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Welcome & Speakers

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Hardness and Alkalinity Management within Source Water Vulnerability

Agenda

- What is Water Quality?
- Management of Dissolved Solids
- Management of Water Hardness
- Management of Alkalinity & De-Alkalization
- Membrane – Reverse Osmosis
- Take Control of Organics
- Q&A

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What is Water Quality?

Water quality depends on how it is being used.

WATER CYCLE MANAGEMENT

TO MANAGE WATER QUALITY
you need understand the water.

TO UNDERSTAND THE WATER
you need monitor it.

TO MONITOR THE WATER
you need measure it.

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Factors Affecting Source Water Quality

- Temperature
- Total Suspended Solids (TSS)
- Total Dissolved Solids (TDS)
- Organics
- Microbiological

Industry and Processes Have Different Water Quality Guidelines

Cooling Tower Feedwater

- < 100 ppm Alkalinity
- < 200 ppm Total Hardness

Boiler Water

- Dependent on boiler pressure
- Need low hardness

Carbonated Soft Drinks

- <85 ppm Alkalinity
- < 100 ppm Total Hardness

Boiler Pressure Guidelines

Pressure PSI	Silica mg/L	Total Hardness	Total Alkalinity	Oxygen	Iron	Copper
100	15 – 25	75.00	900.00			
200	10 – 20	20.00	800.00			
300	7.5 – 1.5	2.00	700.00			
500	2.52 – 5.0	2.00	600.00	0.03		
600	1.3 – 2.5	0.20	500.00	0.03		
750	1.3 – 2.5	0.10	300.00	0.03	0.05	0.02
900	0.8 – 1.5	0.05	200.00	0.007	0.02	0.015
1000	0.2 – 0.3	0.05	50.00	0.007	0.02	0.015
1500	0.3 max	0.00	0.00	0.005	0.01	0.01
2000	0.1 max	0.00	0.00	0.005	0.01	0.01
2500	0.05 max	0.00	0.00	0.003	0.003	0.002
3200+	0.02 max	0.00	0.00	0.002	0.002	0.001

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Hach Provides Analytical Solutions Appropriate for Every Application and Process

- Eliminate Sampling and Analytical Error
- Real Time Measurement - Always
- Online Systems for Analysis and Control

Simple Test Kits

Extensive Laboratory Systems

Online Systems for Analysis and Control

This is especially critical when determining the exhaustion of zeolite softening process.

Management of Dissolved Solids

In clarified and disinfected water the concentration and types of dissolved solids present are a primary concern with quality of the water for direct use in a production and/or utility process.

By concentration, the primary dissolved constituents of most untreated waters are the minerals:

- Cations (+): Calcium, Magnesium and Sodium
- Anions (-): Bicarbonate, Chloride and Sulfate

Other dissolved constituents of concern in lower concentrations:

- Iron, Manganese, Aluminum
- Nitrate/Nitrite

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Management of Water Hardness

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Water Hardness

- Hardness: Typically the sum amount of calcium (Ca) and magnesium (Mg) in water expressed as mg/L $CaCO_3$
- Hardness is the primary cause of scale in heat exchange equipment, boilers, pipelines.
- It can interfere with commercial and industrial processes such as dyeing, beverages, etc.
- Treatment includes water softening, reverse osmosis, demineralization, internal boiler water treatment and surface-active agents.

NOTE: In water quality ……….Hardness is always a consideration even if there is not s stated specification. Understanding the relationship of hardness to TDS and its relation to alkalinity is critical.

Example: $CaSO_4$ and/or $CaCl_2$ can affect flavor profile.

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Causes of Hardness

Minerals contributing to hardness include:

- Primarily - Calcium and Magnesium
- To a lesser extent -iron, strontium, aluminum, zinc and manganese.

Hardness then is generally expressed as the total concentration of calcium and magnesium ions present in the water and its units of measurement are as mg/L $CaCO_3$.

17.1 mg/L ~ 1 grain/gal

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Expression of Hardness

As a guideline

- Very soft < 30 mg/L
- Soft 30-75 mg/L
- Moderately hard 75-150 mg/L
- Hard 150-300 mg/L
- Very hard >300 mg/L

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Chemistry of Water Hardness

Water hardness may be of two types:

Carbonate & *Non-carbonate*

Carbonate hardness: Bicarbonates of calcium and magnesium

Also referred to as temporary hardness, which is typically removed by precipitation or ion exchange

Non-carbonate hardness: Hardness contributed by calcium and magnesium sulfates, nitrates, chlorides

Also referred to as permanent hardness, which is typically removed by ion exchange

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Methods for Softening Water

Softening methods generally fall into four categories; precipitation, reverse osmosis, membrane, and ion exchange.

Precipitation: typically is accomplished with the lime-soda process.

Zeolite Softening: Ion Exchange of Hardness with Sodium

Membrane: Nanofiltration and Reverse Osmosis

Ion Exchange/De-mineralization: is accomplished with a variety of naturally occurring and synthetic substances

- **Anion Bed:** Removes anions
- **Cation Bed:** Removes cations
- **Mixed Bed:** Remove cations and anions

Methods for Softening Water

Precipitation: Alkalinity Not Reduced

Zeolite Softening: Alkalinity Not Reduced

Membrane:

- **Nano Filtration:** Some Reduction of Alkalinity
- **Reverse Osmosis:** Alkalinity Reduced / Removed

Ion Exchange/De-mineralization: Alkalinity Removed

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Precipitation: Lime Softening

- Precipitation / softening processes are for reducing the TDS of resource/raw water for direct use in processes or as an initial stage for further purification.
- **Primarily calcium hydroxide in the form of hydrate lime along or with soda ash and or sodium aluminate is reacted with the raw water hardness and alkalinity to form an insoluble precipitate which can be removed by sedimentation and filtration.**
- This method is used for raw water with hardness levels in the 150 – 500 mg/L as $CaCO_3$ range.

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Precipitation: Lime Softening

There are three primary methods of lime softening:

- Cold Lime Softening
  - Takes place at ambient temperature
- Warm Lime Softening
  - Temperature range of 120-140F
- Hot Process Softening
  - Temperature range of 227 – 240F
  - Good for silica reduction

Lime softening can also reduce iron, manganese, silica and water organics (color-contributing colloids).

As a general description the pH of the water is made alkaline (target >9.4) and at that point calcium forms an insoluble precipitate that can be removed by sedimentation. If magnesium is needed to be removed then the pH is increased to 10.6.

Precipitation: Lime Softening

Lab and online measurement in lime softening. This includes:

- Calcium Hardness
- Total Hardness
- Alkalinity
- pH
- Suspended Solid
- Conductivity
- Silica

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Sodium Zeolite Softening

This is the original ion exchange process and continues to be very common form of water treatment.

Water passes through a bed of zeolite material which exchanges sodium ions for hardness (calcium and magnesium ions).

- If you have a water softener in your home you are performing zeolite softening.

The treated water is now called “soft” because the hardness has been replace with sodium.

- Typically Hardness is reduced to < 2.0 mg/L as $CaCO_3$
- The TDS of the water is not reduced as there is an equivalent amount of sodium in the water as a replacement for the hardness.
  - TDS/EC may actually increase.
- Sodium being extremely soluble is not subject to scaling.

Understanding when the zeolite resin is exhausted (no longer able to exchange the hardness with sodium) is critical.

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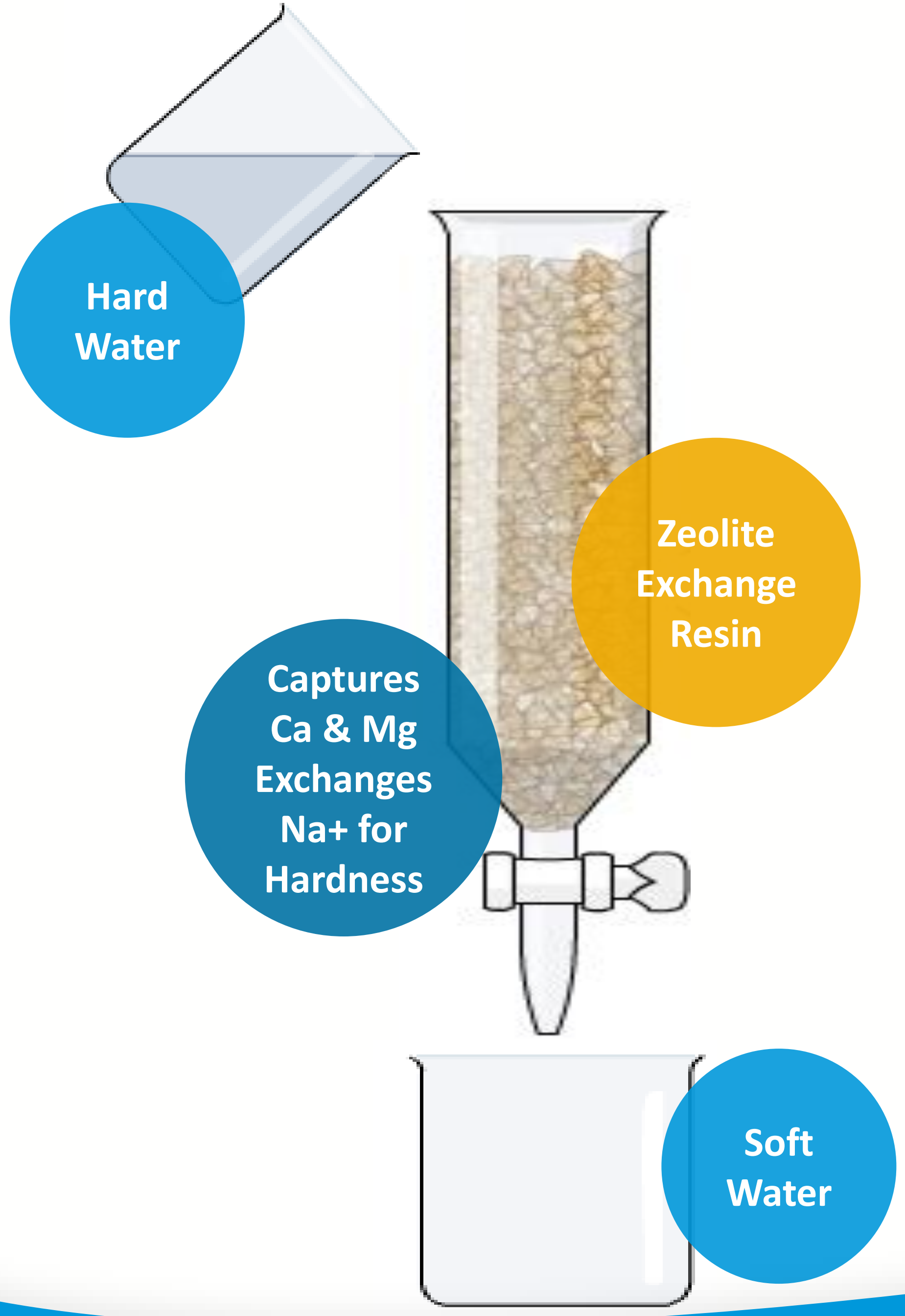

What is Zeolite “Ion Exchange”?

Sodium Zeolite Softening

Although sodium zeolite softeners efficiently reduce the amount of dissolved hardness in a water supply, alkalinity concentrations are not affected.

The concentration of sodium is now equivalent to the amount of sodium originally present in the water plus the sodium from the ion exchange.

- Based on specific limits the sodium will need to be reduced by reverse osmosis.

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Sodium Zeolite Softening

Softening cycle:

- **The length of the softening cycle ends when 1 to 5 mg/L of hardness is detected in the effluent**
- While 1-5 mg/L hardness is typical value for regeneration, that can vary on the quality of water needed.

Sodium Zeolite Softening

Softening cycle:

- Almost all softening units have an alarm on the water meter to indicate when a certain amount of water has passed through the exchange unit
  - This is an estimate only and can result in water loss due to overused regeneration or to hardness breakthrough due to underused regeneration.

Hach's SP-510 Hardness Monitor

- Provides a trip alarm and control
- Does not provide actual concentration of hardness

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Sodium Zeolite Softening

The primary parameter being monitored is to determine when the zeolite resin is exhausted.

- Hach's Hardness Monitor (SP510) has been widely adopted for this application.
    - It is used for auto-regeneration of the zeolite beds.
    - Based on set Points and not actual concentration
    - Set Points Can be Chosen
        - 0.3 mg/L
        - 1 mg/L
        - 5 mg/L
        - 10 mg/L
        - 30 mg/L
        - 50 mg/L
        - 100 mg/L

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Sodium Zeolite Softening

Parameters monitored for pre-zeolite softening

- Total Hardness
- Calcium Hardness
- Suspended Solids –
  - Zeolite softeners will not function efficiently on turbid waters
- pH
- Conductivity
- Iron and Aluminum
  - Can foul the zeolite process

Hach's EZ Series Analyzers, Turbidimeters, pH and Conductivity can provide a complete integrated monitoring package

Sodium Zeolite Softening

Backwash

- Remove trapped suspended solids
- Reset / Fluff the zeolite resin

Brining

- 10% Brine Solution displaces the calcium and magnesium from the exchange sites on zeolite and replaces with sodium.

Slow Rinse

- Removes excess brine + Calcium and Magnesium to drain.

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Sodium Zeolite Softening

Water from a properly operated zeolite softener is nearly free from detectable hardness. However, some small amounts of hardness, known as leakage, are present in the treated water. The level of hardness leakage is dependent on the hardness and sodium level in the influent water and the amount of salt used for regeneration.

Hach's EZ Series Hardness Analyzer is very accurate and can detect very low amounts of any hardness in leakage.

- This analyzer then can be used post softening:
    - Continuously monitor the quality of softened water
    - Trigger regeneration
    - Monitor for significant leakage

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Hach's EZ Hardness Analyzer

- Accurate and precise measurement
- Data logging and trending
- Advanced control capabilities
- Wide analytical range capabilities
- Can be configured to work in complex water matrix

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Alkalinity & De-alkalization

Like hardness, alkalinity is a term that isn't a direct measurement of a specific ion but defined by its characteristic behavior (buffer against acidification).

Alkalinity is the capacity of water to resist changes in pH that would make the water more acidic. (It should not be confused with basicity which is an absolute measurement on the pH scale.)

Expression of Alkalinity

Expressed as equivalent calcium carbonate, mg/l $CaCO_3$

- Total Alkalinity – pH titrated to 4.
- Phenophthalein Alkalinity – pH titrated to 8.3
- Hydroxyl Alkalinity – Calculated based on Total and P-Alkalinity.

Alkalinity and Hardness Relationships

If alkalinity > total hardness

- All hardness is carbonate hardness, temporary hardness
- Extra alkalinity comes from other sources such as NaHCO3
- Sodium bicarbonate = alkalinity – total hardness
- Magnesium bicarbonate = total hardness – calcium
- Calcium bicarbonate = calcium

If alkalinity < total hardness

- Non-carbonate, permanent hardness present (hardness from SO4 or Cl-) = total hardness - alkalinity
- Carbonate hardness = alkalinity

(All results and values expressed as CaCO3 equivalents)

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Causes of Alkalinity

In typical waters the primary constituent of alkalinity is the bicarbonate ion (HCO_3^-)

- As pH increases the bicarbonate ion can dissociate to the carbonate ion ($CO_3^{=}$)
- At high pH alkalinity is also represented by the hydroxyl ion (OH^-)

FOR TYPICAL MONITORING AND CONTROL THE VALUE OF TOTAL ALKALINITY IS THE MOST IMPORTANT.

- Total alkalinity includes all three forms which is dependent on the water's pH.

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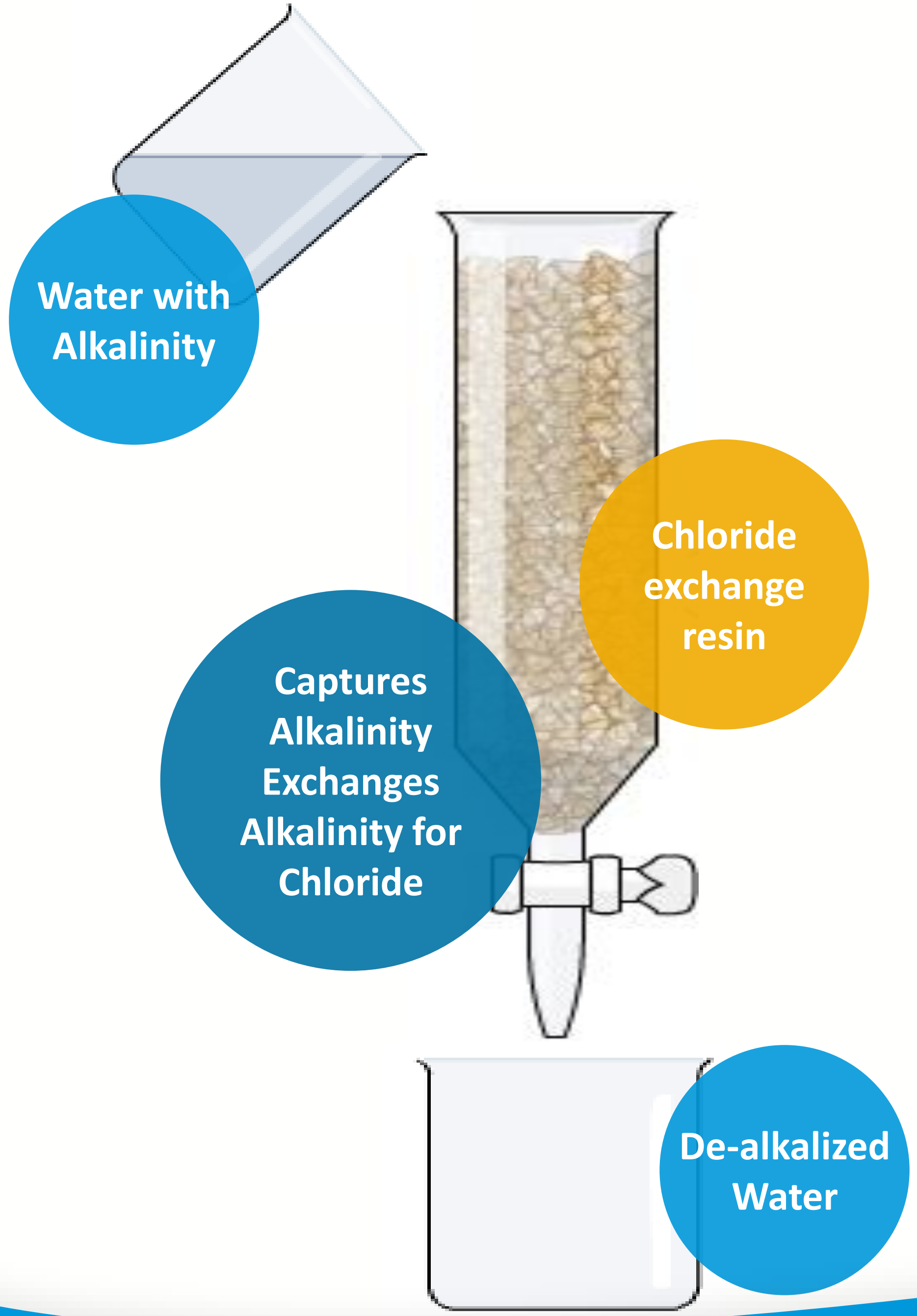
De-alkalization “Ion Exchange”



De-alkalization – Removal of Alkalinity

- Since water softening only reduces hardness and not alkalinity a secondary process is needed.
- Where in zeolite softening Na^+ replaces the Ca^{++} and Mg^{++}, in De-alkalization Cl^- exchanges with HCO_3^- / $CO_3^{=}$.

Hach's EZ Alkalinity Analyzer

- Accurate and precise measurement
- Data logging and trending
- Advanced control capabilities
- Wide analytical range capabilities
- Can be configured to work in complex water matrix

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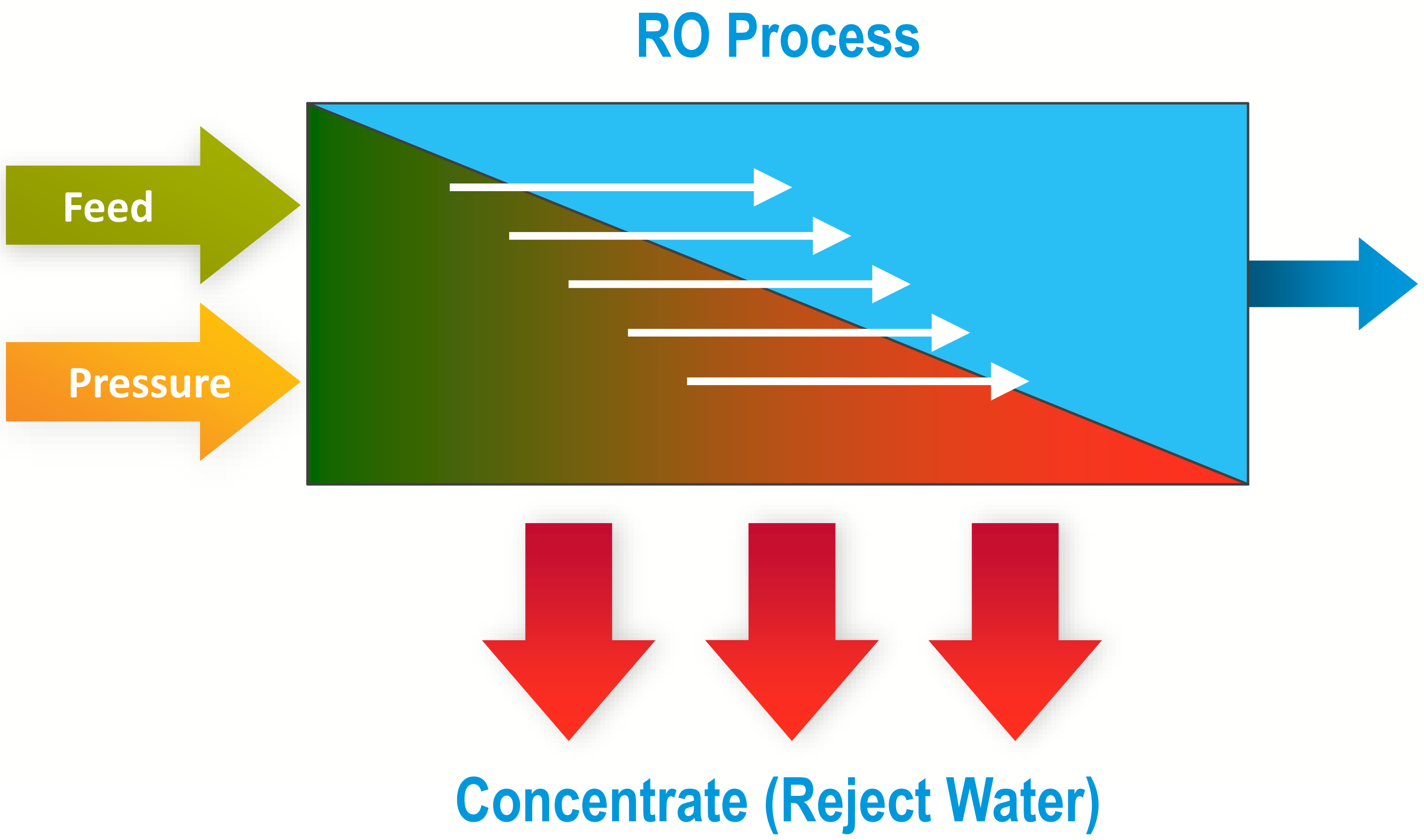
Membrane – Reverse Osmosis

- Reverse Osmosis (RO) uses applied pressure on the higher TDS side to force the water through the membrane, leaving behind the TDS.
- The water that has passed through the membrane has been purified to a percentage of the original TDS.

Reverse Osmosis



- Removes a large percentage of all types of water contaminants
    - (ions, organics, pyrogen, viruses, bacteria, particulates, colloids)
- Low operating costs due to low energy needs
- No need for strong acid and bases cleaning; minimum maintenance
- Good control of operating parameters

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Testing Reverse Osmosis Water Quality

- Reverse osmosis membranes are susceptible to attack by oxidizers
  - Chlorine
  - Bromine
  - Ozone
  - Hydrogen Peroxide
- Concentrations of these oxidizers in the feed water of reverse osmosis will result in destroying or reducing the useful life of the reverse osmosis membrane.
- Typically activated charcoal filters or a reducing agent like sodium bisulfite are used to remove the oxidizer prior to reverse osmosis.

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Take Control of Organics

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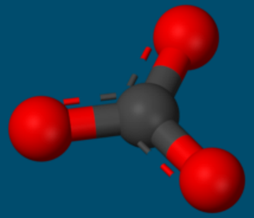
Inorganics and Organics

Iron

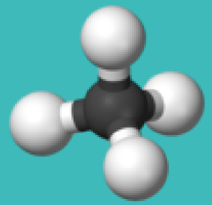


Carbonate

Inorganics

- Hardness (Ca, Mg)
- Alkalinity (Carbonates)
- Carbon Dioxide
- Individual elements

Sucrose



Methane

Organics

- Proteins
- Carbohydrates
- Lipids
- Petrochemicals

Condensate & Water Reuse

Many food processes condense water which can be reused in the plant

- Evaporators
- Condensers
- Spray Dryers

Condensate is valuable because it is PURE and HOT

- Saves resources to purify water
- Saves BTUs in heating

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The Problem

Condensate should be extremely clean, unless there are LEAKS!

Product Contamination into reuse water can quickly cause problems

- Deposits in pipes
- Organic scale inside boilers
- Pitting in metal surfaces

Determining when product contamination occurs can save maintenance costs and increase uptime

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The Problem

Issue #1: Is the water clean enough to reuse? To what degree?

Issue #2: Are their failures in the condenser, evaporator, membrane etc. that allow product to break through?

How much product in the water?

Plugged condenser tubes

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Poll

Alternative: Conductivity

Pros:

- Quick reading of dissolved solids
- Easy to install and maintain
- Helps monitor and control CIP processes
- Controls cycles of concentration in boilers & cooling towers

Cons:

- Weak electrolytes such as organic acids don’t correlate well to conductivity
- Conductivity can’t detect insoluble compounds
    - Won’t catch sugars, fats, proteins, surfactants, etc.

Dirty water is captured for reuse & clean water is diverted

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Solution: Organics Measurement

If we know the carbon content in water, we know how clean it is!

- B3500c Condensate Analyzer
  - In conjunction with a sampler cooler
  - TOC ranges from 0 – 100; 0 – 1000
- Continuously monitor condensate return lines for carbon (product)

When TOC goes high:

Divert condensate to drain to protect equipment.

Alarm to maintenance staff to look for condenser leaks.

Track TOC data over time to seek continuous process improvement.

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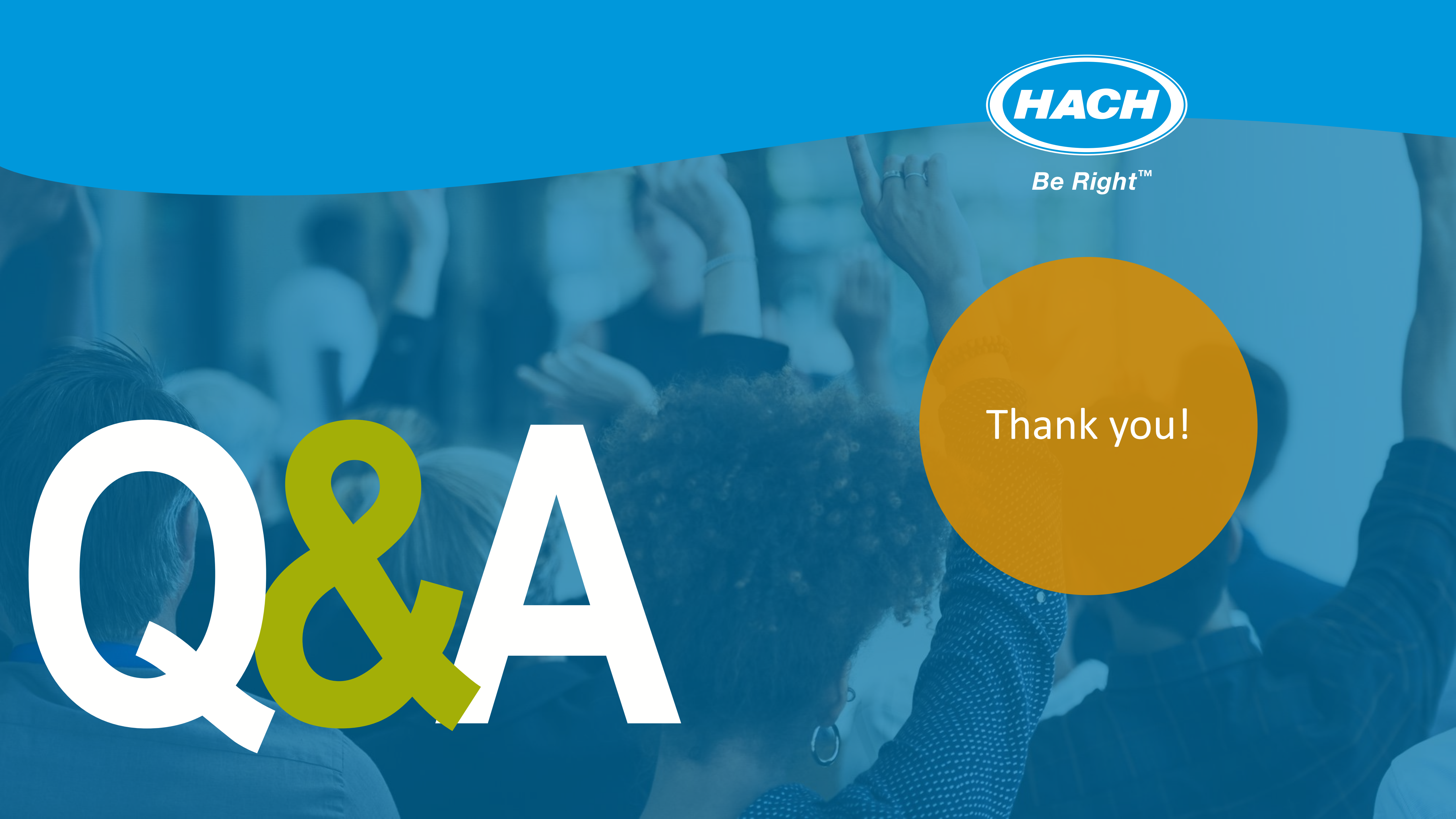
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Thank you!