Cooling Water Treatment

Theory Training

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General Properties of Water

- Some of the properties of water which make it ideal for industrial cooling processes are listed below:
  - Water has the capacity to store and transport heat
  - Water absorbs more heat per pound than any other inorganic substance
  - Water has the following physical properties:
    - One pound of water gives up 144 BTU's upon freezing
    - At atmospheric pressure, water freezes at 32 deg F and boils at 212 deg F
    - Water is most dense at 40 deg F
    - One pound of water, when transformed into steam, releases 970 BTU's
    - Pure water does not exist in nature

General Properties of Water

- There are two main sources of water, note general differences
  - Wells and springs are classified as ground water sources
    - Low suspended solids and dissolved oxygen, high dissolved solids including iron, hardness, and alkalinity, and also high carbon dioxide
  - Rivers and lakes are classified as surface water sources
    - High suspended solids and dissolved oxygen, low dissolved solids including iron, hardness, and alkalinity, and also low carbon dioxide

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Types of Impurities in Water

- Suspended solids
  - Turbidity
    - Finely divided suspended or colloidal matter (clay, silt, dirt, organic matter)
  - Color
    - An arbitrary standard scale used to measure soluble organic materials in water

CATIONS
Ca
Mg
K
Na
Fe, Al, Cu
Zn, Si

ANIONS
Cl
HCO_3
CO_3
SO_4
PO_4
NO_3

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Types of Impurities in Water (cont.)

- Dissolved solids
  - Dissolved mineral solids
    - When rain falls, it scrubs the atmosphere of carbon dioxide
    - Carbon dioxide mixes with water to form a weak acid called carbonic acid
    - The carbonic acid dissolves mineral solids contained in nature, such as:
      - Limestone (calcium carbonate), dolomite (magnesium carbonate), epsom salt (magnesium sulfate), gypsum (calcium sulfate), sand (silica), and common salt (sodium chloride).
    - Minerals containing sodium have a relatively high solubility in water
    - Minerals containing calcium and magnesium have a relatively low solubility in water

Types of Impurities in Water (cont.)

- Dissolved Gases
  - Oxygen
    - Corrosive to metal at elevated concentrations
    - Solubility in water depends on temperature, surface area and pressure
  - Carbon Dioxide
    - Will form carbonic acid, a weak acid, when dissolved in water
    - Carbonic acid dissociates to form bicarbonate and carbonate alkalinity which is pH dependent
    - Solubility in water depends on temperature, surface area and pressure

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Types of Impurities in Water (cont.)

- Miscellaneous Impurities
  - Bacteria that require oxygen and produce carbon dioxide are aerobic bacteria
  - Bacteria that do not require oxygen and produce hydrogen sulfide are anaerobic bacteria
  - Algae favors exposure to sunlight
  - Fungi favors dark secluded areas

Hardness and Alkalinity

- Hardness (calcium and magnesium) and alkalinity (bicarbonate and carbonate) both play a major role in cooling water treatment:
    - The weak acid, carbonic acid, that is formed during rainfall has the ability to dissolve minerals in the earth's strata
    - The acid solution is composed of hydrogen, the positively charged portion of the solution (acidic portion), and a negatively charged counterpart
    - If the earth's strata contains appreciable quantities of limestone and dolomite, then two of the primary reactions between the weak acid and the strata will be with the calcium carbonate and magnesium carbonate

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Hardness and Alkalinity (cont.)

- Hardness (calcium and magnesium) and alkalinity (bicarbonate and carbonate) both play a major role in cooling water treatment:
  - As the mineral dissolves, both the calcium and carbonate (as well as the magnesium and carbonate), go into solution
  - Once dissolved, both the calcium and magnesium (the positively charged portions of the mineral), tend to favor "reverting" back to their natural insoluble state
  - When combined with other mineral impurities, calcium and magnesium will preferentially precipitate out of solution and form an insoluble sludge
  - The reaction of calcium and magnesium in water with soaps and detergents creates an undesirable sludge which can make laundering difficult. The difficulty or "hard to wash condition" led to the the terminology "Water Hardness"

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Solubilities

- The common mineral substances can be classified into four categories based on solubility:
  - Calcium and magnesium compounds rules of thumb
    - Solubility decreases when temperature rises, alkalinity increases, and available carbon dioxide decreases
    - Bottom line: hardness salts are more likely to drop out at high temperatures and pH
  - Sodium compounds rules of thumb
    - Solubility increases as temperature increases. If deposits with sodium are found, it can generally be attributed to extreme concentrations or evaporation to dryness
    - Bottom line: Sodium compounds are rarely a problem caused by water treatment)

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Solubilities (cont.)

- The common mineral substances can be classified into four categories based on solubility *(cont.)* :
  - Silica dioxide rule of thumb
    - Solubility increases as alkalinity increases
  - Iron and manganese compounds rule of thumb
    - Solubility decreases as water alkalinity increases and as the degree of oxidation increases (i.e. oxygen, chlorine, bromine)

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NO_3

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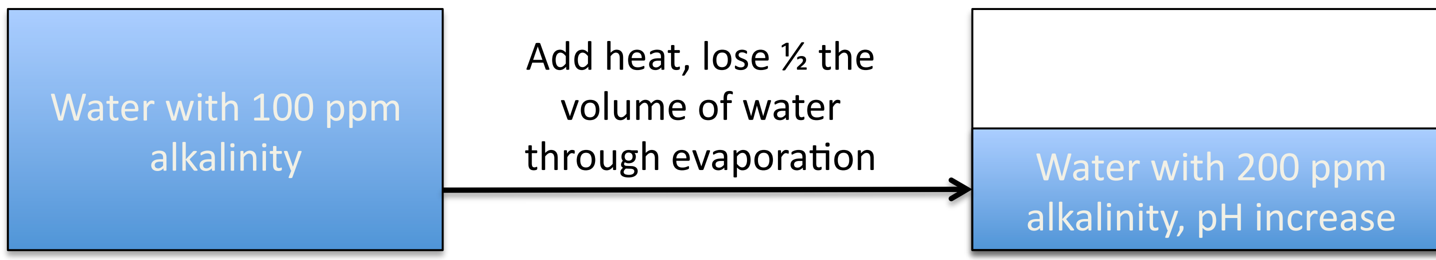
pH and Cycles of Concentration

- Defined exactly, pH is the logarithm of the reciprocal of the hydrogen ion concentration in the reaction

- A more simple explanation is that pH is a number between 0 and 14 that denotes various degrees of acidity and alkalinity, with neutral water at pH 7. Below 7 becomes increasingly acidic, while above 7 becomes increasingly alkaline

pH and Cycles of Concentration (cont.)

- pH is a very important parameter in water treatment, especially in cooling water treatment. As water is cycled, alkalinity concentrates, so subsequently pH increases, example:



- We call this example as being 2 cycles of concentration, where mineral concentrations, as well as conductivity, are doubled

- At UPMC Shadyside, towers average 5 cycles of concentration

Langelier Saturation Index (LSI)

- A numerical value for the scaling potential of calcium carbonate ($CaCO_3$)

- The equation is a numerical combination of:
    - Total dissolved solids
    - Temperature
    - Calcium hardness
    - Alkalinity
    - pH

- A positive LSI is scale forming, a negative LSI is corrosive, and zero is perfect equilibrium

LSI/RSI Calculation

- $LSI = pH - pH_s$
- $pH_s = 9.3 + TDS[F] + Temp[F]$
  $-(Ca[F] + Alk[F])$

Methods of Treatment for High LSI

- Acid Feed
  - By reducing pH in cooling water, the equation

    $$LSI = pH - pH_s$$

    means that LSI will be reduced, therefore calcium carbonate scaling potential is reduced

  - Proper dilution of acid is critical to contact all points of the system. It is ***important to equip the system with safeguards*** if acid feed is lost or inefficient

Methods of Treatment for High LSI #2

- Organic phosphonates combined with polymers can withstand LSI to $^{+}3.0$
- Usually safe to maintain LSI at $^{+}2.5$
- Another method of controlling LSI is softened make-up, but requires manhours for regeneration and maintenance

Cooling Water Treatment

- Objective of a cooling water treatment program:
  - Maintain optimum heat transfer in process equipment and heat exchangers
  - Insure equipment reliability and availability
  - Minimize operating costs
  - Provide predictive treatment recommendations for system operating changes and tower contamination
  - Maintain healthy environment in moist areas around perimeter of tower
  - Assure system circulation to keep all areas with fresh flow on a regular basis

Cooling Water Treatment (cont.)

- Major concern areas:
  - Scale: Formation of insoluble deposits on heat transfer surfaces, usually hardness salts on the most critical (or hottest) areas
    - High potential with high temperatures, high pH, excessive alkalinity, high dissolved solids, and high hardness
  - Corrosion: Loss of metal by reaction with the environment
    - Formation at the anode or cathode setting up an "electrical circuit", or oxidation of base metal
  - Fouling: Microbiological and suspended solids deposition
    - Algae, fungi, or bacteria depending upon location in system, can act as "the glue that holds deposits together"

Corrosion and Scale Control

Treatment Chemicals

Changing Chemistries Over the Years

- Toxic Nature of Chromate
- Desire to Eliminate Acid
- Desire to Operate at High Cycles
- Economic Pressure
- More Effective Inhibitors

Overview

- Carbon Steel Corrosion Process
- How Chemical Treatments Work
- Treatment Programs: *The Last 20 Years*
- The Future

Corrosion Process

ANODE

$Fe \rightarrow Fe^{+2} + 2e^-$

CATHODE

$H_2O + ½O_2 + 2e^- \rightarrow 2OH^-$

Rust Formation

Fe^{+2} hydrated to $Fe(OH)_2$

$Fe(OH)_2$ oxidized to $Fe(OH)_3$

$Fe(OH)_3$ precipitates

Anodic Inhibitors

Inhibit oxidation of iron

Promote gamma - Fe_2O_3

Precipitates fill voids

Anodic Inhibitors

- Chromate
- Nitrite
- Molybdate
- Orthophosphate

Cathodic Inhibitors

Inhibit Cathodic Reaction

Form Barrier Films

High surface pH causes precipitates

$$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$$

Cathodic Inhibitors

- Polyphosphates
- Phosphonates
- Zinc
- Calcium Carbonate

Inorganic Phosphates

- Orthophosphate
- Pyrophosphate
- Tripolyphosphate
- Polyphosphate

Phosphates

- 1940's: Polyphosphate Glasses
- 1950's -1960's: Zinc/Poly Glasses
- 1970's: Phosphate Esters
- 1980's: Stabilized Phosphates

Stabilized Phosphate

1st Stabilized Phosphate Program

Dianodic II™

1st Alkaline Stabilized Phosphate Program

pHreeGUARD™

Calcium Phosphate Inhibition

Inhibitors	Active Dosage (mg/L)	Percent Inhibition
70/30 AA/AM	50	< 25
AA/HPE	17	> 90
1:1 MA:SS	17	> 90
PMA	50	< 20
Polyaspartic Acid (Green)	50	< 20

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Calcium Phosphate Inhibition

Inhibitors	Minimum Effective Dose (mg/L)	Percent Inhibition
60/40 AA/AMPS *(TRC-233, AR-546, CT-40, Acumer 2100, WB65-37AS)*	7-8	>90
AA/AMPS/TBAM *(Acumer 3100)*	7-8	> 90
AA/AMPS/SS *(Goodrite K-798)*	7-8	> 90
AA/AHPSE	8	>90
75/25 AA/AMPS *(TRC-233i, AR-545, Acumer 2000, WB60-45AS)*	9-10	>90
Sulfonated AA Polymer *(Aquatreat MPS)*	9-10	> 90

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All-Organic

- HEDP/AMP
- HEDP/PBTC
- HEDP/ORTHO
- HEDP/HPA

Halogen Stabilizers

- Cyanuric Acid
- Sulfamic Acid
- Monoethanolamine

Chlorine Tolerant

- BAYER: PBTC
- RHODIA: PMAP

Zinc Products

- Zinc/Polyphosphate
- Zinc/Ortho
- Zinc/AMP
- Zinc/HEDP
- Zinc/PBTC
- With Polymer

High Calcite Saturation: 240X (LSI=2.8)

Inhibitors	% Inhinition (active dosage mg/L)	
	20 mg/L	30 mg/L
PEP	91	100
PBTC	72	76
HEDP	58	53
AMP	-	51
HPA		44
PMAP	46	39
PMA		51
Polyaspartic Acid	-	39

Green Chemistry

- Low/Non-Zinc
- Low/Non-Phosphate
- PMAP

Conclusion

- Most Important Development: Improved Polymers
- Polymer of Choice: 60/40 AA/AMPS
- Best High Calcite Saturation Inhibitor: Natcolene PEP
- Future: More Studies Needed for Green Chemistries

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Oxidizing Biocides

- Chlorine based
  - Not as effective above pH 7.5
    - Sodium hypochlorite
      - “Bleach” available at 14%
    - HTH
      - Calcium hypochlorite powder, rapid dissolving
    - Chlorine isocyanurate tablets
      - Organic chlorine rapid dissolving tablets
    - Chlorine dioxide
      - Combination of sulfuric acid and hypochlorite

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Oxidizing Biocides (cont.)

- Bromine based
  - Effective above pH 7.5
    - Stabilized bromine
      - 14% bromine combined with sodium hypochlorite
    - Bromine hydantoin tablets
      - Slow dissolving fed via brominator
    - Bromine isocyanurate
      - Rapid dissolving bromine tablets

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Non-Oxidizing Biocides

- Liquid biocides used to supplement an oxidizing biocide program
  - Fed via pumps on 7 day timer
  - Acts as a poison to kill bacteria/algae/fungi/mold
    - WSCP (142L) - algae, bacteria, fungi
    - Carbamate - bacteria, sulfate reducers, fungi
    - MBT -bacteria, sulfate reducers, fungi
    - Terbuthylazine - algae
    - Isothiazoline - bacteria, sulfate reducers, fungi
    - DBNPA - bacteria
    - Glutaraldehyde - bacteria, sulfate reducers, fungi
    - Thione - bacteria, fungi
    - Triazine - algae
    - DGH - bacteria, sulfate reducers, fungi

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Operation and Testing

- Molybdate Test

1. Add 1.5 mL of tower water to each viewing tube
2. Add tap water to 1st mark of each viewing tube (5 mL mark)
3. Add one Molybdenum 1 Reagent Powder Pillow to one of the tubes
4. Add eight drops of Molybdenum 2 Reagent to the same tube used in Step 3
5. Insert the tube from Step 4 into the right opening of the color comparator
6. Place the blank into the left opening, and hold up to natural light
7. The control display range is 1.1 mg/L to 1.8 mg/L

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Operation and Testing (cont.)

- Total and Free Halogen Test

  1. Fill a viewing tube to the first line (5 mL) with sample water
  2. Add either total or free chlorine powder pillow to the sample
  3. For total chlorine test, allow 3 minute reaction time before reading result
  4. View sample in comparator, control free chlorine 0.1 -0.3 mg/L and total chlorine < 1.0 mg/L.

- Conductivity
  - Control 1600 -2000 umhos conductivity

- Sanicheck Test Kit
  - Control < 10^5bacteria/mL

Review Quiz

- What is the scale that we are most concerned with in recirculating cooling water systems?
- If the makeup water is 400 conductivity, and the tower water is at 2000 conductivity, what are the cycles of concentration?
- What are ways to control legionella bacteria in a cooling tower?
- Where is hardness most likely to drop out of the water solution in a cooling water system?
- What safety equipment is necessary when handling treatment chemicals?