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Electrochemical Studies with Coupled Multielectrode Array Sensors on Corrosion Inhibition of Copper and Affected Metals in the Presence of Ammonia and Other Corrosive Ions In Zero Liquid Discharge Cooling Water

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Presentation Outline

- Wastewater Reuse in Zero Liquid Discharge (ZLD) Towers
- Corrosion of Copper by Ammonia
- Coupled Multielectrode Array Sensor (CMAS) Corrosion Studies
- Municipal Reuse Case History
- Galvanized Metal Study

This technology is patent protected;

US 6,929,749 / Silica Scale Control
US 6,949,193 / Silica Scale Control
US 6,998,092 / Corrosion Inhibition/Silica
US 7,122,148 / Corrosion Inhibition/Silica
Additional patents are pending

Wastewater Reuse in Zero Liquid Discharge (ZLD) Towers

Silica Inhibition Chemistry

Reuse of Wastewater for Cooling Tower Makeup

- Waste water requires treatment to remove suspended solids (TSS) & insoluble organics
- Filtered to remove TSS that would foul softener
- Need high efficiency softening (HES)
- Dissolved solids (TDS) must be low enough to permit ion exchange softening
- Natural high silica and alkalinity desirable
- Ammonia and soluble organics do not have to be removed with ZLD / silica chemistry

Cost Benefits of ZLD Tower Operation

- High efficiency softening lowers salt use (4# per CF resin) and brine waste flow (< 2% MU)
- Typical softening cost of $0.12 per 1000 gallons tower makeup
- Both equipment and operating cost is 10-15% of conventional ZLD / discharge reduction systems
- Optimum water use and discharge reduction
- Reduced wastewater discharge obtained with use of waste heat (low carbon footprint)

ZLD / Silica Chemistry
Expanded Options

- Permits use of alternative water sources such as municipal / industrial reuse, RO reject, and high TDS water sources for tower makeup
- Silica inhibits metals from corrosion by high TDS (azoles needed for copper / ammonia)
- Expands metal selection / cost economy
- Soft water eliminates scale limitations and permits higher temperatures
- Biostatic chemistry mitigates micro-bio activity

Corrosion of Copper by Ammonia

Corrosion Rates of Several Copper Alloys in 0.8% Ammonia at 104° F (40° C)

Alloy	Corrosion Rates	
	mpy	mm/y
Copper	14	0.30
Brass (Cu-Zn, 70:30)	7	0.20
Alloy 905 (Cu-Sn-Zn)	5	0.10
Cu-Mn (95:5)	2	0.05

Source: Radley, Stanley and Moss, Corrosion Technology 6:229:1959

Copper Corrosion Inhibition Study
(Azoles in High Ammonia / ZLD Water)

- Study with 150,000 mg/L TDS / pH 10 / soft tower water inhibited by silica and azoles exposed to ammonia (200-400 mg/L)
- Rapid uninhibited corrosion by ammonia
- Azoles highly effective for inhibiting ammonia attack at high pH / TDS
- High pH treatment method increases azoles effectiveness / cost efficiency

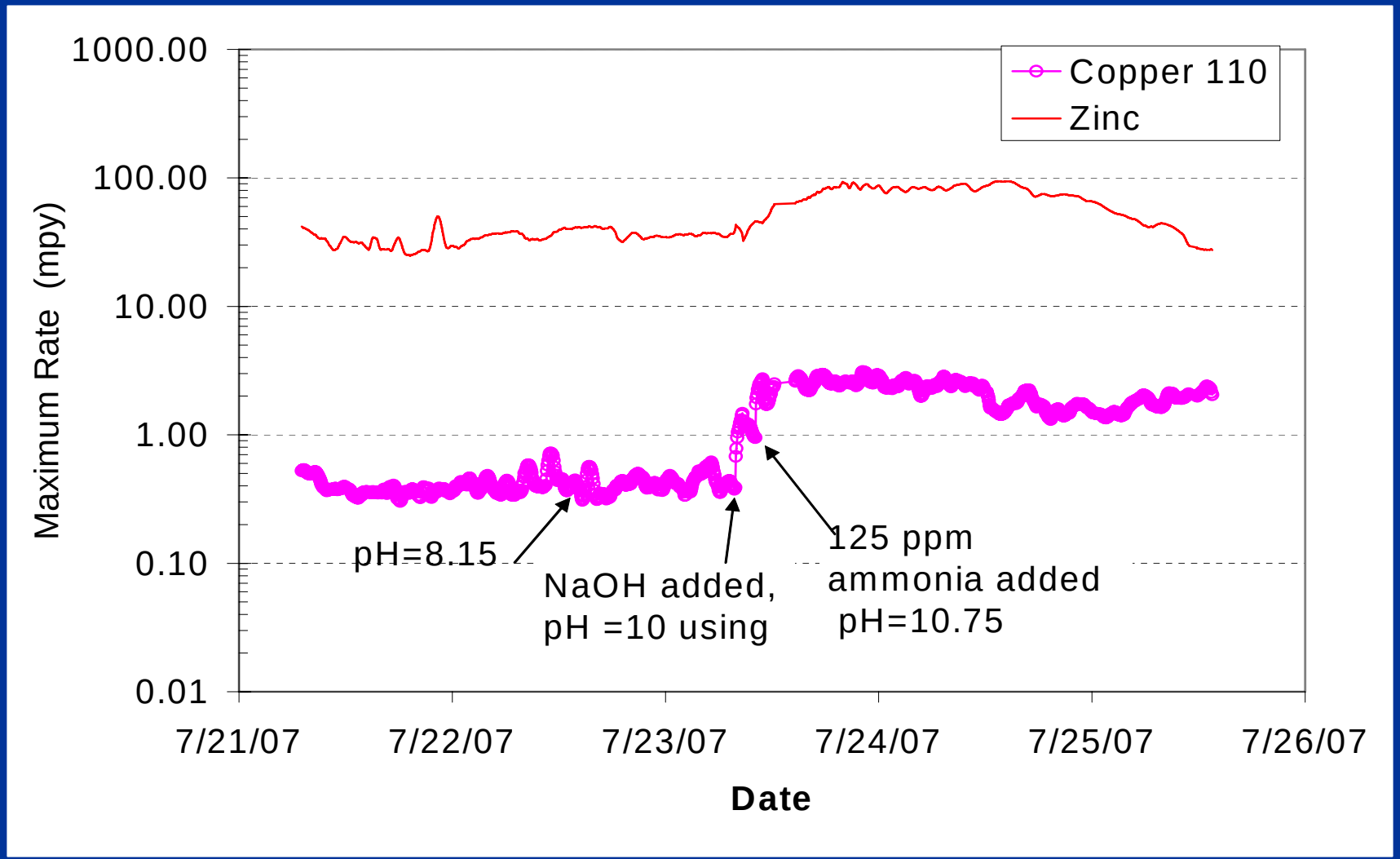
Copper Corrosion Inhibition by TTA (Ammonia / pH 10 and 150,000 TDS)

Copper / TTA / Ammonia Study and Weight Loss Results				
ZLD Tower Water	$NH4^+$, mg/L	TTA, mg/L	Cu, mg/L	CR, mpy Wt. loss
Sample # 1	0	0	0.7	2.5
Beginning	300	0	0.7	
After 48 hours	300	0	40	
Sample # 2	0	0	0.7	0.0
Beginning	300	200	0.7	
After 48 hours	300	200	0.7	

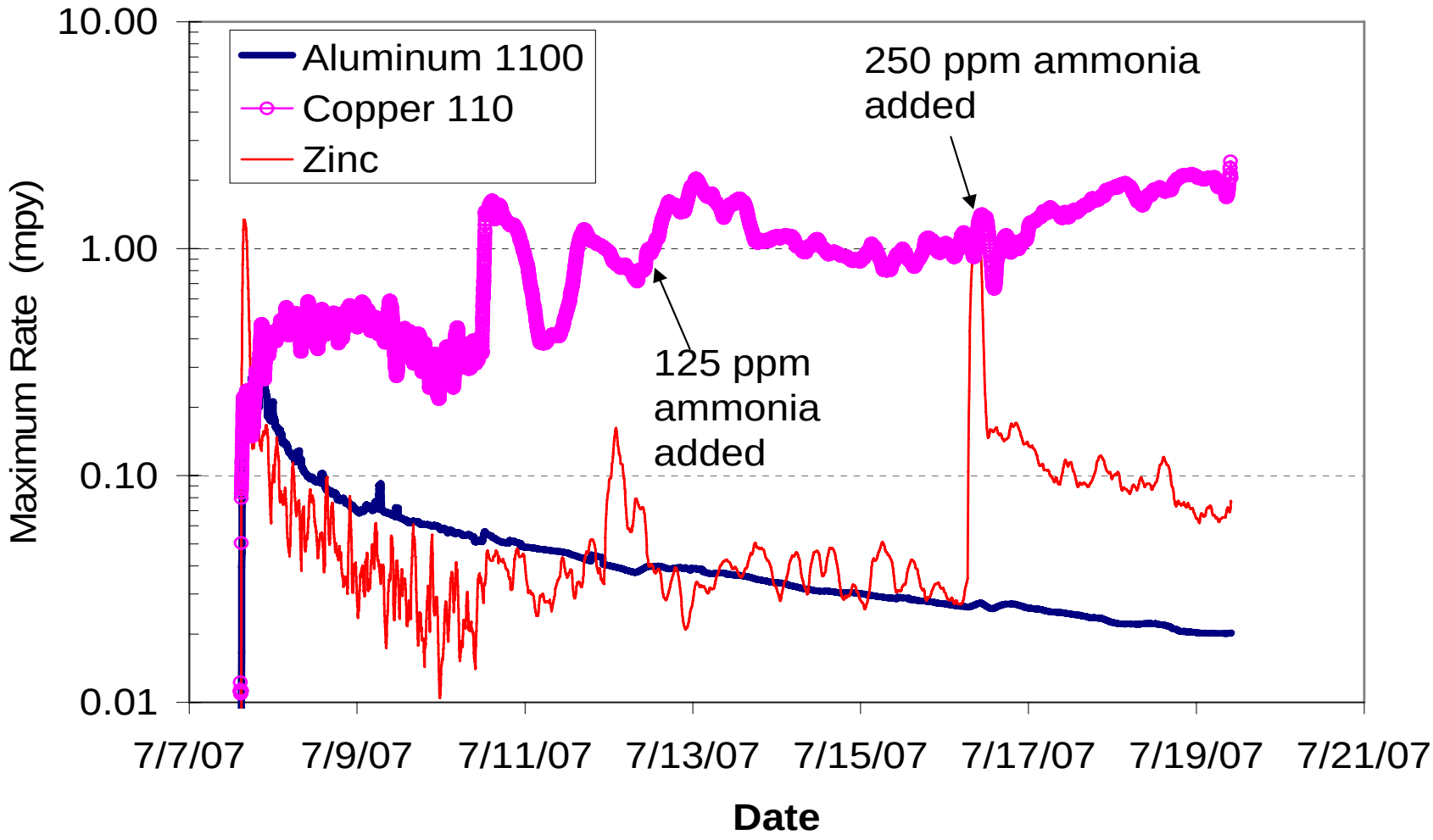
CMAS Corrosion Studies

Localized Corrosive Effects of Ammonia, High TDS, High pH on Copper Zinc and Aluminum

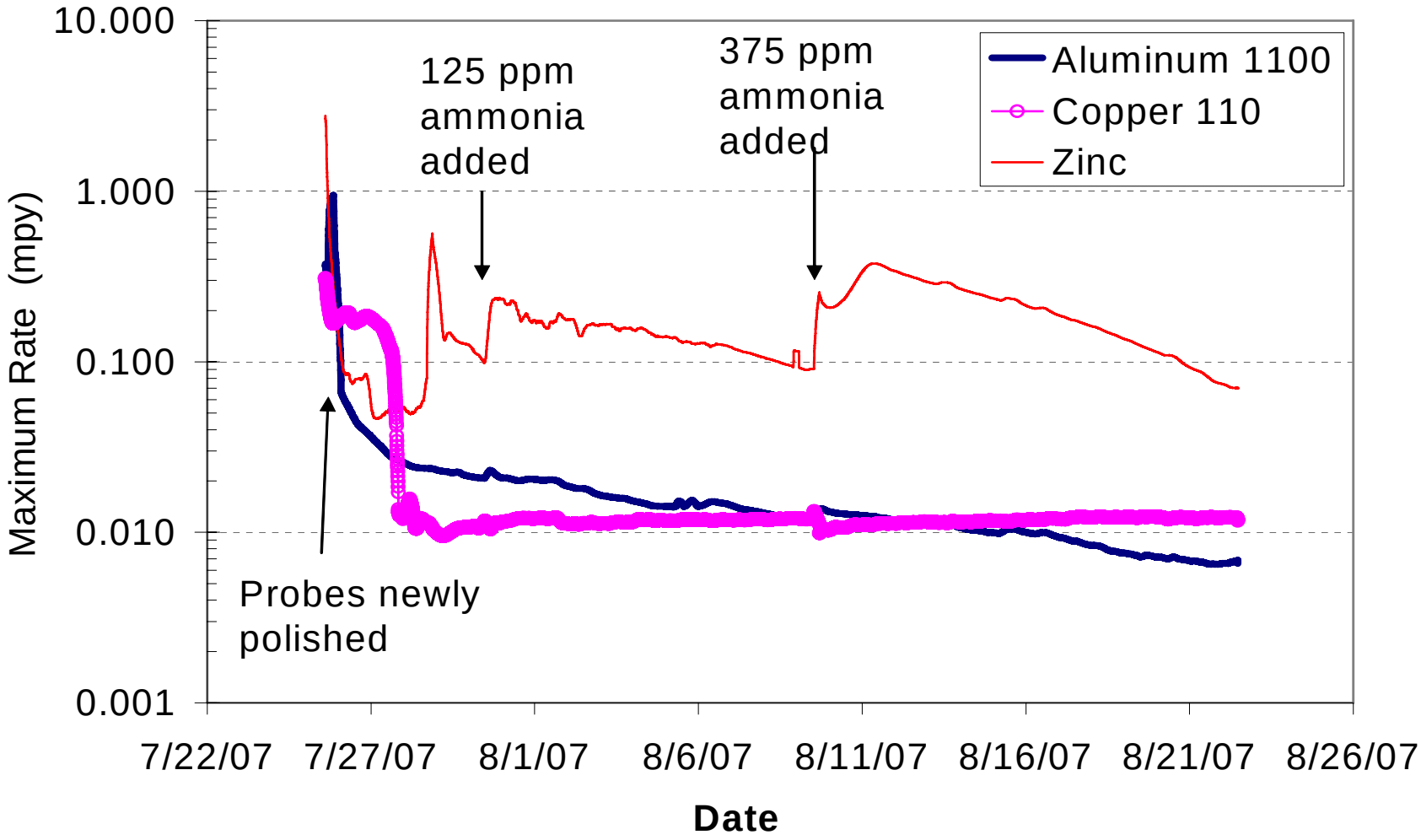
15% NaCl solution with pH adjusted, no Inhibitors, Ammonia / TDS / pH corrosive effect on Cu and Zn



Silica Inhibited ZLD Water, Zn & Al Inhibited, Cu corroded by Ammonia / TDS / pH



ZLD (150,000 TDS) / Silica treated Tower Water: Ammonia and TDS Corrosion of Copper inhibited by TTA



CMAS Study Summary

- Uninhibited localized corrosion rates with ammonia and high TDS were 2.5 mpy for copper and 80 mpy for zinc (room temperature)
- Silica inhibited localized corrosion rates for zinc and aluminum were negligible from ammonia / high TDS; copper was not well inhibited
- Copper was inhibited by TTA to negligible corrosion rate from high ammonia / high TDS

Municipal Reuse Case History

Municipal Reuse water used for makeup to ZLD Tower Operation

Cooling Tower Using High Ammonia (Reuse) Waste Water for Makeup

- High ammonia (34 mg/L) “reuse” makeup water
- High hardness and phosphates limit traditional COC (concentrations of chemistry) of makeup in tower
- High TDS limited traditional corrosion protection
- Copper chiller and absorber tubes at risk from ammonia
- Required multimedia filtered and HES softened makeup
- ZLD / high pH / high TDS with silica & TTA inhibitors
- Ammonia stripped to < 0.5 mg/L at 60 COC by chemistry
- Corrosion of copper inhibited to 0.007 mpy.
- Micro-bio growth (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) Municipal Reuse Waste Water for Makeup

Tower / Soft Makeup COC (Concentration of Chemistry) Ratios			
Sample / Tests (01/04/08)	Tower	Soft MU	COC
TDS, mg/L (Myron L 6P, 442)	66000	1100	60
pH	9.85	7.3	NA
Silica, mg/L SiO_2	530	20	27
Calcium, mg/L $CaCO_3$	18	0.2	NA
Magnesium, mg/L $CaCO_3$	13	0.1	NA
Sulfate, mg/L SO_4	7700	128	60
Chloride, mg/L NaCl	12500	212	59
Tot. Alkalinity, mg/L $CaCO_3$	15000	257	58
Ammonia, mg/L NH_4	< 0.5	38	NA
Total Phosphate, mg/L PO_4	52	0.9	58
TTA, mg/L as tolytriazole	5	NA	NA

Corrosion Rates for ZLD Cooling Tower with Reuse Makeup Water

Linear Polarization and Weight Loss Corrosion Rates (Water treated with silica and TTA inhibitors)		
	Mild Steel (1008)	Copper (110)
Linear Polarization (mpy)	0.2	< 0.1
Coupon Weight Loss with 60 day exposure (mpy)	0.22	0.007

Biostatic Monitoring

- Dip stick cultures 10^{o} Col / ml @ 48 hours
- No bio slime deposits on tower fill
- No slime in chillers or absorbers
- No odor
- No biocide use or handling

Natural Biostatic Chemistry

- Natural source water alkalinity and TDS
- 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

Non-scaling Water Savings

- HES softening provides non-scaling water
- Permits high COC or ZLD operation
- Water use was reduced 30% (reduced tower blowdown)
- Reuse water cost / HCF was 30% less
- Total water use cost reduced 50%
- Equipment ROI less than 12 months
- Minor chemical use (TTA)

Galvanized Coating Passivation Study

ZLD Cooling Water

ZLD Tower Water Chemistry

Tower / Soft Makeup COC (Concentration of Chemistry) Ratios				
Sample / Tests	Tower	Filtered Sample	Soft MU	COC
TDS, mg/L (Myron L 6P)	146,000		251	582
pH	10.07		7.58	
Copper, mg/L Cu	**0.7**	**0.25**	**0.0015**	467
Iron, mg/L Fe	22.2	ND	ND	
Zinc, mg/L Zn	3.8	ND	ND	
Silica, mg/L SiO_2	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		4.5	575
Sulfate, mg/L SO_4	10,260		18	570
Chloride, mg/L NaCl	22,400		38	589
Tot. Alkalinity, mg/L $CaCO_3$	69,400		120	578

Galvanized coupon #283 exposed in ZLD tower for 60 days

vs #282 control before & after coating striped

ZLD Chemistry / Passivation of Galvanized Coatings

- Galvanized coatings protected by silica
- Not affected by high alkalinity / pH / TDS
- Residual copper from source water may deposit on non-passivate coating
- Micro pitting of non-passivate coating
- TTA / azoles (25 mg/L active dose) at start up very effective to passivate coating
- Periodic azoles dose for residual copper

Galvanized Coupon exposed 60 days in ZLD tower with TTA Supplement to Silica Inhibitor

ZLD / Silica / TTA Chemistry Summary

- No scale threat with “ZLD” operation
- Negligible corrosion at very high TDS
- Unaffected by reuse (ammonia) waste water
- Ammonia and organics stripped by chemistry
- Copper protected from ammonia
- Mitigates biological and pathogen growth
- Simple control chemistry
- Reduced water use and discharge cost

Questions?