

**ACS WRM 2008**  
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**Water Resources Management in the US Southwest**

“Green” Chemistry Uses Natural Water Minerals to  
Treat Cooling Towers, Reduce Water Use and  
Eliminate Toxic Discharge to Support  
Water Resources Management

Report by Dan Duke  
Water Conservation Technology International  
[www.water-cti.com](http://www.water-cti.com)

# Presentation Outline

- Water Sustainability & Cooling Towers
- New Corrosion & Scale Control Chemistry
- Fresh Water Case History
- Recycled Water Case History
- Power & Industrial ZLD
- WRM – New Opportunities
- WRM Incentives / Regional Support

# Water Sustainability

- Fresh water supply is diminishing for nature, irrigation, population, industry
- Discharge of organics / toxicants into ecological resources must be eliminated
- Limited water supply, discharge regulations, and cost will restrict use

# Why Cooling Towers?

- They consume second largest quantity (~5%) of fresh water use, following irrigation
- Their primary purpose is to reduce water use
- They evaporate pure water to biosphere
- They concentrate minerals in source water, typically discharging 20-40% of water to sewer
- They discharge organic chemicals and biocides used to control scale, corrosion and bio growth

# Tower Blowdown is Required with Limitations of Chemical Treatment

<u><i>Limit</i></u>	<u><i>Impact</i></u>	<u><i>Control Mechanisms</i></u>
1. Ca/Mg	Scale	<u>Blowdown</u> / Inhibitor / Acid
2. Silica	Deposits	<u>Blowdown</u> / Inhibitor
3. TDS	Corrosion	<u>Blowdown</u> / Inhibitor
4. pH	Corrosion & Scale	<u>Blowdown</u> / Acid

# Cooling Tower Chemicals Discharged with Blowdown & Drift

- 70 million pounds annual discharge of non-oxidizing organic biocides in US
- Most also use halogen biocides, source of AOX (absorbable organic halogens)
- Even greater quantities of organic scale and corrosion inhibitors discharged

# What If

- You could replace 20 to 40% of the fuel in your vehicle tank with water ...
- get the same gas mileage ...
- and eliminate toxic exhaust emissions!

# Cooling Towers .. can use .. Natural Water Chemistry process to ...

- Evaporate over 98% of water used
- Reduce water use by 20-40% (*9-24,000 GPD per 1000 tons cooling load*)
- Use recycled water rather than fresh water
- Save energy used to treat and pump water
- Eliminate biocide and inhibitor discharge
- Mitigate scale, corrosion or bio fouling



# New Corrosion & Scale Control Chemistry

Four US Patents; # 6,929,749;  
# 6,949,193; # 6,998,092; # 7,122,148  
Further US & Foreign Patents Pending

# How The Chemistry Works

- Low solubility ions (Ca/Mg) removed from water
- Remaining TDS in water are very soluble
- Scale limitations eliminated (< 100,000 TDS)
- Soluble silica polymerizes at > 200 mg/L
- Polymerized silica protects metals from TDS
- Excess silica forms non-scaling colloids
- High TDS/pH prohibits bio & pathogen growth

# Natural Water Chemistry

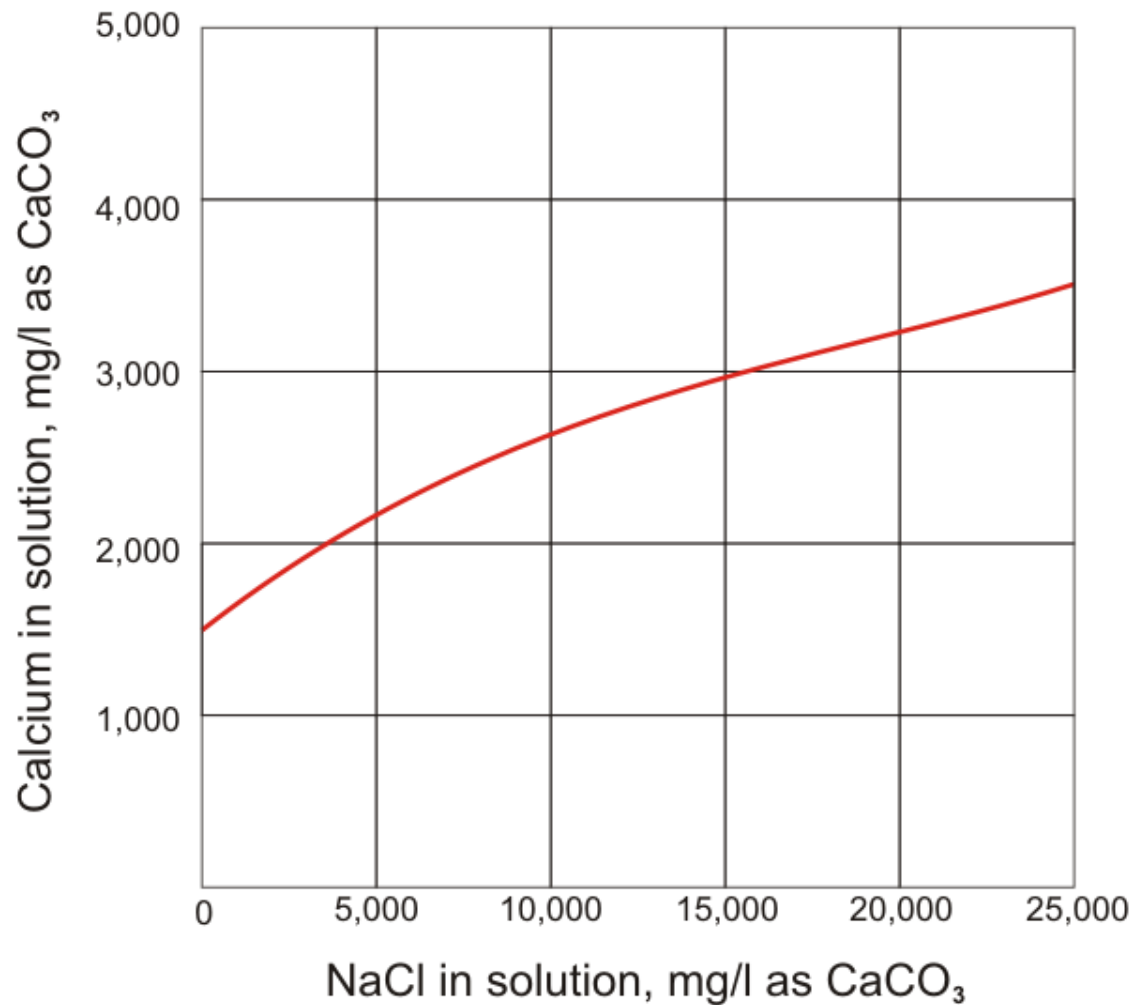
- The major surface water minerals are Ca, Mg, Na, Cl,  $\text{SO}_4$ , carbonate alkalinity and silica
- Ion exchange of Ca & Mg with Na eliminates low solubility salts that scale
- Evaporation of water saturates silica, TDS, and alkalinity (pH) which catalyze polymerization of silica to form amorphous silicates or colloids
- Natural Zeolite exchange and silica colloids occur in nature (geothermal process)

# Highly Soluble Sodium Salts Eliminate Scale Limitations

(Solubility of Ion pairs as sodium salts @ 30° 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)

**Calcium sulfate (gypsum) solubility increases with increasing sodium chloride.**



# Corrosion Control

- Outstanding corrosion protection for mild steel, copper, aluminum, stainless, galvanized metals
- New standard for mild steel; less than 0.1 mpy versus 1-5 mpy for traditional chemical treatment
- Performance vetted by independent corrosion evaluation studies (Dr. Lietai Yang, Corr Instruments, NACE papers 07626 & 88372)

# Natural Biostatic Chemistry

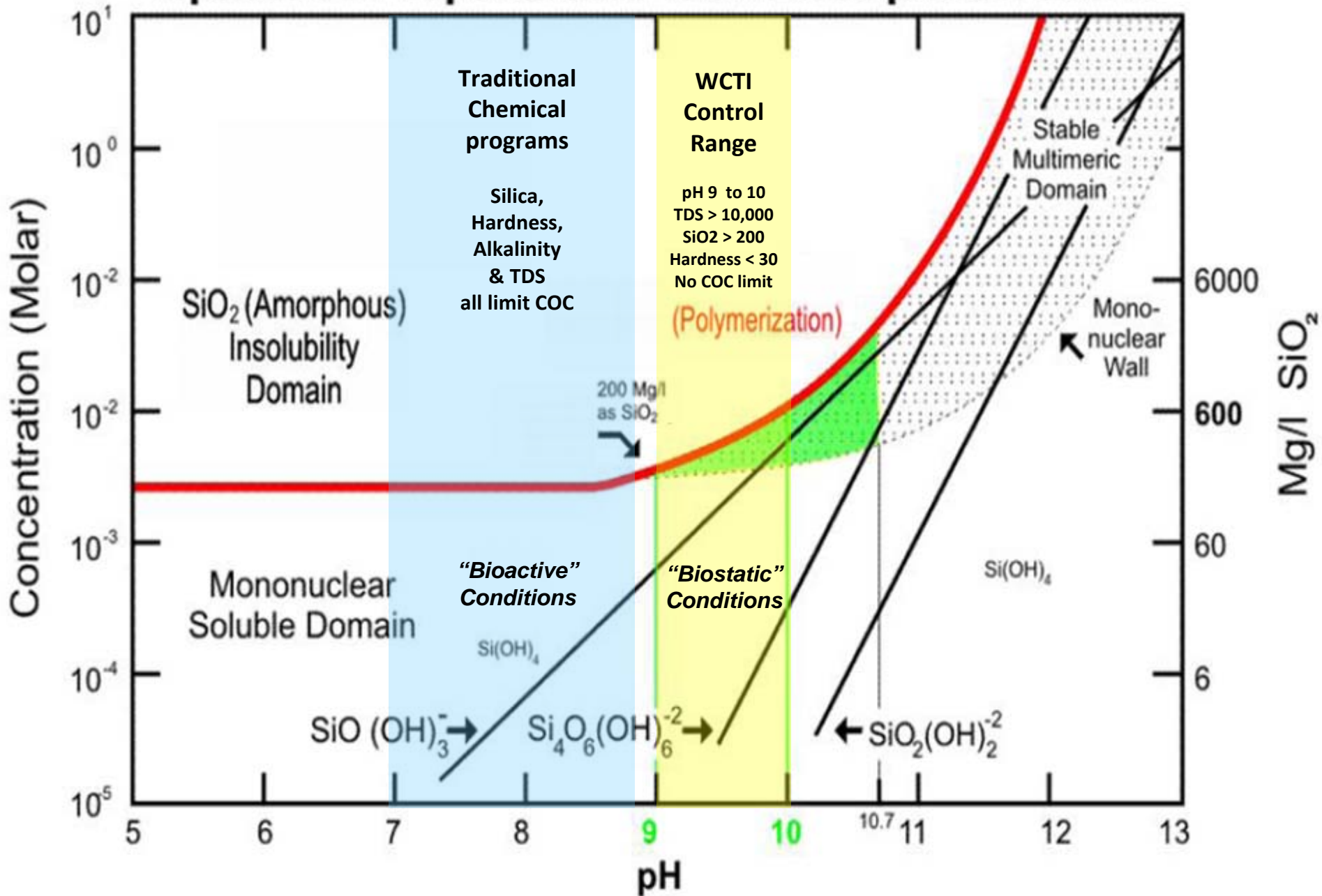
- Elevated pH and TDS are naturally biostatic to bacteria, spores and viruses
- Hydrolysis of peptide chains occurs as water pH is increased (used in wastewater treatment)
- Proteins & enzymes also denatured by high TDS
- Natural pH/TDS increase as water is evaporated and concentrated by reduced tower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

# HES Softening Economy

- Low regenerate use / high efficiency softening (HES) design @ 4# / CF resin
- Exceeds California efficiency standard of 4000 grains hardness removal per pound of salt.
- Typical salt usage cost of \$0.12 per 1000 gallons vs \$2.00-5.00 water & discharge cost
- Cooling tower discharge is reduced from 20-40% to 1-2% of total evaporative use



# Species In Equilibrium with Amorphous Silica



# **Water Resource Management Case History – Fresh Water**

California Steel Mill

# Steel Mill Tower ZLD Water Chemistry

Cooling Tower and Soft Makeup Water Chemistry (COC) Ratios				
Sample / Tests	Tower	Filtered Tower Sample	Soft MU	COC
<b>TDS</b> , mg/L (NaCl Myron L 6P)	<b>146,000</b>	146,000	<b>251</b>	<b>582</b>
pH	10.07	10.07	7.58	
Copper, mg/L Cu	0.7	0.25	0.0015	
Iron, mg/L Fe	22.2	ND	ND	
Zinc, mg/L Zn	3.8	ND	ND	
<b>Silica</b> , mg/L SiO <sub>2</sub>	<b>1,050</b>	1,050	<b>30</b>	<b>35</b>
Calcium, mg/L CaCO <sub>3</sub>	62	12.4	<0.1	
Magnesium, mg/L CaCO <sub>3</sub>	16	8.2	<0.1	
<b>Phosphate</b> , mg/L PO <sub>4</sub>	<b>89</b>	-	<b>0.15</b>	<b>593</b>
Nitrate, mg/L NO <sub>3</sub>	2590	2590	4.5	575
Sodium, mg/L Na	145,000	145,000	250	580
Sulfate, mg/L SO <sub>4</sub>	10,260	10,260	18	570
<b>Chloride</b> , mg/L NaCl	<b>22,400</b>	22,400	<b>38</b>	<b>589</b>
Tot. Alkalinity, mg/L CaCO <sub>3</sub>	69,400	69,400	120	578
(COC) = Concentration of Chemistry				

# **Steel Mill Tower #1 (24 months ZLD) Galvanized Tube Bundle / No White Rust**



# Steel Mill Tower Galvanized Coated Steel Coupon 60 Day Exposure





# Mild Steel Coupons 60 Day Exposure VS Non-exposed

0.017 mpy #1652 VS 0.013 mpy #1664 (control)



# Water Resource Management Case History – Recycled Water

Honda Motors HQ

# High Ammonia Content Recycled Water

- Municipal “recycled” use in central plant with 2500 tons capacity - copper condenser tubes
- Ammonia = 38 mg/L
- TDS = 730 mg/L
- Total hardness = 224 mg/L
- Total Phosphate = 0.9 mg/L

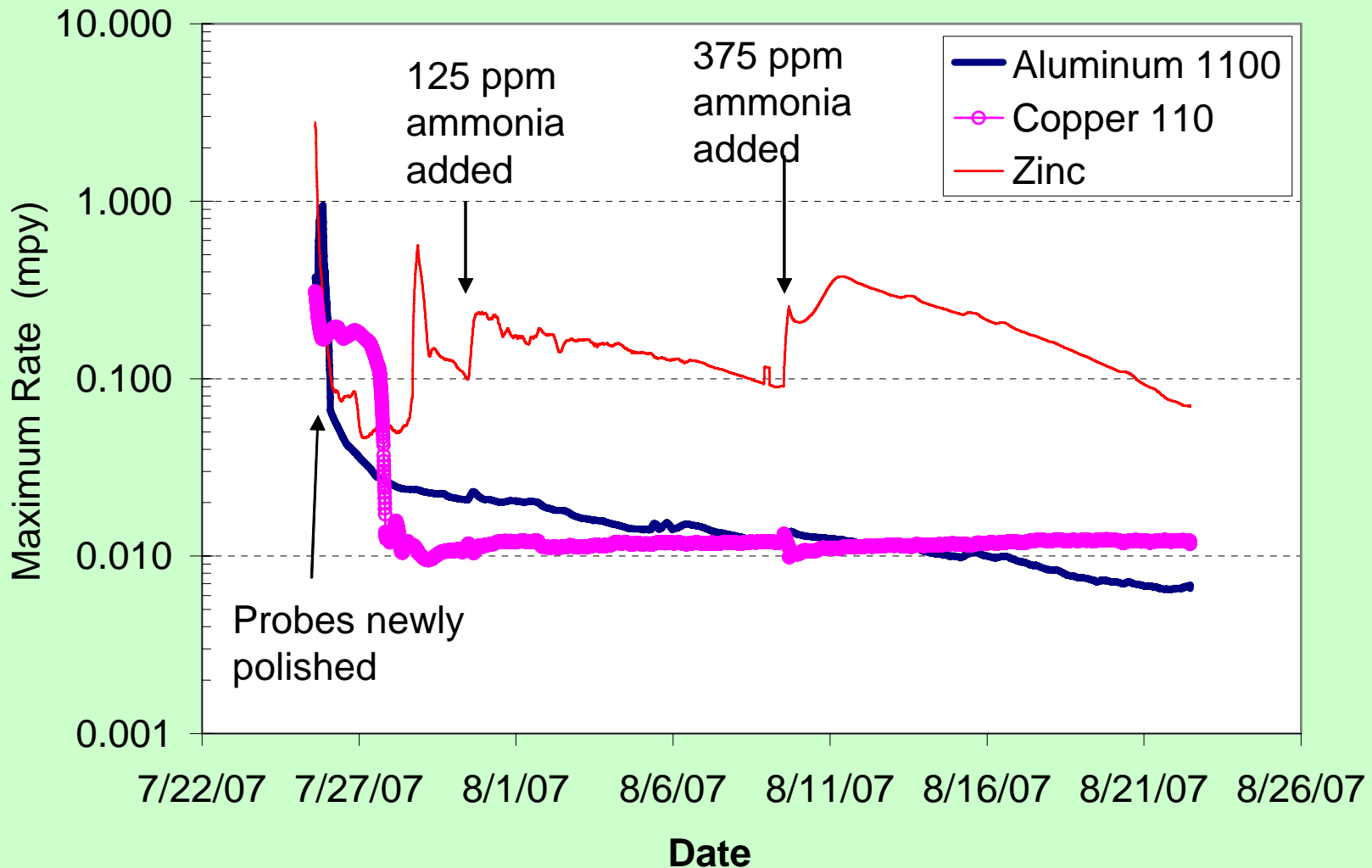


# ZLD Cooling Tower

## (California Title 22) Recycled Makeup

ZBD Tower / Soft Reuse Makeup COC Ratios (concentrations of chemistry)			
Sample / Tests (01/04/08)	Tower	Soft MU	COC
<b>TDS, mg/L (NaCl Myron L 6P)</b>	<b>66,000</b>	<b>1100</b>	<b>60</b>
pH	9.85	7.3	NA
Silica, mg/L SiO <sub>2</sub>	530	20	27
Calcium, mg/L CaCO <sub>3</sub>	18	0.2	NA
Magnesium, mg/L CaCO <sub>3</sub>	13	0.1	NA
Sulfate, mg/L SO <sub>4</sub>	7700	128	60
Chloride, mg/L NaCl	12500	212	59
Tot. Alkalinity, mg/L CaCO <sub>3</sub>	15000	257	58
<b>Ammonia, mg/L NH<sub>4</sub></b>	<b>0.5</b>	<b>38</b>	NA
<b>Total Phosphate, mg/L PO<sub>4</sub></b>	<b>52</b>	<b>0.9</b>	<b>58</b>
TTA, mg/L as Tolytriazole	5	NA	NA
(COC) = Concentration of Chemistry			

# ZBD / Silica treated Tower Water, with TTA Supplement: Ammonia Corrosion of Copper, Zinc & Aluminum Inhibited



# Treatment Results

- Ammonia < 1 mg/L at 60 COC tower water
- Copper corrosion rate at < 0.05 mpy
- Mild steel corrosion rate < 0.2 mpy
- Micro-biological growth from ammonia and organics mitigated ( $10^0$  Col / ml)
- No scale, fouling or efficiency losses
- Annual chemical cost (\$80,000) eliminated
- Blowdown water use savings (\$32,000)

# **Power / Industrial ZLD**

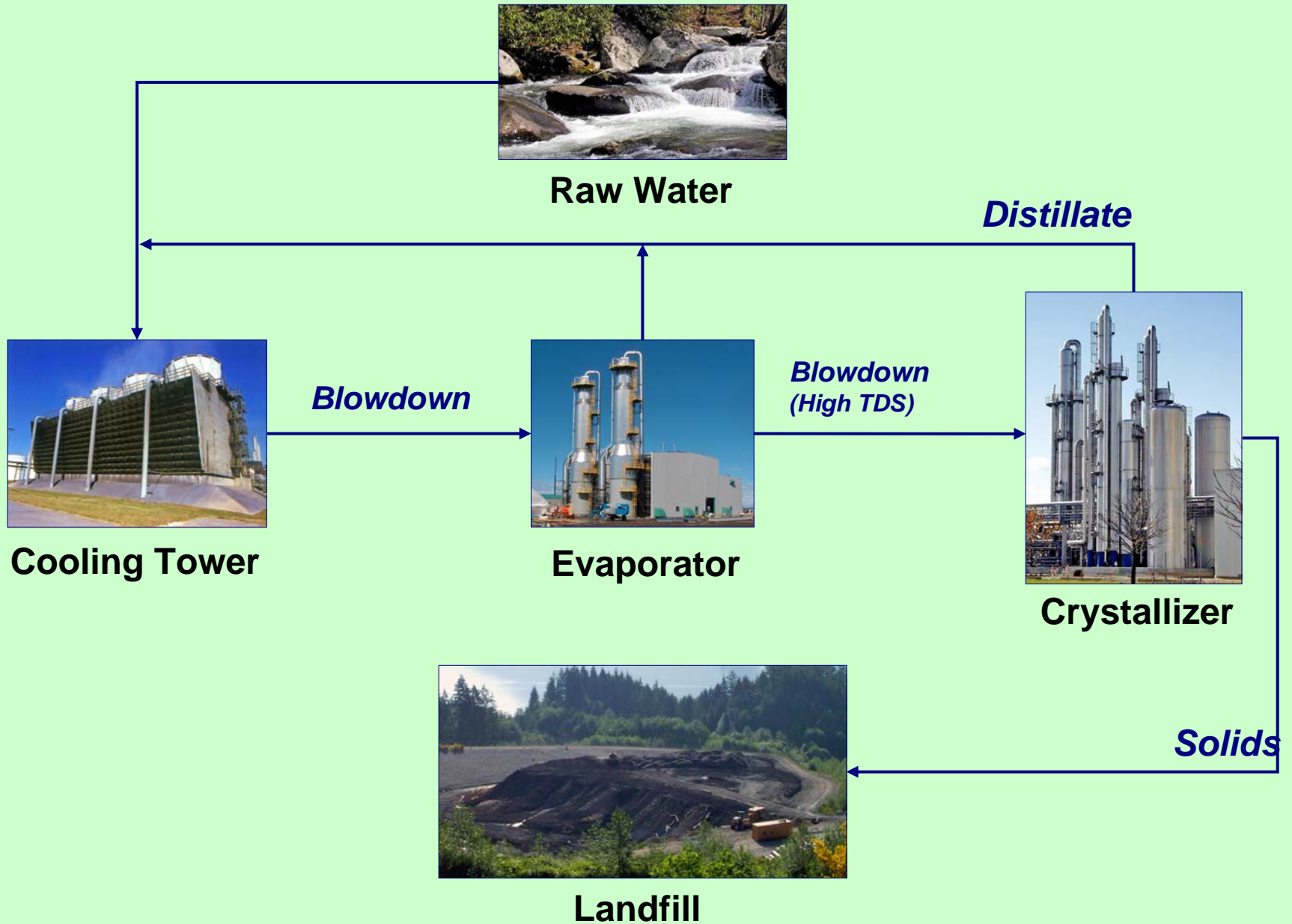
(Site Processed Discharge)

# Power Plant ZLD Approaches

- Require combination of chemical precipitation, reverse osmosis, evaporator and crystallizer stages to recover water and produce dry solids
- Capital cost can be 10% of power plant facility
- Operational costs 15% of power plant facility
- Parasitic energy consumption for ZBD systems is a major operational cost
- Complex operation, control and maintenance
- Still use organic chemicals and biocides
- Costs passed on in higher rates to consumers

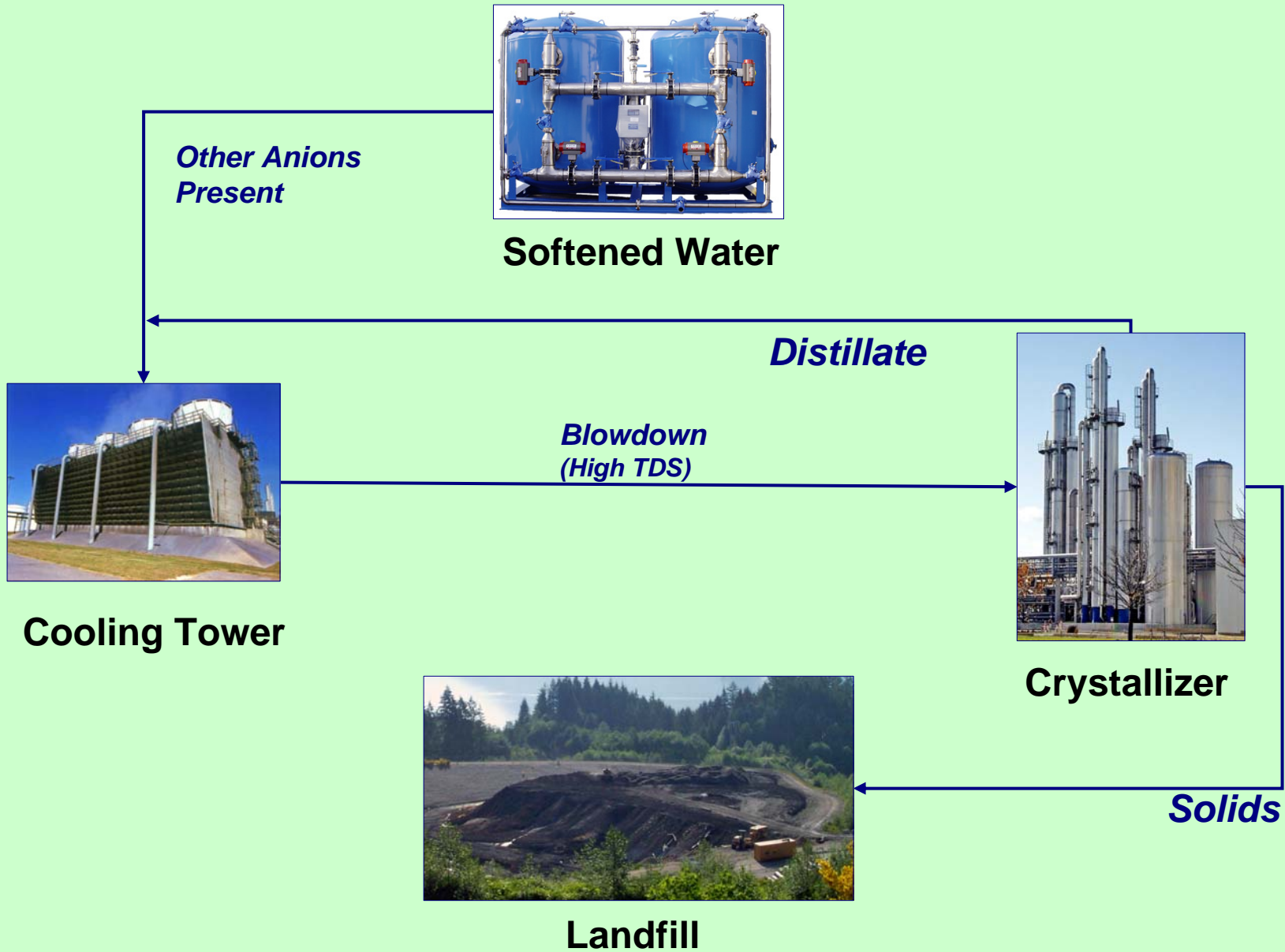
Option A

Conventional Average Cycles of Concentration



**Option B**

**Pre-Treated Make-up with Silica Inhibition Program**





Raw Water

*Other Anions Present*



Cooling Tower

*Blowdown (High TDS)*



Evaporation Pond



# Evaporation Pond

- Utilize waste heat from cooling load to reduce waste discharge volume
- Relatively small land use is required for pond with reduced discharge volume
- Waste disposal parasitic energy consumption is averted

# Water Resources Management

## New Opportunities

- ZBD reduces water use by 20-40%
- Even greater conservation with waste water use
- No blowdown or pH control systems required
- No chemical storage and feed systems required
- Minimize discharge of organics and toxicants
- HES cost efficient removal of scale ions
- Low investment cost (ROI < 12 months)
- 50% to 75% less cost than chemical treatment

# Natural Technology / Waste Heat Ideal for Recycled Water Use

- Use cooling waste heat to evaporate recycled water (minimize parasitic energy use and WTP capacity costs)
- Reduce fresh water energy cost (22% of CA energy use)
- High TDS in recycled water does not cause corrosion
- Biostatic chemistry mitigates biological growth from ammonia and organics (major reuse limitation)
- Non chemical approach exploits natural water minerals
- Qualifies for “green” chemistry, LEED, LEAN processes
- Nitrification of waste water not required

# Expanded Economic Options

- Potential tower water sources include recycled water, RO reject, boiler BD, high TDS water
- Use lower cost and efficient heat transfer metals (mild steel, copper, aluminum) for economy
- Mitigates micro-biological and pathogen growth to minimize biocide dependency
- Lowers discharge loading to sewer
- Lowers waste volume for other disposal options (haul, evaporation ponds, crystallizers, ect)

# Current Recycled & High Silica Water Applications

- Honda CHQ - 2500T (waste water reuse)
- CSUDH – 1500T (potable to reuse)
- Boeing CHQ – (national program pilot)
- Yahoo & Microsoft Data Centers – (industrial reuse & 35-70 silica)
- Intel – Philippines (>100 mg/L silica)

# Water Resource Management Incentives & Support

# **LEED (gain up to 5 points)**

## **Green Building Association**

- WE 2.0 - Innovative WW Technologies (1)
- WE 3.1 - Water Use Reduction – 10% (1)
- WE 3.2 - Water Use Reduction – 20% (1)
- WE 4.1 – Chemical use reduction (1)
- WE 4.2 – Non Potable (recycled) Use (1)

# LOW CARBON FOOTPRINT (Green Energy / Chemistry)

- ✓ Minimize heat transfer loss
- ✓ Avoid high energy consuming devices
- ✓ Eliminate manufactured chemicals



# **LEAN**

## **(natural resource efficient)**

- ❖ Minimize water use and disposal cost
- ❖ Optimize energy use (heat transfer) and cost
- ❖ Reduce capital expense / investment
- ❖ Reduce equipment cleaning and replacement
- ❖ Reduce variables for work flow improvement
- ❖ Reduce chemical handling and storage
- ❖ Reduce operator time and safety risks
- ❖ OEE - Optimize Equipment Efficiency

# Regional Support

- Municipal Distributor Water Conservation Incentives - MWD & Seattle PU
- California Sustainability Alliance
- National Water Research Institute
- Washington State DOE – Quincy Model
- 2009 CA Water Reuse Association – joint paper with West Basin MWD

# Summary

- “ZBD” operation now cost viable for all towers
- Negligible corrosion at high TDS
- Use waste or recycled water makeup
- Ammonia and organics impact mitigated
- Eliminates organic and toxicant discharge with biocides and inhibitor treatment chemicals
- Reduced water use and discharge cost
- **LOW CARBON, LEED and LEAN opportunity**