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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

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Presentation Outline

- Objectives of Study
- Silica Chemistry and Inhibition Mechanisms
- Laboratory Studies of Silica Corrosion Inhibitor
- Field Studies of Silica Corrosion Inhibitor
- Conclusions

Objectives of Study

- Establish confidence in transferring laboratory / pilot data to full operations
- Verify that silica chemistry can prevent corrosion in high TDS waters
- Demonstrate silica chemistry qualifies as “green” inhibitor chemistry and tool for water conservation

Silica Chemistry
and Inhibition Mechanisms

Limitations of Current Alkaline 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

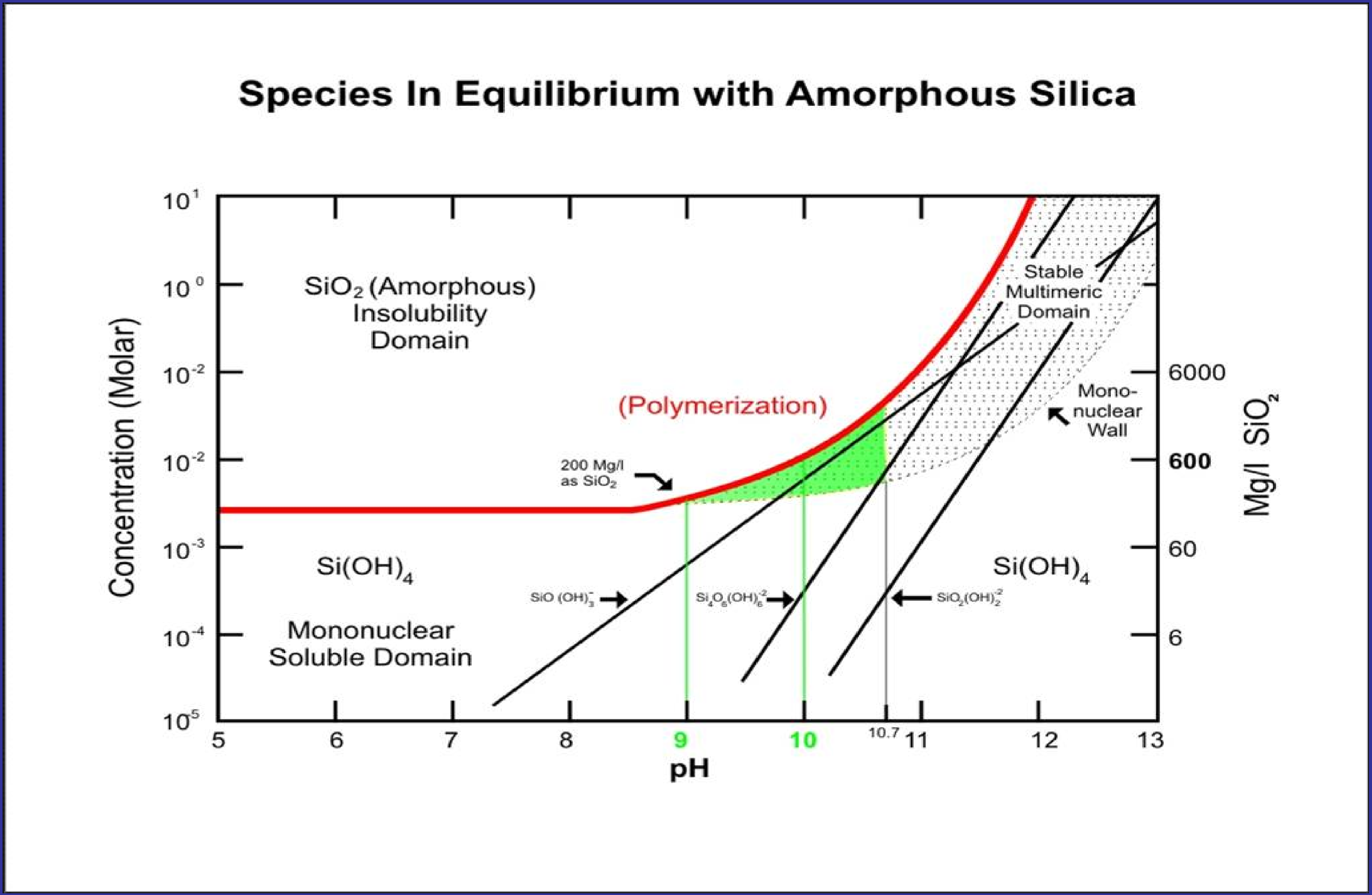
Silica Chemistry Approach

- Soften makeup water, no scale ions
- Concentrate TDS, eliminate blow down
- Control pH to 9 to 10 range
- Concentrate silica to 200-600 mg/L
- No silica saturation limitations
- Chemicals not needed for most waters

Silica Inhibitor Chemistry

- Evaporative concentration of alkalinity, sodium, and silica in makeup
- Silica equilibrium and corrosion inhibition attained above pH 9 and 200 mg/L silica
- System chemistry and temperature of water catalyze silica polymerization
- Excess silica forms non scaling colloids

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



Silicate Anodic Mechanism

- Monomeric silica is polymerized to multimeric silicates by system chemistry
- Silicates hydrolyze to negatively charged colloidal particles
- Colloidal silicate migrates to anodic sites on metal and react with metal oxides
- Silica forms self repairing silicate gels on metal surface

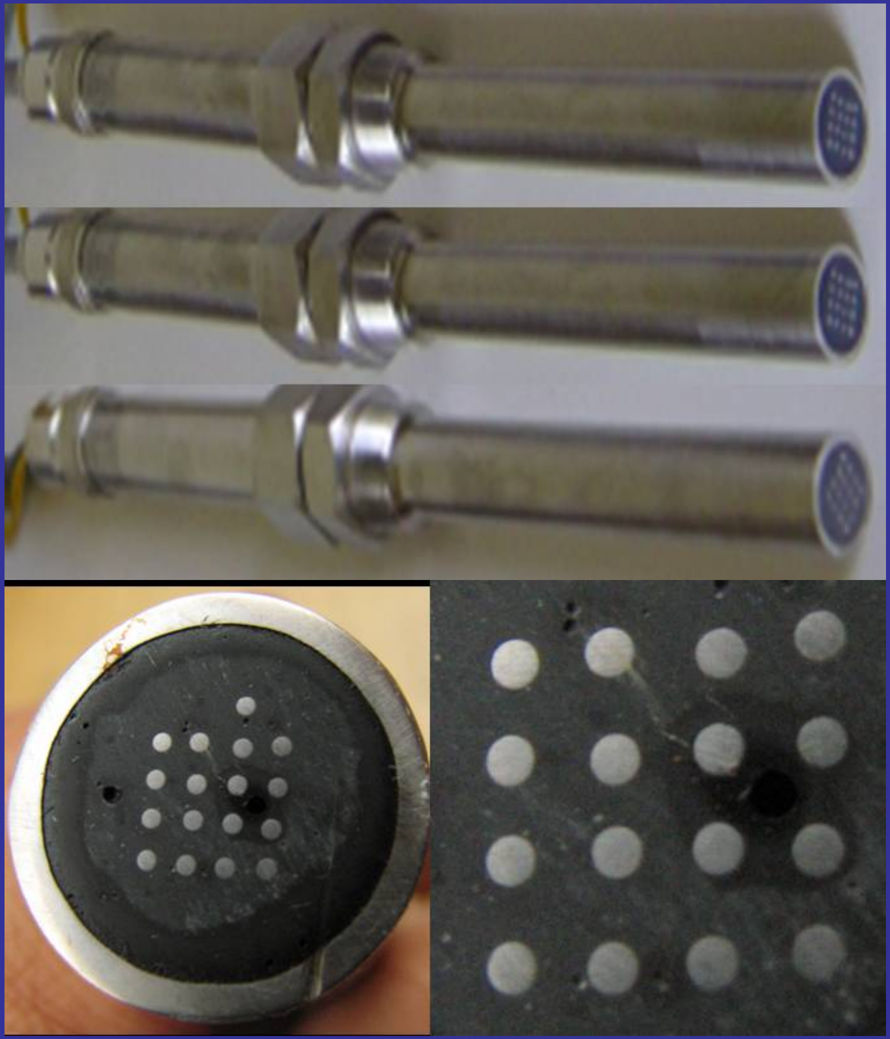
Silica Cathodic Mechanism

- Saturated silica, in equilibrium with amorphous silica, is attracted to metals
- Cathodic gel layer forms on metals for total barrier to corrosion
- Even amphoteric metals (Al, Zn) are protected by silica gel layer at high pH
- Gel layer growth is self limiting

Laboratory Studies of Silica Corrosion Inhibitor

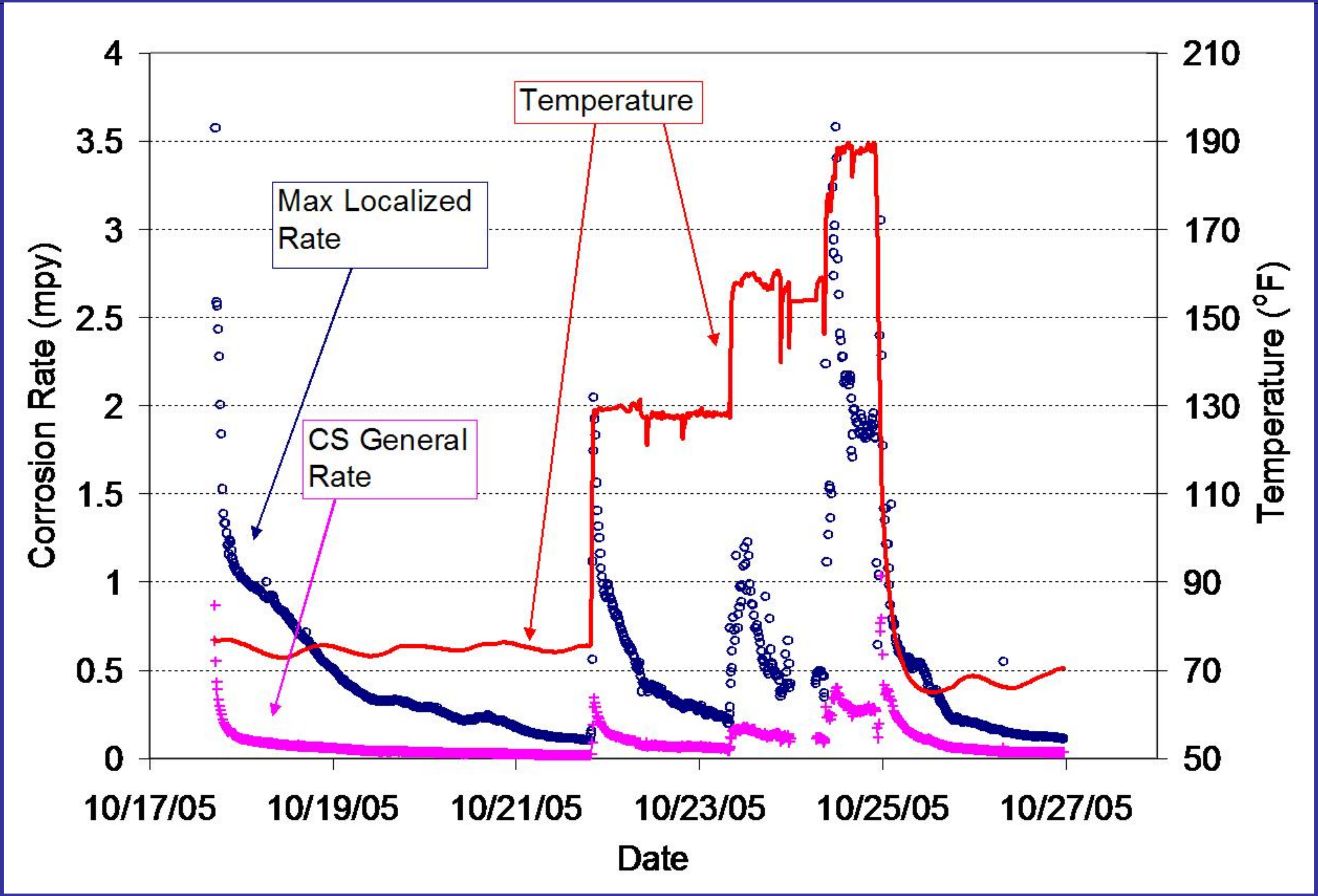
at High TDS / Temperatures

High TDS / High Temperature Corrosion Inhibition Studies

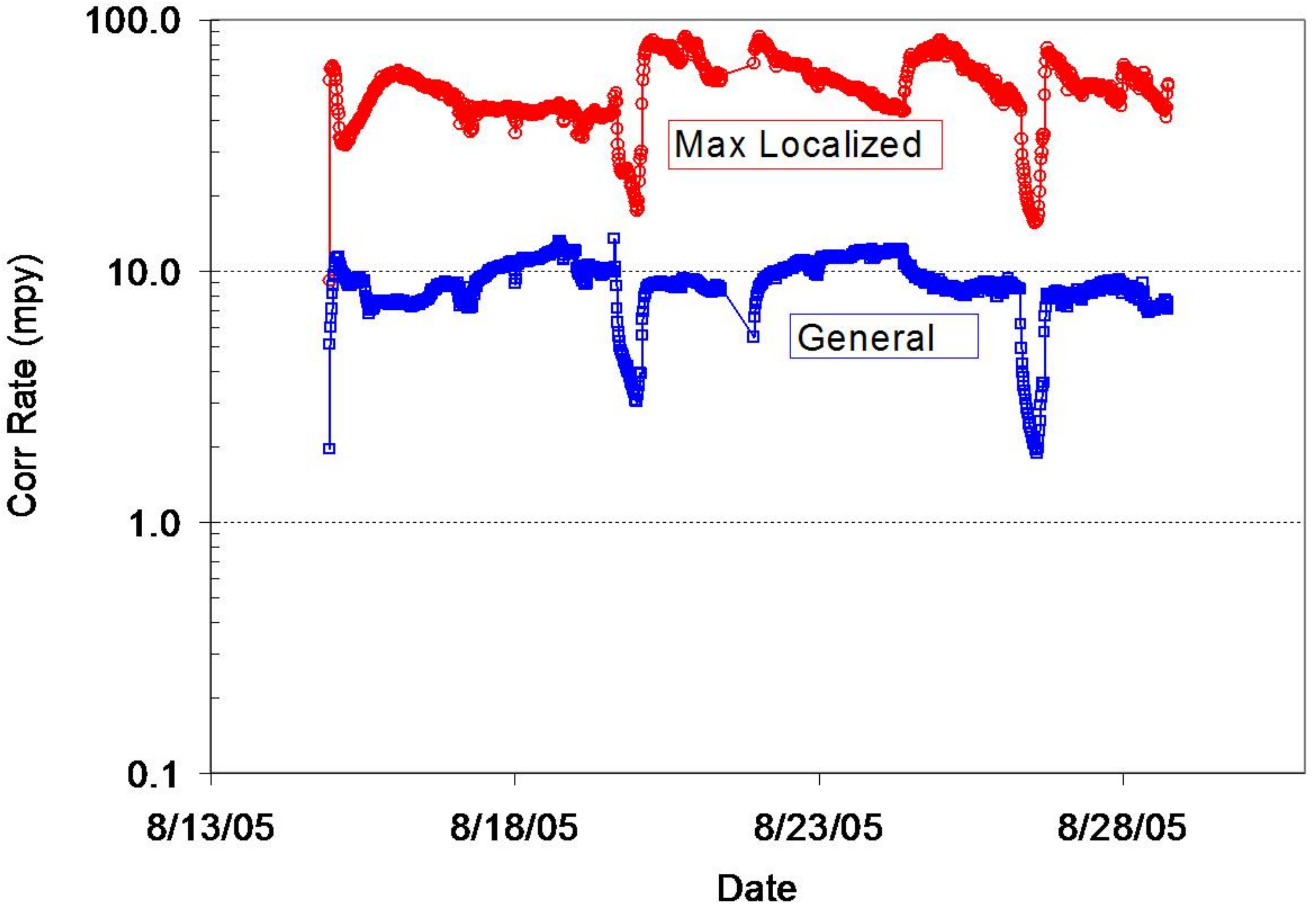


- Used real time coupled multi-electrode array corrosion probes
- Probes measured peak localized and general corrosion rates
- Test water chemistry:
  - 50,000 conductivity
  - 450 ppm silica
  - 9000 ppm chloride
- Temperatures:
  - 77º F; 130º F; 160º F; 190º F **(25º C; 54º C; 71º C; 88º C)**
- Metals: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

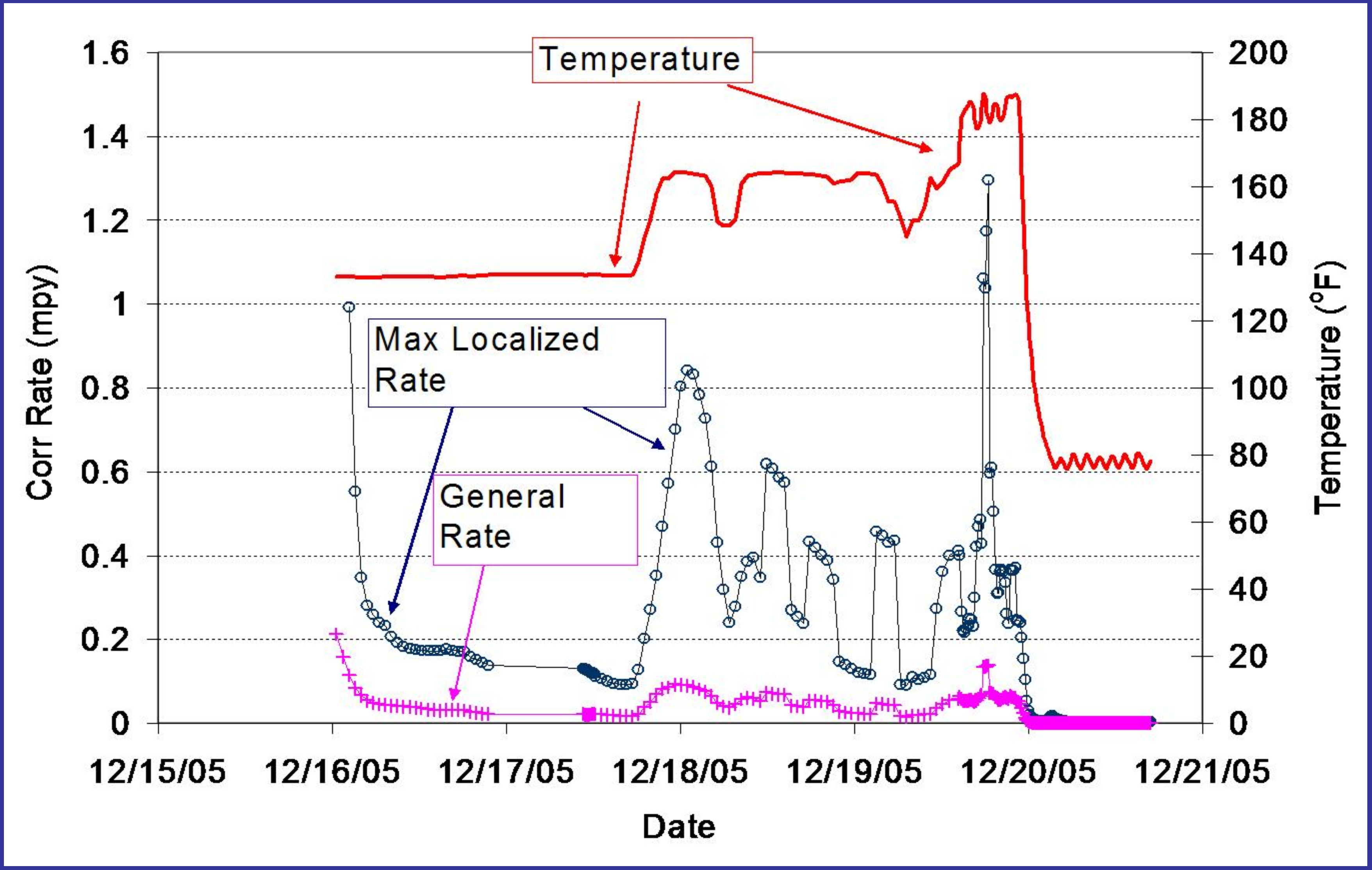
Localized and General Corrosion Rates of Carbon Steel in High Silica - High TDS Water



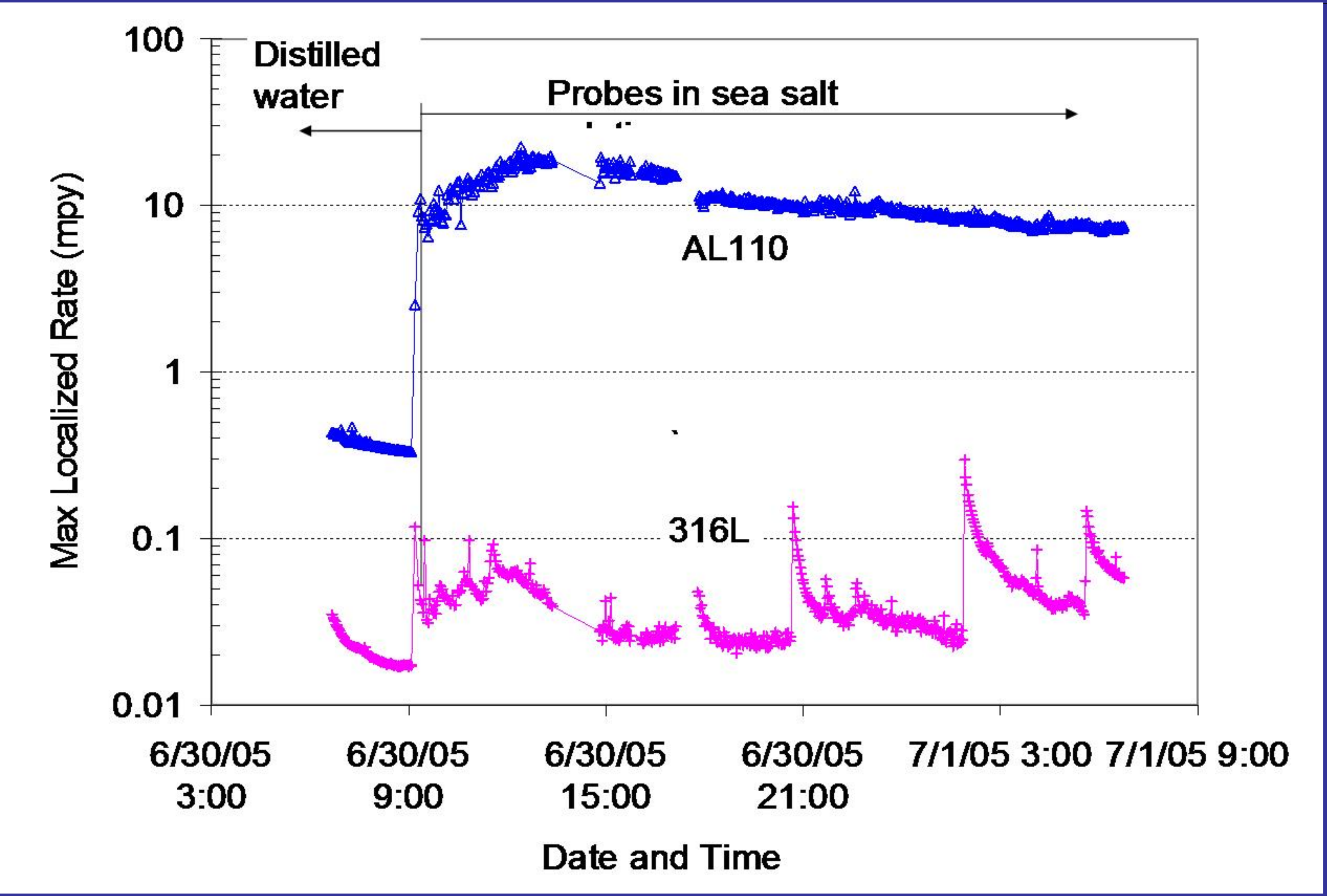
Localized and General Corrosion Rates of Carbon Steel in Unprotected Seawater at Room Temperature



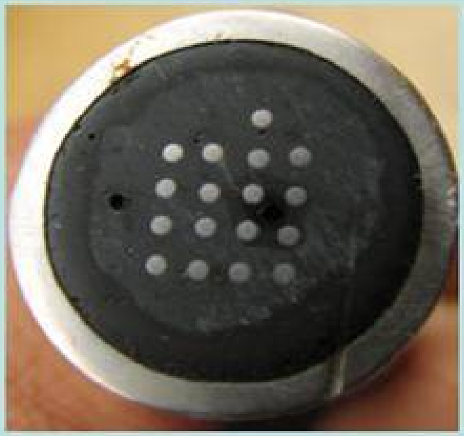
Localized and General Corrosion Rates of Aluminum 1100 in High Silica - High TDS Water

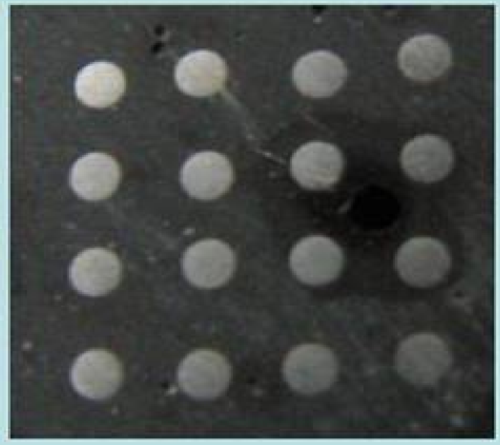


Localized and General Corrosion Rates of Aluminum and 316L SS in Unprotected Waters at Room Temperature



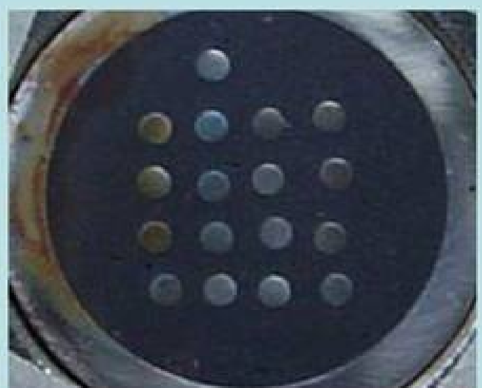
Post-Test Probes – Steel Localized Corrosion at 40 mpy in Unprotected Brine vs. < 0.2 mpy in Silica Inhibited Brine





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

Carbon steel



316L Probe

Three weeks in seawater at room temperature

Silica Inhibitor Bench Study Results

- CS, Cu, Al, Zn, SS corrosion mitigated to very low rates from 77º to 190º F
- Aluminum corrosion less than steel, even at pH 10 (amphoteric metal)
- 316 SS chloride attack mitigated
- Localized corrosion (pitting), typically 10-40X general rates, equally mitigated

Field Studies of
Silica Corrosion Inhibitor

“Green” Inhibitor Chemistry

- System chemistry derived from concentration of (soft) makeup water ions and silica
- No organic or discharge restricted chemicals are required
- Natural, non-toxic chemistry
- Limited or no biocide use
- Blow down not required

Field Study #1
Industrial Solvents Processor

- Four years application, solvent separation process using vacuum distillation
- Tube & Shell Exchangers, 304SS, Shell Side 450º F, no deposit on tubes
- Both Corrator and 60 day coupon techniques; CS < 0.2 mpy, Cu < 0.1 mpy, 304SS negligible
- “ZLD”, soft water MU, no chemicals

Cooling Tower No. 1 - Makeup & Tower Concentration of Chemistry (COC) Ratios

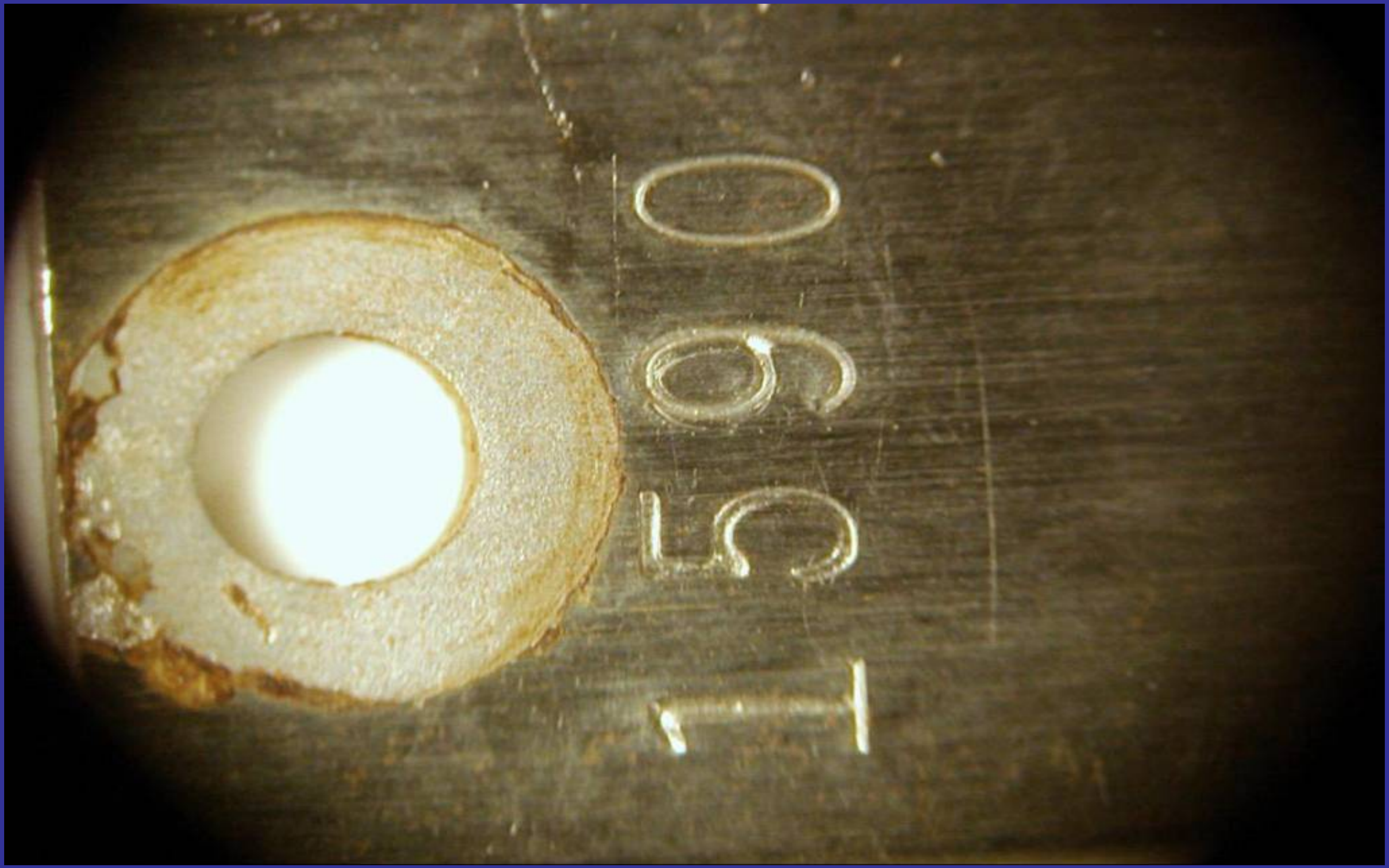
Tests	*Tower*	*Makeup (soft)*	*COC*
Conductivity, μmhos	33,950	412	82
pH	10.01	8.23	-
Turbidity, NTU Neat	3	0.08	-
Silica, mg/L SiO_2	382	9.5	40
Calcium, mg/L $CaCO_3$	16.0	0.15	-
Magnesium, mg/L $CaCO_3$	3.33	0.05	-
Chloride, mg/L	6040	80	76
Tot. Alkalinity, mg/L	13200	156	85

Field Study #2
Refrigeration Chiller Condensers

- Trane enhanced tube condensers with three years operation on silica chemistry
- Corrator; CS rates reduced from 8.0 mpy to 0.5 mpy in 2 weeks
- Both Corrator and 60 day coupon techniques; CS < 0.2 mpy, Cu < 0.1 mpy
- “ZLD”, soft water MU, no chemicals

Cooling Tower No. 2 - Makeup & Tower Concentration of Chemistry (COC) Ratios			
Tests	*Tower*	*Makeup (soft)*	*COC*
Conductivity, µmhos	66,700	829	80
pH	9.61	7.5	-
Turbidity, NTU Neat NTU Filtered (0.45µ)	4 2	0.08 -	- -
Silica, mg/L SiO_2	306.4	11	28
Calcium, mg/L $CaCO_3$	21.5	0.20	-
Magnesium, mg/L $CaCO_3$	0.65	0.05	-
Chloride, Mg/L	17,900	216	83

Carbon Steel Corrosion Coupon #1590
(0.2 mpy @ 62 days - corrosion under mount)



Carbon Steel Coupons
60 day exposed (#1652) @ 0.017 mpy and non-exposed (#1664) control @ 0.013 mpy

Field Corrosion Summary

- CS coupon and Corrator rates < 0.2 mpy
- Cu coupon and Corrator rates < 0.1 mpy
- Galvanized steel “white rust” mitigated
- Coupon mount bias correction shows CS corrosion less than 0.020 mpy!

Other Benefits of Silica Chemistry

- Permits use of reclaimed waste water or brackish water sources
- Biological propagation is impeded at elevated TDS & pH
- Simple control with “ZLD” or reduced blow down, eliminates chemicals

Field Application Experience

- Four years of evaluation / application
- Commercial, Institutional, Food, Chemical, and Steel industry applications
- Marley, BAC, Evapco and other towers
- System materials: galvanized, stainless, copper, plastic, fiberglass, and concrete

Silica Inhibitor Conclusions

- Excellent corrosion inhibitor at high TDS
- Excellent inhibitor at high temperatures
- Protects all metals, mitigates “white rust”
- Permits “ZLD”, water savings, no scale
- Can use reclaim / reuse waste waters
- Provides “green” water chemistry

Conclusions on Pilot Study Method

- Study results corroborate four years of field corrosion study results
- The method facilitates efficient (time/cost) selection of inhibitors or metallurgy
- The method accurately predicts localized (pitting) rates, unlike traditional methods
- Quantifying localized corrosion is crucial to selecting required metallurgy and inhibitors

Questions?