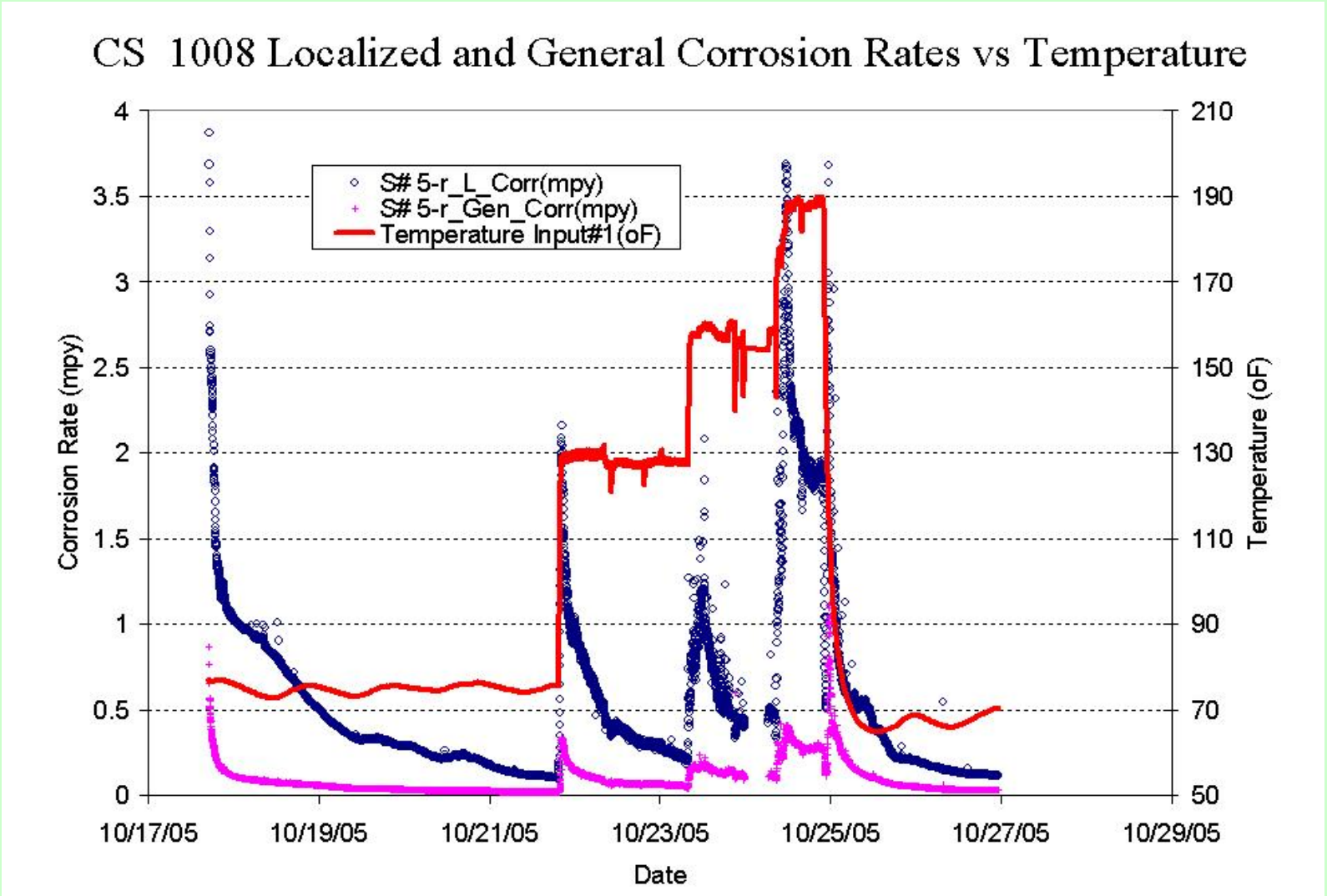
High Temperature Corrosion Inhibition Studies

High Temperature Corrosion Inhibition Studies

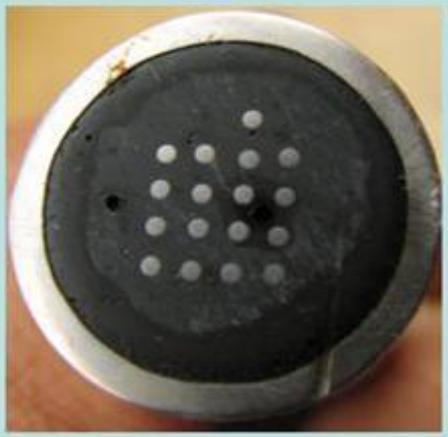


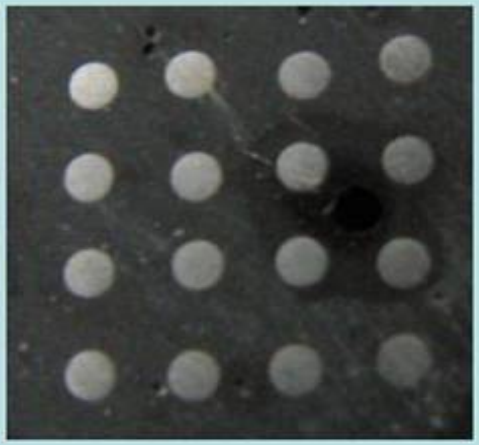
- Used real time coupled multi-electrode array corrosion probes
- Probes measured peak localized and general corrosion rates
- Test water chemistry:
  - 50,000 TDS / conductivity
  - 450 ppm silica
  - 9000 ppm chloride
- Temperatures:
  - 77^{o} F; 130^{o} F; 160^{o} F; 190^{o} F **(25^{o} C; 54^{o} C; 71^{o} C; 88^{o} C)**
- Metals:
  - CS1008; 316L SS; AL1100; Cu 1100; Zn

Silica Inhibited Study / High Temp

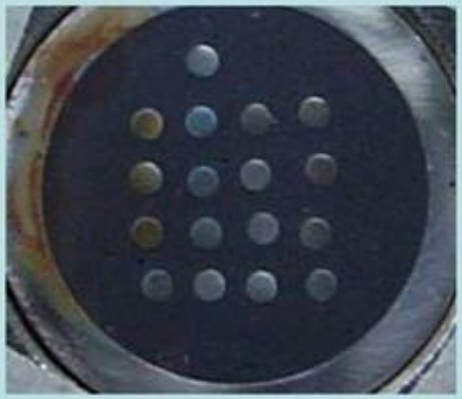


Post-Test Probes – Steel Localized Corrosion at 40 mpy in Unprotected Brine vs. < 0.2 mpy in Silica Inhibited Brine





Carbon steel, one week in high-silica brine solution (pH=10) at up to 190 °F



Three weeks in seawater at room temperature

Carbon steel

316L Probe

Other ZLD Benefits and Current Studies

Other ZLD / Silica Benefits

- Use reclaim waste water, grey water, RO reject, brackish water sources
- Protect metals from corrosion by high chlorides, sulfates, alkalinity, ammonia, organics
- Excellent aluminum, steel, copper protection
- Expands metal selection / cost economy options
- Mitigates micro-biological and pathogen proliferation, reduces biocide use
- Potential for mineral or regenerate recovery (concentrate volume efficient processes)

Inhibition of Copper / Other Alloys from Ammonia Corrosion

- Research with 150,000 TDS / high pH / soft tower water with ammonia (200-400 mg/L).
- Study found silica/azoles inhibit copper and other alloys from corrosion by ammonia.
- Azoles increasingly effective at high pH / TDS in silica treated soft water.
- Study underway with high ammonia “reclaim” water, used in refrigeration copper chiller and absorber tubes confirms inhibition results.
- Micro-biological growth in ammonia / phosphate rich reclaim water is mitigated.

Tower Ammonia Stripping

In a waste stream, ammonium ions exist in equilibrium with ammonia.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

1. Below pH 7, virtually all the ammonia is soluble ammonia ions.
2. Above pH 12, virtually all the ammonia is present as a dissolved gas.
3. Between pH 7 and 12, both ammonium ions and dissolved gas exist together.
4. Percentage of dissolved gas increases with pH / temperature.
5. Elevated pH and temperature favor removal of ammonia from solution as the gas when water is scrubbed over a tower.

Application Experience

- Four years of application and evaluation
- Customers include Industrial, Food, and Commercial/Institutional systems.
- Tower system metals include mild steel, copper, galvanized, stainless, aluminum.
- Cooling towers include Marley, BAC, Evapco, Delta.

ZLD / Silica Program Summary

- No scale with “ZLD” operation
- Negligible corrosion at extreme high TDS
- Excellent inhibition at high temperatures
- Al, Zn, Cu protected at high pH (10)
- Mitigates biological and pathogen growth
- Use reclaim or grey water makeup
- “Green” chemistry / simple control
- Reduce water use and discharge cost

Questions?