ΧΗΜΙΚΗ ΤΕΧΝΟΛΟΓΙΑ ΤΟΥ ΝΕΡΟΥ : ΠΡΟΒΛΗΜΑΤΑ ΚΑΙ ΛΥΣΕΙΣ ΒΑΣΙΣΜΕΝΕΣ ΣΕ ΧΗΜΙΚΕΣ ΠΡΟΣΕΓΓΙΣΕΙΣ

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Τμήμα Χημείας

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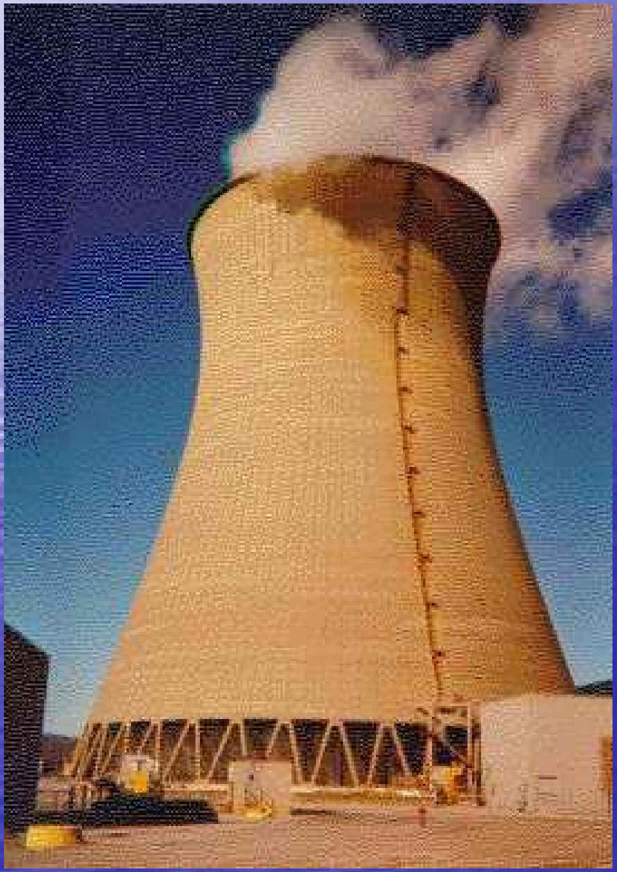
Agenda

- Introduction
- Basic Types of Cooling Systems
- Fundamentals of Cooling Water
- Cooling System Problems
- Treatment Programs
- Questions

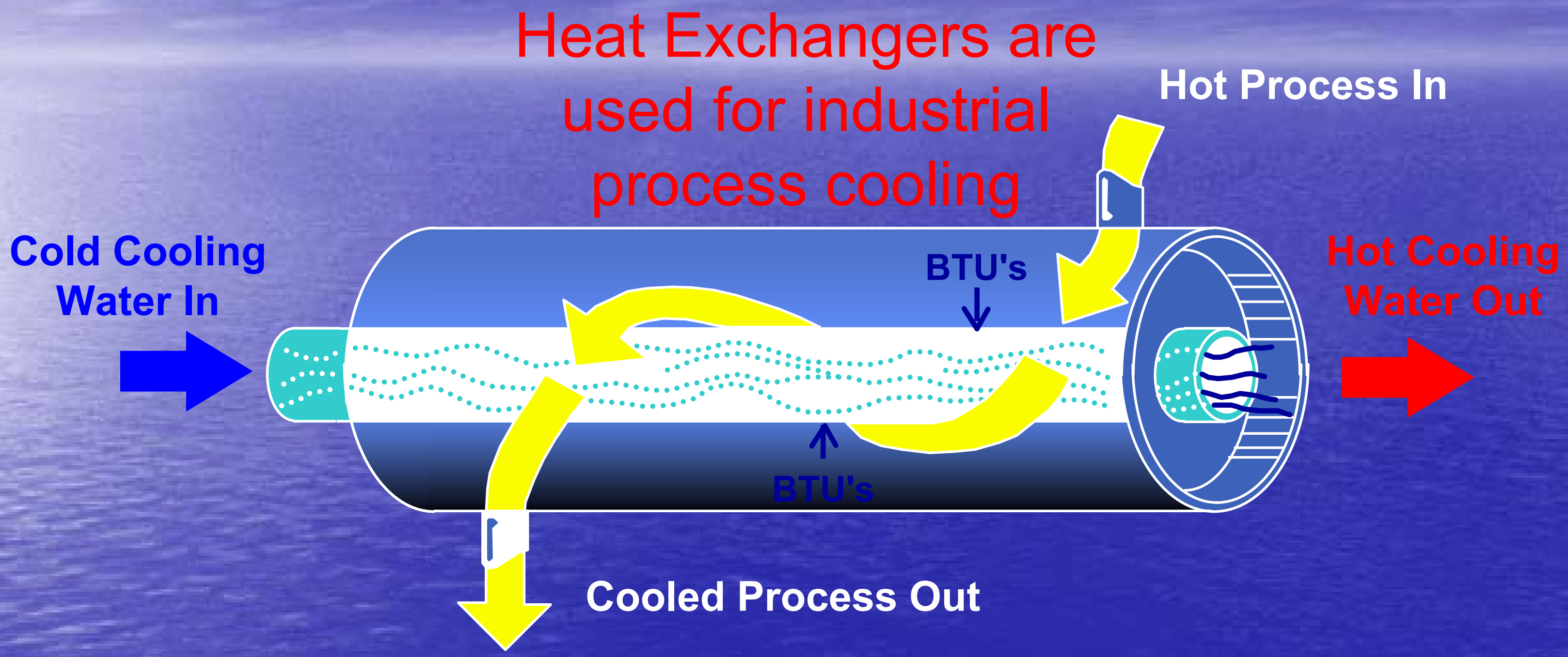
TYPES OF COOLING WATER SYSTEMS

THE COOLING PROCESS



- The purpose of cooling systems is to transfer heat from one substance to another
- The substance that gives up its heat is “cooled”
- The substance that receives the heat is the “coolant”

Simple Heat Transfer



<u>Common Measurement of Heat</u>

A BTU is the amount of heat required to raise the temperature of 1 lb. of water 1°F

Basic Types of Cooling Water Systems

There are three basic types of cooling water systems commonly used in industry…

1. Once Through
2. Closed Recirculating
3. Open Recirculating

ONCE THROUGH COOLING WATER SYSTEMS

Once Through Systems

- Simplest type of system
- Water passes water through heat exchangers only one time
- Discharged back to original source
- No recirculation occurs - mineral content of water remains unchanged

Once Through Systems

EXAMPLES

- Potable Water Systems
- Process Water
- General Service

CHARACTERISTICS

- Avg. Temp. Change: 4.4-5.6°C
- Amount of Water Used: Large ⇨

Once Through Systems

A once-through cooling water system uses large volumes of water to achieve the cooling process…

Once Through Systems

- Large volumes of water used
- Large volumes of water discharged
- Water intake source typically seawater, lake water, or river water
- Discharge water returned to the same source, but in a different location to prevent recycling

Once Through Systems

Advantages

- Low capital/operating costs: Pumps, etc.
- Water undergoes minimal temperature change

Disadvantages

- Large volumes of water required
- Environmental concerns: Thermal pollution
- Cost: Expensive to treat large volumes

Once Through Systems

Considerations

Environmental

- Intake/Discharge restrictions
- Plants under increased pressure to reduce water usage

Seasonal

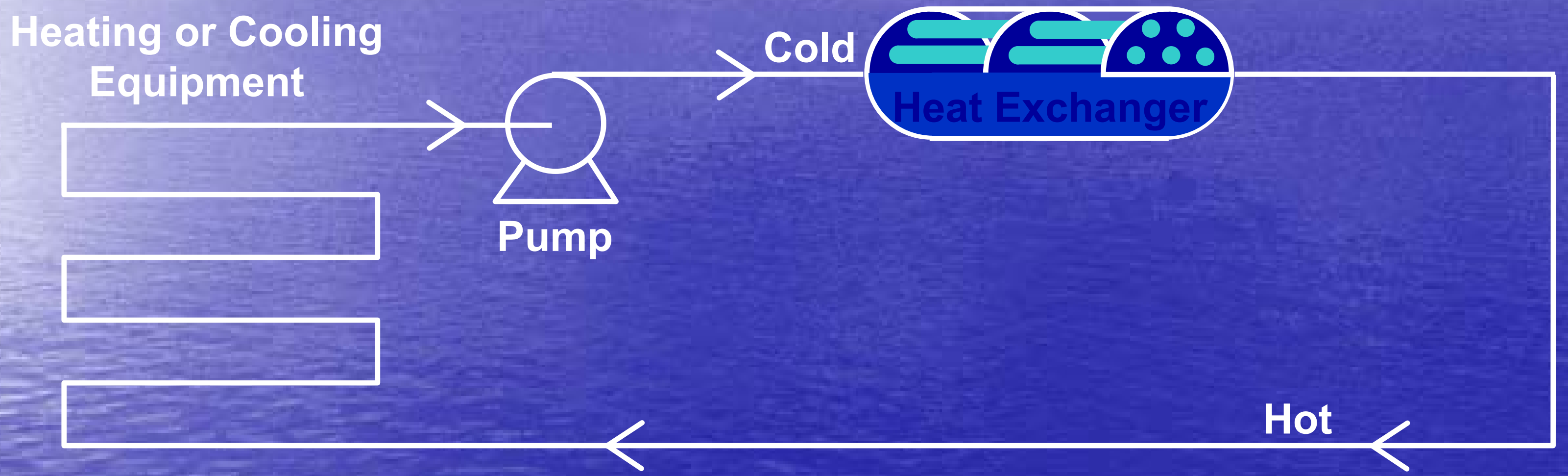
- Water must meet minimal requirements
- Availability: Reliable supply needed
- Quality: Degrades during 'dry times'

CLOSED RECIRCULATING WATER SYSTEMS

Closed Recirculating Systems

A closed recirculating system (closed loop) removes heat from a process by using a fixed volume of cooling water that is not open to the atmosphere. No water is evaporated.

Closed Recirculating Systems



EXAMPLES

- Diesel Engine Jackets
- Automobile Radiators
- Chilled Water Systems

CHARACTERISTICS

- Avg. Temp. Change: 5.6-10°C
- Amount of Water Used: Low

Closed Recirculating Systems

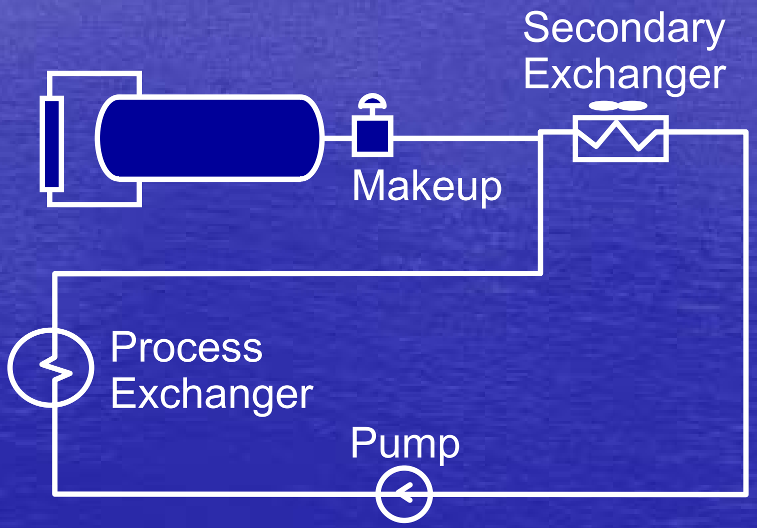
Situations When Closed Loops are Useful...

- Critical Processes: High heat flux systems
- Discharge Restrictions: Volume/thermal
- Water Source Limitations: When water is not plentiful
- Extended Equipment Life: Easier to control corrosion in closed systems (e.g. chillers)

Closed Recirculating Systems

Three Basic Parts of a Closed Loop…

- Pump
- Primary Heat Exchanger
- Secondary Heat Exchanger



TYPICAL SYSTEM

Closed Recirculating Systems

- Water temperatures range from -1 °C in a chiller system to 662 °C in a hot water heating system.
- No *theoretical* water loss from the system
- Water losses occur from leaks around expansion tanks, seals and valves
- Losses average 0.1-0.5% of system capacity per day

Closed Recirculating Systems

Major Problems

- Corrosion
  - Corrosion Product Build-up
  - Plugging: Small orifices, ports, valves
- Microbiological Growth/Fouling

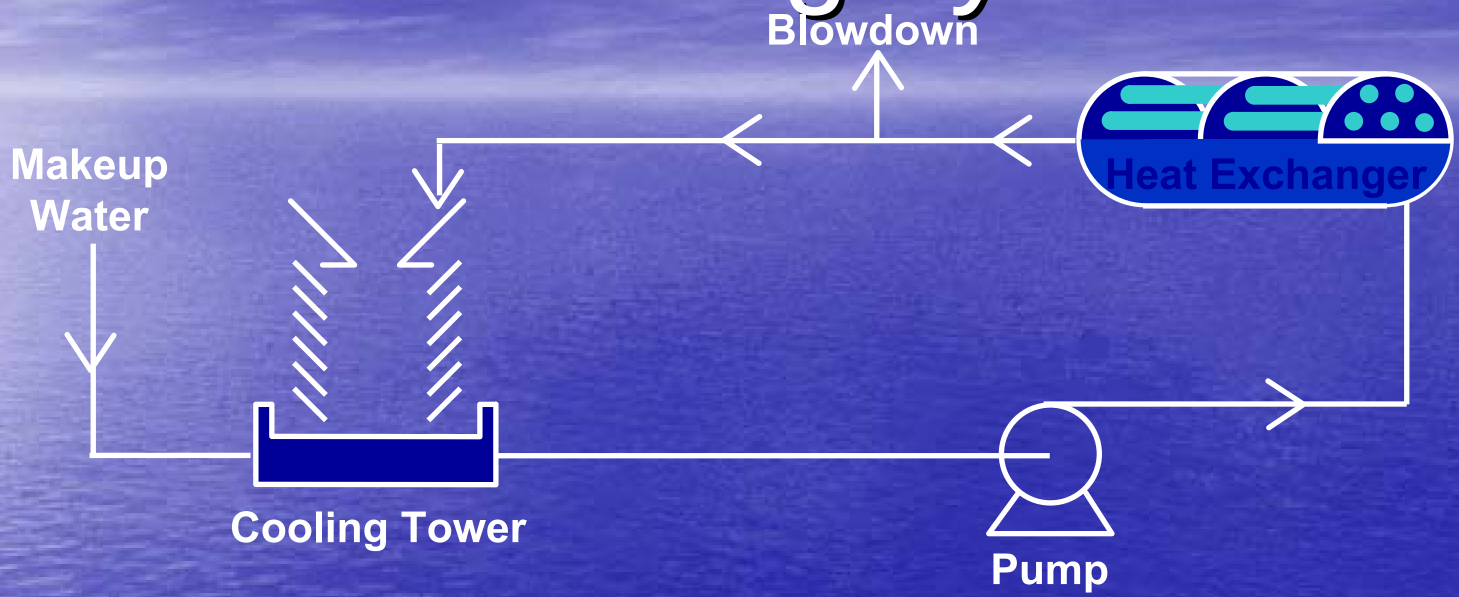
...Scale is generally not a concern in closed loops

OPEN RECIRCULATING WATER SYSTEMS

Open Recirculating Systems

Open recirculating systems are open to the atmosphere at the tower. As the water flows over the tower, heat picked up by the process is released by evaporation. The cooling water then returns to the heat exchangers to pick up more heat.

Open Recirculating System



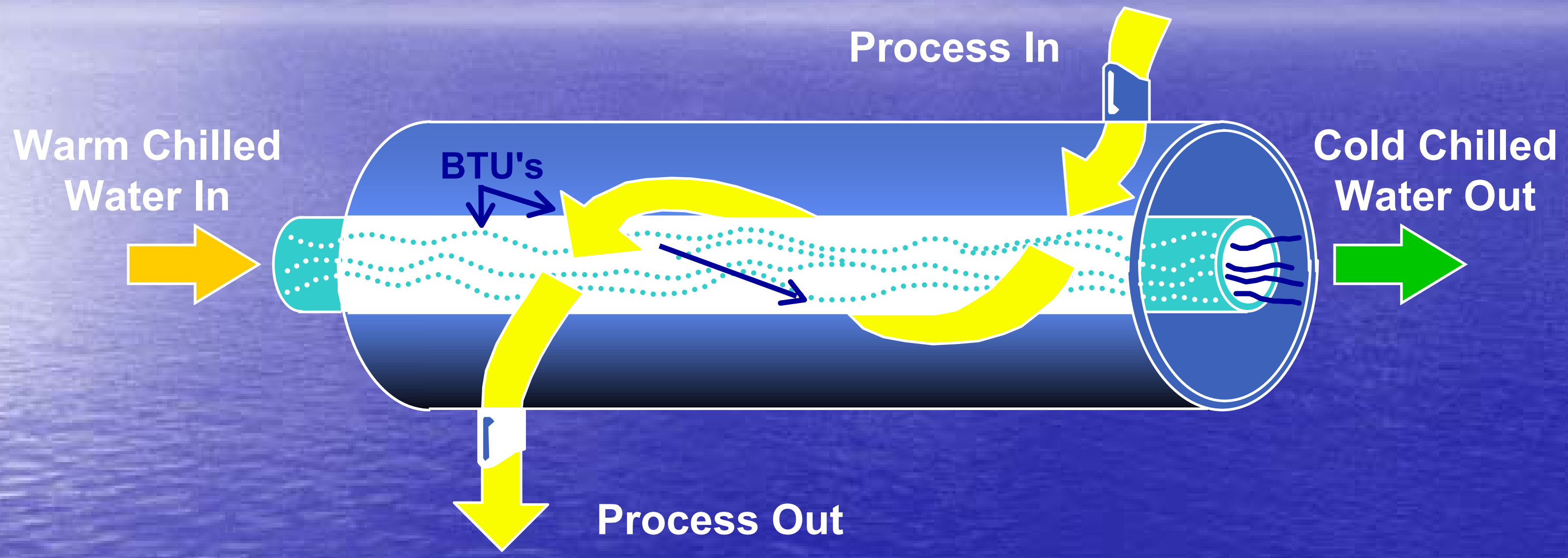
EXAMPLES

- Spray Ponds
- Cooling Towers
- Evaporative Condensers

CHARACTERISTICS

- Avg. Temp. Change: 11.1-16.7°C
- Amount of Water Used: Moderate

Heat Transfer Principle



Open recirculating systems work on the basis of two principles...

- HEAT TRANSFER
- EVAPORATION

Open Recirculating Systems

Heat Transfer

- Process in which heat is transferred from one substance to another.

Evaporation

- Process by which the hot cooling water releases its heat to the atmosphere so that it can return cool water back to the heat exchangers

Open Recirculating Systems

Cooling tower provides two conditions that enhance the evaporation process…

- Break water into tiny droplets, thus providing more escape routes for water molecules to evaporate.
- Fans provide rapid flow of air through the tower which removes evaporated water molecules and allows even more to escape.

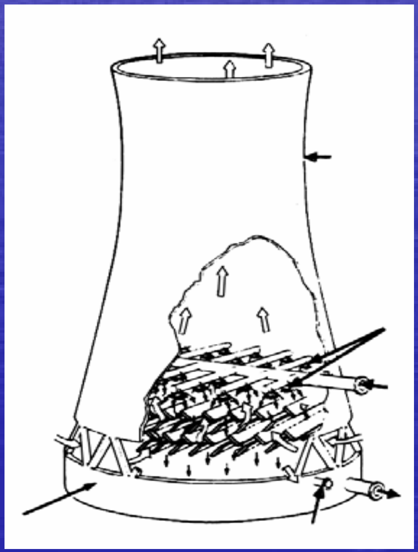
Open Recirculating Systems

Three Classifications of Open Recirculating Cooling Towers...

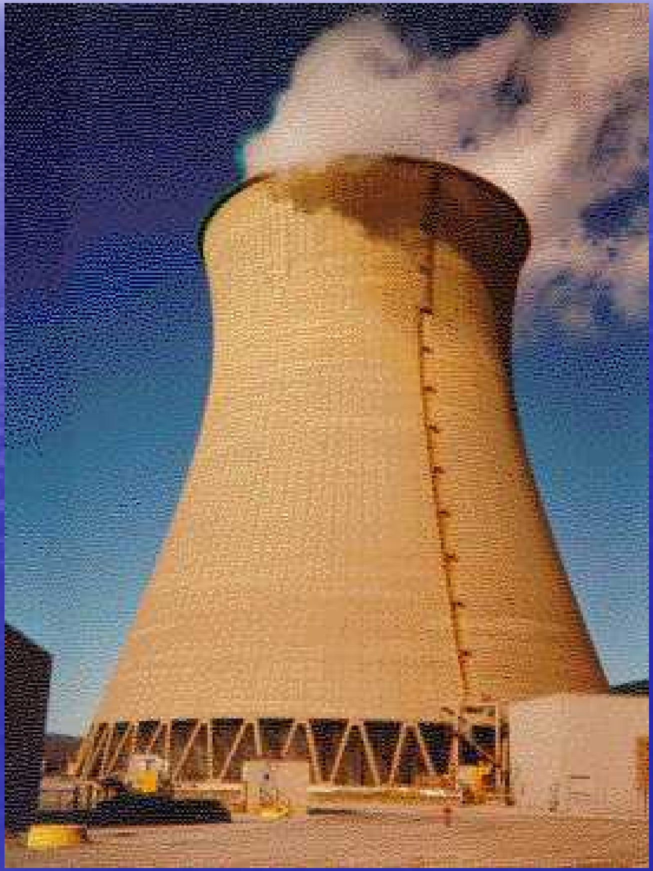
1. Natural Draft
2. Mechanical Draft
3. Evaporative Condensers

Natural Draft Cooling Tower

- Hot air rises…
- Draws cool, dry, outside air through the water, which enhances evaporation
- Moist, warm air naturally rises up & out of the tower
- Shape causes air to move more quickly through the the lower section, where the water is flowing



Hyperbolic Natural Draft Cooling Tower



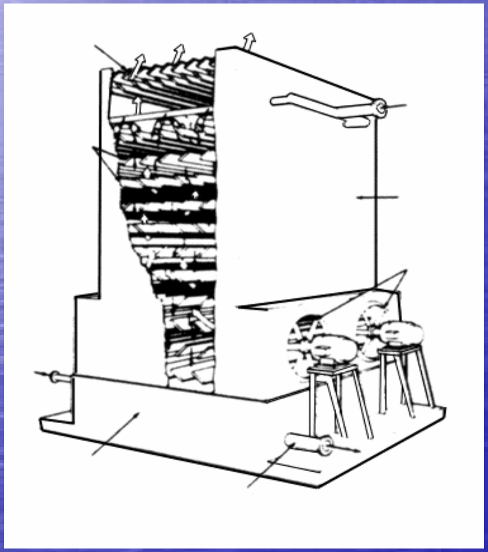
Mechanical Draft Towers

Use mechanically operated fans to move air through the cooling tower...

Forced Draft Towers

Induced Draft Towers

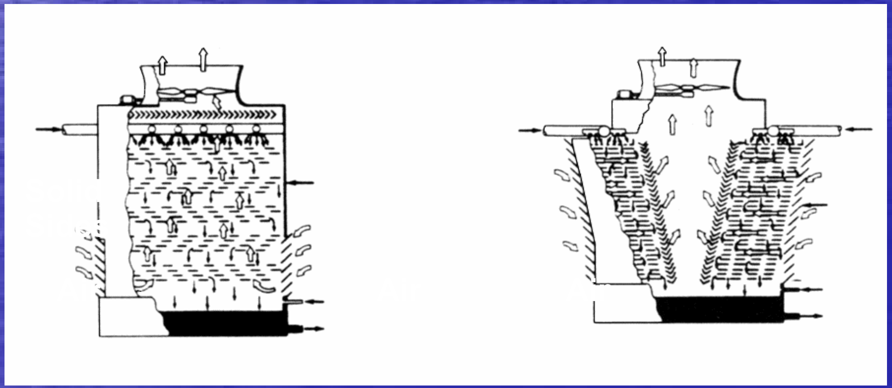
Forced Draft Towers



- Push air through tower
- Use limited to smaller systems due to high horsepower required

Induced Draft Towers

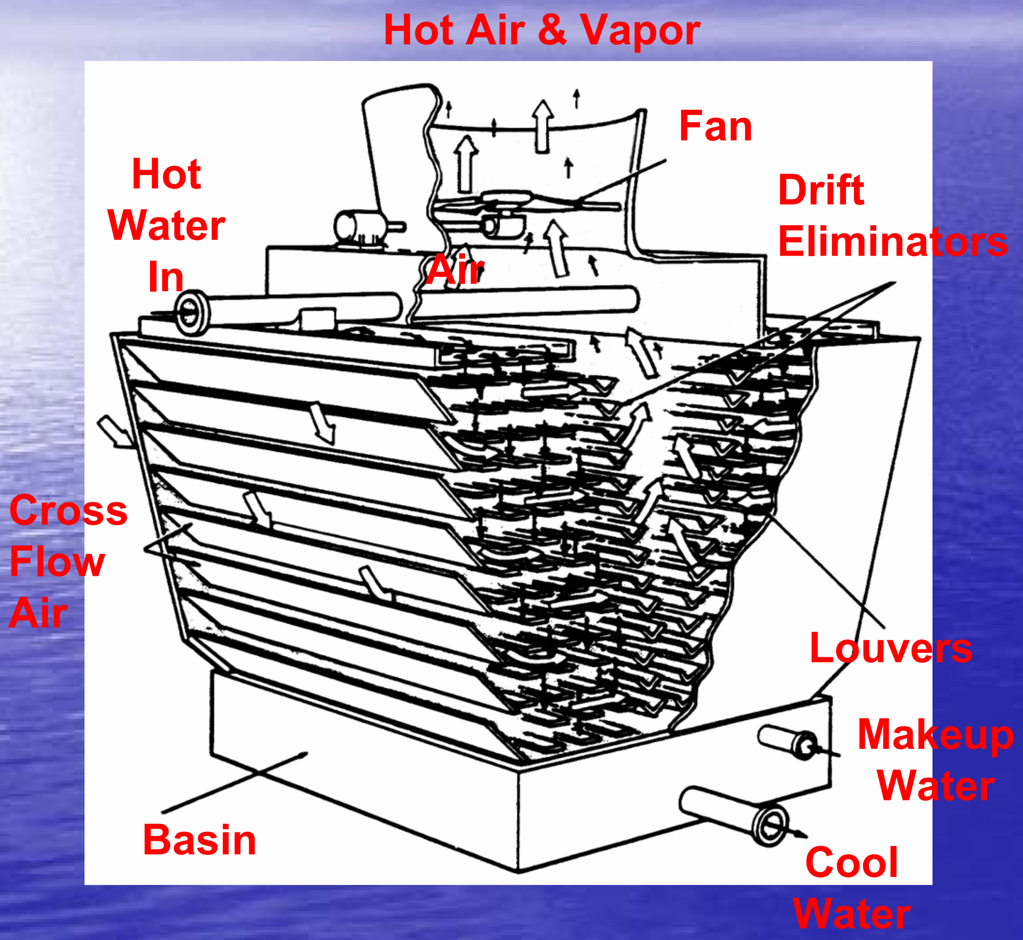
- Pull air through tower
- Classified as either counterflow or crossflow
- Classification depends on flow of air with respect to cooling water



Evaporative Condenser

- A cooling tower that combines a closed recirculating cooling system with an open recirculating one
- Instead of having the recirculating water open to atmosphere at the tower, the water is carried inside of cooling coils

Cooling Tower Components



- Basin
- Cold Well
- Drift Eliminators
- Louvers
- Cells
- Fill
- Spray Nozzles

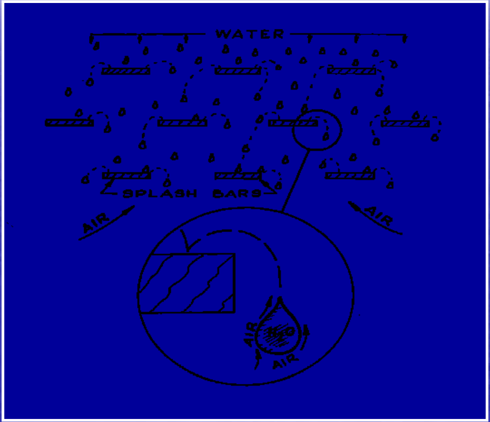
Cooling Tower Components

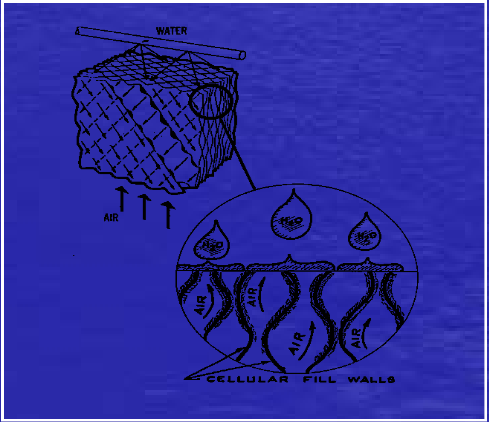
- **TOWER BASIN:** Area under the cooling tower where CW is collected and held until it is pumped back to the exchangers.
- **COLD WELL:** Deeper part of tower basin where the screens & pumps are installed to circulate the water.
- **DRIFT ELIMINATORS:** Removes entrained water droplets from the air leaving the tower. The moisture laden air is forced to change direction and water droplets are removed.
- **LOUVERS:** Sloping boards on the outside of the towers where air enters. Prevent water spray from leaving the tower.
- **CELLS:** Cooling towers are divided by partitions that separate it into distinct sections. Each cell has its own fan system.

Tower Fill

- Increases contact between air & water
- Breaks water into small drops or a film as it cascades through the tower
- Two types of fill

Splash Fill





Film Fill

Tower Fill

Splash-Type Fill:

- Bars made of wood or plastic are used to break water into droplets

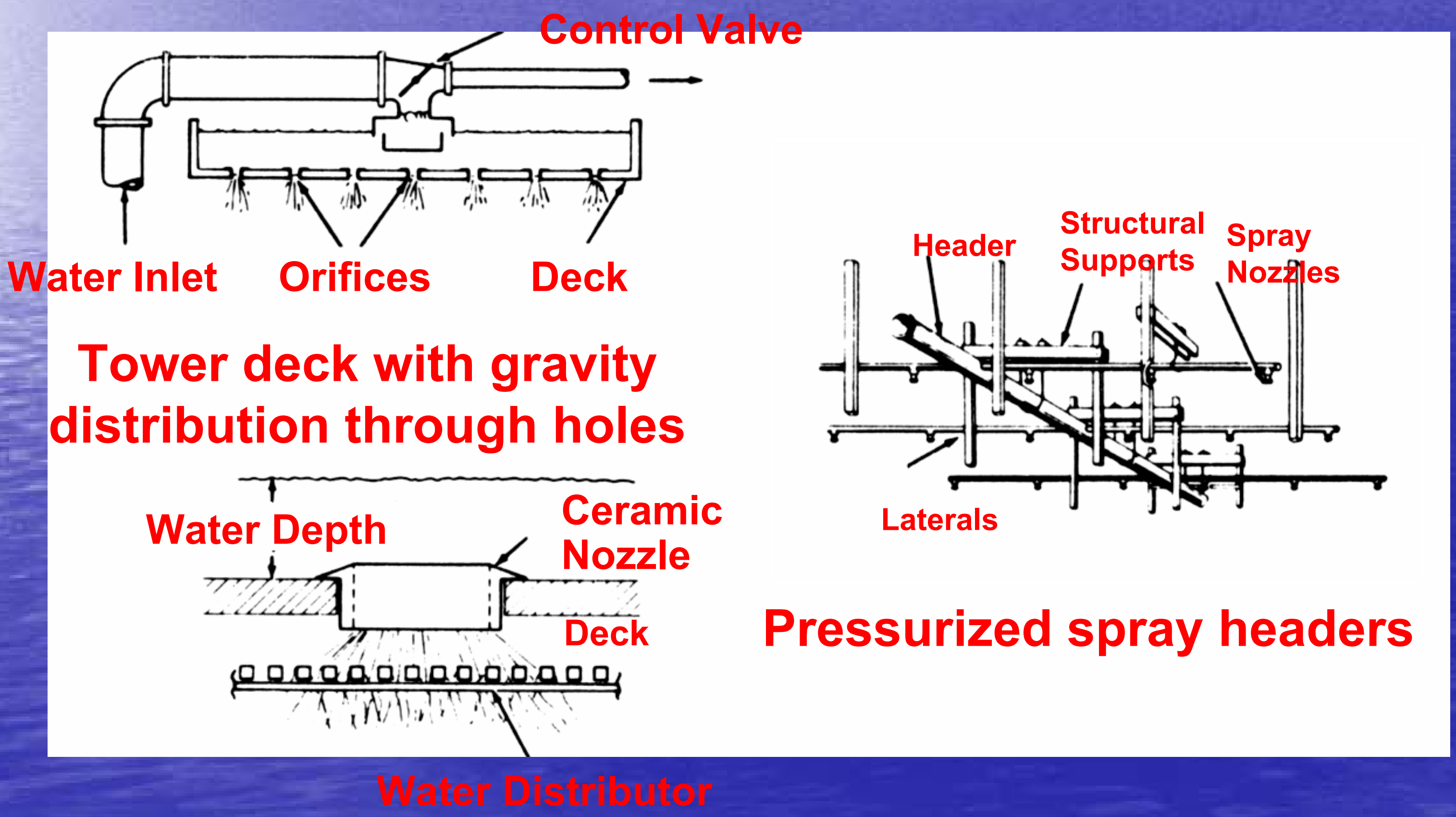
Film-Type Fill:

- Plastic, wood or metal packing that divide inlet water into thin films which maximize exposed surface area
- Film packing allows greater air flow and generally results in improved tower efficiency

Spray Nozzles

Inlet Water Distribution System

Spreads hot water uniformly across the top of the tower



Open Recirculating Water Systems

- Efficient operation of the cooling water system is critical to the production process in any industrial plant.
- Optimal operation of cooling water systems are dependent on two things:
  ① Maintain good mechanical control
  ② Maintain good chemical control

FUNDAMENTALS
OF
COOLING WATER

Why Use Water for Cooling?

- Plentiful; Readily Available; Cheap
- Easily Handled: Pumpable
- Can carry large amounts of heat
- Does not expand/contract much at normally encountered temperatures
- Does not decompose

Why Use Water for Cooling?

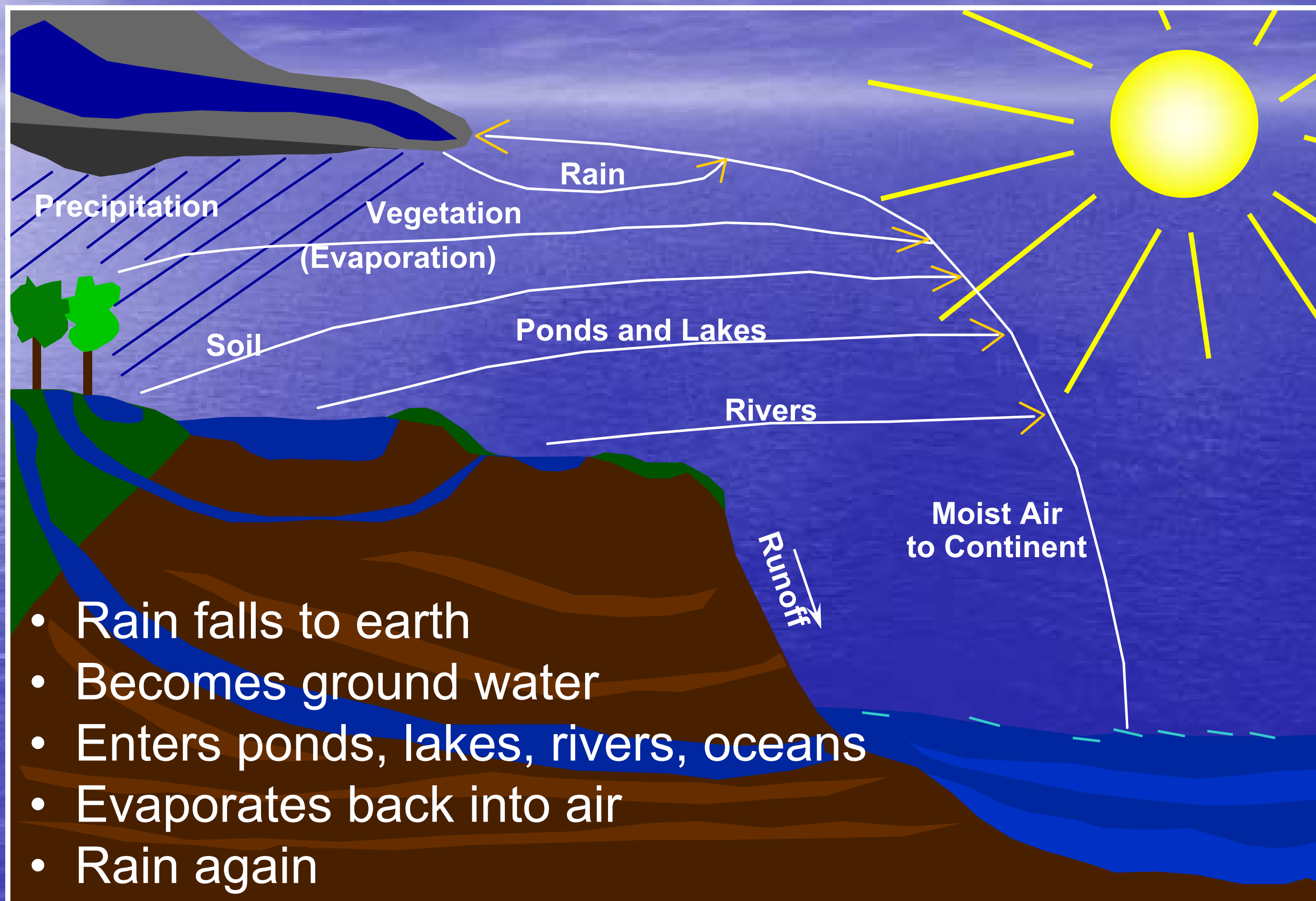
- Specific Heat: Measure of how well a substance absorbs heat
- Water can absorb more heat than virtually any other substance that would be considered for industrial cooling
- Minor increases in temperature
- Minimal environmental impact
- Everything is compared to water: Specific Heat = 1.0

Why Isn't Water Perfect for Cooling?

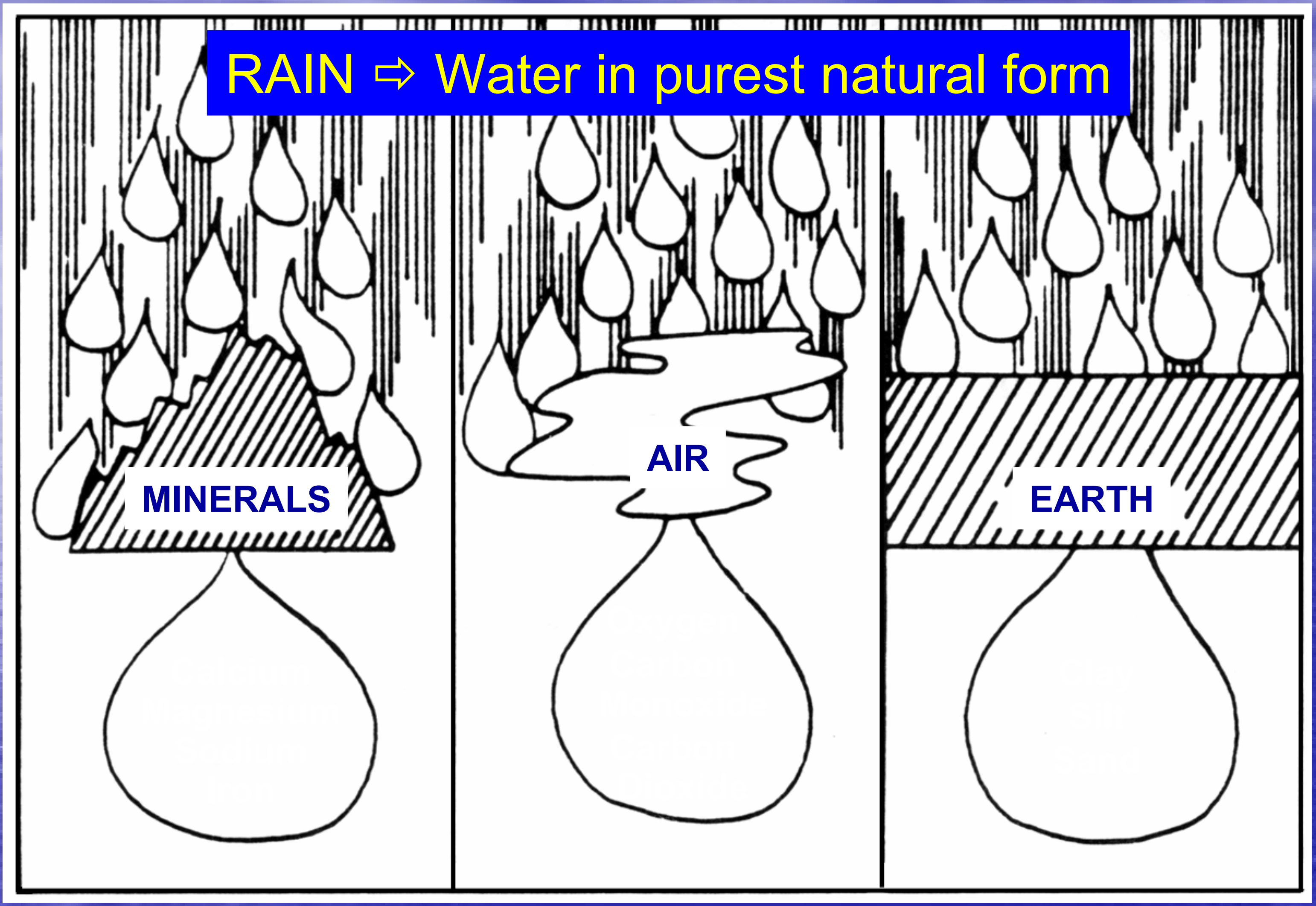
- Dissolves everything it touches: Metal; earth; stone
- Unique dissolving ability has earned water the title…

Universal Solvent

Hydrologic Cycle



- Rain falls to earth
- Becomes ground water
- Enters ponds, lakes, rivers, oceans
- Evaporates back into air
- Rain again



(1) Dissolved Solids (2) Dissolved Gases (3) Suspended Matter

Water contains 3 types of impurities

Two Sources of Water

Surface Water

- Low in dissolved solids
- High in suspended solids
- Quality changes quickly with seasons & weather

Ground Water

- High in dissolved solids
- Low in suspended solids
- High in iron & manganese
- Low in oxygen, may contain sulfide gas
- Relatively constant quality & temperature

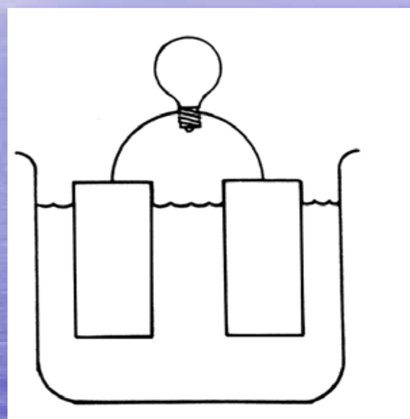
What Chemical Properties of Water Are Important?

Important Properties of Water

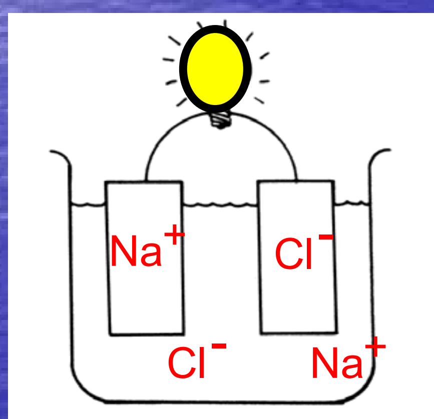
1. Conductivity
2. Hardness
3. Alkalinity
4. pH

Conductivity

Pure Distilled Water



Distilled Water with Salt



- Measure of water's ability to conduct electricity
- Pure water will not conduct an electrical current
- As minerals accumulate, conductivity increases

Conductivity

- Proportional to amount of dissolved solids in the water
- Used to measure TDS
- Micromhos (μmhos)
- Calcium, magnesium, alkalinity, silica, sodium
- ⇧ Conductivity
- ⇧ Corrosion/Scale Potential

Did you know?

The oceans alone contain enough dissolved matter to bury all of the land on earth under 112 feet [34 meters] of mineral deposits

Hardness

- Amount of Calcium & Magnesium present
- Hardness reacts with other minerals such as carbonate alkalinity, phosphate, & sulfate
- Tendency to come out of solution & form hard deposits in heat exchangers
- Ca/Mg inversely soluble with temperature
- Potential for hardness deposition affected by alkalinity levels

Alkalinity

- Carbonate & Bicarbonate Ions
- React with hardness to form scale (e.g. Calcium Carbonate)
- Must maintain within specified range
- ⇧ Alkalinity: Scale/deposition
- ⇩ Alkalinity: Corrosion

pH

Measure of hydrogen ions present in water...

H+ ions ⇧ -- pH ⇩

H+ ions ⇩ -- pH ⇧

pH

- pH 7.0 ⇨ ‘Neutral’ not ‘pure’ water
- Balance between hydrogen & hydroxyl ions in the water
- Maintaining good pH control critical to cooling system operation
- Short pH excursions can be detrimental
- Low pH: Corrosion
- High pH: Scale

Evaporation

Process by which hot water returns from the unit heat exchangers, releases it’s heat to the atmosphere, is cooled, and returns back to the process

Evaporation

Each 10°F [6°C] drop in temperature results in an avg. 0.85% of recirculated cooling water

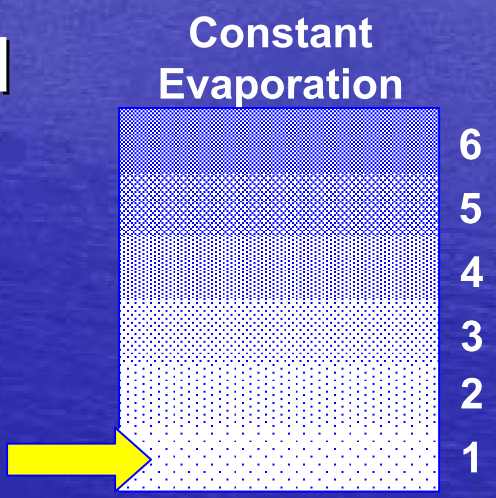
$$ER = (RR)*(dT/10)*(.85)$$

Where:

- ER: Evaporation Rate [gpm]
- RR: Recirculation Rate [gpm]
- dT: Temp drop across tower [DegF]

Concentration of Dissolved Solids

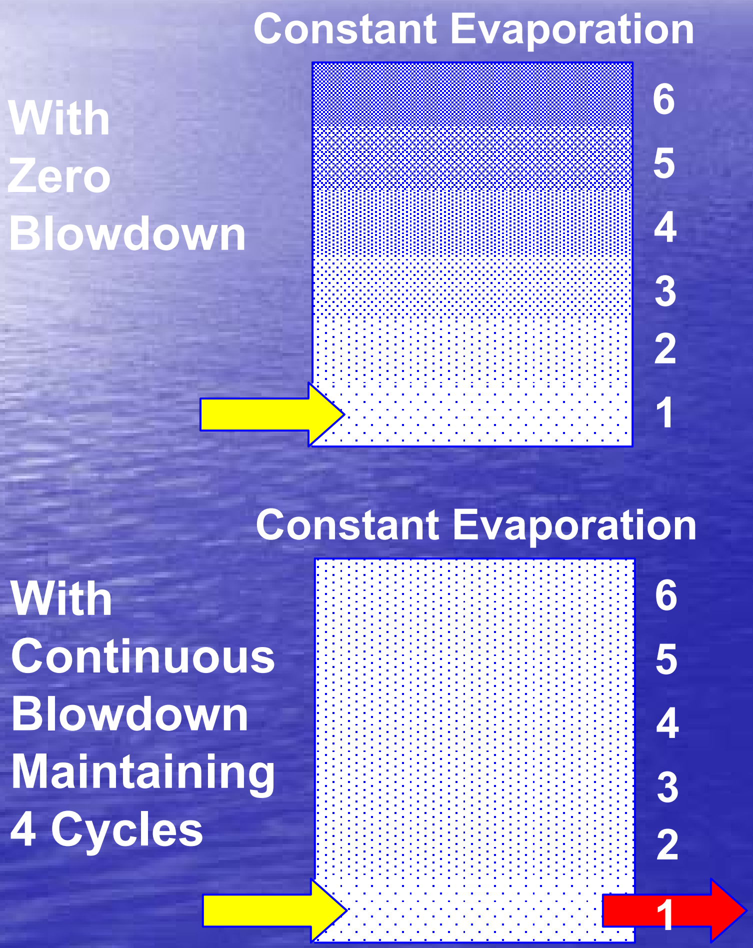
- Only pure water can evaporate
- No dissolved solids leave the liquid water
- If there are no other water losses from the system, the evaporation process causes an increase in the concentration of dissolved solids in the recirculating cooling water.



Concentration of Dissolved Solids

- Mineral scale will form if the dissolved solids concentration in the cooling water becomes too high
- Supersaturation

Impact of Blowdown on Concentration Ratio



Blowdown:

- Deliberate discharge of water to prevent the dissolved solids from getting to high

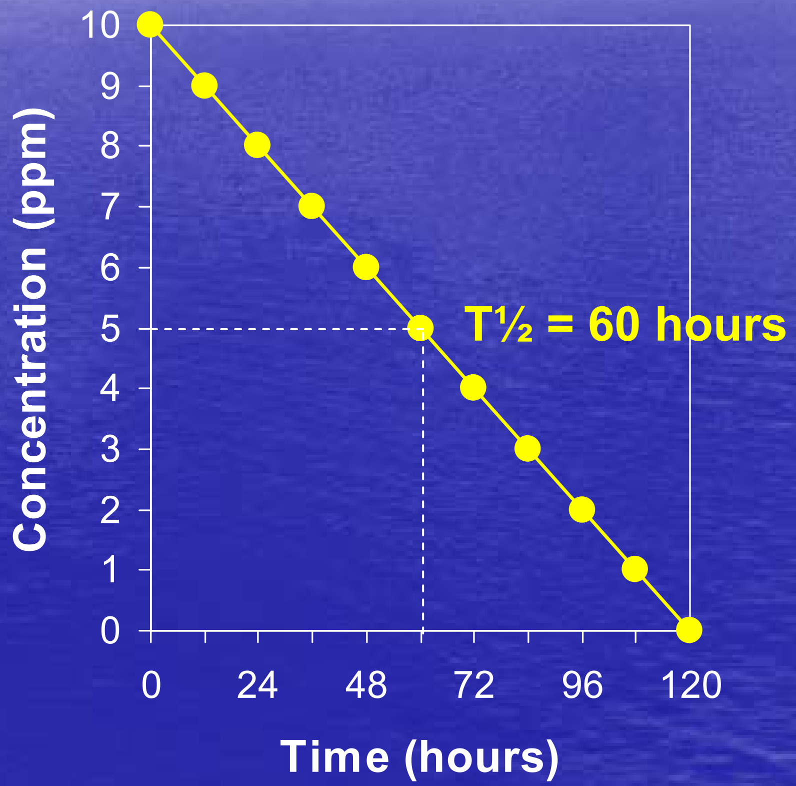
Makeup Water

- Amount of water required to replace water lost by evaporation and blowdown

Makeup = Evaporation + Blowdown

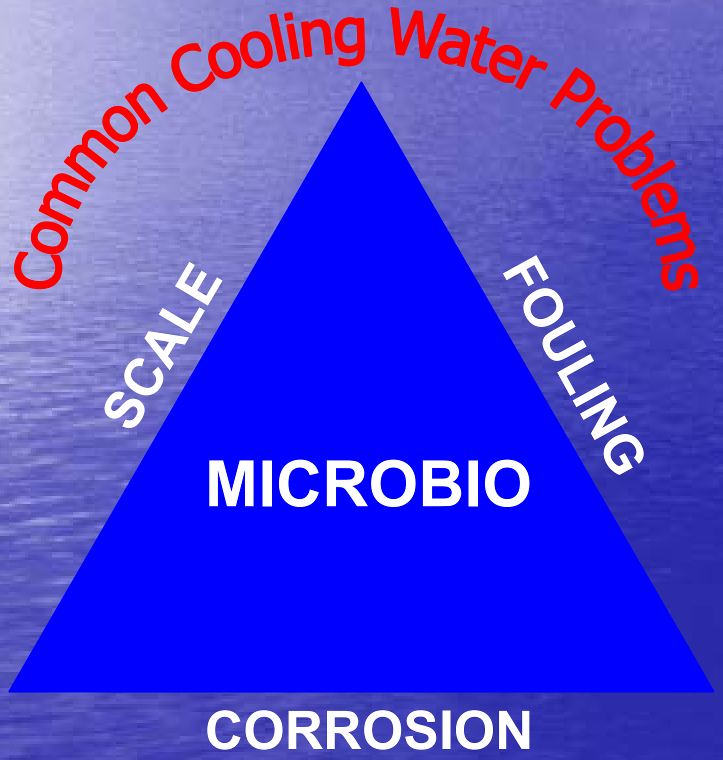
Holding Time Index

- Amount of time required for the concentration of any ion to reach one-half of it's original concentration
- Important for proper selection & dosing of treatment chemicals



COMMON COOLING SYSTEM PROBLEMS

Cooling System Problems



Left unchecked these problems cause

- Loss of heat transfer
- Reduced equipment life
- Equipment failures
- Lost production
- Lost profits
- Increased maintenance costs
- Plant shutdown

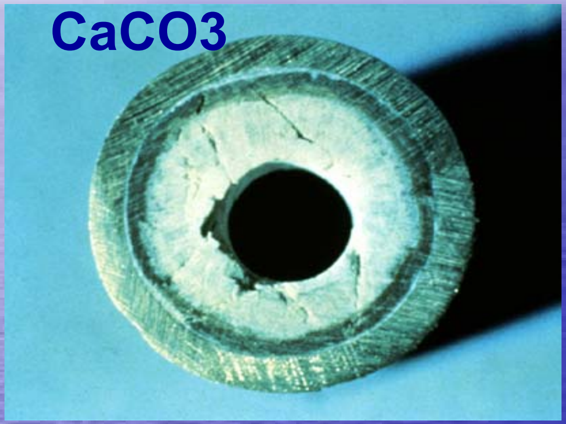
MINERAL SCALE

Mineral Scale

- Cooling Water contains many different minerals -- normally these minerals are dissolved in the water
- Under certain conditions minerals can come out of solution and form into hard, dense crystals called SCALE

Precipitation

Mineral Scale



Scaled Heat Exchanger Tubes

Common Scales

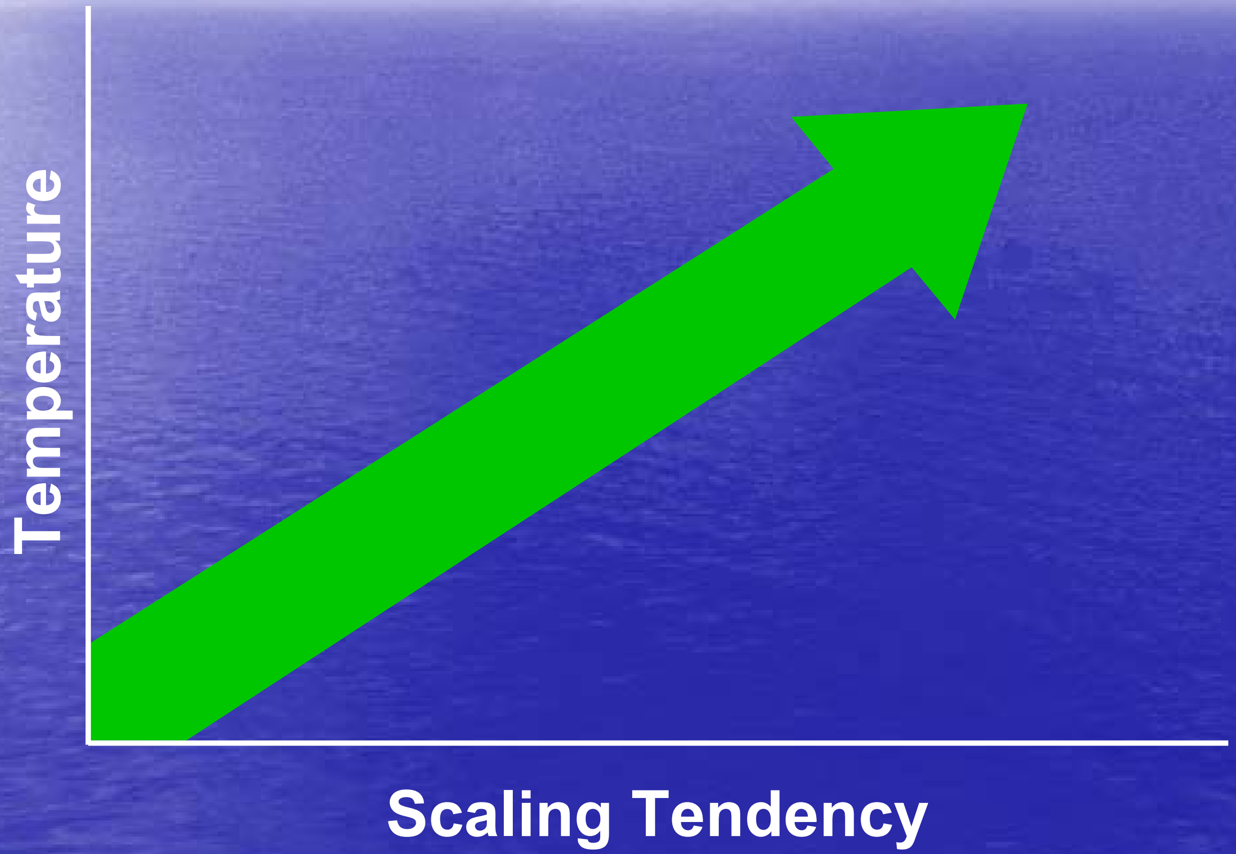
- Calcium Carbonate
- Magnesium Silicate
- Calcium Phosphate
- Calcium Sulfate
- Iron Oxide
- Iron Phosphate
- Others...

Mineral Scale

The Following Factors Affect Scale Formation…

- ⇧ Mineral Concentration
- ⇧ Water Temperature
- ⇧ Water pH
- ⇧ Suspended Solids
- ⇩ Water Flow Velocity

Temperature & Scale Tendency



Mineral Scale

- Scale forms in hot areas of cooling systems
- Reduces heat transfer efficiency
- Mechanical/Chemical cleaning
- Under deposit corrosion (pitting)
- Plant shutdown
- Equipment replacement

Preventing Mineral Scale

- Limit concentration of scale forming minerals: Blowdown, clarify/filter MU
- Feed acid to reduce pH & alkalinity: Reduces scaling -- increases corrosion
- Mechanical design changes: Increase water velocity, backflush, air rumble
- Apply chemical scale inhibitors

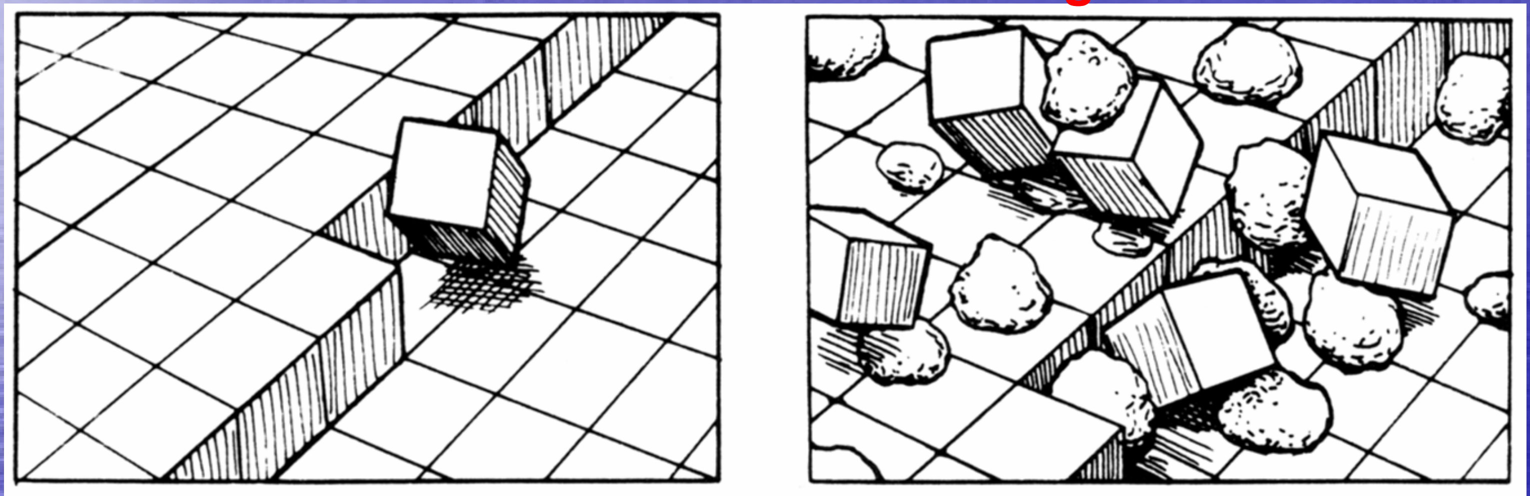
Mineral Scale

Three Classifications Of Scale Inhibiting Chemicals Are...

- Crystal Modifiers
- Sequestrants
- Dispersants

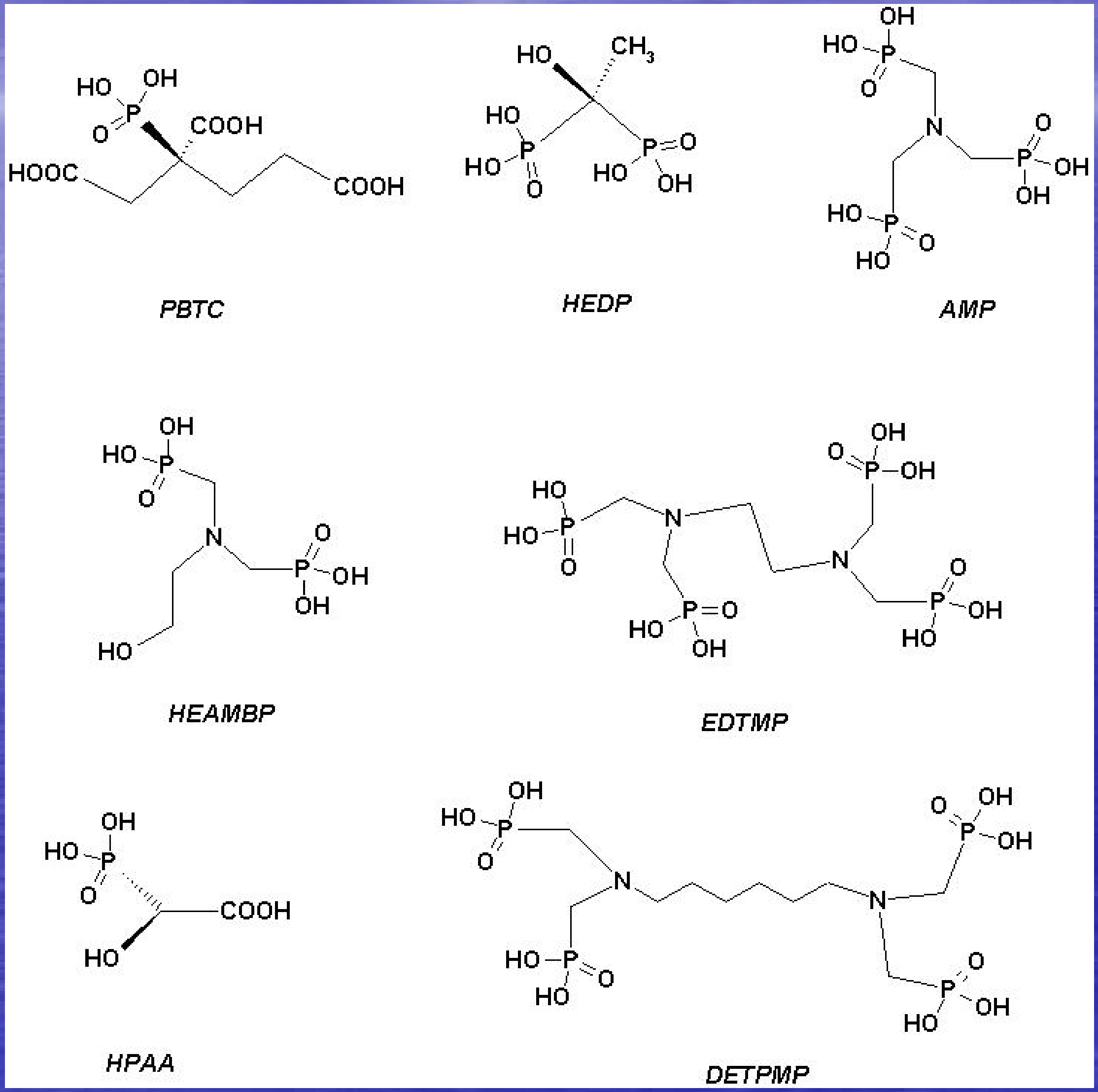
Crystal Modifiers

Minerals do not align in a tight matrix



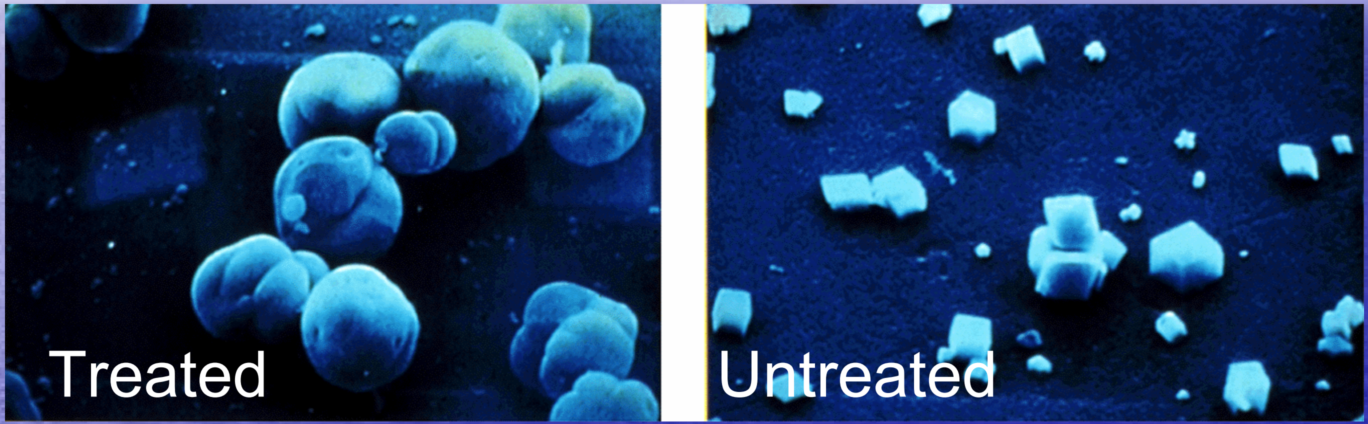
Organophosphonates & organic dispersants distort the crystal structure of scale so that it does not become tightly adherent

Representative Phosphonates



Sequestrants

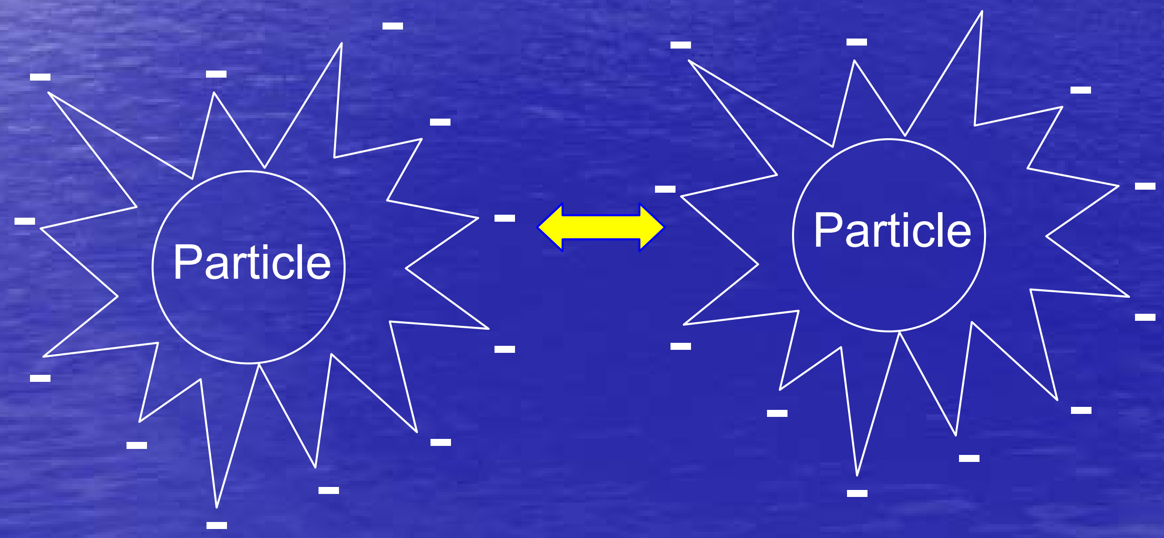
$CaCO_3$



Polyphosphates & anionic dispersants form a complex with troublesome minerals to prevent them from forming scale

Dispersants

Compounds such as polyacrylates are large molecules that impart a charge causing scale forming minerals to repel each other

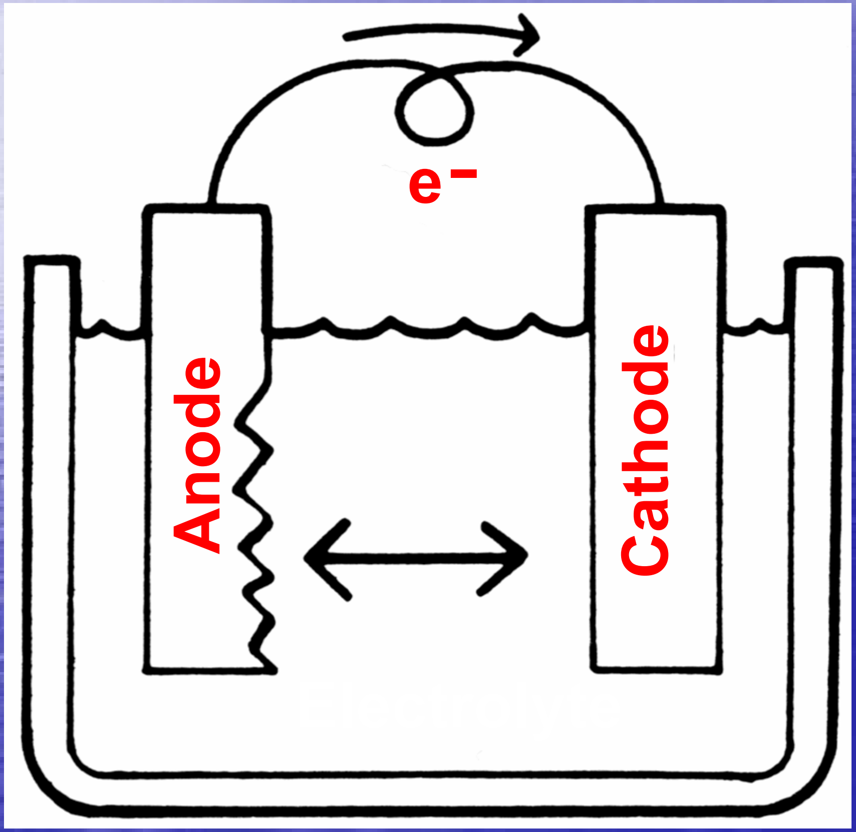


CORRORSION

CORROSION

Corrosion is the mechanism by which metals are reverted back to their natural “oxidized” state

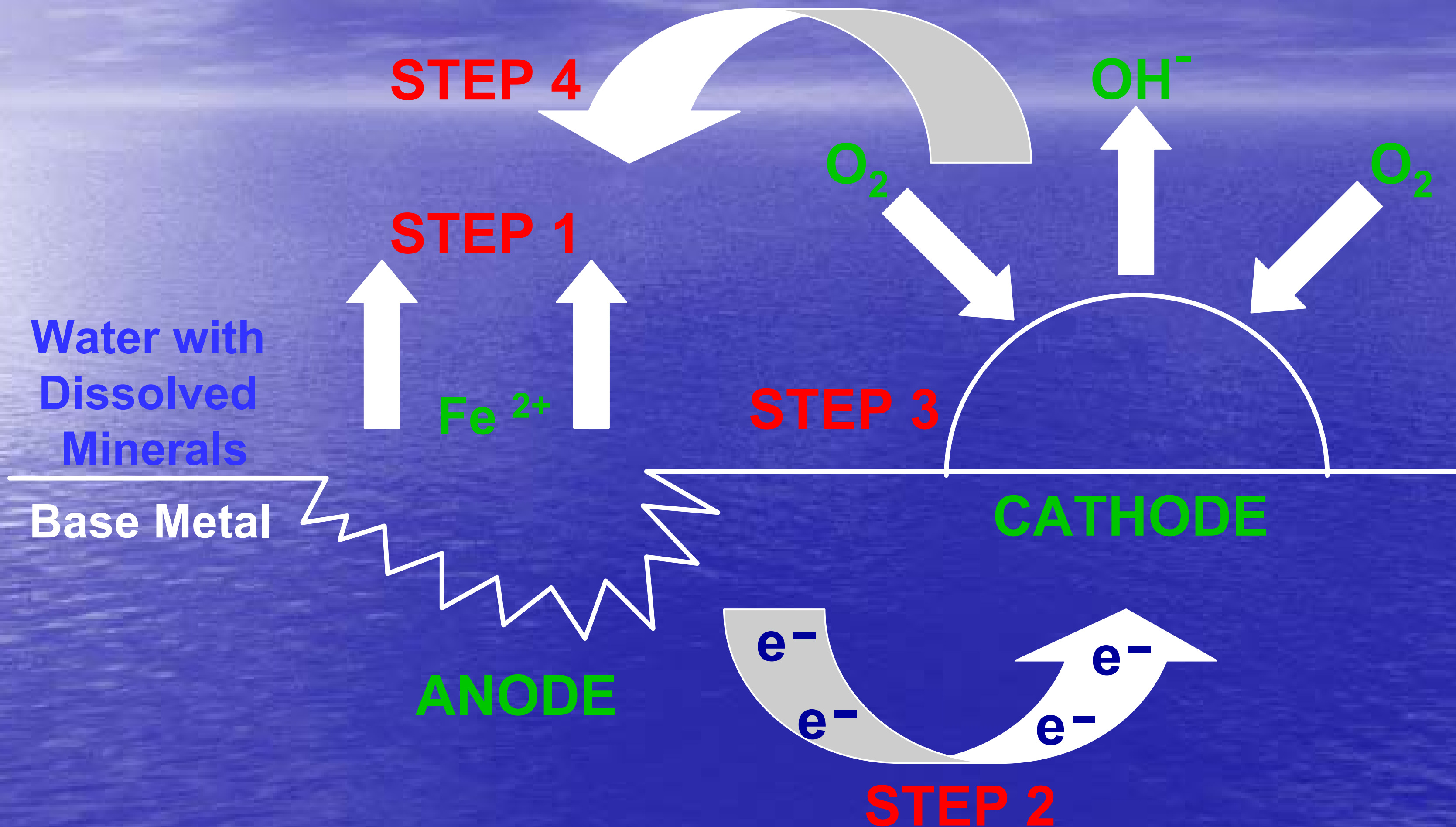
Corrosion



Battery Analogy

- Anode
- Cathode
- Electrical Circuit
- Metal lost at anode

Simplified Corrosion Cell



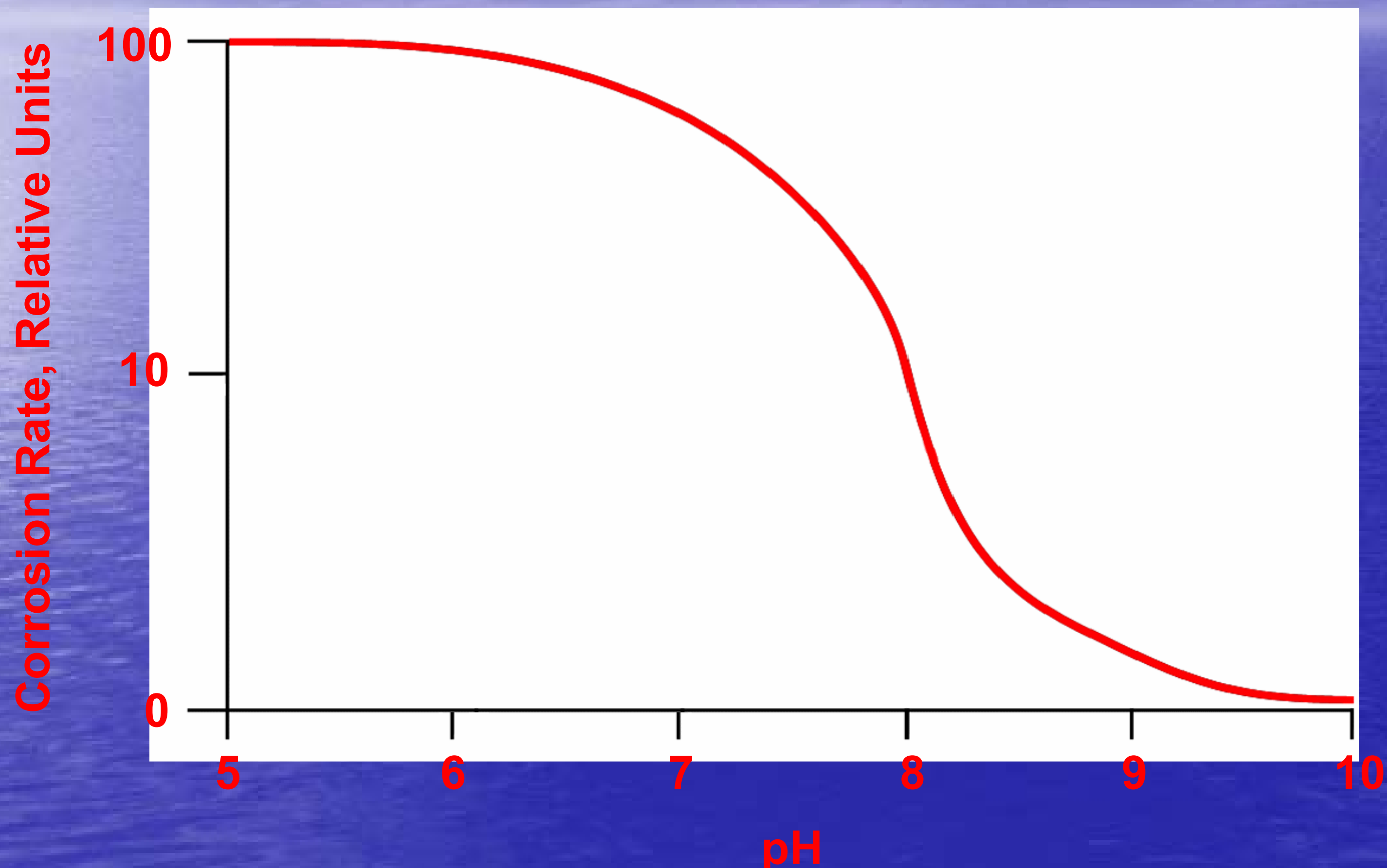
Four Step Corrosion Model

- Step 1: At the anode, pure iron begins to break down in contact with the cooling water. This step leaves behind electrons.
- Step 2: Electrons travel through the metal to the cathode.
- Step 3: At the cathode, a chemical reaction occurs between the electrons and oxygen carried by the cooling water. This reaction forms hydroxide.
- Step 4: Dissolved minerals in the cooling water complete the electrochemical circuit back to the anode.

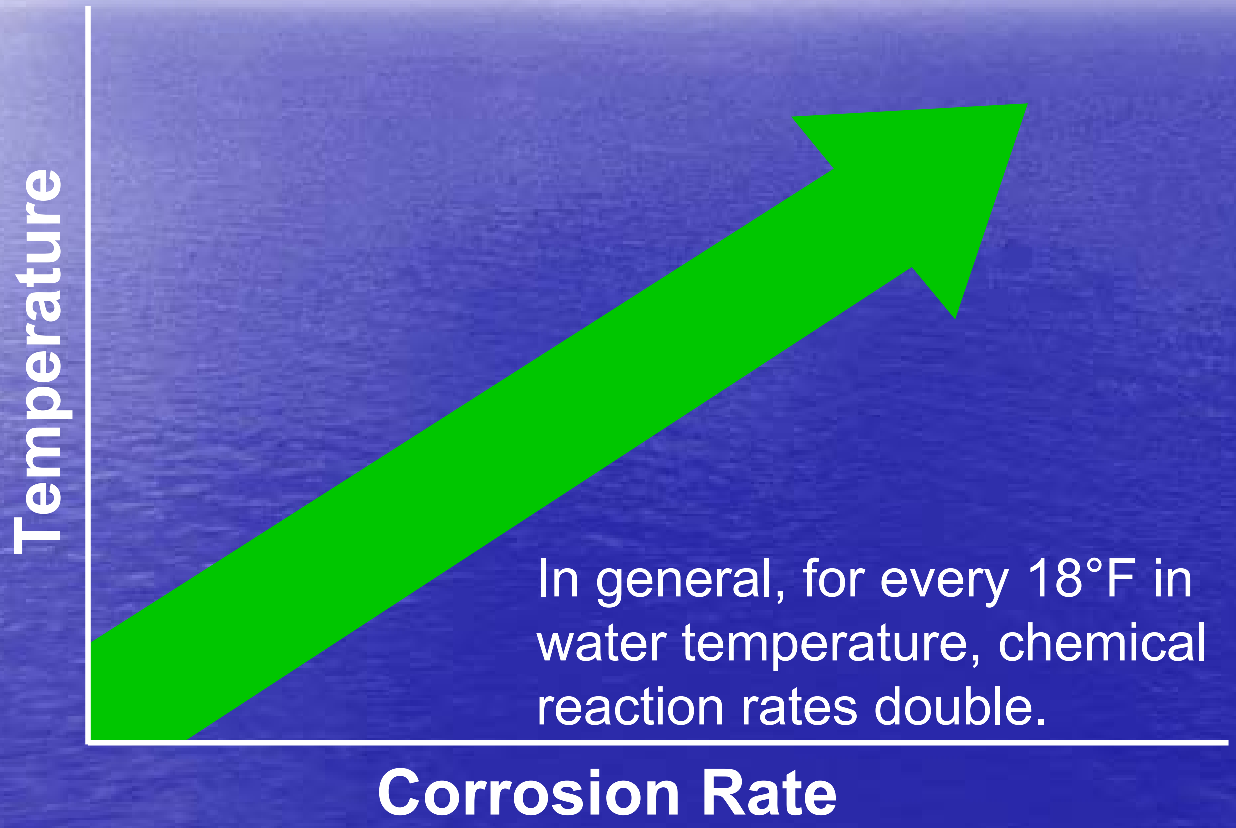
Factors Influencing Corrosion

- pH
- Temperature
- Dissolved Solids
- System Deposits
- Water Velocity
- Microbiological Growth

Corrosion Vs. pH



Corrosion Vs. Temperature



Other Causes of Corrosion

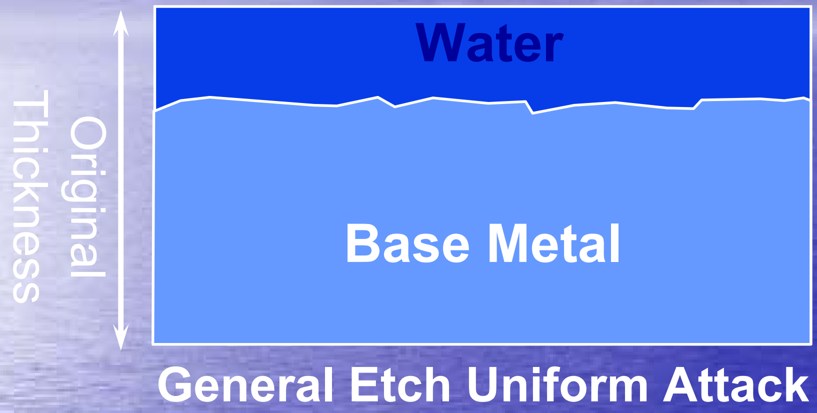
- ⇧ Dissolved Solids
  - – Complete circuit from cathode to anode
- ⇧ System Deposits
  - Anodic pitting sites develop under deposits
- ⇔ Water Velocity
  - Too low = deposits
  - Too high = Erosion
- ⇧ Microbiological Growth
  - Deposits; Produce corrosive by-products

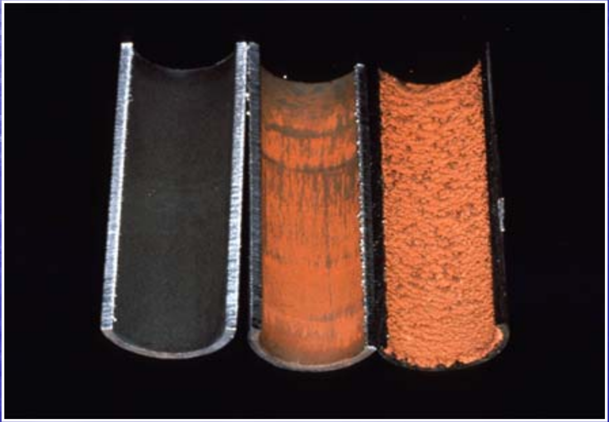
Types of Corrosion

All cooling system metallurgy experiences some degree of corrosion. The objective is to control the corrosion well enough to maximize the life expectancy of the system…

1. General Corrosion
2. Localized Pitting Corrosion
3. Galvanic Corrosion

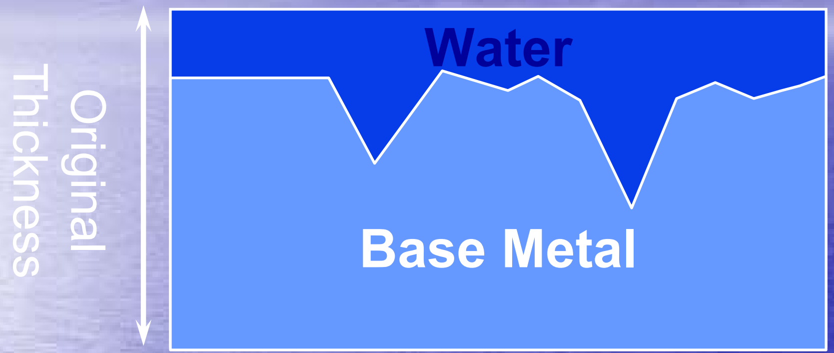
General Corrosion



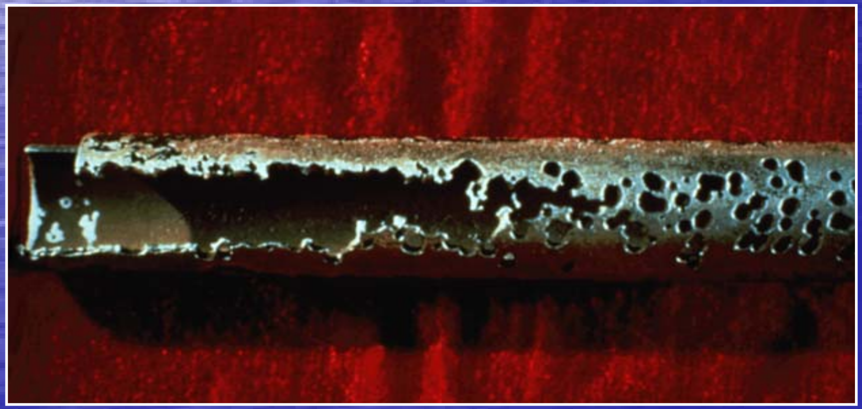


- Preferred situation
- Take a small amount of metal evenly throughout the system
- Anode very large

Pitting Corrosion



Localized Pitting Attack



- Metal removed at same rate but from a much smaller area
- Anode very small
- Often occurs under deposits or weak points
- Leads to rapid metal failure

Galvanic Corrosion

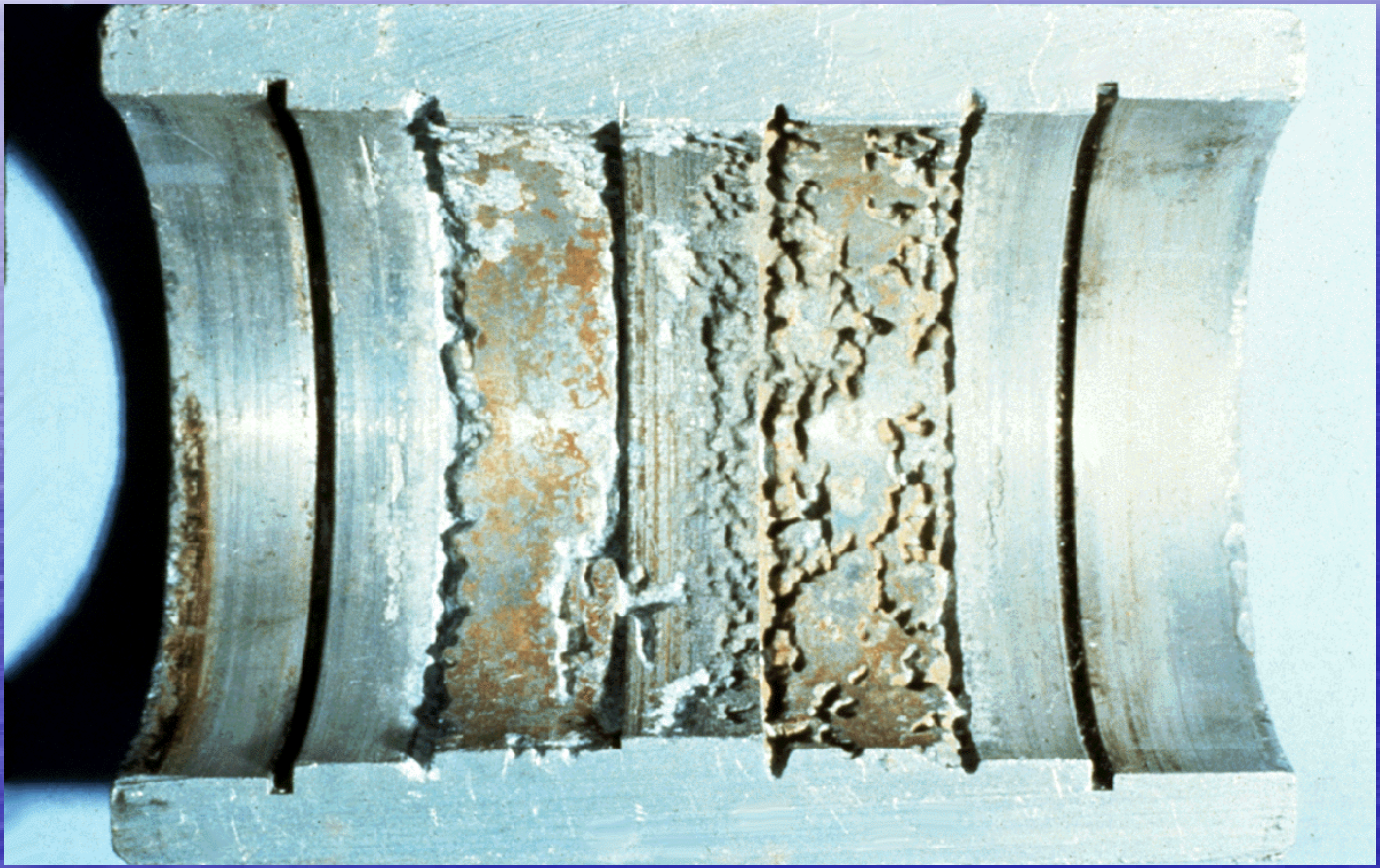
- Occurs when two different metals are in the same system
- More reactive metal will corrode in presence of less reactive metal
- Potential for galvanic corrosion increases with increasing distance on chart

Active End

Magnesium
Galvanized Steel
Mild Steel
Cast Iron
18-8 Stainless Steel Type 304 (Active)
18-12-3 Stainless Type 316 (Active)
Lead Tin
Muntz Steel
Nickel (Active)
76-Ni-16 Cr-7 Fe Alloy (Active)
Brass
Copper
70:30 Cupro Nickel
67-Ni-33 Cu Alloy (Monel)
Titanium
18-8 Stainless Steel Typ 304 (Passive)
18-12-3 Stainless Steel Type 316 (Passive)
Graphite
Gold
Platinum

Passive End

Galvanic Corrosion



Effects of Corrosion

- Destroys cooling system metal
- Corrosion product deposits in heat exchangers
- Heat transfer efficiency is reduced by deposits
- Leaks in equipment develop
- Process side and water side contamination occurs
- Water usage increases
- Maintenance and cleaning frequency increases
- Equipment must be repaired and/or repaired
- Unscheduled shutdown of plant

Methods To Control Corrosion

- Use corrosion resistant alloys: $
- Adjust (increase) system pH: Scale
- Apply protective coatings: Integrity
- Use “sacrificial anodes”: Zn/Mg
- Apply chemical corrosion inhibitors

Anodic Corrosion Inhibitors

- Stop corrosion cell by blocking the anodic site
- Severe localized pitting attack can occur at an unprotected anodic sites if insufficient inhibitor is present

Anodic Inhibitors

- Chromates (carcinogenic !)
- Nitrites
- Orthophosphates
- Silicates
- Molybdates

Cathodic Corrosion Inhibitors

- Stop corrosion cell by blocking the electrochemical reaction at the cathode
- Corrosion rate is reduced in direct proportion to the reduction in the size of the cathodic area.

<u>Cathodic Inhibitors</u>

- Bicarbonates
- Polyphosphates
- Polysilicates
- Zinc

General Corrosion Inhibitors

- Protect metal by filming all surfaces whether they are anodic or cathodic

General Inhibitors

- Soluble Oils
- Tolyltriazoles
- Benzotriazoles

FOULING

Fouling

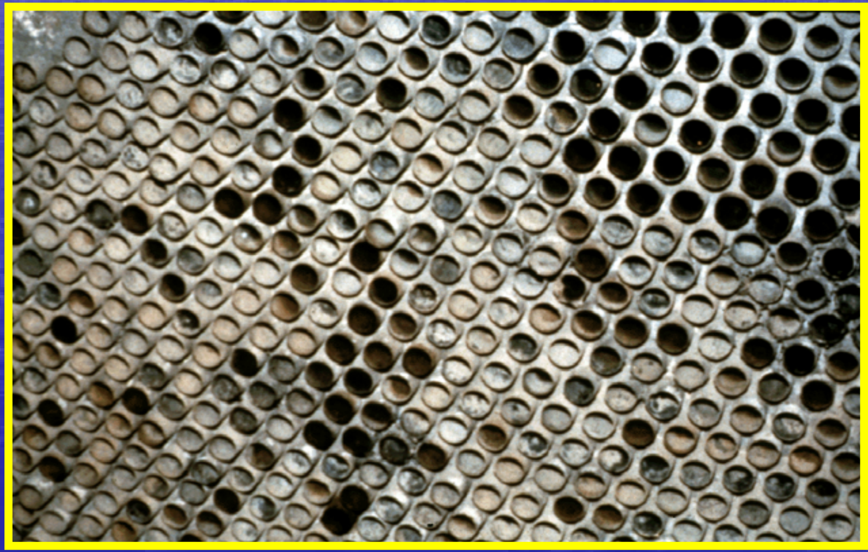
FOULING is the accumulation of solid material, other than scale, in a way that hampers the operation of equipment or contributes to its deterioration

Common Foulants
Suspended Solids

- Silt, Sand, Mud and Iron
- Dirt & Dust
- Process contaminants, e.g. Oils
- Corrosion Products
- Microbio growth
- Carryover (clarifier/lime softener)

Factors Influencing Fouling

- Water Characteristics
- Water Temperature
- Water Flow Velocity
- Microbio Growth
- Corrosion
- Process Leaks



Effects of Fouling

- Foulants form deposits in hot and/or low flow areas of cooling systems
- Shell-side heat exchangers are the most vulnerable to fouling
- Deposits ideal for localized pitting corrosion
- Corrosive bacteria thrive under deposits
- Metal failure results

Economic Impact of Fouling

- Decreased plant efficiency
- Reduction in productivity
- Production schedule delays
- Increased downtime for maintenance
- Cost of equipment repair or replacement
- Reduced effectiveness of chemical inhibitors

Fouling

Three Levels Of Control Can Be Employed To Address The Effects Of Fouling…

1. Prevention
2. Reduction
3. Ongoing Control

Preventing Fouling

Prevention

- Good control of makeup clarification
- Good control of corrosion, scale, & microbio

Reduction

- Increase blowdown
- Sidestream filter

Ongoing Control

- Backflushing, Air rumbling, Vacuum tower basin
- Chemical treatment

Fouling

Chemical Treatment

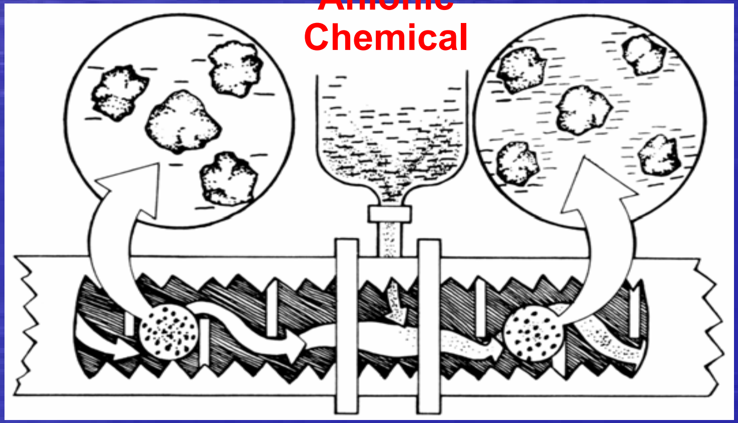
- Charge Reinforcers
- Wetting Agents

Charge Reinforcement Mechanism

- Anionic polymers increase strength of charge already present on suspended solids
- Keep particles small enough so they do not settle out

Slightly anionic suspended particle

Highly Anionic Chemical

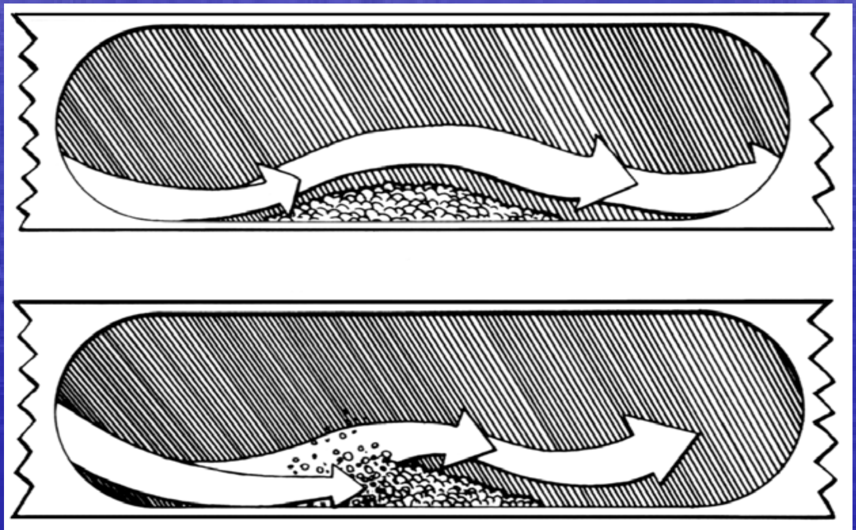


Suspended Solid which has adsorbed highly anionic chemical

Wetting Agents

- Surfactants
- Penetrate existing deposits
- Wash away from metal surfaces

Particle Build-up



With Wetting Agent

MICROBIOLOGICAL GROWTH

Microbiological Growth

- Water treatment is about managing three fouling processes…
  - ⇨ Corrosion
  - ⇨ Scale
  - ⇨ Microbio

The microbial fouling process is…

- The most complex
- The least understood
- The hardest to measure and monitor
- Controlled using the least desirable, most expensive, & potentially hazardous products

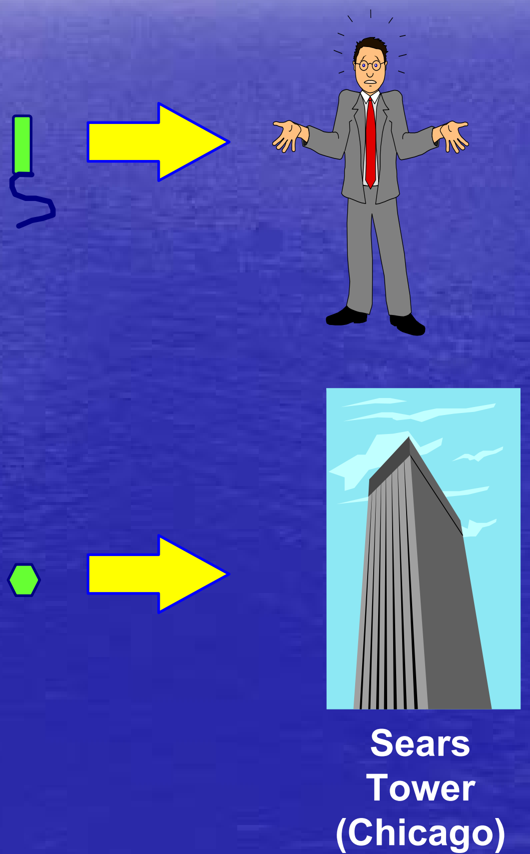
Microbiological Growth

Three Kinds Of Troublesome Microorganisms In Cooling Water…

1. Bacteria
2. Algae
3. Fungi

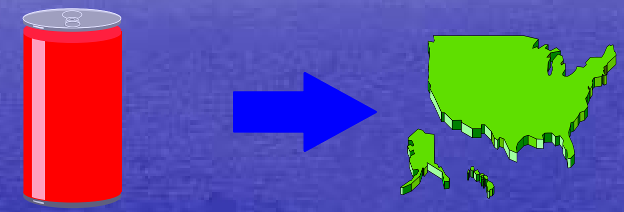
Bacteria

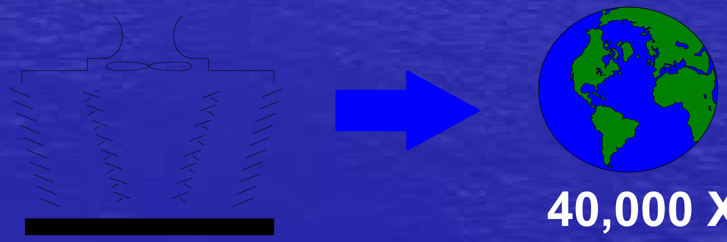
- Bacteria extremely small
- Compared to a human, a bacteria is like a grain of sand to the Sears Tower
- Size allows many (millions) to fit into a small volume of water...



Bacteria

- There are as many bacteria in 330 mL of cooling water as there are people living in the United States
- There are 192000 times as many bacteria in a 240000 L cooling system as there are people in the world!



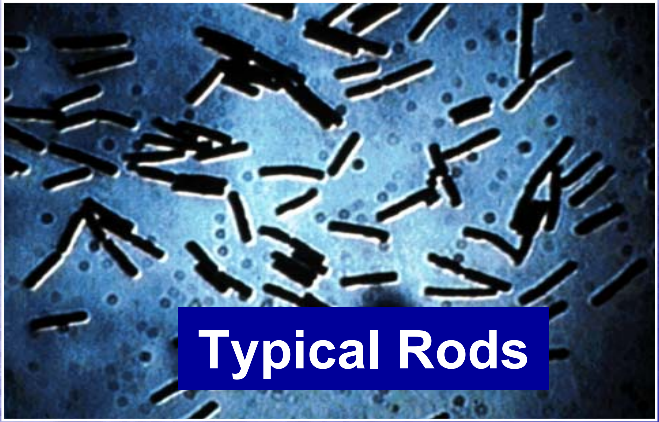


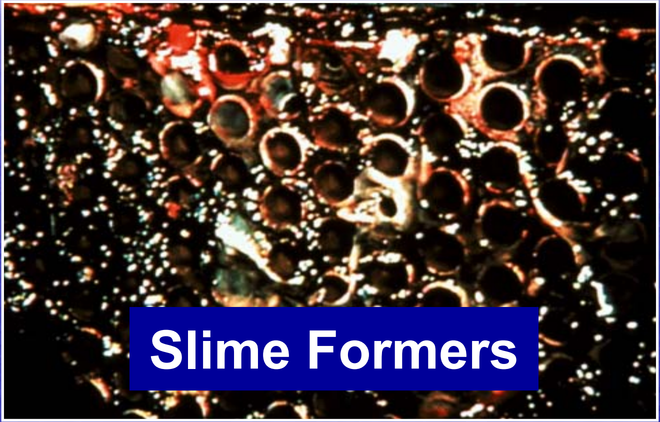
Bacteria

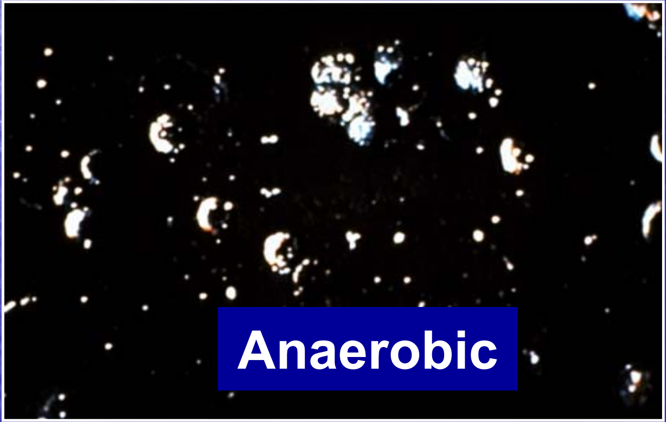
Types of Bacteria

1. Slime Forming
2. Anaerobic Corrosive
3. Iron Depositing
4. Nitrifying
5. Denitrifying

Bacteria







Bacteria

- Produce acidic waste that lowers pH and causes corrosion
- Produce large volumes of iron deposits that foul
- Produce acids from ammonia that increase corrosion & lower pH
- Form sticky slime masses that foul & cause reduced heat transfer

Two Classifications of Bacteria

Planktonic:

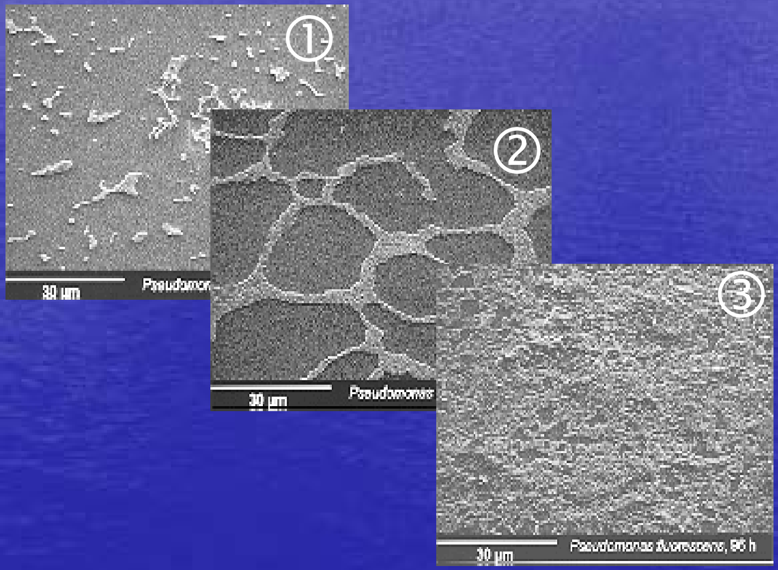
- Free-floating bacteria in bulk water

Sessile:

- Bacteria attached to surfaces
- Over 95% of bacteria in a cooling system are sessile and live in BIOFILMS

Biofilms

- Contribute to all cooling water problems
- Underdeposit corrosion
- Trap silt & debris which foul heat exchangers and tower fill
- Provide nucleation sites for scale formation



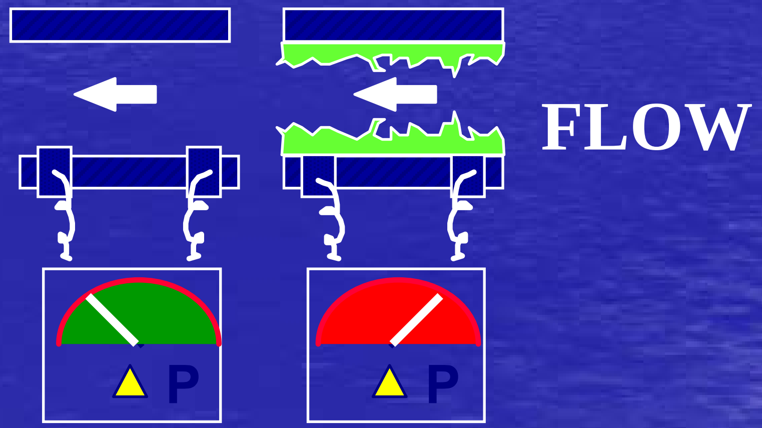
Biofilm Formation

Biofilms

- More insulating than most common scales ⇨
- Reduce heat transfer efficiency
- Increase dP across heat exchangers & reduce flow
- Health risks (legionella)

Foulant	Thermal Conductivity
CaCO3	1.3-1.7
CaSO4	1.3
CaPO4	1.5
MgPO4	1.3
Fe Oxide	1.7
Biofilm	0.4

Common biofilms are 4 times more insulating than $CaCO_3$ scale!



Algae

- Require sunlight to grow
- Found on tower decks & exposed areas
- Form “algae mats”
- Plug distribution holes on tower decks
- Plug screens/foul equipment
- Consume oxidants
- Provide food for other organisms

Fungi

- Use carbon in wood fibers for food
- Destroy tower lumber by either surface or internal rotting (deep rot)
- Loss of structural integrity of tower

Factors Affecting Growth of Microorganisms

- Microorganism Sources: Air or Makeup water
- Cooling systems provide the ideal environment for microbiological growth
  - Nutrients: Ammonia, oil, organic contaminants
  - Temperature: 70-140°F acceptable
  - pH: 6.0 - 9.0 ideal
  - Location: Light/No Light
  - Atmosphere: Aerobic/Anaerobic

Controlling Microbiological Growth

- Water Quality
  - – Eliminate organic contaminants (food)
  - – No food = No "bugs"
- System Design Considerations
  - – Clean basin, plastic, cover decks
- Chemical Treatment with Biocides

Microbiological Growth

Chemical Treatment With Biocides

- Oxidizing Biocides
- Non-oxidizing Biocides
- Biodispersants

COOLING WATER TREATMENT PROGRAMS

Treatment Programs

- Moly-Phosphonate
- Alkaline Zinc
- Stabilized Phosphate
- Dispersants
- All Organic
- Oxidizing Biocides
- Non-Oxidizing Biocides

MOLYBDATE-PHOSPHONATE PROGRAM (Moly/Phosphonate)

Moly/Phosphonate Program

- Designed for system with corrosive (low hardness &/or alkalinity) waters
- Molybdate-based corrosion inhibitor
- Phosphonate for scale inhibition
- Dispersant polymer for fouling protection

Moly/Phosphonate Program

- Well suited to aluminum industry
- Works well in high heat flux systems where heat transfer surfaces experience high skin temperatures
- Provides protection over a wide range of operating parameters
  - ⇨Calcium: 0-500 ppm
  - ⇨M-Alkalinity up to 2,000 ppm

Moly/Phosphonate Programs

- Molybdate “workhorse” of program
- Surface active *anodic* corrosion inhibitor
- Does not depend on controlled deposition
- Promotes rapid oxidation of metal surfaces to form a tightly adherent layer of metal oxides
- Protective layer impermeable to other anions, especially chlorides and sulfates

Moly/Phosphonate Program

General Control Guidelines

• Molybdate:	6-16 ppm (as MoO_4)
• Phosphonate:	1-2 ppm (as PO_4)
• Calcium:	0-500 ppm
• M-Alkalinity:	50 -2,000 ppm
• HTI:	120 Hours max.
• Temperature:	135-180°F [57-82°C]
• Conductivity:	2,000 micromhos max.

Moly/Phosphonate Program Benefits

- Improved Heat Transfer
  - Reduced energy costs
- Reduced Corrosion
  - Extended equipment Life & reliability
- No impact on quenchability
  - Production not negatively impacted

ALKALINE/ZINC PROGRAM

Alkaline/Zinc Program

- Uses low levels of zinc together with ortho phosphate for corrosion control
- Polymeric dispersant used for general dispersancy & scale control
- Attractive cost performance under high stress conditions
- Basic program can be customized to fit system needs

Alkaline/Zinc Program

- Zinc provides cathodic corrosion protection
- Ortho phosphate provides anodic corrosion protection
- The key to the success of the alkaline zinc program is the polymer dispersant

Alkaline/Zinc Program

<u>Polymer Dispersant</u>

- Maintains zinc & phosphate in soluble form at higher pH’s than they would under normal circumstances
- Operating at higher pH’s allow program to provide excellent corrosion protection at very low levels of zinc (< 1.0 ppm)
- Also provides scale control

Alkaline/Zinc Program

General Application Ranges

- Dependent on Calcium & M-Alkalinity
- Ca 200 ppm M-Alkalinity 1,500 ppm
- Ca 1,000 ppm M-Alkalinity 300 ppm

Alkaline/Zinc Program

General Control Guidelines

Zinc (soluble):	0.5-2.0 ppm
Ortho PO4:	Extremely variable
Insoluble PO4:	1.5 ppm or 40% of total PO4
Calcium:	15-1,000 ppm
M-Alkalinity:	50 -1,500 ppm
HTI:	120 Hours max.
Temperature:	160°F [71°C] max.
Conductivity:	6,000 micromhos max.

STABILIZED PHOSPHATE PROGRAM

Stabilized Phosphate Program

- Uses high levels of orthophosphate to provide corrosion protection
- Polymeric dispersant provides calcium phosphate stabilization
- Supplemental Tolyltriazole (TT) used for yellow metal protection

Stabilized Phosphate Program

- Operates at near-neutral pH
- High levels of ortho phosphate (10 -17 ppm) provide anodic corrosion inhibition
- Poly phosphate & calcium complex provide cathodic corrosion protection
- Dispersant polymer for CaPO4 stabilization

Polymer Dispersant

- Key to program is polymeric dispersant
- Inhibit inorganic scales such as calcium carbonate & calcium phosphate
- Keep particles suspended in water -- control foulants such as:
  - ⇨Manganese & iron oxides
  - ⇨Suspended solids like mud & silt

Polymer Dispersant

- Mechanism: Charge Reinforcement
- Polymer adsorbs onto particles & increases the ± charge naturally present
- Treated particles repel each other
- Reduces chances of collision & agglomeration
- Prevents formation of deposits

Stabilized Phosphate Program

Excellent choice when…

- Restrictions on use of heavy metals
- Bulk water temperature < 150°F
- Low make-up calcium &/or M-alkalinity
- High incoming O-PO4 levels

Stabilized Phosphate Program

General Control Guidelines

• Total O-PO4:	8 -17 ppm (Ca dependent)
	2.0 ppm insoluble max.
• Calcium:	15 -1,000 ppm
• pH:	6.8-8.4 (Ca dependent)
• HTI:	96 Hours max.
• Temperature:	150°F [66°C] max.
• Conductivity:	7,500 micromhos max.

Stabilized Phosphate Program

Properly controlled programs

- Excellent protection against corrosion and scaling

Poorly controlled program causes

- Severe Corrosion
- Scaling
- Fouling

ALL ORGANIC PROGRAM

All Organic Program

- Non-heavy metal/phosphate program
- All Organic programs use high pH & alkalinity conditions to provide corrosion protection in a scale forming cooling system environment
- Organic scale inhibitors prevent mineral deposits

All Organic Program

- All organic components make this a very environmentally acceptable program
- Contains no heavy metals that can be precipitated (e.g. zinc sulfide)
- Contains no inorganic phosphates to precipitate with iron in low-pH localized leak areas

All Organic Program

- Operates under alkaline conditions at pH’s between 8.5-9.4
- Designed for systems where makeup calcium & M-Alkalinity cycle naturally to within program guidelines
- Supplemental acid/caustic feed may be required to maintain proper M-Alk.
- Maintaining the proper calcium-alkalinity relationship is *critical*

All Organic Program

General Control Guidelines

• Calcium:	80-900 ppm
• M-Alkalinity:	300-500 ppm Temperature dependent
• pH:	8.5-9.4
• HTI:	48 Hours max.
• Temperature:	110-140°F [43-60°C]
• Conductivity:	4,500 micromhos max.

All Organic Program

Properly controlled programs

- Excellent protection against corrosion and scaling

Poorly controlled program causes

- Severe Corrosion
- Scaling
- Fouling

OXIDIZING BIOCIDES

Oxidizing Biocides

- Penetrate microorganism’s cell wall and “burn-up” the internals of the organism
- Effective against all types of bacteria
- No microorganism resistant to oxidizers
- Kill *everything* given sufficient concentration levels & contact time

Oxidizing Biocides

- Broad-spectrum effectiveness makes oxidizers primary biocide in large cooling water applications

<u>Oxidizers</u>

- Gas Chlorine
- Bleach
- Acti-Brom
- BCDMH
- Stabilized Bromine

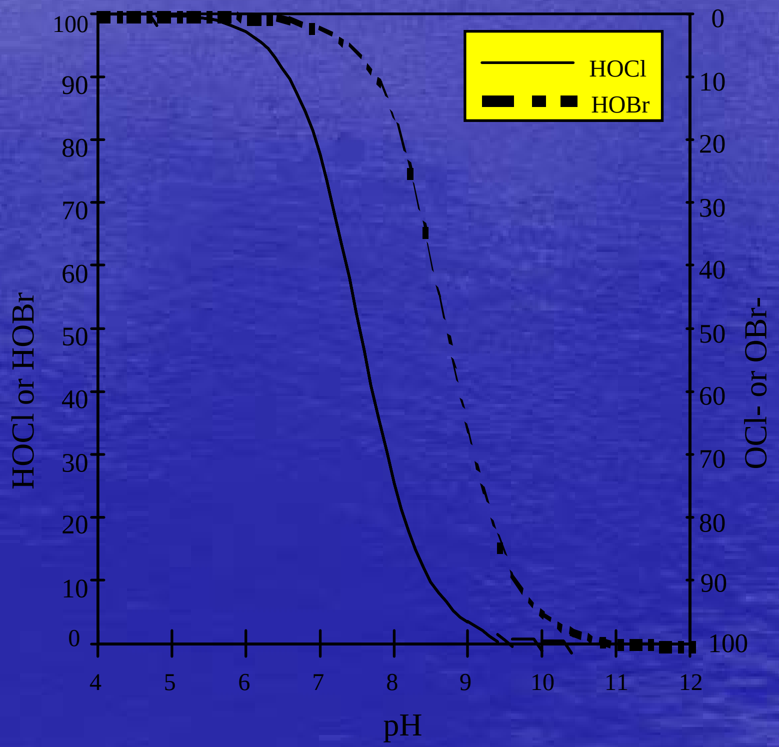
Oxidizing Biocides

- Biocide effectiveness pH dependent
- Cl_2 ⇨ HOCl & OCl^-
- Br ⇨ HOBr & OBr^-
- HOCl/HOBr Biocidal
- @ pH=8.0

  HOCl: 22%

  HOBr: 83%

⇨ Bromine more biocidal



Chlorine Advantages

- Economical
- Traditional technology

Chlorine Disadvantages

- Slower kill at high pH
- Consumed by ammonia, sulfides, iron, manganese, & hydrocarbons
- Volatile and easily stripped, thus high usage rates
- High residuals (or slug feeding) cause wood delignification
- High feed rates and residuals can cause higher corrosion rates
- Poor control (or slug treatment) leads to degradation of water treatment compounds -- e.g. organophosphates and triazoles
- Chlorinated organics, e.g., THM's, are toxic, regulated, and persistent in the environment

Bromine Advantages

- Higher biocidal activity at significantly lower dosages than chlorine
- Increased kill rate - better recoverability from upsets
- More active over a higher, wider pH range
- No decrease in biocidal activity in the presence of ammonia since bromamines are as active as HOBr
- Lower halogen residuals in the effluent
- Brominated organics are less persistent than chlorinated organics in receiving water
- Lower residuals: less wood delignification, less tolytriazole and organic phosphate degradation, and less corrosion
- Less mechanical stripping (at pH <8.0)

Bromine Disadvantages

- Bromine is more aggressive to HEDP (phosphonate)
- A chlorine source is needed to generate ACTI-BROM on site.
- Dry products have fixed bromine to chlorine ratio.
- Low residual can be difficult to control.
- Lower residual or intermittent feed can result in lack of algae control

NON-OXIDIZING BIOCIDES

Non-Oxidizing Biocides

- Organic compounds that react with specific cell components
- Interfere with metabolism or destroy cell wall

Non-oxidizing Biocides

- Generally not used as the primary biocide in larger systems due to cost
- Typically slug fed at high dosages
- Often used for clean-up or contingency reasons

Non-Oxidizing Biocides

- Different microorganisms exhibit different levels of resistance to various non-oxidizing biocides
- Specific to type of microorganism
- Work within specific (limited) pH ranges
- Carefully regulated by EPA
- Safety/Handling issues

Non-Oxidizing Biocides

Common Non-Oxidizers

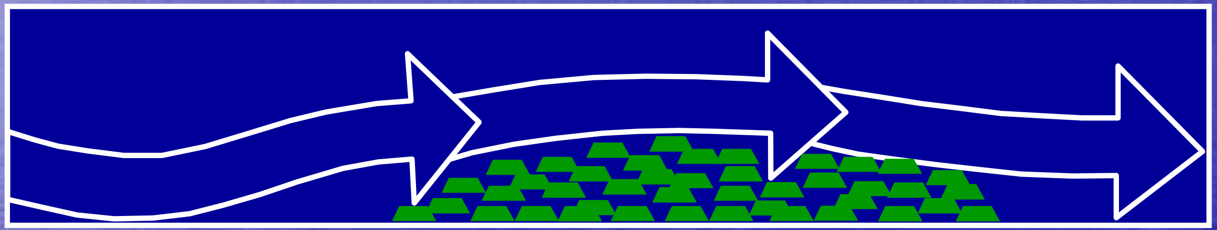
- Isothiazoline
- Glutaraldehyde
- DBNPA
- Quaternary Amines
- Glut/Quat Combo

Non-Oxidizing Biocides

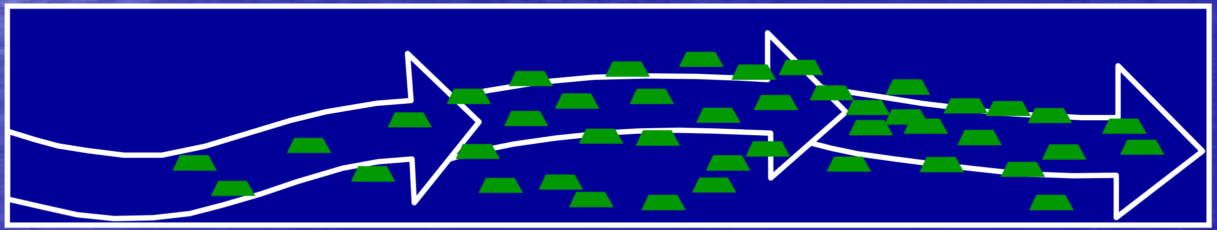
- No practical method of directly testing levels of non-oxidizing biocides in CW
- Optimal dosage & application frequency should be determined through indirect measurement
- Microbio counts, sessile monitoring, ATP, toxicity testing, biofouling monitors

Biodispersants

Before Biodispersant



After Biodispersant



Do not kill -- Penetrate deposits and increase the effectiveness of oxidizing & non-oxidizing biocides.