Henan Qingshuiyuan Technology., Ltd

ChemTreat

Power Plant

Cooling Water Technology

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Agenda

- Types of Cooling Systems
  - Heat Transfer
  - Basic Calculations
  - Cooling Tower Basics
- Deposit Control
  - Scale
  - Silt
  - Deposit Control
  - Cleaning
- Corrosion Control
  - Corrosion Cell
  - Corrosion Inhibitors
  - Electrochemistry
  - Non-P, Non-Zn Inhibitors
- Automation
  - Hardware
  - Software

Please feel free to ask questions as we move through the presentation

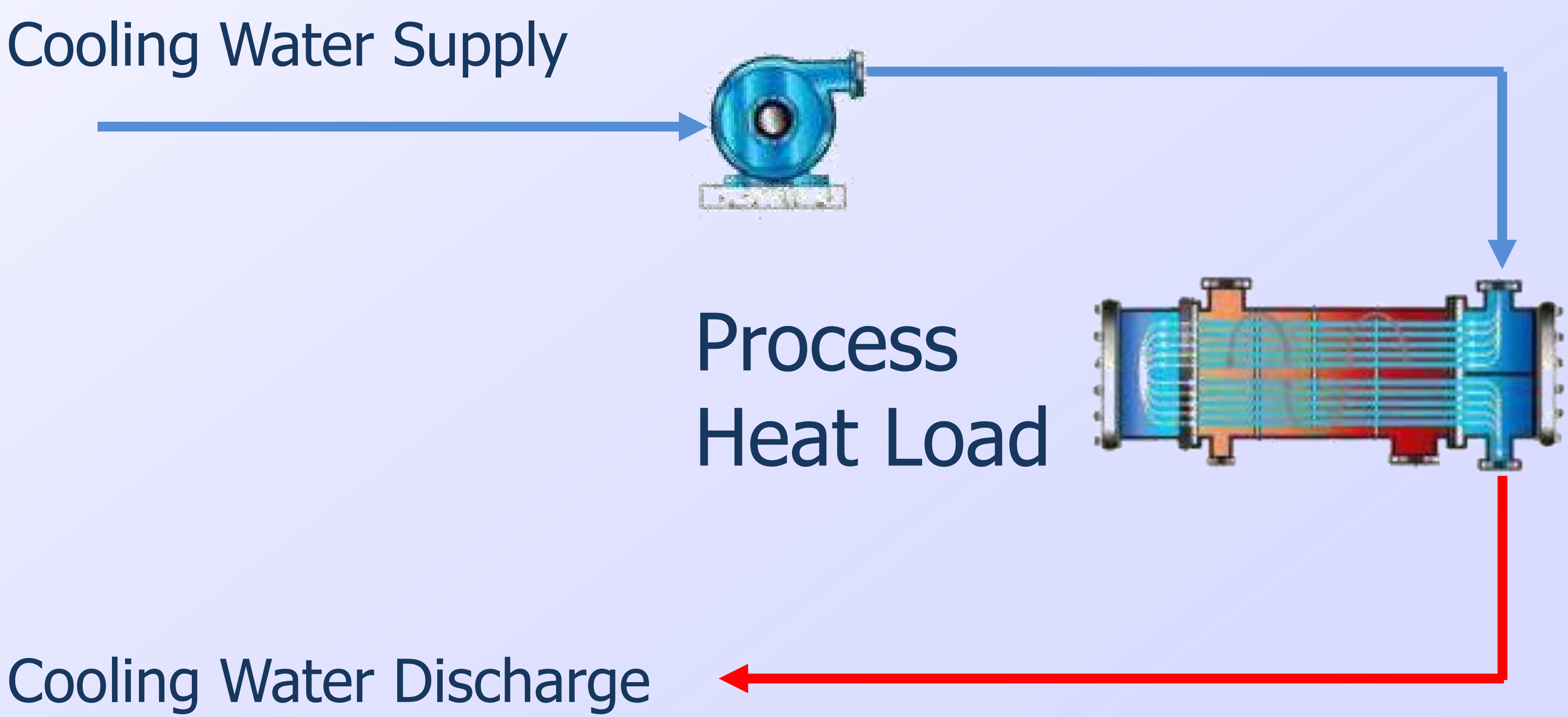
Cooling Water Systems

Remove *Heat* (BTU's)

1. Temperature Change "Sensible Heat"
   - "Heat capacity" - C_p = 1 BTU/lb-°F (1 cal/g-°C)
   - Heat transferred - $Q = m \times C_p \times (T_h - T_c)$
2. Evaporation
   - "Latent Heat" - LH = 1,000 BTU/lb (556 cal/g)
   - Heat transferred - $Q = m \times LH$

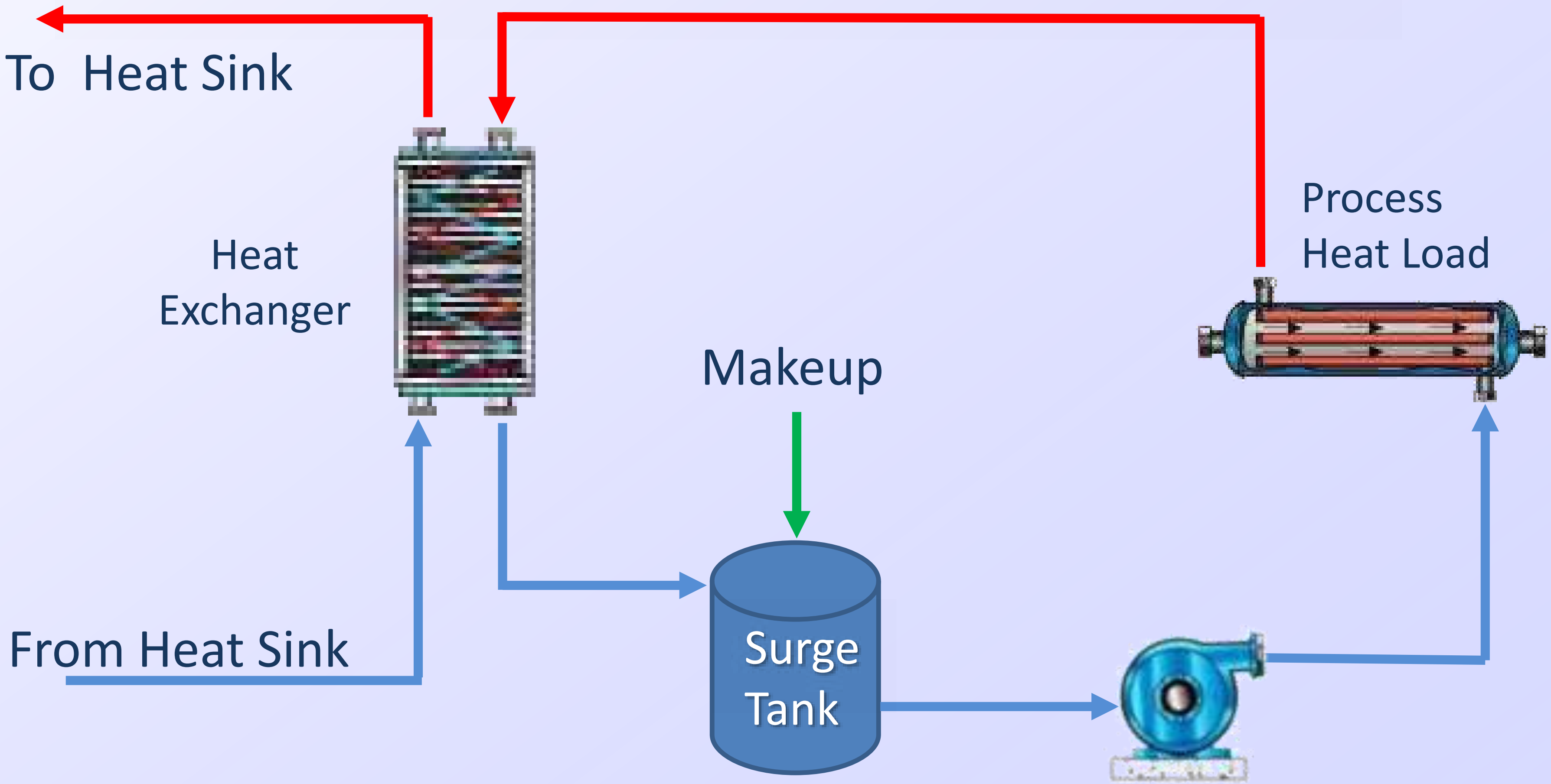
How do power plant cooling systems use these properties?

Once - Through System



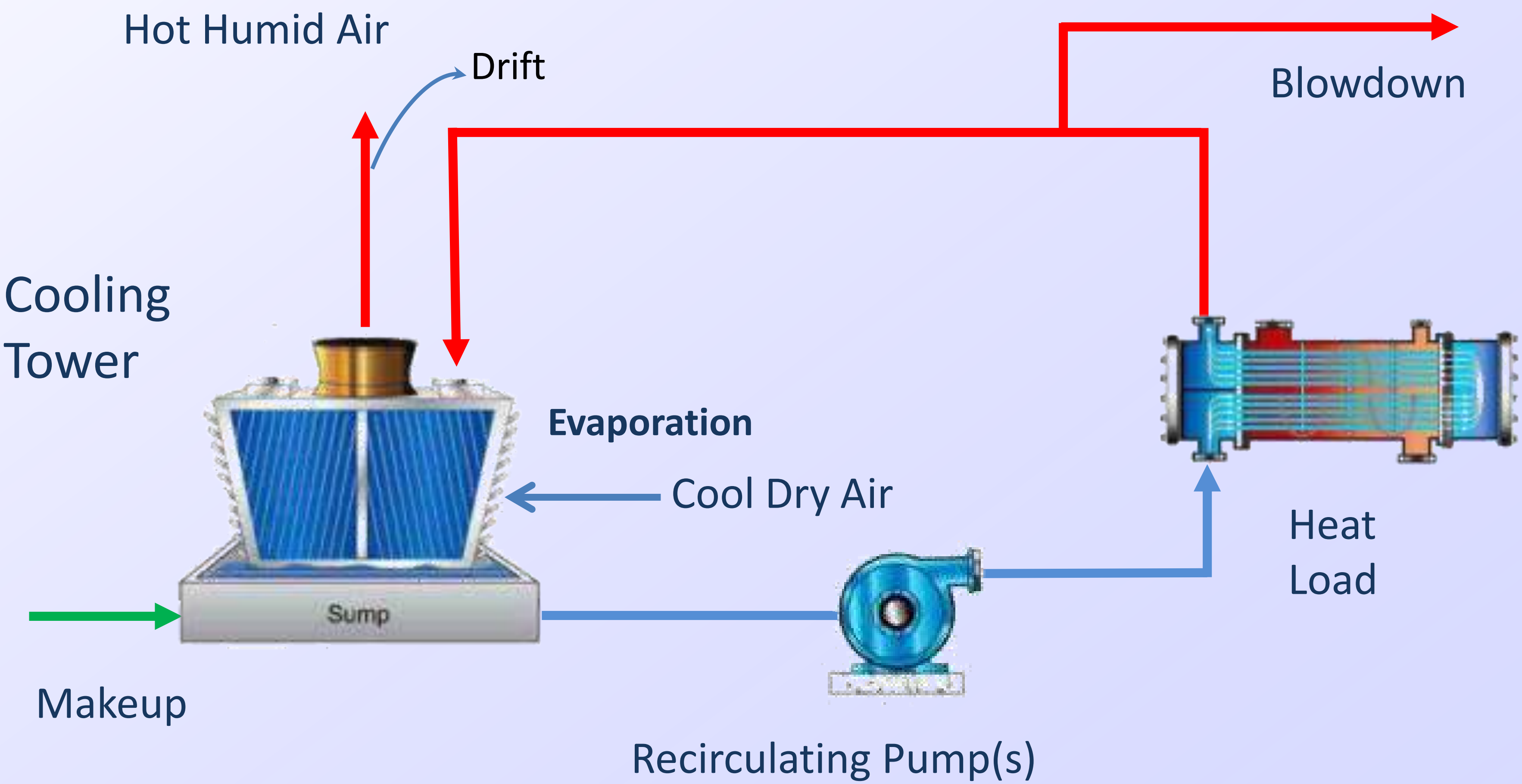
Q (Btu/hr.) = mCp(Tout - Tin) = gpm x 500 (Tout - Tin)

Closed Recirculating Cooling System



What plant heat exchangers use closed cooling?

Open Recirculating Cooling System



$$Q = mLH = m \times 1{,}000 \text{ Btu/lb} = mCp(Tout - Tin)$$

Power Cooling System Designs By Age

- Older plants
  - Often have copper alloys – 90: Cu:Ni, Admiralty Brass, Bronze
    - Better heat transfer, less biofouling
  - Limited use of closed cooling water systems in fresh water plants
    - Much small bore piping directly on cooling tower
    - Susceptible to corrosion and silt
    - Need to identify how the auxiliary cooling is handled
  - Once through cooling water
    - Limited ability to treat for anything, due to large flows
    - Threshold calcium carbonate scale inhibitor
    - Biofouling Control
    - Seawater – “Macrofouling” (mussels, barnacles)
- Newer plants, especially combined cycle
  - No copper alloys anywhere (except possibly chillers)
  - “Circ Water” or Condenser Cooling Water
    - Services the condenser, 90%-95% of cooling load
    - Operates directly off the cooling tower
  - “Aux Cooling Water” or “Service Water”
    - Lube oil, compressors, bearings, hydrogen coolers, air ejector intercooler, etc.
    - All on a closed loop behind an alloyed Plate exchanger
    - All small bore piping is on a closed loop

Once Through Cooling Systems

Macrofouling is often the biggest problem

- Saltwater Organisms
  - Mussels
    - *Mytilus* genus (Chilean mussel, Blue Mussel, etc)
    - *Perna* genus (Brown mussel, Green Mussel, Scorched Mussel
    - Oyster, Ribbed Mussel
  - Barnacles
  - Hydrazoans, Bryozoans
  - Tunicates (Sea Squirts)
  - Sponges
  - Tubeworms
- Freshwater Organisms
  - Golden mussel *(Limnoperna fortunei)*
  - Asiatic Clam *(Corbicula fluminea)*
  - Zebra Mussel *(Dreissena polymorpha)*
  - Quagga Mussel *(Dreissena bugensis)*
  - Bryozoans *(Ectoprocta)*

Macrofouling Organisms Are Difficult to Control

Especially In Seawater

- Many species with varied growth habits
- Grow rapidly, especially in warm water
- Very fertile organisms
- Colonize surfaces in dense populations
- Shells are large enough to block condenser tubes
  - When organism dies, shells break loose and are transported into the system
- Difficult to control
  - Mechanical
  - Physical
  - Thermal
  - Coatings
  - Chemicals
    - Oxidizing (chlorine)
    - Non-Oxidizing

Let's look at some common control methods

Physical Control Methods

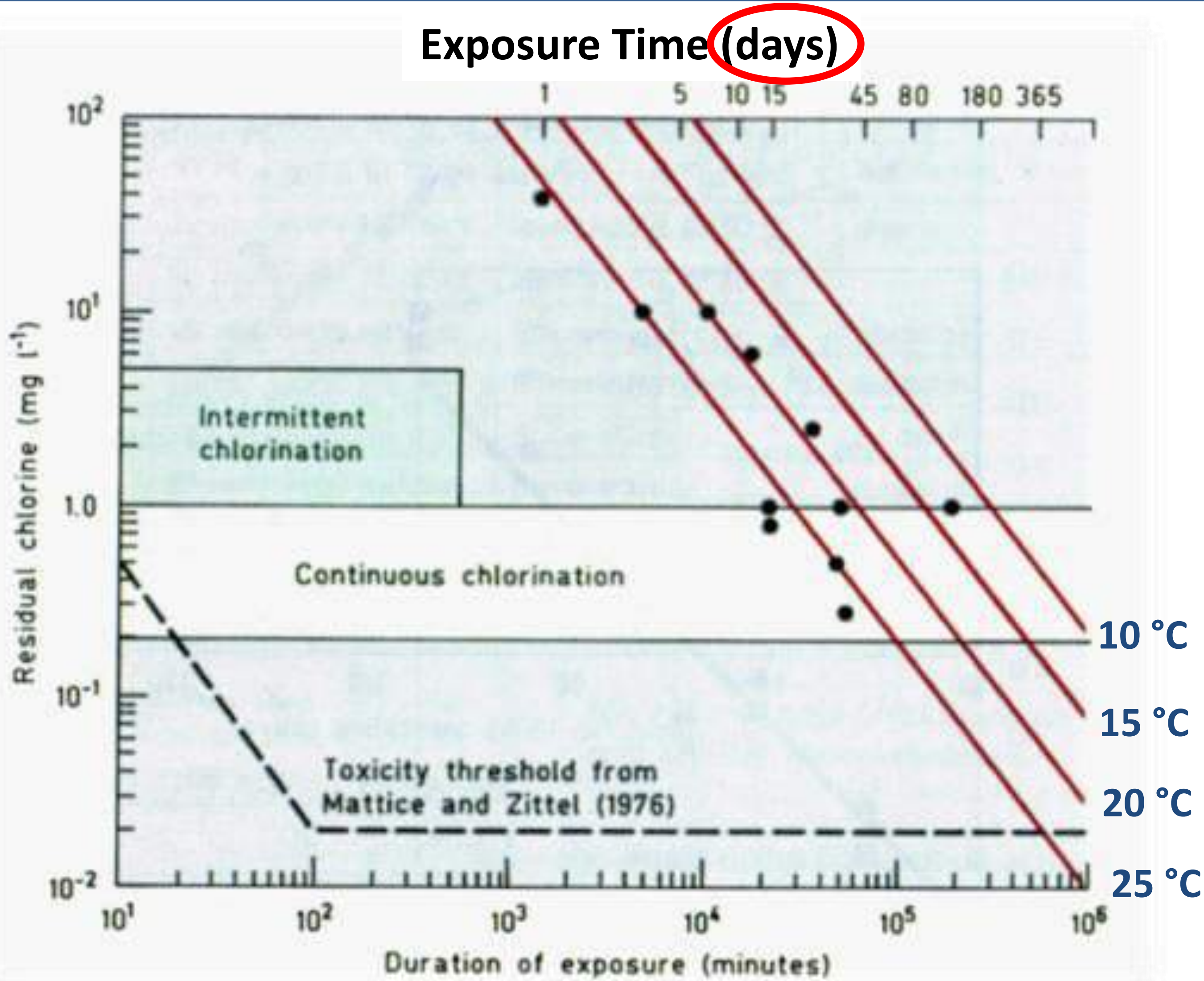
- Physical Removal
  - Low Capital Cost
  - Environmentally Benign
  - Annual Frequency
- Limitations:
  - Equipment Generally Off-Line
  - De-Water or Underwater
  - Labor Intensive for Long Tunnels
  - Small Piping Inaccessible
- Desiccate / Freeze
  - Equipment must be off-line
  - Function of Time, Temp., Humidity
    - Equations Given in Paper

Oxidizing Biocides

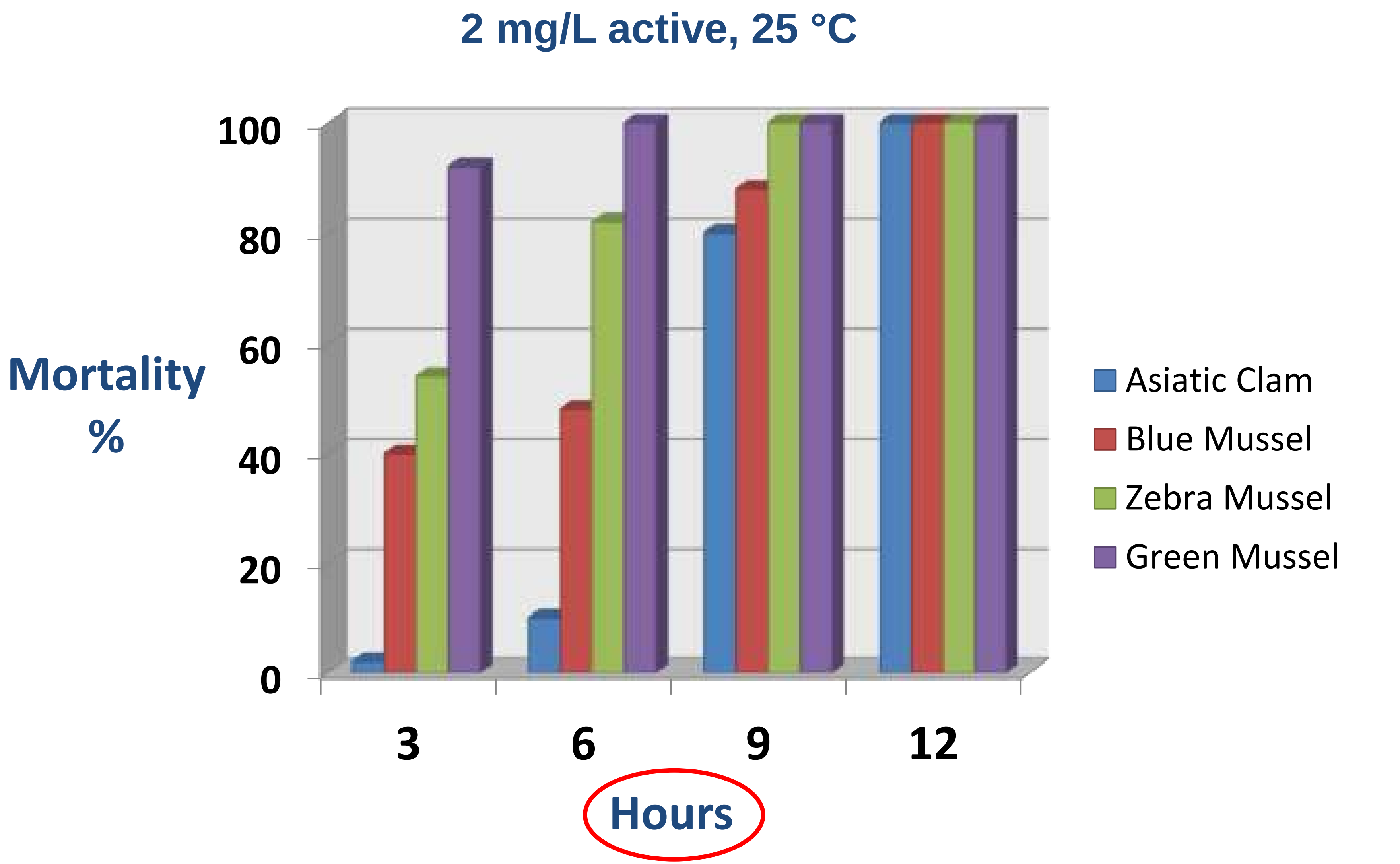
Chlorine, ClO_2, Bromine, Peroxide, Ozone

- Effective, Familiar Compounds
- Limitations
  - Oxidants Are Readily Detected by Mollusk
    - Mollusk Closes Shell and Ceases Siphoning
    - Require Long Exposure Times
    - Continuous or semi-continuous chlorination
  - Large Quantities
    - Expensive
  - Corrosive To System Metallurgy
  - Environmental Impact
    - Not Selective
- In seawater systems, electrochlorinators are common

Effect of Continuous Chlorination On Blue Mussels (*Mytilus*) Vs. Temperature

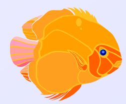


Cationic Surfactants
Effective In Short Exposure Time



ADVANTAGES OF *SHORT EXPOSURES*

Environmental

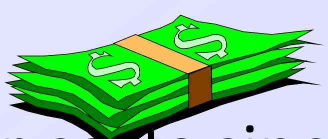


- Reduced impact on entrained plankton
- Less chemical released to the environment

Operations

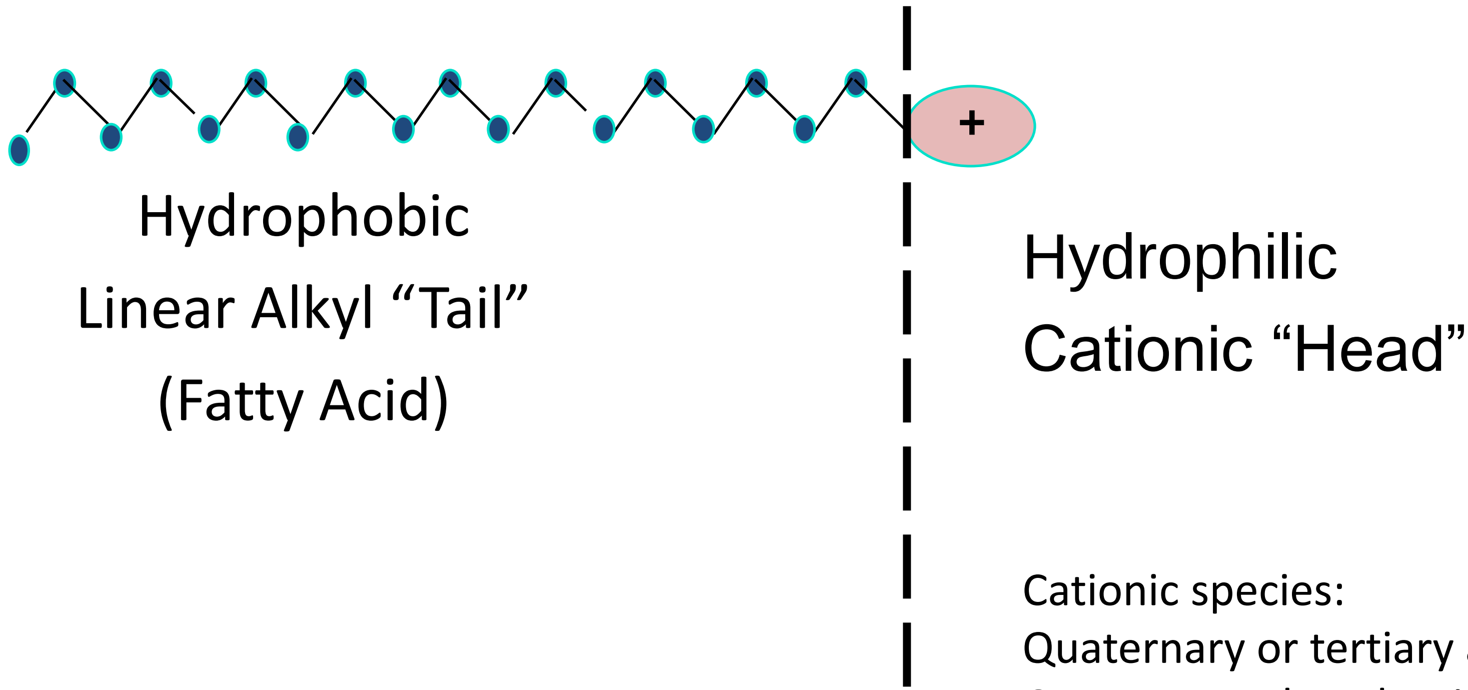
- No permanent tanks, dikes, or feed equipment
- Treatment concentrations easily verified during entire application

Costs



- Lower costs since far less chemical is required

Cationic Surfactant



Cationic species:
Quaternary or tertiary amine
Quaternary phosphonium

Mollusks do not sense surfactant as readily as oxidizing chemicals
Do not close shell to avoid contact

Common Cationic Surfactants

- ADBAC Quat
  - Alkyl dimethyl benzyl ammonium chloride
  - Effective dosage
    - 2-4 ppm active
    - 12-24 hours
    - Once every 7-14 days
- TTPC
  - Triphenyl tetradecyl phosphonium chloride
  - Effective dosage
    - 0.2-1 ppm active
    - 10x more effective than Quat

Molluscicide Industrial Application Example

Application on 42,000 m3/day Thermal Desalination Plant

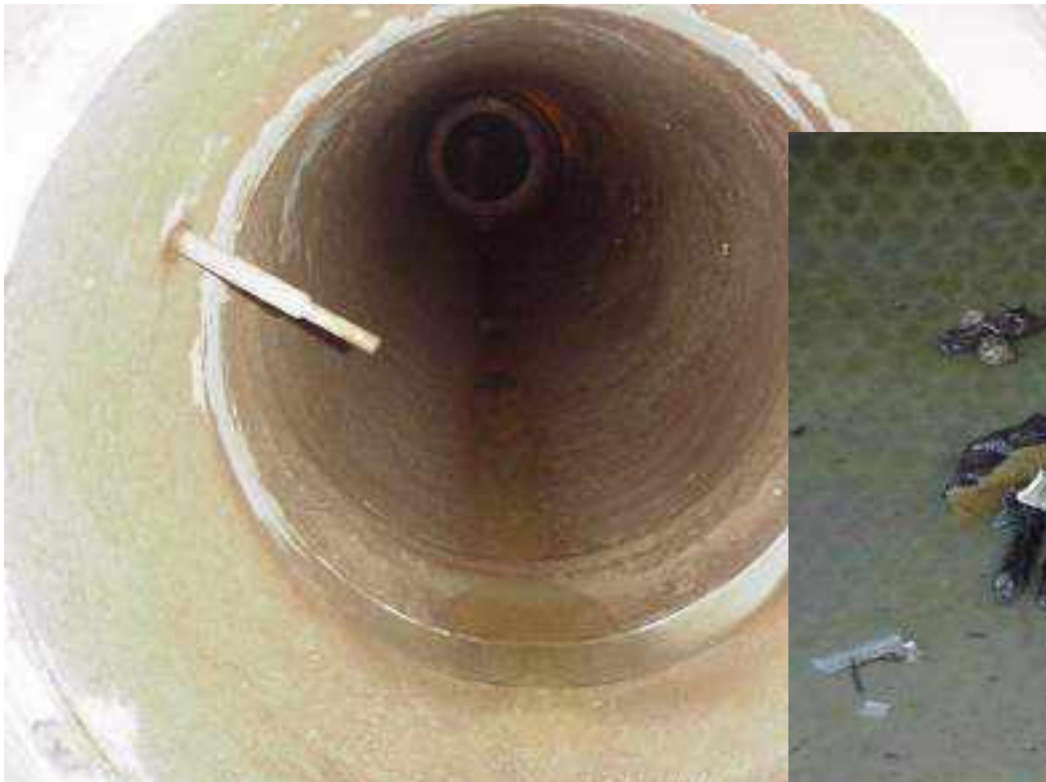
- Unit had a history of being taken out of service every 3 months to clean
- Dosage:
  - Once every 2 weeks
  - 12 hours
  - 4.5 mg/L product
- Monitoring
  - Performance Ratio
    - 9.5 Vs. historical 8.7
  - Product carryover to distillate <0.1 mg/L
  - Residual effluent to sea within limits

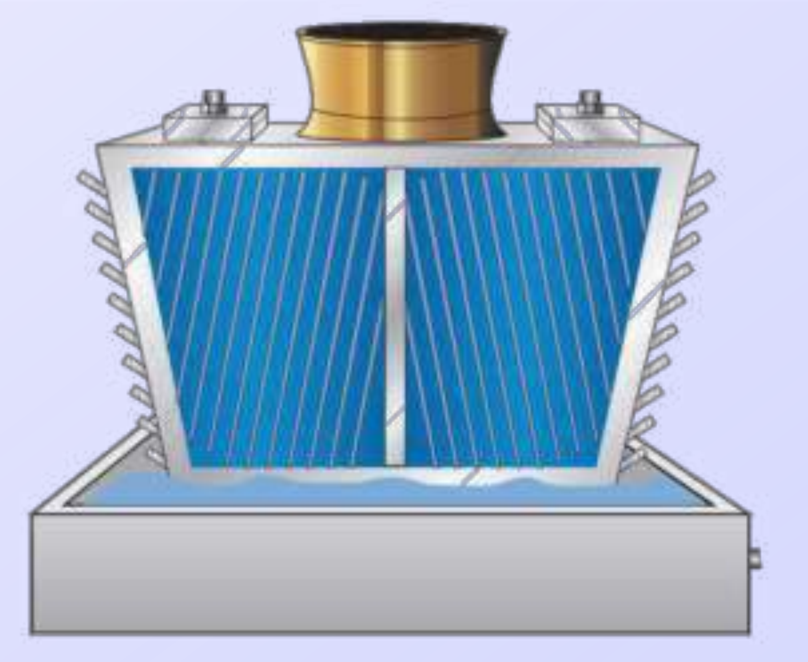
Typical Macrofouling on Condensers After 3 Months Operation

Condensers Clean After 3 Months Using Molluscicide

Molluscicide applied once every 14 days at 4.5 mg/L

Piping Clean - Small Amount of Debris

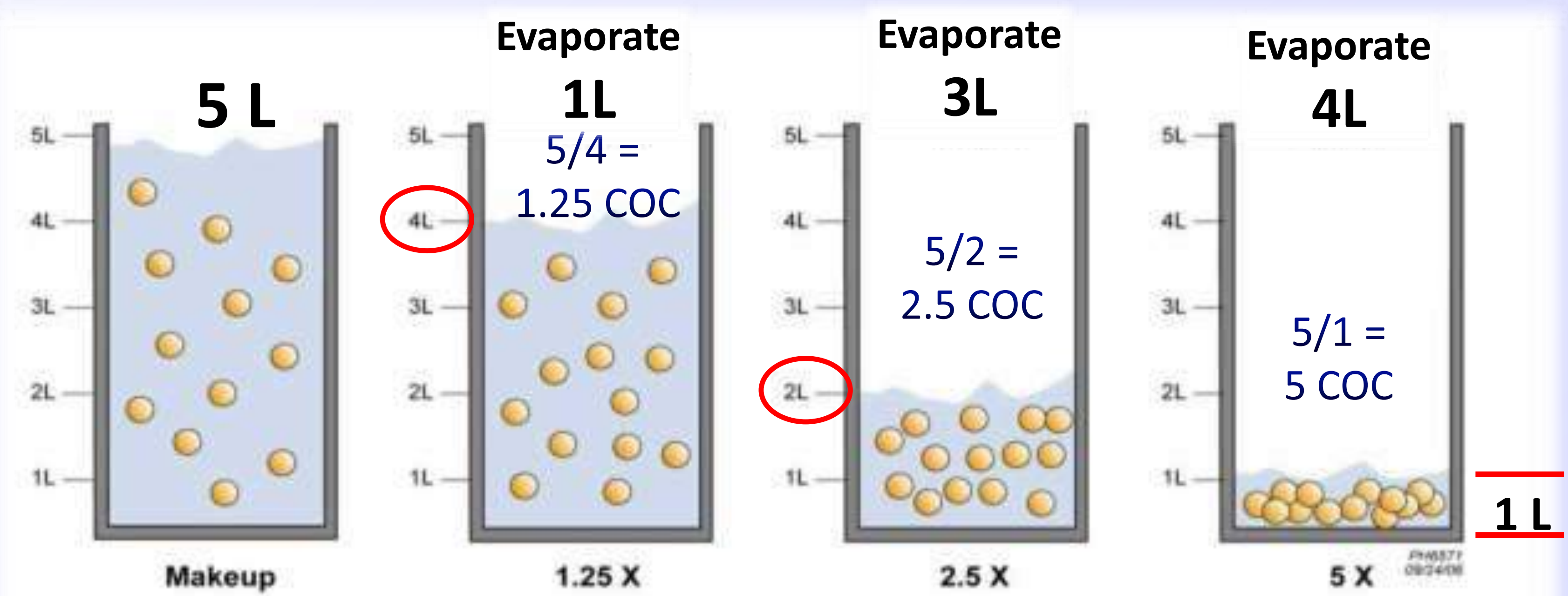




COOLING TOWERS

Evaporation Over A Cooling Tower

Only The Pure Water Is Lost - Salts and Suspended Particles Are Concentrated



1) *Precipitation of Sparingly Soluble Salts*
2) *Corrosivity Increases With Dissolved Salts*
3) *Higher Ionic Strength Causes Most Particles to Settle Faster*
4) *Higher Dissolved Solids Can Cause Drift Issues*

Cycles of Concentration

"Concentration Ratio"

"Cycles", "COC, "CR", "C"

$$C = \frac{MU}{BD} = \frac{I_{BD}}{I_{MU}}$$

Flow Basis — Ion Basis

MU = Makeup flow

BD = Blowdown flow

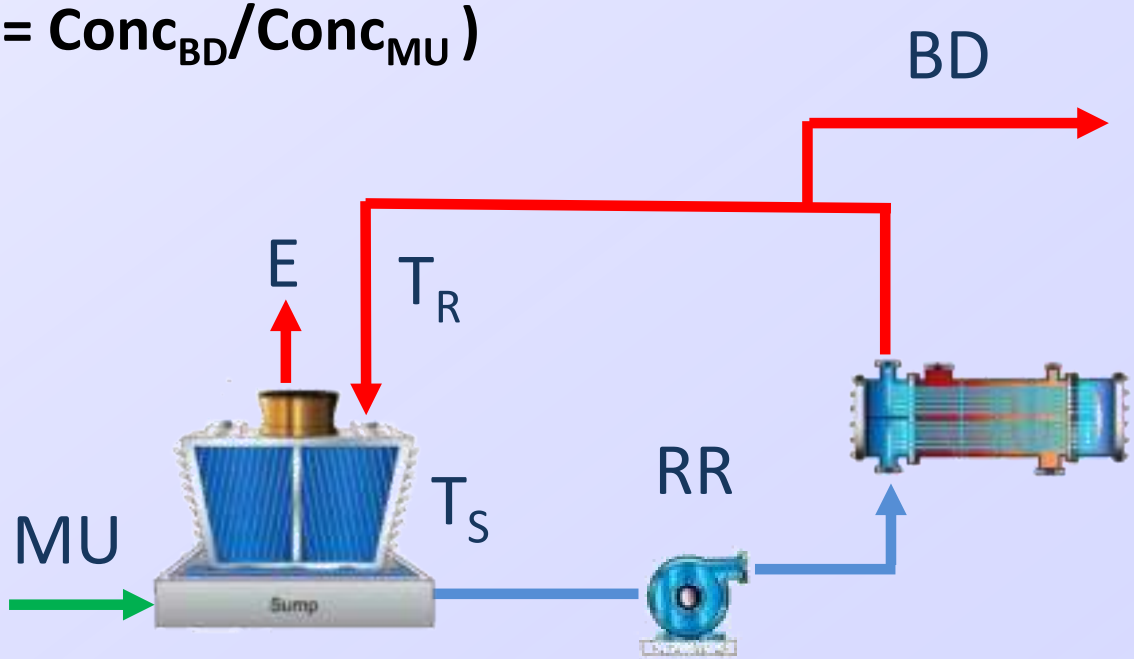
I_{BD} = Any ion in Blowdown

I_{MU} = Same ion in Makeup

Conductivity Ratio Is Often Used To Automate COC Control

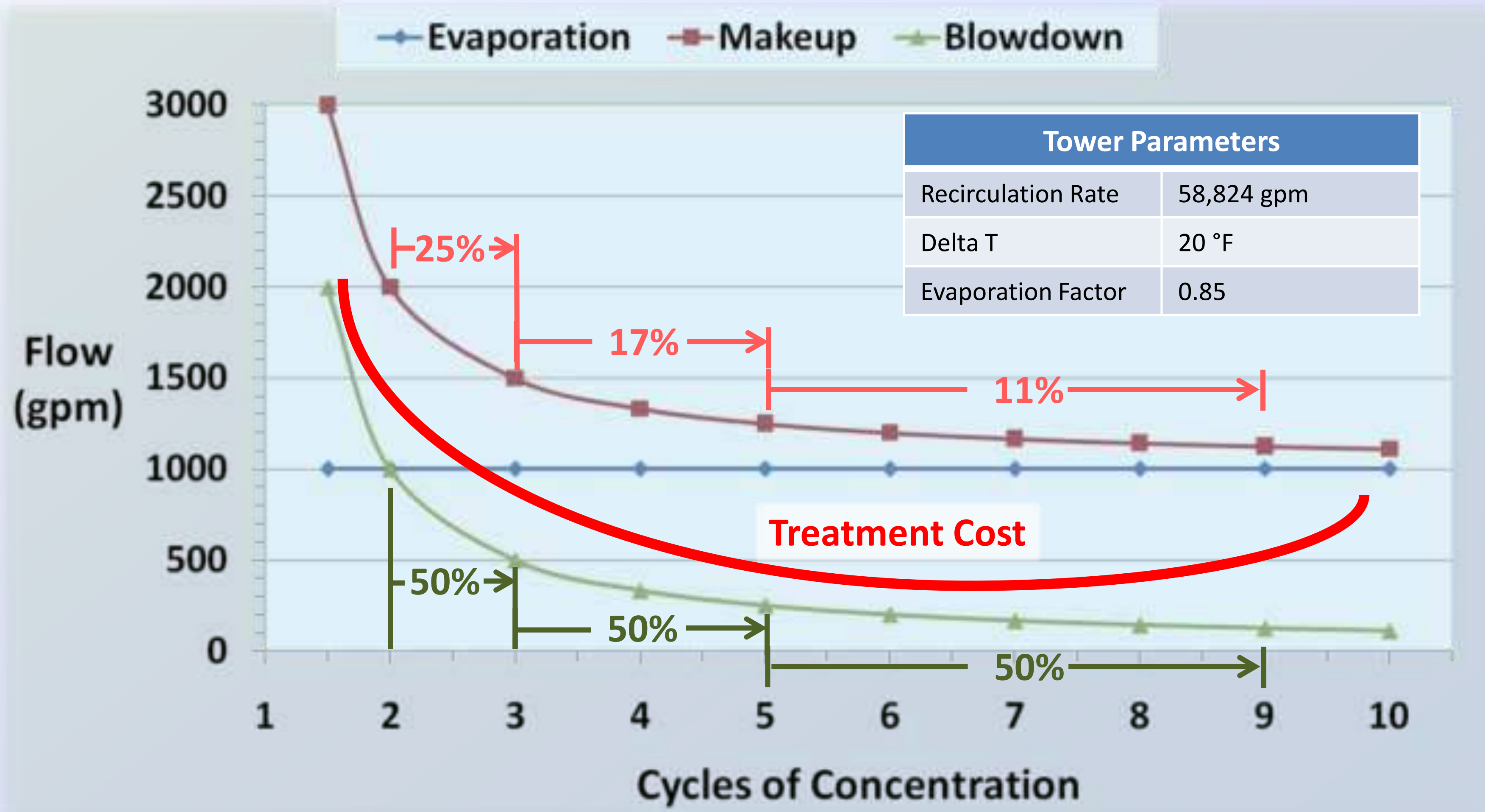
Combined Energy and Mass Balance

- $E = (RR * (T_R - T_S) * f)/556$ *(for °C)*
- $MU = BD + E$
- $C = MU/BD$ (also, $C = Conc_{BD}/Conc_{MU}$)
  - $C = (BD+E)/BD$
  - $BD*C = BD+E$
  - $BD*C – BD = E$
  - $BD*(C-1) = E$
- $BD = E/(C - 1)$



Cooling Systems Are Major Consumers of Fresh Water Resources

Reducing Water & Chemical Usage By Increasing Cycles



The trend is toward ever higher cycles for better water efficiency

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Makeup Water Quality & System Constraints Vary WIDELY

Site	Mineral, VA	Lansing, MI	Gila Bend, AZ	Grey Water, McAllen, TX	Sayreville, NJ	Brooks, OR
pH	7.0	7.8	7.7	7.4	4.4	7.7
Cond	70	729	2,297	2,400	178	203
M-Alkalinity	28	299	70	118	0	99
Ca Hardness	9	231	99	393	19	45
Mg Hardness	10	125	8	191	11	49
Iron	0.1	0.4	0.7	0.1	8.8	0.2
Sodium	3	13	387	291	12	8
Potassium	2	2	9	26	2	2
Chloride	4	16	584	443	20	8
Sulfate	6	66	137	412	31	1
Nitrate	0	1	16	75	0	0
Ortho PO4	0.0	0.0	0.0	10.0	0.0	0.8
Silica	11	14	26	23	10	45

Major impact on Materials of Construction and Achievable COC

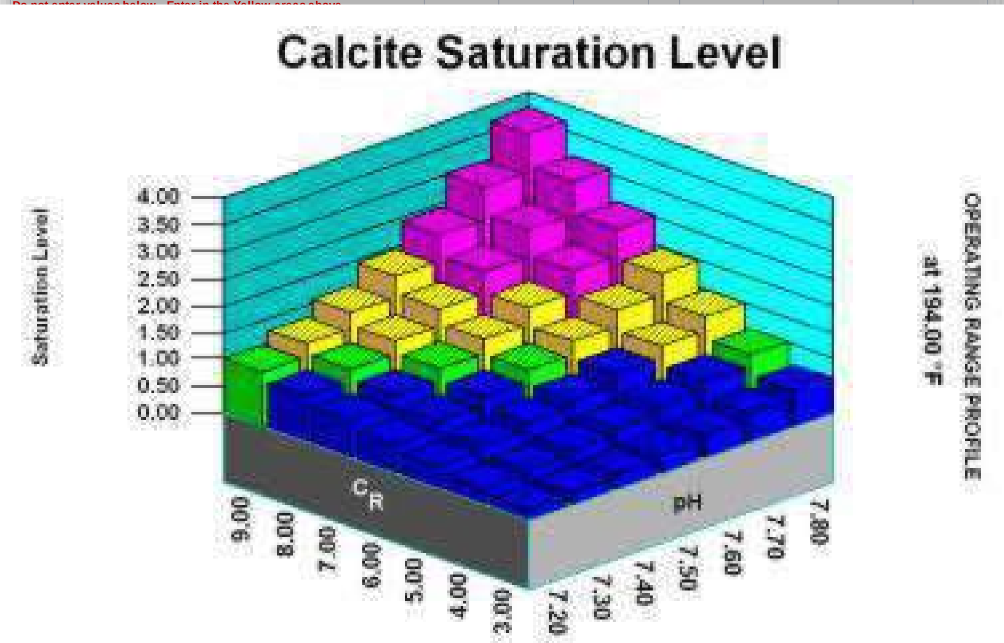
Modeling Software Can Be a Big Help

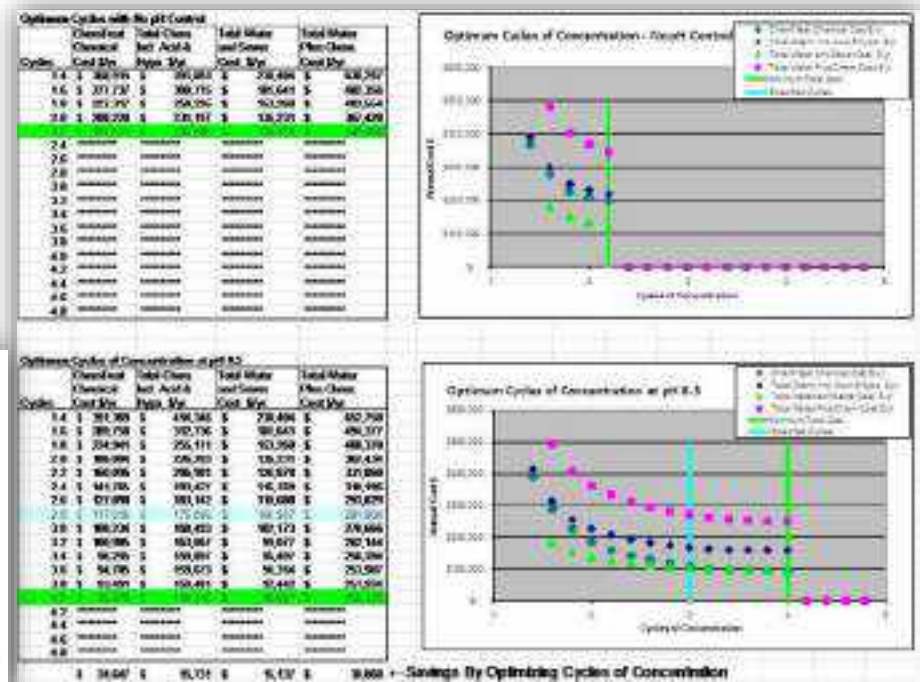
% Sample 1	Date:	Avg 10-8-07	Calculated
75	MU	Tower	Cycles
pH	8.20		
Cond	1,825.00		-
M-Alkalinity	199.25		
Ca Hardness	37.69		-
Mg Hardness	15.39		-
Iron	0.17		-
Copper	0.90		-
Zinc	0.00		-
Sodium	470.75		-
Potassium	2.67		-
Chloride	128.75		-
Sulfate	693.50		-
Nitrate	8.00		-
Ortho PO4	0.05		-
Silica	49.98		-
Manganese	0.05		-
Aluminum	0.05		-
TSS	-		-
M-Alk + SO4	893	-	-

% Sample 2	Date:	Max 10-8-07	Calculated
15	MU	Tower	Cycles
pH	7.20		
Cond	132.00		-
M-Alkalinity	53.20		
Ca Hardness	8.60		-
Mg Hardness	9.60		-
Iron	0.25		-
Copper	0.00		-
Zinc	0.01		-
Sodium	4.00		-
Potassium	2.86		-
Chloride	4.97		-
Sulfate	7.05		-
Nitrate	0.75		-
Ortho PO4	0.58		-
Silica	8.66		-
Manganese	0.11		-
Aluminum	0.00		-
TSS	4.80		-
M-Alk + SO4	60	-	-

% Sample 3	Date:		Calculated
10	MU	Tower	Cycles
pH	7.50		
Cond	66.00		-
M-Alkalinity	18.96		
Ca Hardness	8.60		-
Mg Hardness	9.60		-
Iron	0.10		-
Copper	0.00		-
Zinc	0.01		-
Sodium	4.00		-
Potassium	0.58		-
Chloride	4.97		-
Sulfate	7.05		-
Nitrate	0.75		-
Ortho PO4	0.58		-
Silica	8.66		-
Manganese	0.11		-
Aluminum	0.17		-
TSS	4.80		-
M-Alk + SO4	26	-	-

Note: Molybdate reactive silica from the Lab DR5000 was used for the silica analysis because we believe it is more representative than silca by ICP, which can include non-reactive silica.





Software should evaluate:

- Blends of water sources
- Costs of each source
- Achievable cycles for each blend
- Total treatment cost

- Commercially Available – French Creek
- Water treatment company
- Consultant
- Write your own

Power Plant Cooling Water Technology

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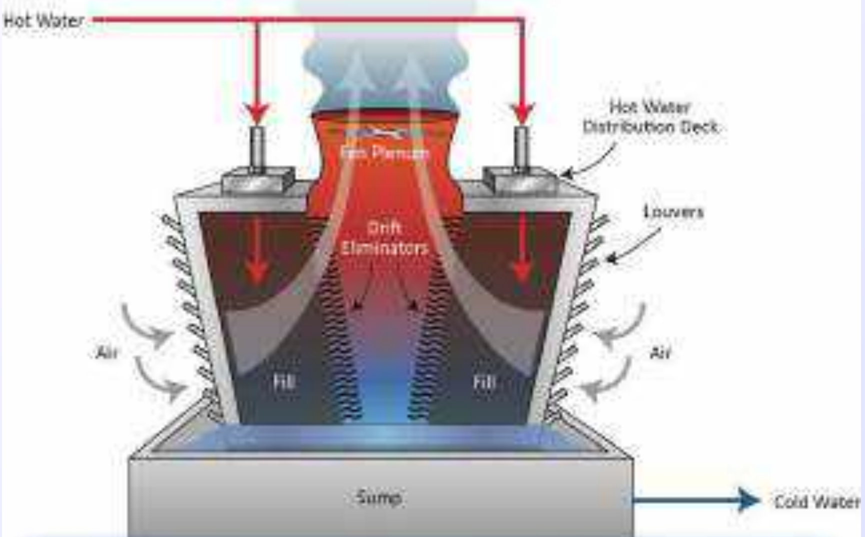
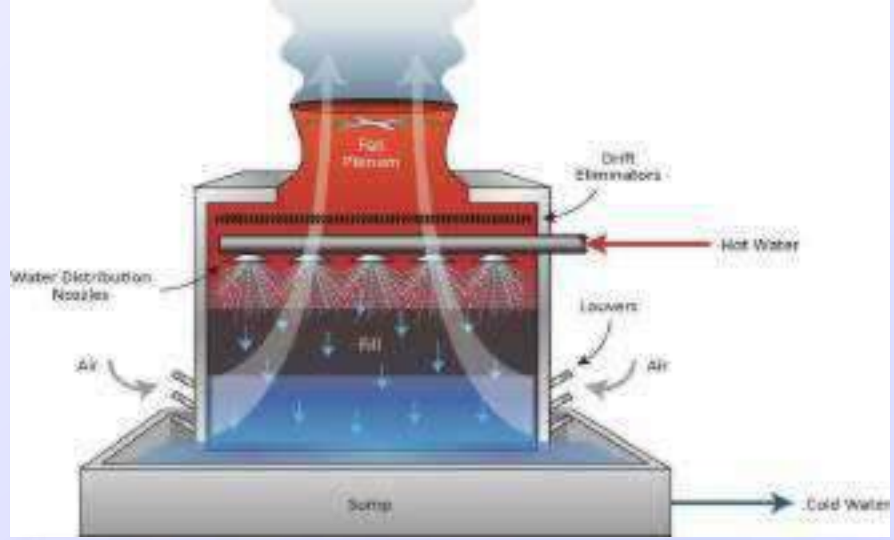
Cross-Flow Induced Draft



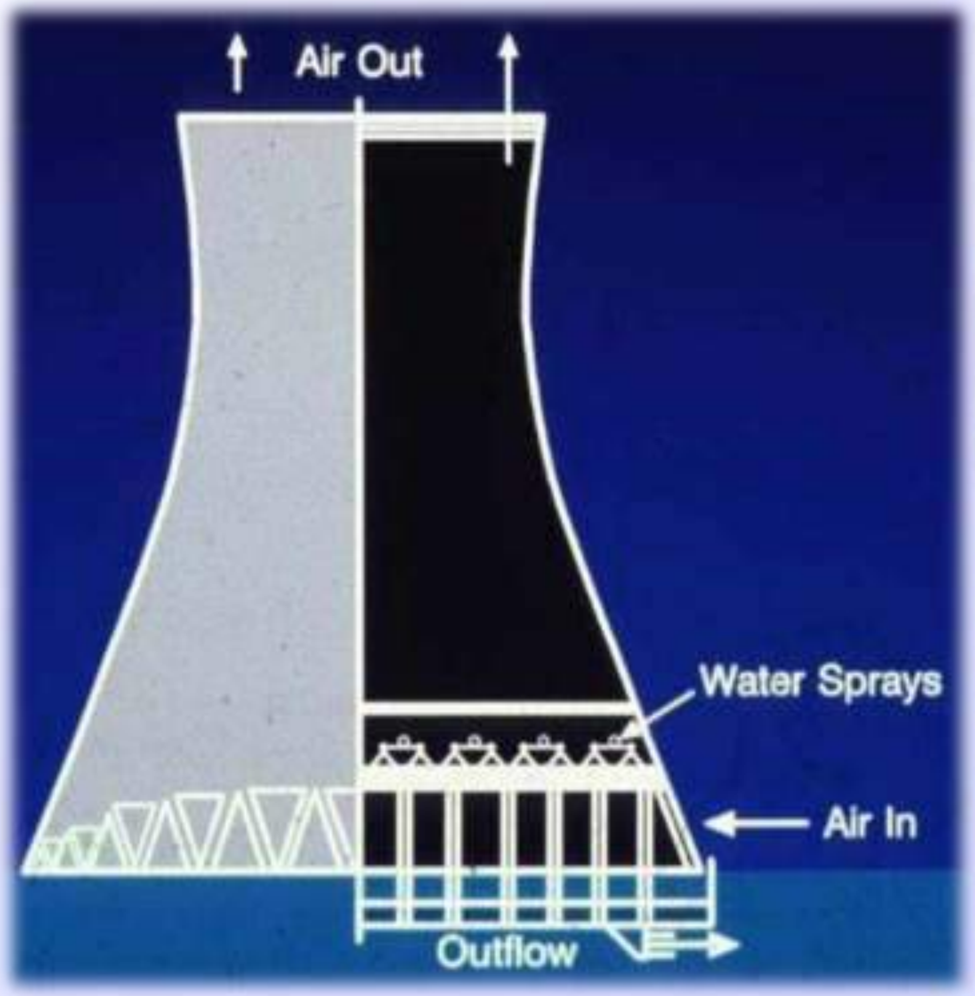
Counter-Flow Induced Draft



Air flow direction Across the Water flow

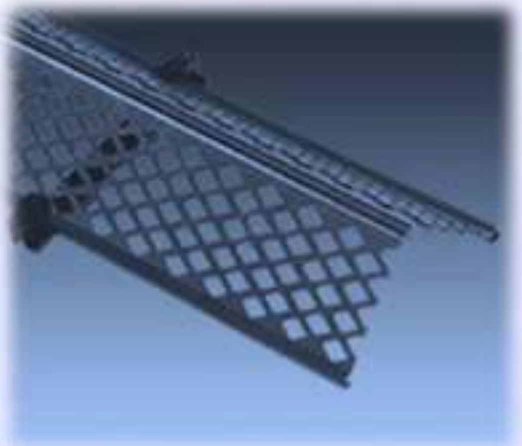
Air flow direction is Counter to Water flow

Natural Draft - *Counter-Flow and Cross-Flow*



Power Plant Cooling Water Technology

Splash Fill
Older Cooling Towers

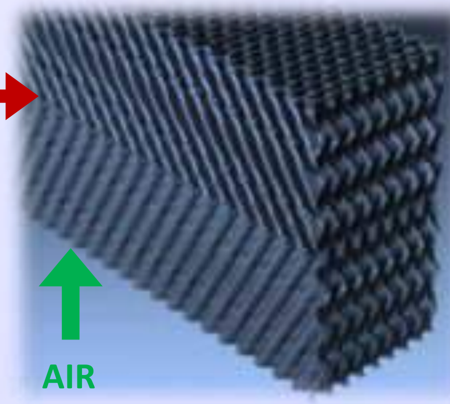


Open pattern – Fouling resistant

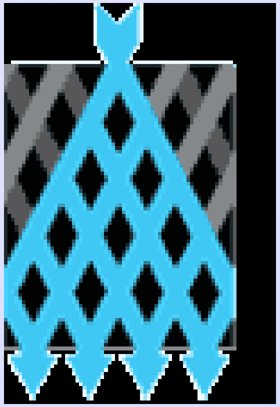
Film Fill
Newer Cooling Towers

WATER

WETTED SURFACE



AIR



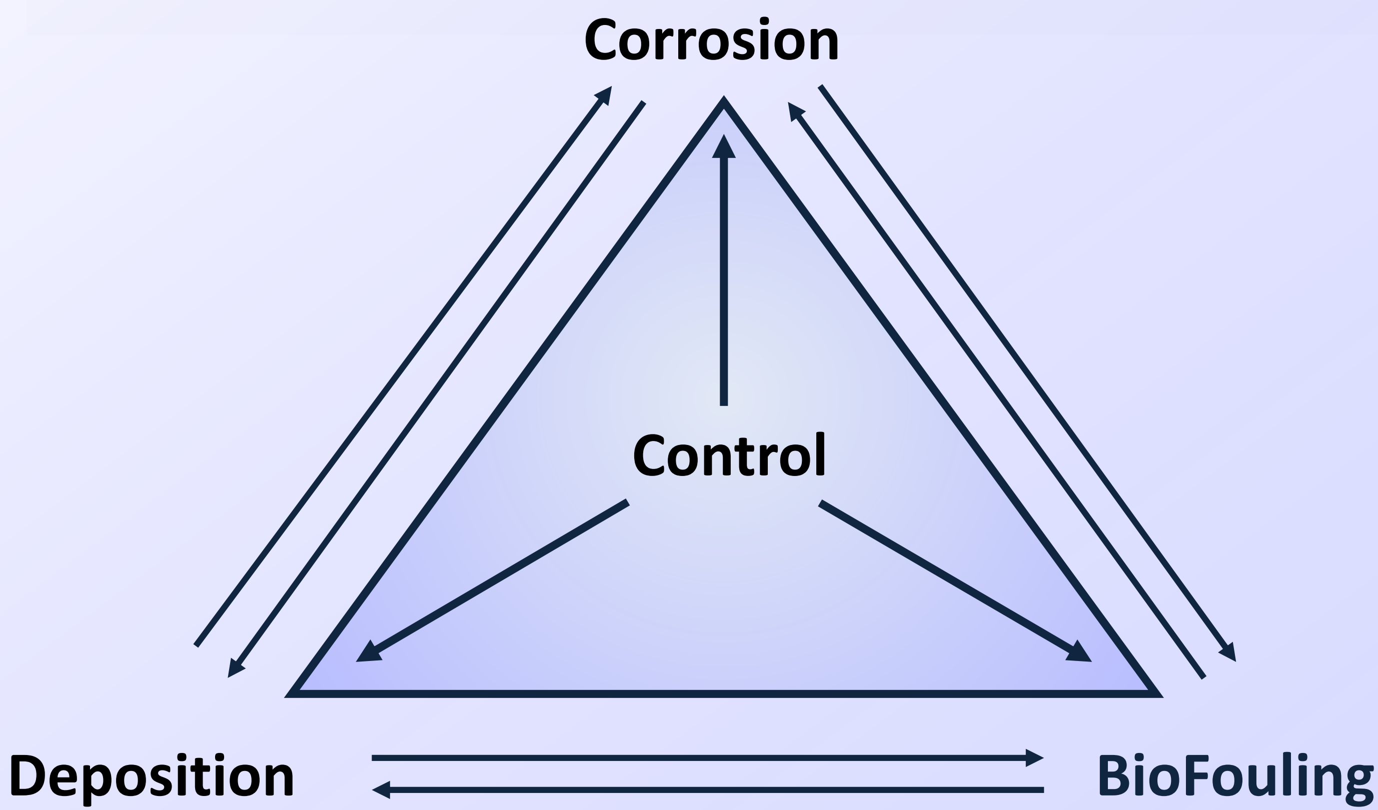
Tight passages – More efficient

The Combination of Slime and Suspended Solids Can Be Devastating to High Efficiency Fill

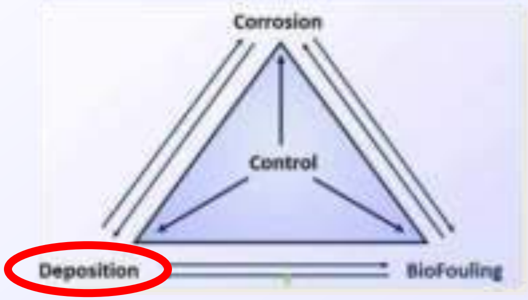
QSY Polymers and Phosphonates Help To Control These Deposits

Periodic Cleaning With H2O2 Peroxide Can Help

Fundamental Cooling System Triangle



Power Plants Are Less Concerned About Steel Corrosion Because They Use Corrosion Resistant Alloys And Coatings



Over-Cycling

Mineral Scales

Suspended Solids

DEPOSIT CONTROL

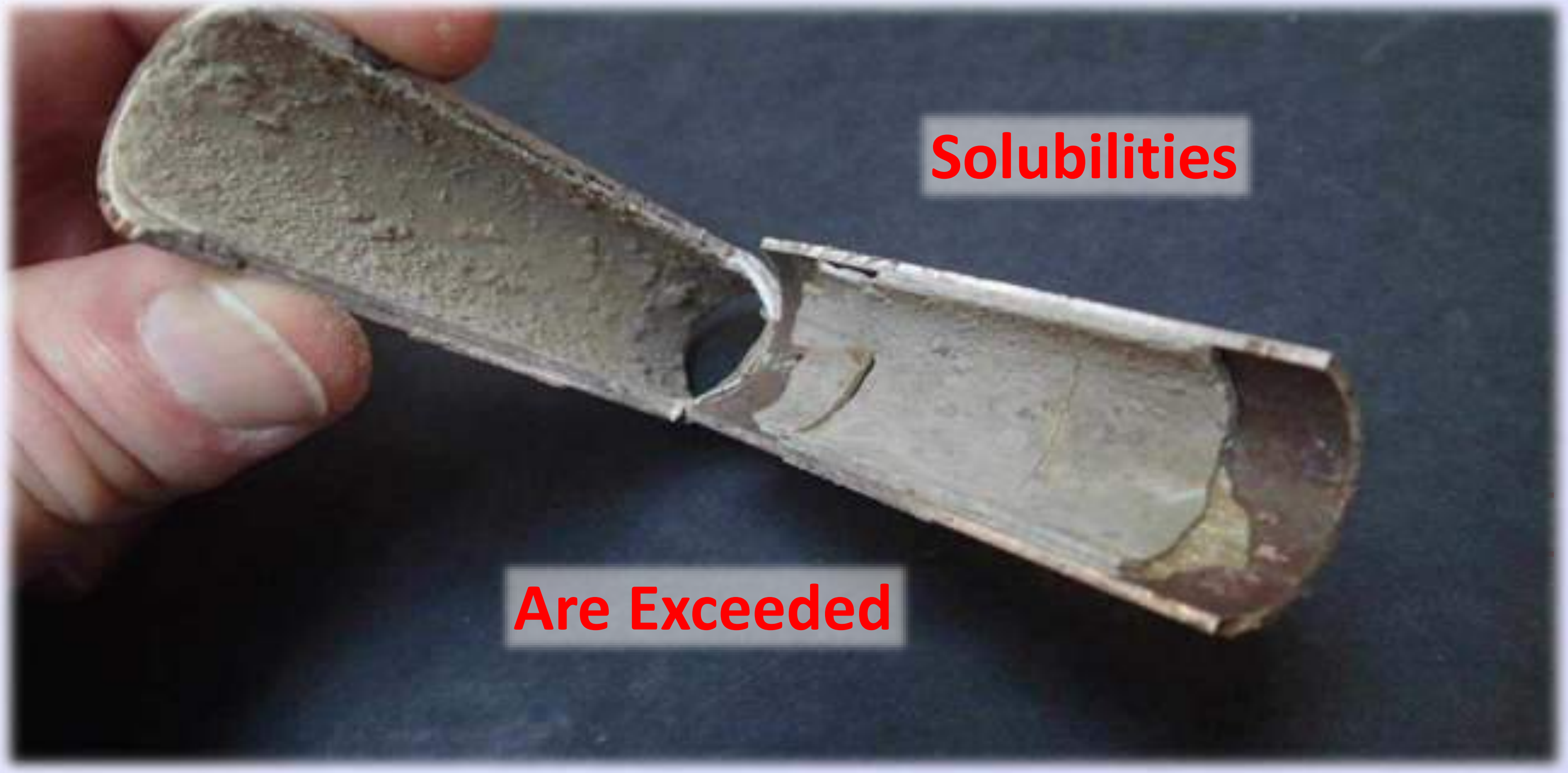
Types of Deposition

- Scaling
  - Mineral scale
  - Dissolved minerals exceed solubility when concentrated
- Fouling
  - Suspended matter
    - Enter with makeup water
    - Enter as dust particles in air
  - Transient corrosion products
  - Hydrocarbon or process leaks
  - Debris

How does scale form?

Evaporation Over A Cooling Tower

Only The Pure Water Is Lost - Salts Are Concentrated



What factors affect scale formation?

Scale Formation

Function of:

- Concentration of Ions
- pH
- Temperature
- Presence of Solid Seeding Material
- (Water Velocity)

Cooling Tower pH Chemistry Simplified

$H_2O \leftrightarrow H^+ + OH^-$

H^+ = Acid = Low pH

OH^- = Caustic = High pH

Evaporation concentrates minerals:

HCO_3^- (bicarbonate) $\rightarrow OH^- + CO_2\uparrow$

pH increases

$HCO_3^- + OH^- \rightarrow H_2O + CO_3^=$ (carbonate)

$Ca^{++} + CO_3^= = CaCO_3\downarrow$

Calcium carbonate scale

Add sulfuric acid:

$H_2SO_4 + 2OH^= \rightarrow H_2O + SO_4^=$

$Ca^{++} + SO_4^= \rightarrow CaSO_4\downarrow$?

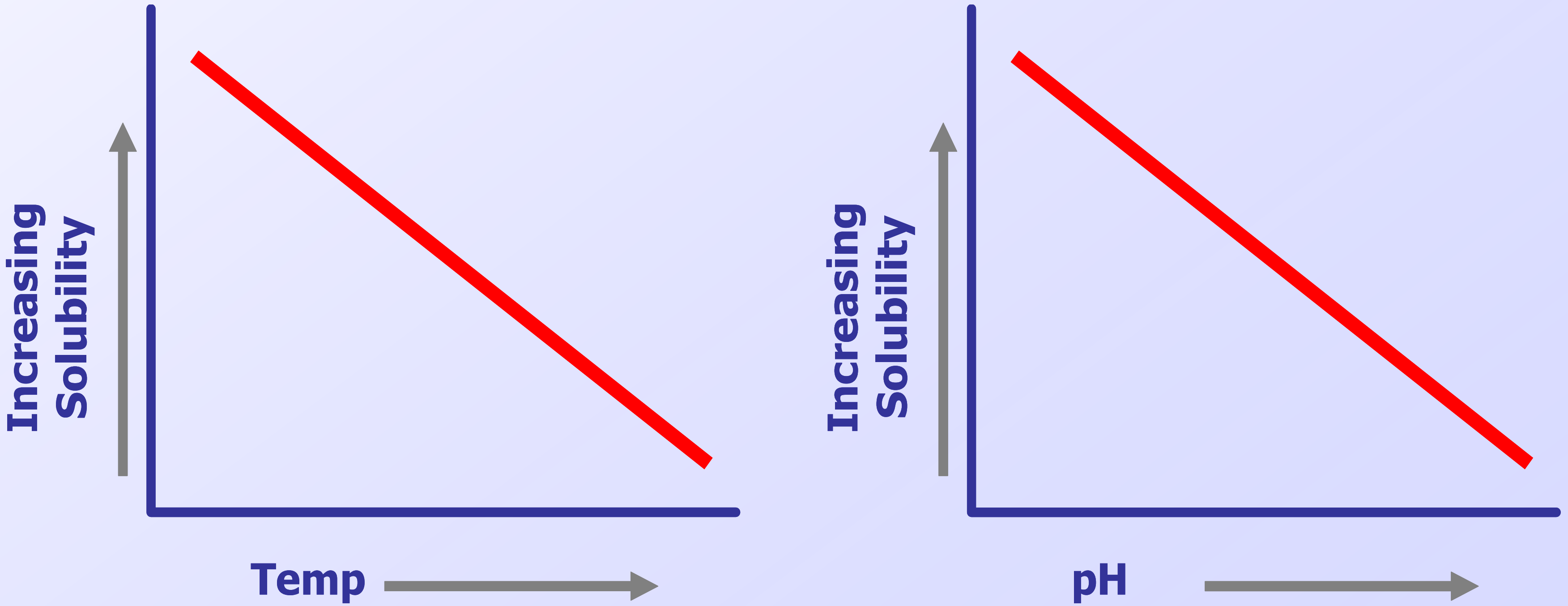
Calcium sulfate scale (gypsum)

More soluble than CaCO3, but…

Countermeasures – Add acid, Remove "hardness", Add scale inhibitors

Most Troublesome Scale Forming Minerals

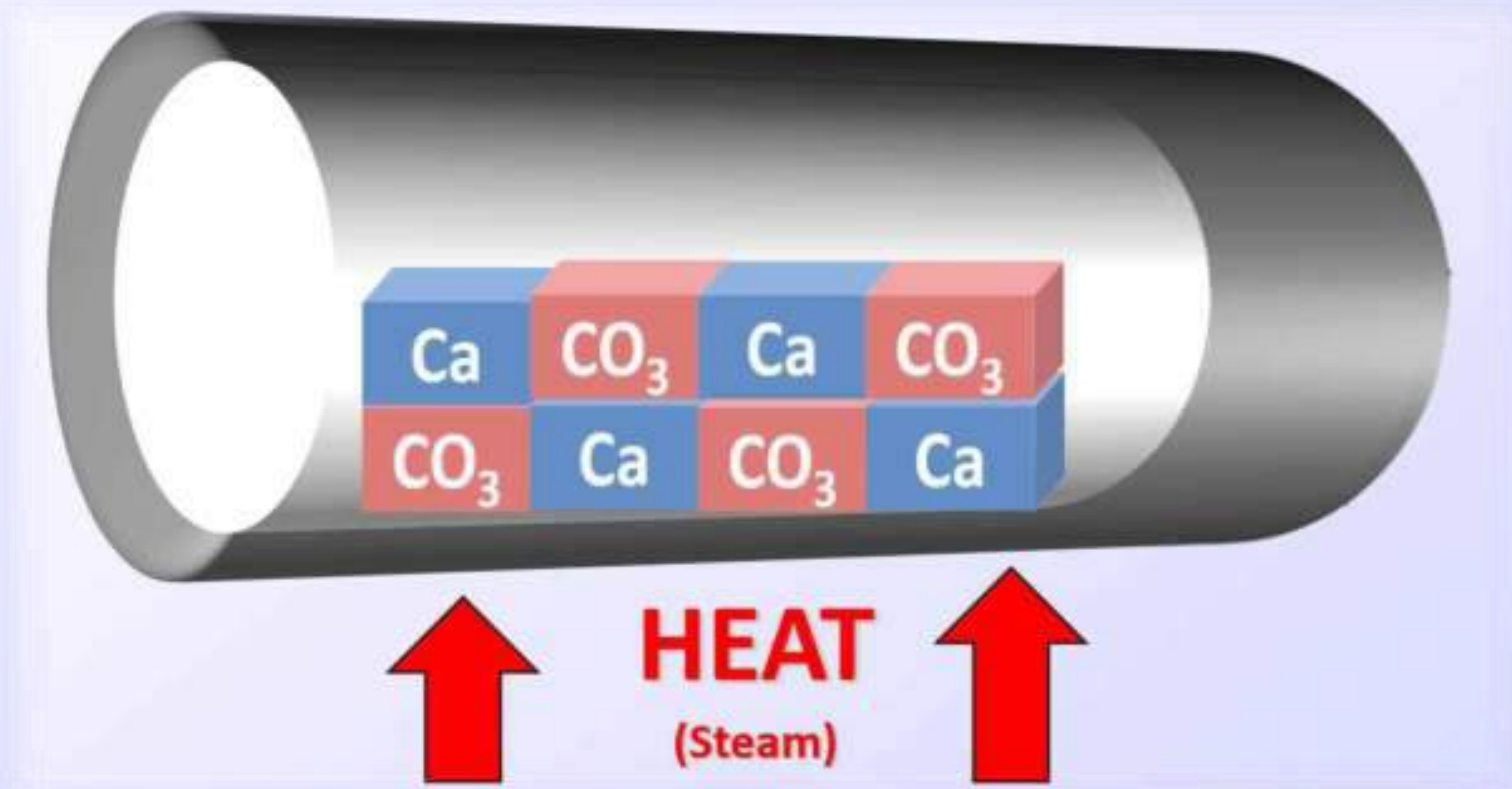
Inverse Solubility with Temperature and pH



Why is inverse solubility a problem?

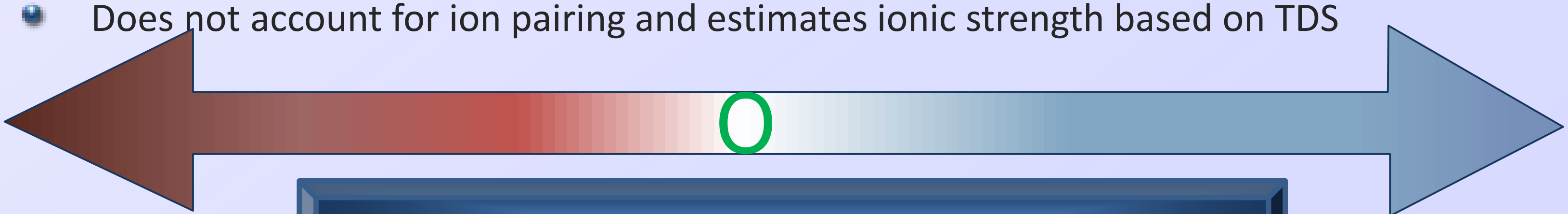
Calcium Carbonate Is Inversely Soluble With Temperature

- Soluble ions in solution join together in a regular crystalline lattice on the heated surface
- Like building blocks



$CaCO_3$ – *LSI - Langelier Saturation Index*

- $LSI = pH – pH_s$
  - pH = Actual pH
  - pH_s = Saturation pH
  - pH_s = function of Ca, M-Alk, TDS, & T
  - “There’s an App for that”
- Interpreting LSI
  - Negative – Scale is not possible
  - Positive – Scale is Possible
  - >1.0 – Scale is Likely without treatment
  - 3.0 is the max. recommended by ChemTreat with proper treatment
  - Typically, operate <2.5 with scale inhibitor
- Overestimates scaling tendency in high TDS waters
  - Does not account for ion pairing and estimates ionic strength based on TDS

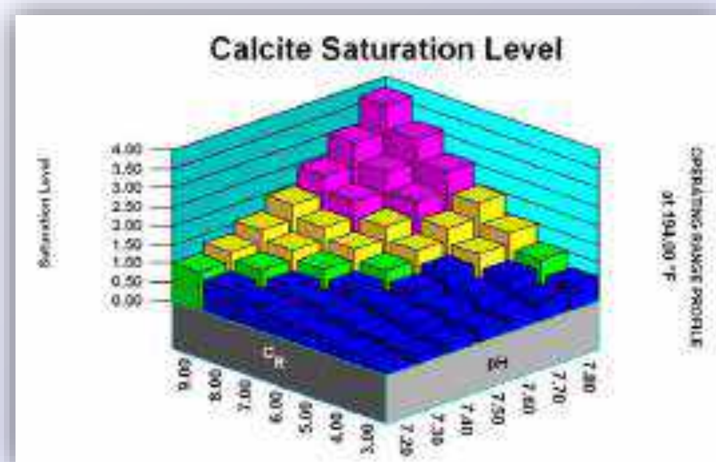


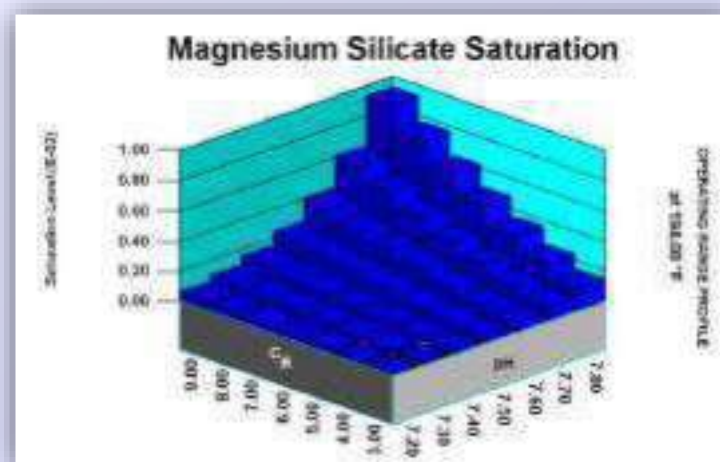
– Corrosion

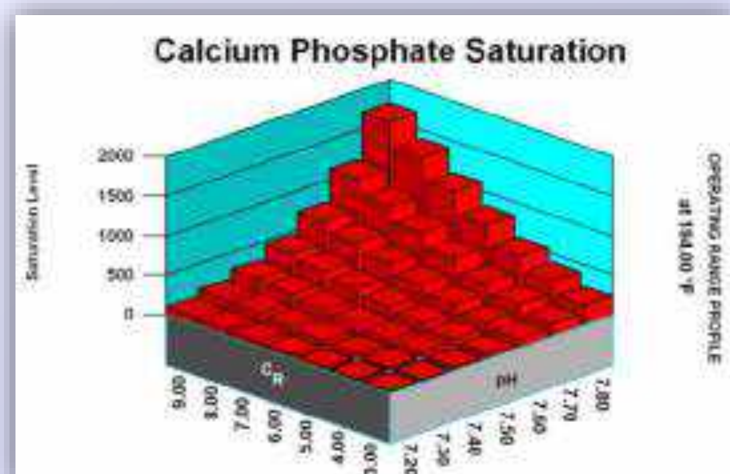
What is the chemistry basis for this index?

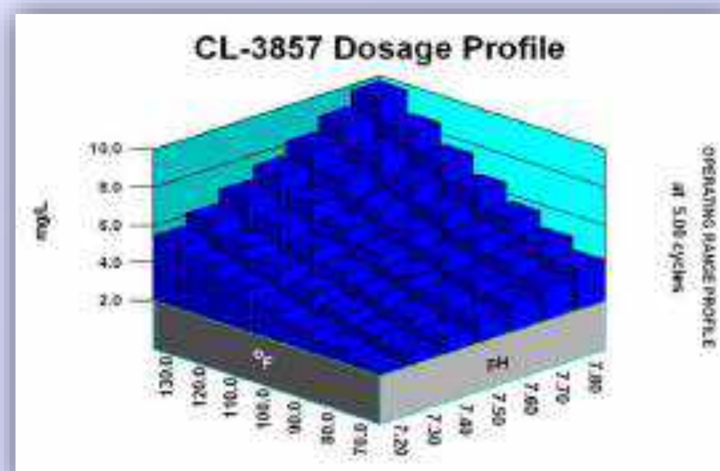
+ Scale

Work Smarter – Use Modeling Software





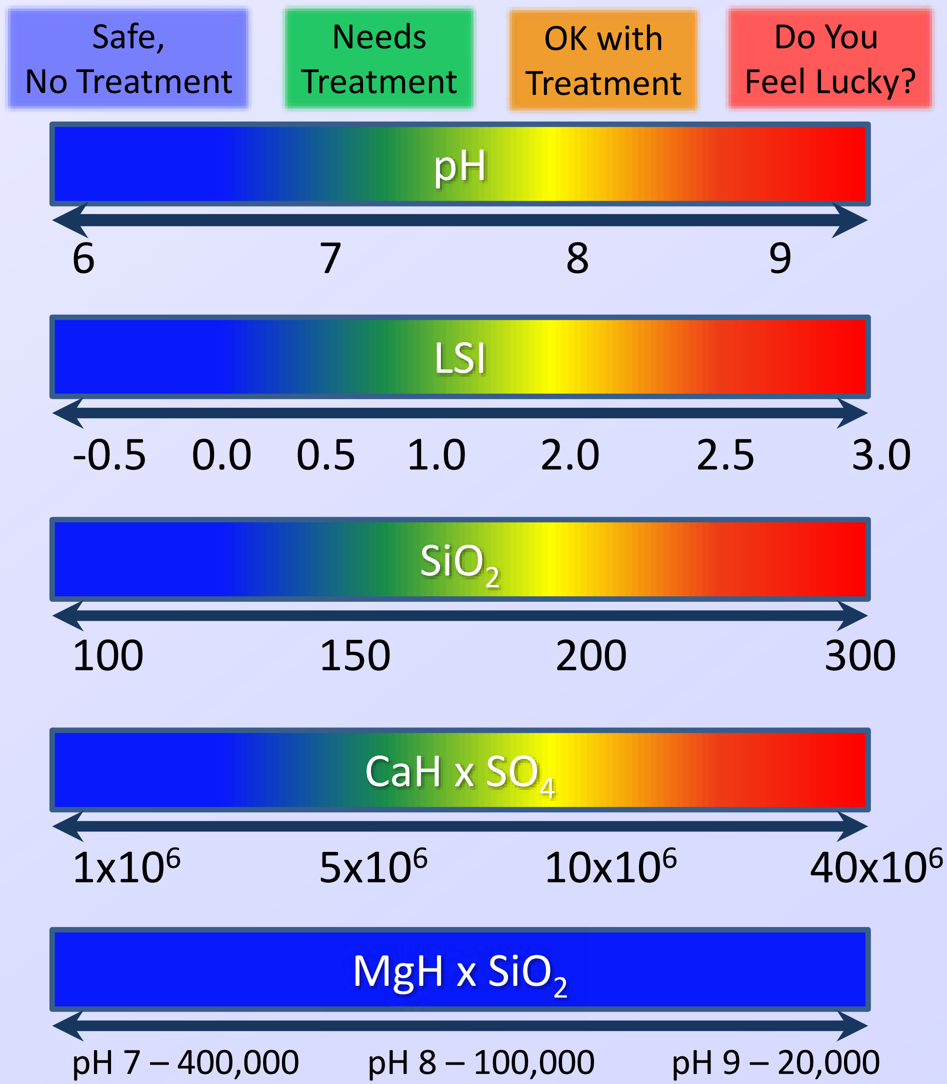




French Creek WaterCycle Output

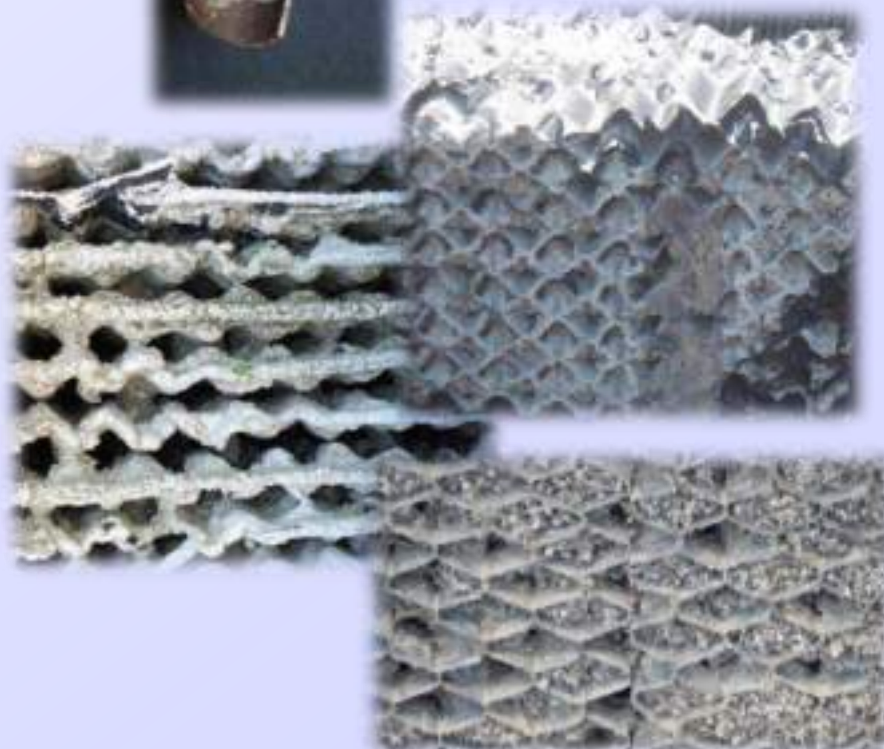
Predicting Mineral Scaling

- Proprietary software
  - Write your own
  - Work with cooperating chemical or consulting company
- Commercially available software
  - Consider French Creek Software
    - WaterCycle (Cooling)
    - Hyd-RO-Dose
    - DownHole SAT
  - PHREEQE
  - WATEQ4F
- Manufacturer specs.
  - "When all else fails, read the instructions"
  - Tend to be conservative



Where Is Scale Likely To Occur?

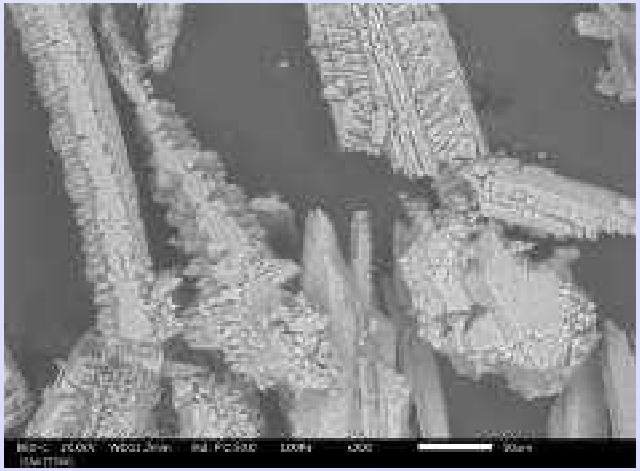
- Heat transfer surfaces
  - Temp drives kinetics
  - Minerals w/inverse solubility with temperature
- Cooling tower fill
  - Evaporation concentrates minerals
    - Calcium Sulfate
  - Minerals with normal solubility with temperature
    - Silica
  - Minerals with inverse solubility with pH
    - pH increases w/ CO_2 off-gas
    - Calcium carbonate



Chemically Controlling Mineral Scaling

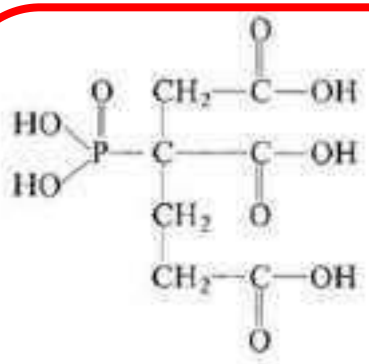
- “Threshold Inhibitors”
  - Adsorb onto growing crystal embryo
  - Distort orderly growth pattern
  - Encourage dissolution of the embryos into ions
  - Contrast to Chelation
- Phosphonates (Organic Phosphates)
  - PBTC, HEDP, AMP, HPAA, DETPMP, and others
  - Generally most effective, but can be degraded by oxidizers and UV light
- Polymers
  - Polymaleate, polyacrylate, polymers, copolymers, oligomers
  - Less effective at low dosage, but more stable and non-P
  - Also used in combination with phosphonates to disperse and distort crystal nuclei

Without Scale Inhibitor,300X

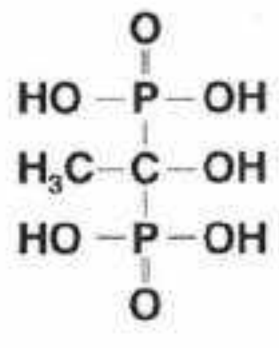


With Scale Inhibitor,300X

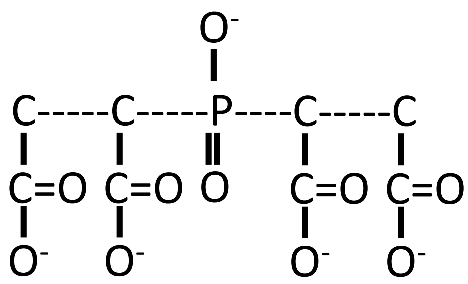
Example Organic Phosphates (Phosphonate / Phosphinate)



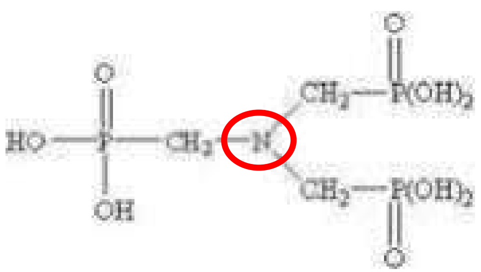
PBTC



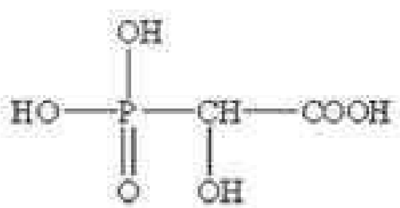
HEDP



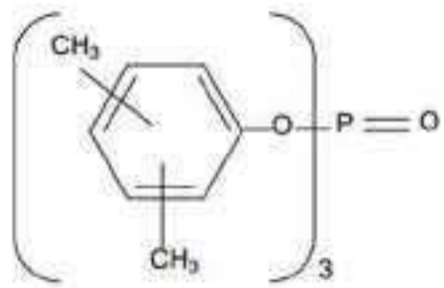
PSO
(Simplified)



AMP
(DETPMP, PAPEMP, others)



HPAA



Trixylenyl phosphate
(Fyrquel phosphate ester)

Controlling Fouling by Suspended Solids

- Solid particles enter the cooling system
  - Makeup water
  - Air
  - Process leaks
- Mechanical control
  - Remove suspended solids from makeup water using appropriate pretreatment (clarifiers, softeners, and filters)
  - Install sidestream filters (~2-5% of recirculation flow)
- Re-configure for higher water velocity
- Feed chemical dispersants and/or surfactants to keep them in suspension and prevent them from depositing

Best to Employ a Combination of Mechanical and Chemical Methods

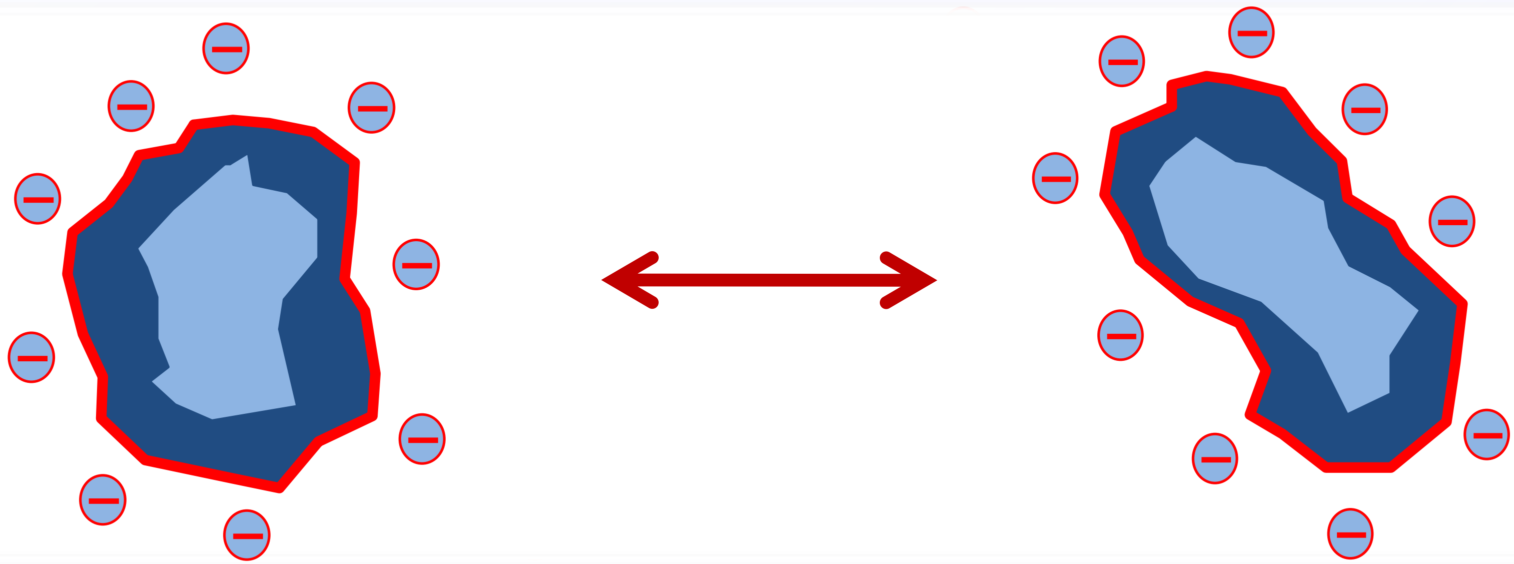
Chemical Control of Suspended Solids

"Dispersion"

Clay particles naturally have a negative surface charge

Anionic polymeric Dispersants adsorb onto suspended solids...

...Reinforcing negative charges



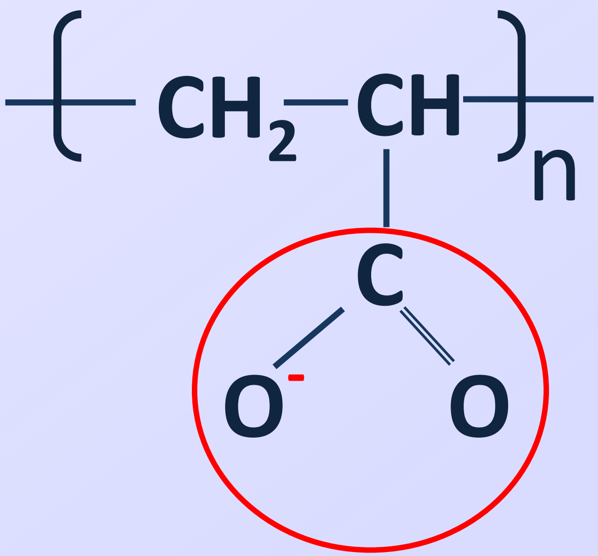
Causing them to repel

What are some common dispersants?

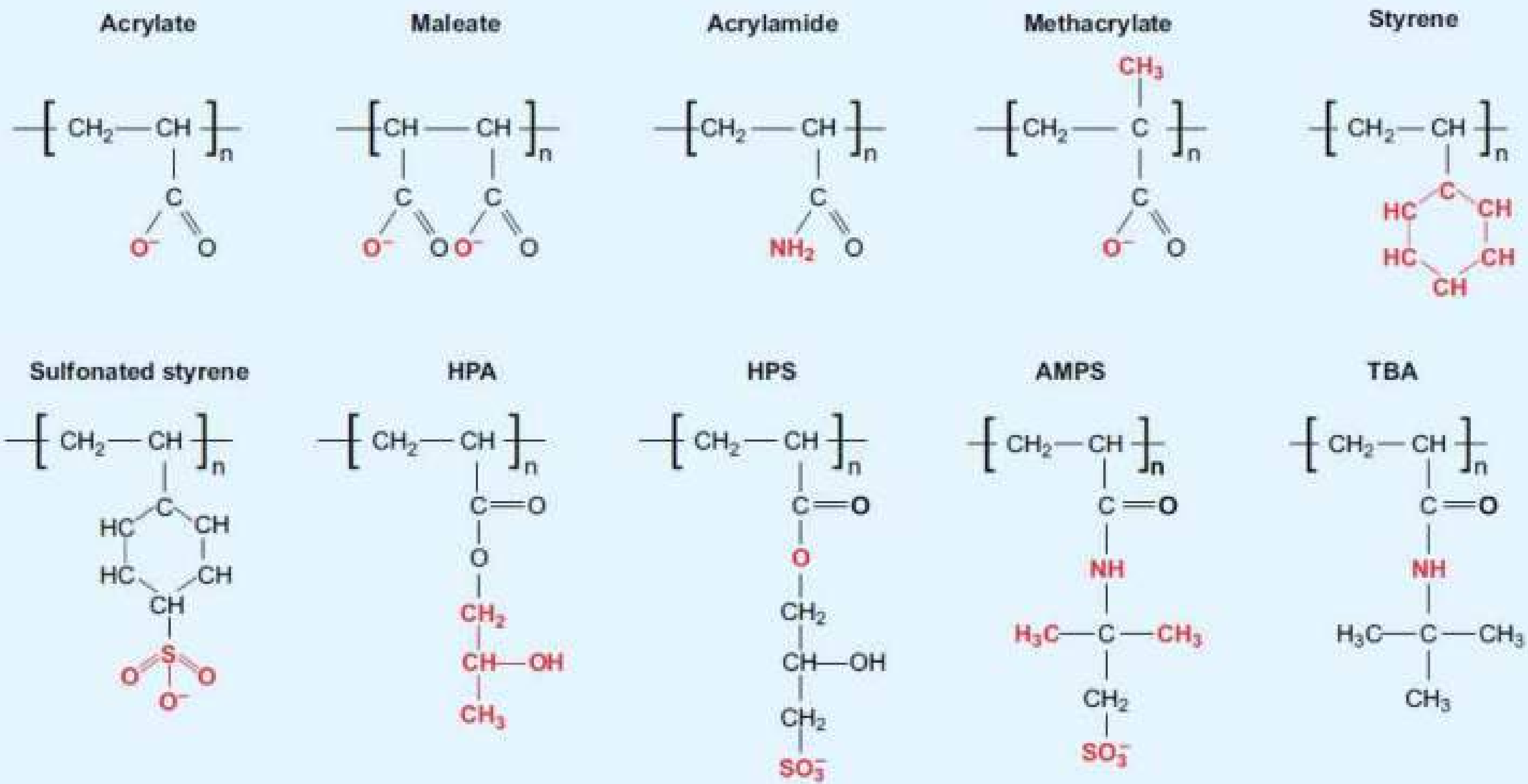
Typical Dispersants

- Homopolymers
  - PAA, PMA,
- Copolymers
  - SS/MA, AA/HPA, AA/AMPS, AA/HPSE, etc.
- Terpolymers
  - "HSP", "STP", AA/AMPS/TBA, AA/AMPS/SS
- Quad polymers
- Typical cooling tower dosage of 2-10 ppm active

Polyacrylic acid



Charged carboxylic acid group

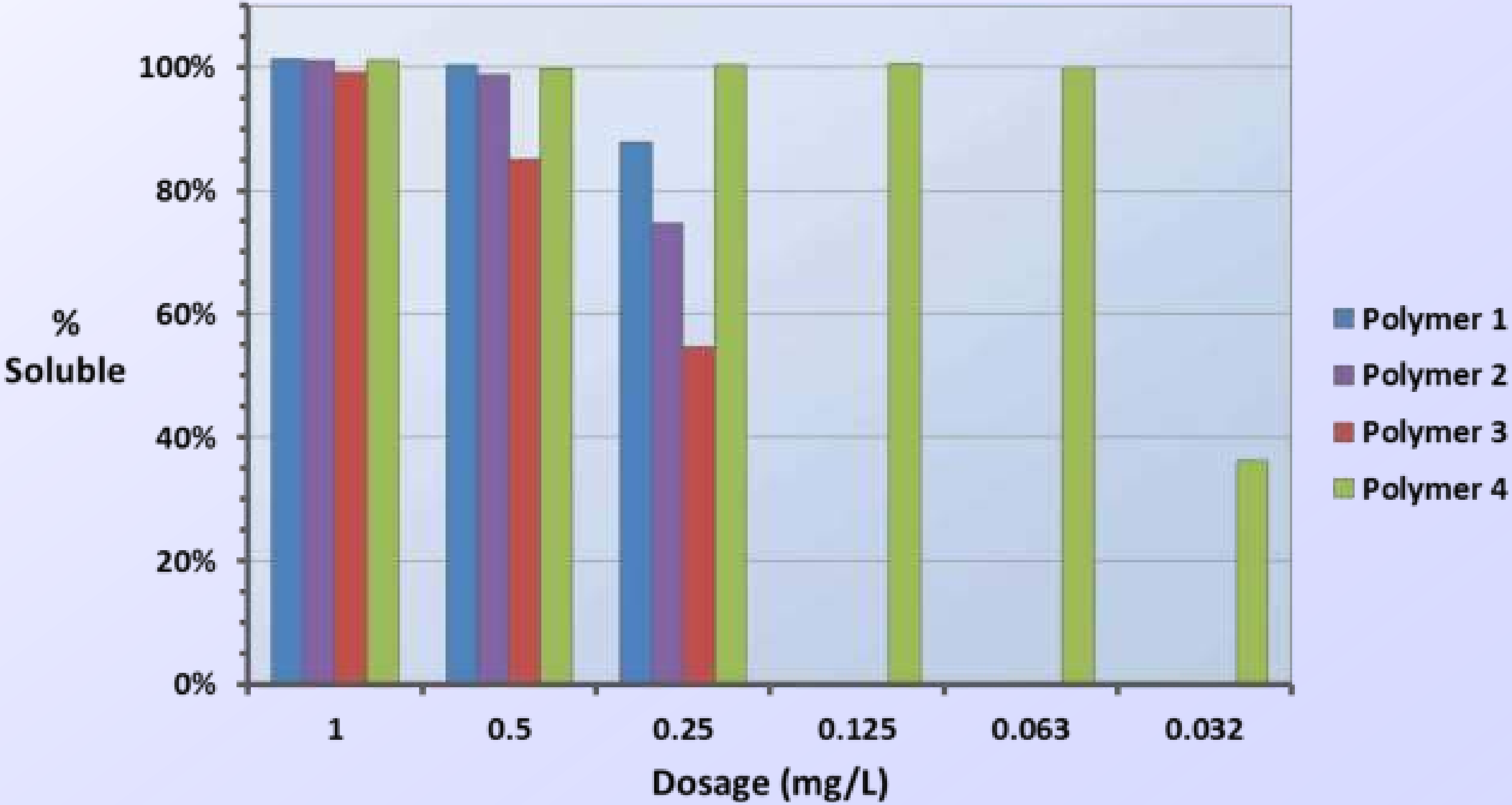


- Generally, carboxylic acid functionality performs best on carbonates and sulfates
- Generally, sulfonic acid functionality performs best on phosphates, zinc, Mn, iron

Calcium Sulfate Scale Inhibition

Percent Soluble after 18 Hr. at 50 °C

Conditions: 7,060 mg/L $SO_4^{=}$, 7,350 mg/L Ca^{+2} (as CaCO3)



Polymers vary widely in performance and are tailored for specific requirements

Iron and Manganese Stabilization

Often Use a Combination of Sequestration and Dispersion

Water: Tap + 100 ppm CaH, 100 ppm MgH, 50 ppm M-Alk

3 ppm Fe^{2+} + 2 ppm Mn^{2+}

pH 8.5 and ~25 ppm Chlorine

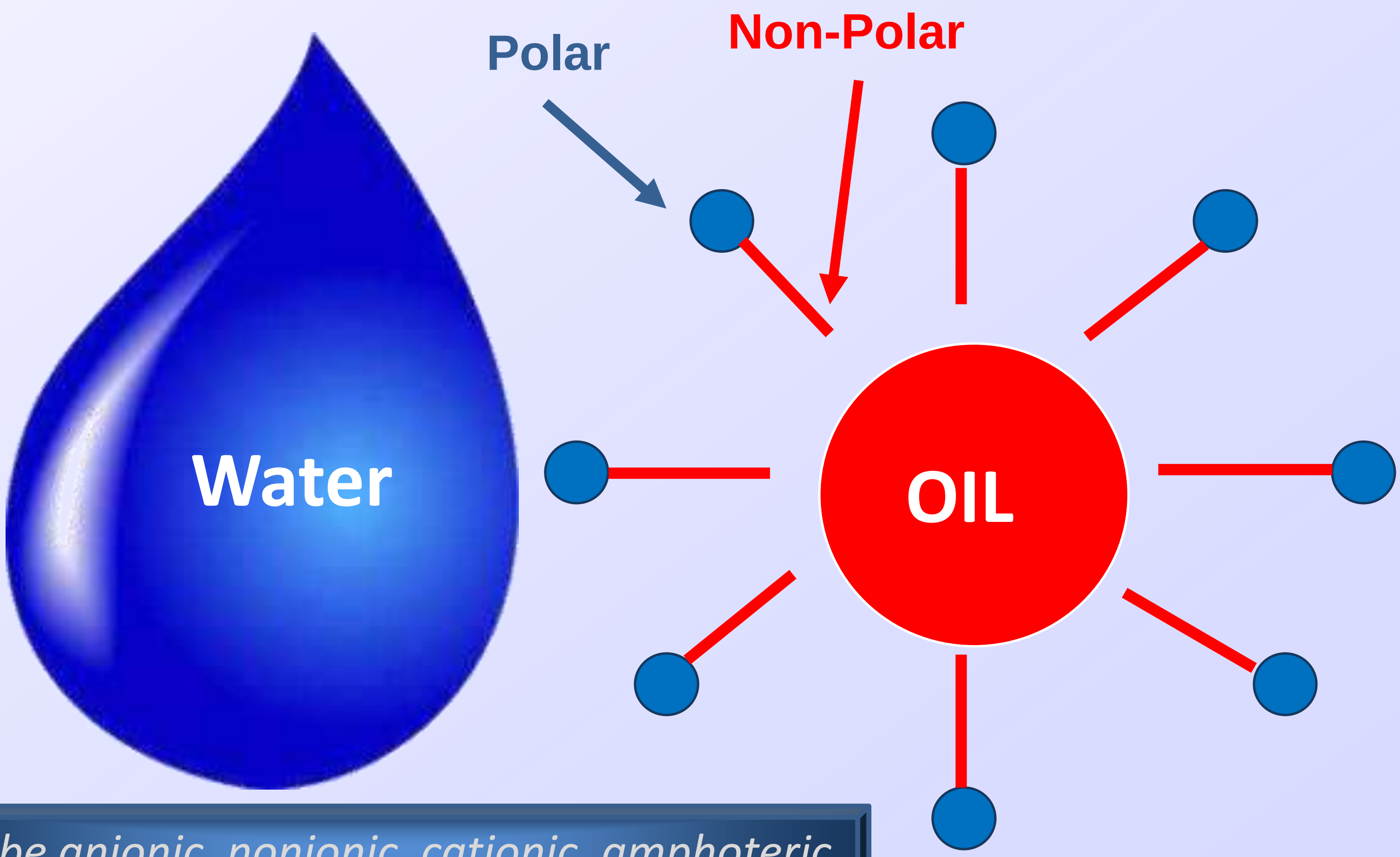
Untreated Blank

25 ppm CL4822

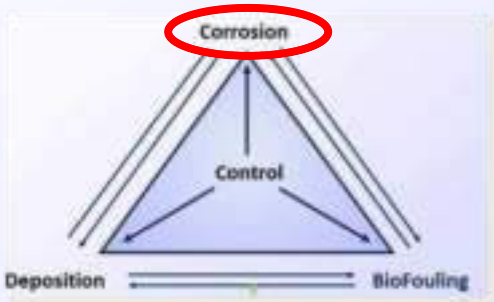
Manganese Is A Special Concern For Corrosion Of Stainless Steel and Brass

Oil Dispersion and Biofilm Penetration

- SURFACTANTS -



Can be anionic, nonionic, cationic, amphoteric



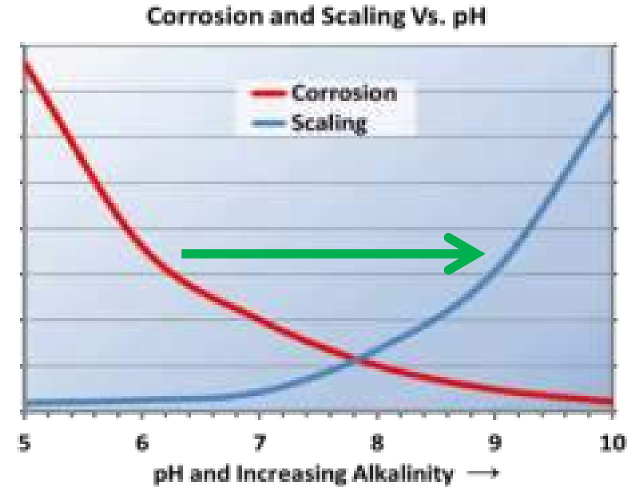
Selecting Materials that are appropriate for the Water Chemistry

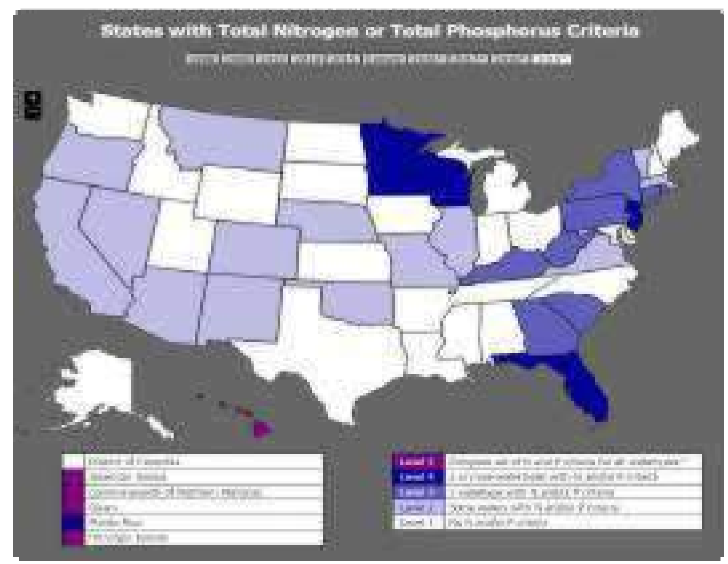
Selecting Treatment Chemistry appropriate for the Materials and Water

CORROSION RISK

Brief History of Cooling Water Corrosion Inhibitors

- 1970’s and earlier – Chromate
  - Excellent corrosion inhibitor
  - Non-Fouling
  - Banned globally due to human health effects
- 1980’s-’90’s
  - Phosphate and Zinc replace chromate
    - Less effective corrosion inhibitors
    - Operate at higher pH
    - Organic phosphorus scale inhibitors
- 2000’s
  - Zinc restricted due to aquatic toxicity
  - USEPA Priority Pollutant list
  - USEPA Toxic Pollutant list
- 2010’s and beyond
  - Phosphate restricted as an aquatic nutrient





Phosphorus Has Adverse Impacts on the Environment

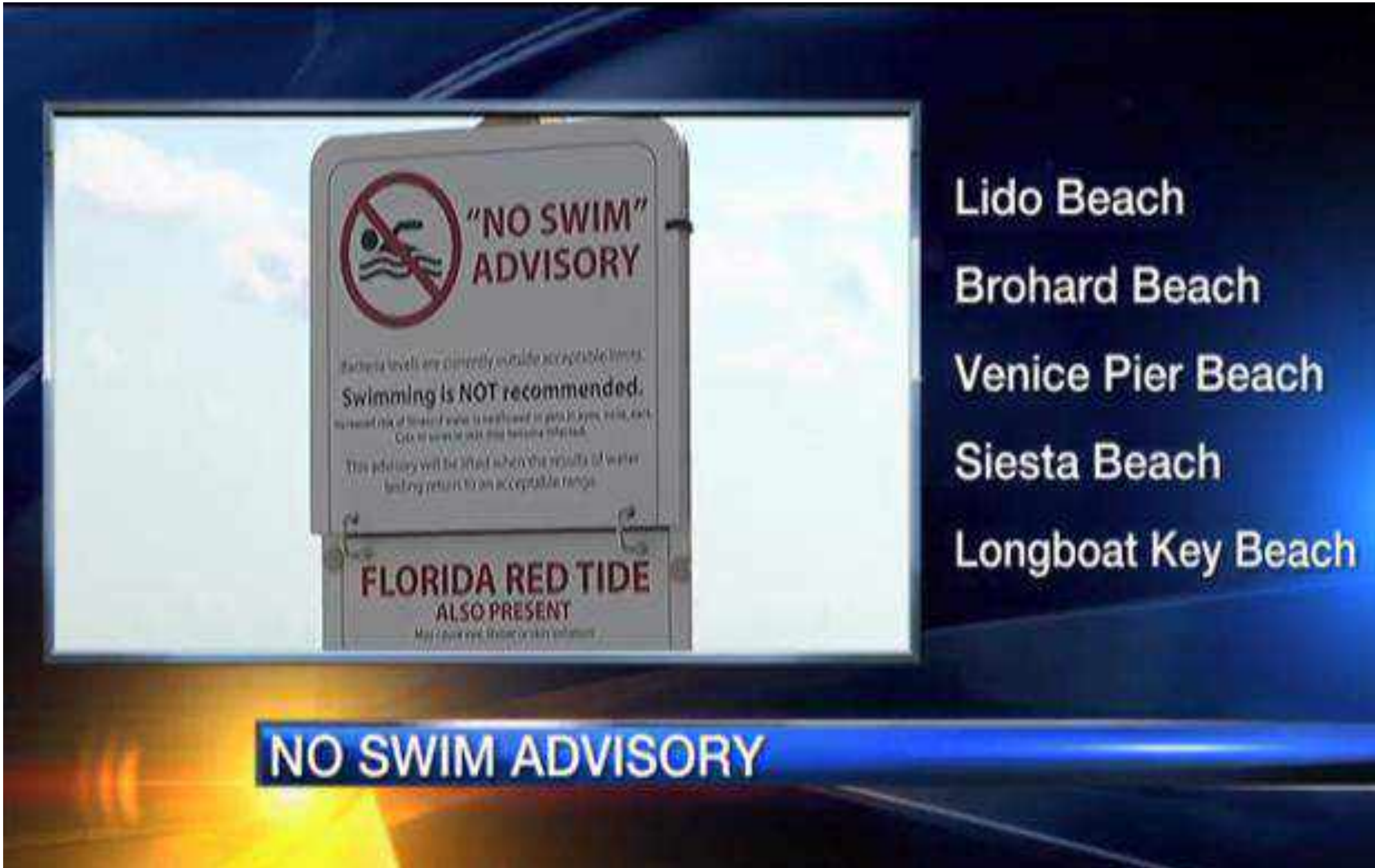
- Redfield Ratio for Algae
  - 106C : 16N : 1 P
- Blue-green algae
  - Cyanobacteria
  - Nitrogen fixing
  - C from bicarbonate/CO_2
- Algae support other organisms
  - Fix inorganic bicarbonate into organic carbon
- P also required by Bacteria
  - 45-50C : 9-10N : 1P
- Food for “higher life forms”
  - Amoeba
  - Protozoa

Phosphorus Is The Limiting Nutrient For Algae

Photo Credit - Jesse Allen and Robert Simmon - NASA Earth Observatory, Public Domain, https://commons.wikimedia.org/w/index.php?curid=16981673

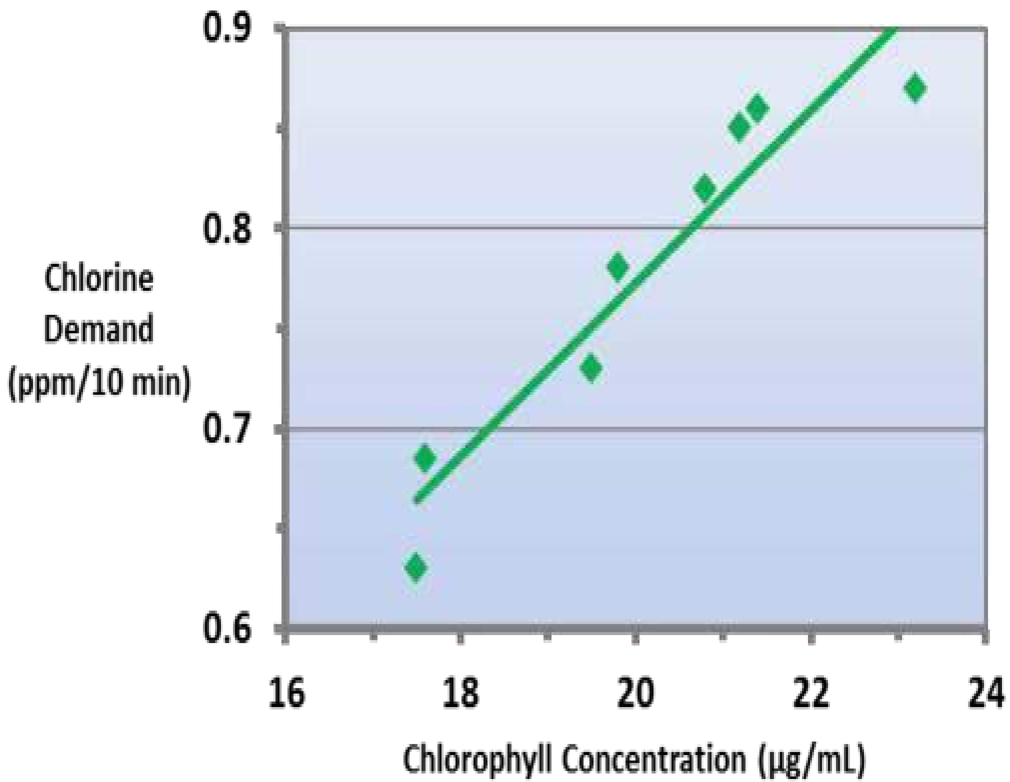
Last Summer's Phosphorous Fiasco – Florida Gulf Coast

Red Tide, Brown Tide, Millions of Pounds of Rotting Fish



Phosphorous Also Adversely Affects Cooling Systems

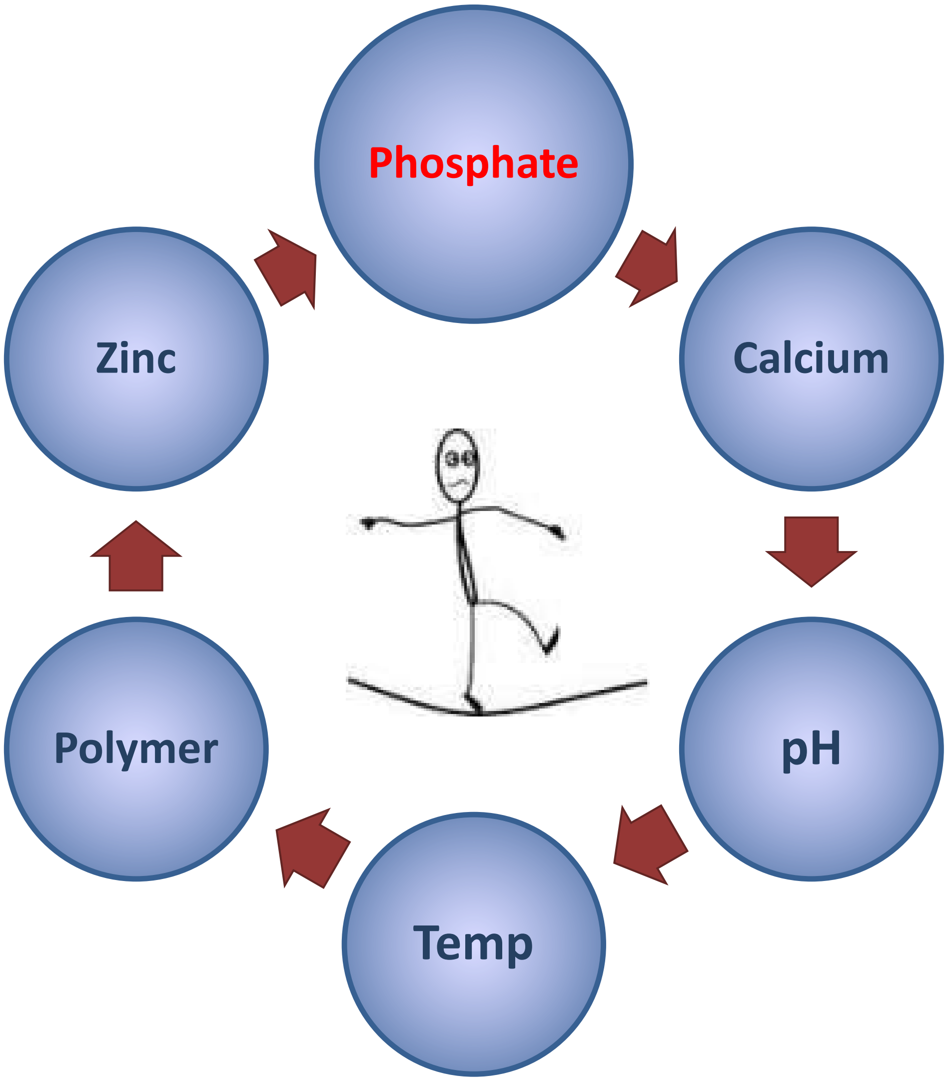
Impacts Chlorine Demand and Treatment Cost



No P → No algae → Less chlorine → Less corrosion → Lower Cost

Sustainable Microbiological Control

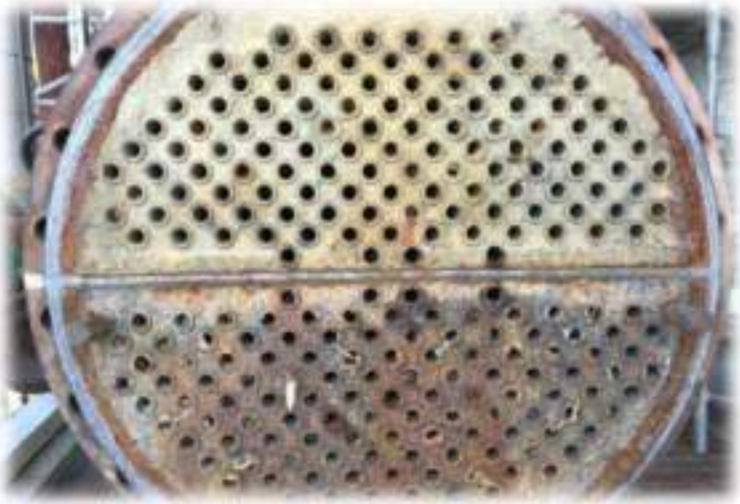
Phosphate Treatment Juggling Act



- Difficult to Control
- Lots of Phosphate
- Lots of Polymer to keep phosphate soluble
- Prefers Low pH to get more phosphate into solution
- Effective Only on Steel
- Lots of Nutrients
  - Increases chlorine and biocide usage
- = Lot$ of Co$t
- Lots of Risk
  - pH control
  - Lose polymer
  - Over/Under feed of $PO_4^{=}$
  - High temp HX fouling

Performance Problems With Phosphate and Zinc

- Hard to control
  - Balance PO_4, Zn, Ca, pH, T, & Polymer
  - Too Little → Corrosion
  - Too Much → Fouling
  - Solubility decreases with temperature
- Only effective against steel corrosion
  - Copper, aluminum, stainless steel?
- Precipitates with Iron and Aluminum
  - Forms deposits and consumes PO_4
  - Use more expensive organic coagulants
- Trouble with Low Hardness waters
  - Requires calcium to form $Ca_3(PO_4)_2$ film
- Algae nutrient
  - Increases chlorine demand
- Tightening discharge regulations
  - Phosphate regulated as nutrient
  - Zinc as Toxic, Priority Pollutant



Corrosion on the Cold Inlet
Fouling on the Hot Outlet

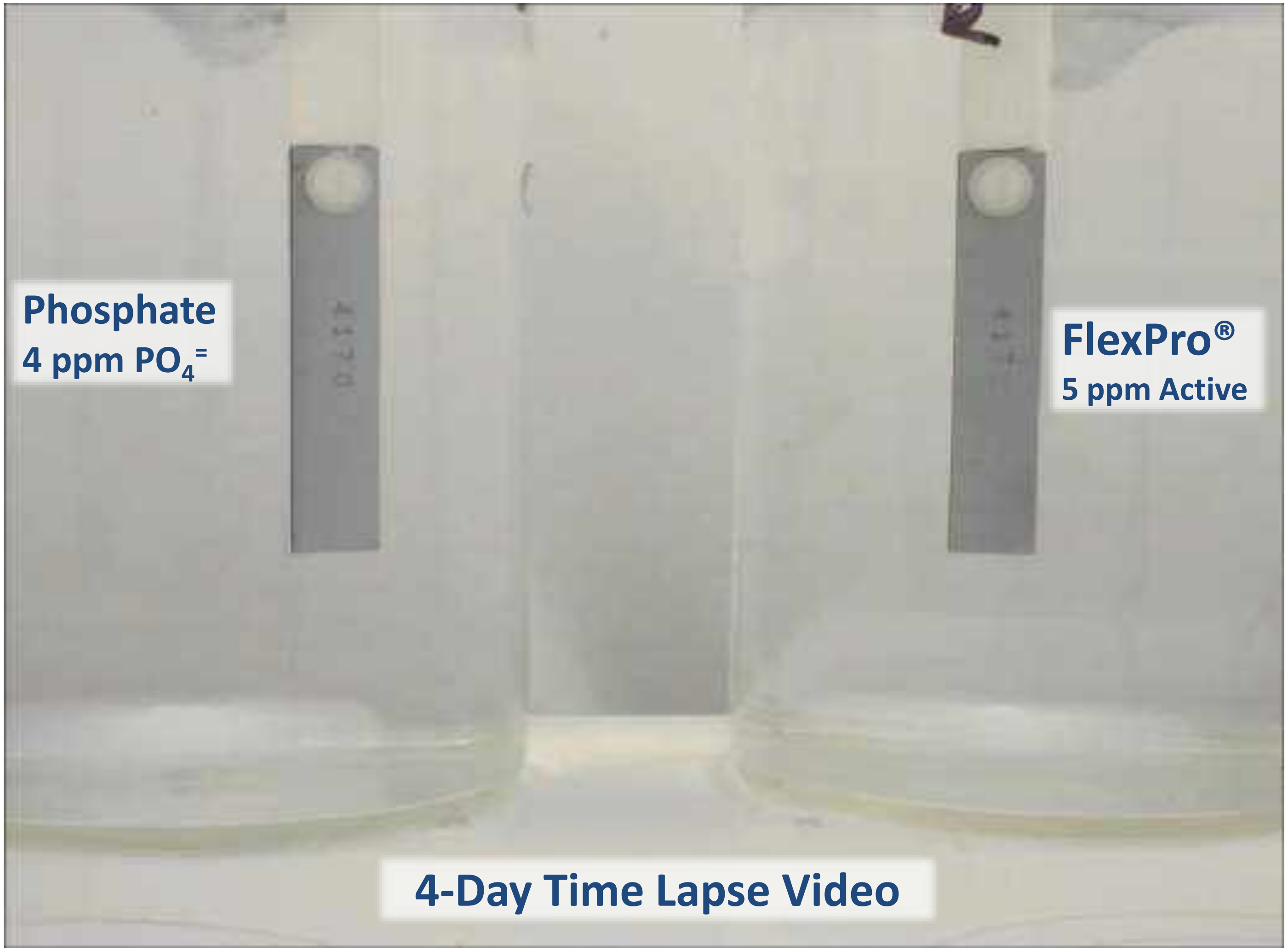
Algae requires phosphate

What If We Could Do Away With Phosphate and Zinc?

What If You Could Operate Without Phosphate or Zinc and Reduce Corrosion?

- No calcium phosphate or zinc deposits
  - Scorching hot, low flow bundles open Clean
- Improved Profitability
  - Longer turnaround cycles
  - Improved Efficiency
- Less chlorine for biological control
  - Lower chloride
  - Lower cost
  - Lower hazardous chlorinated bypoducts
- Longer heat exchanger life
  - Lower cost alloys
- Improved environmental compliance
- Better performance

FlexPro® Non-P and Non-Zn
Superior Corrosion Inhibition and Non-Fouling

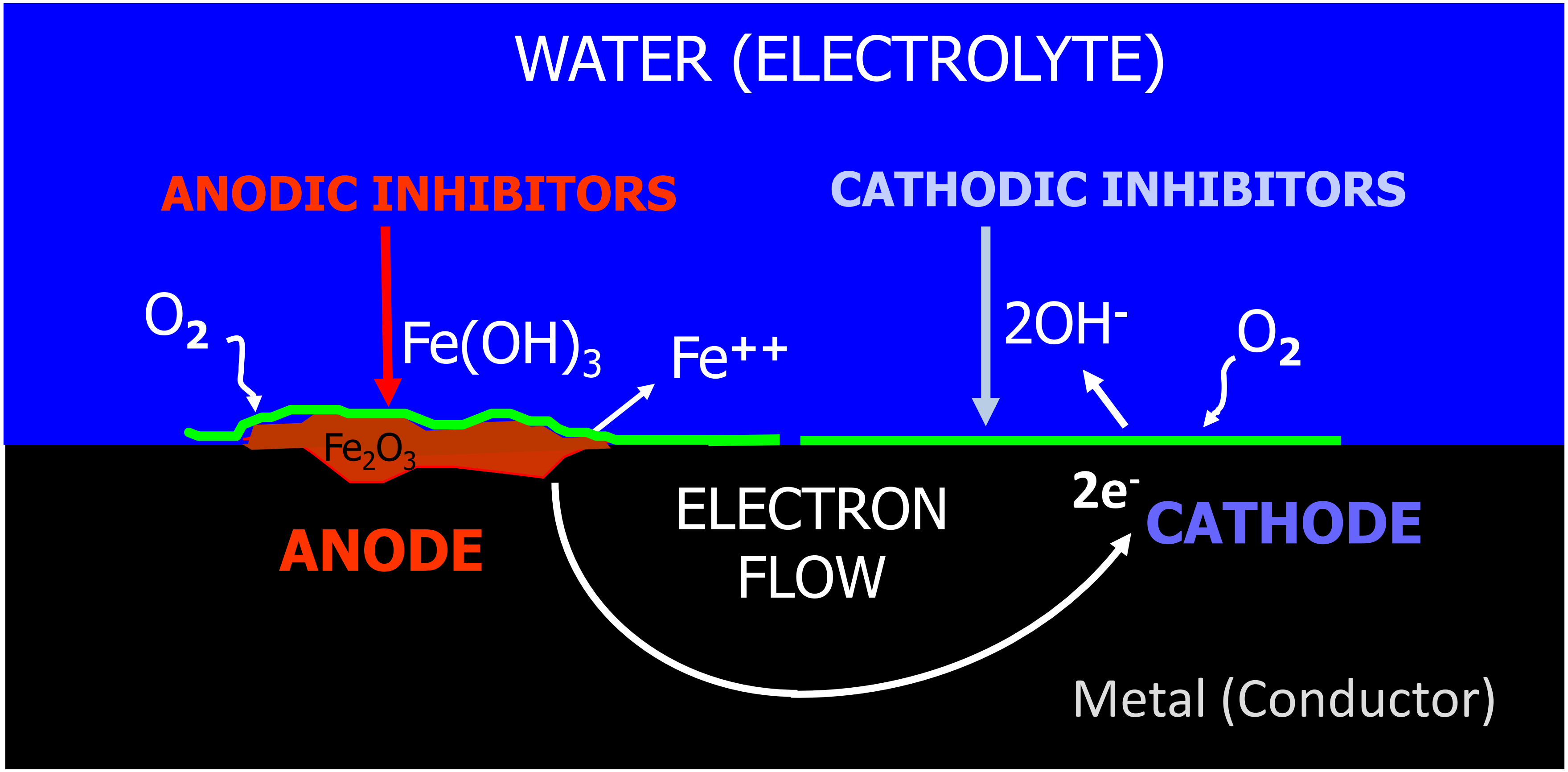


Conditions: pH 8.0, 25 ppm Calcium (as $CaCO_3$), 108 ppm Cl^-, 30 ppm $SO_4^{=}$, 40 °C, 4-day test

Non-P and Non-Zinc Corrosion Inhibitor

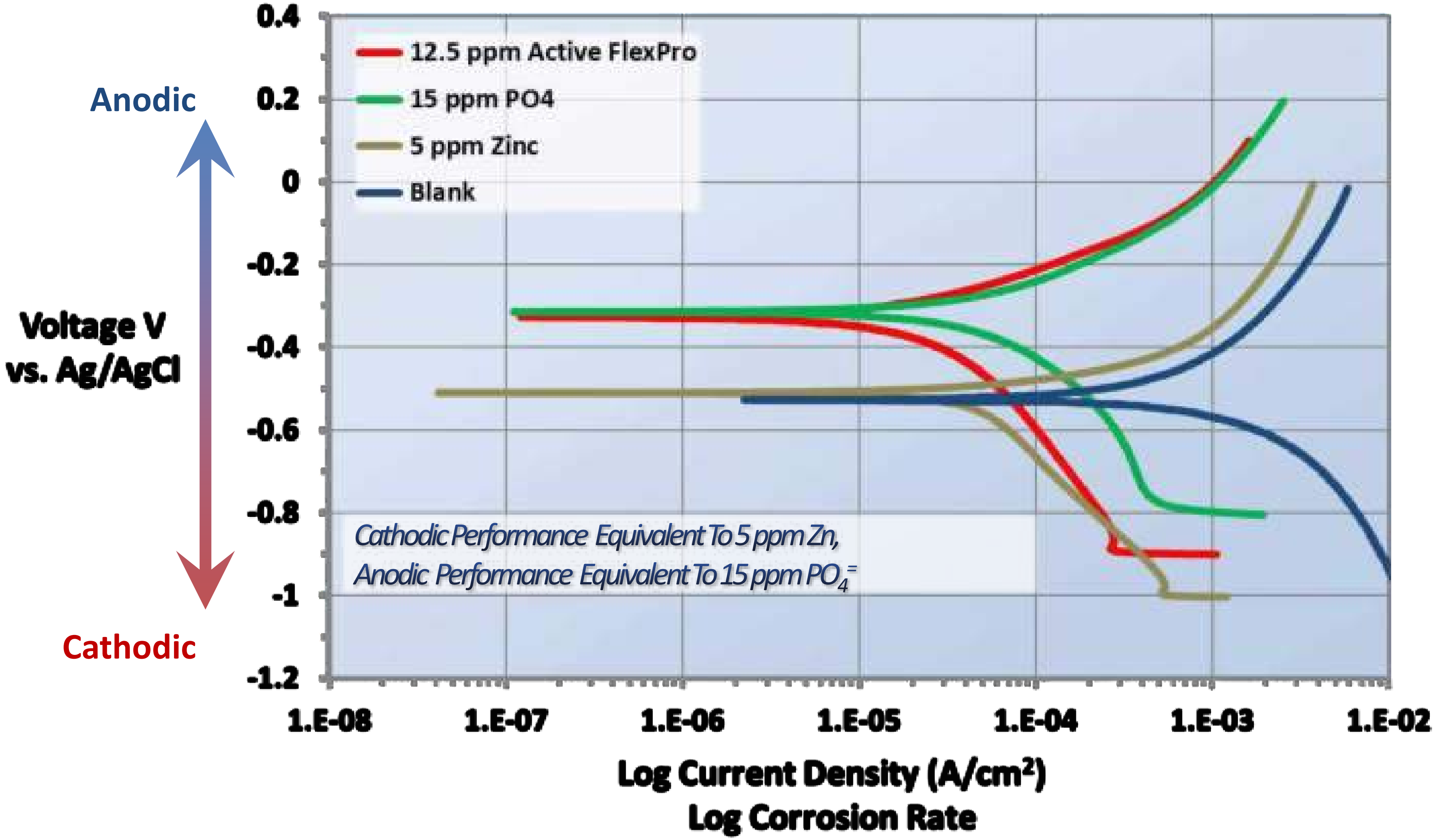
- FlexPro®
  - Flexible new corrosion inhibitor developed by ChemTreat
  - Binds directly with metal to form a truly Passive surface
    - Treat the Metal, Not the Water
    - Performance is independent of Calcium
    - Non-fouling – No issues with high pH excursion
    - Easy to control – Cannot be overfed
  - Inhibitor film is much more persistent than phosphate barrier layer
    - Resists corrosion during low pH excursions and standby
    - Effective on multi-metals – Steel, Stainless Steel, Al, & Cu
  - Non-P – Reduces algae and chlorine demand
  - Non-Zn – No USEPA Priority Pollutants or Toxic Pollutants
- What is the active ingredient?
  - RPSI – Reactive Polyhydroxy Starch Inhibitor

How Do We Inhibit Corrosion?



Best to Inhibit Both Anodic and Cathodic Reactions!

Advanced Electrochemical Techniques to Develop and Assess Corrosion Inhibitors



Midwest Cogeneration Plant On Great Lakes

High Hardness, High Sulfate Corrosive Water

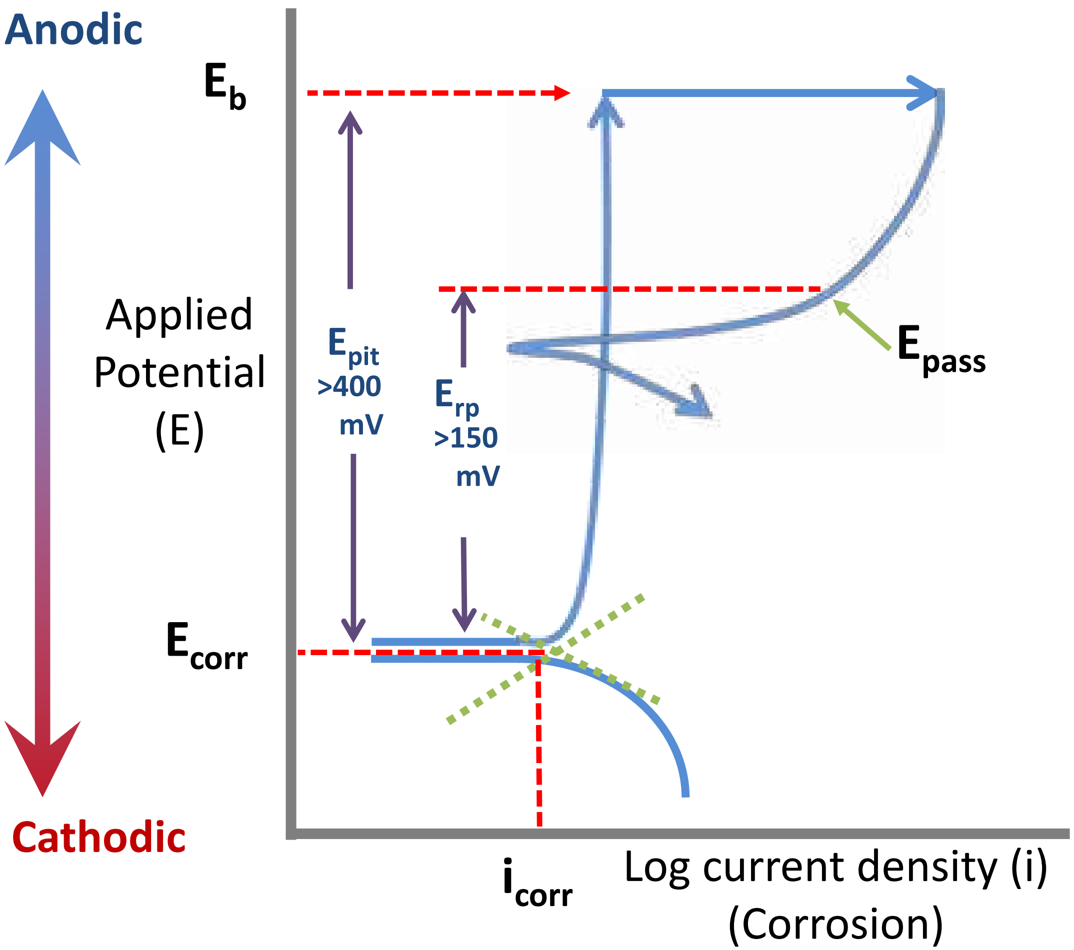
Analyte	ppm
pH	8.64
Conductivity	2,552
M-Alkalinity	267
Ca (as $CaCO_3$)	469
Mg (as $CaCO_3$)	672
Sodium	189
Chloride	324
Sulfate	807
LSI @120 °F	2.2
Larson-Skold	4.9

Previous Low P Program

FlexPro® Non-Phosphorus Program

7 years experience with FlexPro® at this site

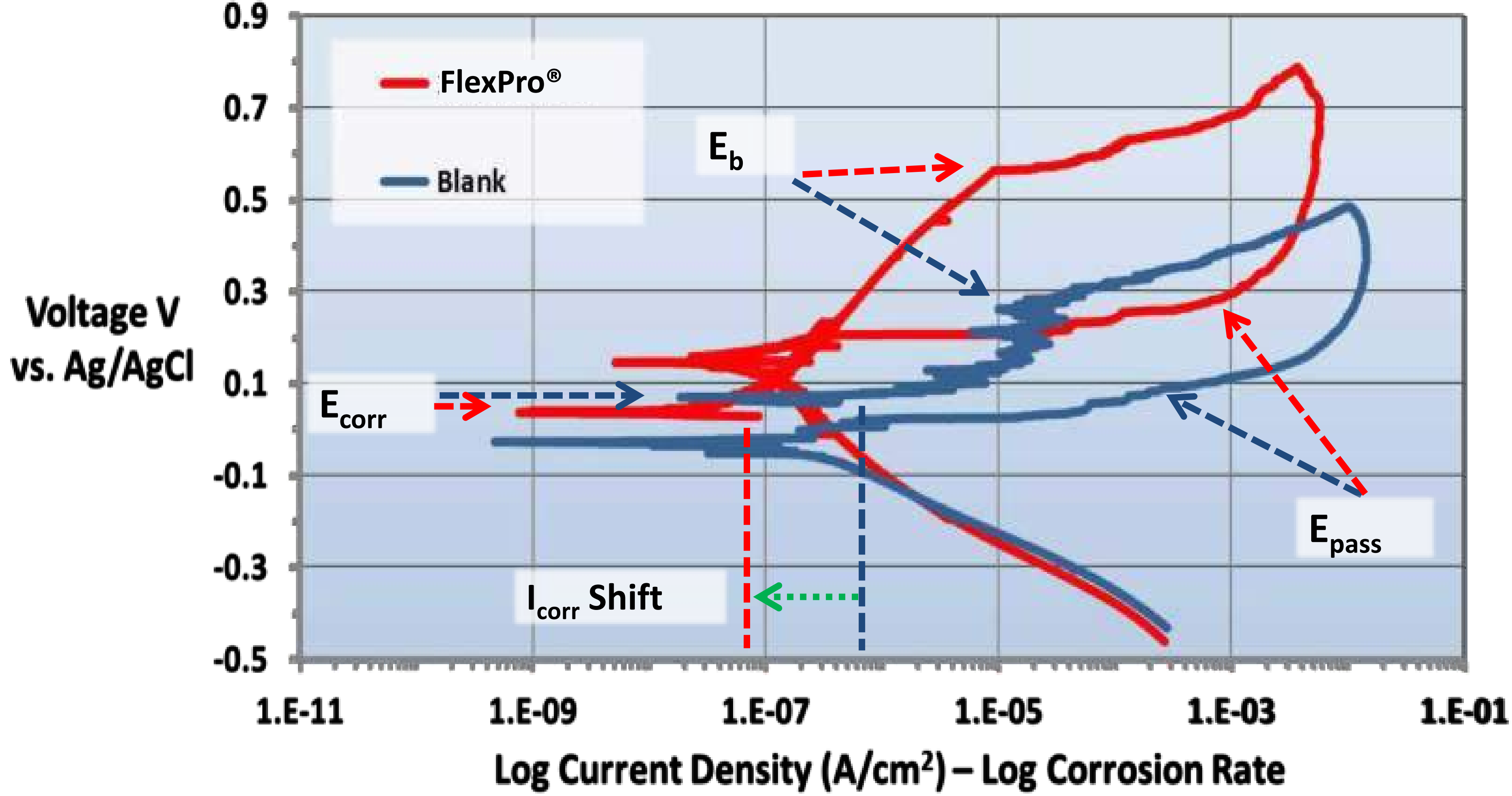
Evaluating Stainless Steel Pitting Tendency



1. E_{pit} > 400 mV
2. E_{rp} >150 mV
3. I_{corr} – Lower is better
4. Hysteresis Loop – Smaller is better

FlexPro® Non-P Chemistry Inhibits Stainless Steel Corrosion

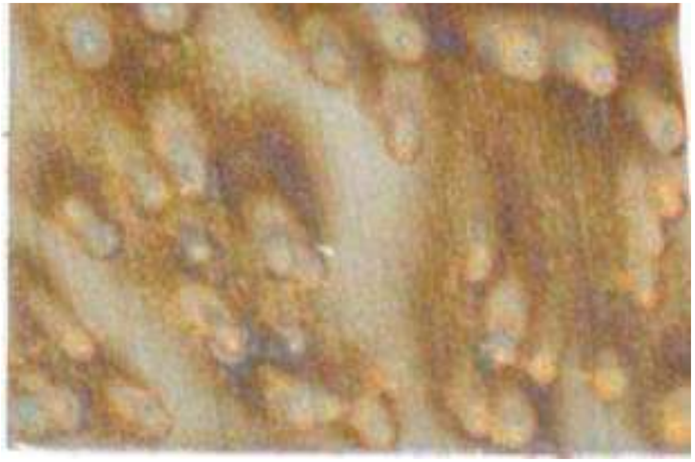
Type 304 SS – Tap water + 750 ppm Chloride, 65 °C (150 °F)



ChemTreat Can Evaluate Stainless Steel Alloys In Your Water

Electrochemical Data – Type 304 SS Electrodes

Treatment	E_{corr} mV	E_{pit} mV	E_{rp} mV	I_{corr} µA/cm^2
Blank	62	180	-5	0.68
FlexPro®	39	518	219	0.072



Untreated 304SS Electrode

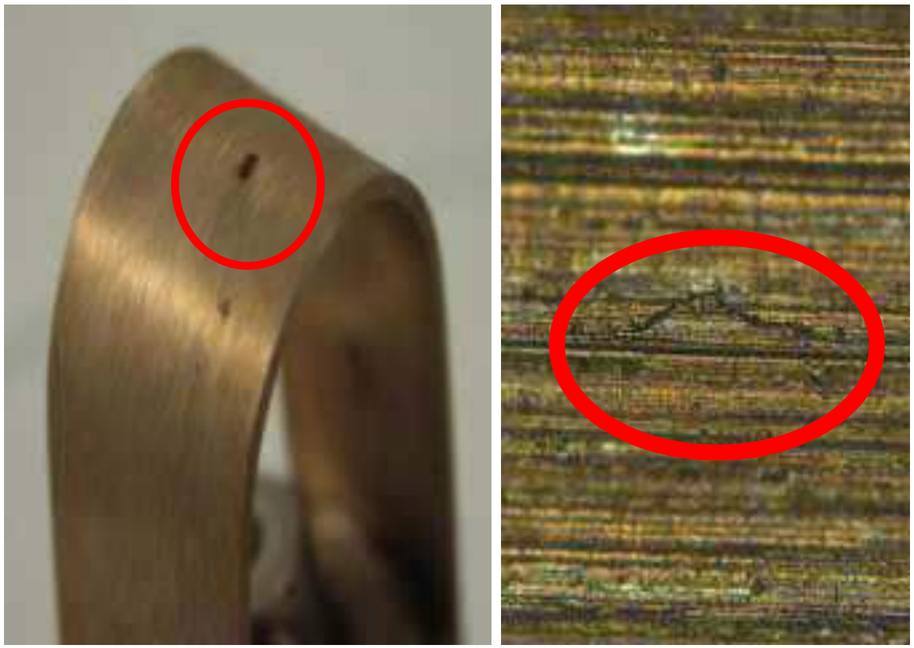
FlexPro® 304SS Electrode

Only FlexPro® Can Protest Stainless Steel In High Chloride Waters

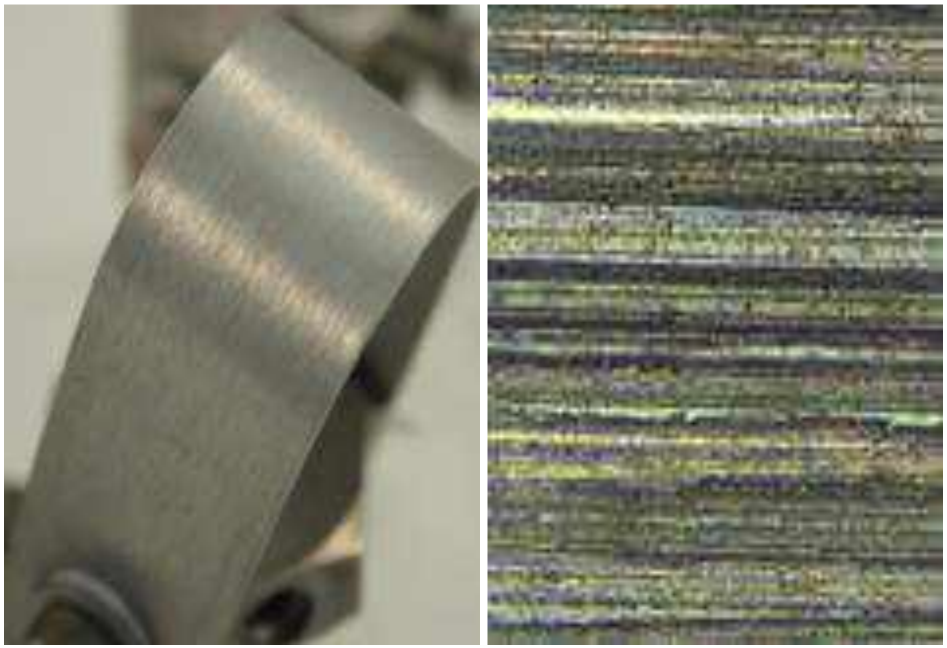
FlexPro® Protects Against Stress Corrosion Cracking

Type 304 SS U-Bend – 1,000 mg/L Cl^-, 105 °C, pH 8.0 - 8.2, Under Air, 15 days

Untreated



FlexPro®



- Type 304 SS, U-bend stressed specimens
- Richmond tap water + 1000 ppm Chloride
- Temperature: 221 ^{o}F, under air pressure
- Duration: 15 days

Untreated Shows Tarnish, Pitting, and Cracking

Sustainable – Aquatic Effects and EH&S

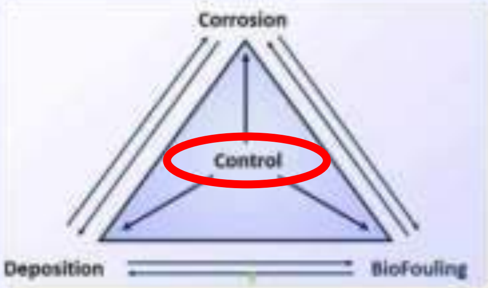
- Initial goal to develop an environmentally sustainable alternative to phosphate and zinc
  - Requires minimal aquatic effects as well as non-P (& non-Zn)
- Range of Non-P Products
  - Typical "100 ppm" product
    - Ceriodaphnia – 2,967 mg/L LD_{50}
    - Minnow – 3,536 mg/L LD_{50}
      - 3,500 mg/L 7d NOEL
- Environmental Health & Safety
  - Many products in the Non-P family formulated at pH 3.0 -3.5
  - Less hazardous than most products it replaces
    - Strong alkali, pH >12
    - Strong acid, pH <2
  - No flash point
  - Not DOT regulated
  - No California Prop 65
  - HMIS rating 1-0-0-X
    - 0-4 Scale

Able to Permit FlexPro® Where Nothing Else Could Be Permitted

FlexPro® Technology Development History

8 Years, 14 Major Publications

- International Water Conference – November 2010
  - Development of Next Generation Phosphorus Free Cooling Technology
- Electric Utility Chemistry Workshop – May 2011
  - Development and Application of Phosphorus Free Cooling Technology
- Cooling Technology Institute – February 2014
  - Development & Application of Phosphorus Free Cooling Water Treatment
- Southwest Chemistry Workshop – August 2014
  - Cooling System Layup and Passivation
- EPRI Electric Power Research Institute – August 2015
  - Advances in Cooling System Passivation and Layup
- International Water Conference – November 2015
  - Advances in Pretreatment, Passivation, and Layup of Cooling Systems
- Cooling Technology Institute – February 2016
  - Advancements in Cleaning and Passivation of Cooling Systems
- North American Energy Services – May 2016
  - Phosphorus- and Zinc- Free Cooling Technology
- Cooling Technology Institute – February 2017
  - Can Rusted Surfaces Be Effectively Passivated To Reduce Further Corrosion?
- AIChE – March 2017
  - Benefits of Non-Phosphorous Cooling Water Chemicals on Refinery Economics
- World Energy And Engineering Congress – September 2017
  - Development And Application Of Non-P Corrosion Inhibitors For Cooling Water Systems
- International Water Conference – November 2017
  - A Holistic Approach to Microbiological Control In Cooling Systems And The Environment
- EPRI-CTI – August 2018
  - Mitigation of a Flow Limiting Corrosion and Fouling Issue on a U-tube Condenser at Athens Energy Biomass Plant
- International Water Conference – November 2018
  - Grey Water – A Sustainable Alternative for Cooling Water Makeup



Automation

Instrumentation

Communication

CONTROL

Reduce Risk and Improve Performance

Automate Your Cooling System

Vastly improved electronics, software, and Communication

Typical Cooling Tower Automation System

Better Data. Better Decisions.

- Wide range of sensors for monitoring and controlling:
  - Conductivity
  - pH
  - ORP / Chlorine
  - Corrosion rate
  - Biofouling
  - Scaling
  - Treatment chemical dosage
  - Tank level
  - Performance
- Cell modem for accessibility via smart phone, tablet or PC from virtually anywhere
- 24/7 open web-based water management software platform

Most effective as Tools, Not substitutes for Trained Professionals

Product Monitoring Technology

- Old Methods
  - Molybdate tracer
    - Molybdate use is increasingly prohibited
    - Requires sampling, reagents, disposal
    - Difficult to do in-line
  - Wet chemistry
    - Requires sampling, reagents, disposal
    - High cost and maintenance for on-line analyzers
- New Methods
  - Electronic Sensors !
  - No Reagents
  - In-line or hand held
  - No sample conditioning
  - Reliable, low-cost
  - Digital output, MODBUS connection
- Genesis of "Big Data"

Bluetooth Tank Level Sensor with Integral Display

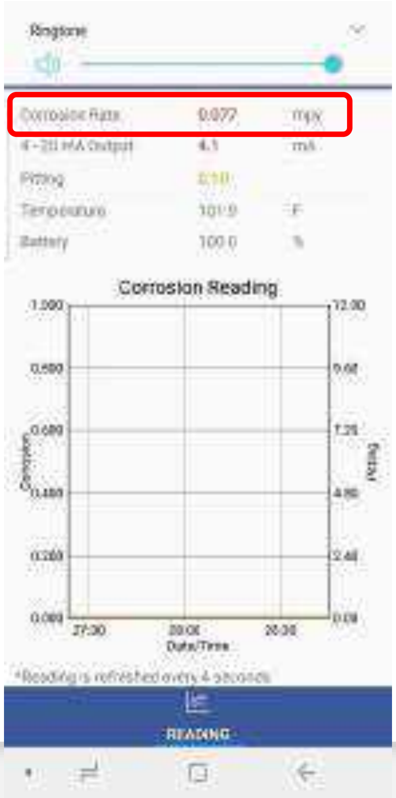
Sensors & Controller

Smartphone Application

Advanced Sensors

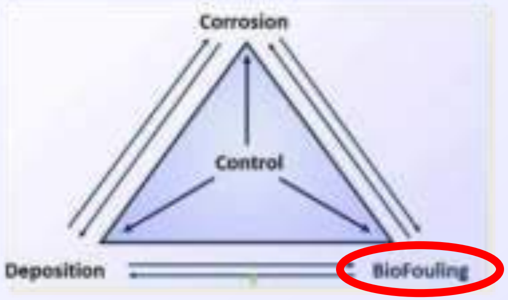
- **Halogen Stable Triazole**
  - Corrosion Inhibitor for Copper
- Patent-Pending Technology
- Just One Press to Measure
  - No reagents
  - No UV Pen
  - No cuvette
  - No lab
  - No waiting
- Compensated for interferences
- Waterproof
- Faster and better than wet chemistry

- **Wireless corrosion rate**
- Bluetooth connectivity to cellphone
- 10x better sensitivity
  - 0.001 mpy
- Built-In data recording



Goal – Enable In-Line Tracking Of All Chemicals

- PTSA – Inert fluorescent tracer for cooling systems
  - Fluorescein is not chlorine-stable, but can be used for Boiler and RO
  - NDSA for high pressure boiler
- Tagged Polymer!
  - Tag a non-P polymer for calcium carbonate scale control
    - AA/MA
    - Unique in the market
  - Tag a polymer for calcium phosphate, zinc, iron, and silt
    - AA/AMPS
    - Something better? AA/AMPS/Non-ionic
- Need sensors for calcium, alkalinity, silica, magnesium
- Need lower cost, practical deposition sensor
- Corrosion rate meter – Need accurate pitting indicator
- Improved sensor for chlorine
- Implement level control sensors and reporting
- We have acceptable sensors for conductivity, pH, and ORP



Airborne Pathogens

Cellular Plastic Fill Selection

Nutrients

MICROBIOLOGICAL CONTROL

How Do We Control Microbes?

- Reduce microbes entering the system
  - Pretreatment with chlorine or other antimicrobial
- Control nutrients entering the system
  - Process leaks
  - Phosphate and nitrogen
- Control sunlight entering the water
- Apply antimicrobial chemicals to the cooling system
  - Oxidizing
    - Chlorine, bromine, chlorine dioxide
    - Mostly non-specific across organism types
  - Non-oxidizing
    - Many types – Isothiazolin, DBNPA, Glutaraldehyde, Quat Amine & Phosphonium
    - Effectiveness is more specific to the organism
    - Can be difficult to permit

Oxidizing biocides are usually primary for cooling towers

Appearance of Raw Water Pond

Polyphosphate – Summer 2014

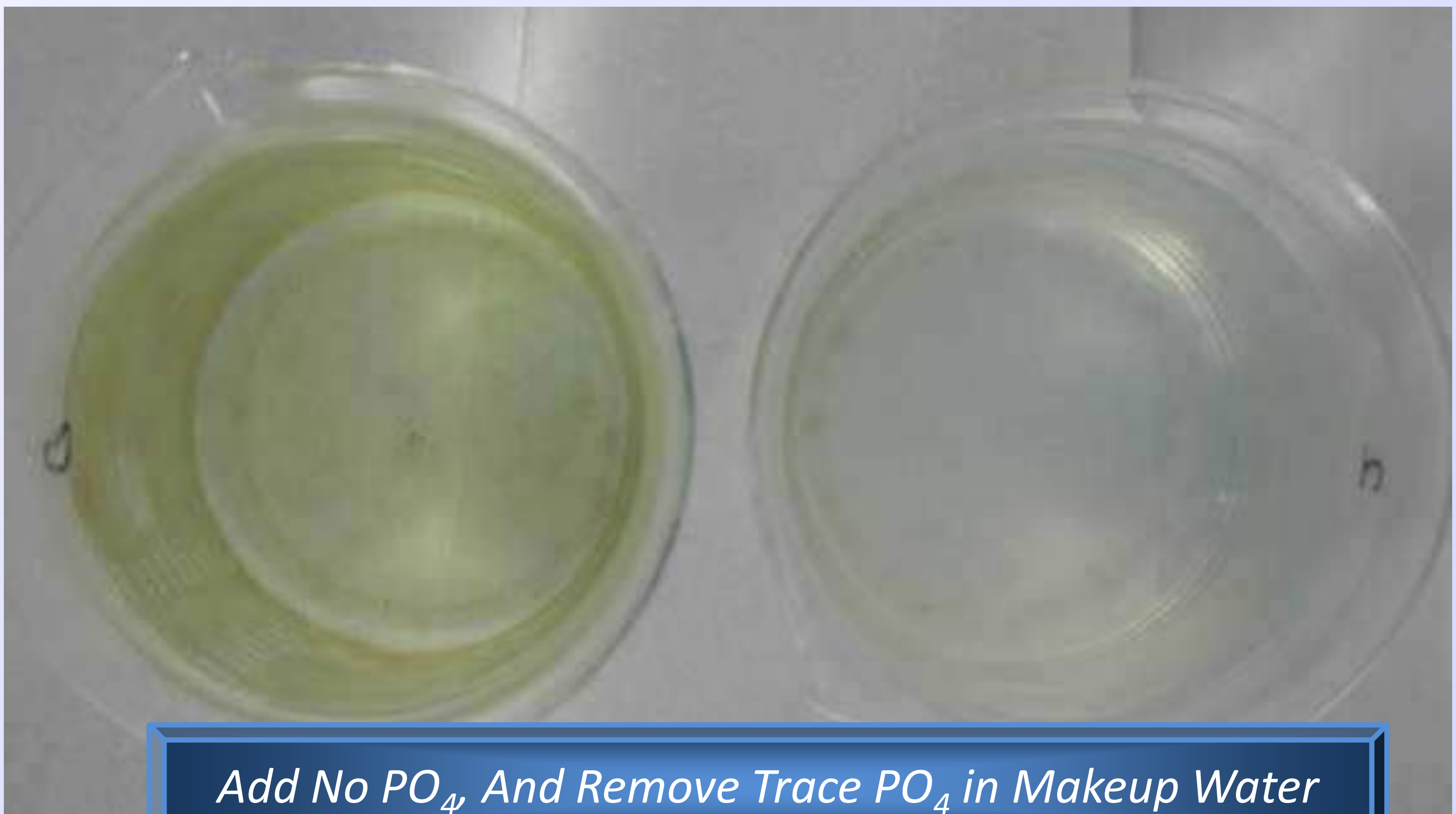
Non-P, Non-Zn – Summer 2017

"Looks like the Caribbean"

70% Reduction in Hypochlorite Usage

New Technology For Algae Control In Cooling Towers

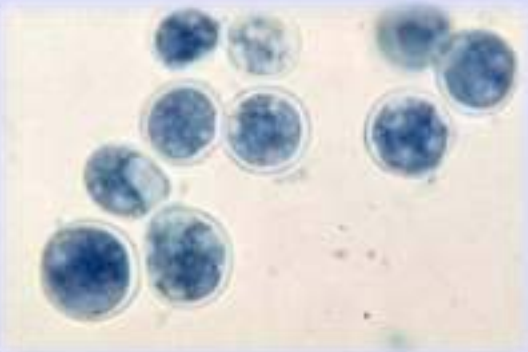
- Binds phosphate so tightly that Algae can't metabolize it
- Holistic approach to algae control
  - Less chlorine demand and cost
  - No chlorinated byproducts (THM and AOX)



Add No PO_4, And Remove Trace PO_4 in Makeup Water

Fungi Control

- Fungi degrade complex organics into simpler organics
  - Molds and Yeasts
  - Tower lumber
  - Organic leaks in Process industries
  - Lignin and Fiber in Paper industry
  - Poorly treated POTW effluent
- Tower lumber is generally the only fungi concern for Power
  - Primarily in the mist zones in plenum
  - Difficult to control – Not fully wetted
  - Consider preservative spraying
  - Best bet – Replace with Plastic



Cooling Tower Lumber Wood Rot

- Particularly troublesome in the plenum area
- Antimicrobials – limited effectiveness in areas not fully wetted
- Inspect timbers
  - Wood rot / delignification
  - Surface algae / fungus
- Fungal attack beneath the thin preservative layer
- Brown rot fungi oxidize primarily the cellulose, leaving the darker lignins

Brown Rot Fungi – Testing for Internal Decay

- Fungal attack occurred beneath the thin preservative layer
  - Not always obvious
- Brown rot fungi prefer softwoods
  - Wood shrinks and cracks
  - Penetrates deep into the wood
  - Also called Dry Rot (seems to conduct moisture into kiln dried lumber in areas that seem dry)
    - Rhyzomorph ("roots") conduct moisture into the wood interior

Oxidizing Biocides

Chlorine Gas

Sodium Hypochlorite ("Bleach")

Both react with water to produce HOCl ("hypochlorous acid")

$Cl_2 + H_2O \rightarrow HOCl + HCl$

- HOCl = "Hypochlorous acid" - Antimicrobial
- HCl = "Hydrochloric acid", lowers pH

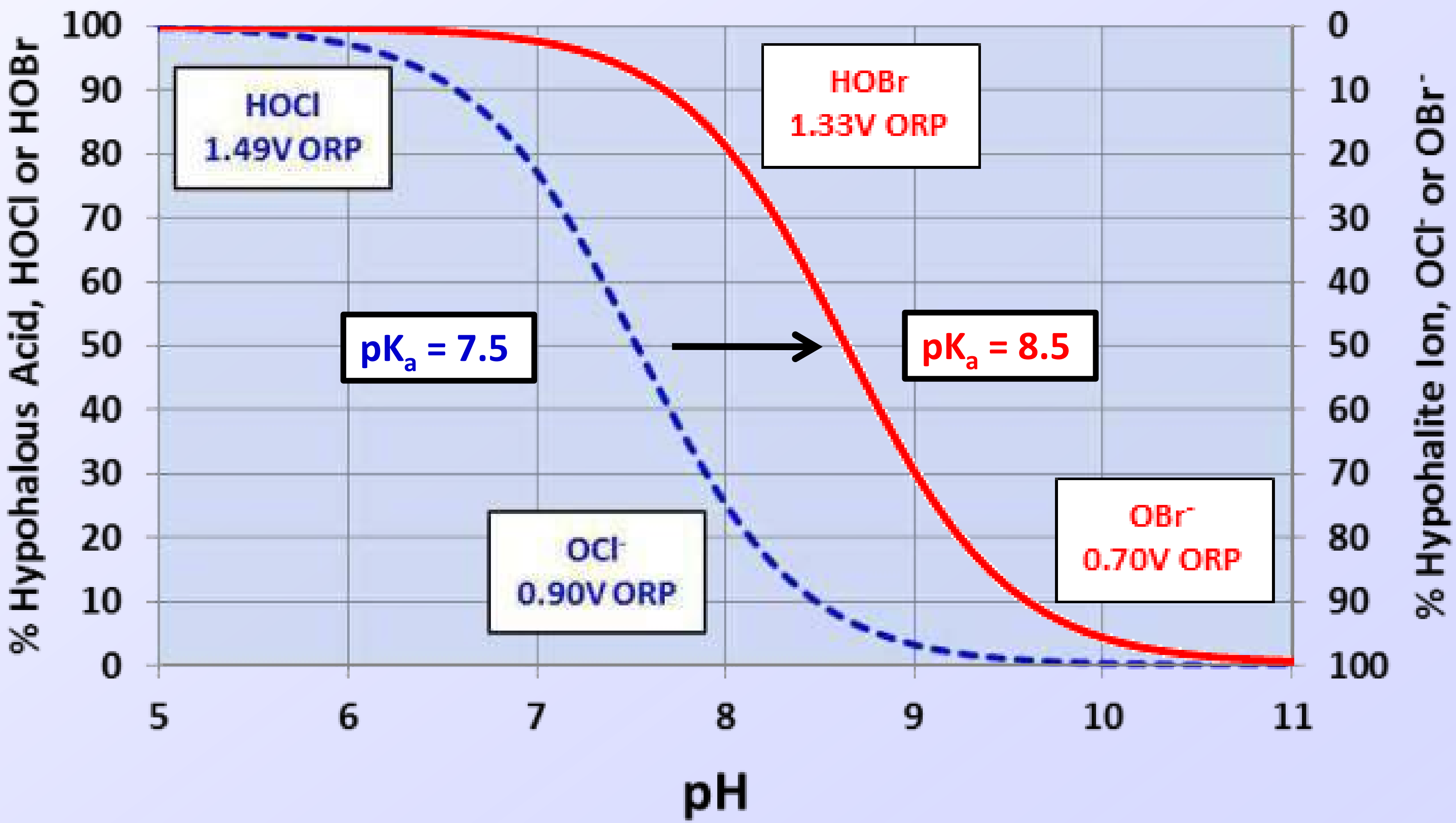
$NaOCl + H_2O \rightarrow HOCl + NaOH$

- Also produces HOCl
- NaOH = "Caustic", raises pH

$HOCl \leftrightarrow OCl^- + H^+$

- HOCl is a weak acid in equilibrium with OCl-
- Both are considered "Free Available Chlorine" (FAC)
- HOCl is faster acting as a biocide
  - Electrical neutrality and smaller effective diameter allow it to penetrate rapidly through cell walls

Hypochlorous Acid and Hypobromous Acid – *Dissociation Curves*



At pH 8.5, 50% of the Bromine is in the most effective form Vs. 5% for Chlorine

Generating Bromine Using Chlorine

(Sodium Hypobromite Liquid Is Not Stable)

- $HOCl + NaBr \rightarrow HOBr + NaCl$
- Bromine is a "weaker" acid (higher pKa)
  - Less dissociated at alkaline pH
    - More HOBr and less OBr^-
  - Faster acting
  - Effective at lower residuals
- Less tendency to "tie up" with ammonia
  - Chloramines are not very effective on algae
  - Residuals dissipate faster than chloramines
- ! Less corrosive to copper alloys than chlorine
- Bromide has become expensive
  - Shifting to lower ratios of Br:Cl
  - 4:1 or even 8:1
  - Considerable reactivation in the bulk water, especially for high cycles

A New Trend –

Intentionally Adding Ammonia or Amines

- Why?
  - Cooling towers have Long residence time, so contact time is less important if a continuous residual is maintained
  - Chloramines and bromamines are weaker oxidizers, and less reactive toward non-bacterial demand
    - Lower halogen usage due to less oxidation side reactions
    - Biofilm penetration with less consumption
  - Act as chlorine stabilizers to reduce chlorine consumption
  - Less THM's produced (with non-bromine forms)
    - "Total Halogenated Methanes", or "Tri-HaloMethanes"
- Common ammonia and amines
  - Ammonium sulfate, ammonium bromide, sulfamic acid, hydantoin
- Potential disadvantages
  - Slower reaction time may require dechlorination
  - Chloramines are very weak on algae

Chlorine Dioxide for Microbiological Control

- Overcomes issues associated with chlorine & bromine
  - Not affected by pH
  - Much less corrosive to copper alloys
  - Does not tie up with ammonia to form weak chloramines
  - More effective at penetrating biofilms – Generally shot-fed
  - More effective on macrofouling (zebra mussels, Asiatic clams)
  - More effective in highly contaminated systems (grey water)
- Disadvantages
  - Higher cost per pound than chlorine or bromine
  - Generated on site using 2 or 3 chemicals for large cooling systems
    - Sodium chlorite, hydrochloric acid, (optional sodium hypochlorite)
    - Sodium chlorate, hydrogen peroxide, excess sulfuric acid
  - Requires more care to handle safely than most cooling chemicals
  - Chlorite reaction product does not dechlorinate with bisulfite
    - Aquatic effects in Ceriodaphnia WET tests at 0.05 mg/L

Non-Oxidizing Antimicrobials ("Biocides")

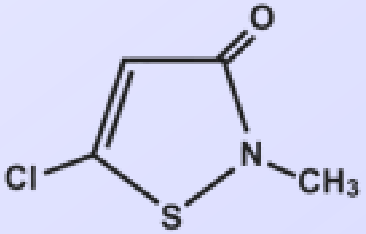
- React with specific cell components as compared to more indiscriminate oxidation
- Why non-oxidizing antimicrobials?
  - Better penetration of biofilms (sessile bacteria)
    - Not consumed by extraneous reactions
    - Some types disrupt biofilms
  - More persistent
    - Lay-up
    - Dead Legs
    - Stagnant conditions
  - More effective on algae and macrofouling organisms
  - Less corrosive to system metallurgy
- Why not?
  - Generally more expensive as the primary antimicrobial
  - Effectiveness is more specific and selective to the type of organism
    - Requires greater skill and care in selection and application

Non-Oxidizing Antimicrobials

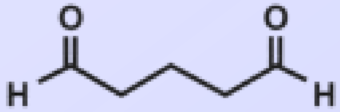
- React with specific cell components as compared to more indiscriminate oxidation
- Two general classes
  - Metabolic inhibitors
    - Enzyme poisons
    - Alter protein structure
    - Disrupt metabolic cycles
    - Effective at low active concentration
  - Surface active agents
    - Cationic hydrophilic head – Hydrophobic tail
    - Adhere to negatively charged microbes and biofilm
    - Alter cell membrane permeability
    - Penetrate biofilms
    - Generally require higher concentrations
    - Will foam to some extent

Common Metabolic Inhibitors

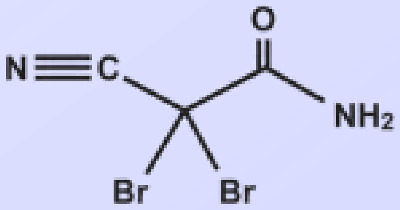
- Isothiazolin
  - Broad spectrum bacteria and fungi
  - Slow acting
  - Electrophilic attack on thiol enzyme groups



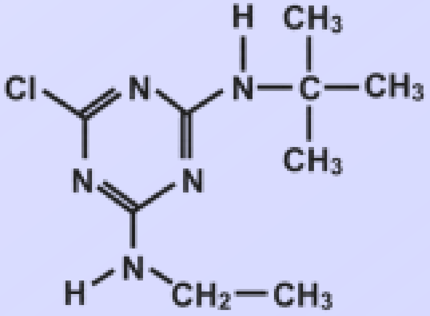
- Glutaraldehyde
  - SRB and broad spectrum
  - Effective in reducing environments
  - Reacts with cell walls and proteins



- DBNPA DiBromo-NitriloPropionAmide
  - Fast kill, broad spectrum
  - Hydrolyzes (breaks down) relatively quickly
  - Reacts with sulfhydryl groups on amino acids

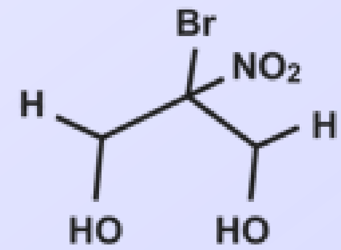


- Terbuthylazine (TBZ)
  - Photosynthesis inhibitor – effective only on algae
  - Synergistic with chlorine
  - Binds to proteins in chlorophyll-containing structures

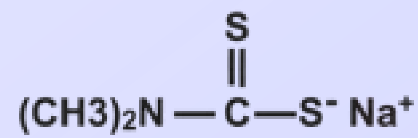


Common Metabolic Inhibitors

- BNPD (Bromo NitroPropane Diol)
  - Broad spectrum, but especially *Pseudomonas* bacteria
  - Hydrolyzes at higher pH
  - Directly attacks, or catalyzes oxidation of, cysteine amino acids



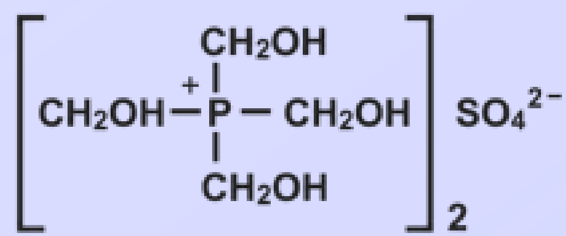
- Dithocarbamates
  - Broad spectrum, primarily fungi
  - Not compatible with chlorine
  - Chelate metal ions required by enzymatic processes



- MBT (Methylene Bis(Thiocyanate)
  - Effective on bacteria and fungi
  - Hydrolyzes quickly at pH >8
  - Not compatible with chlorine
  - Attacks amines, sulfhydryl groups, complexes iron

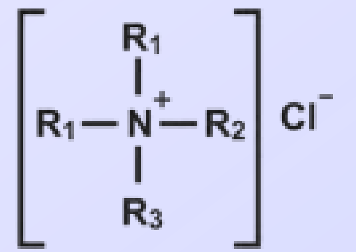
$NCS - CH_2 - SCN$

- THPS (Tetrakishyhydroxymethyl Phosphonium Sulfate)
  - Broad spectrum – effective in reducing environments
  - Oil field applications - Dissolves iron sulfide
  - Not compatible with chlorine
  - Reacts with disulfide amino acids in cell wall

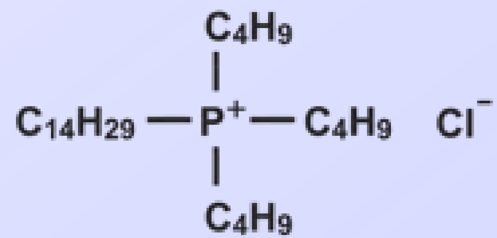


Common Cationic Surface Active Agents

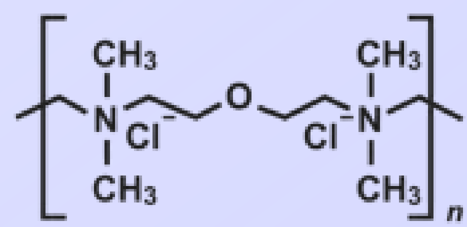
- Quaternary amines
  - ADBAC or DiAlkyl, Dimethyl Ammonium Chloride
  - Broad spectrum, but particularly algae & mollusks
  - Cationic – can interfere with anionic dispersants
  - Attack cell walls, affecting permeability



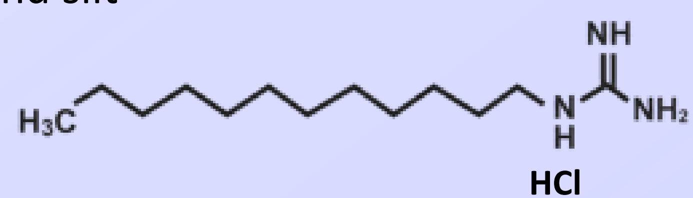
- TTPC – TributylTetradecylPhosphoniumChloride
  - Broad spectrum, especially SRB, mollusks, and algae
  - Disrupts biofilms
  - Cationic – can interfere with anionic dispersants



- Polyquaternary ammonium Compounds
  - Bacteria and very good on algae
  - Non-foaming
  - Prone to precipitate with anionic dispersants and silt

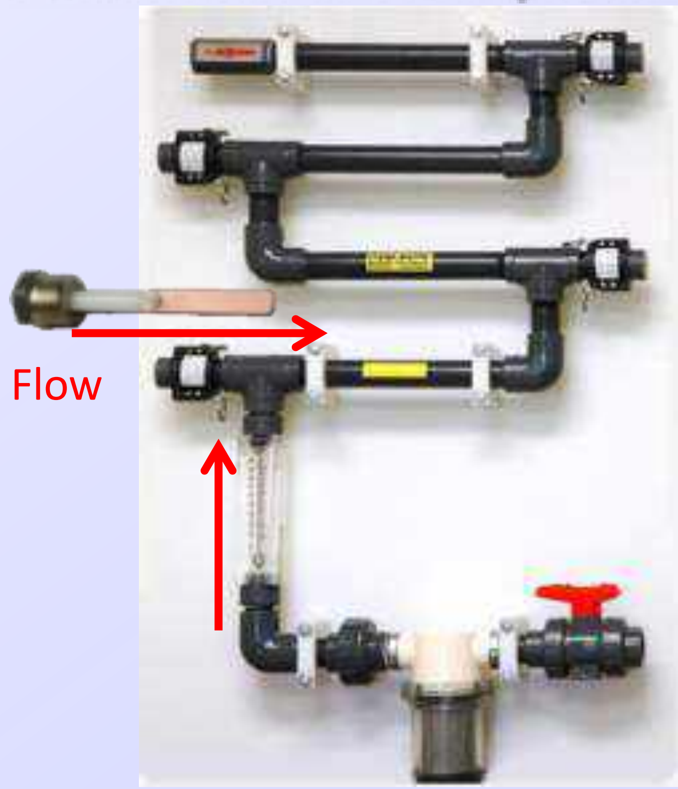


- DGH – DodecylGuanidine Hydrochloride
  - Broad spectrum, especially SRB and algae



- **Bypass coupon rack**
- PVC
  - 1” preferable ASTM
  - ¾” acceptable (to me)
  - Clear plastic can be useful, but cover it
- Match marks to align coupon so flow impinges on edge instead of flat side
  - Cam-lock nice feature vs. threaded
- Provides insight on corrosion rate, mechanism, deposition, & sessile bacteria
- Flow control should be added
  - 3-6 fps
- Pre-weighed test specimens
  - Metals representative of system
  - There is no ASTM standard surface finish
  - Clean and re-weigh after exposure
  - Copper coupons downstream of others
- Flow direction
  - Bottom to top (keep full)
  - From holder to tip (debris)
- By convention, on hot return water (more severe)
- By convention 90 days or 30 days (initial corrosion rates are higher)
- Shutoff /isolation valve
- Retractable coupon holders can also be used
  - Requires full port valve
  - Flow velocity is often erosive

Corrosion Coupons



Power Guidelines	Steel	Copper Alloys
Excellent	< 3mpy	<0.1 mpy
Acceptable	< 5 mpy	<0.3 mpy
Unacceptable	>7 mpy	>0.5 mpy

Corrosion Standards

Source: EPRI Open Cooling Water Chemistry Guideline

Table 0-3
Assessment of Carbon Steel General Corrosion Rates

mm/year (mm/y)		mils/year (mpy)		Description
From	To	From	To	
<0.03		<1.18		Negligible or Excellent
0.03	0.08	1.18	3.15	Mild or Very Good
0.08	0.13	3.15	5.12	Good
0.13	0.20	5.12	7.88	Moderate to Fair
0.20	0.25	7.88	9.85	Poor
>0.25		>9.85		Very Poor to Severe

- Higher than other industries
- Newer combined cycle plants often want <2 mpy
  - Despite having very little exposed steel

Thank You!

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