REINHOLD ENVIRONMENTAL Ltd.

2018 APC & Wastewater Round Table & Expo Presentation

July 23 & 24, 2018 in Lexington, KY / Hosted by East Kentucky Power Coop

Eliminating Phosphorus from Power Plant Wastewater Discharge

2018 APC-Wastewater PCUG Conference

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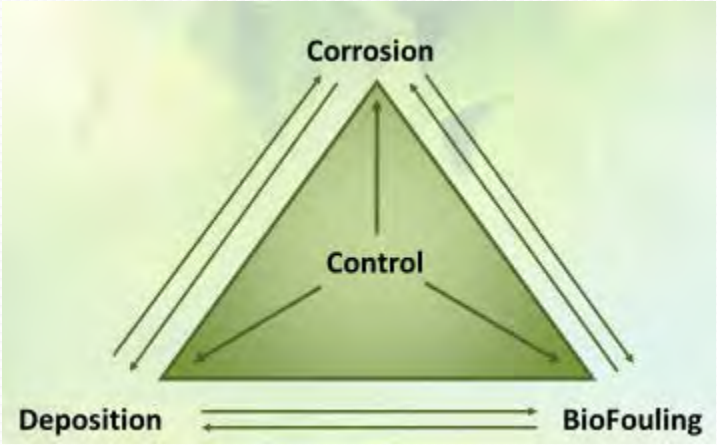
Introduction

- Much focus has been given to plant discharge issues other than cooling towers.
  - Now, more scrutiny is being placed on cooling tower blowdown (CTBD), in part due to phosphorus (as phosphate) discharge. But,
    - phosphate/phosphonate blends have been the core of most CT treatment programs for four decades.
- New chemistry has been developed that eliminates phosphorus-based compounds and also improves corrosion protection.

Agenda

- Cooling system treatment basics
- Review of previous treatment programs
  - Benefits and drawbacks
  - Why evolution has been necessary
- Issues with phosphorus discharge
- Polymer treatment to the rescue
- Wastewater treatment applied to makeup water

The Cooling System Triangle



- Each factor can influence the others.
- Discharge and makeup issues increasingly have an influence.

Some Quick Basics

- Primary Issues for Cooling Water Treatment
  - In untreated water, calcium carbonate is usually the leading deposit.
    - $Ca^{2+} + 2HCO_3^- + \text{heat} \rightarrow CaCO_3\downarrow + CO_2 + H_2O$
  - Regarding corrosion, the predominant mechanism in open recirculating systems is attack from dissolved oxygen in the water.
  - Microbiological fouling

The Good Old Days

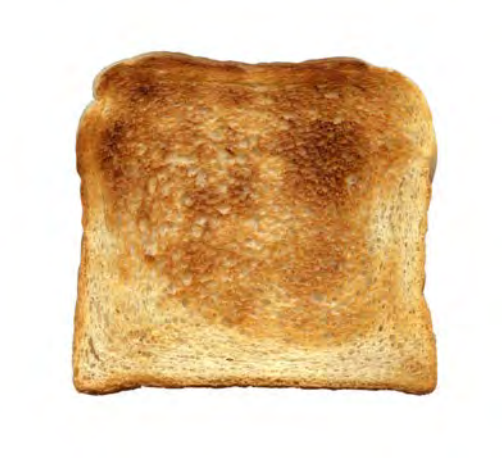
- A program that worked remarkably well for many systems was sulfuric acid/chromate treatment.
  - Acid reduced the potential for $CaCO_3$ scale.
    - $H_2SO_4 + 2HCO_3^- \rightarrow 2CO_2\uparrow + SO_4^{2-} + H_2O$
    - Common pH range of 6.5 to 7.0
      - A range that minimizes many other scales.
    - Acid addition is still sometimes used with modern programs.
  - Addition of disodium chromate (Na_2CrO_7) allows chromium oxides to form a layer on carbon steel. This pseudo-stainless steel layer is very protective.

Trouble in Paradise

- Use of chromates introduces hexavalent chromium (Cr^{6+}) to the environment.
- Cr^{6+} is toxic to humans and other organisms.
- Chromium treatment was banned for open recirculating systems, and has disappeared from almost all closed cooling water systems as well.
  - (Closed systems are typically never truly closed.)

Trouble in Paradise

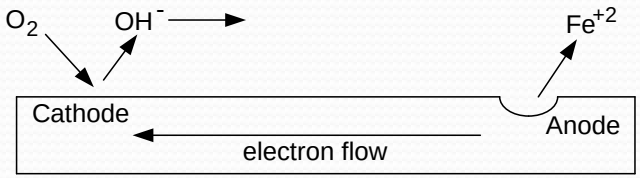
- So, although acid/chromate often worked very well, the method became toast.



- What could replace this treatment?
  - The answer was nothing nearly as simple.

A Brief Look at Fundamental Corrosion

- Corrosion is an electrochemical process, although in some cases mechanical factors are an influence.



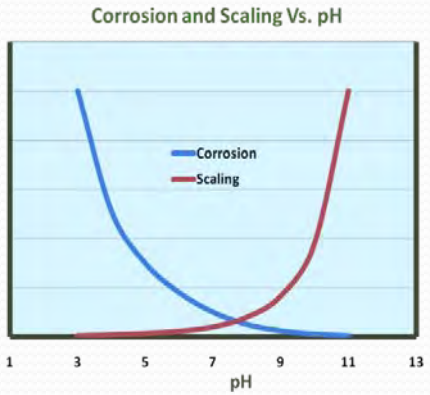
Anode Reaction: $Fe \rightarrow Fe^{+2} + 2e^-$

Cathode Reaction: $1/2\,O_2 + H_2O + 2e^- \rightarrow 2OH^-$

- Corrosion control chemistry is designed to reduce reactions at anodes, cathodes, or both.

A 180° Turn in Treatment

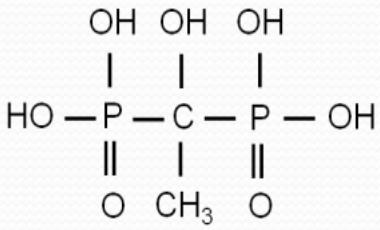
- For four decades, phosphate/phosphonate blends have been the core of cooling tower treatment.
  - Operate at a mildly alkaline pH to reduce general corrosion.
    - $PO_4^{3-} + H_2O \Leftrightarrow HPO_4^{2-} + OH^-$
  - Phosphate and polyphosphates form precipitates at anodes and cathodes to help reduce the corrosion current.
    - $3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2\downarrow$ (At the anode)
    - $3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2\downarrow$ (At the cathode)
  - Zinc often added as a cathodic inhibitor
    - $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$



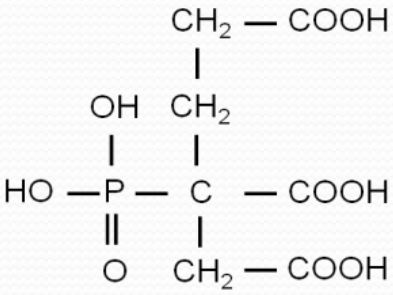
Phosphate/Phosphonates

- Especially in the early days, calcium phosphate [$Ca_3(PO_4)_2$] deposition became almost as great a problem as calcium carbonate had been.
- Phosphonates (organic phosphates) were increasingly utilized and perfected to help control scale, but resist self-deposition.

HEDP

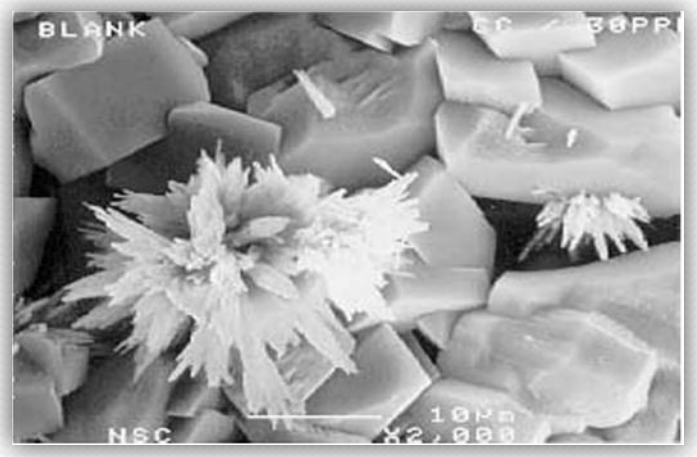


PBTC



Phosphate/Phosphonates

- A primary mode of scale control by phosphonates is crystal modification.
  - Crystals still form, but structure is weak and they do not adhere to metal surfaces.



Without inhibitor

With inhibitor

Phosphate/Phosphonates

- Treatment formulations must control other deposits that can form due to alkaline pH operation, including:
  - Magnesium and calcium silicates
  - Calcium sulfate
  - Calcium fluoride
  - Manganese dioxide (can also induce galvanic corrosion of stainless steel)

Trouble in Paradise(?) 2

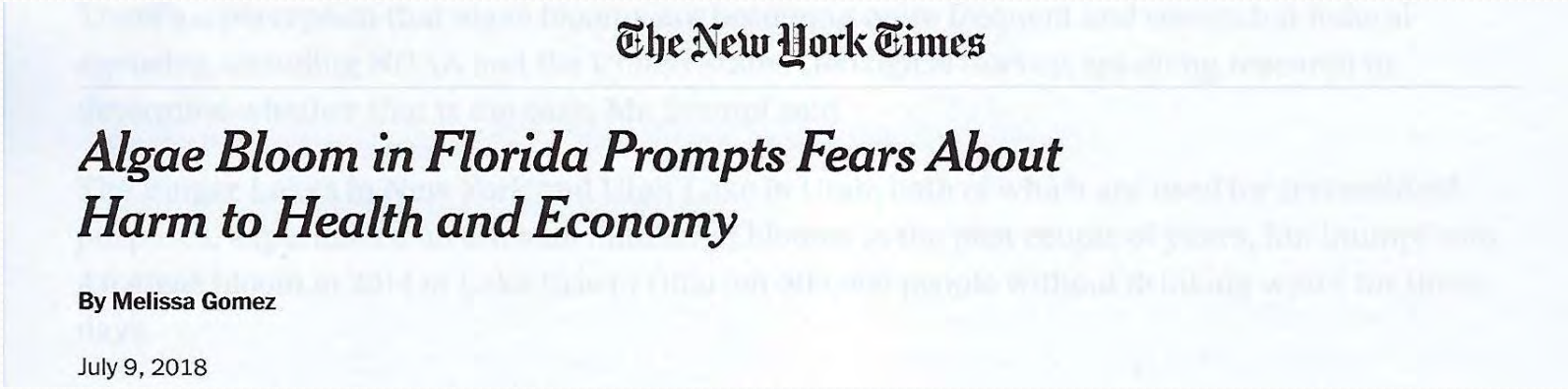
- Phosphate/phosphonate programs have often proven difficult to control.
  - The precipitates that reduce corrosion may wash away.
  - Under- or over-feed of chemical can lead to corrosion or severe deposition.
  - Changes in water chemistry can affect the program. Sophisticated controls are often needed.
- Now of increasing concern is the issue of phosphorus discharge.

Phosphorus Issues

- Phosphorus is a primary nutrient for all life, including microorganisms.
- Toxic algae blooms have become a huge concern in many receiving bodies of water around the country.

Giant blue-green algae bloom in Lake Erie

Phosphorus Issues



The New York Times

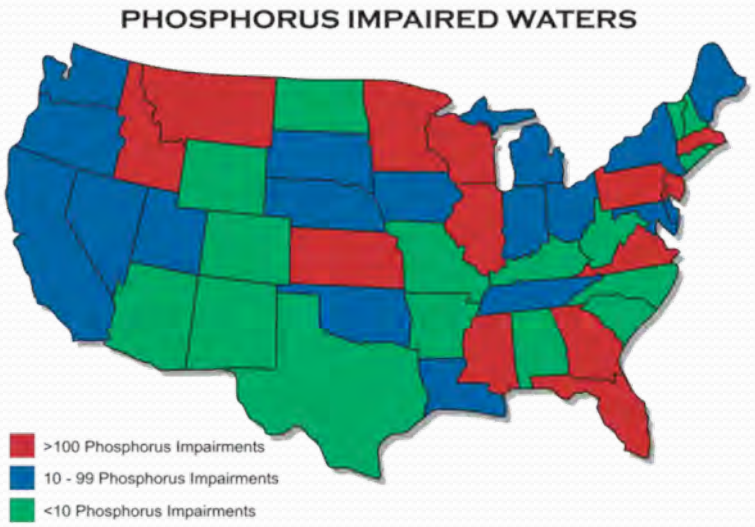
Algae Bloom in Florida Prompts Fears About Harm to Health and Economy

By Melissa Gomez

July 9, 2018

Phosphorus Issues

- States have the power, apart from the EPA, to develop discharge permits.
- Phosphorus is being increasingly regulated, along with:
  - Ammonia
  - Copper, zinc, and other metals
  - Sulfate
  - TDS

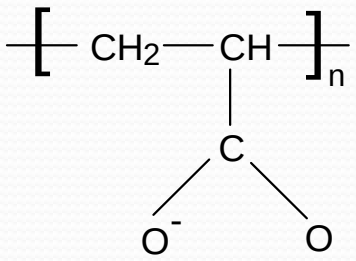


Non-P Chemistry to the Rescue

- Researchers have been diligently working on solving the two-headed issue of improved corrosion/scale control and elimination of phosphorus discharge.
- Some versions of non-phosphorus (non-P) chemistry have now reached maturity, with demonstrated full-scale results.

Non-P for Scale Control

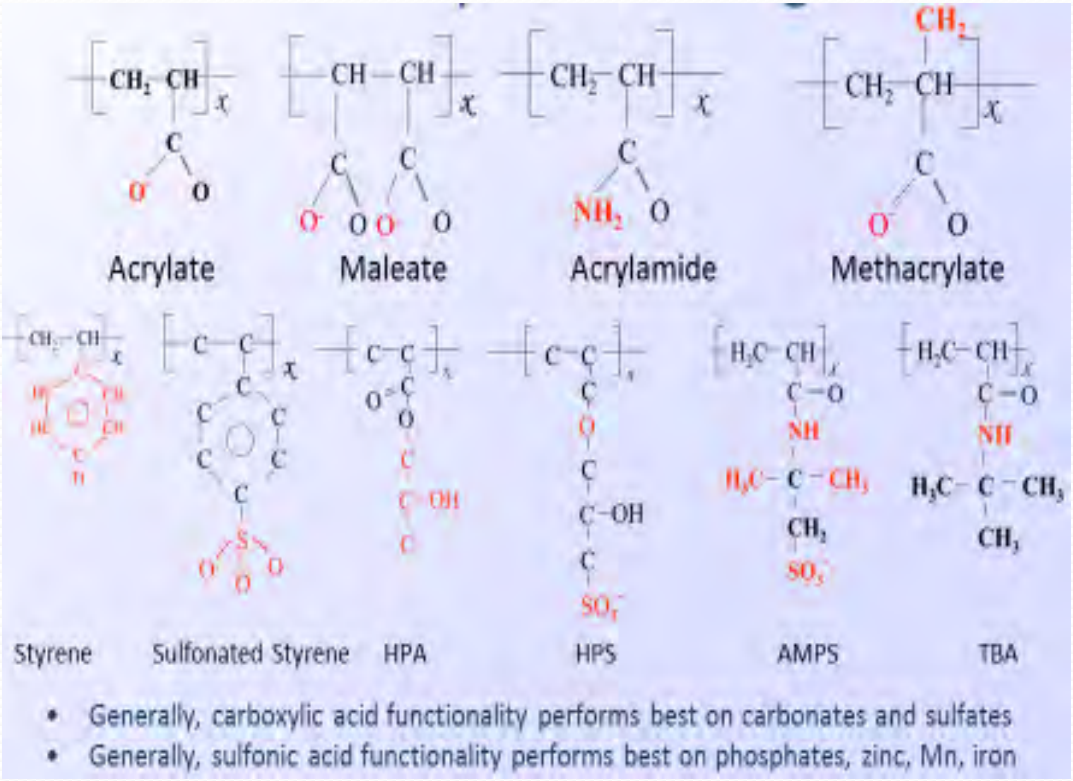
- Polymers for scale control have been around for quite some time, and indeed are necessary in phosphate-phosphonate programs to inhibit calcium phosphate deposition.
- The most basic polymers rely on the carboxylate functional group in various configurations to control scale.



Carboxylate functional group on a section of the polymer chain

Non-P for Scale Control

- Co-, ter-, and even quad-polymers have been developed to control other scales.



Non-P

- A low parts-per-million (ppm) dosage can often be quite effective. The polymers act by:
  - Crystal modification
  - Ion sequestration
- But what about corrosion control?

Non-P Corrosion Control

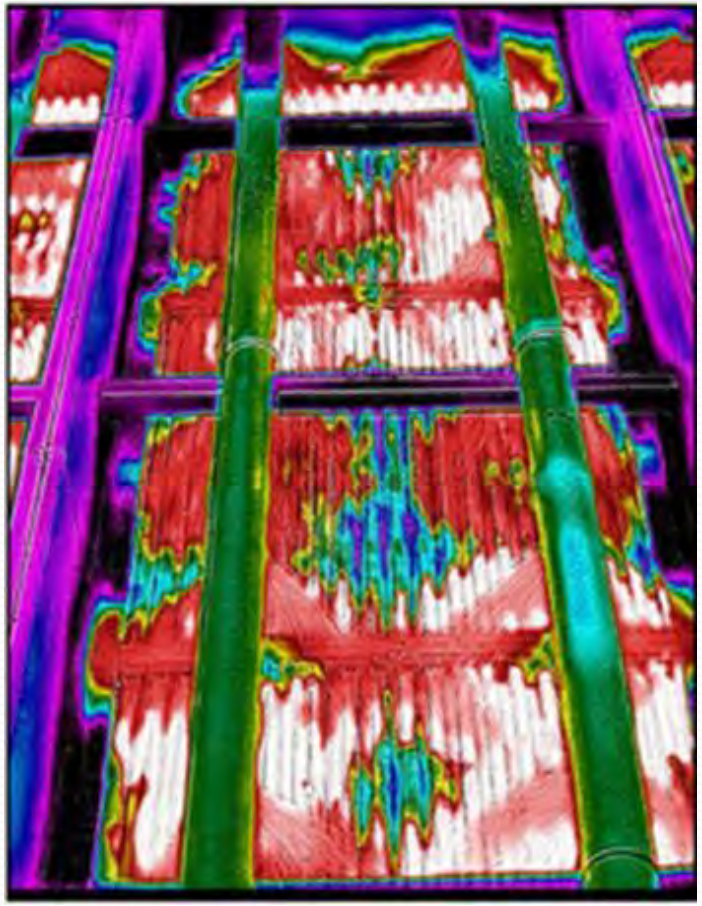
- One product successfully being used goes by the generic chemical name of:
  - Reactive polyhydroxy starch inhibitor (RPSI)
- The hydroxyl (OH) and oxygen groups on the carbon chains attach to metal surfaces. The carbon-chains then form a protective film.
  - Similar technology with azoles (active nitrogen groups) has been used for years for copper alloy protection.

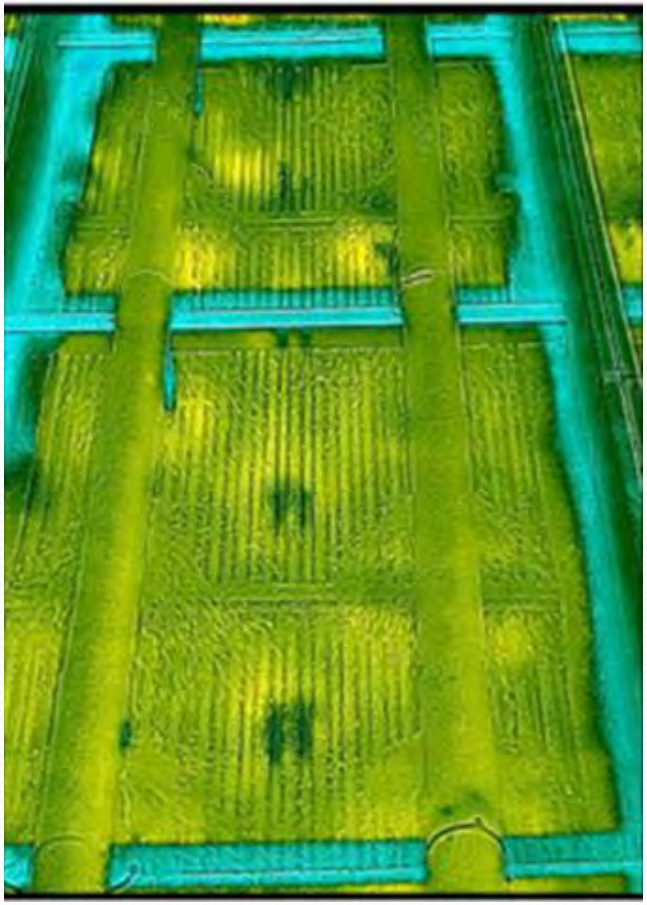
Non-P Corrosion Control

- As contrasted to phosphate/phosphonate programs, RPSI does not rely on deposition products to inhibit anodic and cathodic reactions.
- The next two slides show the results of the chemistry in the cleaning solution (and subsequent standard treatment) of a wet-surface air cooler (WSAC®) at a natural gas liquid (NGL) fractionation plant on the U.S. Gulf Coast.
- Data from another full-scale application showed a corrosion rate reduction of nearly two orders of magnitude.

RPSI Visual Results

RPSI Thermal Images





Non-P Treatment

- Direct costs for non-P treatment are not significantly higher than for phosphate-phosphonate programs.
- Economics become even better over the long-term due to reduced corrosion.
- Modern control systems are now available to feed and track chemistry.

And Now for Something Completely Different

Wastewater Techniques for Makeup Water Treatment

- By choice or mandate, alternatives to fresh water are being selected as makeup to new plants.
- A common choice is secondary effluent from a Publicly Owned Treatment Works (POTW), aka grey water.

WWT for MU Water

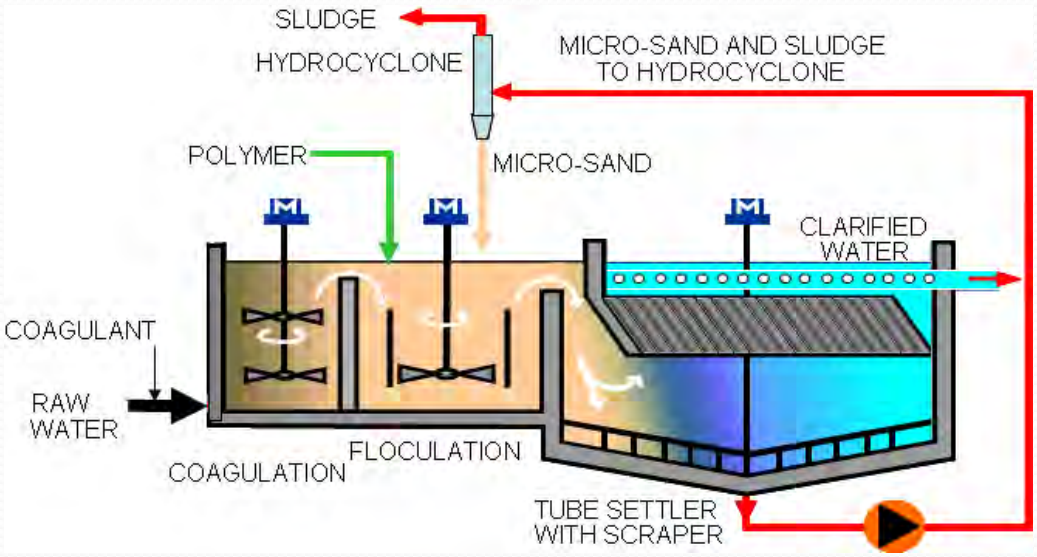
- Grey water usually has much higher levels of several critical impurities.
  - Ammonia (NH_3)
  - Nitrite/nitrate (NO_2/NO_3)
  - Organic compounds
  - Phosphate
  - Suspended solids
- These are food and nutrients in cooling water.

WWT for MU Water

- Clarification is a potential first step.
  - Removes suspended solids and possibly some organic materials.
  - Iron or aluminum coagulants will precipitate most of the phosphate.
  - If the process includes lime softening, additional phosphate removal may be accomplished.
    - Lime softening clarifiers generate large volumes of sludge.

WWT and MU Water

- New clarification technologies are available to replace the old gigantic circular clarifiers with slow rise rates.



Actiflo® clarifier schematic. Courtesy of Veolia Water Technologies.

WWT for MU Water

- Clarification does nothing for nitrogen species, and most organics typically remain in the water.
- If left untreated, the water may still be of such poor quality that film fill cannot be used in the cooling tower.

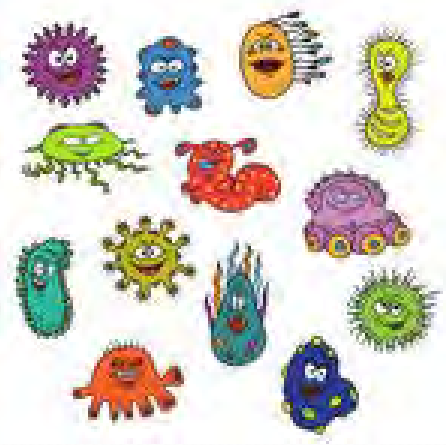
- Modern biological treatment techniques are available.

WWT for MU Water

- Biological treatment for wastewater has been around for decades.
  - Activated sludge and return activated sludge (RAS)
  - Trickling filters
- Employ beneficial microorganisms to consume organics and ammonia.
- Can be very effective, but:
  - Require large volumes or long contact periods.
  - Basic process only converts ammonia to nitrate.
    - NO_3 may still be problematic in cooling systems or the discharge.

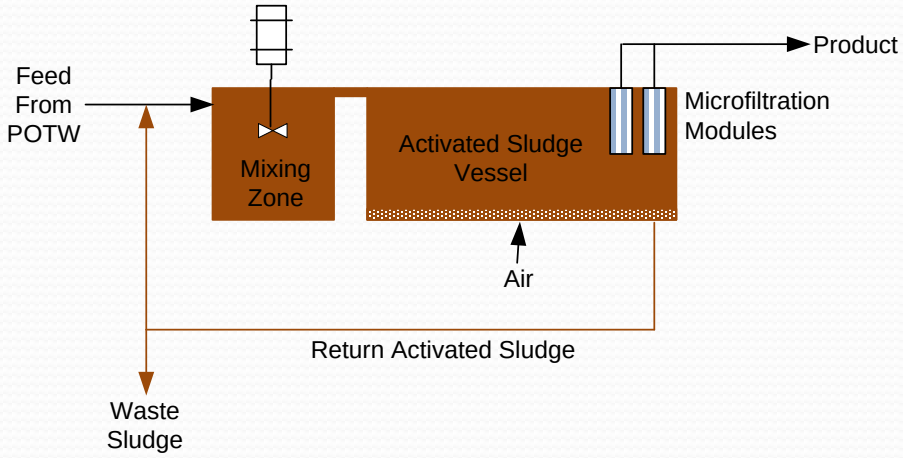
WWT for MU Water

- Modern technologies are available that rapidly speed up the process, with a much smaller footprint.
- Two increasingly popular methods are:
  - Membrane bioreactors (MBR)
  - Moving bed bioreactors (MBBR)



MBR

- Fundamental MBR process is based on RAS, but with much faster reaction rates than conventional RAS.
- Effluent passes through microfiltration membranes and is very clean.



MBR

- MBR is becoming more common for municipal wastewater treatment.
  - I had the opportunity to tour the Smith & Loveless MBR plant for the city of De Soto, Kansas. Crystal clear effluent.
- Basic MBR only converts ammonia to nitrite/nitrate.
- Anoxic and anaerobic stages can be added to these systems and others, in which the bacteria extract oxygen from NO_2 and NO_3, converting the compounds to elemental nitrogen.
  - Odors can be a problem with anaerobic processes.
- A key maintenance item is keeping the membranes clean. Air and water scouring are common cleaning methods.

MBR

- The photo below is of an advanced MBR with an anaerobic stage, which converts nitrogen species to elemental nitrogen.

AnMBR® system. Photo courtesy of Evoqua.

MBBR

- Employs a substrate to which the beneficial microbes attach to improve the process.
  - Advanced version of the old trickling filter
- In MBBR, the media is mobile plastic disks.

Illustration courtesy of Veolia Water Technologies.

MBBR

- Like MBR, the primary MBBR process involves activated sludge, but the process can be expanded to provide for nitrite/nitrate conversion to elemental nitrogen.
- Unlike MBR, filtration of MBBR effluent must be done externally. Micro- or ultra-filters can also be used for this procedure.

Some Brief Comments About Microbiological Fouling Control

- Time constraints prevent a major discussion about cooling water microbiological fouling, but:
  - It can be the 800-pound gorilla in the room when it comes to cooling system upsets.
  - A key aspect is preventing organisms from settling and establishing protective slime films.
  - Bleach is still used at many plants, but its effectiveness decreases with rising pH.
  - "New" oxidizers such as monochloramine and monobromamine may be effective against established colonies. On-site bleach production is also somewhat common.
  - Non-oxidizing biocides, fed on a periodic basis, can also be effective.

Conclusion

- Power plant water treatment must be viewed holistically, from makeup through the unit processes to discharge.
- New chemistry and equipment technologies have emerged to better control water chemistry throughout the process and reduce employee stress.

Thank you!

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