13th Annual GC&EC
Green Corrosion Inhibition and Water Treatment Session

Sustainable Natural Green Chemistry (NGC) for Cooling Water Treatment

Report by Dan Duke
Water Conservation Technology International

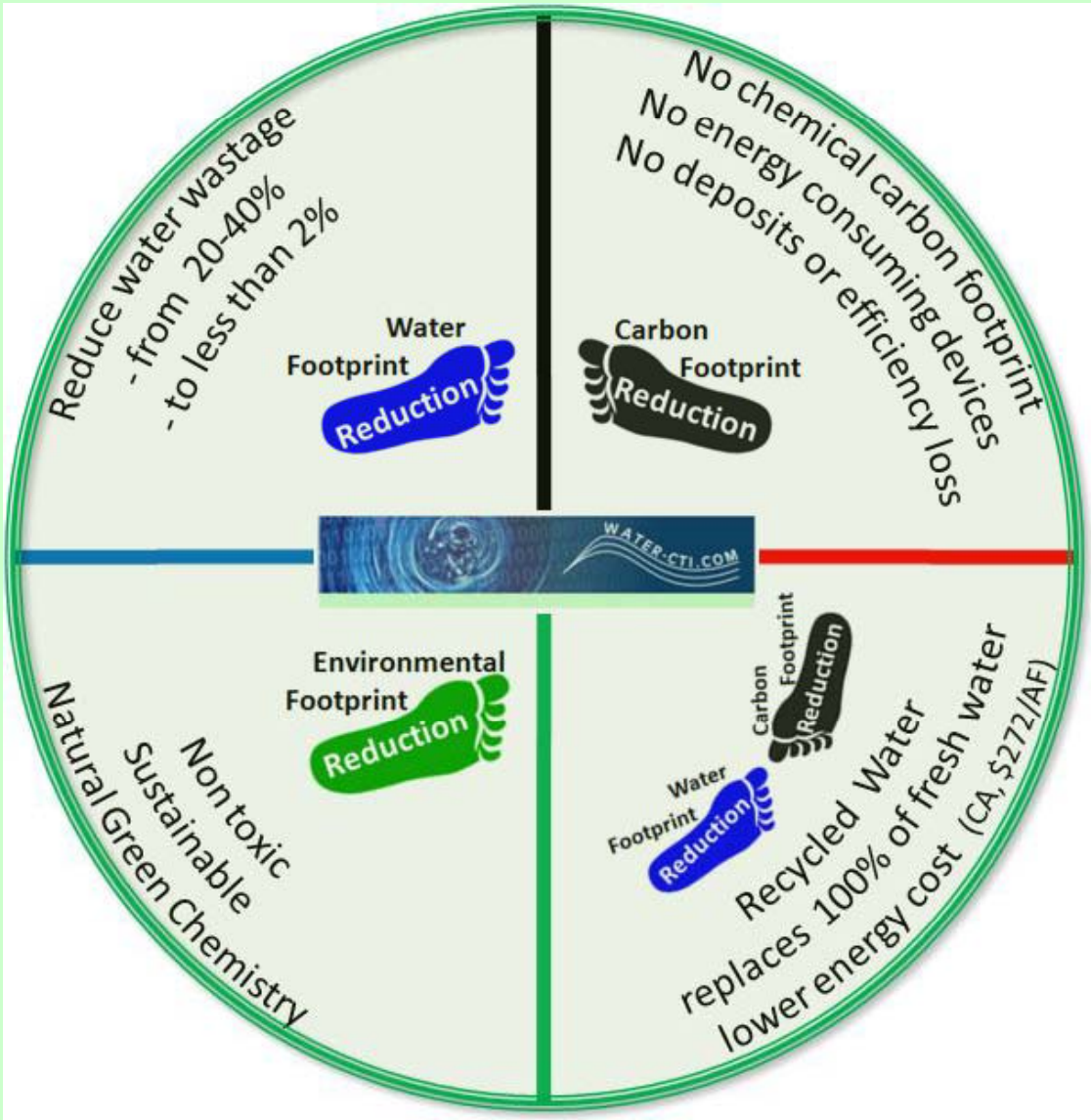
Presentation Outline

- Cooling Water Treatment - Green Challenge
- Organic and Toxic Chemical Discharge
- NGC – How it Works – Why it’s Green
- ZBD - Conserve Water & Environment
- Case History – Recycled Water Use

Cooling Water Treatment

Green Challenge

Cooling Towers Challenge Water Treatment to Reduce Major Water, Carbon and Environmental Foot Prints



Contributors

- Corr Instruments – Lie Yang, PhD
- Anderson Engineering - Eric Anderson
- The Boeing Company – Roger Sampair
- Yahoo, Inc. – A.D. Robinson
- West Basin Utility District – Joe Walters
- NACE / CONRAD – Mike Rogers
- Paul Labine Associates – PhD Chemistry

NGC technology is patented

(Licensed by Water Conservation Technology International)

US 6,929,749 / Scale Inhibition
US 6,949,193 / Scale Inhibition
US 6,998,092 / Corrosion Inhibition
US 7,122,148 / Corrosion Inhibition
US 7,517,493 / Corrosion Inhibition

Green Chemistry Priorities

- Less toxic, less hazardous, biodegradable
- Innocuous feedstock, renewable, natural process
- Eliminate energy and material intensive processes

What Cooling Tower Systems Do

- Consume power to evaporate pure water and remove heat from cooling water
- Consume second largest (5%) individual quantity of fresh water after irrigation
- Concentrate minerals in source water that are discharged to sewers or streams
- Discharge organic chemicals and biocides used for scale, corrosion and bio control

Water Sustainability Challenges

- Fresh water supply for nature, irrigation, population, industry are diminishing
- Water source quality is deteriorating
- Costs for water acquisition, transport (energy) and purification increasing rapidly
- Sewers / WTPs overloaded by discharge
- Organics, toxicants and TDS (source minerals) are limiting water reuse

Deteriorating Water Quality Causes More Discharge for Chemical / NCD Treatments

Water Treatment Priorities For Cooling Tower Operators

- Reduce 20-40% water discharge costs
- Eliminate toxic and hazardous chemicals
- Eliminate energy loss from scale / fouling
- Mitigate corrosion of system metals
- Reduce capital and maintenance costs
- Obtain assured supply of water

WCTI Priorities for R&D

- Eliminate tower discharge (ZBD)
- Replace corrosion & scale chemicals
- Replace biocides & toxicants
- Eliminate chemical handling hazards
- Reduce power use / remove deposits
- Minimize treated discharge (1-2% HES)
- Use recycled water (replaces 100% fresh water and source energy use)

Green Reality vs Green Incentive

- Many green concepts are economically unfeasible or pass high costs to consumers
- Sustaining water or energy or environment should not result in respective poor tradeoffs
- Cost efficient technologies are needed to incentivize commercial and industrial tower operators to replace non-green chemistry

Organic & Toxic Chemicals

Discharged by Cooling Towers

Function & Composition of Chemicals Discharged by Cooling Towers

Product Function	Chemical Composition
Biocides to control bio-growth	organic – non oxidizing halogens - oxidizing
Dispersants for deposit control	organic hydrocarbons
Steel corrosion inhibitors	organic, phosphate, zinc, molybdate
Copper corrosion inhibitors	organic hydrocarbons
Scale inhibitors	organic, phosphate esters, polyphosphate

Quantities of Chemicals Discharged by Tower Blowdown

- 70 million pounds annual discharge of non-oxidizing organic biocides in US
- Even greater halogen biocide use, source of AOX (absorbable organic halogens)
- Over 400 million pounds annual discharge of deposit, scale and corrosion inhibitors
- Over 500 billion gallons annual tower water blowdown is the vehicle

Natural Green Chemistry (NGC)

How it Works

Why it’s Green

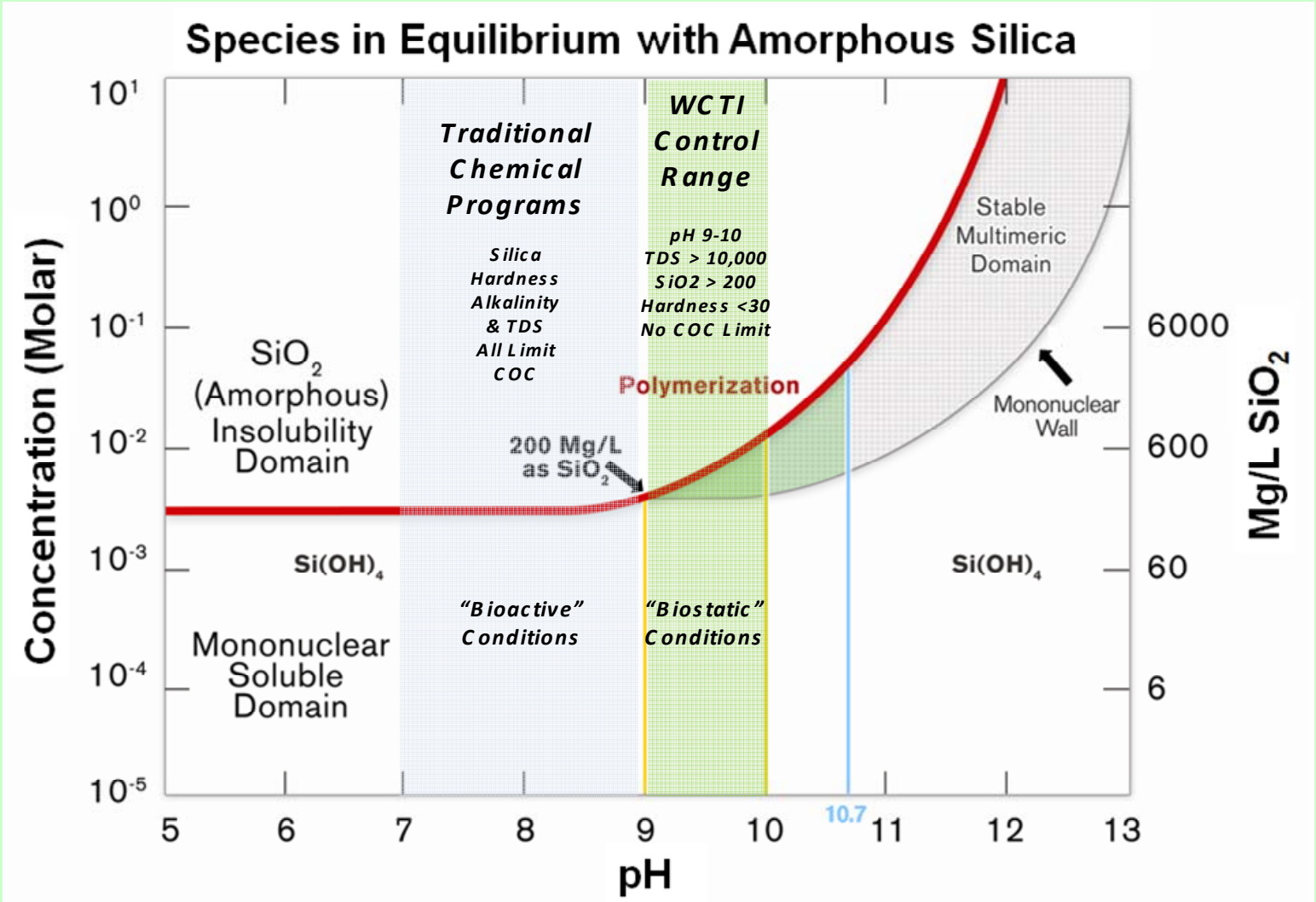
Natural Chemistry Process

- Major minerals in water are Ca, Mg, Na, chloride, sulfate, carbonate and silica
- Exchange Ca & Mg (low solubility ions) with innocuous Na (salt or NaCl)
- Silica polymerized to amorphous silicates by saturation of silica, TDS, alkalinity (pH) with water evaporation
- Zeolite exchange / silica polymerization (natural processes that occur in nature)

How NGC Inhibits Corrosion

- Soft tower water permits 20 to 500 COC (concentrations) of soluble ions versus typical 2 to 5 COC (with hard water)
- Natural tower water chemistry and temperature catalyze silica polymerization
- Silicates form self limiting protective film on all metal surfaces
- Excess silica forms non-scaling and stable silica colloids

Silica Concentration / pH Dependent Relationship



Natural Biostatic Water

- Elevated pH and TDS are naturally biostatic to bacteria, spores and viruses
- Hydrolysis of peptide chains occurs as water pH is increased (used in wastewater treatment)
- Proteins & enzymes also denatured by high TDS
- Natural pH/TDS increase as water is evaporated and concentrated with zero tower blowdown
- Report by Anderson Engineering (water-cti.com)

Eliminate Tower Discharge and Reduce TDS Loadings to Sewer by 70-100% (Recycled Water Example)

TDS Discharge to Sewer with 1000 Ton Tower Load (13,140,000 GPY) Evaporation					
	MU TDS	Tower COC	Discharge TDS	Gal / Year Discharge	# / Year TDS Discharge to Sewer
Tower BD (Chemicals & low COC)	730	2.5	1,825	8,239,000	**125,604**
NGC / ZBD Tower Operation	730	75	54,750	0	**"0"**
HES Softener Waste	-	-	22,700	181,028	**33,146**
Brine Line, Haul or Evaporate Pond	-	-	-	181,028	**"0"**

Reduced Discharge / TDS Disposal to Evaporation Pond

Soft water, soluble ions Present

Raw Water

Cooling Tower

HES / Tower Discharge (High TDS)

Evaporation Pond

NGC Will Remove Existing Scale Deposits!
Reduce *Water* use and save *Energy*

(100 mg/L silica in makeup water to tower)

Performance Measurements	**Chemical Treatment**	**NGC**
Tower COC (TDS concentrations)	**1.4**	**80 (ZBD)**
Tower Water Wasted	**70%**	**1%**
Tower Fill / Exchanger	Visible Scale / Deposits	Removed / Clean Surfaces
Average Planktonic Count	10^4 – 10^5 CFU/ml	10^0 CFU/ml
Average Sessile Count	10^6 CFU/cm^2	10^1 CFU/cm^2
Average Biocide Usage	2.0 – 2.5 gpd	0.05 gpd
Exchanger Amperage Loading	**34**	**25**

NGC Bottom "Green" Line

- No corrosion or scale inhibitors used
- No biocides or toxic chemical discharge
- No energy consumed by fouling / NCDs
- 20-40% or more water use reduction
- Discharge reduced to 1-2% innocuous softener waste (neutral mineral salts)
- Provides TDS discharge load reduction
- Equally effective using recycled water

Zero Blow Down (ZBD)

How NGC / ZBD chemistry
sustains water, energy, environment

Chemical and NCD (non-chemical device) Limitations

- Primarily rely on stability index chemistry (LSI) to control scale and corrosion potential (need Ca)
- Must discharge tower water due to solubility limitations of scaling mineral salts
- Rely on chemical inhibitors, acid and biocides to limit scale, corrosion and fouling potential
- Neither chemicals nor NCD significantly reduce water use / discharge volume
- Corrosion inhibition is ineffective at high TDS
- Vulnerable to scale and mineral deposits

Energy Efficiency Losses From Low Solubility Mineral Deposits

NGC - Highly Soluble Sodium Salts Eliminate Scale Limitations

(Solubility of Ion pairs as sodium salts @ 30^{o} C)

- Sodium Chloride (36% ~ 360,000 mg/L)
- Sodium Carbonate (16% ~ 160,000 mg/L)
- Sodium Sulfate (48% ~ 480,000 mg/L)
- Sodium Ortho-Phosphate (26% ~ 260,000 mg/L)

➢ Non-common ion effect also increases solubility (increased calcium solubility in seawater)

NGC / ZBD Expand
Treatment Options & Performance

- NGC permits cost viable ZBD operation with small or large cooling tower systems
- “State of Art” corrosion & scale inhibition at TDS levels from 5,000 to 150,000 mg/L
- Discharge eliminated without corrosion, scale, or bio-fouling; and reduced pathogen risk
- Ideal for high silica / hardness / TDS water; and includes recycled water sources

High Efficiency Softening (HES) Equipment (Low Investment Cost / Excellent ROI)

- Equipment with low salt use design (4# salt / CF resin), provides 30-50% salt use reduction
- Typical regeneration cost from $0.07 to $0.22 per 1000 gallons of treated water
- Typical tower water use and discharge cost savings are $3.00 - $12.00 /1000 gallons
- Capital cost recovery typically 3 to12 months
- Municipal water conservation incentives
- 75% reduction in regeneration waste volume

Other NGC Opportunities

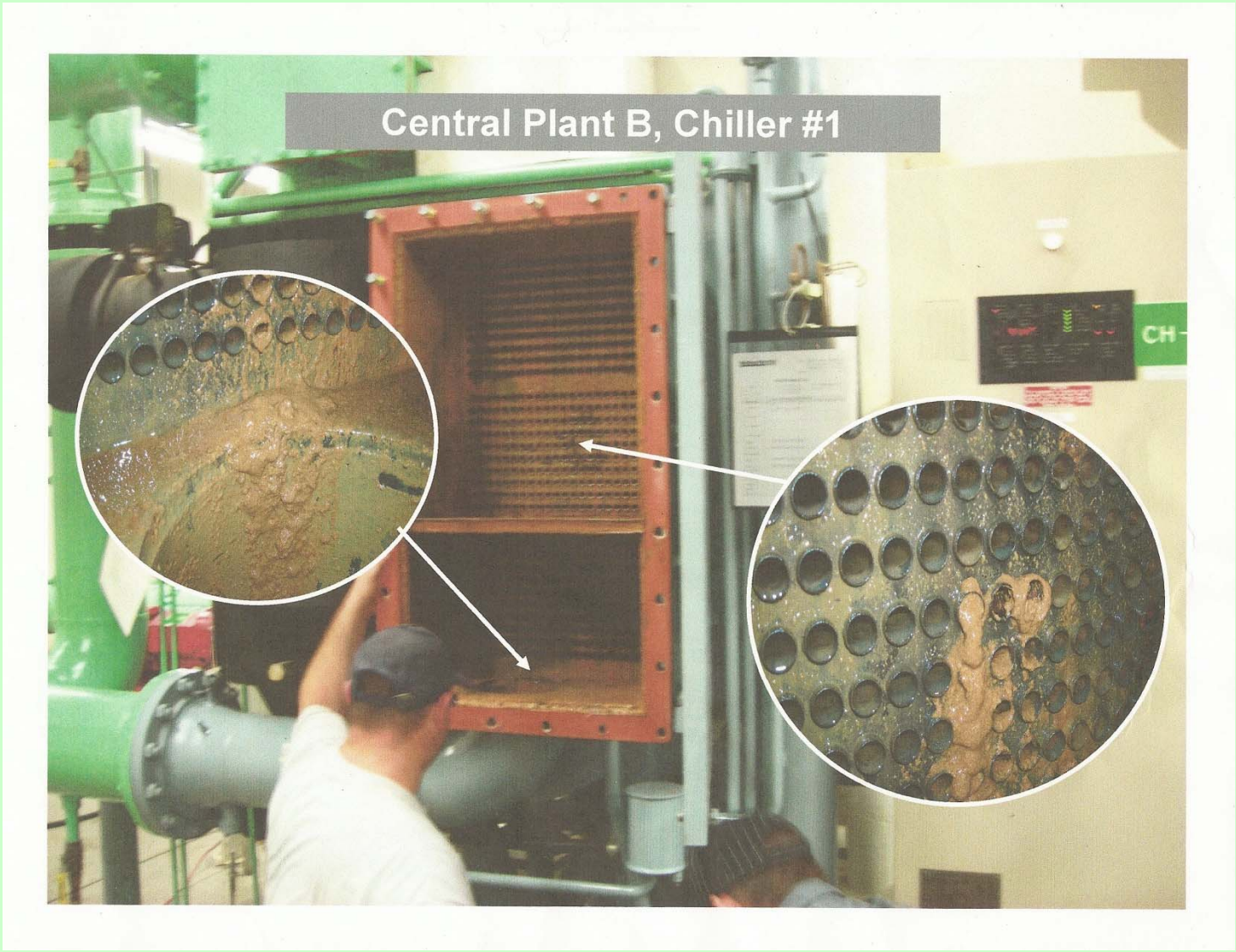
- RO reject reuse as tower makeup (with softened feedwater)
- Use lower cost metals (steel, aluminum, no longer vulnerable to corrosion and scale)
- Use more heat transfer efficient metals (aluminum, copper, steel)
- Regeneration waste recovery and reuse

Case History

Recycled Water Use
(treated municipal sewage)

Challenges With Recycled Water in Cooling Towers

- Suspended solids increase fouling
- Ammonia attacks copper / alloys
- Increased bio-fouling
- Increased scale and corrosion
- Increased water wastage and sewer loading
- Increased chemical cost (2-4X)



Cooling tower systems become incubators for biogrowth, fouling, under deposit corrosion.

Customers Control Recycled Water (RW) Quality and Benefits

- Use high efficiency filtration (HEF) on site
- Use high efficiency softening (HES) on site
- Reduce water & chemical costs 50-75%
- Maintain energy efficient operation
- Acquire additional building LEED points
- Water restriction guarantees (recycled)

Natural Chemistry Process permits Towers to …

- Reduce tower water use by 20-40%
  (9,000-24,000 GPD per 1000 tons load)
- Evaporate over 98% of water used
- Replace 100% fresh water with recycled
- Save $272 /AF in energy cost (CA)
- Operate with natural bio-static water
- Eliminate scale, corrosion and bio fouling

Auto HQ Plant / Recycled Water

- Five central plant cooling towers, Trane copper tube chillers/absorber, plate & frame exchanger
- HEF & HES Pre-treat systems
- Recycled Water Quality

- Ammonia = 38 mg/L
- TDS = 730 mg/L
- Hardness = 224 mg/L
- Total PO4 = 0.9 mg/L
- Turbidity = 3 ntu Avg.

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.

Tower ZBD Chemistry with NGC Treated Recycled Water

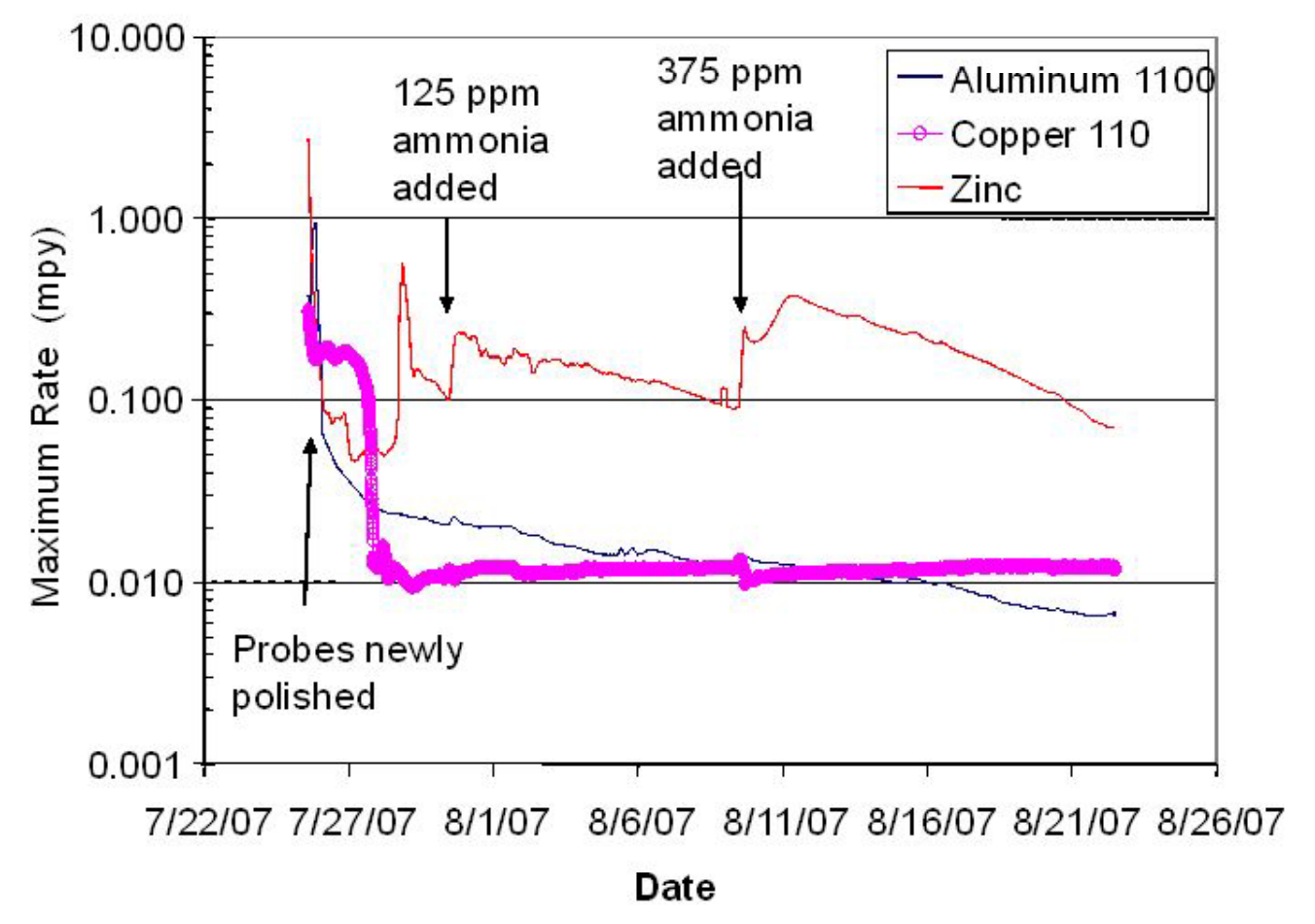
ZBD Tower / Filtered and Softened Recycled Makeup Water COC (Concentration of Chemistry) Ratios			
Sample / Tests	Tower	Soft MU	COC
TDS, mg/L (NaCl Myron L 6P)	**30,000**	1100	**27**
Ph	9.8	7.1	NA
Silica, mg/L SiO_2	**350**	24	**15**
Calcium, mg/L $CaCO_3$	13	0.2	NA
Magnesium, mg/L $CaCO_3$	6	0.1	NA
Sulfate, mg/L SO_4	3300	127	26
Chloride, mg/L NaCl	5800	214	27
Tot. Alkalinity, mg/L $CaCO_3$	5300	192	28
Ammonia, mg/L NH_4	0.5	34	NA
Total Phosphate, mg/L PO_4	**16**	0.6	**27**
TTA, mg/L as tolytriazole	15	NA	NA

Corrosion of Copper Alloys by Ammonia

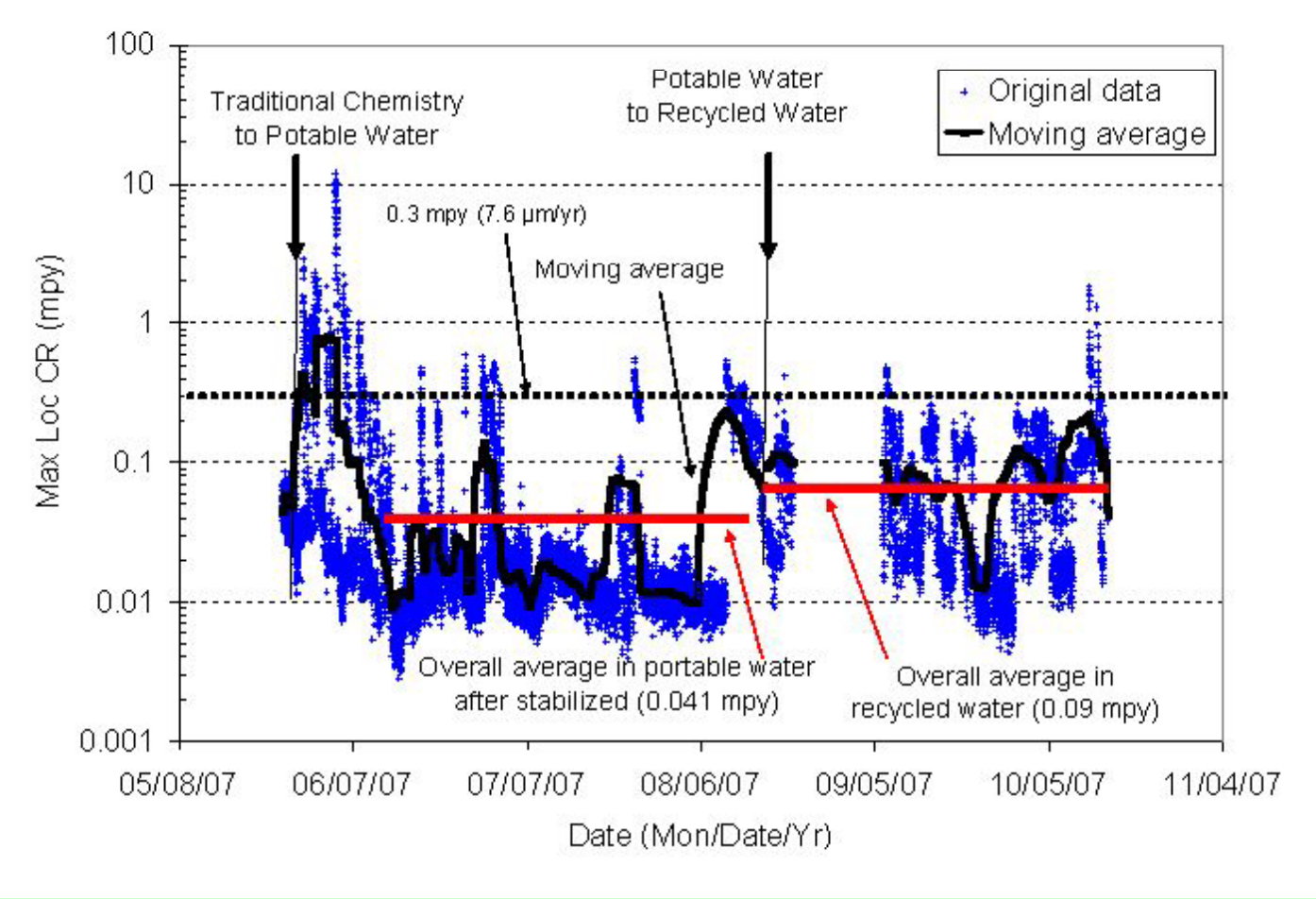
- Ammonia in recycled water is aggressive to brass makeup valves (untreated, failed in less than 12 months, replaced with stainless).
- Don’t use copper pipe for restrooms!
- Typical copper corrosion is presented below.

Corrosion Rates of Copper Alloys in 0.8% Ammonia at 104° F			
Alloy	Corrosion rate		
	mdd	**mpy**	mm/y
Copper	85	**14**	0.36
Cartridge Brass (70:30 Cu-Zn) 260	49	**7**	0.2
Gun Metal (88:10:2 Cu-Sn-Zn) 905	30	**5**	0.1
Copper-manganese alloy (95:5 Cu-Mn)	9	**2**	0.05
Source: After J.A Radley, J.S. Stanley and G.E. Moss, Corrosion Technology 6:229:1959			

Corrosion Studies With Ammonia in Silica and Azoles Treated Water



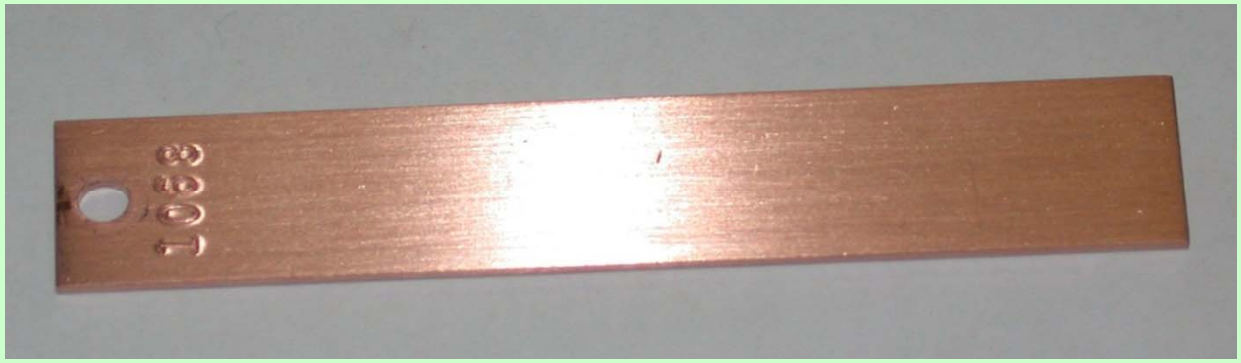
Copper Corrosion (CMAS study)
Chemical vs ZBD Potable vs ZBD Recycled



Copper Corrosion Results (CMAS)
Chemical / ZBD Potable / ZBD Recycled

- The impact of ammonia (NGC treated water) on localized corrosion was a very minor increase from 0.04 to 0.09 mpy
- ZBD corrosion rates on potable and recycled water were well below the 0.3 mpy localized rate with chemicals and potable water

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).

Results: ZBD Tower Chemistry Study for Recycled Water

- Ammonia stripped in tower to < 1 mg/L.
- Ammonia does not affect silica protection of steel, aluminum and zinc.
- Azoles are highly effective for copper protection from ammonia in ZBD water (patent pending).
- Biostatic tower chemistry was not affected by recycled organics and phosphate nutrients.

Steel Mill - Mild Steel Coupons
60 Day Exposure VS Non-exposed
0.017 mpy (1652) VS 0.013 mpy (1664 control)

Steel Mill – Galvanized Tubes – 30 Months Service
No White Rust at up to 146,000 mg/L TDS
Galvanized Coupon after 60 days exposure

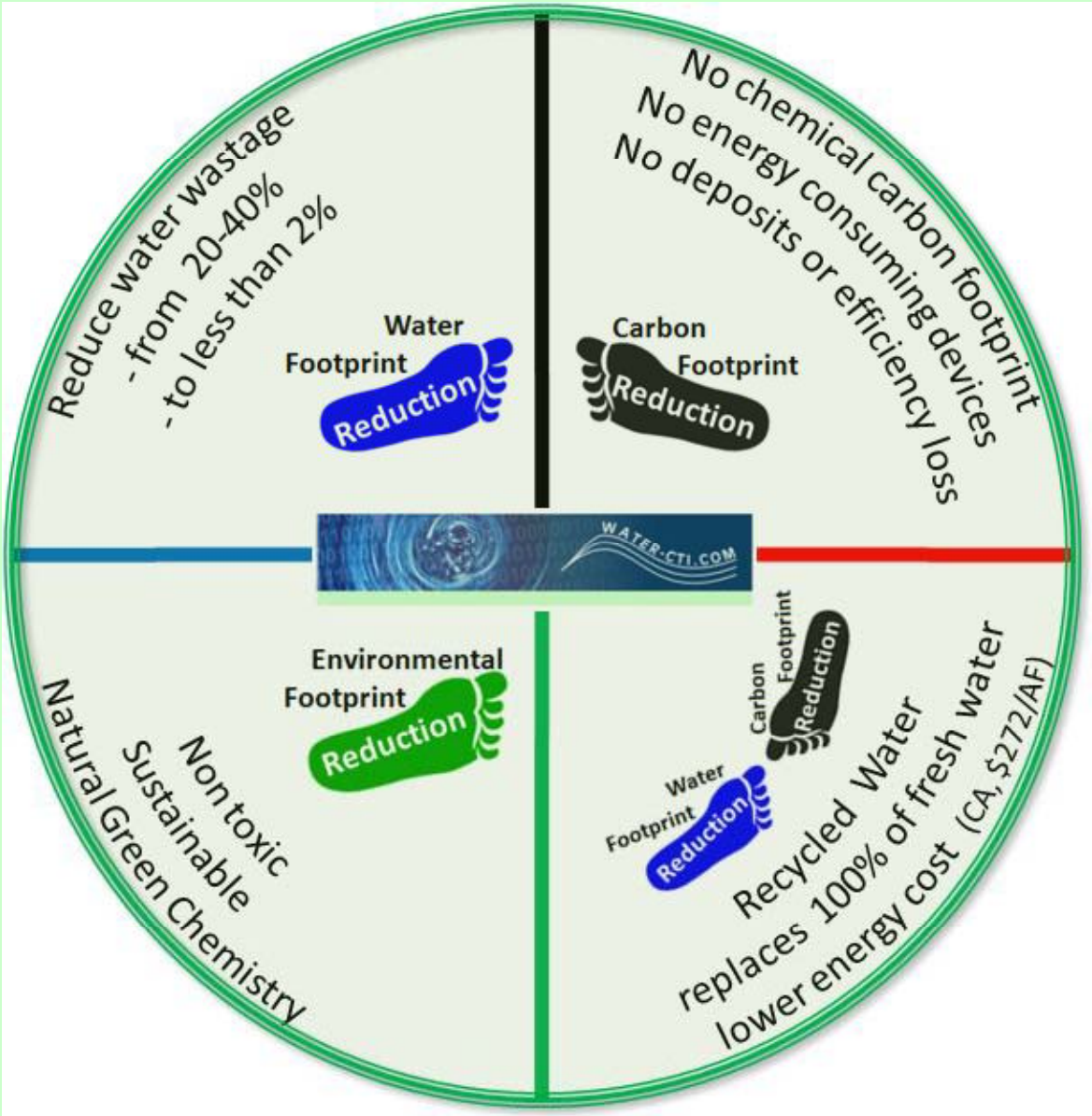
Recycled & High Silica Source Water Projects

- West Basin – Honda, CSUDH, Toyota, LAX, Air Products
- Boeing – Multiple Western US Sites
- Major US Data Centers – (industrial reuse / 35-70 silica)
- Major Chip Manufacturers – Philippines (>100 mg/L silica)

Summary: Recycled Use Expansion in Cooling Towers

- 100% fresh water reduction with recycled water
- ZBD reduces water wastage by 20-40%
- Reduced TDS and toxics to sewer
- HEF / HES cost efficient water quality upgrade
- Quick ROI (< 12 months) from savings
- Water restriction guarantees - Recycled Water
- 50% to 75% less cost than chemical treatment
- Green / energy conserving technology

NGC Can Reduce These Foot Prints



Questions?