CONRAD 2006

Potential Use of Process-affected Water (Recycle Water – RCW)

& High Saline Basal Water as Recirculating Cooling Water

Water Conservation Technology International, Inc.

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Presentation Outline

- Silica Chemistry / How It Works
- Corrosion Inhibition Mechanisms
- Field Case Studies / High TDS
- High Temperature / TDS Corrosion Studies
- Potential Saline Basil / RCW Reuse
- Conclusions / Pilot Study

Aqueous Discharge Reduction

Major 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

Pre-Treatment

- Ca/Mg removal eliminates scale potential
- Pre-treat alternatives are simple and economical (cost less than discharge).
- Sodium cycle or WAC exchange of Ca/Mg depending on source water TDS.

How Silica Is Controlled

- Pre-treat removes polyvalent metal ions.
- Ca/Mg in tower water maintained below level achieved by cold lime softening.
- High 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 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.

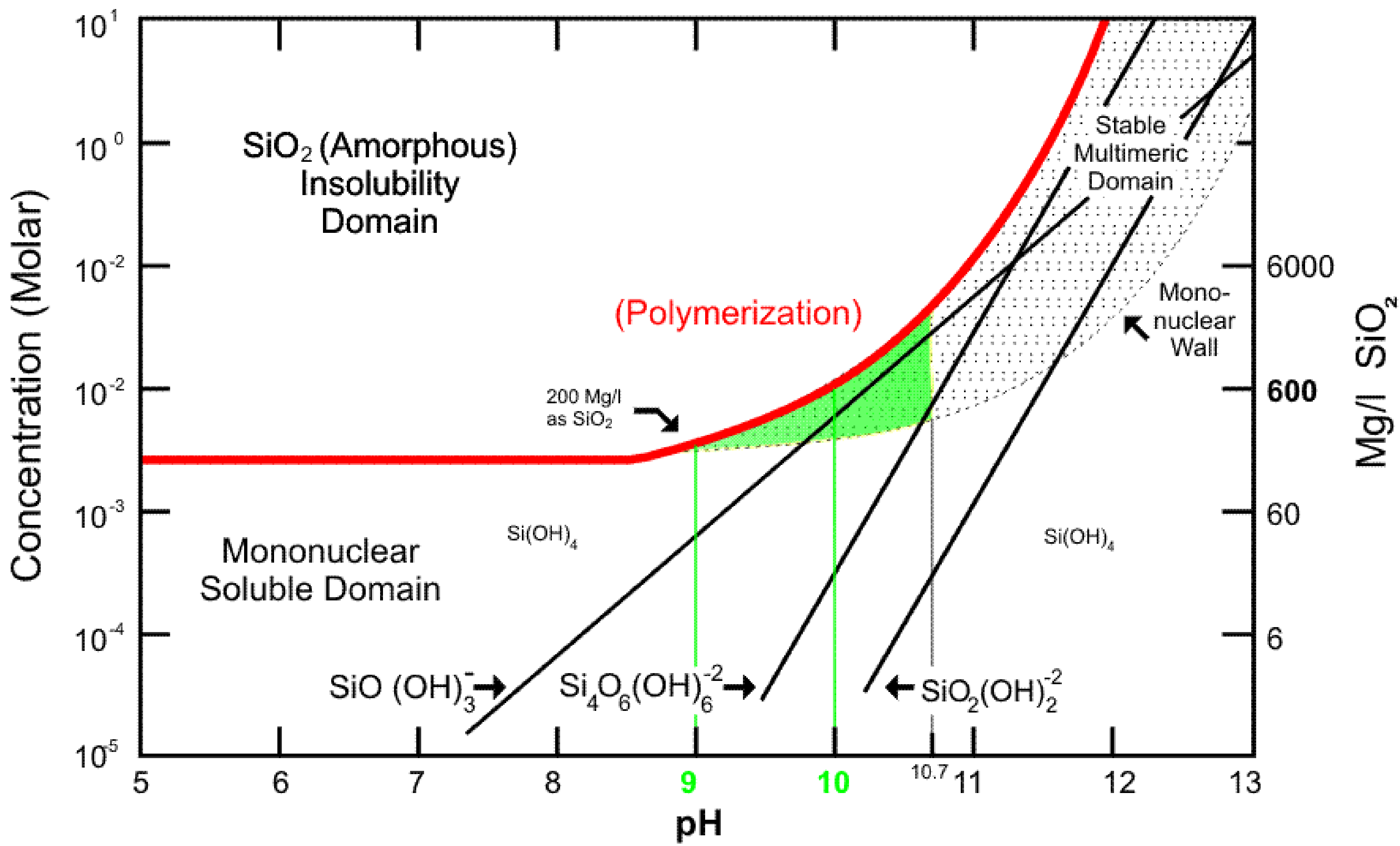
Silica Chemistry

- 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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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 232 C., 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			


1560

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			

High Temperature Corrosion Studies

With Silica Inhibition Chemistry

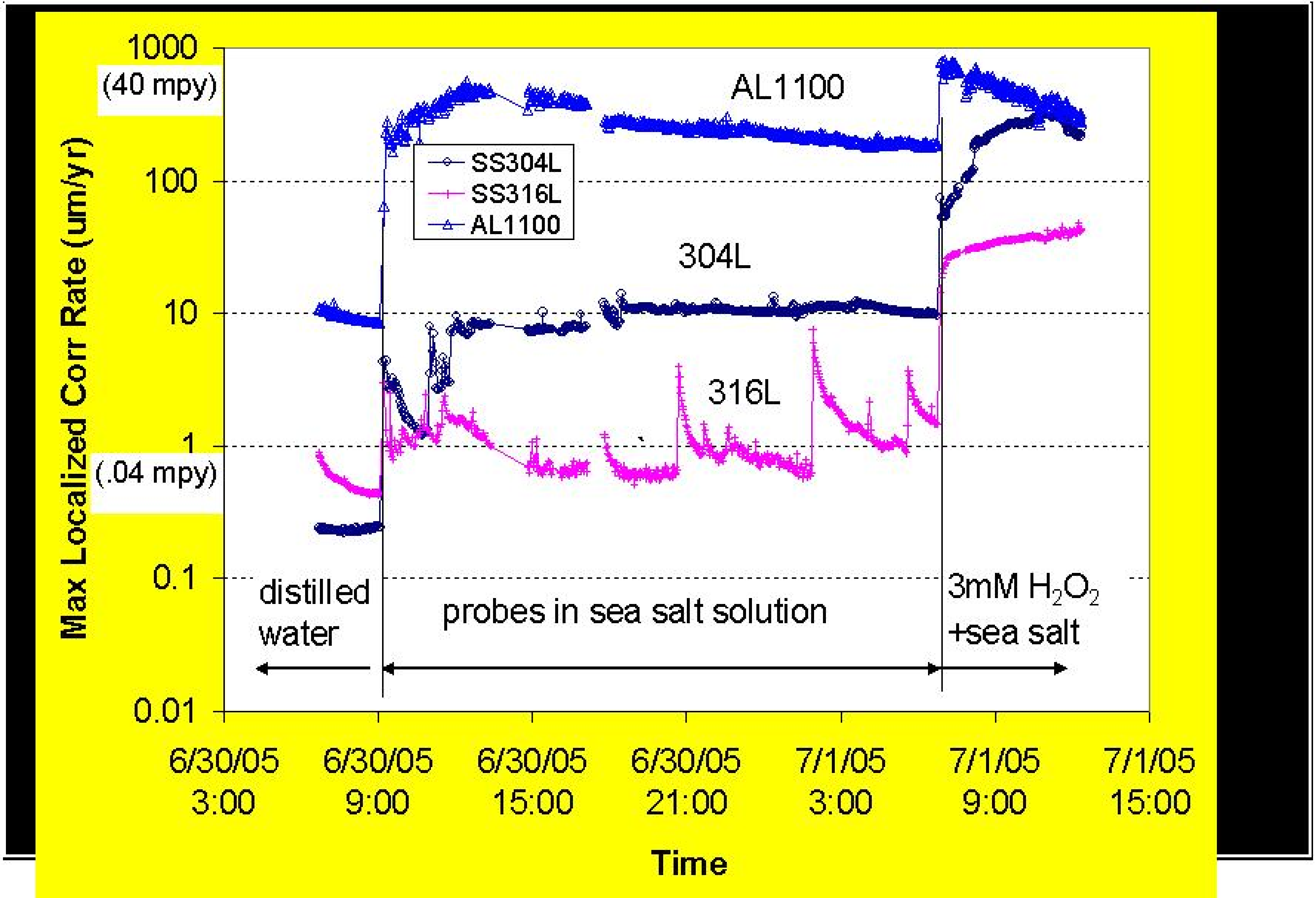
High Temperature / High TDS Corrosion Inhibition Studies

- 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

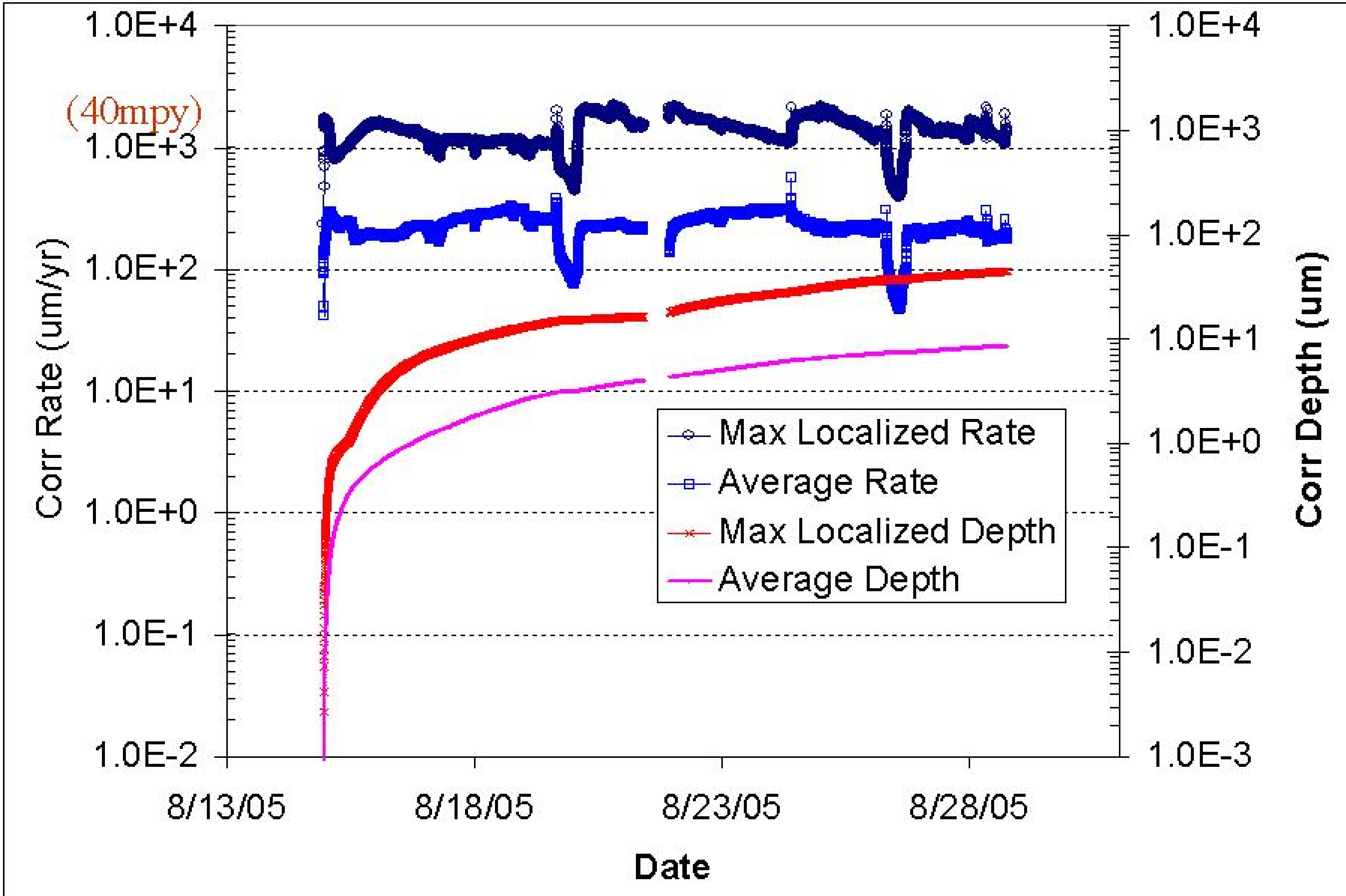
Unprotected Metals in Sea Salt

- 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.

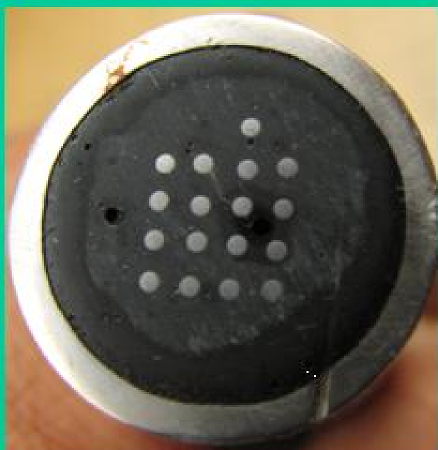
Direct Comparison of Max Localized Corrosion Rates from Three Alloys

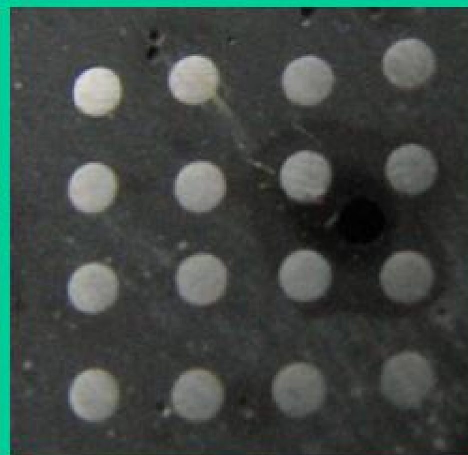


Corrosion Rates and Corrosion Depth from a Type 1008 Carbon Steel Probe



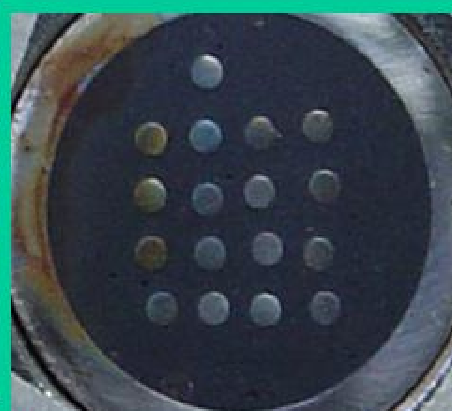
Comparison of Post test Probe Appearances





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

Mild steel



316L Probe

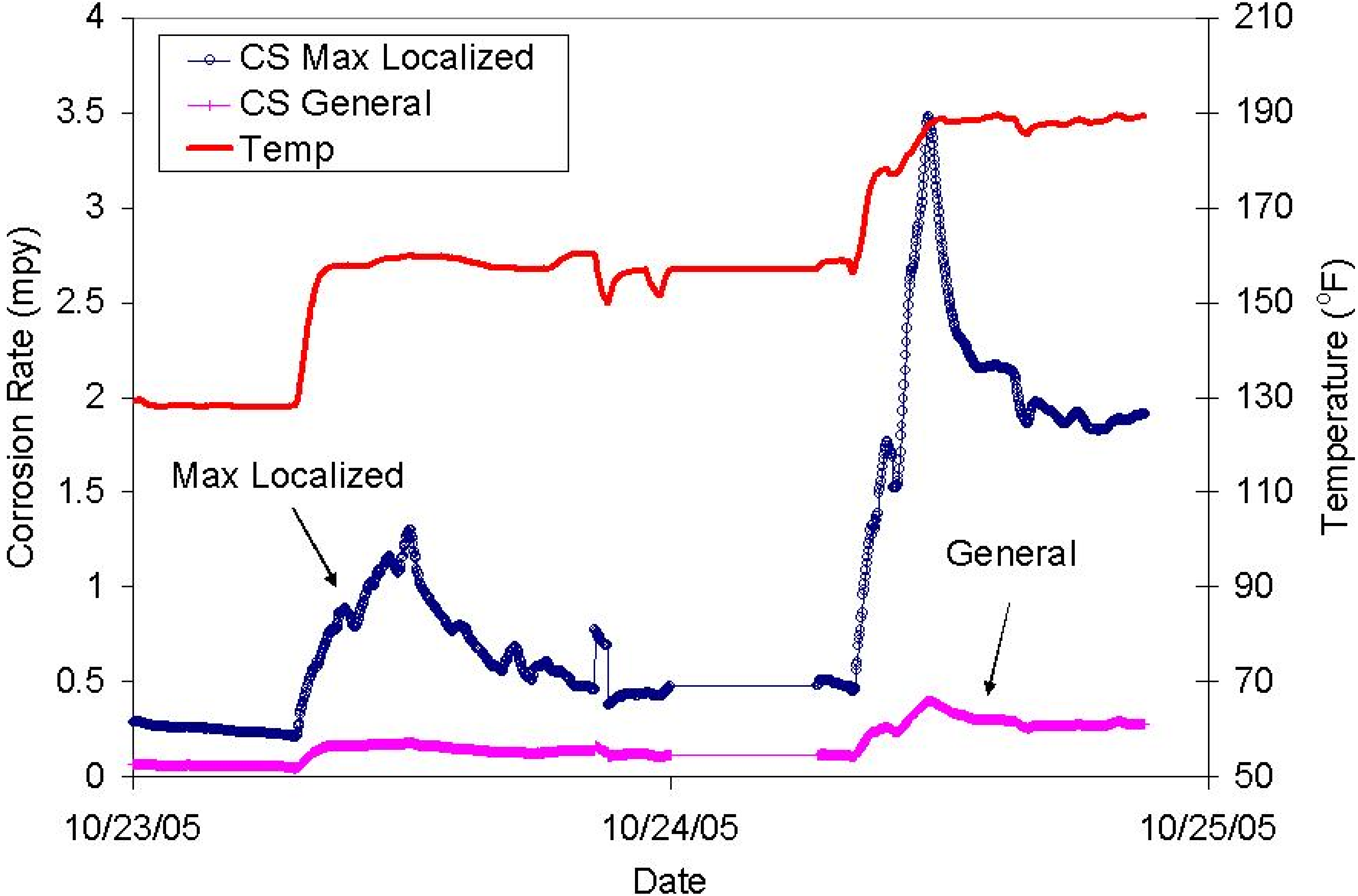
Three weeks in seawater at room temperature

Courtesy:

Corr Instruments

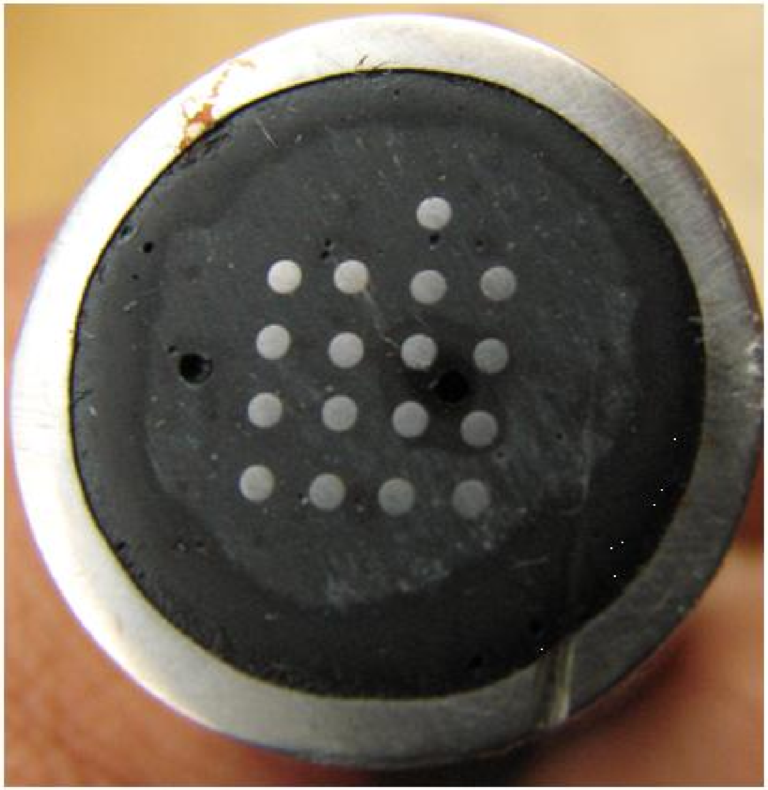
High Temp / Silica Study Results

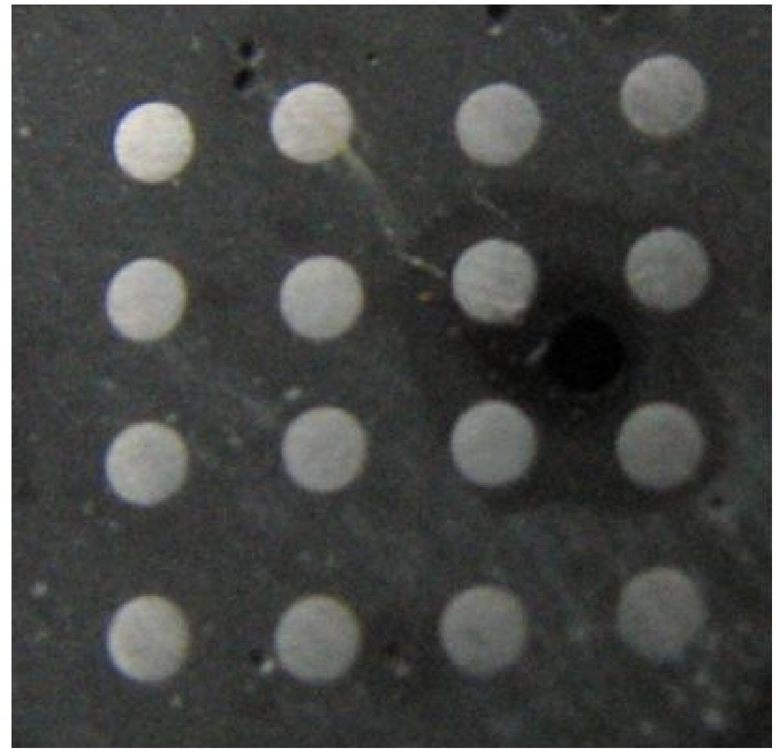
- Outstanding mild steel localized and general corrosion rates at all temperatures.
- Chloride impact on 316 stainless steel is minimal at high temperature.
- Soft metal (Al, Zn, Cu) protection very good at higher temperatures.
- Aluminum protection improved at higher temperatures.

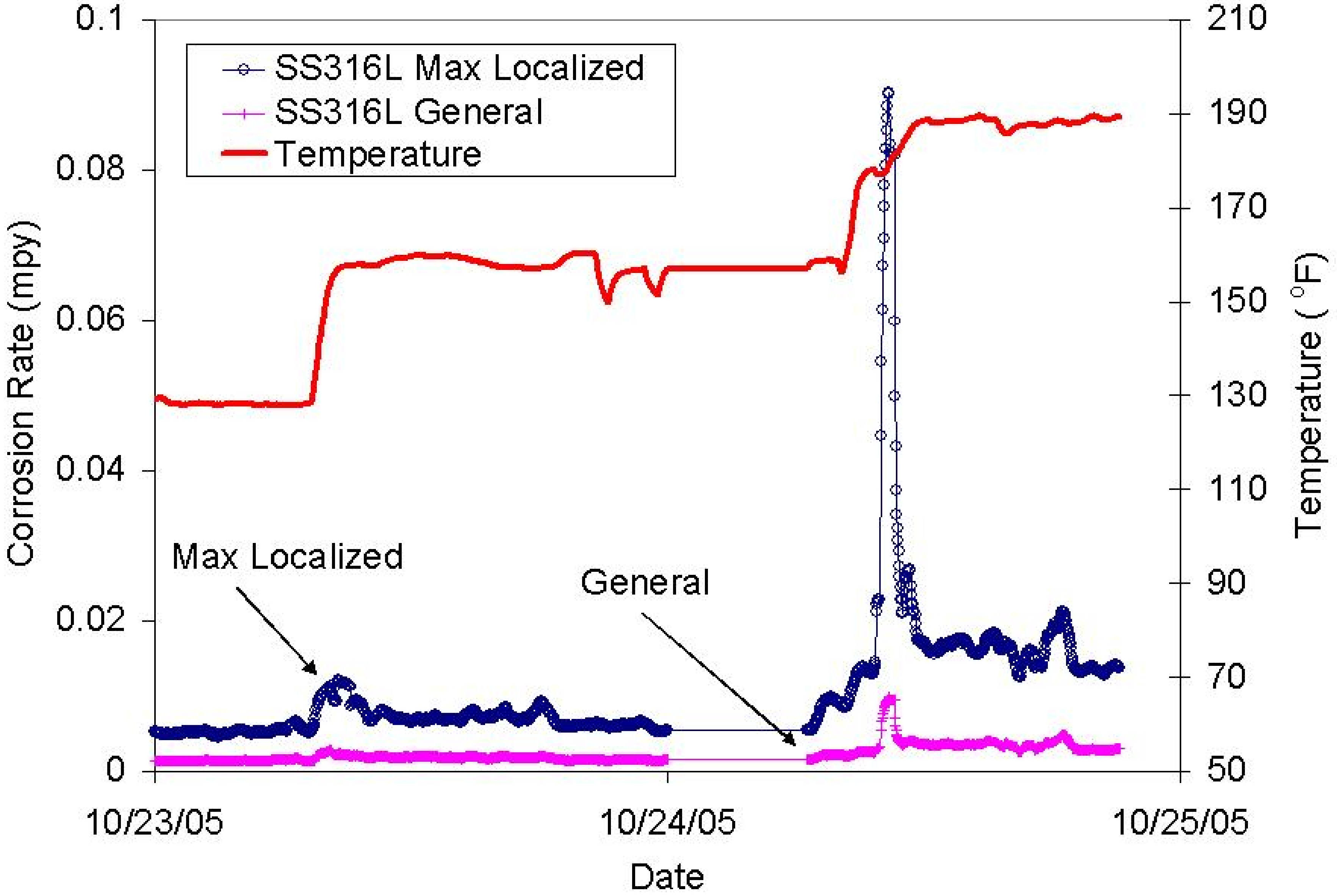


Protected by patents, US 6,929,749;
US 6,949,193; US 6,998,092

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



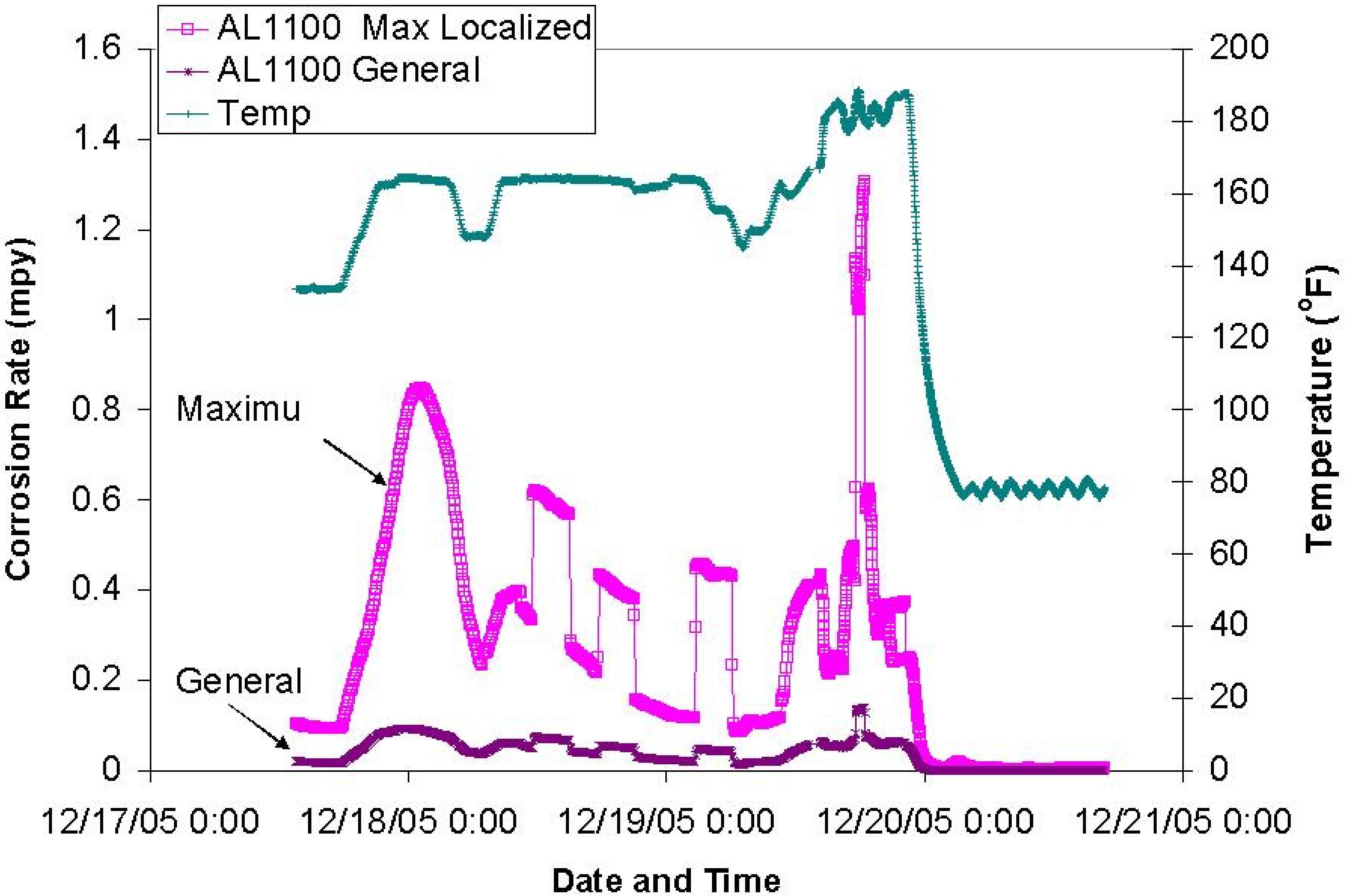




0.1
0.08
0.06
0.04
0.02
0
Corrosion Rate (mpy)
210
190
170
150
130
110
90
70
50
Temperature (°F)
SS316L Max Localized
SS316L General
Temperature
Max Localized
General
10/23/05
10/24/05
10/25/05
Date

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



AL1100 Max Localized
AL1100 General
Temp
Corrosion Rate (mpy)
Temperature (°F)
Maximu
General
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
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

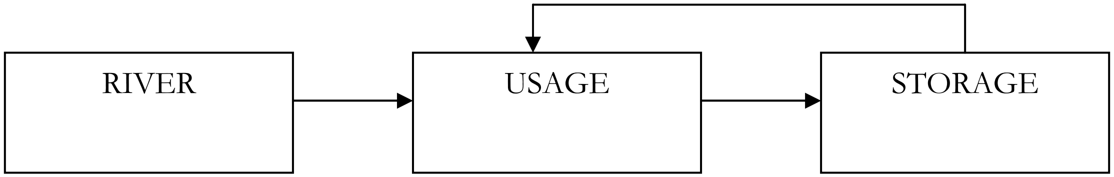
- Potential use with brackish or recycled waste water sources.
- Biological propagation is limited by elevated TDS & pH.
- Simple program control with reduced blow down, limited chemistry adjustments.

Potential Saline Basil / RCW Reuse

Water Conservation Impact

Saline Basal / RCW Reuse

OPEN PIT OPERATIONS



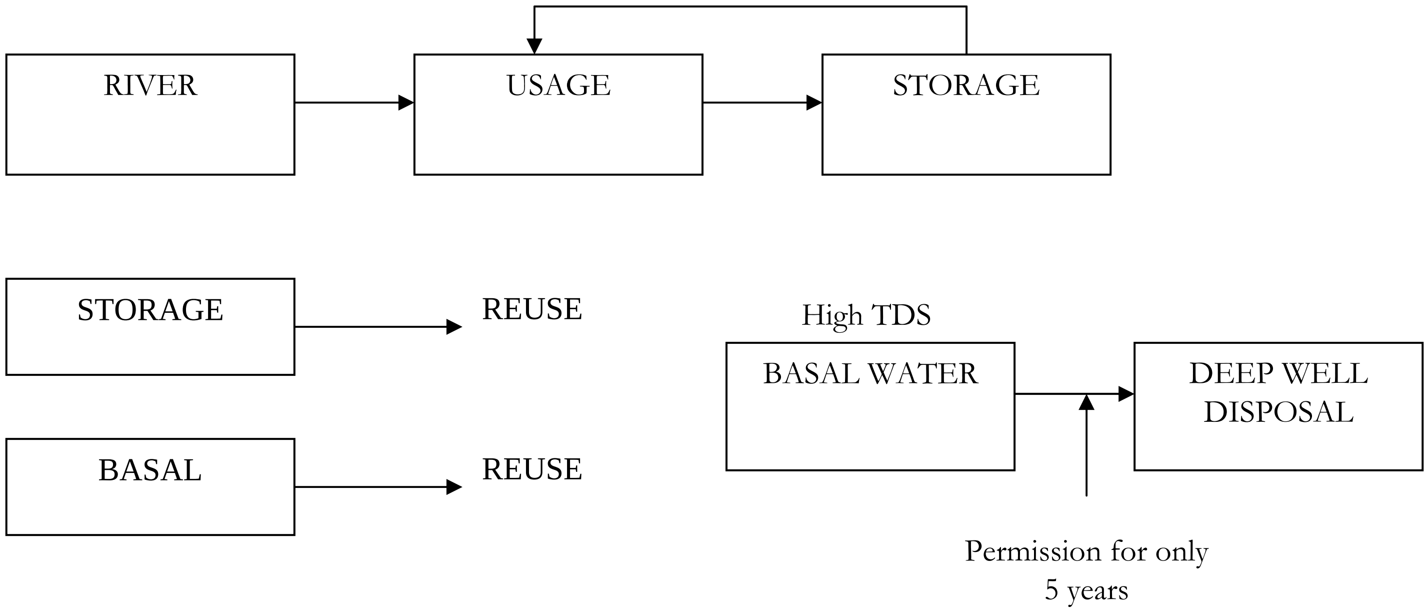
<u>ISSUES</u>

- Limit on what can be withdrawn from river
- Not enough storage

Saline Basal / RCW Reuse

<u>SOLUTION</u>

- Treat & reuse inventory in place of river import



Saline Basal / RCW Reuse

Use As Recirculating Cooling Water

REUSE OPTION – CURRENT METHODS

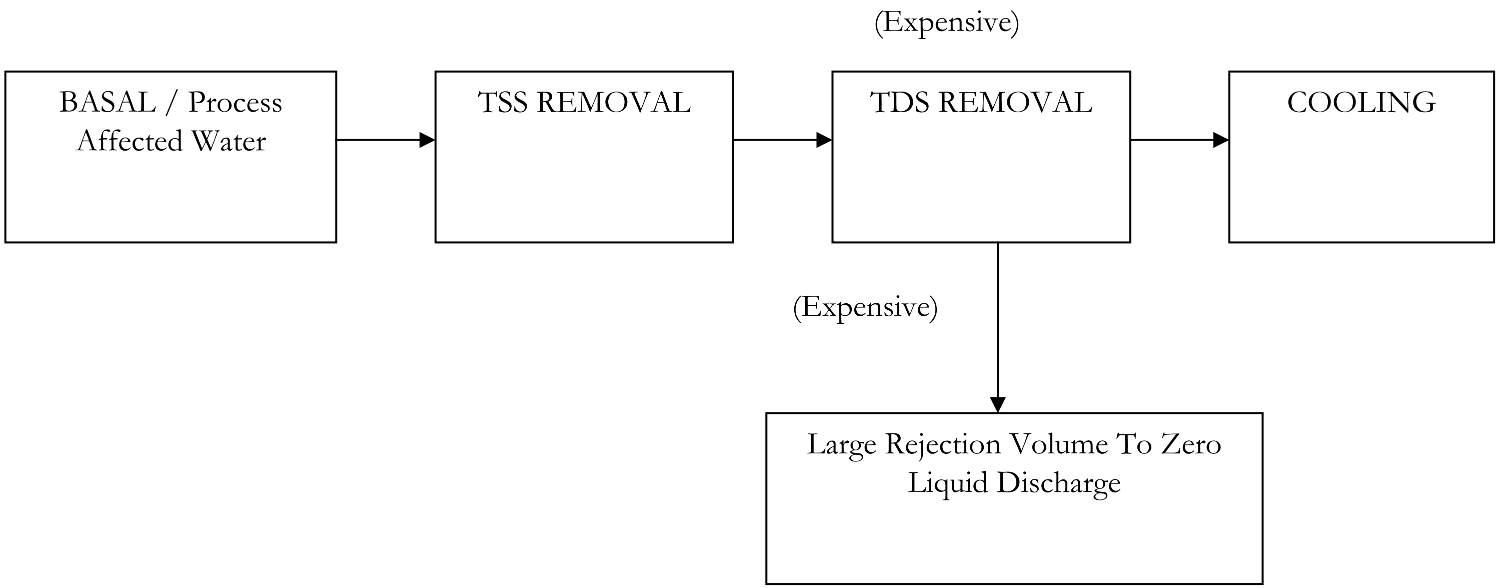
- High TDS limits use without removal
- TDS removal significantly more expensive
- TDS rejection / disposal volume high

REUSE OPTION - WCTI

- Remove only TSS & Hardness
- Reduce Storage Volume with Tower Evaporation
- System wastage / disposal volume is small

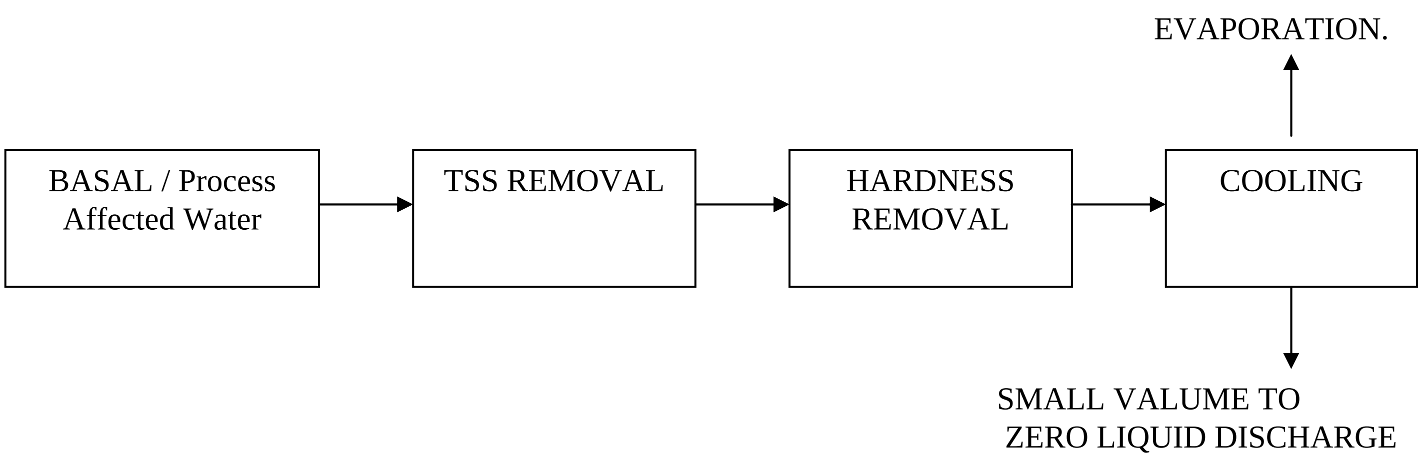
Saline Basal / RCW Reuse

TDS Removal-Reject Expense Prohibitive



Saline Basal / RCW Reuse

Hardness Removal Very Cost Feasible



Protected by patents, US 6,929,749; US 6,949,193; US 6,998,092

Today's Water Use *versus* Reuse

Issue	***Today***	***WCTI***	***Comments***
Makeup	River	Basil / PA	Stay within import limit
Blowdown	Large volume	Small volume	Reduce Storage & Disposal
Chemicals	$$$	None	20% more MU needed
Pre-treat	None	$	20% less MU needed

Conclusions

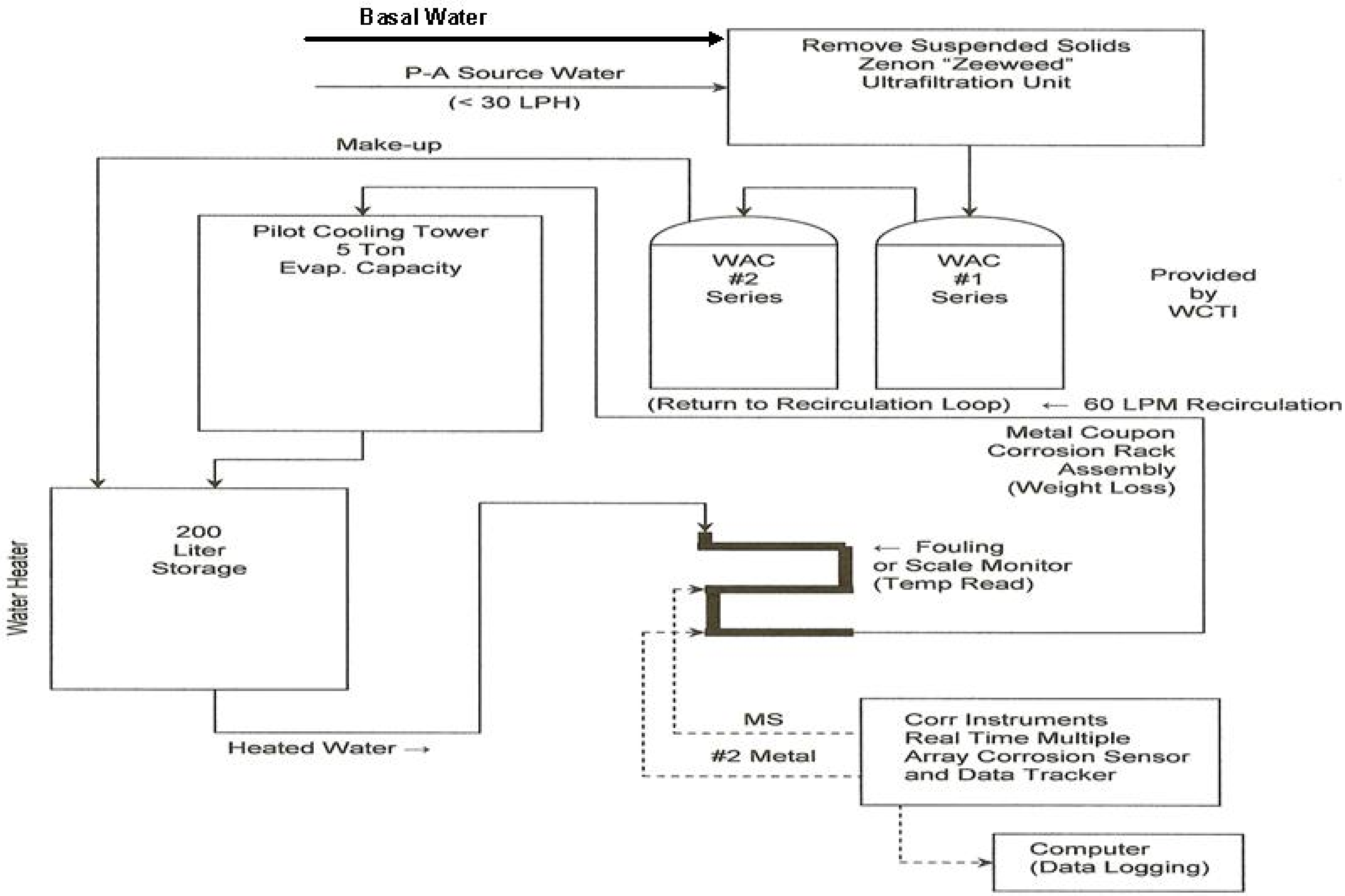
- Excellent corrosion inhibition @ high TDS
- Pre-treatment controls scaling potential
- Maximum aqueous use reduction
- Use of saline basil or RCW water feasible
- Lower total cost of treatment
- NEXT STEP
  - Pilot demonstration

Proof of Concept

CONRAD / ARC / CANMET

Pilot Study

PROCESS-AFFECTED WATER PILOT STUDY AS COOLING TOWER MAKE-UP



Questions?

Comments?