NACE CORROSION 2008 TEG 096X Symposia – Paper 1414

Zero Liquid Discharge Cooling Tower Treatment at CSI

John Kubis

Water & Enviro Tech Company, Mission Viejo CA

Jeff Reed California Steel Industries, Fontana CA

Presentation Outline

- New ZLD technology
- How Silica Chemistry Works
- ZLD / Soft Water / No Scale
- CSI Results With ZLD Tower Operation
- Typical ZLD Installation
- ZLD / Silica Chemistry Summary

New ZLD Technology

Prior ZLD Limitations

- Cost feasible only for large systems
- Combinations of pre-treat and side stream treatment to remove TDS and precipitates
- Extensive capital and operational costs
- Increased TDS and solids disposal volumes
- Scale and corrosion control still limited by traditional chemical treatment

New ZLD Technology

- New inhibitor chemistry permits high TDS / Zero Liquid Discharge
- State of art corrosion & scale protection
- Corrosion mitigated at 5,000-150,000+ TDS
- Calcium not needed for corrosion inhibition
- Eliminates scale, corrosion, and bio fouling
- Ideal for high silica or "reuse" makeup waters

New ZLD Chemistry Benefits

- Scale risk removed by HES pre-treatment
- Ideal corrosion protection (<0.1 MPY) for steel, copper, galvanized and aluminum
- Reduces tower blow down discharge cost
- Reduces water consumption cost
- No chemical handling & storage
- Natural "green" silica chemistry

How Silica Chemistry Works

How Silica Chemistry Works

- Proprietary HES softening system removes scale forming ions from tower makeup water
- Unlimited water concentrations (500X)
- Polymerized silica protects metals at high TDS
- Excess silica polymerized to colloidal forms
- High pH/TDS biostatic to micro-bio growth
- Patented technology US 6,929,749; US 6,949,193; US 6,998,092; US 7,122,148; additional patents pending.

Silica Chemistry

- Removal of polyvalent cations and increased pH eliminate silica deposition and traditional scales
- Monovalent cations, alkalinity, temperature, time and COC polymerize silica to silicates
- Silicates hydrolyze into negatively charged colloidal particles, then migrate to and react with metal oxides or existing silicate surfaces
- Silicates forms self-repairing gels on metal surface

Corrosion Inhibition by Silica

- Polymerized silicates, in saturated equilibrium with amorphous silica, are attracted to metals
- Gel layer on metal forms barrier to corrosive ions
- Gel layer growth is self limiting molecular film
- Even amphoteric metals (Al, Zn) are protected by silicate gel layer from high pH and TDS

ZLD / Soft Water / No Scale

High Solubility of Sodium Salts (30° C)

- Sodium Chloride (35.7% ~ 357,000 mg/L)
- Sodium Carbonate (16%)
- Sodium Sulfate (48%)
- Sodium Ortho-Phosphate (25.8%)
- ZLD Towers COC balance all of above
- Non-common ion effect (example, higher calcium solubility in seawater)

CaSO₄ Solubility in NaCl

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



CSI Results with ZLD Tower Operation

EC West Tower ZLD Chemistry

EC West Tower - Concentration of Chemistry (COC) Ratios						
SAMPLE / TESTS	Tower	Filtered	Makeup	COC		
TDS, mg/L (Myron L)	141,000	Tower	251	562		
pH	10.05		7.58			
Copper, mg/L Cu	0.6	0.2	0.0015			
Iron, mg/L Fe	19	ND	ND			
Zinc, mg/L	3.5	ND	ND			
Silica, mg/L SiO ₂	960		30	32		
Calcium, mg/L C a C O ₃	35	7.5	< 0.1			
Magnesium, mg/L C a C O 3	15	7.7	< 0.1			
Phosphate, mg/L PO ₄	82		0.15	547		
Sulphate, mg/L SO ₄	9995		18	555		
Nitrate, mg/L NO ₃	2450		4.5	544		
Chloride, mg/L NaCl	21000		38	552		
Alkalinity, mg/L C a C O 3	67,000		120	558		

CSI - EC WEST Tower – 27 months Galvanized Tube Bundle / No White Rust (141,000 TDS)



16

CSI - EC WEST Tower Galvanized Coated Steel Coupon 60 Day Exposure



CSI - EC WEST Tower - Mild Steel Coupons 60 Day Exposure VS Non-exposed 0.017 mpy #1652 VS 0.013 mpy #1664 (control)



EC 10 Tower ZLD Chemistry

EC 10 Tower - Concentration of Chemistry (COC) Ratios						
SAMPLE / TESTS	Tower	Filtered	Makeup	COC		
TDS, mg/L (Myron L)	146,000	Tower	251	582		
pH	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	3.8	ND	ND			
Silica, mg/L SiO ₂	1050		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		
Sulphate, mg/L SO ₄	10260		18	570		
Chloride, mg/L NaCl	22400		38	589		
Alkalinity, mg/L CaCO3	69,400		120	578 19		

CSI - EC #10 Tower – 24 months Galvanized Tube Bundle / No White Rust (146,000 TDS, 105° / 77° F)



CSI Results Summary

- ZLD provided 98% discharge reduction
- Water usage reduced 30%
- No scale on heat transfer surfaces
- No corrosion of galvanized bundles
- No biological fouling or growth
- Chemical use and handling eliminated
- Six cooling towers now using ZLD

Typical ZLD Installation

Typical ZLD Installation

- Tower makeup water passes through HES.
- Scale risk eliminated by removal of hardness.
- Blow down is reduced to ZLD, or < 5% range.
- No chemical feed or control systems required.
- Corrosion almost zero for all metals.
- Environmentally friendly / no toxic chemicals.
- Just maintain salt tank / low usage design.



ZLD HES Cost / ROI

- HES low salt use design (4# / CF resin)
- 30-50% salt use reduction
- Less than 2% treated flow regenerate waste
- Treated cost average, \$0.12 /1000 gallons
- Typical water savings of \$3.00 /1000
- Equipment cost recovery < 12 months
- Municipal rebates now common

ZLD / Silica Chemistry Summary

"Green" Inhibitor Chemistry

- System chemistry derived from concentration of (soft) makeup water ions and silica
- Natural, non-toxic source water chemistry
- Organic corrosion and scale inhibitors are not required or discharged
- Limited or no microbiological control agents
- Blow down is not required

Other Benefits of Silica Chemistry

- Permits use of reuse waste water, RO reject, high TDS and silica water sources
- Protect metals from high chlorides, sulfates, alkalinity, ammonia, organics
- Protects galvanized and aluminum metals
- Expands metal selection / cost options

ZLD / Silica Program Summary

- No scale with "ZLD" operation
- Excellent corrosion inhibition at high TDS
- Excellent high temperature inhibition
- Permits Al, Zn use at high pH (10)
- Mitigates biological and pathogen growth
- Permits municipal and "grey" waste water reuse
- Natural "green" chemistry to reduce water use and sustain water sources / environment

