CONRAD 2007

Water Use and Discharge Minimization Using Silica / ZLD Approach for Evaporative Cooling Towers

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Presentation Outline

- Limitations of Traditional Treatment
- Silica Corrosion Inhibition Chemistry
- New ZLD Technology
- Power / Industrial ZLD Example
- Cascaded ZLD Operation
- Steel Mill ZLD Case History
- Waste Water Use (Ammonia / Organics)

Limitations of Traditional Cooling Water Treatment

Inhibitors & Blowdown

Limits of Traditional Cooling Water Treatment

Limit	**Impact**	***Control Mechanisms***
1. Ca/Mg	Scale	Blowdown / Inhibitor / Acid
2. Silica	Scale	Blowdown / Inhibitor
3. TDS	Corrosion	Blowdown / Inhibitor
4. pH	Corrosion / Scale	Blowdown / Acid

Impact of Soft / DM Water on Traditional Corrosion Control

- Traditional corrosion inhibitors do not function effectively without calcium (soft water)
- Requires precise pH control to stabilize corrosion inhibitors and prevent deposition
- Use of chlorine / bromine biocides further increases soft water corrosiveness
- Organic inhibitors degrade with long retention time, must be blown down and replenished
- Requires blowdown / limits discharge reduction

Silica Corrosion Inhibition

Advantages With
Zero Liquid Discharge

Silica Corrosion Inhibition Chemistry

- Requires soft water (Soft or DM)
- Not affected by low or high TDS
- Not affected by ammonia, soluble organics
- Control chemistry provides ammonia striping
- Control chemistry eliminates biocide use
- Permits almost unlimited tower water (makeup) concentration to minimize discharge

How Silica Chemistry Works

- Pre-treat to remove low solubility ions (Ca/Mg)
- Eliminates scale limitations in towers (100X)
- Other TDS very soluble (Evap Cooler 800X)
- Soluble silica polymerizes at > 200 mg/L
- Polymerized silica protects metals from TDS
- Excess silica forms amorphous colloids
- High TDS/pH prohibits bio & pathogen growth
- US Patents # 6,929,749; # 6,949,193; # 6,998,092; and # 7,122,148

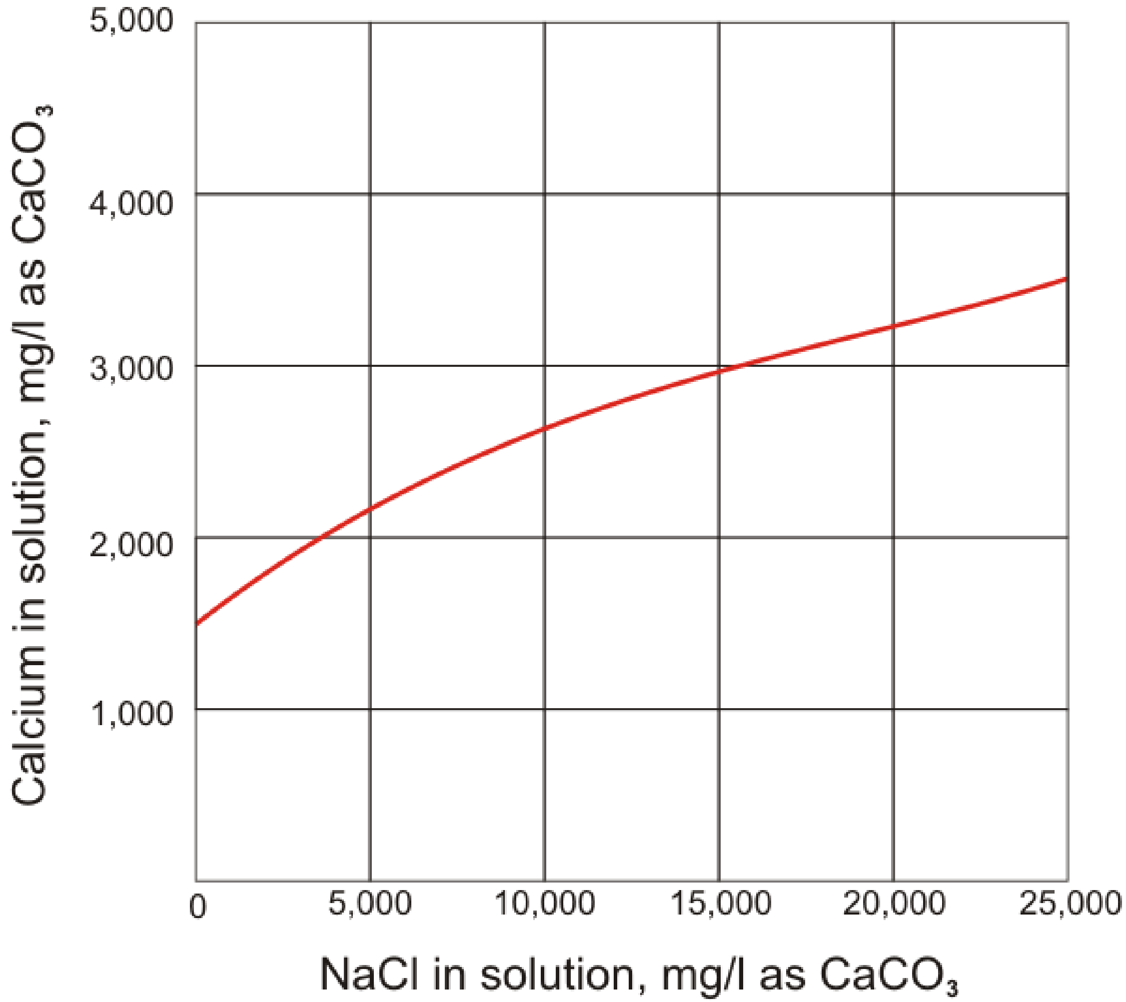
Hard Water / Low TDS Chemistry
Major Ion Relationships @ 2-5 COC

Cations		Anions
Ca^{+2} (60%)		Cl^{-}
Mg^{+2} (30%)	SiO_2	SO_4^{-2}
Na^{+} (10%)	⟺	CO_3^{-2}
		OH^{-}

Softened Water / High TDS Chemistry
Major Ion Relationships @ 20-800 COC

Cations		Anions
-		Cl^-
-	SiO_2	SO_4^{-2}
Na^+ (99%)	⟺	CO_3^{-2}
		OH^-

Calcium sulfate (gypsum) solubility increases with increasing sodium chloride.



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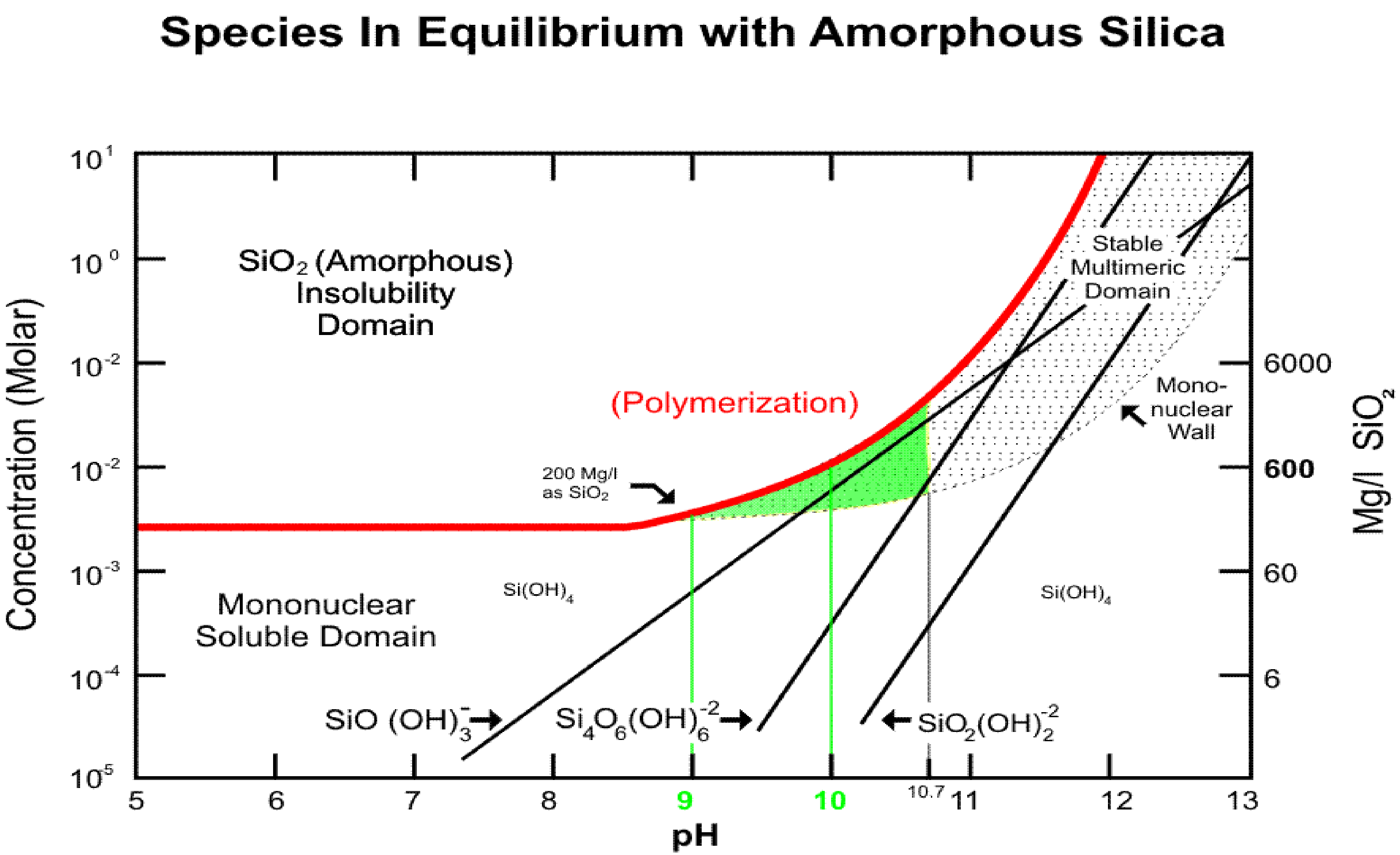
Relationship between Soluble, Insoluble and Polymerized Silica Species at Varying pH and Concentration (no polyvalent metals)



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New ZLD Technology

Prior ZLD Limitations

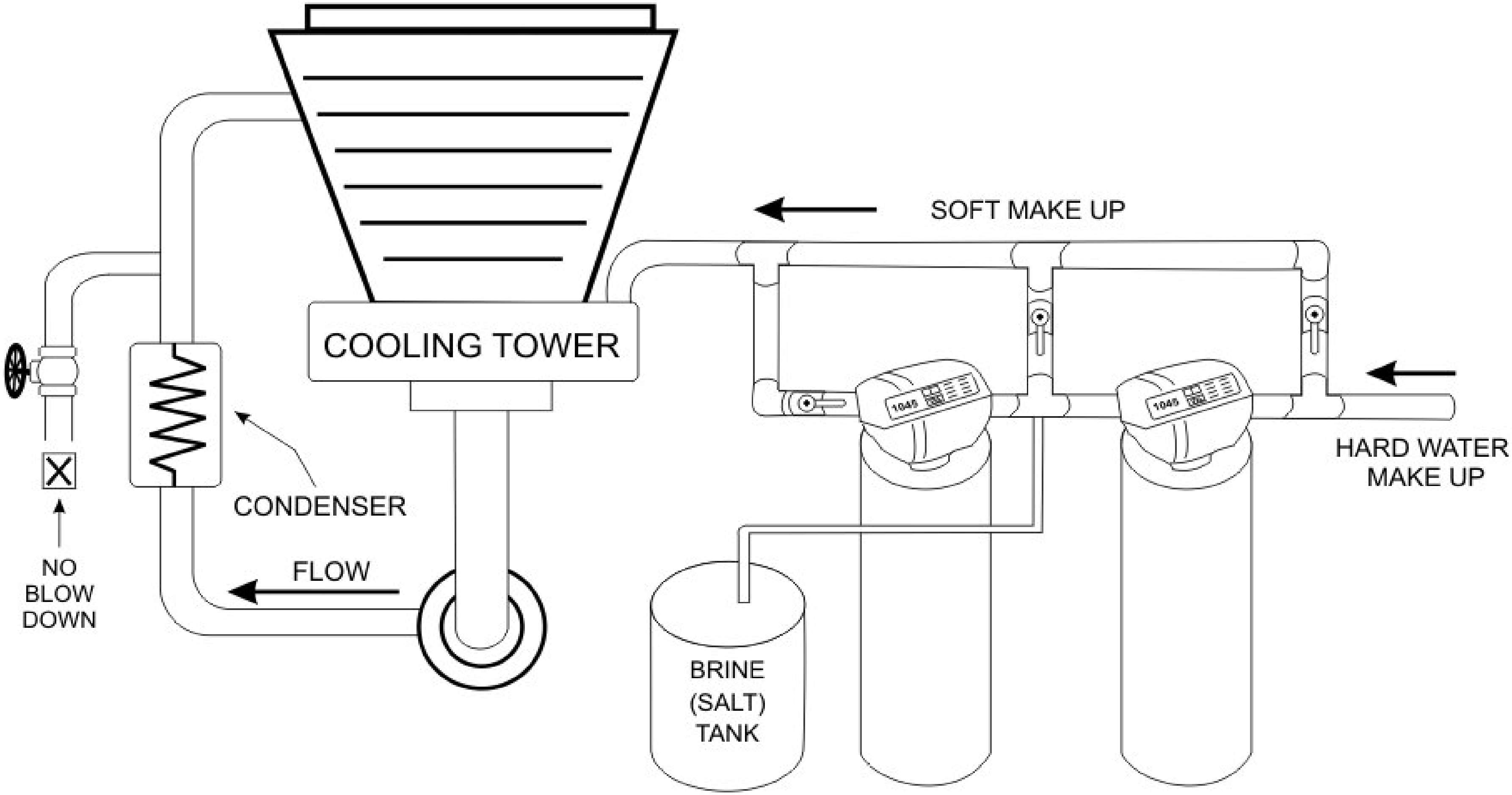
- Combinations of pre-treat and side stream treatment to remove TDS and precipitates
- Extensive capital and operational costs prohibitive unless mandated
- Corrosion, deposition and biological control still required
- Increased solids disposal from chemicals

New ZLD Technology

- Tower evaporation (waste heat) recovers water
- ZLD operation (High TDS) is very cost viable for either small or large systems
- “State of Art” corrosion & scale inhibition
- Effective operation at up to 200,000 mg/L TDS
- Reduces water use and discharge without risk of scale, corrosion and bio fouling
- Ideal for wastewater use / disposal.

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



Preconditioning Tanks
(Softening)

Typical ZLD Installation

ZLD HES Equipment Economy

- Low regenerate use / high efficiency softening (HES) design @ 4# / CF resin
- Typical regenerate usage cost of $0.12 per 1000 gallons tower makeup
- Equipment and operating cost is 15% of conventional ZLD / TDS reduction systems
- Evaporative energy provided by process (cooling system) waste heat

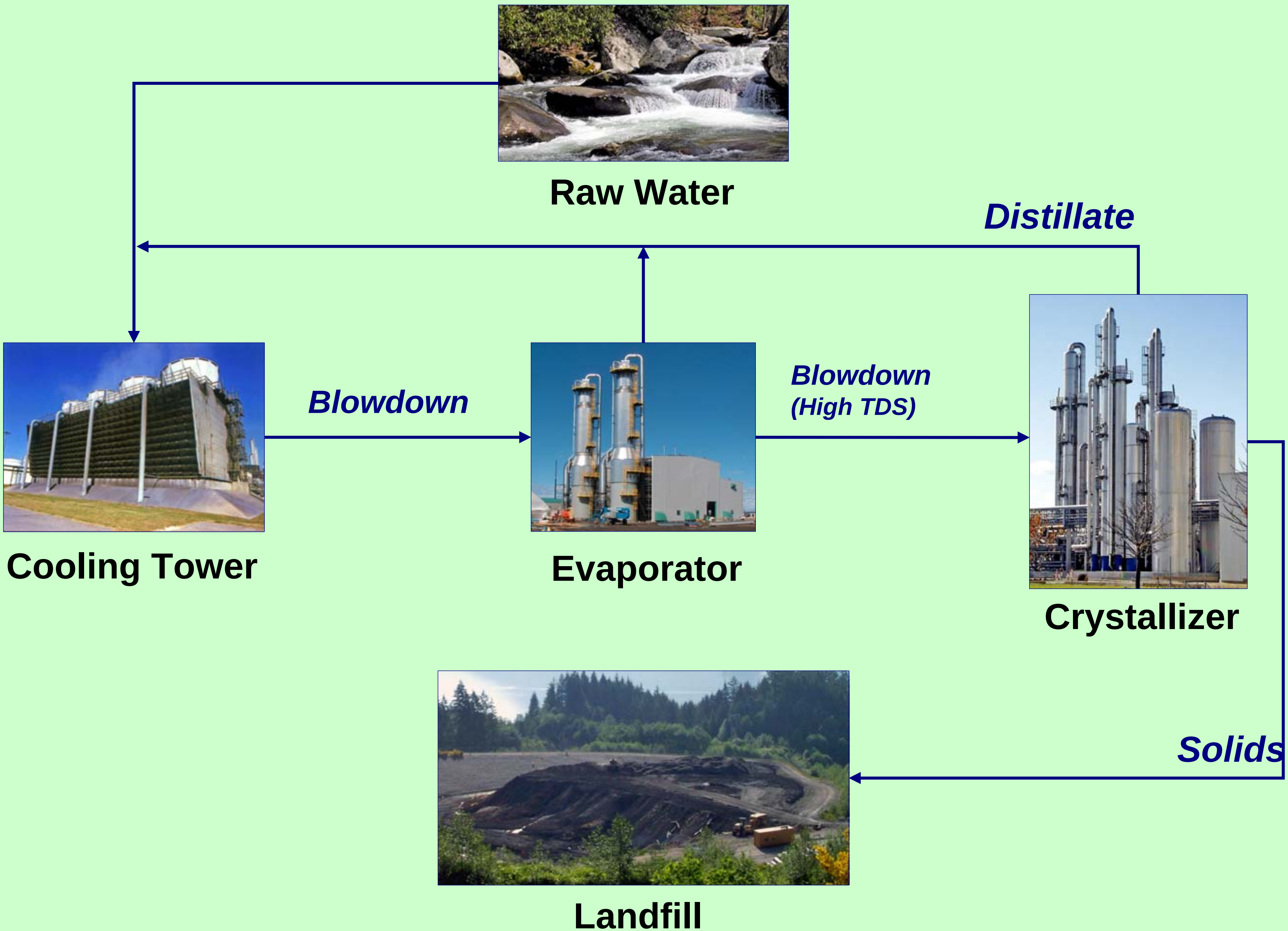
Power / Industrial ZLD

(Site Discharge Processing)

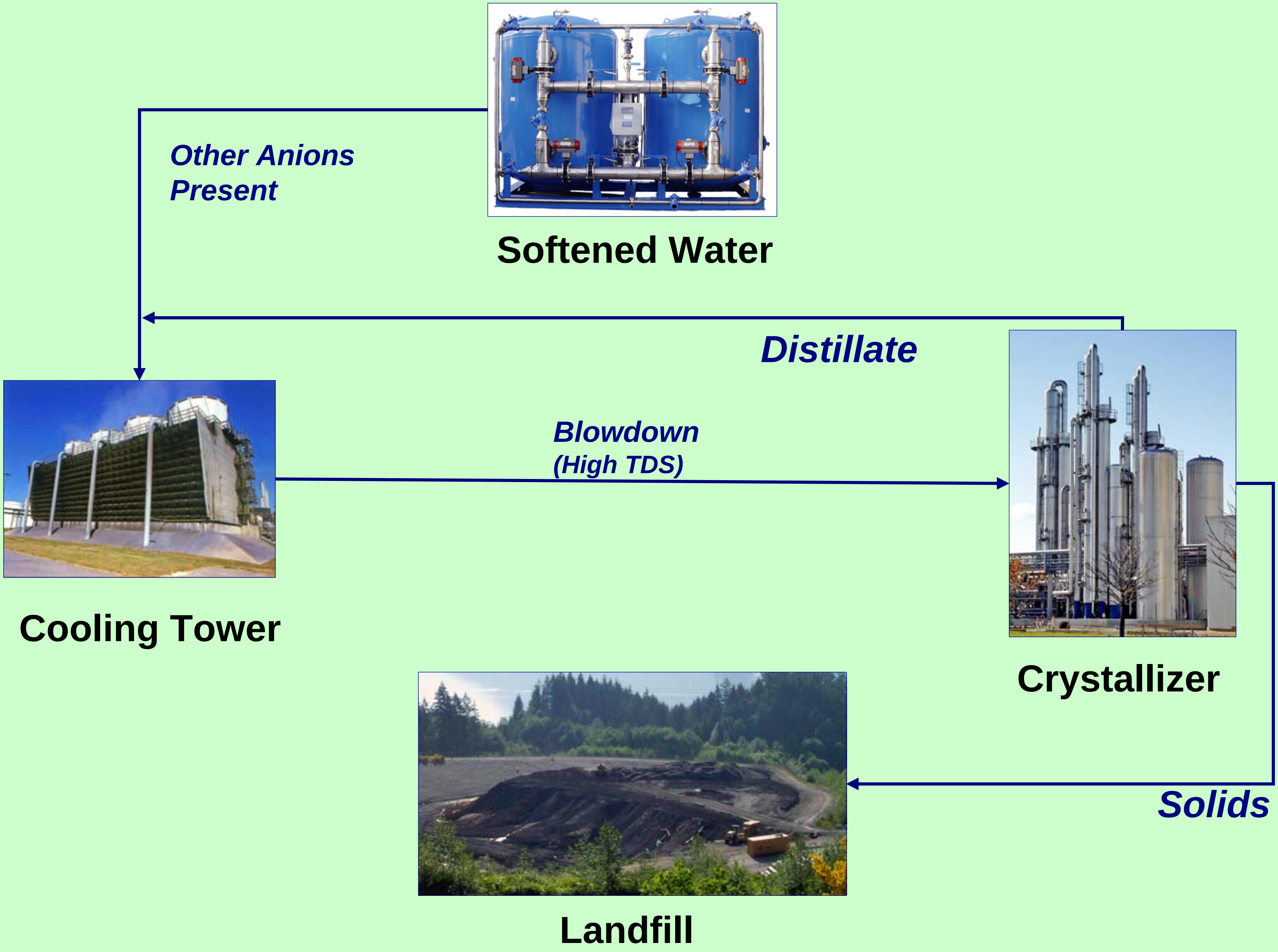
Prior Power ZLD Approaches

- 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 costs 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



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



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

Option C Raw Water Option with Evaporation Pond

Raw Water

Other Anions Present

Cooling Tower

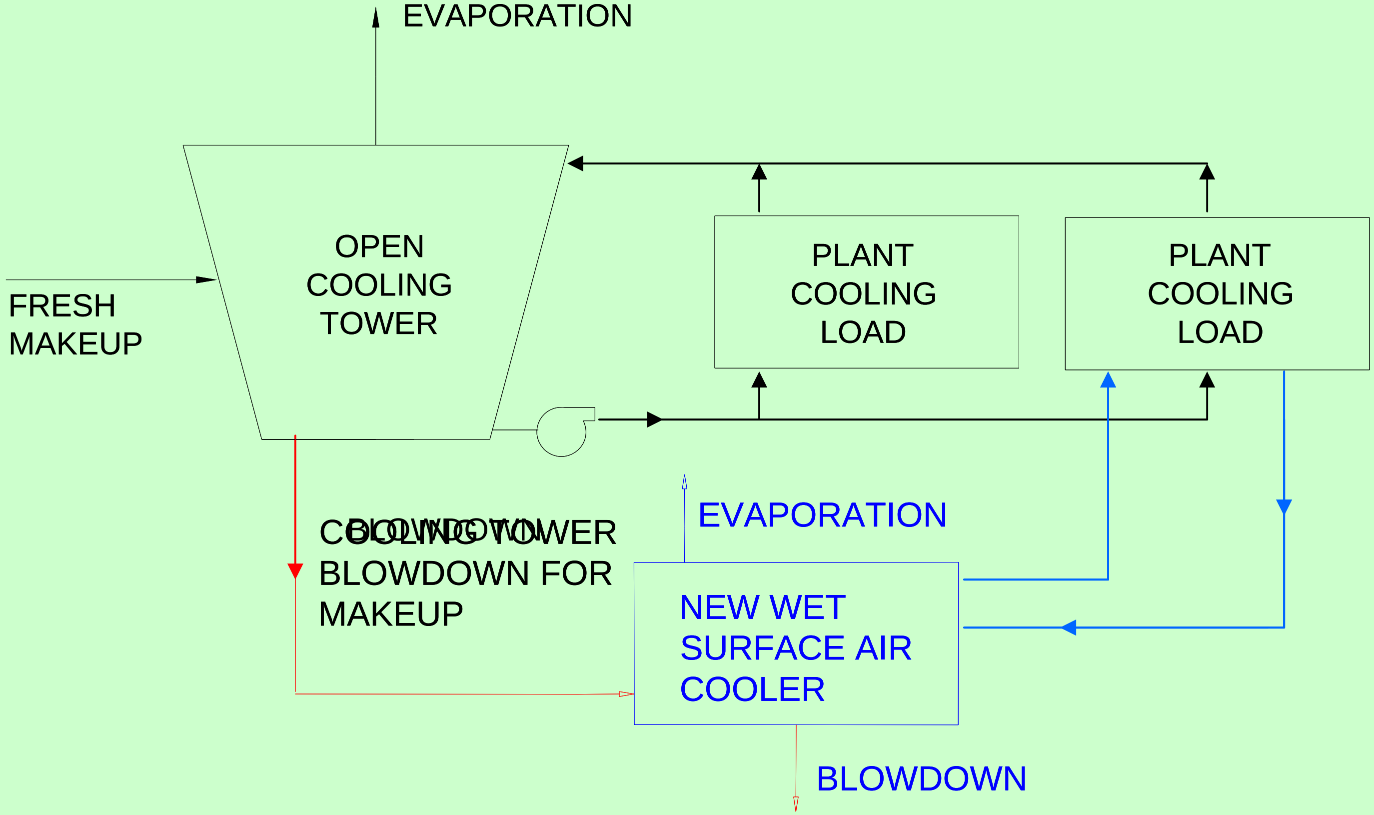
Blowdown
(High TDS)

Evaporation Pond

Cascaded ZLD Operation

Reduce Process Tower COC
and Reduce Discharge

De-Bottlenecking / Reducing Discharge in Existing Open Loop Systems



Cascaded BD to Evap Cooler

- Small Evap Cooler provides 2nd stage evaporation for blowdown in ZLD operation
- Low heat flux metal exchange surface
- Low cost metal construction (mild steel)
- Evap Coolers can approach unlimited TDS concentrations with ZLD / silica chemistry
- Minimize water quality effects (chlorides) on critical exchanger metals (stainless)
- Reduce BD discharge & disposal cost

ZLD Case History

Steel Mill

Steel Mill Tower ZLD Water Chemistry

Cooling Tower and Soft Makeup Water Chemistry (COC) Ratios				
Sample / Tests	Tower	Filtered Tower Sample	Soft MU	COC
TDS, mg/L (NaCl Myron L 6P)	146,000	146,000	251	582
pH	10.07	10.07	7.58	
Copper, mg/L Cu	0.7	0.25	0.0015	
Iron, mg/L Fe	22.2	ND	ND	
Zinc, mg/L Zn	3.8	ND	ND	
Silica, mg/L SiO_2	1,050	1,050	30	35
Calcium, mg/L $CaCO_3$	62	12.4	<0.1	
Magnesium, mg/L $CaCO_3$	16	8.2	<0.1	
Phosphate, mg/L PO_4	89	-	0.15	593
Nitrate, mg/L NO_3	2590	2590	4.5	575
Sodium, mg/L Na	145,000	145,000	250	580
Sulfate, mg/L SO_4	10,260	10,260	18	570
Chloride, mg/L NaCl	22,400	22,400	38	589
Tot. Alkalinity, mg/L $CaCO_3$	69,400	69,400	120	578
(COC) = Concentration of 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)

Waste Water Use

Waste Water Makeup
to Silica / ZLD Treatment

ZLD / Silica Expands Options

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

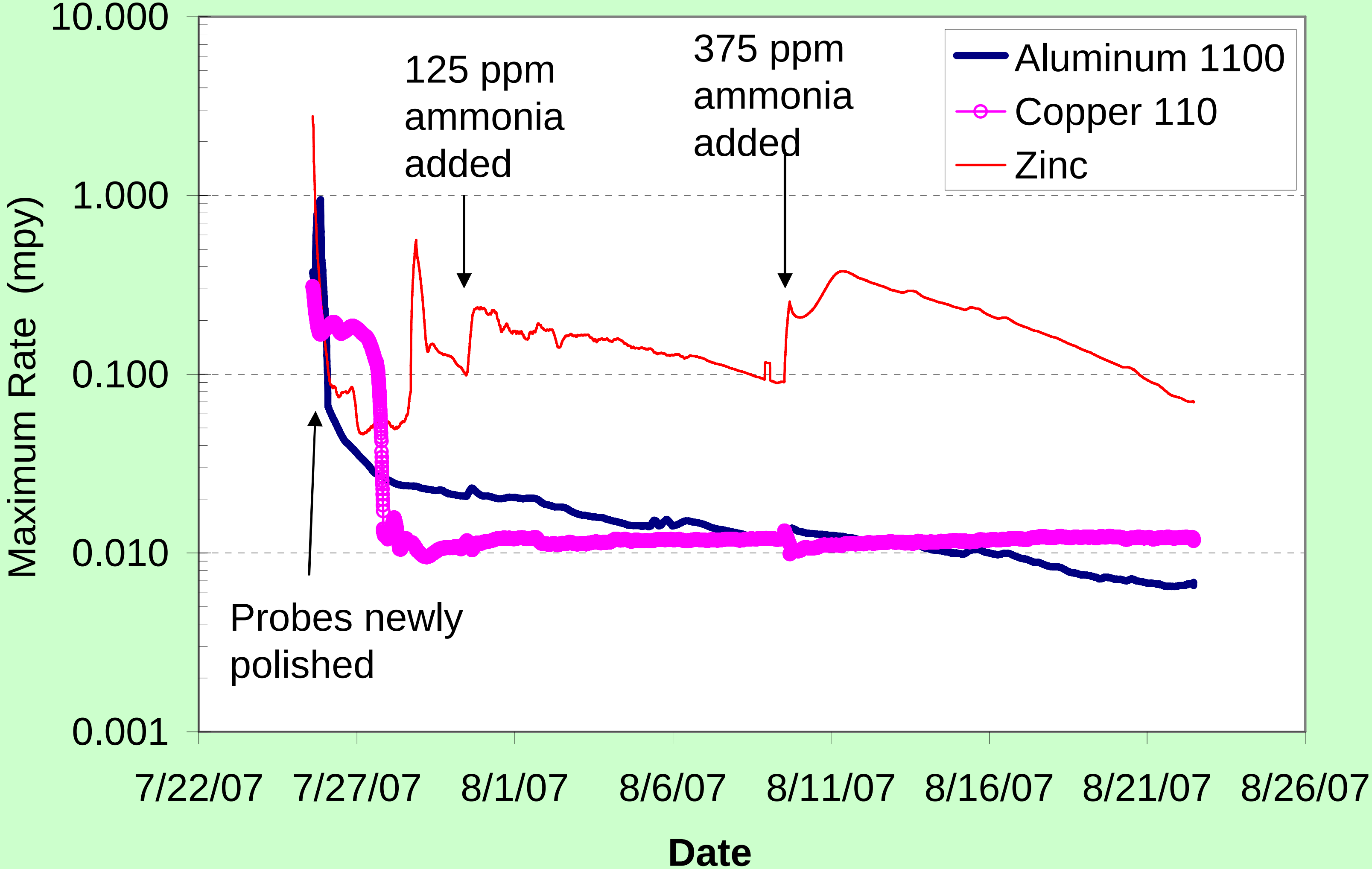
Reclaim / Waste Water Makeup

- Must be low hardness
- Waste water sources require treatment to remove TSS & insoluble organics.
- Must be filtered to remove suspended solids that would foul softening processes used.
- TDS must be low enough to permit ion exchange softening.
- Ammonia and soluble organics do not have to be removed for ZLD / silica chemistry.

Inhibition of Copper Corrosion by Ammonia

- Research with 150,000 TDS / pH 10 / soft tower water inhibited by Silica / Azoles exposed to ammonia (200-400 mg/L).
- Study shows silica/azoles provide highly effective inhibition of copper corrosion.
- High pH increases effectiveness of azoles in silica treated high TDS / soft water.

ZLD / Silica treated Tower Water, with TTA Supplement: Ammonia Corrosion of Copper, Zinc & Aluminum Inhibited



Case History Using High Ammonia (Reclaim) Waste Water

- High ammonia (34 mg/L) “reclaim” makeup water to system with copper chiller and absorber tubes
- Ammonia < 1 mg/L at 20 tower COC
- Ammonia attack inhibited with copper corrosion at < 0.1 mpy.
- Micro-biological growth from ammonia and organics mitigated (10^o Col / ml).

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.

ZLD Cooling Tower using (California Title 22) Reclaim Waste Water as Makeup

ZLD Tower / Soft Reclaim Makeup Chemistry (COC) Ratios			
Sample / Tests	Tower	Soft MU	COC
TDS, mg/L (NaCl Myron L 6P)	**20,000**	1100	**18**
pH	9.7	6.7	NA
Silica, mg/L SiO_2	280	24	**12**
Calcium, mg/L $CaCO_3$	10	0.2	NA
Magnesium, mg/L $CaCO_3$	4	0.1	NA
Sulfate, mg/L SO_4	2300	127	18
Chloride, mg/L NaCl	**3700**	214	17
Tot. Alkalinity, mg/L $CaCO_3$	3800	192	20
Ammonia, mg/L NH_4	**0.5**	**34**	NA
Total Phosphate, mg/L PO_4	**12**	**0.6**	**20**
TTA, mg/L as Tolytriazole	50	NA	NA
(COC) = Concentration of Chemistry			

ZLD Cooling Tower Corrosion Test Data

Reclaim Water Makeup

CORRATOR, COUPON & CMAS CORROSION TEST DATA		
Specimen Type	**Mild Steel**	**Copper**
Test location	Tower Loop	Tower loop
Corrosion Rate (mpy)	**< 0.2**	**< 0.1**

ZLD / Silica Program Summary

- No scale threat with “ZLD” operation
- Negligible corrosion at extreme high TDS
- Use reclaim or waste water makeup
- Ammonia and organics stripped by process
- Copper protected from ammonia
- Mitigates biological and pathogen growth
- Simple control chemistry
- Reduce water use and discharge cost

Questions?

Water Conservation Alternatives

Zero Liquid Discharge

ZLD / Silica Technology For Water Conservation

- ZLD reduces 2nd highest water use 20-40%.
- Reclaim water use cost is 30% of potable water.
- Blowdown and pH control systems not required.
- Chemical storage and feed systems eliminated.
- Reduced discharge volume and toxicant load.
- HES removal of only scaling ions (Ca & Mg) is highly cost and water use (waste) efficient.

Tower Discharge Reduction Alternatives TDS Impact (recycle or makeup)

- Traditional ion exchange TDS removal (DI) regeneration wastage is 8-10% of processed MU flow. Total discharged TDS from regeneration waste is increased 3X.
- Reverse osmosis wastage is 20-40% of processed MU flow (~BD). TDS discharge is increased 2X when pre-softening and pH increase are used to increase water recovery (10% wastage, HERO).

Cooling Tower Discharge Volume Reduction With HES

- High efficiency softening (HES) of tower MU permits discharge volume reduction.
- No additional energy cost as cooling tower evaporates water with waste heat.
- HES regeneration water wastage is < 2% of processed flow.
- HES regeneration produces less TDS than low cycle BD / MU traditional treatment.

Alternative Tower Discharge Reduction Costs

- Capital cost for HES is < 15% of cost for DI or RO approaches per unit of MU water recovered (example, $12,000 versus $80,000 for 40 GPM).
- Operating cost for HES is < 20% of cost for DI or RO (energy, pre-treatment, regenerate use) approaches per unit of water recovered.
- CT BD recycle treatment requires equivalent capital and operating cost (smaller volume / higher TDS), plus filtration and added TDS solids disposal.
- These alternatives still require use/cost of traditional CT inhibitors & biocides.

Drift Permitting

- Reducing CT discharge volume results in higher TDS concentration in tower water.
- Permit applications use cooling tower drift control design data from manufacturer.
- Recent permits use 5% of TDS value for PM 10 per Reisman & Frisbie Study.
- Use of these two factors relegate most tower PM to < 5 tons/Year, which are not regulated in US.

WCTI Licensee Services

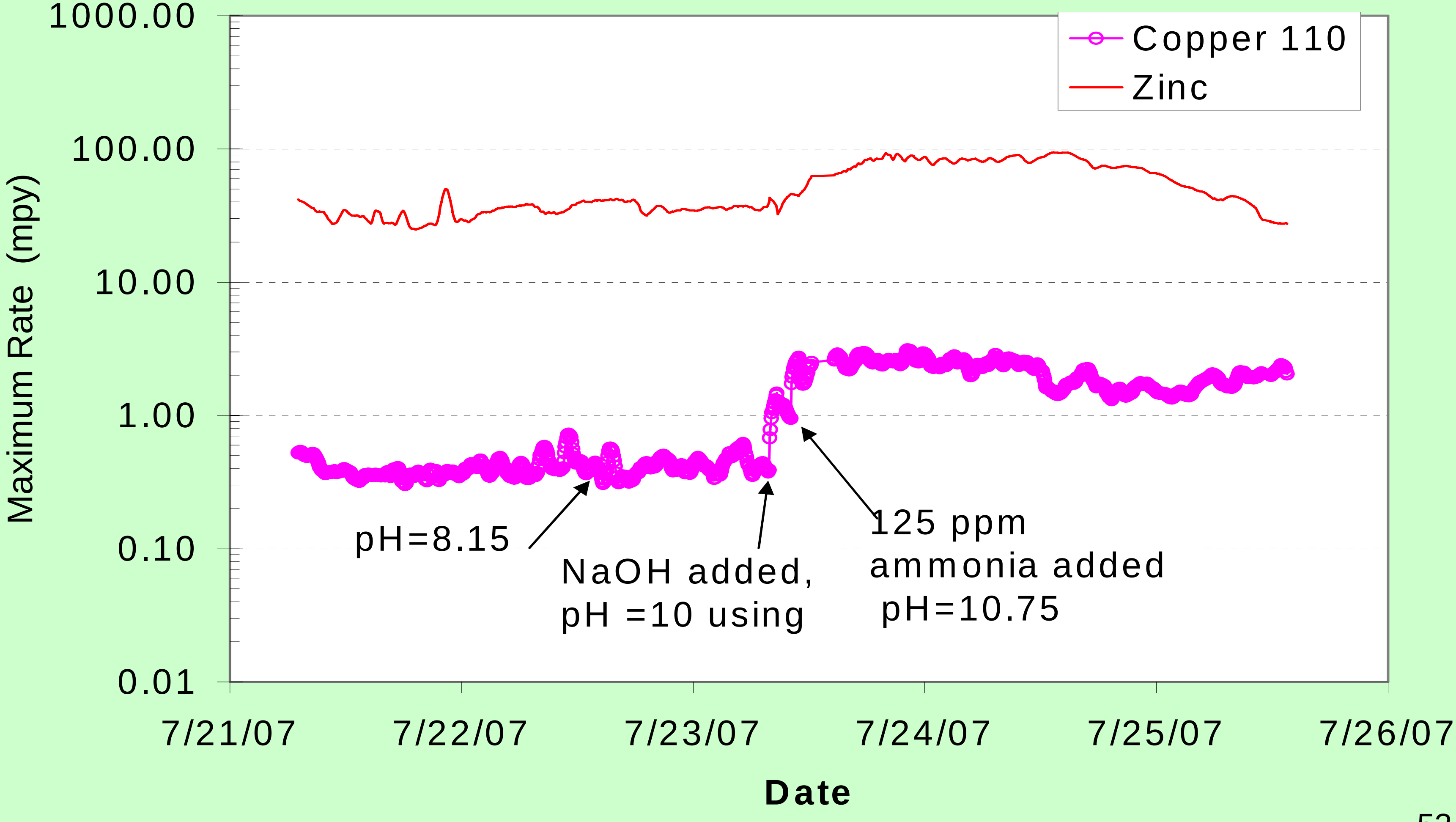
- Treatment chemistry operating control standards and transition
- Equipment design and installation support
- Equipment performance certification
- Equipment operational review & support
- Technical support to licensee
- R&D updates and reports to licensees

Ongoing Research & Development Technical Association Review

- NACE
- IWC
- CTI
- AWT
- CONRAD
- AIST
- AWWA
- ASHRAE
- ACS/GCE

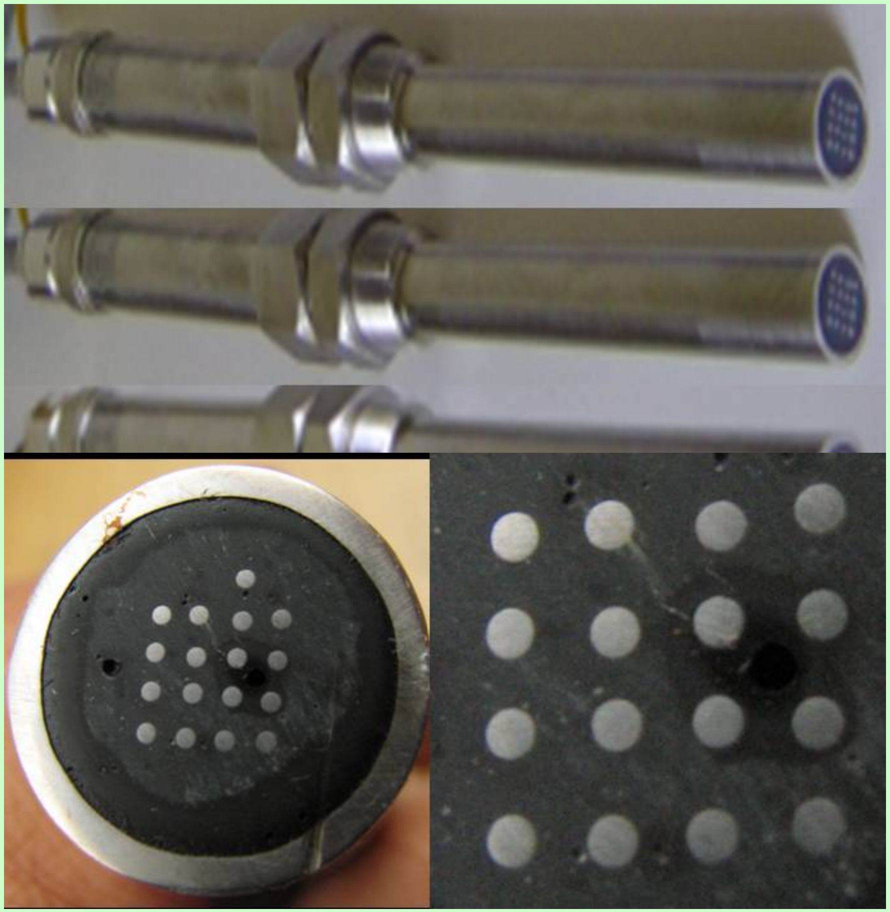
- Water Conservation
- Sustainable Environment
- R&D Studies
- Technical Exchange
- Symposia Papers
- Reports & Journals
- Pre-treat R&D
- Testing Standards
- Green Chemistry

15% NaCl solution with pH adjusted, no Inhibitors Ammonia Effect on Corrosion of Copper and Zinc



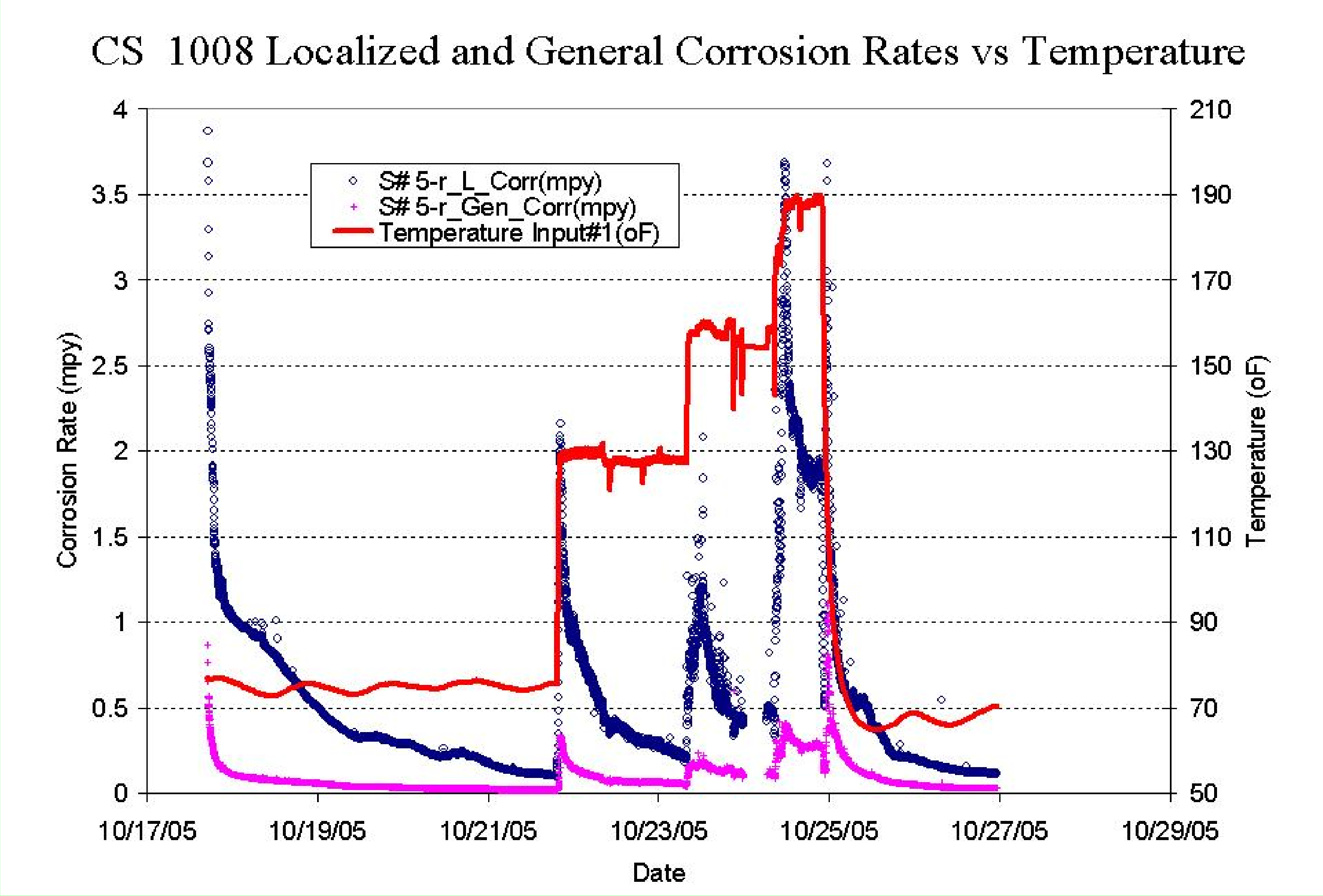
High Temperature Corrosion Inhibition Studies

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



The Effect of Silica and Temperature on Corrosion Rates in High (50,000 mg/L) TDS Waters

Metals	Test Solution	º F	º C	General (mpy)	Max Loc (mpy)
CS 1008	Sea Salt	77	25	-	60
CS 1008	Tower / Silica	77	25	0.02	0.1
CS 1008	Tower / Silica	130	55	0.1	0.2
CS 1008	Tower / Silica	160	71	0.2	0.4
CS 1008	Tower / Silica	190	88	0.2	1.9
SS 316 L	Sea Salt	77	25	-	0.04
SS 316 L	Tower / Silica	77	25	< 0.002	< 0.005
SS 316 L	Tower / Silica	130	55	< 0.01	< 0.01
SS 316 L	Tower / Silica	160	71	< 0.01	< 0.01
SS 316 L	Tower / Silica	190	88	< 0.01	0.013
AL 1100	Sea Salt	77	25	-	20
AL 1100	Tower / Silica	77	25	< 0.05	< 0.1
AL 1100	Tower / Silica	130	55	0.002	0.009
AL 1100	Tower / Silica	160	71	< 0.05	0.2
AL 1100	Tower / Silica	190	88	< 0.06	0.37
Zn	Sea Salt	77	25	8	80
Zn	Tower / Silica	77	25	< 0.05	< 0.01
Zn	Tower / Silica	130	55	< 0.2	0.4
Zn	Tower / Silica	160	71	-	2.0
CU 110	Sea Salt	77	25	-	0.4
CU 110	Tower / Silica	77	25	< 0.05	< 0.2
CU 110	Tower / Silica	130	55	< 1.0	3.0
CU 110	Tower / Silica	160	71	-	4.0

Fresh Water Reduction / Discharge Reduction