Aqueous Discharge Minimization
NACE 2006

New Technology for Evaporative Cooling Water Discharge Reduction and Corrosion Protection

Water Conservation Technology International, Inc.

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Presentation Outline

- Objectives
- Silica Chemistry / How It Works
- Corrosion Inhibition Mechanisms
- Field Case Studies
- High Temperature Corrosion Studies
- Water Conservation Impact
- Conclusions

Objectives

- Provide high TDS tolerant water treatment
- Permit discharge reduction
- Eliminate scale limitations
- Protection from corrosion
- Permit use of high salt or recycle water
- Provide economical & simple control

Aqueous Discharge Reduction

Priority of Limiting Factors

Factor	***Limit***	***Control Mechanisms***
1. Ca/Mg	LSI 2.5-3.0	Blowdown / Inhibitor
		Acid / Ca&Mg Reduction
2. Silica	150-180 Mg/l	Blowdown / Inhibitor
		Silica Reduction
3. TDS	Corrosion	Blowdown / Inhibitor

Silica Chemistry

How It Works

Silica / Scale Control

- Minimize polyvalent metal co-precipitant ions and salts.
- Prevents surface nucleation/reaction sites.
- Permits maintenance of higher concentrations of soluble and stable silica.
- Silica precipitates are non-adherent form.

Pre-Treatment

- Pre-treatment alternatives are simple and economical (cost less than discharge).
- Sodium cycle or WAC exchange of Ca/Mg depending on source water TDS.
- Proper pre-treatment design can reduce regenerate usage by 30-50%.

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

<u>Cations</u>

Ca^{+2} (60%)

Mg^{+2} (30%)

Na^{+} (10%)

SiO_2 ⟺

<u>Anions</u>

Cl^{-}

SO_4^{-2}

CO_3^{-2}

OH^{-}

Pre-treated / High TDS Chemistry
Major Ion Relationships @ 20-100 Conc.

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

High TDS Corrosion Control

- Silica based protection of metals, highly resistant to TDS corrosive impact.
- Method conversion of monomeric & colloidal silica in source water to corrosion inhibiting forms.
- Permits maximum aqueous discharge reduction without corrosion impact.

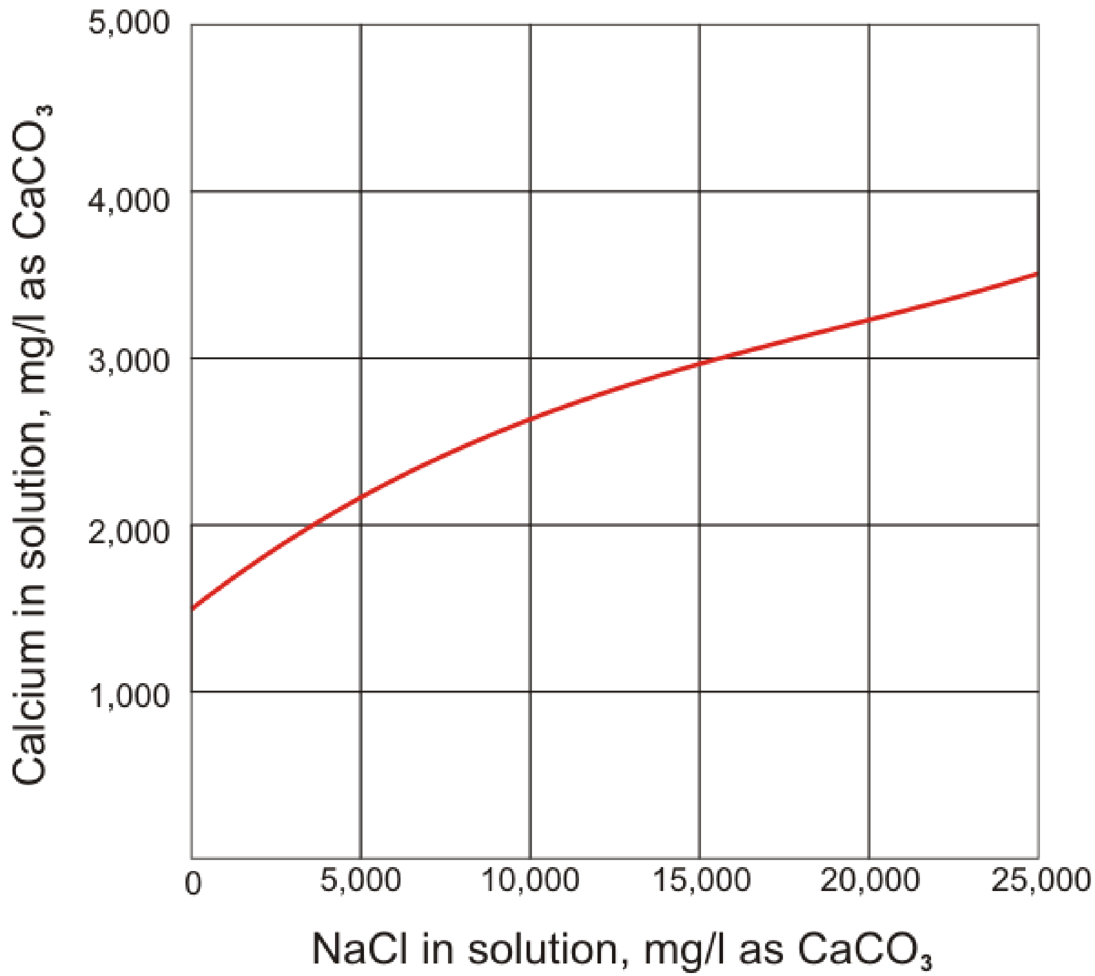
How Silica Is Controlled

- Pre-treatment removes divalent metal ions.
- Control Ca/Mg in treated systems below level achieved by cold lime softening.
- Elevated ionic strength increases solubility of remaining metal salts (sea water effect).
- Control pH at 9 to 10 range.
- Concentration of silica to 200-600 Mg/l.

High Ionic Strength Effect

- Solubility of Ca/Mg increases at higher ionic strength.
- 2-3X solubility increase at zero blowdown.
- Seawater solubility example

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



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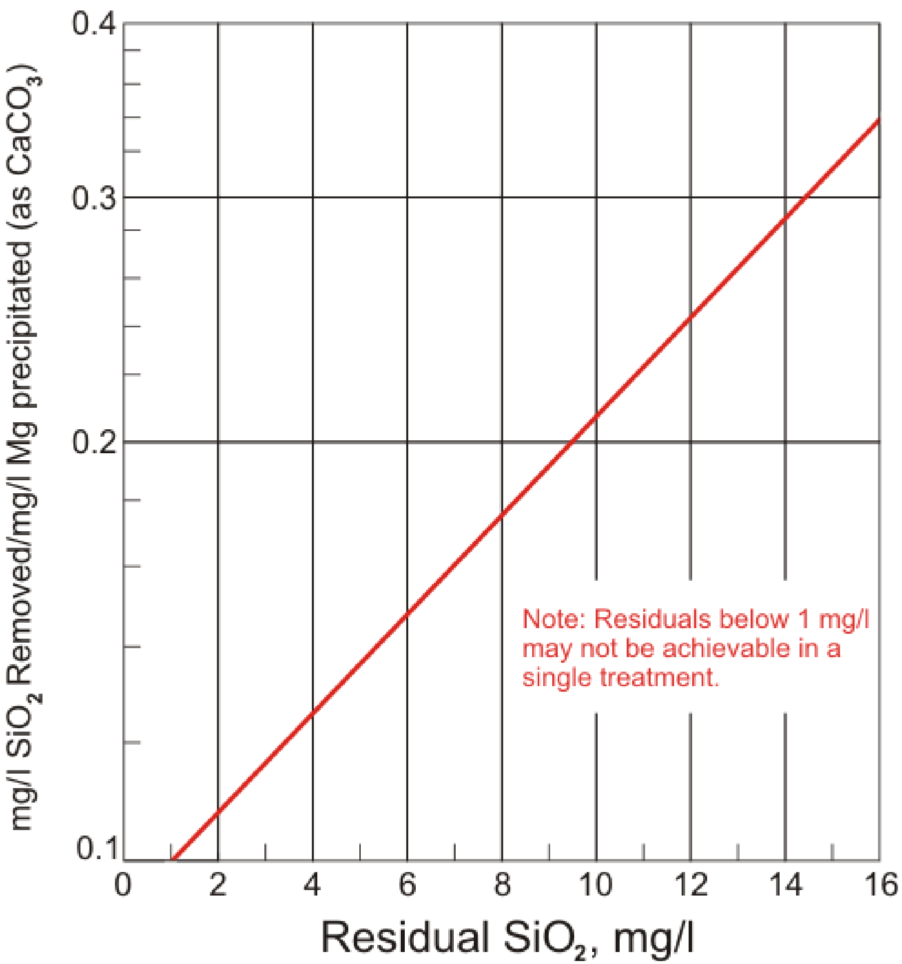
Excess Silica Reduction

- Excess silica is incrementally adsorbed to form small quantities of non-adherent amorphous precipitate in basin.
- Adsorbs on trace multivalent metal salts from source water or scrubbed from air.
- Freundlich isotherms illustrate silica adsorption in precipitation processes.

Freundlich isotherms showing adsorption effectiveness of $Mg(OH)_2$ toward SiO_2



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High TDS Corrosion Control

- Silica chemistry protects metals, highly resistant to TDS corrosive impact.
- Method converts monomeric & colloidal silica in source water to corrosion inhibitor.
- Permits maximum aqueous discharge reduction without corrosion impact.

Prior Silica Limitations

- Earlier studies focused on silica precipitation and removal from water for a number of technical and economic reasons.
- Silica in source water does not contribute to corrosion inhibition and was a scale threat with prior water treatment practices.
- Current discharge reduction, accompanied by high TDS levels, requires extensive re-examination of corrosion protection mechanisms.

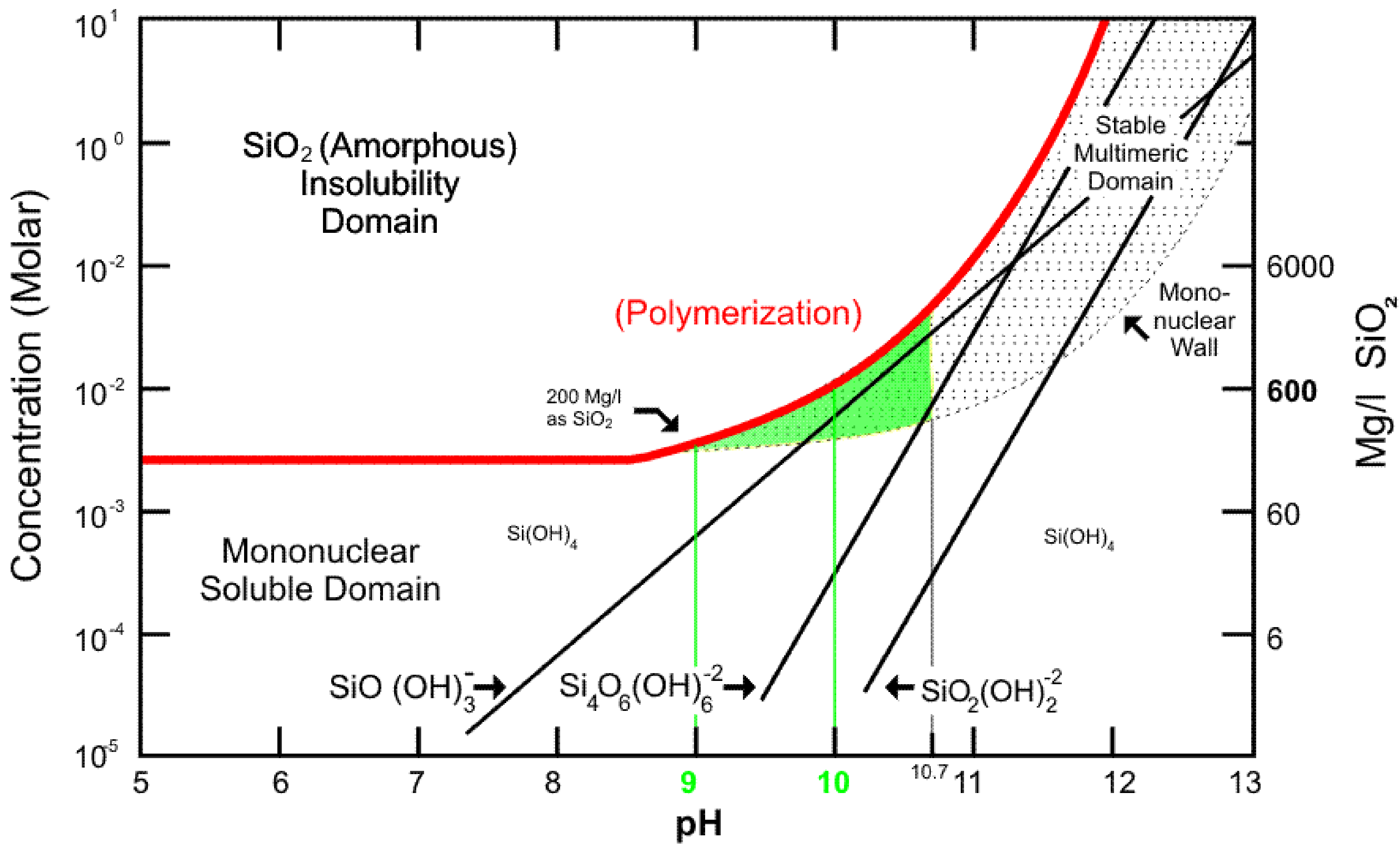
Silica Chemistry

- In the absence of polyvalent metal ions, silica solubility and behavior is very different than common expectations.
- Exchange of polyvalent metal ions with mono valent metal ions, and control of alkaline chemistry, increases monomeric silica solubility and transforms silica to larger corrosion inhibiting particles.

Equilibrium Chemistry

- We are familiar with the role of $CaCO_3$ solubility equilibrium in deposition control and corrosion inhibition mechanisms for most "alkaline" program chemistry.
- This chemistry looks at a comparable role for silica solubility equilibrium and impact on corrosion inhibition mechanisms.

Species In Equilibrium with Amorphous Silica



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Other Contributing Factors

- High levels (>0.3N) of monovalent (sodium) salts reduce colloidal silica solubility, which precipitate (non adherent) as amorphous silica.
- Colloidal silica particles grow by adsorbing smaller particles, thus reducing soluble silica levels detected by molybdic acid test.
- Colloidal silica solubility increases at elevated temperature surfaces (versus polyvalent metal salts of silica).

Corrosion Inhibition Mechanisms

Silica Chemistry

Silicate Anodic Passivation

- Monomeric silica converted to multimeric silicates in aqueous system chemistry.
- Silicates hydrolyze to negatively charged colloidal particles.
- Colloidal silicate migrates to anodic sites on metal and react with metal oxides.
- Forms self repairing silicate gels, with self limiting growth on metal surface.

Silica Cathodic Film Passivation

- At saturated silica concentration, in equilibrium with amorphous silica, cathodic gel formation provides exceptional corrosion protection.
- Amphoteric metals (Al, Zn) are protected by silica gel layer, contrary to high hydroxyl ion level.
- Method controls ions (Ca/Mg) that normally interfere with silica anodic/cathodic mechanisms that protect metal surfaces.

Field Case Studies

Silica Chemistry

Case History #1

Industrial Solvents Processor

- Three years application, solvent separation process using vacuum distillation.
- Tube & Shell Exchangers, 304S, Shell Side 450 F., deposit free tube surfaces.
- Corrator and 60 day weight loss; 304S negligible, MS < 0.2 mpy, Cu < 0.1 mpy.
- No chemical inhibitors utilized.

Industrial Solvents Processor

Industrial Solvents Processor	Chemistry Residual Ratios		
SAMPLE / TESTS	Tower	Makeup	Conc
Conductivity (Un-neutralized)	33,950	412	82.4
pH	10.01	8.23	
Turbidity, NTUs, Neat	3	0.08	
Copper, mg/L Cu	ND	ND	
Zinc, mg/L	ND	ND	
Silica, mg/L SiO2	382	9.5	40.2
Calcium, mg/L CaCO3	16	0.2	
Magnesium, mg/L CaCO3	3.33	0.05	
Iron, mg/L Fe	ND	ND	
Aluminum, mg/L Al	ND	ND	
Phosphate, mg/L PO4	ND	ND	
Chloride, mg/L	6040	80	75.5
Tot. Alkalinity, mg/L	13200	156	84.6
ND = Not Detected; Conc = Concentration of chemistry			

Case History #2

Refrigeration Chiller Condensers

- Trane enhanced tube condensers.
- Two years operation with technology.
- Approach temperature maintained at design.
- Corrator; MS from 8.0 to 0.5 mpy, 2 weeks.
- 60 day weight loss; MS < 0.2 mpy, copper < 0.1 mpy.
- No chemical inhibitors utilized.

Refrigeration Chiller Condensers

Refrigeration Chiller Condensers	Chemistry Residual Ratios		
SAMPLE / TESTS	Tower	Makeup	Conc
Conductivity (Un-neutralized)	66,700	829	80
pH	9.61	7.5	
Turbidity, NTUs			
Neat	4	0.08	
Filtered (0.45 micron)	2	-	
Zinc, mg/L	ND	ND	
Silica, mg/L SiO2	306.4	11	28
Calcium, mg/L CaCO3	21.5	0.2	
Magnesium, mg/L CaCO3	0.65	0.05	
Chloride, Mg/L	5,000	60	83
Sulfate, Mg/L	7,950	106	75
Alkalinity, Mg/L CaCO3	12,000	155	77
ND = Not Detected; Conc = concentration of chemistry			

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US 6,949,193; US 6,998,092

Corrosion Protection Performance

- Highly effective passivation
- < 0.2 MPY Mild Steel
- < 0.1 MPY Copper
- Negligible Stainless Steel corrosion
- Passivation of white rust


1590


120

High Temperature Corrosion Studies

With Silica Inhibition Chemistry

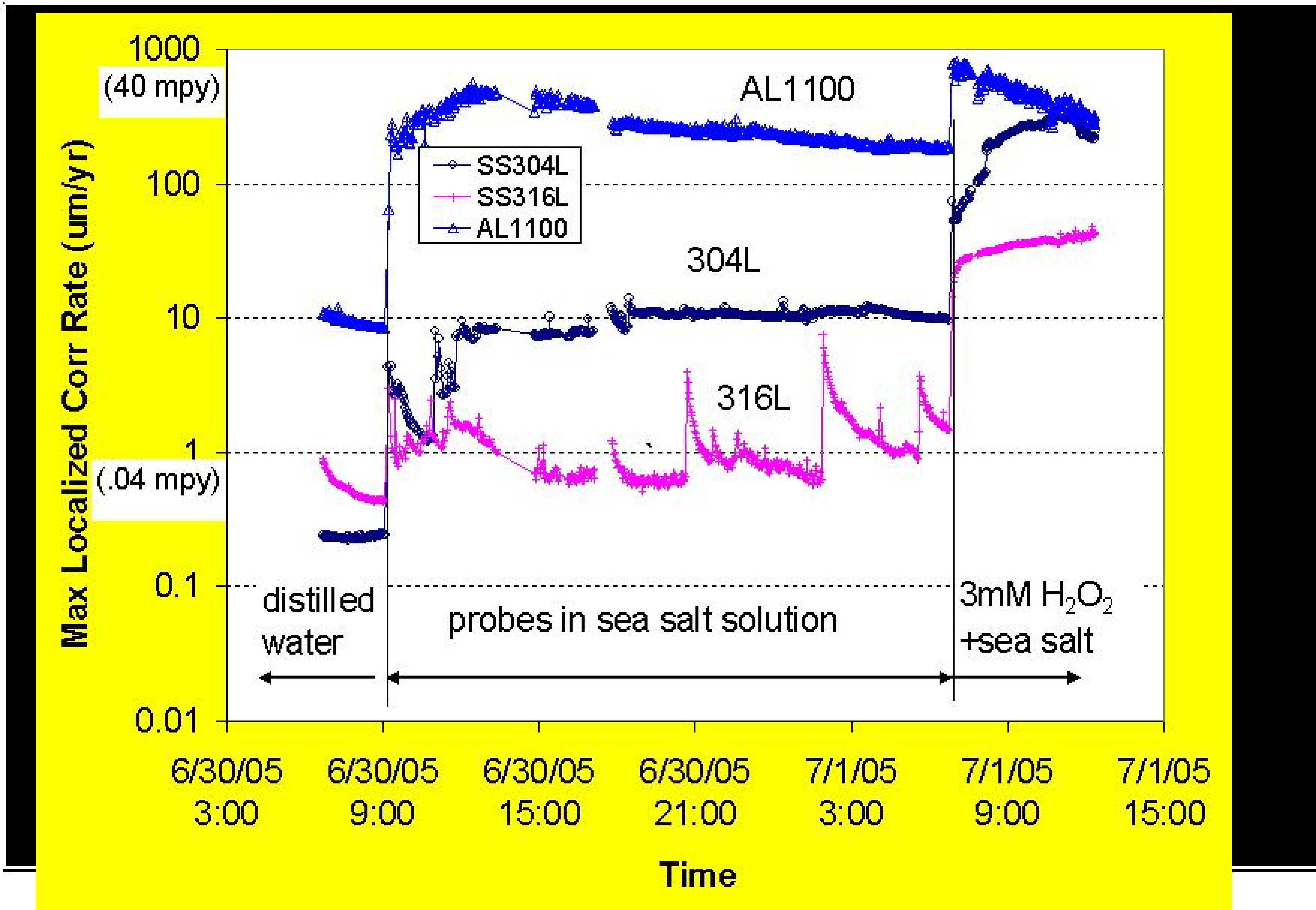
High Temperature / High TDS Corrosion Inhibition Studies

- Study conducted with real time coupled multi-electrode array corrosion sensors.
- Measurement of peak localized corrosion rates; and average rates for metals.
- Test Water Chemistry: 50,000 conductivity; 450 Silica; 9000 chloride.
- Temperatures: 20^{o} C; 55^{o} C; 72^{o} C; 88^{o} C

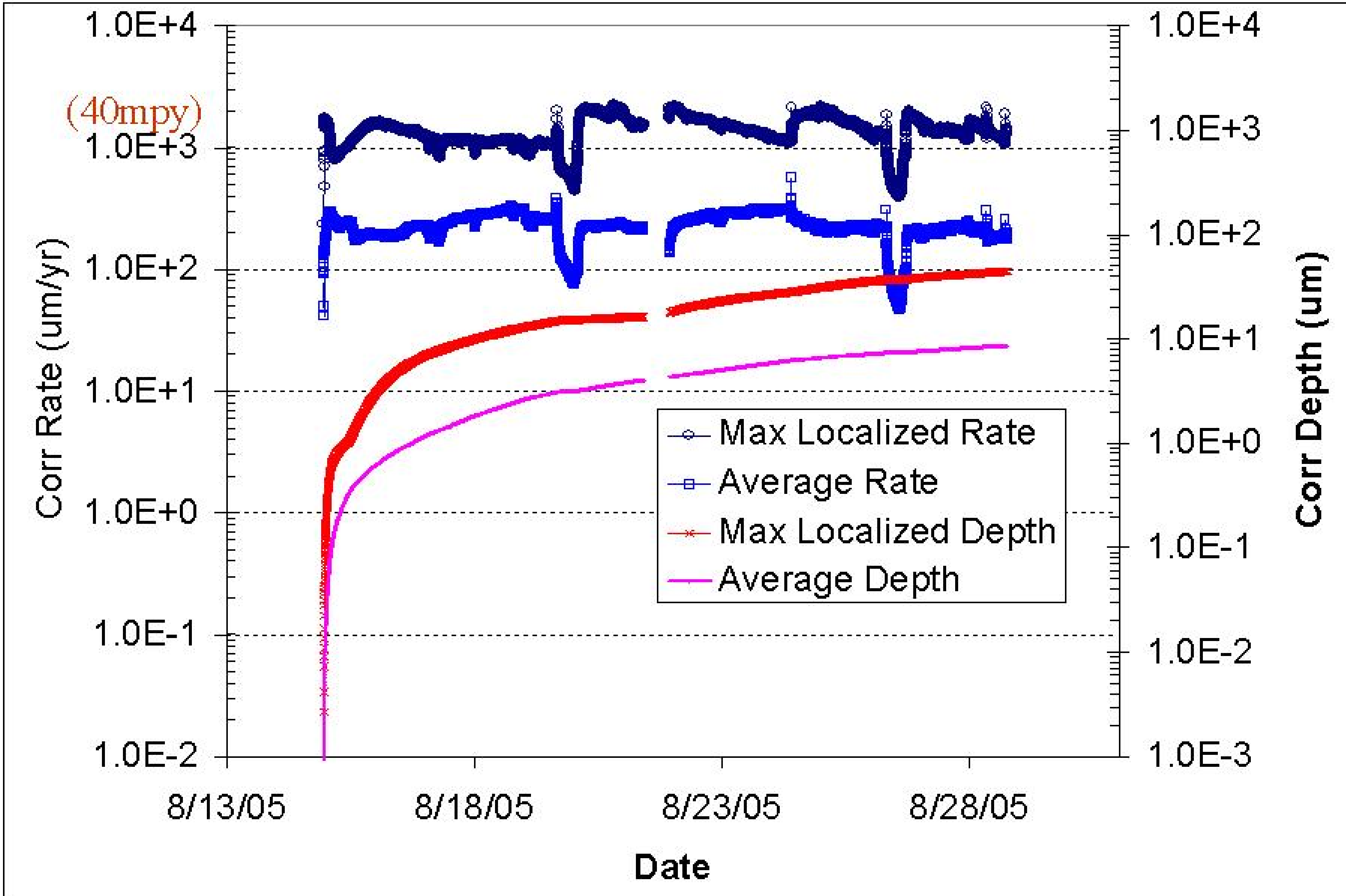
Unprotected Metals in Sea Salt

- High TDS (0.5 N sea salt) impact on CS, AL and SS metals @ 20^{o} C.
- Corrosion approaches 40 MPY localized for mild steel and aluminum.
- Higher temperatures will further increase unprotected corrosion rates in salt.
- Corrosion of steel and aluminum was 40-80X higher than silica inhibited study.

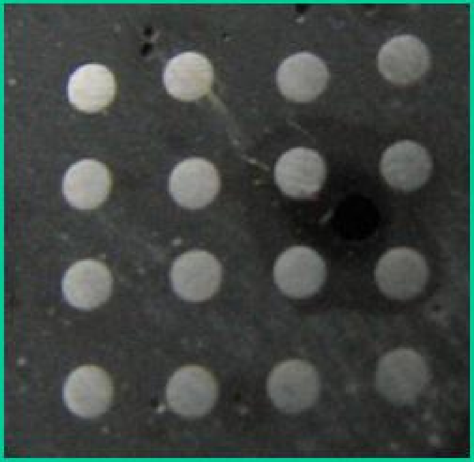
Direct Comparison of Max Localized Corrosion Rates from Three Alloys



Corrosion Rates and Corrosion Depth from a Type 1008 Carbon Steel Probe

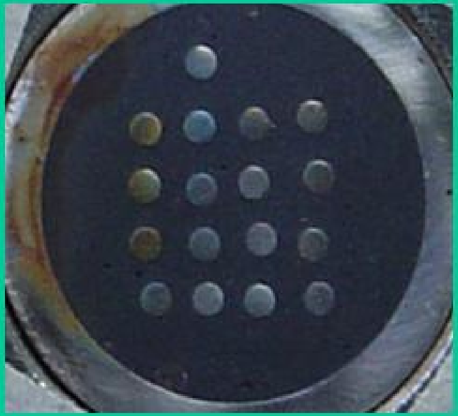


Comparison of Post test Probe Appearances

Carbon steel, one week in High-Silica Brine Solution at up to 88 °C

Mild steel



316L Probe

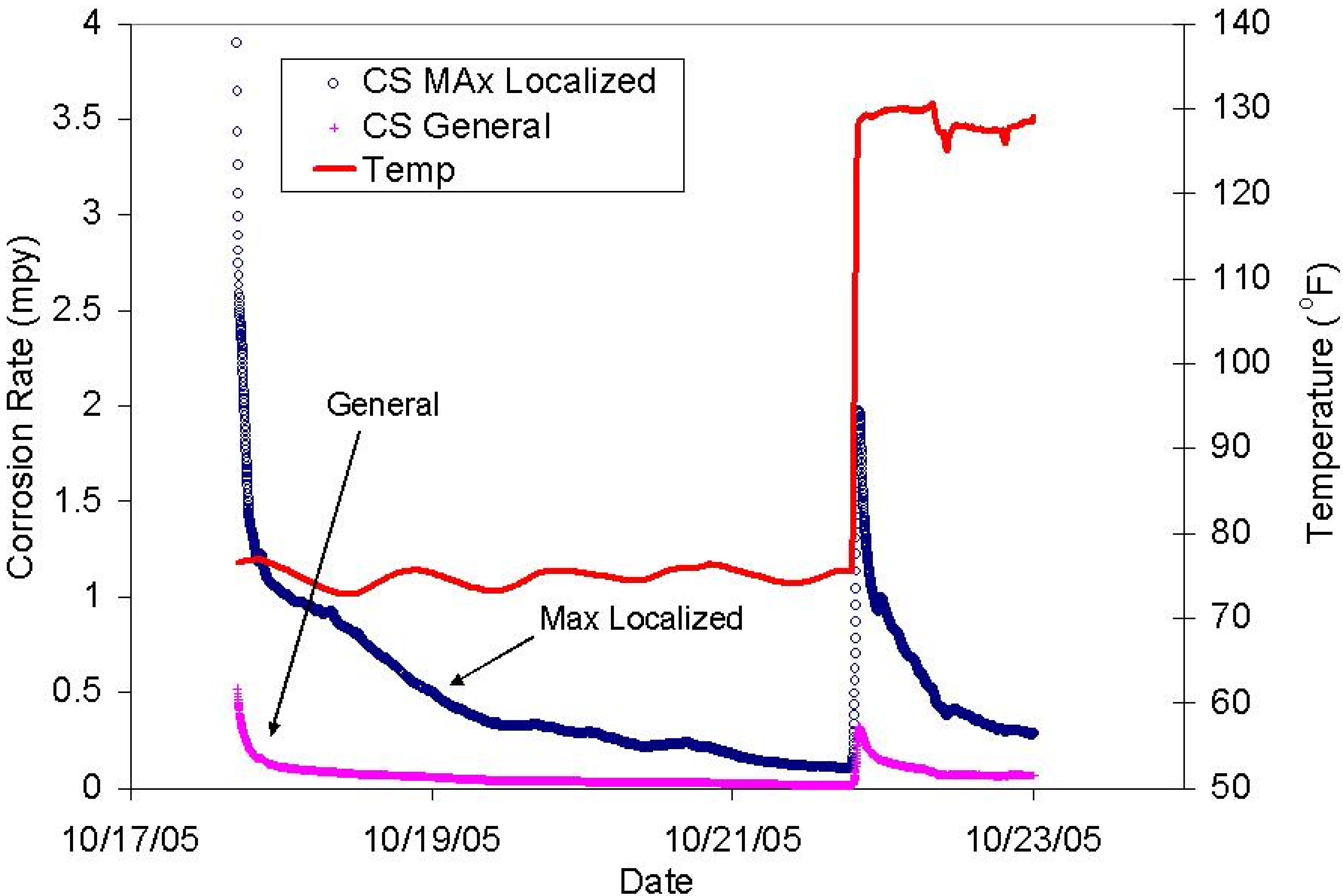
Three weeks in seawater at room temperature

Courtesy:

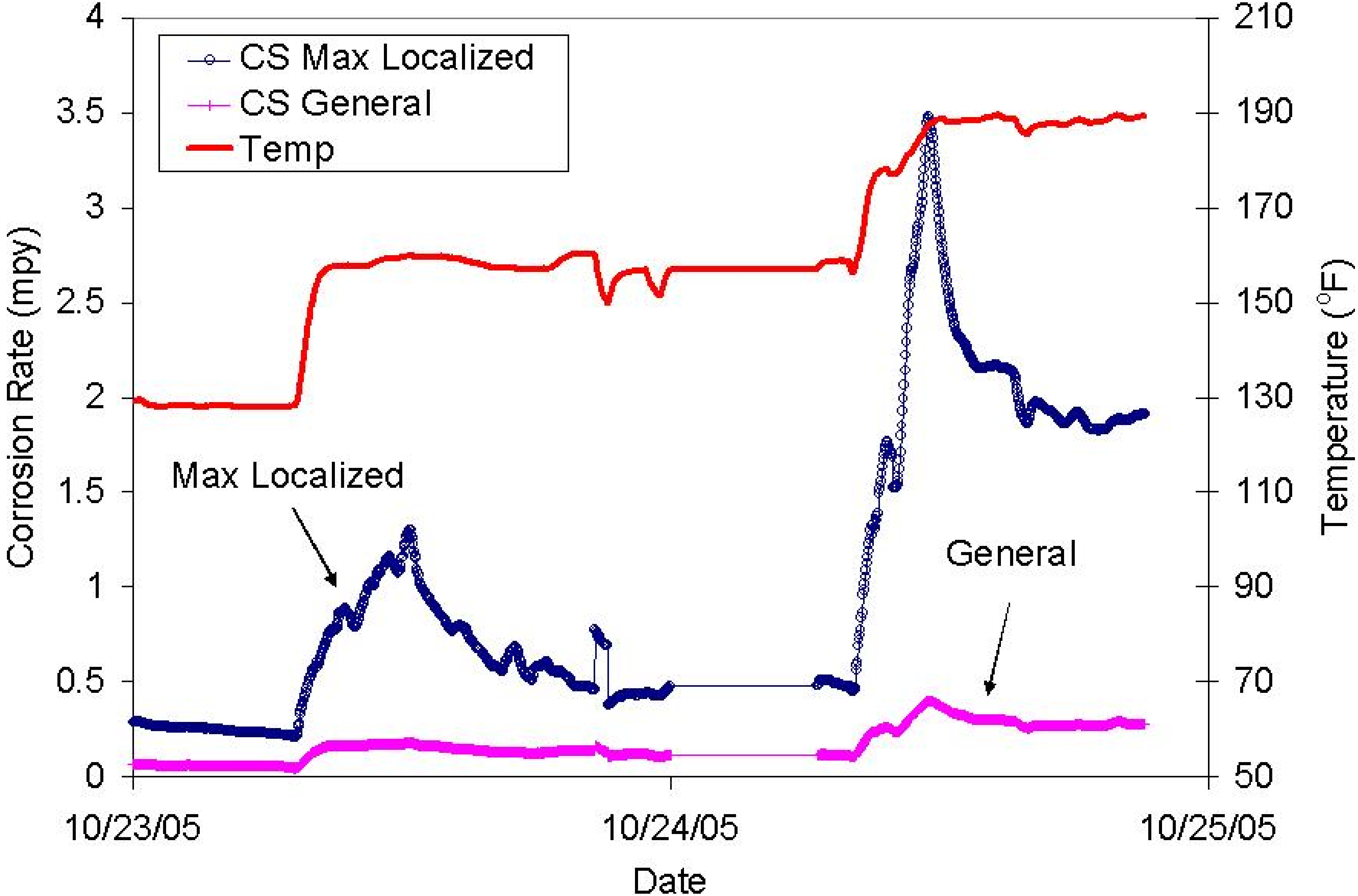
Corr Instruments

High Temp / Silica Study Results

- Outstanding mild steel localized and general corrosion rates at all temperatures.
- Chloride impact on 316 stainless steel is minimal at high temperature.
- Soft metal (Al, Zn, Cu) protection very good at higher temperatures.
- Aluminum protection improved at higher temperatures.



CS MAx Localized
CS General
Temp
General
Max Localized
Corrosion Rate (mpy)
Temperature (°F)
Date
4
3.5
3
2.5
2
1.5
1
0.5
0
140
130
120
110
100
90
80
70
60
50
10/17/05
10/19/05
10/21/05
10/23/05



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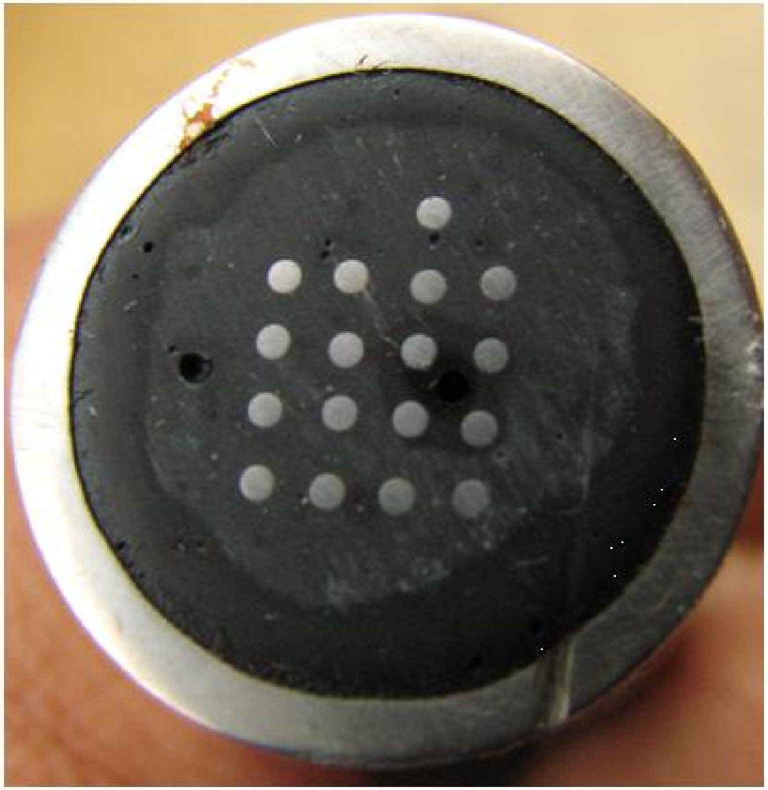
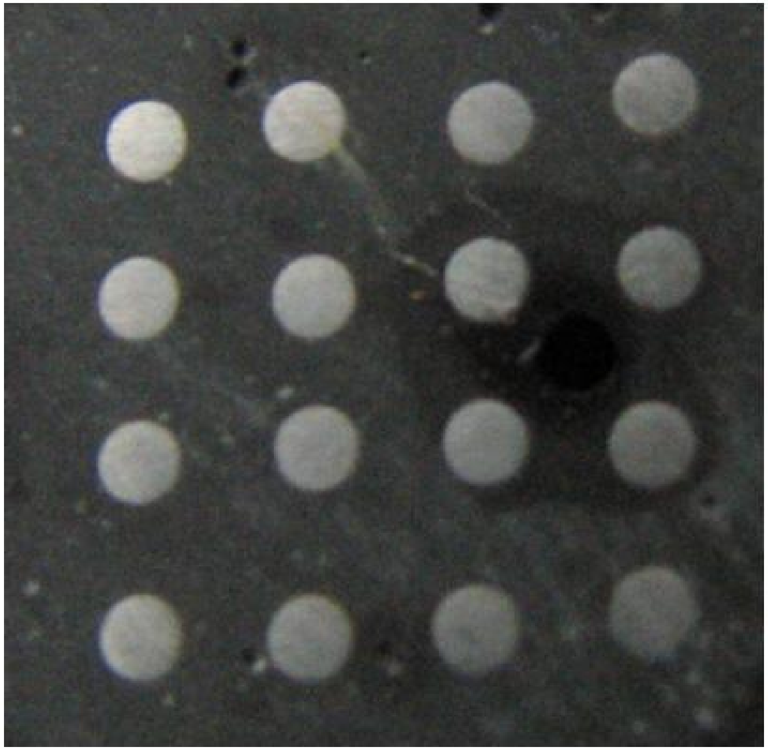
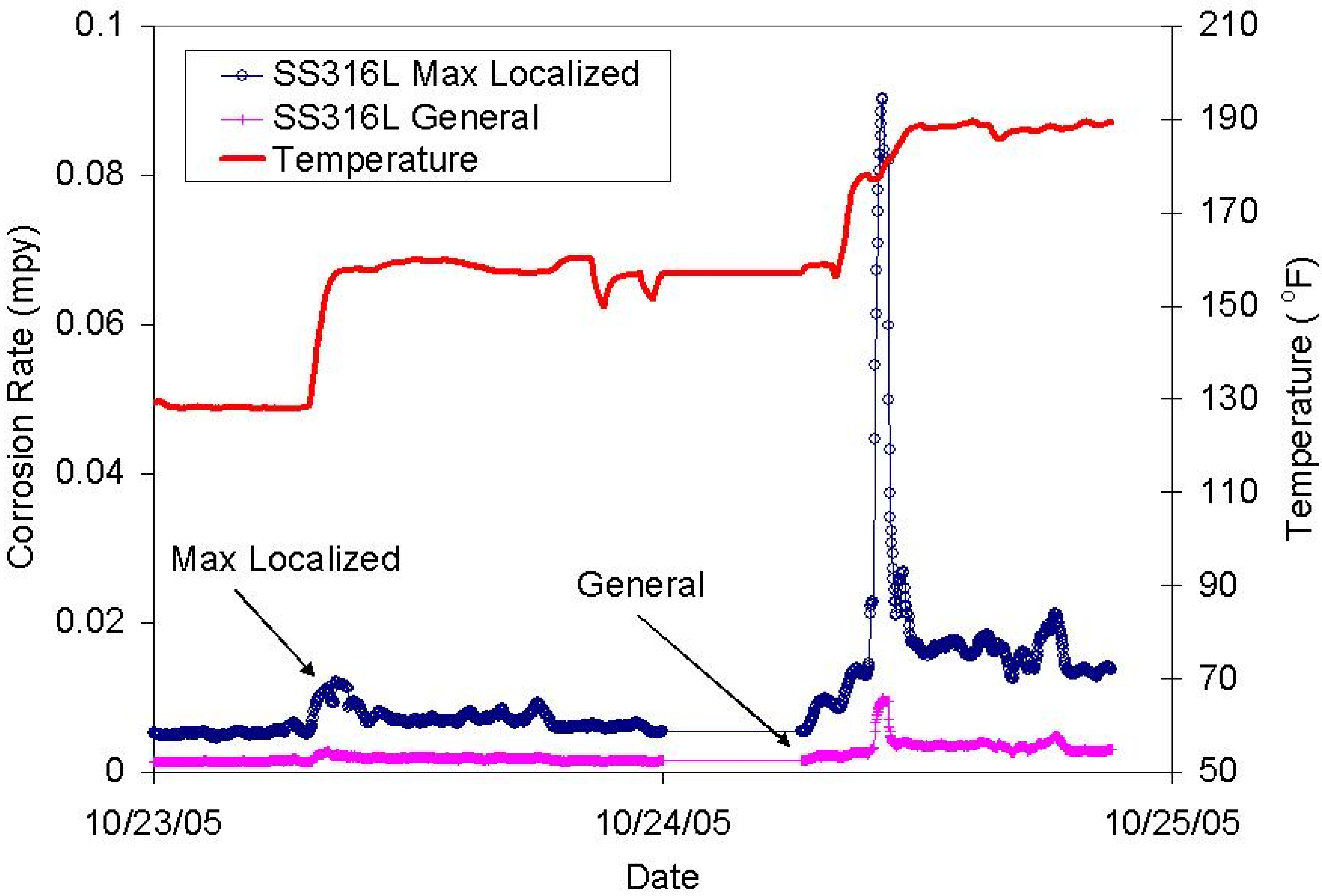
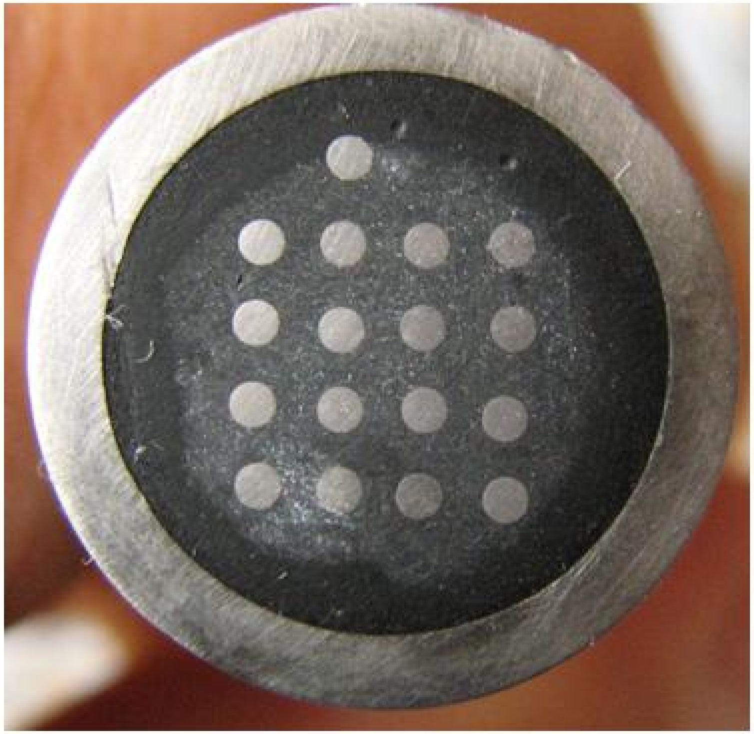
Carbon Steel probe after 88 ^{o} C test
No rust can be seen, before cleaning





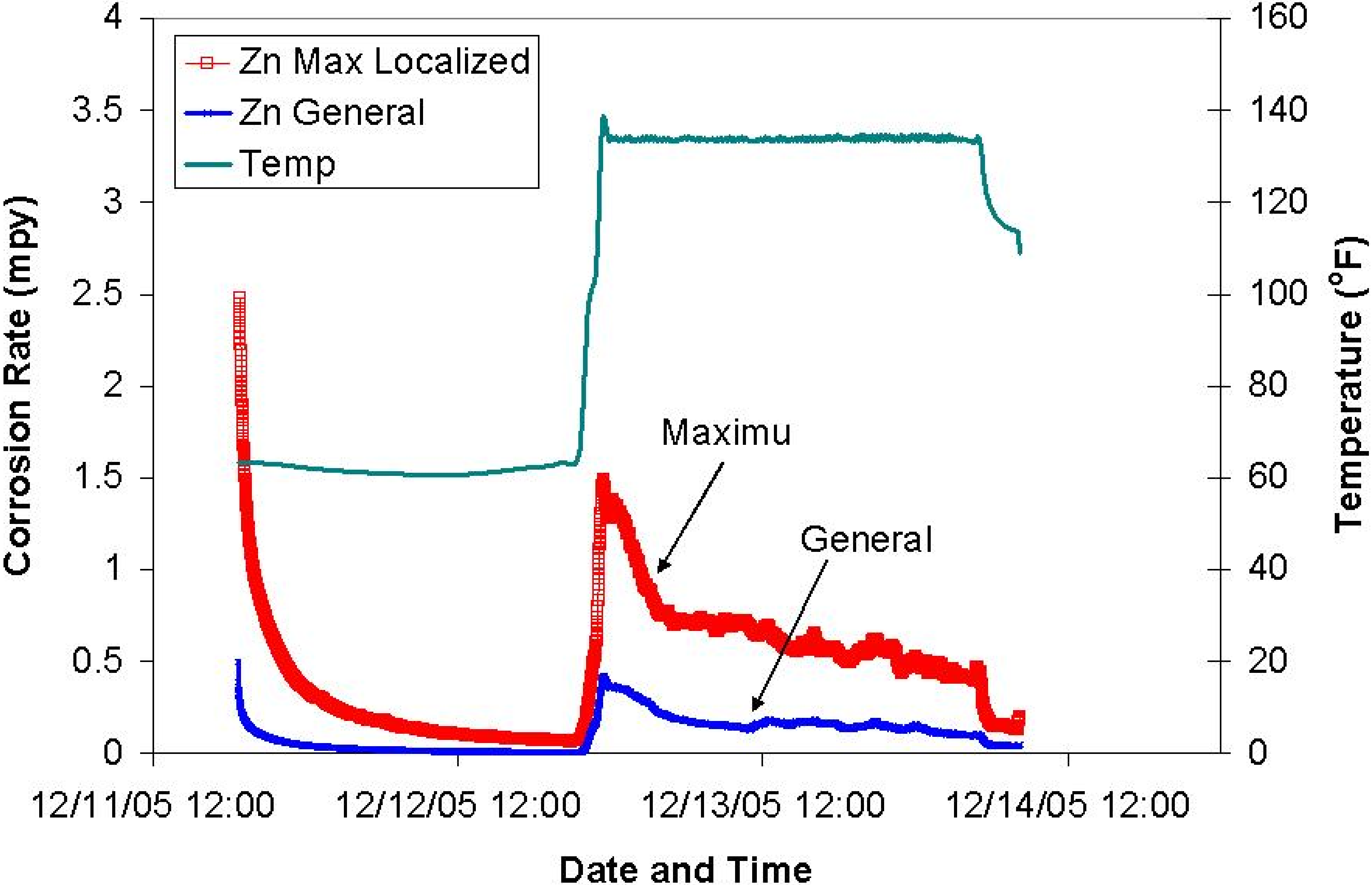

0.1
0.08
0.06
0.04
0.02
0
Corrosion Rate (mpy)
210
190
170
150
130
110
90
70
50
Temperature (°F)
SS316L Max Localized
SS316L General
Temperature
Max Localized
General
10/23/05
10/24/05
10/25/05
Date

SS probe after 88 ° C test
No rust can be seen, before cleaning

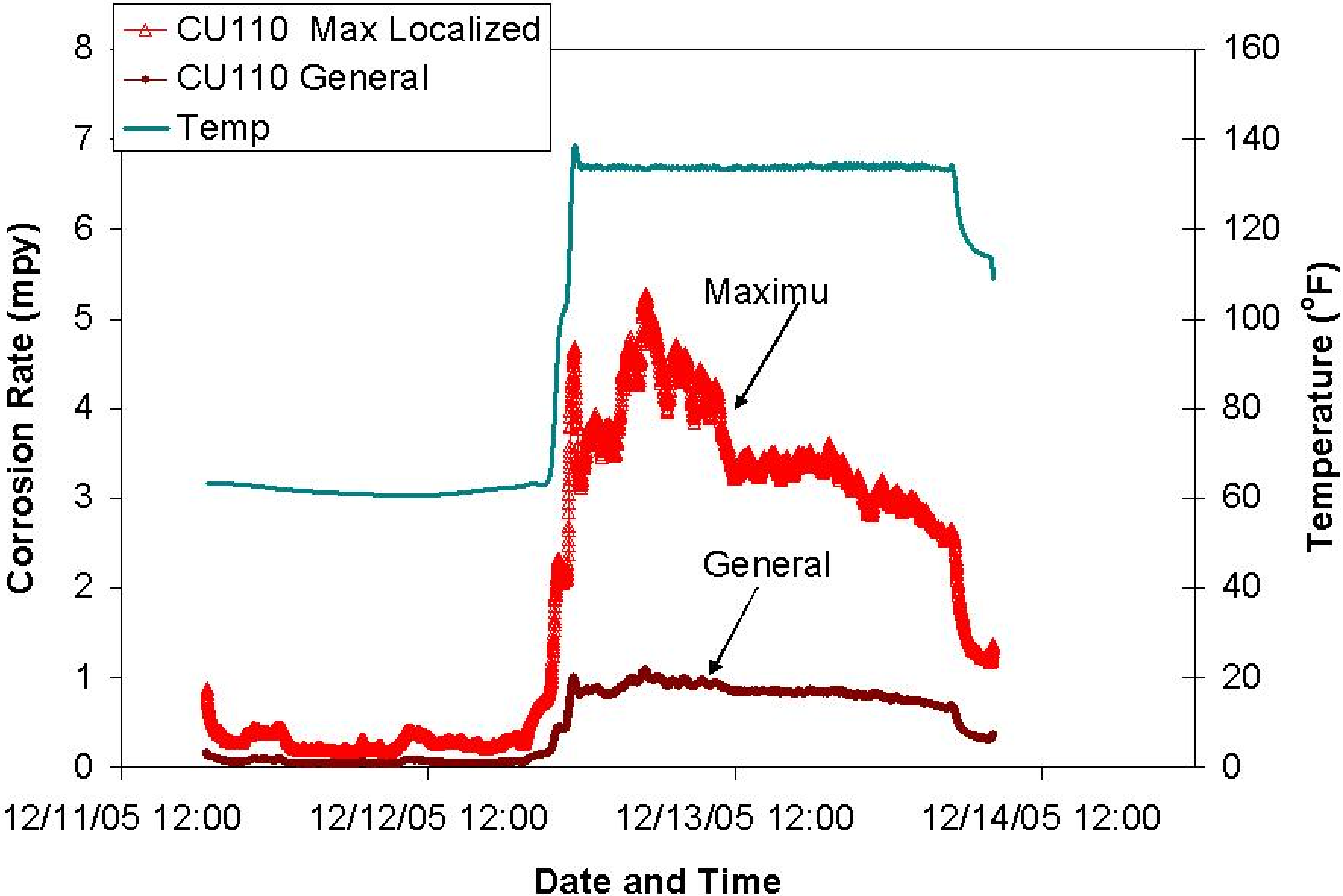


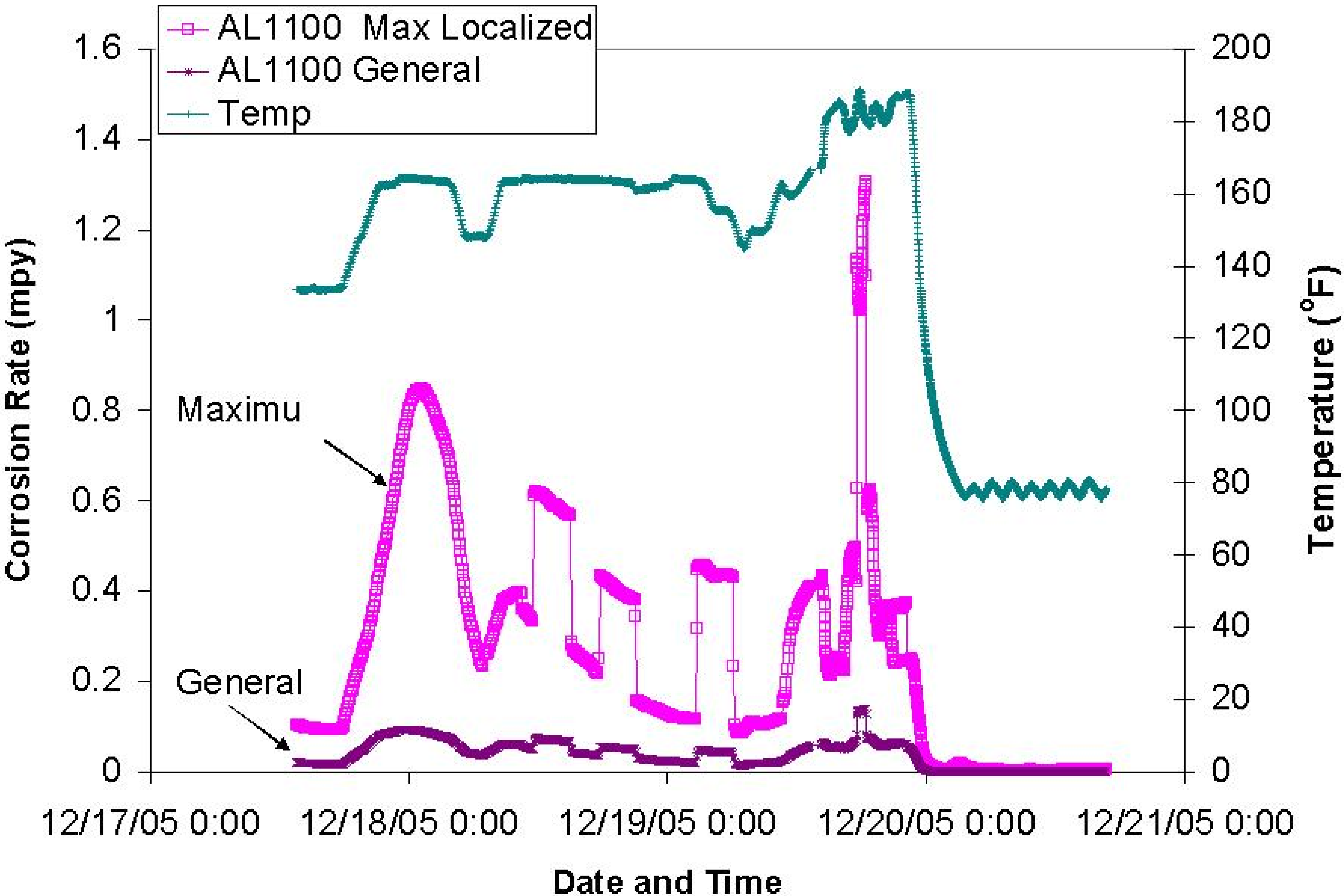
Soft Metals / Silica Study

- Aluminum, Zinc and Copper
- Temperatures: 20^{o} C; 55^{o} C; 72^{o} C
- Protection very good for Zinc & Aluminum
- Aluminum passivation at 72^{o} C



Zn Max Localized
Zn General
Temp
Corrosion Rate (mpy)
Temperature (°F)
4
3.5
3
2.5
2
1.5
1
0.5
0
160
140
120
100
80
60
40
20
0
Maximu
General
12/11/05 12:00
12/12/05 12:00
12/13/05 12:00
12/14/05 12:00
Date and Time


CU110 Max Localized
CU110 General
Temp
8
7
6
5
4
3
2
1
0
Corrosion Rate (mpy)
160
140
120
100
80
60
40
20
0
Temperature (°F)
Maximu
General
12/11/05 12:00
12/12/05 12:00
12/13/05 12:00
12/14/05 12:00
Date and Time


AL1100 Max Localized
AL1100 General
Temp
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
180
160
140
120
100
80
60
40
20
0
Corrosion Rate (mpy)
Temperature (°F)
Maximu
General
12/17/05 0:00
12/18/05 0:00
12/19/05 0:00
12/20/05 0:00
12/21/05 0:00
Date and Time

Other Benefits of Silica Chemistry

- Potential use with brackish or recycled waste water sources.
- Biological propagation is limited by elevated TDS & pH.
- Simple program control with reduced blow down, infrequent chemistry adjustments.

Ammonia Removal

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

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

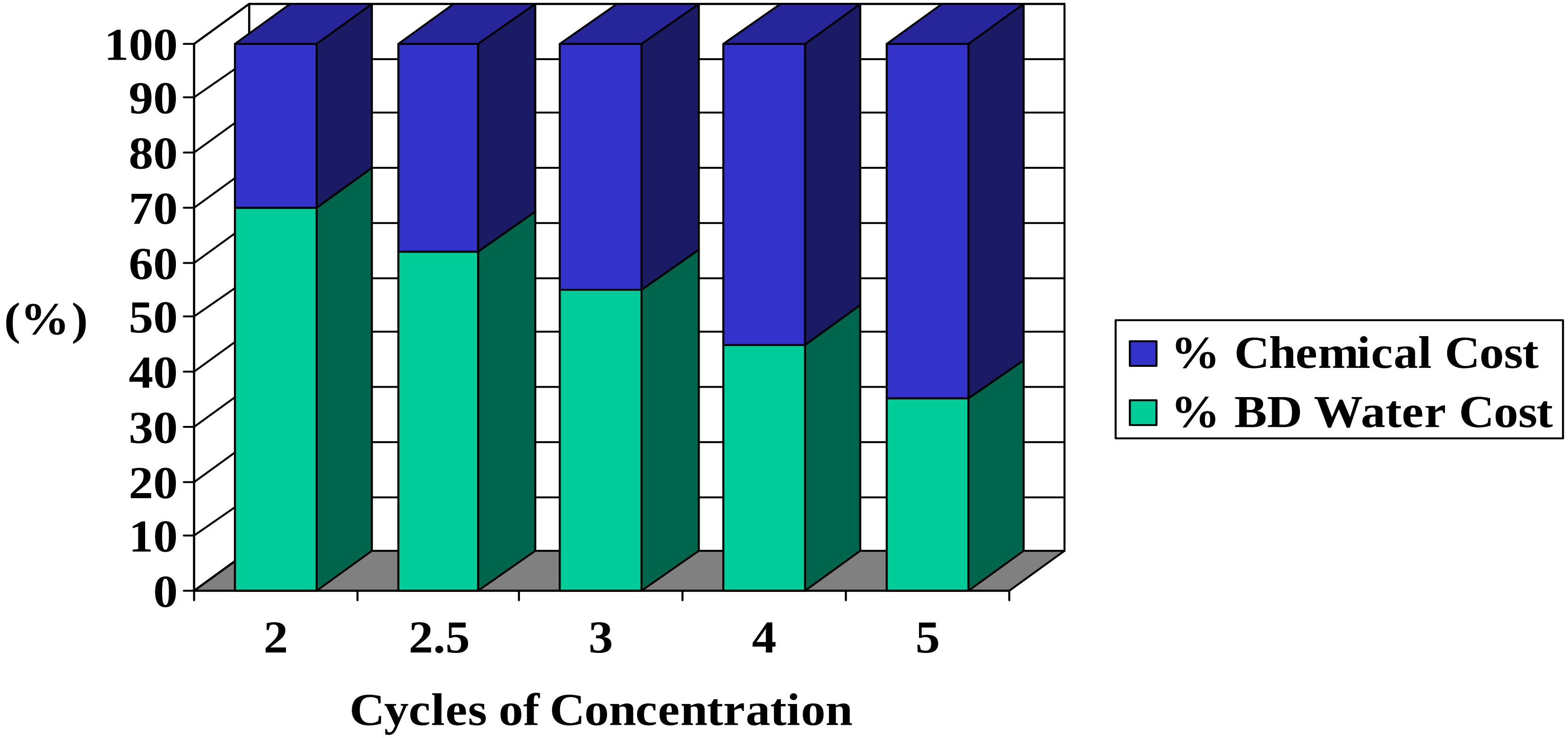
1. Below pH 7, virtually all the ammonia will be soluble ammonia ions.
2. Above pH 12, virtually all the ammonia will be present as a dissolved gas.
3. The range between 7 and 12, both ammonium ions and dissolve gas exist together.
4. Percentage of dissolved gas increases with temperature and pH. Where temperature and pH favor removal of ammonia from solution.

Water Conservation Impact

Discharge Reduction Redefines Cost for Water Treatment

Aqueous Blowdown Treated Cost

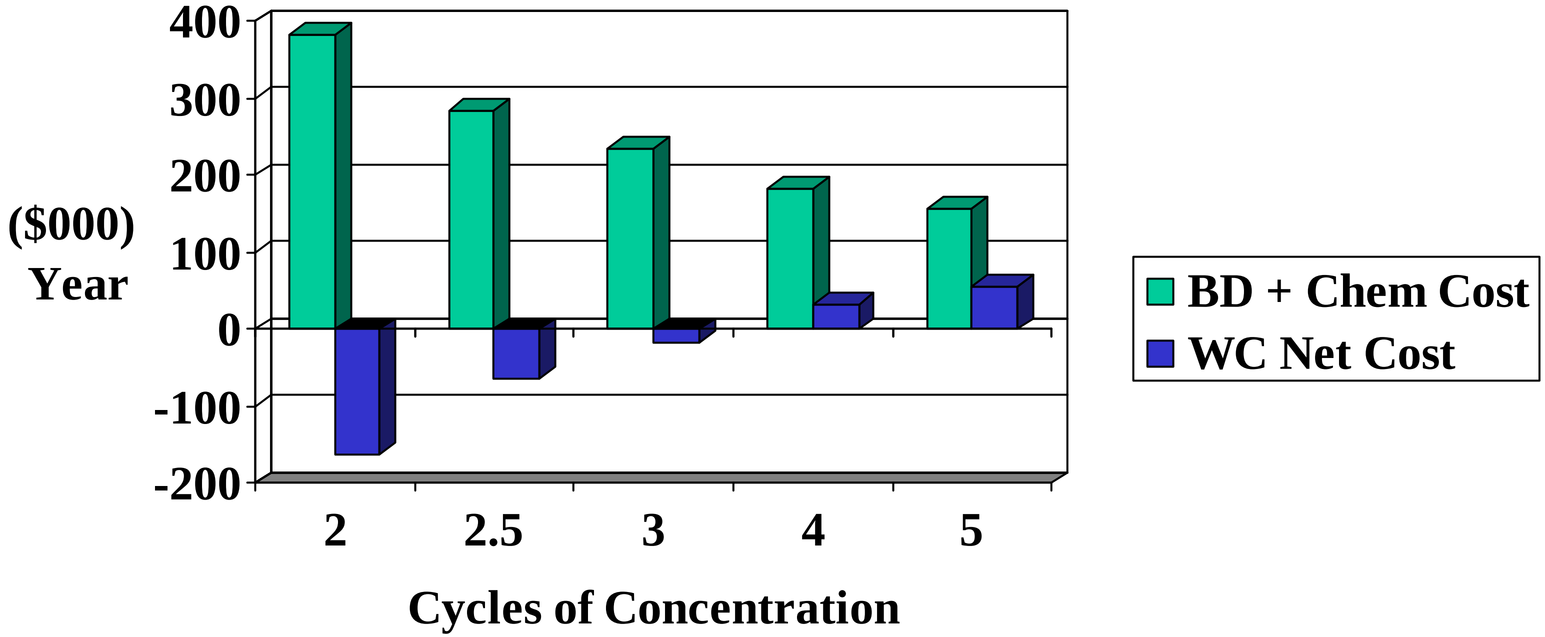
Chemical Cost + Blowdown Water Cost



Water Conservation Program Net* Cost
<u>versus</u> Blowdown + Chemical Cost

*Includes pre-treat & service costs

250 GPM Evaporative Load Example



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Application Experience

- Three years of application and evaluation
- Customers include Chemical Processing, Commercial/Institutional, Food Processing.
- Cooling towers include Marley, BAC, Evapco, Delta.
- Tower construction materials include galvanized, stainless, plastic & fiberglass.

Conclusions

- Excellent corrosion protection @ high TDS
- Pre-treatment controls scaling potentials
- Maximum aqueous discharge reduction
- Can use normal and high TDS waste waters
- Simple & reliable program control
- Lower total cost of treatment

Questions?