ΧΗΜΙΚΗ ΤΕΧΝΟΛΟΓΙΑ ΤΟΥ ΝΕΡΟΥ:
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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 purpose of cooling systems is to transfer heat from one substance to another. The substance that gives up its heat is "cooled" and the substance that receives the heat is the "coolant".
Simple Heat Transfer

Heat Exchangers are used for industrial process cooling.

Common Measurement of Heat
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

CHARACTERISTICS

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

EXAMPLES

- Potable Water Systems
- Process Water
- General Service
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

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

**EXAMPLES**
- Diesel Engine Jackets
- Automobile Radiators
- Chilled Water Systems

Diagram showing the flow of a closed recirculating system with Heating or Cooling Equipment, Pump, Cold Heat Exchanger, and Hot.
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
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

**CHARACTERISTICS**
- Amount of Water Used: Moderate

**EXAMPLES**
- Spray Ponds
- Cooling Towers
- Evaporative Condensers
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 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

**Diagram:**
- 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

Tower deck with gravity distribution through holes

Pressurized spray headers
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
Water contains 3 types of impurities:

1. Dissolved Solids
2. Dissolved Gases
3. Suspended Matter

RAIN ★ Water in purest natural form
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

- 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**

ACIDIC | BASIC
--- | ---

*pH SCALE*

Hydrogen Ions Increase

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |

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 its 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 evaporation rate. The formula for evaporation rate (ER) is:

$$ER = (RR) \times \left( \frac{dT}{10} \right) \times 0.85$$

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

Constant Evaporation

With Zero Blowdown

With Continuous Blowdown Maintaining 4 Cycles
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 its original concentration
- Important for proper selection & dosing of treatment chemicals

\[ T_{\frac{1}{2}} = 60 \text{ hours} \]
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.
Mineral Scale

Common Scales

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

Scaled Heat Exchanger Tubes
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

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.
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

STEP 1

Water with Dissolved Minerals
Base Metal

STEP 2

O₂

Fe²⁺

STEP 3

STEP 4

OH⁻
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

Graph showing the relationship between Corrosion Rate and pH, with the Corrosion Rate on a logarithmic scale and pH on a linear scale.
In general, for every 18°F in water temperature, chemical reaction rates double.
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

- 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
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.

Cathodic Inhibitors
- 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 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
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 192,000 times as many bacteria in a 240,000 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

Typical Rods

Slime Formers

Anaerobic

Iron Depositing
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
Biofilms

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

<table>
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<th>Foulant</th>
<th>Thermal Conductivity</th>
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<tr>
<td>CaCO3</td>
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<tr>
<td>CaSO4</td>
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<tr>
<td>CaPO4</td>
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<tr>
<td>MgPO4</td>
<td>1.3</td>
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<tr>
<td>Fe Oxide</td>
<td>1.7</td>
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<tr>
<td>Biofilm</td>
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</tbody>
</table>

Common biofilms are 4 times more insulating than CaCO3 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 MoO₄)
- **Phosphonate**: 1-2 ppm (as PO₄)
- **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 orthophosphate 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

Polymer Dispersant

• 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.
- 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 $\pm$ 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

- 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

- **Oxidizers**
  - Gas Chlorine
  - Bleach
  - Acti-Brom
  - BCDMH
  - Stabilized Bromine
Oxidizing Biocides

- Biocide effectiveness pH dependent
- \( \text{Cl}_2 \rightarrow \text{HOCl} & \text{OCl}^- \)
- \( \text{Br} \rightarrow \text{HOBr} & \text{OBr}^- \)
- HOCl/HOBr Biocidal
- @ \( \text{pH}=8.0 \)
  - HOCl: 22%
  - HOBr: 83%

\( \Rightarrow \) 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.