

# GC&EC 2007

## Green Analytical Chemistry Session

### Paper 41237

“Green” Corrosion & Scale Inhibitor process  
converts Natural Chemistry in source water to  
protect Cooling Tower system metals  
operating with Zero Liquid Discharge

Report by Dan Duke

Water Conservation Technology International

# This technology is patent\* protected;

US 6,929,749 / Silica Scale Control

US 6,949,193 / Silica Scale Control

US 6,998,092 / Corrosion Inhibition/Silica

US 7,122,148 / Corrosion Inhibition/Silica

Additional patents pending

\*Licensed by Water Conservation Technology International

# Presentation Outline

- Cooling Towers / Green Issues
- Organic and Toxic Chemical Discharge
- How ZLD / Silica Chemistry Works
- Why it's Green / Natural Biostatic Chemistry
- Zero Liquid Discharge / Conserving Resources
- Case History
- High TDS / Temperature Corrosion Studies
- Other ZLD Benefits / Future Studies

# Cooling Towers

Green Issues

# What Cooling Towers Do

- Evaporate pure water into biosphere when removing heat from water used to cool processes or comfort systems
- Consume second largest (5%) individual quantity of fresh water after irrigation
- Concentrate minerals in source water that are discharged to sewers or streams
- Discharge organic chemicals and biocides used for scale, corrosion and bio control

# What If

- You could replace 25 to 40% of the fuel in your vehicle tank with water ...
- get the same gas mileage ...
- and eliminate toxic exhaust emissions!
  
- Would you be pleased?

# What You Can Do With Cooling Towers

- Reduce cooling tower water use and discharge by 25-40% in most systems
- Eliminate use and discharge of chemicals and biocides
- Eliminate heat transfer loss from scale or fouling which conserves energy
- Virtually eliminate corrosion of metals
- Reduce capital, operating and energy cost

# Sustainability Issues

- Fresh water supply is diminishing for nature, irrigation, population, industry.
- Discharge of organics and toxicants increasing in both water and air.
- Energy resources increasingly limited.
- Greenhouse gas intensity increasing.
- Sustainability of usable water and energy sources is critical.

# Reality versus Incentive

- Some green approaches used only under forced compliance, and cost is passed to consumer
- Economic incentive is needed to promote commercial and industrial application
- We need cost effective technologies that can replace current non-green approaches
- Utilities and government regulators should champion conservation of water and energy
- But sustaining water, energy or environment should not require respective poor tradeoffs

# Organic & Toxic Chemicals

Discharged by Cooling Towers

# Cooling Tower Chemicals Discharged with Blowdown & Drift

- 70 million pounds annual discharge of non-oxidizing organic biocides in US
- Most also use halogen biocides, source of AOX (absorbable organic halogens)
- Even greater quantities of dispersant, scale and corrosion inhibitors discharged
- Very few green chemistry options [handout, or at [water-cti.com](http://water-cti.com)]

# Function & Composition of Chemicals in Cooling Tower Discharge

<b>Product Function</b>	<b>Chemical Composition</b>
Biocides	Organic* / halogen** * US, 70-80 MM Lbs./yr ** Source of AOX
Dispersants	Organic hydrocarbons
Steel Corrosion	organic, phosphate, zinc, molybdate
Copper Corrosion	Organic hydrocarbons
Scale Inhibitors	Organic, phosphate esters, polyphosphate

# How ZLD / Silica Chemistry Works

Why it's Green

# How ZLD / Silica Chemistry Works

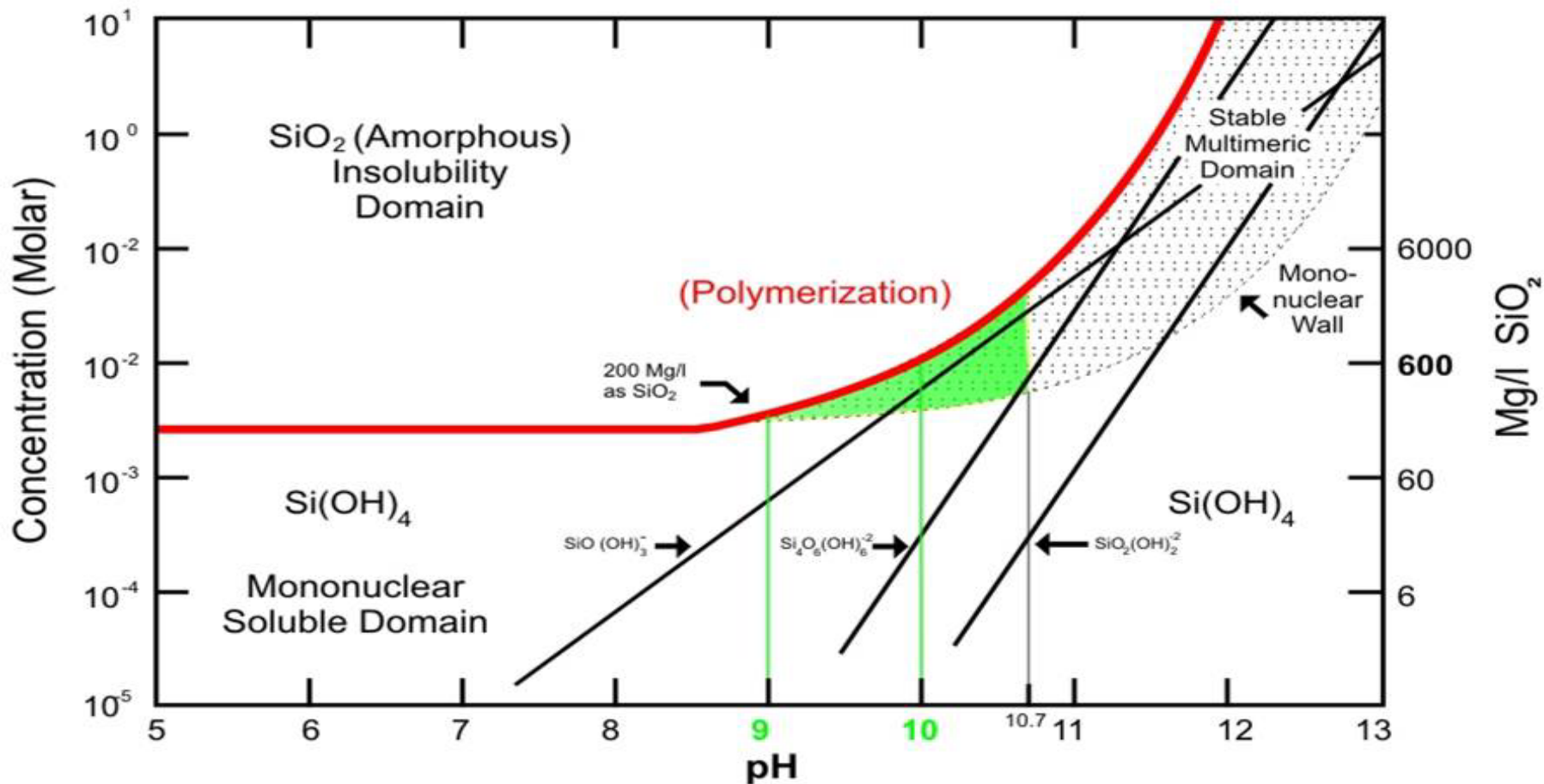
- Pretreatment removes scale forming ions (hardness) from make-up to tower
- Permits concentration of soluble ions in water (20 to 600 versus typical 2 to 5)
- Soluble silica concentrated to  $> 200$  mg/L
- Elevated pH catalyzes silica polymerization
- Polymerized silica inhibits metal corrosion
- Excess silica polymerized to colloidal forms

# Natural Water Chemistry

- Major minerals in water are Ca, Mg, Na, chloride, sulfate, carbonate and silica
- Zeolite exchange, colloids occur in nature
- Exchange of Ca & Mg with Na replaces low solubility salts (scale)
- Silica polymerized to amorphous silicates and colloids with saturation of silica, TDS, alkalinity (pH) through water evaporation

# Relationship Between Soluble, Insoluble and Polymerized Silica Species at Varying pH and Concentration

## Species In Equilibrium with Amorphous Silica



# 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\* [\*available at [water-cti.com](http://water-cti.com)]

# Zero Liquid Discharge (ZLD)

How ZLD / silica chemistry can  
sustain water, energy, environment

# Typical Current ZLD Technology

- Requires combination of chemical precipitation, reverse osmosis or evaporators and crystallizer stages to recover water and dry solids
- Cost feasible only for large systems (Power)
- Capital cost can be 10% of power plant facility
- Operational cost 15% of power plant facility
- Costs passed on in higher rates to consumers
- Energy use is largest portion of operating cost
- Added energy use produces greenhouse gases
- Still use organic chemicals and biocides

# New ZLD Technology

- New approach permits ZLD attainment with existing evaporative cooling tower system
- Provides “State of Art” corrosion & scale inhibition with TDS levels from 2,500 to 150,000 mg/L
- Discharge eliminated without corrosion, scale, bio fouling; and reduced pathogen risk
- Ideal for high silica / hardness / TDS water
- ZLD / silica approach is very cost viable for both small and large systems

# Example 500 MW Power / ZLD Comparison

(Final Dry Solids Produced by Crystallizer)

<u>Current ZLD</u> ; CTBD to LS/IE/HERO or LS/BC	<u>New ZLD</u> ; 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

# New ZLD Pretreatment Cost

## (Economical / Excellent Payback)

- Equipment with low regenerate design (4# salt / CF resin), provides 50% reduction in salt use
- Typical regeneration cost from \$0.07 to \$0.22 per 1000 gallons of treated water
- Typical tower makeup water and discharge cost savings is \$2.00 - \$3.00 per 1000 gallons
- Provides equipment cost recovery < 12 months
- Many municipalities now rebate cost to purchase and install water conservation equipment

# Small System Cost Examples

- Pretreatment system to provide makeup flow from 2 to 10 GPM at \$3500 installed cost
- ZLD will save \$2400 to \$6200 /Yr in water cost with a 300 ton evaporative load with blowdown rates from 25% to 40% of makeup
- Cost economy improves with increasing size
- For 3000 ton load, installed cost is \$36,000 and ZLD water savings are \$30,000 to \$66,000 /Yr
- Program testing and service provider fees are equivalent or less than chemical approaches

# Case History

# Steel Mill Tower - ZLD Chemistry

<b>Tower / Makeup - Concentration of Chemistry (COC) Ratios</b>			
<b>SAMPLE / TESTS</b>	<b>Tower</b>	<b>Makeup</b>	<b>COC</b>
<b>TDS, mg/L</b>	<b>146,000</b>	<b>251</b>	<b>582</b>
<b>pH</b>	<b>10.05</b>	<b>7.58</b>	
<b>Copper, mg/L Cu</b>	<b>0.7</b>	<b>0.0015</b>	
<b>Iron, mg/L Fe</b>	<b>ND</b>	<b>ND</b>	
<b>Zinc, mg/L</b>	<b>ND</b>	<b>ND</b>	
<b>Silica, mg/L SiO<sub>2</sub></b>	<b>1,250</b>	<b>30</b>	<b>42</b>
<b>Calcium, mg/L CaCO<sub>3</sub></b>	<b>62</b>	<b>&lt; 0.1</b>	
<b>Magnesium, mg/L CaCO<sub>3</sub></b>	<b>16</b>	<b>&lt; 0.1</b>	
<b>Nitrate, mg/L NO<sub>3</sub></b>	<b>2590</b>	<b>4.5</b>	
<b>Sodium, mg/L NaCl</b>	<b>145,000</b>	<b>250</b>	<b>580</b>
<b>Sulphate, mg/L SO<sub>4</sub></b>	<b>10,260</b>	<b>18</b>	<b>570</b>
<b>Chloride, mg/L NaCl</b>	<b>22,400</b>	<b>38</b>	<b>589</b>
<b>Tot. Alkalinity, mg/L CaCO<sub>3</sub></b>	<b>69,400</b>	<b>120</b>	<b>578</b>
ND = Not Detected; COC = Concentration of Makeup Chemistry			

**Steel Mill Tower**  
**Galvanized Coated Steel Coupon**  
60 Day Exposure



Steel Mill Tower – 15 months service  
Galvanized Tubes (bottom) / No White Rust  
(146000 TDS, 105 to 77 deg F drop)



Steel Mill Tower - Mild Steel Coupons  
60 Day Exposure VS Non-exposed  
0.017 mpy #1652 VS 0.013 mpy #1664 (control)

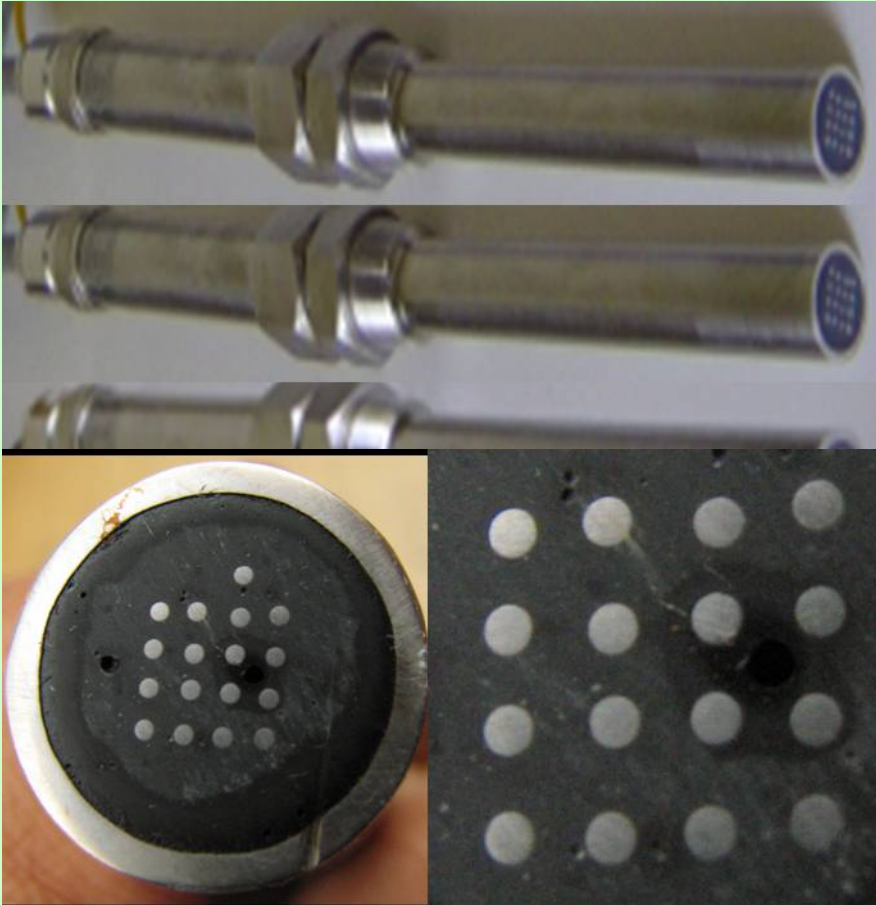


# Steel Mill ZLD Impact

- 30% reduction in tower makeup water
- 98% reduction in wastewater volume
- Design heat transfer efficiency
- New galvanized metals protected
- No chemical use, storage or handling

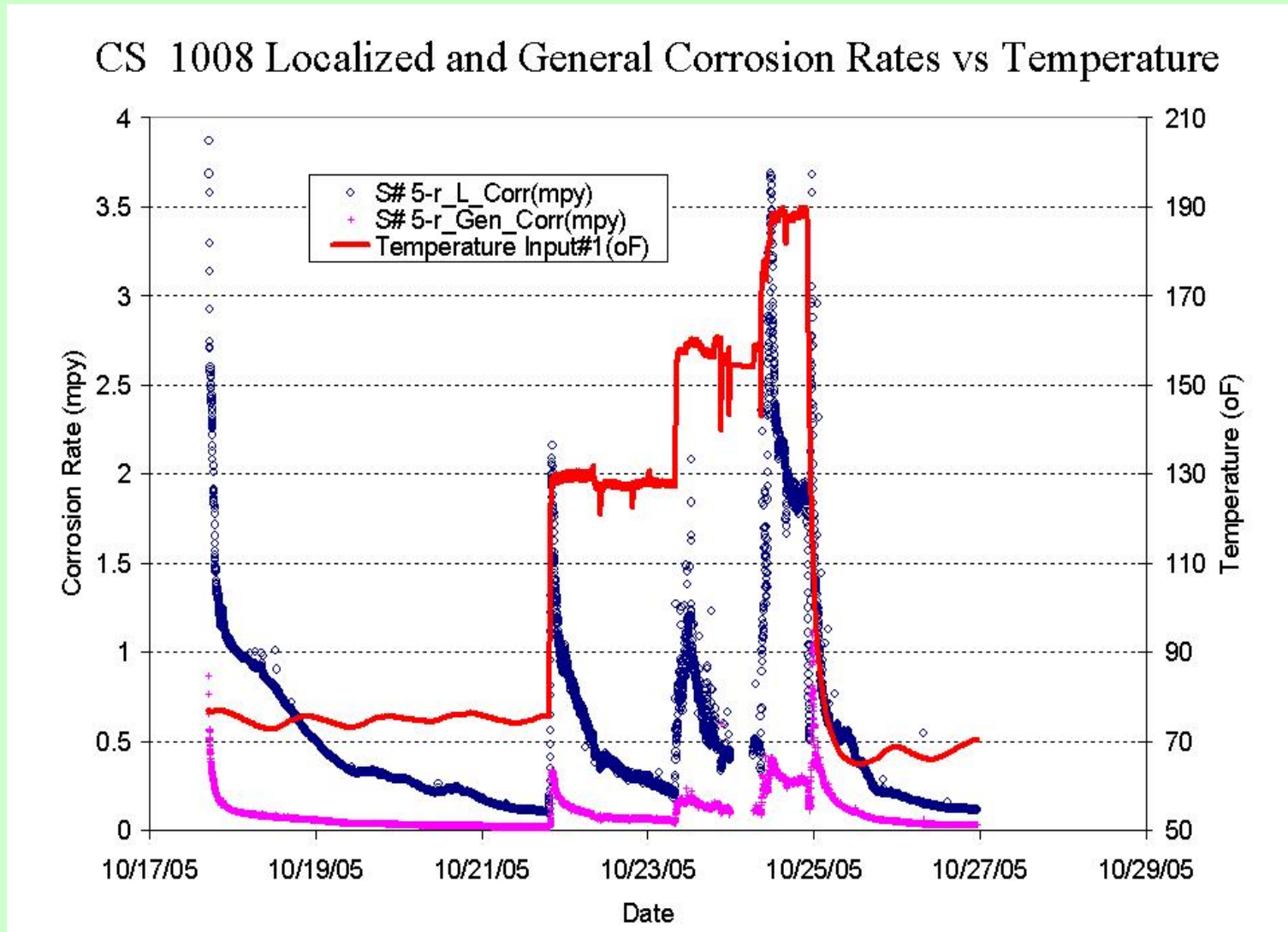
# High TDS / Temperature Corrosion Inhibition Studies

# High TDS / High Temperature Corrosion Inhibition Studies

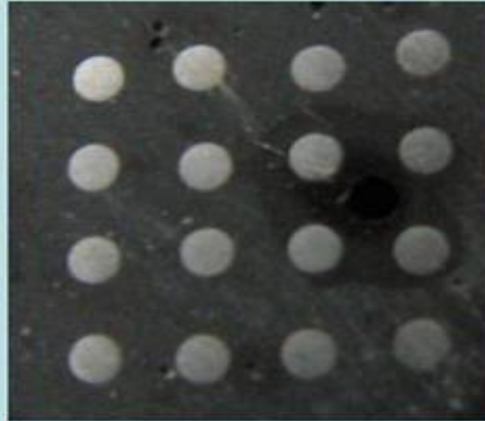
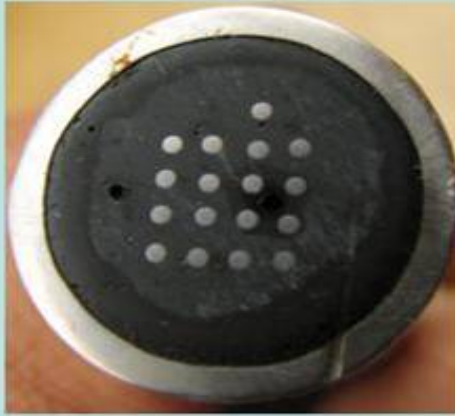


- Used real time coupled multi-electrode array corrosion probes
- Probes measured peak localized and general corrosion rates
- Test water chemistry:
  - 50,000 conductivity
  - 450 ppm silica
  - 9000 ppm chloride
- Temperatures:
  - 77° F; 130° F; 160° F; 190° F  
**(25° C; 54° C; 71° C; 88° C)**
-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

# Silica Inhibited Study / Carbon Steel



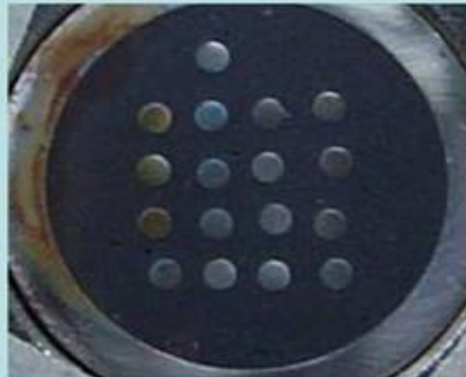
# Post-Test Probes – Steel Localized Corrosion at 40 mpy in Unprotected Brine vs. < 0.1 mpy in Silica Inhibited Brine



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



Carbon steel



316L Probe

Three weeks in seawater at room temperature

# Corrosion Inhibition Results at High Temperature and 50,000 TDS

Metals	Inhibitor / Solution	Temp (°F)	Temp (°C)	General (mpy)	Max Loc (mpy)
<b>CS 1008</b>	<b>Sea Salt</b>	<b>77</b>	<b>25</b>	<b>***</b>	<b>40.0</b>
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
<b>SS 316 L</b>	<b>Sea Salt</b>	<b>77</b>	<b>25</b>	<b>***</b>	<b>0.04</b>
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
<b>AL 1100</b>	<b>Sea Salt</b>	<b>77</b>	<b>25</b>	<b>***</b>	<b>20.0</b>
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
<b>Zinc</b>	<b>Sea Salt</b>	<b>77</b>	<b>25</b>	<b>8.0</b>	<b>80.0</b>
Zinc	Silica	77	25	< 0.05	< 0.01
Zinc	Silica	130	55	< 0.2	0.4
Zinc	Silica	160	71	***	2.0
<b>CU 110</b>	<b>Sea Salt</b>	<b>77</b>	<b>25</b>	<b>***</b>	<b>0.4</b>
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

# Other ZLD Benefits and Future Studies

# Other Potentials for ZLD / Silica

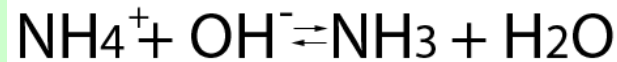
- Use with reclaimed waste water, RO reject, or brackish water sources
- Protects common metals from chlorides, sulfates, alkalinity, ammonia, organics
- Mitigation of micro-biological and pathogen growth will support waste water reuse
- Expanded metal options for improved heat transfer and economy
- Potential mineral or regenerate recovery from tower water (volume efficient process)

# Inhibition of Corrosion by Ammonia In Wastewater Sources

- Mitigation of ammonia corrosion of copper and microbiological bloom is critical to permit use of phosphate and ammonia rich “grey” water in cooling towers
- WCTI conducted studies with ZLD / silica inhibited tower water and high ammonia (200 mg/L)
- The study found silica and Tolytriazole or Benzotriazole (azoles) will inhibit corrosion of copper by ammonia
- Azoles are more effective in high pH / ZLD water, with synergy of inhibition mechanisms with silica
- Beginning ZLD study using “grey” water with high ammonia content in a tower with copper exchangers

# Ammonia Removal

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



1. Below pH 7, virtually all the ammonia will be as soluble ammonia ions.
2. Above pH 12, virtually all the ammonia will be present as a dissolved gas.
3. The range between 7 and 12, both ammonium ions and dissolved gas exist together.
4. Increased temperature and pH favor ammonia removal when water is over scrubbed over a cooling 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.
- Cooling towers sold by Marley, BAC, Evapco, others.

# ZLD / Silica Summary

- No scale with “ZLD” / energy efficiency
- Near zero corrosion, less than 0.1 mpy for steel versus typical 2 to 5 mpy (0.051 to 0.126 mm/yr)
- Corrosion inhibition at high temperature / pH / TDS for all common metals (Fe, Cu, Al, Zn, SS)
- Protects aluminum, zinc at high pH
- Natural biological and pathogen mitigation
- Silica is non-toxic and is non-nutrient
- Energy conservation / cost reduction with ZLD cooling tower waste heat
- Potential wastewater and “grey” water reuse
- Green chemistry with no chemical discharge
- ZLD is cost effective for large and small applications
- Sustains water, energy and environment with use of existing operating equipment and resource costs

***... please help sustain our water sources  
and environment!***



# Questions?