LOCALIZED AND GENERAL CORROSION OF COPPER IN AZOLES AND SILICA INHIBITED ZERO BLOWDOWN COOLING WATER IN AN AUTOMOTIVE PLANT

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Challenges When Using Recycled Water in Cooling Towers

- Suspended solids increase system fouling
- Ammonia attacks copper / alloys
- Nitrification expensive for waste water utilities
- Organics & phosphates promote bio-fouling
- Increased scaling & corrosive ions
- Increased blow down water wastage
- Increased chemical treatment cost (2-4X)
- Increased toxics and organics discharge

Real Time CMAS Field Study Objectives

- Insure protection of customer system assets (copper tubes) from localized corrosion
- Verify dynamic impact of ZBD system chemistry (soft, high TDS, high pH water) on ammonia reduction and copper corrosion in the system
- Detect effects of change to recycled water (ammonia) on azoles-inhibited copper corrosion (not detected by LPR and weight loss)
- Confirm CMAS lab results for inhibition by azoles in ZBD / ammonia chemistry

ZBD / Silica / Azoles
Tower Chemistry Control Targets

AY2

- Suspended solids: < 0.5 NTU in makeup
- Total hardness: < 30 mg/L
- Soluble SiO_2 : > 300 mg/L (corrosion inhibition)
- pH: > 9.5 (biostatic control & NH_3 strip)
- TDS: > 10,000 mg/L (biostatic control)
- Ammonia: < 1.0 mg/L (pH control / tower strip)
- Tolytriazole: 5-50 mg/L for copper inhibition (usage minimal with zero blow down)

Slide 4

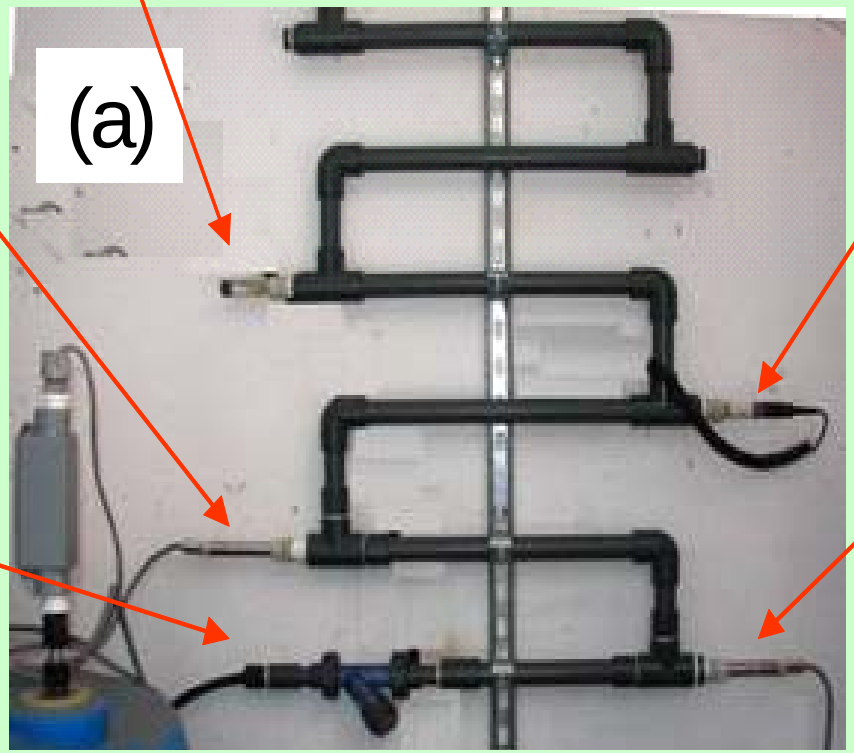
AY2 Too many acronyms. Reviewer may not allow

Andrew Yang, 1/22/2009

ZBD Tower Chemistry with Potable (PMU) and Recycled Makeup (RMU), and Tower COC Ratios during CMAS Study Period.

Automotive Plant Sample / Tests	Soft PMU	Tower PMU	COC PMU	Soft RMU	Tower RMU	COC RMU
TDS, mg/L (Myron L 6P)	350	9000	24	1100	19000	17
pH	7.7	9.8	NA	7.1	9.6	NA
Silica, mg/L SiO_2	12	250	20	24	280	12
Calcium, mg/L $CaCO_3$	0.1	15	NA	0.2	13	NA
Magnesium, mg/L $CaCO_3$	0.1	7	NA	0.1	6	NA
Sulfate, mg/L SO_4	-	-	-	127	2030	16
Chloride, mg/L NaCl	-	-	-	214	3640	17
Tot. Alkalinity, mg/L $CaCO_3$	150	3300	22	192	2900	15
Ammonia, mg/L NH_4	-	-	NA	34	0.5	NA
Total Phosphate, mg/L PO_4	-	-	-	0.6	9.5	16
TTA, mg/L as tolytriazole	-	20	NA	NA	25	NA

Test Probes Assembly



Metal coupons

Inlet

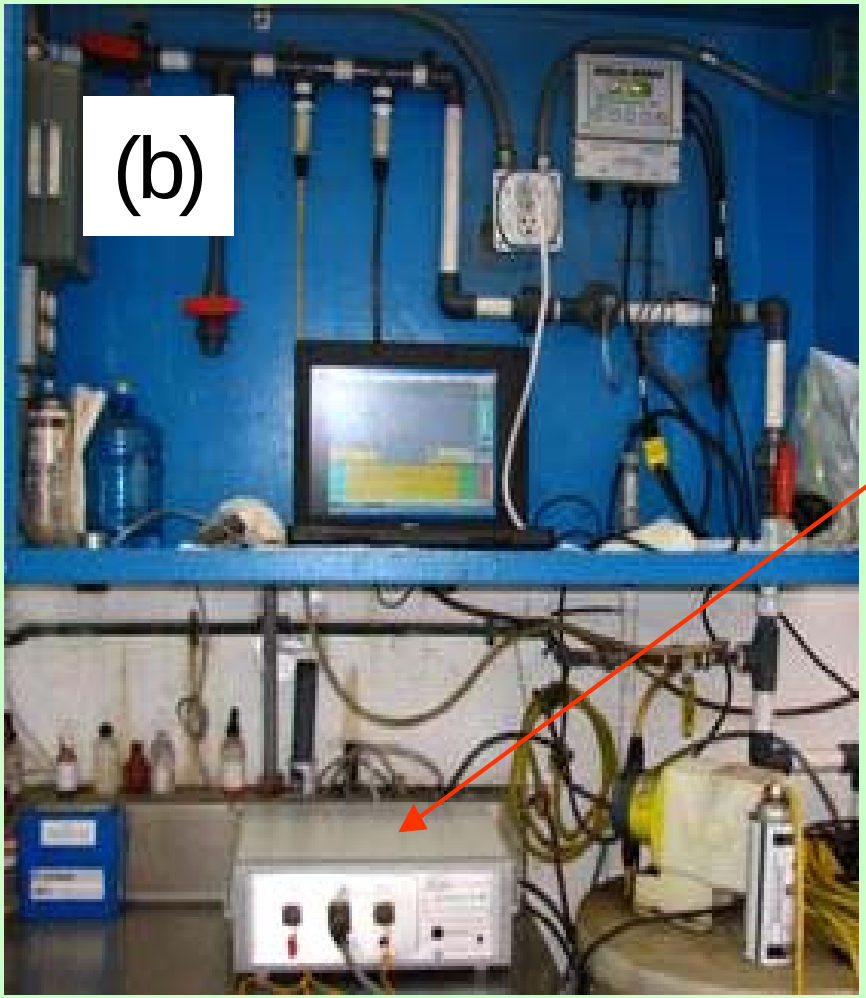
Linear polarization probe for general corrosion

Copper CMAS probe

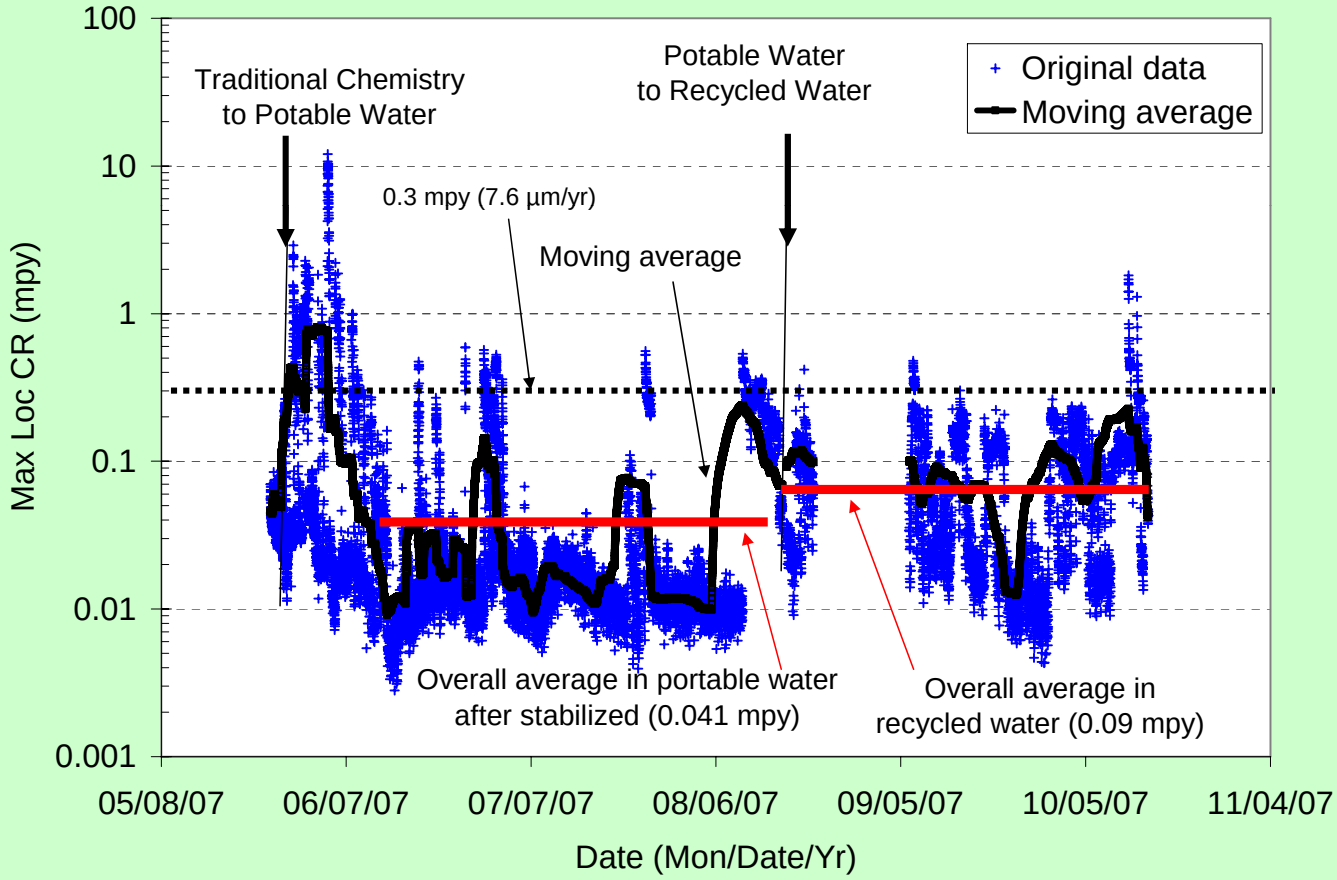
Carbon steel CMAS probe

Outlet

Test Station & Analyzer



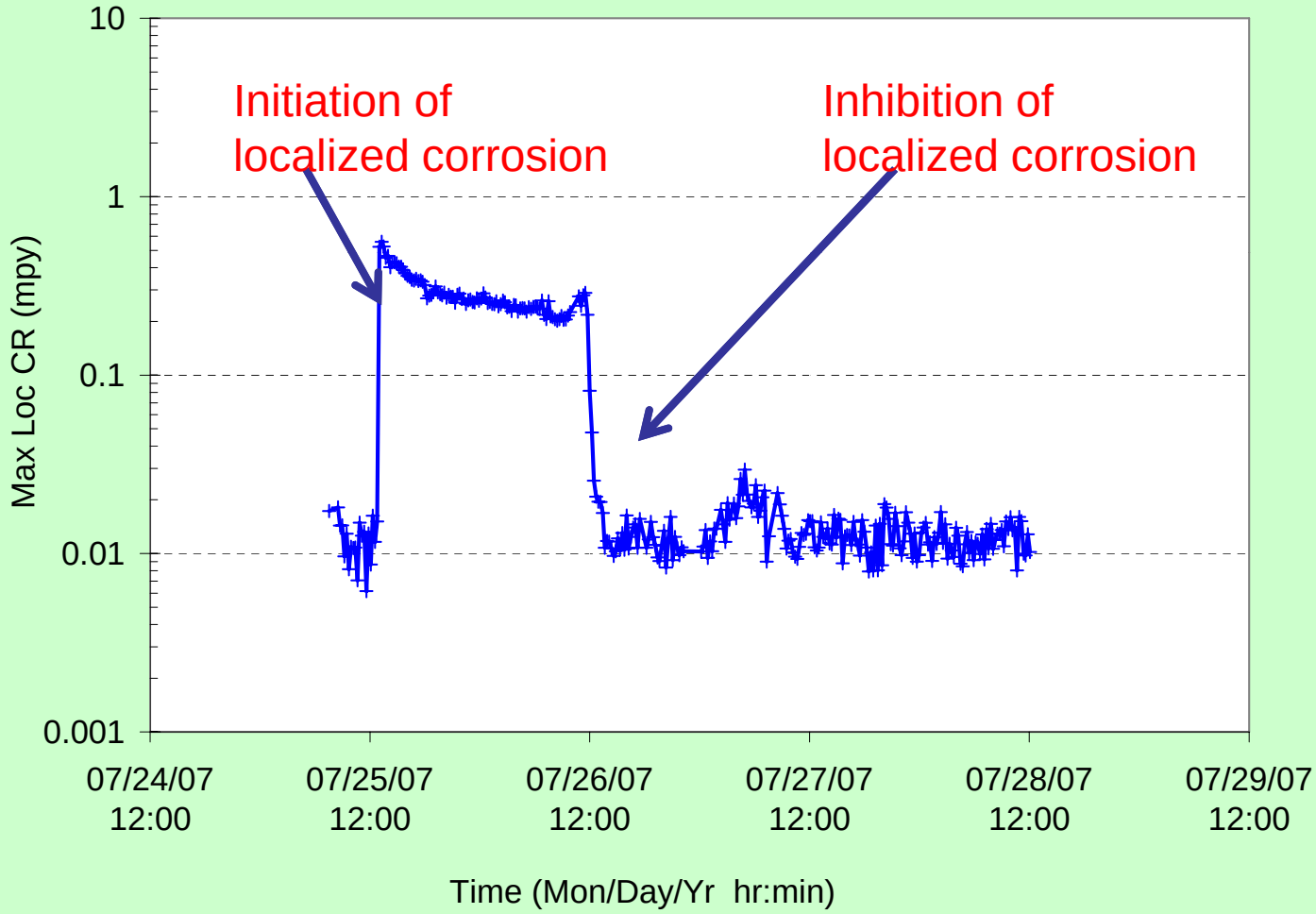
Localized Corrosion Rate (CMAS) for Copper with Transition from Traditional Treatment to ZBD Potable Treatment in May and ZBD Recycled Treatment in August.



Copper Corrosion Rates by CMAS for ZBD Potable and Recycled Water

- The impact of ammonia (recycled water) on localized corrosion was an increase from 0.04 to 0.09 mpy
- CMAS detected only low level short term events, with rapid inhibition restoration
- Overall localized corrosion rates exceptionally low
- Corrosion rate for both potable and recycled water were well below the 0.3 mpy rate measured before transition from traditional chemical treatment

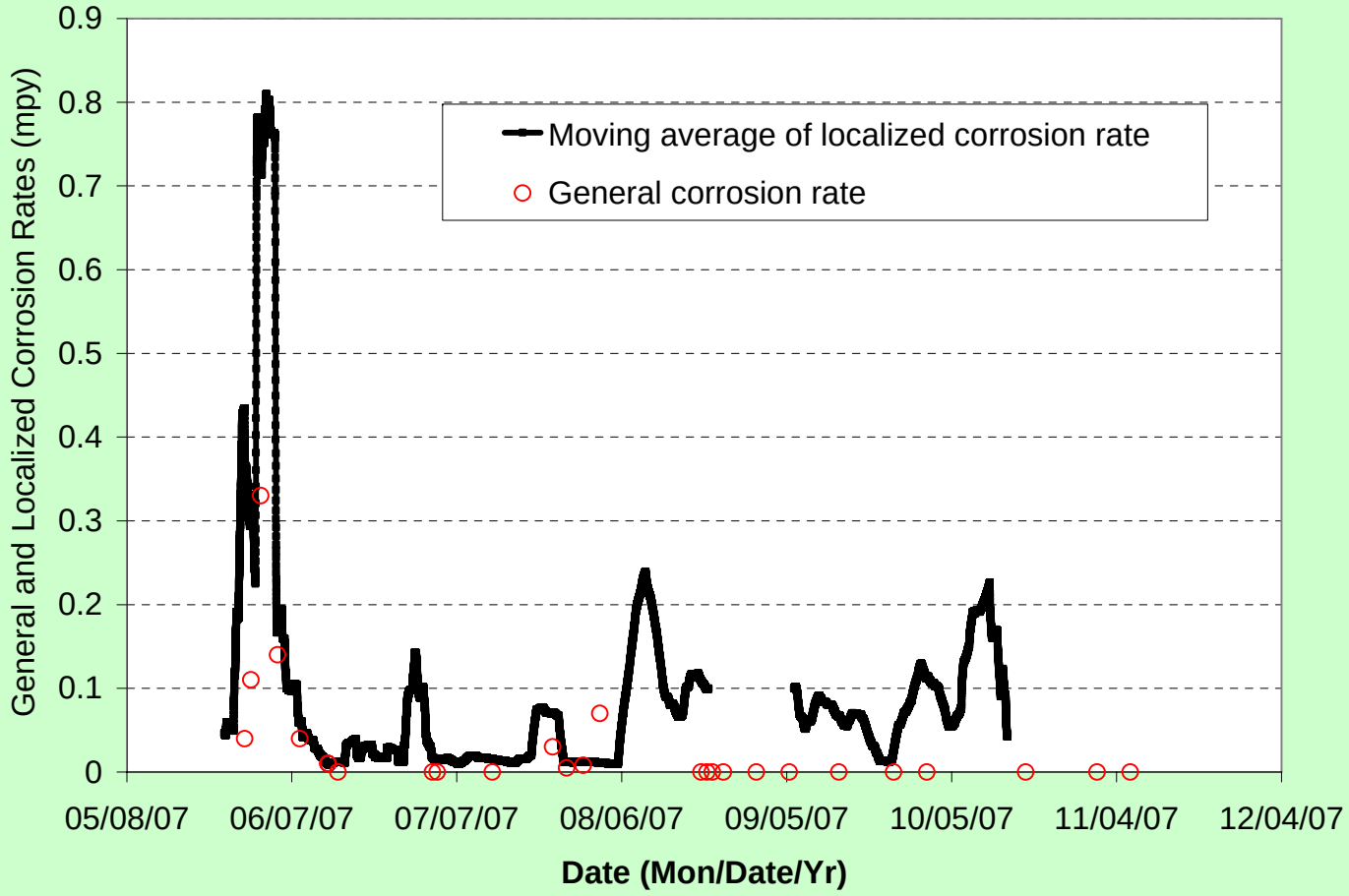
Enlarged View for a Typical Short-term Low-Level Localized Corrosion Event.



Short Term Event and Localized Corrosion Inhibition

- CMAS short-term localized event to 0.5 mpy in July on potable water
- Rapid return to low variability results and exceptionally low localized corrosion rates

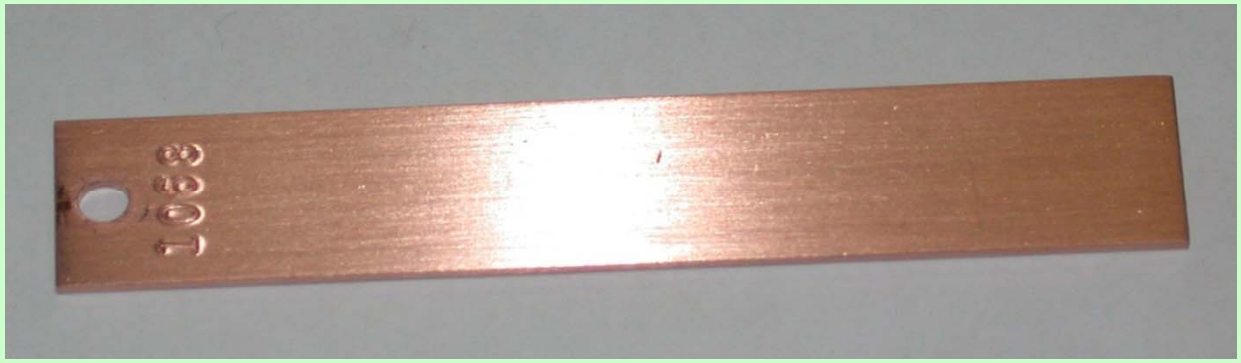
General Corrosion Rates from LPR Probe Compared to Low Level Localized Rate from CMAS Probe



LPR versus CMAS Detection of Localized Copper Corrosion

- LPR copper rates were 0.04 to 0.33 mpy for first 20 days (transition)
- LPR at 0.00 to 0.03 mpy after transition, lacking sensitivity to detect localized rates
- CMAS localized copper rates averaged 0.05 mpy after transition
- CMAS detected copper shift from 0.04 to 0.09 mpy moving average with recycled water (ammonia)

Coupon Weight Loss Results



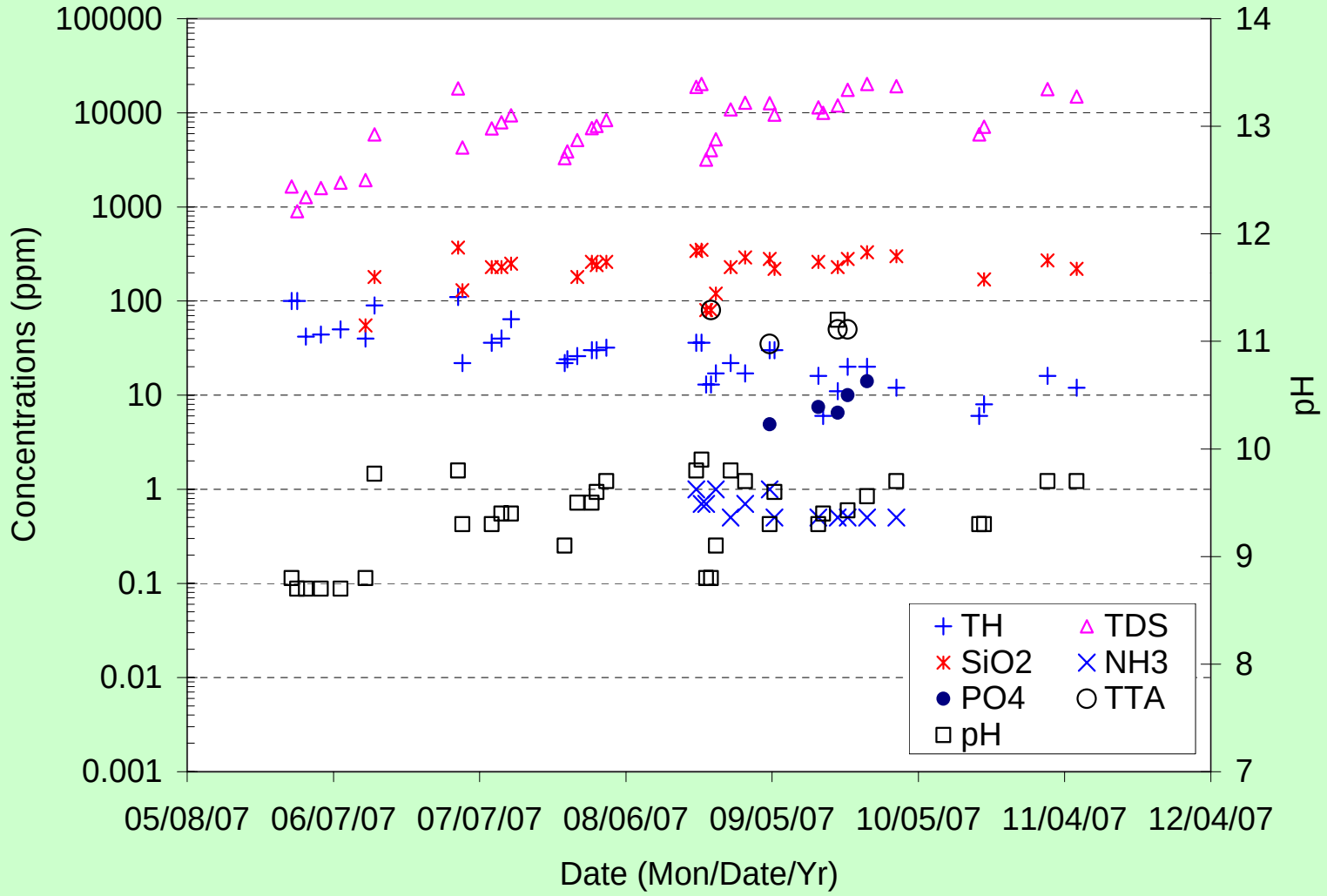
Copper coupon, exposed 99 days, 0.16 mpy corrosion rate (high under mount corrosion bias).

Carbon steel coupon exposed 99 days with 0.426 mpy corrosion rate (high under mount corrosion bias).

Coupon Weight Loss Results

- Copper coupon appearance (no pitting) and low rate of 0.16 mpy confirms CMAS results during ammonia exposure. Note that coupon rate is higher due to under mount corrosion bias.
- Mild steel rate of 0.426 mpy compares to prior potable ZBD / silica results, but higher due to under mount corrosion bias.
- Mild steel rates have been measured at 0.05 mpy with alternative weight loss method.

Chemistry of Tower Water during CMAS Monitoring Period



Note: TH– total hardness

Tower Water Chemistry

- Variations from control targets occurred with both potable and recycled water
- No chemistry differences other than ammonia appeared to impact results
- No correlations of other chemical parameters or impact were attempted

Summary: How Silica / Azoles / ZBD Tower Chemistry Performs with Use of Recycled Water

- Ammonia is stripped in tower to < 1 mg/L.
- Ammonia does not affect silica's corrosion inhibition for steel, aluminum and zinc.
- Ammonia will penetrate silica inhibition film to corrode uninhibited copper.
- Azoles are highly effective in inhibiting localized attack of copper by ammonia in ZBD water.
- Biostatic tower chemistry is not affected by organics and phosphate nutrients.

Conclusions

- CMAS provides rapid real time verification of effective inhibition to copper localized corrosion
- CMAS detects very low shifts in copper localized corrosion from ammonia exposure
- CMAS verified rapid azoles inhibitor film formation and stabilization for copper
- Mitigation of recycled water issues can be attained with use of ZBD / silica / azoles chemistry.