REINHOLD ENVIRONMENTAL Ltd.

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Water Treatment for the Modern Power Industry

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Introduction

- This paper is a break from the norm at this conference, but water (and increasingly wastewater) treatment and chemistry are critical issues at any steam generating plant.
- I spent many years at two utilities and much time since dealing with these issues. (And also wet-limestone scrubbers and SCRs)

Outline

- The importance of proper water/steam chemistry
- Makeup water treatment evolution
- Current thinking regarding water/steam process chemistry
- Increasing importance of wastewater treatment

Water is not just water!

- Poor makeup water treatment and process upsets can lead to problems like this.

Photo courtesy of Mel Esmacher, GE Water.

Impurity Consequences

- Impurities such as chlorides, hardness compounds and others cause waterwall scaling and corrosion. Failures can occur within days or even hours of a major upset.
- Contaminants can be introduced directly to steam via attemperation or excessive concentration in drums. They can cause,
  - Superheater/reheater fouling
  - Deposition on turbine blades
  - Turbine blade corrosion

Makeup Water Treatment Guidelines

- Per EPRI, below are established guidelines for makeup water system effluent.
  - Sodium, < 3 ppb
  - Silica, < 10 ppb
  - Chloride, < 3 ppb
  - Sulfate, < 3 ppb
  - TOC, < 300 ppb

The Old Days

- In the last century, a makeup system would often look like;
  - Clarification/sand filtration → Cation exchange → Anion exchange → Mixed-bed ion exchange polishing

- This technology would do the job, but with much acid and caustic usage due to frequent regenerations.

A Transformation

- In the last three decades, water treatment schemes have greatly evolved. A very common scenario today is;
  - Primary filtration (often micro- or ultrafiltration) → Reverse osmosis (single-pass or two-pass) → Polishing either with exchangeable mixed-bed "bottles," or by electrodeionization (EDI)

Factors That Have Influenced This Transformation

- Modern filtration systems without clarifiers can often provide the necessary pre-treatment ahead of RO.
- RO can remove 99+ percent of the dissolved ions in the water.
- Polishing devices such as exchangeable mixed-bed bottles or EDI operate very well with RO-treated influent.

Technology Overview

Micro- and Ultrafiltration

- Micro- and ultrafiltration, (MF and UF by acronym) mechanically remove fine particulates.
- MF filtering range: 0.05 to 5 microns.
- UF filtering range: 0.005 to 0.1 microns.
- While several designs are available, most if not all utilize hollow fiber membranes to filter particulates.

MF Types

- Several reputable companies manufacture MF systems.
- In one design, the hollow fibers hang within the water to be purified, and a vacuum pulls water through the membranes.
- In the other major design, pressurized water is pumped through vessels containing the fibers, where the water is forced through the membranes.

Microfilter pressure vessel skid. Photo by Brad Buecker.

Hollow Fibers

Hollow fibers in a cutaway view. Photo courtesy of the Pall Corporation.

MF and UF, Additional Details

- UF and particularly MF operate with very low driving pressures, thus the membranes can be manufactured from durable material. The typical choice is polyvinylidene fluoride, PVDF, although at least one manufacturer offers ceramic membranes for high temperature applications.
- PVDF is tolerant to oxidizing biocides, so a continuous chlorine or bromine treatment may be applied to prevent microbial growth.

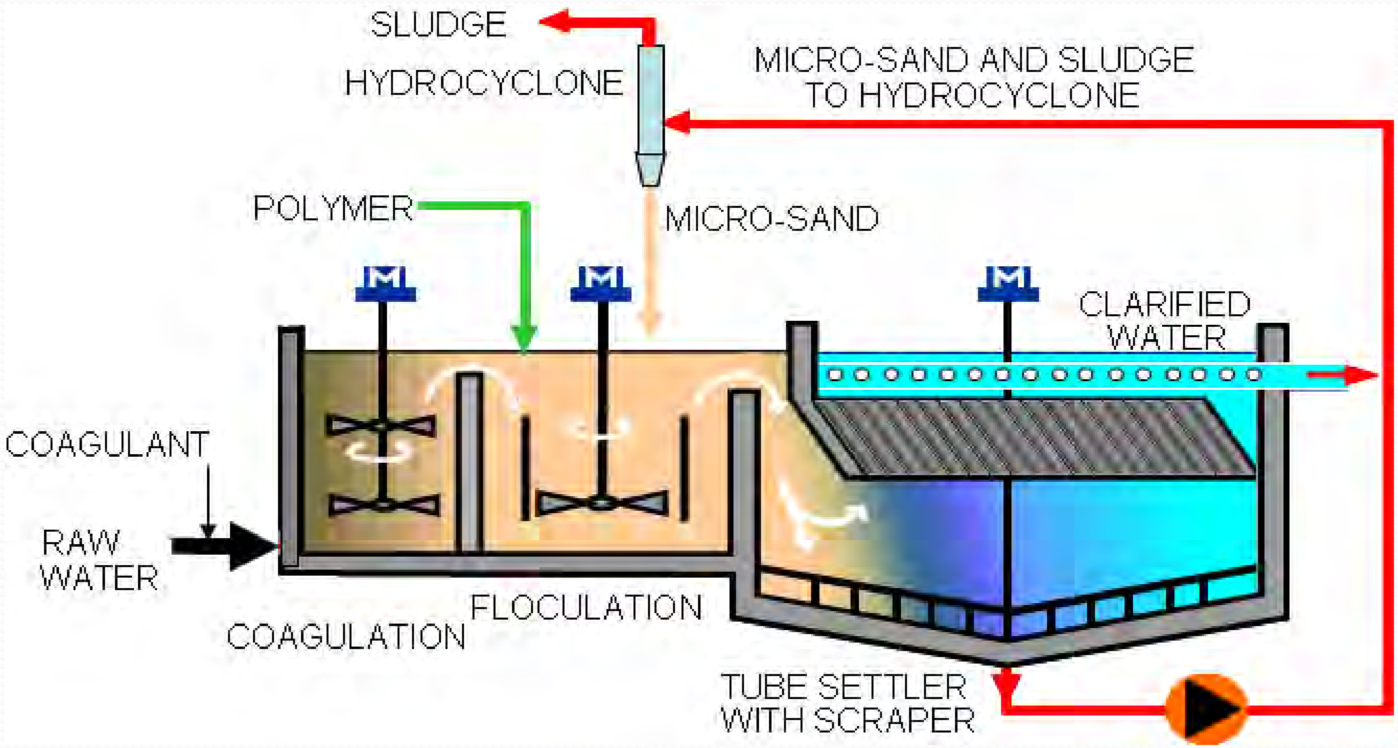
An Additional Driver for Proper Pre-Treatment

- Existing and new regulations, such as Title 22 in California, are requiring more plant owners to use recycled water instead of fresh water for makeup.
- Recycled water is often more variable than fresh water supplies. Variable constituents include,
  - Suspended solids
  - Organics
  - Ammonia and phosphate

A Note About Clarifiers

- Clarifiers still have a place in many applications, particularly if the raw water exhibits the following characteristics.
  - High hardness (calcium and magnesium)
    - Lime and soda ash softening
  - Intermittent or continuous high suspended solids content
    - Excursions that could overwhelm MF or UF units.

A Modern Clarifier Design

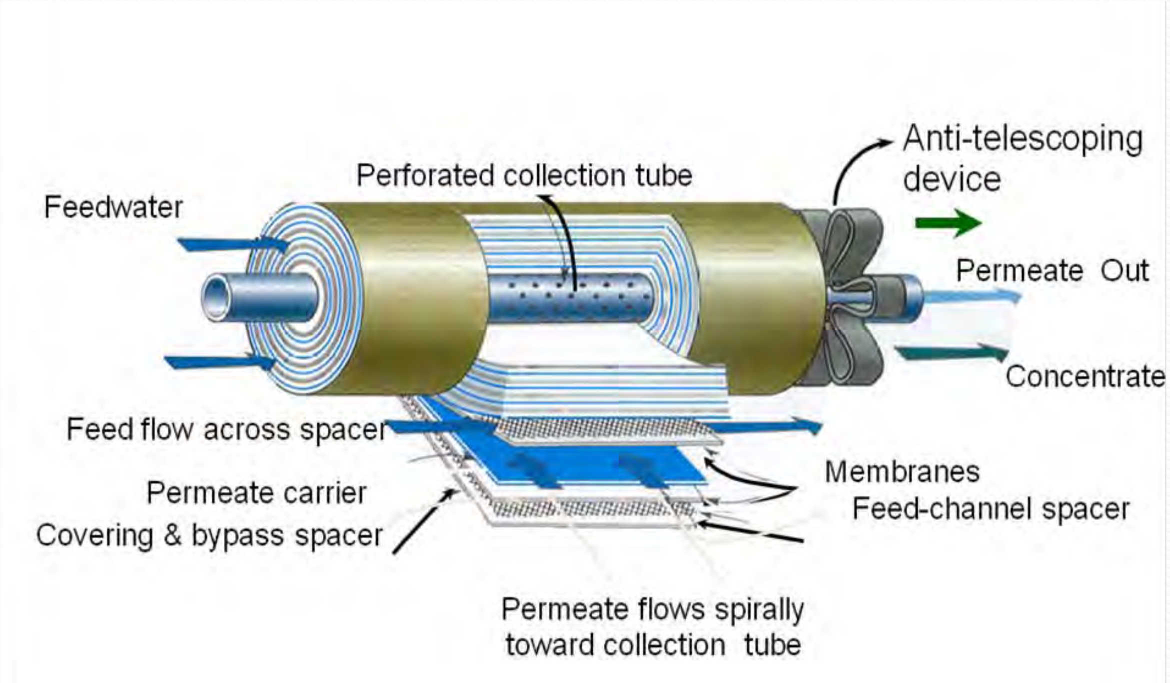


Schematic of an Actiflo® clarifier.
Illustration courtesy of Veolia.

Primary Dissolved Solids Removal Reverse Osmosis

- Clarifiers/filters, microfilters, and ultrafilters remove suspended solids, but dissolved solids remain.
- Prior to commercial development of RO units, ion exchange resins were exclusively utilized to remove the dissolved ions necessary to produce high purity water.
- The high ion load to demineralizers resulted in short run lengths and high acid and caustic usage for regeneration. Enter reverse osmosis.

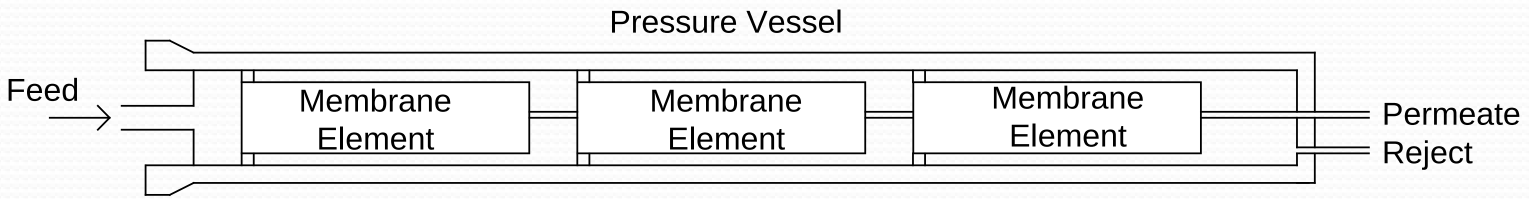
RO Membrane Design



Spiral-wound design. The flat membrane sheet and spacer materials are wound around a perforated central core. Feed-water must be at pressure to provide the driving force.

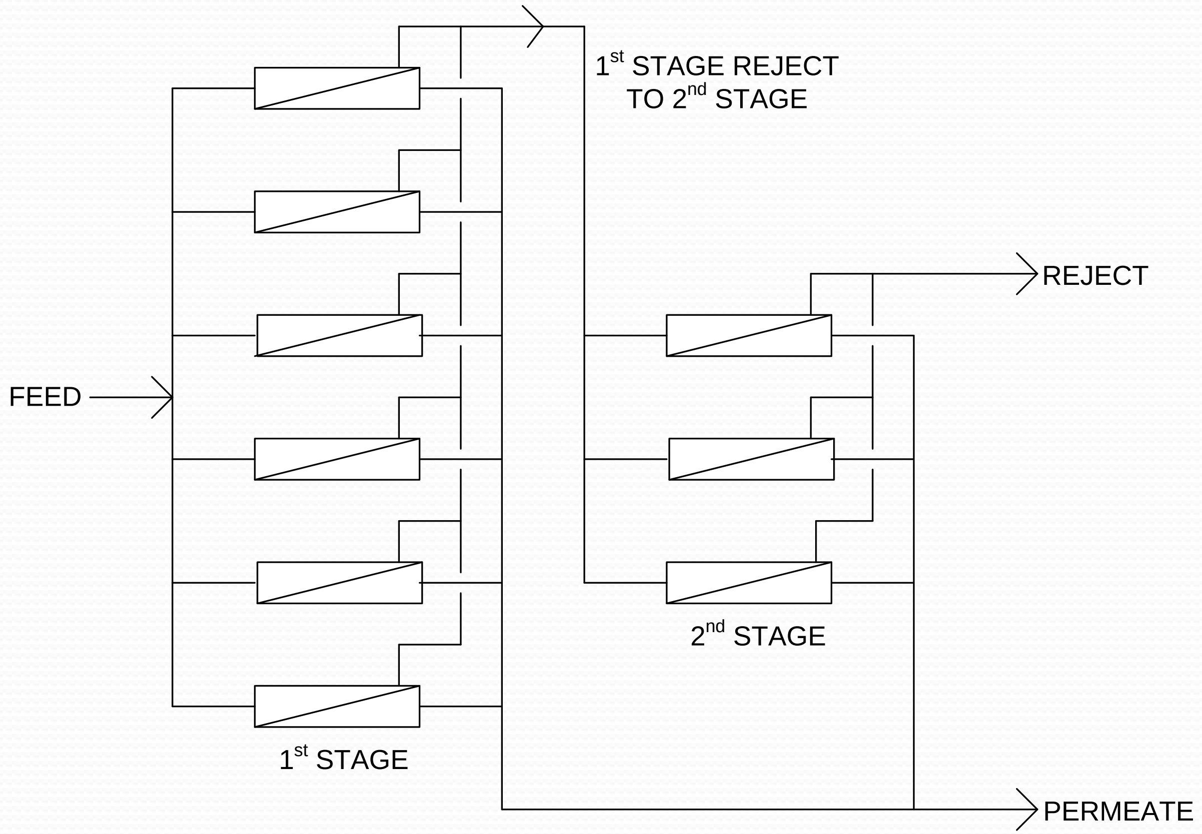
RO Pressure Vessel Layout

- Several spiral wound membrane elements are placed in series within a pressure vessel.



- Pressure vessels are then sized and arranged per permeate flow requirements.

Two Stage, Single-Pass RO System Schematic



Typical for "normal" waters is 50% recovery from the first stage followed by 50% recovery from the second stage.

Two-Pass RO

- A quite common application nowadays is two-pass RO, where the permeate of the first pass is treated in a second RO pass.

- The water from the second pass is pure enough to be polished by mixed-bed ion exchange or EDI.
  - The second pass reject is recycled to the first pass inlet.

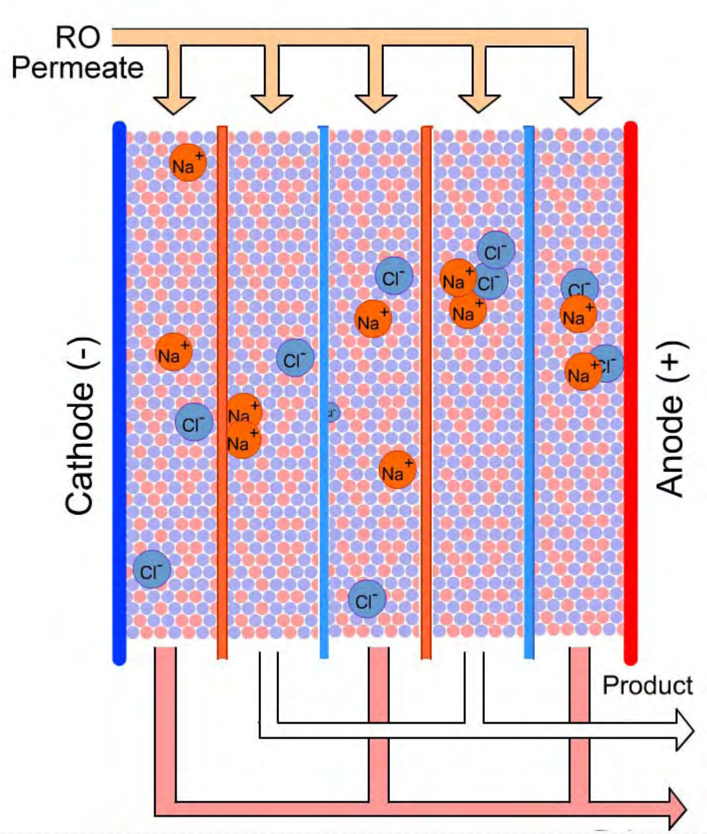
Polishing

- The permeate from a two-pass RO may reach the following quality:
  - Specific conductivity, 0.5 to 1 μS/cm
  - Total dissolved solids, 0.5 ppm
- This is not quite pure enough for high-pressure steam generators. Permeate polishing is needed.

Polishing Choices

- Two methods currently predominate for polishing.
  - Exchangeable mixed-bed units, commonly termed “bottles” that a vendor replaces on an as-needed basis.
    - No capital cost other than piping from the RO to the MB bottle station
  - Electrodeionization
    - EDI is a permanent system that utilizes ion exchange, membranes, and electrolysis to purify water.

The EDI Process



EDI process. Illustration courtesy of Siemens Water Technologies

Water/Steam Chemistry: Current Trends

Chemistry Lessons (Not Always) Learned

- Chemistry for coal-fired steam generators has significantly evolved over the last 30 years.
- HRSG chemistry is very similar, but the importance of many issues is not always recognized.
  - Feedwater/low-pressure boiler chemistry
    - Flow accelerated corrosion (FAC). Some plant personnel still insist on feeding oxygen scavengers.
    - Transport of FW corrosion products to the boiler
  - Operating with condenser tube leaks
    - Boiler corrosion including hydrogen damage

Chemistry Lessons (Not Always) Learned

- Steam Chemistry Issues
  - Mechanical carryover of corrosive compounds to the superheater, reheater and turbine
  - Vaporous carryover of impurities
- Poor Layup Practices
  - Severe oxygen attack of components
  - Generation of huge volumes of particulates that carry over to the steam generator

What Causes These Problems, A Feedwater Examination First

- Unless the condensate/feedwater network contains copper alloys (very unlikely with HRSGs), do not feed oxygen scavengers.

- The combination of oxygen scavenger feed with ammonia or amine injection for pH control is known as all-volatile treatment reducing [AVT(R)].

- The reducing environment produced by AVT(R) causes metal dissolution at flow disturbances. This is known as single-phase, flow-accelerated corrosion (FAC).

Single-Phase FAC

- The combination of a reducing environment generated by an oxygen scavenger and flow disturbances can cause this →
- Fatalities have resulted from FAC-induced failures.

Photo courtesy of Dave Johnson, ChemTreat.

FAC, continued

- <u>Two-phase</u> FAC may occur with water/steam mixtures, at such locations as deaerators and LP drums.

Controlling FAC

- Methods to minimize single- and two-phase FAC
  - No oxygen scavenger feed. Allow oxygen that enters the condensate via condenser air in-leakage to remain. This is known as all-volatile oxygenated treatment [AVT(O)].
    - $\leq$10 ppb O_2 has been the standard
  - Maintain feedwater pH at or near 9.8.
  - Fabricate HRSG LP waterwall tube elbows from 2¼ chrome steel.
  - Perform NDT of susceptible locations.

Boiler Water Treatment

- Most high-pressure drum units still operate on phosphate treatment, but many power plant chemists have converted to EPRI's phosphate continuum (PC) program.
  - Only tri-sodium phosphate [$Na_3(PO_4)$] is utilized, with perhaps a bit of caustic (NaOH) at startup.
  - Phosphate concentration maintained below 3 ppm, and often 1 ppm or lower.
  - Free caustic alkalinity must not exceed 1 ppm to prevent under-deposit caustic gouging.

Boiler Water Treatment

- Alternatives to phosphate treatment
  - Straight caustic (free hydroxide at or below 1 ppm)
  - All-volatile treatment (AVT) utilizing the ammonia added to the feedwater for pH control.

- None of the modern programs offer much protection against impurity ingress.

Boiler Water Chemistry

- Operating a unit with condenser tube leaks (or other contaminant source), and where the condensate/feedwater system has no condensate polisher, is a potential recipe for disaster!

- Even trace amounts of impurities, most notably chloride but also sulfate and caustic, can concentrate under porous deposits and cause major damage.

Steam Issues

- Continuing research shows that even trace impurities in steam can cause significant turbine fouling and damage.
  - Chloride-induced stress corrosion cracking (SCC) and pitting in LP blades and rotors
  - Caustic-induced SCC
  - Silica deposition on turbine blades
  - Other deposition

Steam Issues

- Contaminants may enter steam by three principal mechanisms.
  - Mechanical carryover in drums
    - Sodium, chloride, sulfate, hydroxide and phosphate via,
      - Poor drum design, failed steam separators, improper operation, excessive boiler water dissolved solids (foaming)
  - Vaporous carryover
    - Excessive silica in the boiler water
    - (Copper in high-pressure units that have copper alloy feedwater heaters. Some remaining coal plants.)
  - Steam attemperation
    - Any impurities in the feedwater

Water/Steam Chemistry Monitoring: Important Samples

- Makeup System Effluent
  - Silica and specific conductivity
    - These measurements will indicate breakthrough of impurities from the makeup water treatment system. The system effluent should have sodium less than 3 ppb and silica less than 10 ppb.
- Condensate Pump Discharge
  - Cation conductivity (CC), sodium, dissolved oxygen (DO)
    - Cooling water in-leakage will immediately cause an increase in conductivity. The cation conductivity must be maintained below 0.2 µS (sometimes 0.15 µS) to minimize corrosion from oxidizing treatment programs.
    - Sodium is a straightforward measurement and a great supplement to CC. Normally less than 3 ppb, often less than 1 ppb.
    - DO needs to be less than 10 ppb for proper control of AVT(O) or AVT(R) programs. Concentrations in excess of 10 ppb indicate excess air in-leakage to the condenser.

Water/Steam Chemistry Monitoring

- Economizer Inlet
  - DO, pH, specific conductivity (SC)
    - DO measurements supplement those of the condensate pump discharge. In fact, a shared analyzer may be used.
    - The need for pH monitoring is a "no-brainer" to maintain a consistent alkaline environment. A pH in the mid- to upper-9 range is recommended.
    - SC is typically the guiding data for ammonia control due to the sensitivity of the readings in high-purity water.

Water/Steam Chemistry Monitoring

- Boiler Water
  - SC, CC, pH, sodium, silica, ammonia, phosphate (if necessary)
    - SC is important to ensure that impurities do not reach excessive levels in the boiler water and influence carryover contamination.
    - CC is useful in determining the concentration of harmful impurities vs. the conductivity induced by treatment chemicals.
    - As with feedwater chemistry, pH measurement helps to ensure that conditions are being maintained in an alkaline regime.

Water/Steam Chemistry Monitoring

- Boiler Water, cont.
  - Sodium
    - Sodium is an important measurement to track the chemistry of phosphate treatment programs, and to monitor for potential carryover issues.
  - Silica
    - Silica is typically monitored by grab sample analysis each shift or at least daily to ensure that concentrations remain below levels which would cause excessive carryover to the turbine.
  - Ammonia
    - Shift or daily grab sampling is needed to calculate the influence of ammonia boiler water alkalinity.
  - Phosphate
    - Continuous or shift grab sampling to track the performance of the boiler water treatment program.

Water/Steam Chemistry Monitoring

- Main/Reheat Steam
  - CC, sodium, silica
    - CC is the guideline used by turbine manufacturers. The common limit is ≤ 0.2 μS.
    - Sodium is a critical measurement for evaluating carryover. Current guideline is ≤ 2 ppb.
    - Silica is typically analyzed by grab sampling on a shift or daily basis. It is needed to monitor for vaporous carryover. Current guideline is ≤ 10 ppb.

Other Useful Sample Points or Samples: Periodic Analyses

- Saturated steam to evaluate mechanical carryover
- Makeup water and condensate pump discharge total organic carbon (TOC)
  - Organic carbon breakdown in steam can produce small-chain acids that cause turbine corrosion. Concentration should be less than 300 ppb (MU), 200 ppb (CPD).
- Main/reheat steam for chloride, sulfate (≤ 2 ppb), and TOC (≤ 100 ppb)
  - Helpful to evaluate carryover

A Look at Wastewater Treatment

- We have been seeing a continual stream of combined-cycle request-for-proposals (RFPs).
- Not one has called for a once-through cooling system, undoubtedly due to impending 316b regulations.
  - Most call for cooling towers, the remainder air cooled condensers.
- Many plants are facing restrictions on cooling tower and auxiliary wastewater discharge quantity and/or quality.
  - 40CFR 423, individual state regulations, etc.

Wastewater Treatment

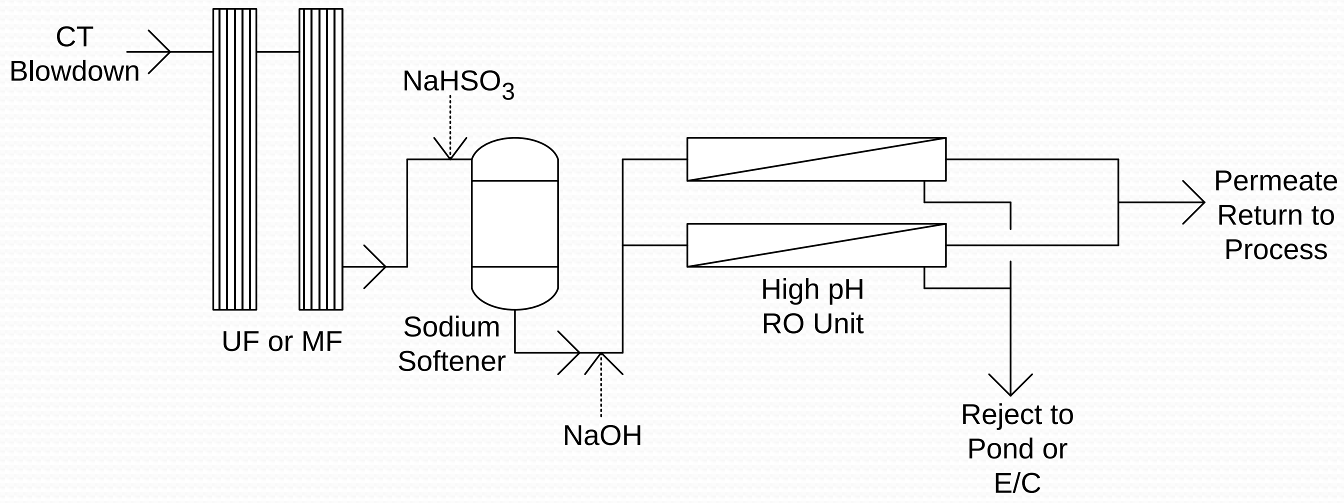
- Wastewater constituents being regulated include,
  - Suspended solids
  - pH
  - Oil and grease
  - Phosphate and ammonia
  - Copper and zinc
  - Sometimes a limit on total dissolved solids (TDS)

{ Traditional NPDES samples

Wastewater Treatment

- Many of the techniques outlined in previous slides are being applied to wastewater treatment to reduce the discharge volume. Emerging technologies include HERO® (High Efficiency Reverse Osmosis), licensed by Aquatech and GE, and OPUS®, licensed by Veolia.

Core Design of RO-Based WWT Systems



Core Design of RO-Based WWT Systems

- UF or MF for particulate removal
- Sodium bisulfite ($NaHSO_3$) feed to remove oxidizing biocides
- Sodium softening to remove calcium and magnesium hardness
- Caustic injection to keep silica in a soluble form
- RO to recover ~ 90 percent of the water

Concerns

- The process is not foolproof. Recent issues we have encountered include;
  - Some standard cooling water chemicals may foul the UF membranes.
    - The membrane manufacturer and type can greatly influence fouling.
    - Coagulants may not be effective at converting the chemicals into filterable flocs.
  - Low quality backwash water can cause scaling of UF membranes.
  - Clarification of the influent stream may be required.

Concerns

- Even with 90 percent water recovery, a liquid stream still remains. Possible disposal solutions include;
  - Evaporation ponds
  - Deep-well injection
  - Thermal evaporation/crystallization
  - Truck the liquid off-site to a waste disposal company.

Concerns

- A difficulty with cooling towers is the significant, continual water requirement due to evaporation.
  - Perhaps 1,000 to 3,000 gpm as compared to only a tenth or less of that for makeup water treatment.
- Restrictions on fresh water withdrawal are influencing cooling tower makeup, too. Replacement supplies include,
  - Recycle water
  - Poor quality surface or well water

Summary

- Water chemistry is extremely important for reliable plant operation.
- Failures can cause outages that cost a plant millions. FAC has caused fatalities.
- Wastewater treatment and water recycling are becoming much more important.

Thank you!

I always enjoy discussing power plant issues.
Please feel free to contact me at the following address.

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