Boiler Water Chemistry: Getting From the Source to the Boiler

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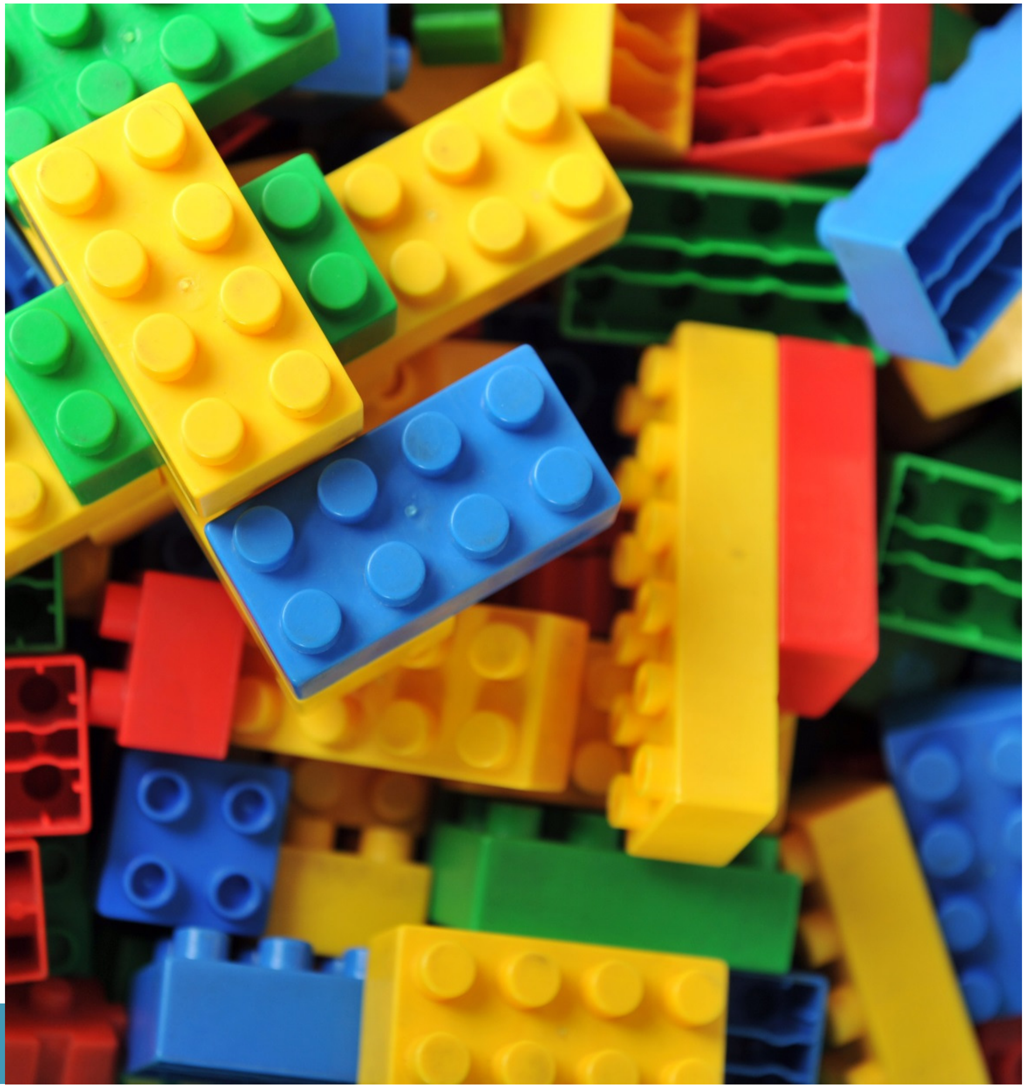
Goals

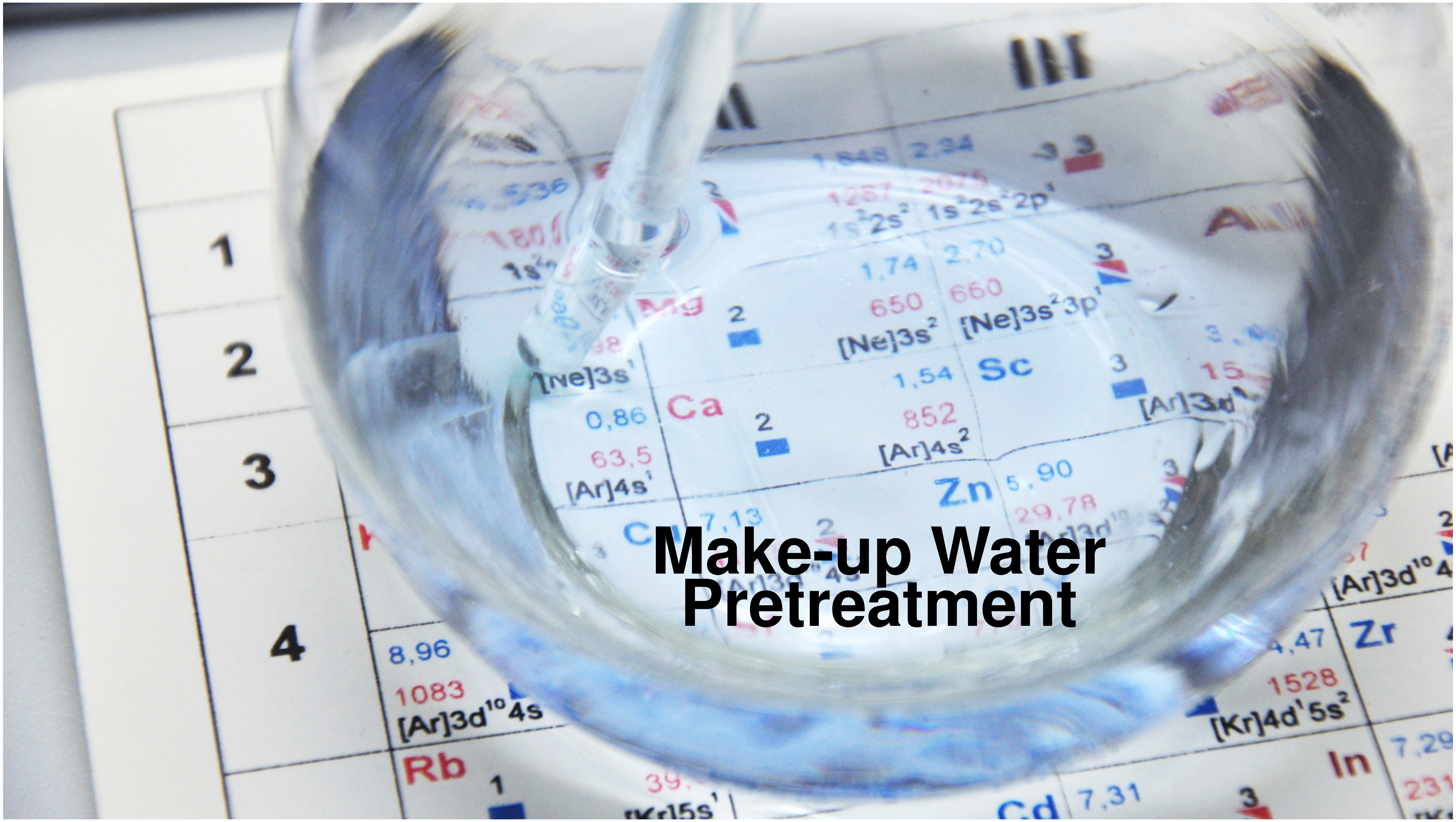
- Minimize Scaling
- Limit Deposition
- Prevent Corrosion
- Prevent Efficiency Loss
- Maximize Life of the Asset

Water is an excellent heat transfer medium, but it must be properly treated in both steam and hot water systems or problems will ensue robbing the system of energy and reducing the life of the asset.

Multiple Components for a Successful Boiler Water Treatment Program

- Makeup Water Pretreatment
- Internal Treatment
- Monitoring and Control





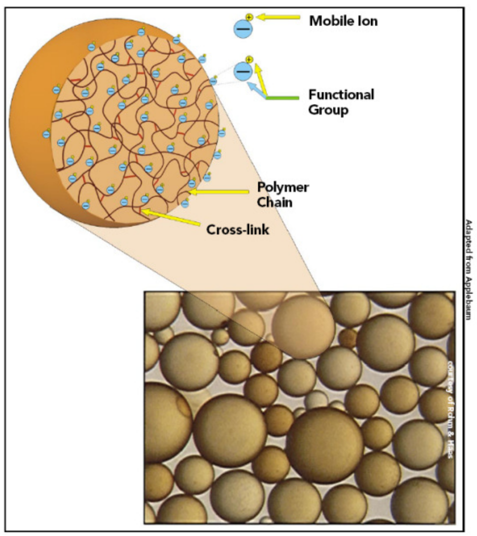
Make-up Water Pretreatment

Contaminants of Concern

- **Sodium:** Alkaline conditions, Stress corrosion cracking
- **Sulfate:** Acidic conditions, Stress corrosion cracking
- **Chloride:** Acidic conditions, Pitting, general corrosion, denting, stress corrosion cracking
- **Calcium & Magnesium :** Deposits, Under-deposit corrosion
- **Silica:** Deposits, Under-deposit corrosion
- **Corrosion Products:** Deposits, Under-deposit corrosion
- **Dissolved Gases:** Pitting

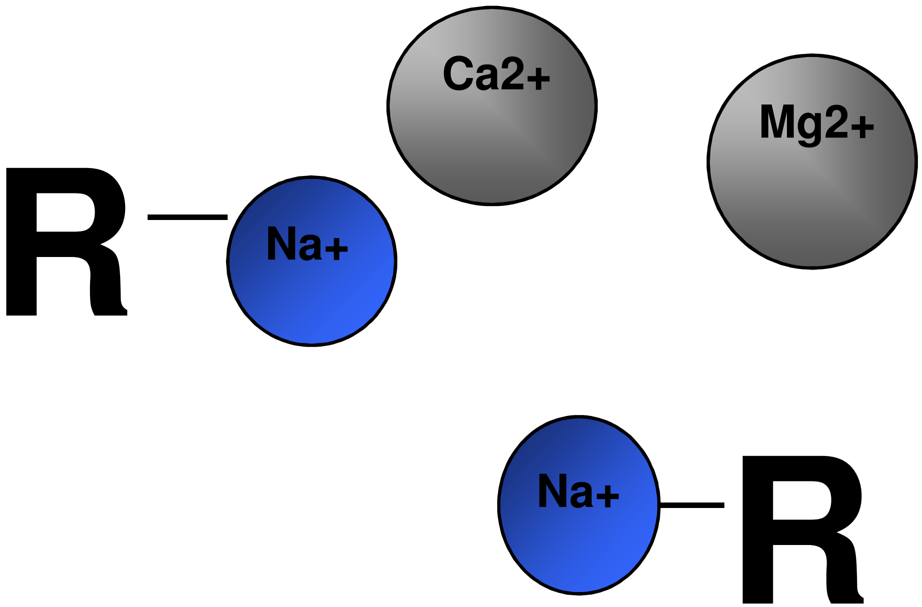
Ion Exchange Softening

- Removal of Calcium and Magnesium
- Replace with Sodium (operates Na Cycle)



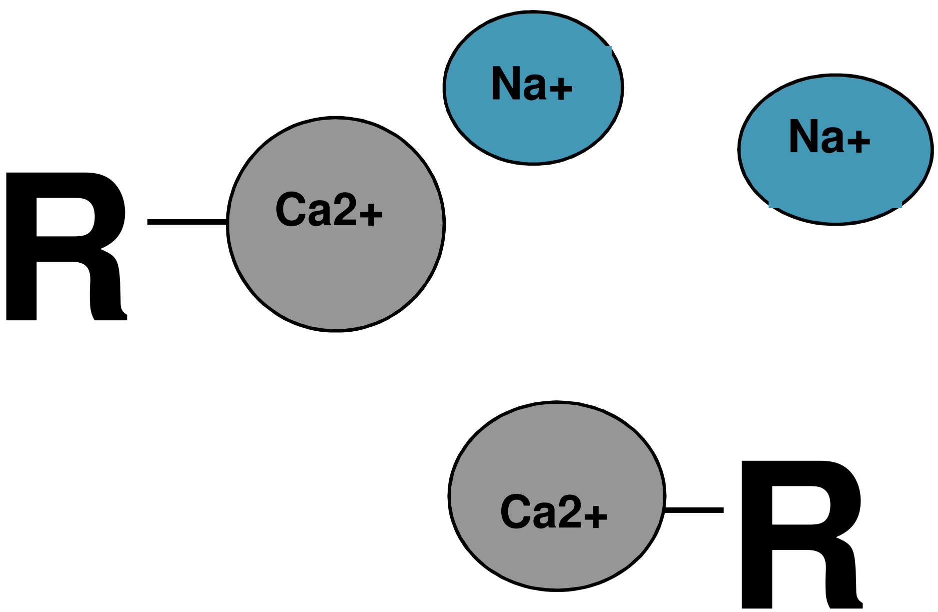
Ion exchange resin is an activated, synthetic, organic, copolymer matrix comprised of porous beads with a typical diameter of 0.01 - 0.04 inch.

Hardness Removal
Sodium Softening



- Removes hardness in the form of Calcium (Ca^{2+}) and Magnesium (Mg^{2+})
- Also good for Barium removal
- Strong Acid Cation Resin in Sodium Form

Regeneration



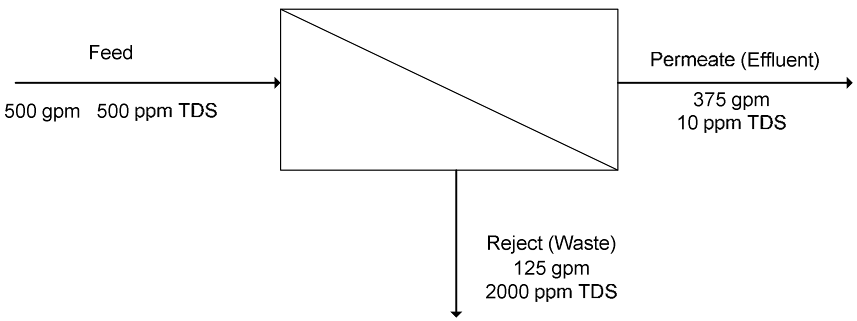
- Softening regenerated using sodium chloride (NaCl)
- The strength of the NaCl solution used determines the ion exchange capacity of the unit.

Dealkalization

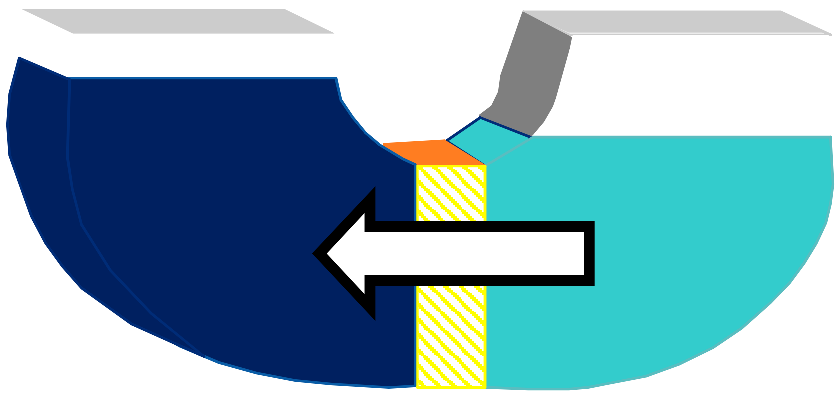
- Removal of Alkalinity
  - Bicarbonate and Carbonate
- May also remove Sulfate and Nitrate
- Replace with Chloride (operates Cl Cycle)
- Strong Base Anion Resin in Chloride form
- Regenerated with salt (brine) solution

Reverse Osmosis

- Semi-permeable membrane
- Reverse the process of osmosis
- Remove dissolved solids (TDS)



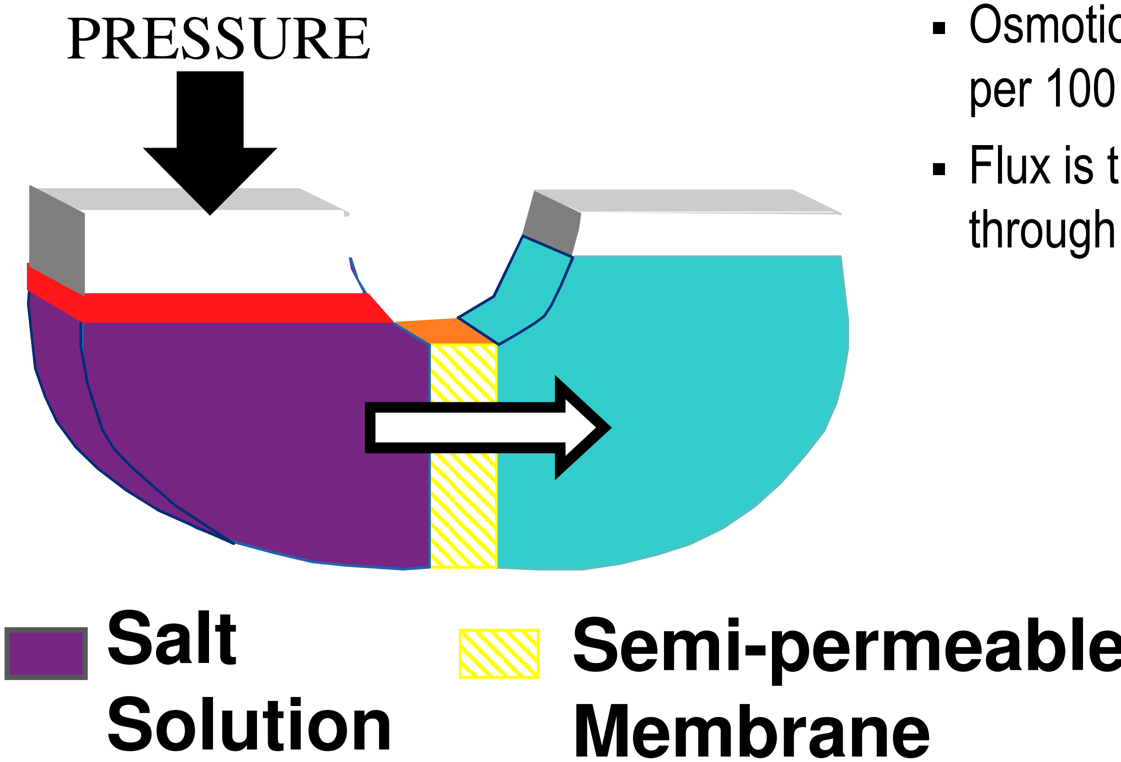
What is Osmosis ?



- The transport or diffusion of water across a semipermeable membrane
- Semipermeable - Salt will not pass; water will
- Water passes from the solution of lower concentration to higher concentration.
- Water will rise on the side of the more concentrated solution due to water migration.
- Difference is elevation is the Osmotic Pressure.
- Will continue until differential head stops the flow.

1000 mg/L Salt Solution **Semi-permeable Membrane** **Pure Water**

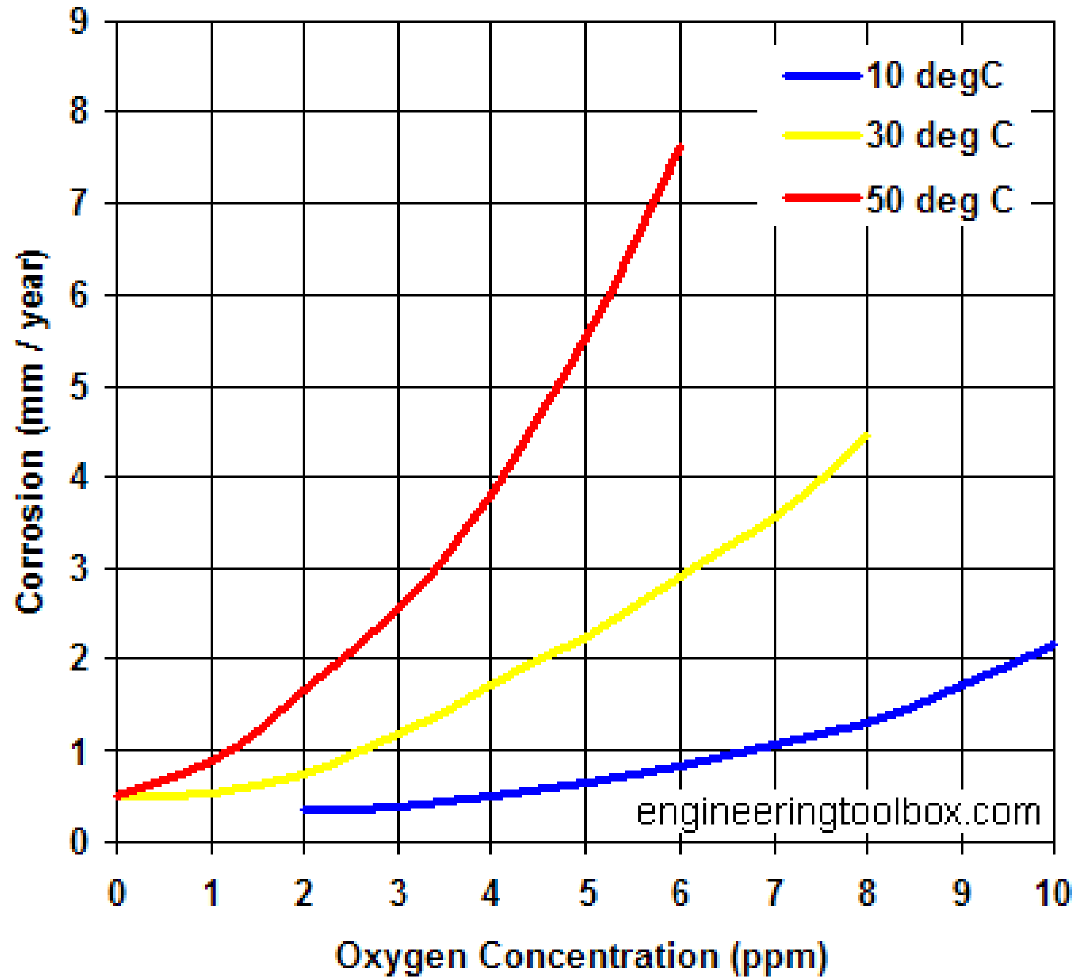
Reversing Osmosis



- Application of pressure so to stop water flow is called OSMOTIC Pressure
- Osmotic Pressure: Generally about 1 PSI per 100 mg/L TDS difference
- Flux is the rate that water permeates through the membrane. (GFD or LMH)

Oxygen Corrosion

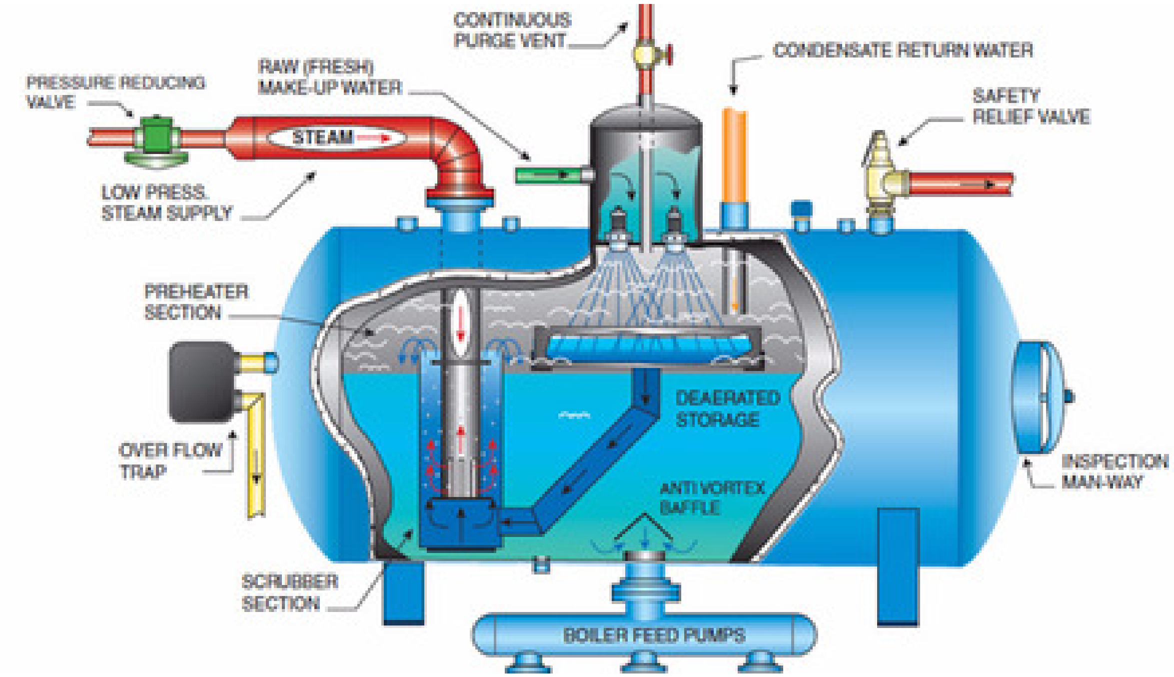
- Corrosion potential increases with increasing temperature
- Dissolved oxygen is ~ 10X more corrosive than carbon dioxide
- O_2 removed mechanically and/or chemically



Graph courtesy of: www.engineeeringtoolbox.com

Mechanical Deaeration

- Gas solubility in solution decreases as temperature increases and approaches saturation temp
- Sprays and/or trays and/or packed column increase surface area of water
- Increased surface area increases contact with steam reducing solubility of gases and facilitating removal

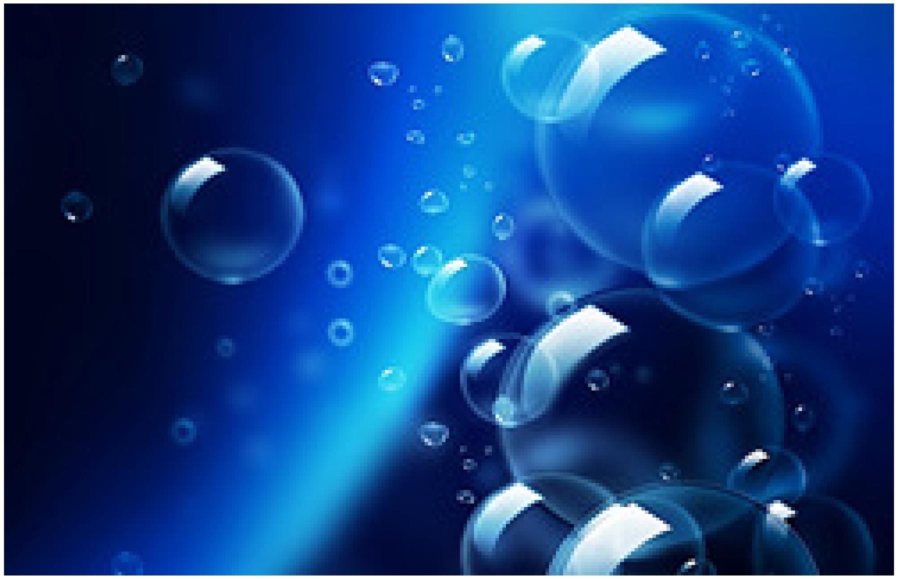


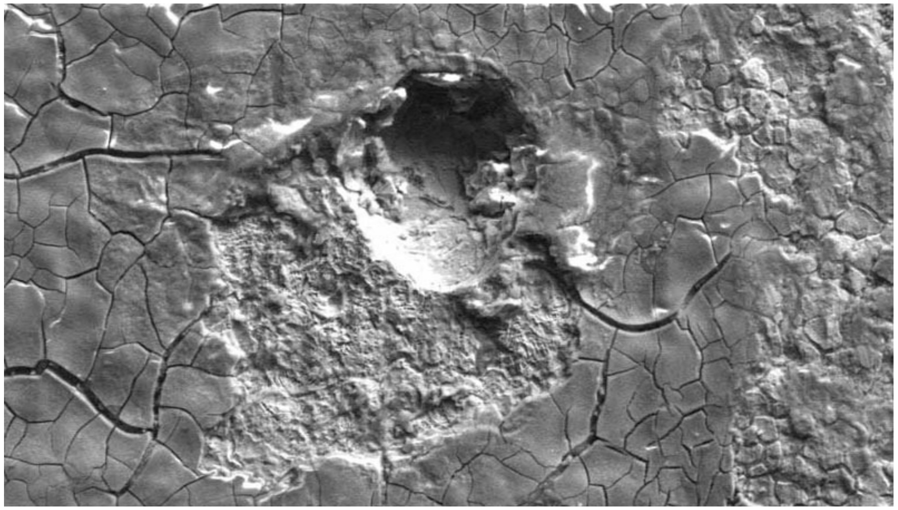
INTERNAL TREATMENT

Oxygen Scavengers

- O_2 removed mechanically and/or chemically
- Removes trace O_2 left by DA/FW tank
- Reducing agents
- Volatile (900 psig +) & non-volatile (<600 psig) types

Volatile	Nonvolatile
Hydrazine N_2H_4	**Sodium Sulfite Na_2SO_3**
Carbohydrazide H_6N_4CO	**Erythorbic Acid $C_2H_8O_6$**
Diethylhydroxylamine (DEHA)	
Methylethylketoxime (MEKO)	





Condensate and Feedwater pH Control: Neutralizing Amines

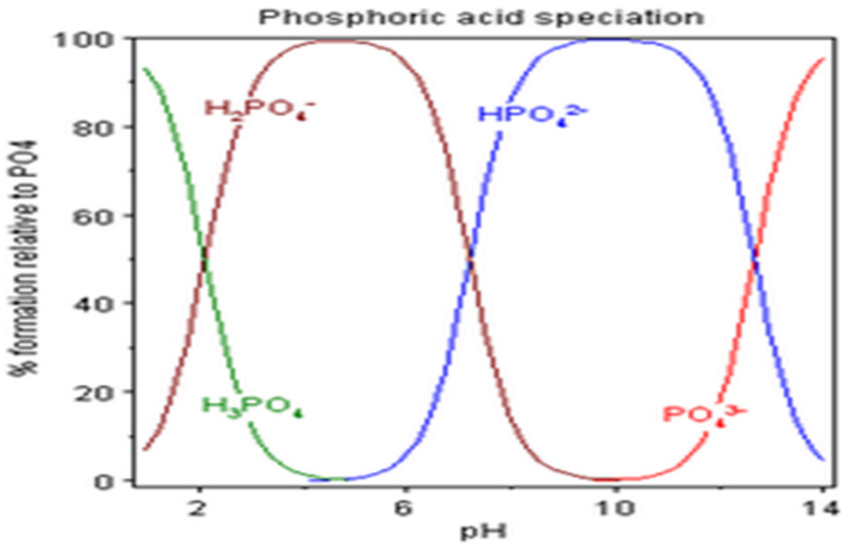
- Neutralize the acid (H^+) generated by the dissolution of carbon dioxide or other acidic process contaminants in the condensate
- Short chain organic with amine group
- Most common: Morpholine, Cyclohexylamine, Diethylaminoethanol, Dimethlyisopropanolamine, Ammonia
- Differ in cost, consumption rate and distribution ratio
- FDA has limits regarding neutralizing amines (other than ammonia) when steam contacts food or food products
- Ineffective against DO based corrosion

Condensate and Feedwater pH Control: Filming Amines

- Protect against oxygen and carbon dioxide corrosion by replacing the loose oxide scale on metal surfaces with a very thin amine film barrier
- High molecular weight amines or amine salts containing chains of 10 to 18 C atoms
- Most common: Octadecylamine, Hexadecylamine, Dioctadecylamine, Ethoxylated Soya Amine (ESA)
- Most effective applied to clean metal
- Limited acceptance by FDA
- Often blended with neutralizing amine and emulsifiers
- Must be continuously fed

Boiler Treatment: Phosphate Treatment Programs

- One of the oldest treatment programs
- Precipitating chemistry
- Dosed based on hardness – can be used with high hardness FW
- Blowdown and scale formed depends on amount hardness
- Various different programs for different concerns, pressures, and FW purity level
- Controlled by monitoring of pH, PO_4 and blowdown of precipitate



Boiler Treatment: Threshold Scale Inhibitors

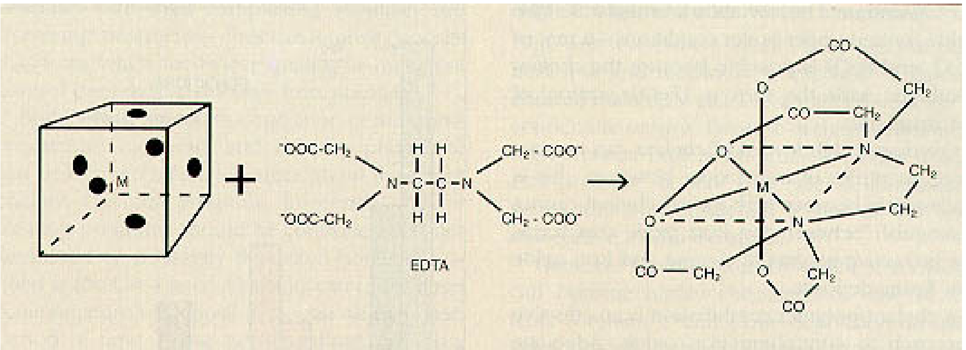
- Hybrid programs that combine phosphonate and polymer
- Distorts crystal structure and prevents scale formation
- Low pressure <300 psig
- Firetube boilers
- Better able to handle moderate to severe hardness upsets

Boiler Treatment: All Polymer Programs

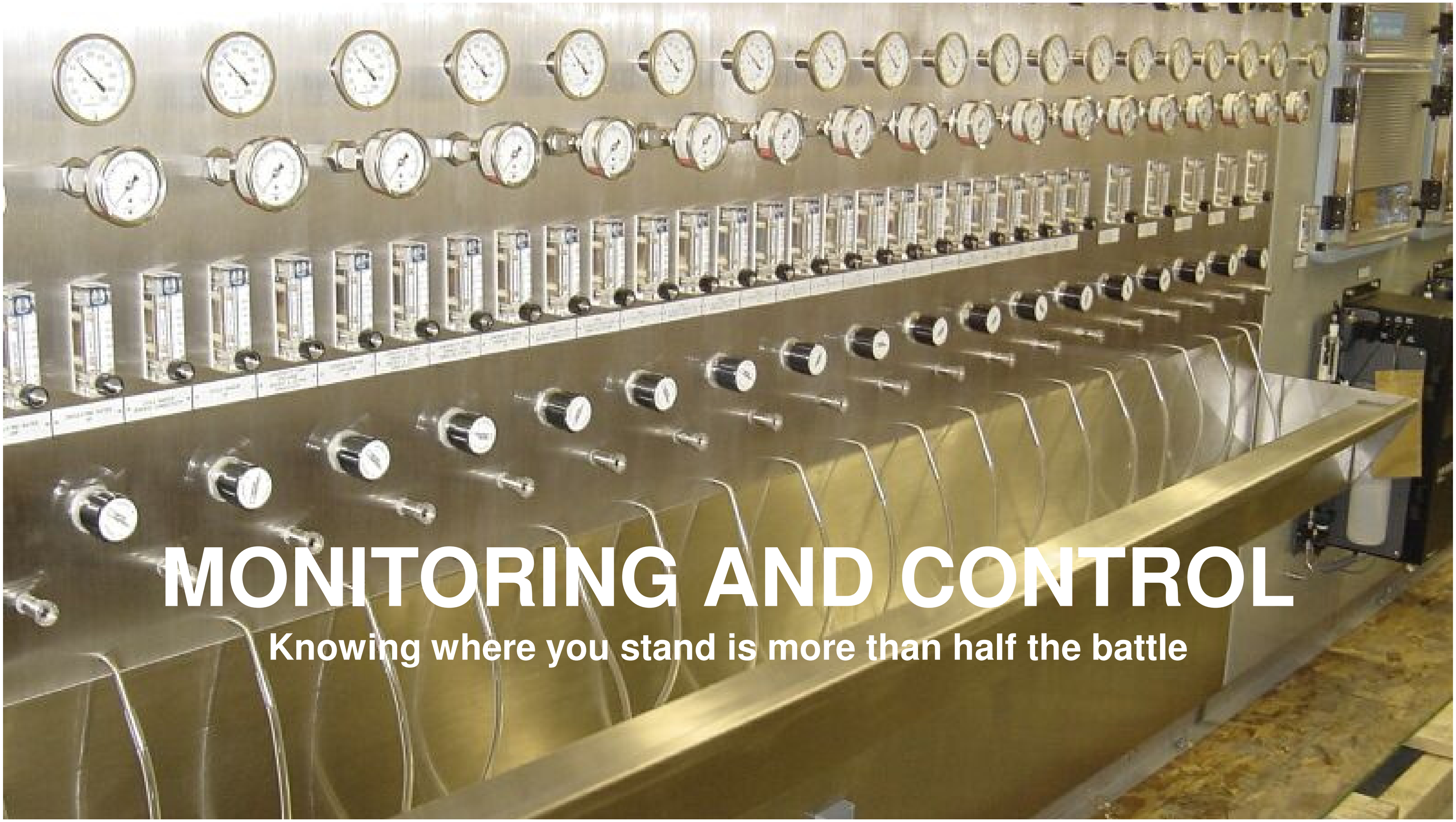
- Monomers having carboxylic acid functional groups (polycarboxylates)
- Act as dispersants and weak sequestrants
  - Maintain solubility of Ca, Fe, and Mg
- Limited to <900 psig and 50 COC
- Subject to challenges of thermal degradation
- Can be corrosive if overfed
- Produce very clean heat transfer surfaces
  - No precipitate is formed, blowdown can often be reduced.

Boiler Treatment: Chelant Chemistries

- Depend on sequestration – chelants bind with ions - keep them in soluble state
- Conditions sludge and solubilizes hardness
- Typical chemicals: NTA and EDTA
- Control by measurement of residual chelant – dosed based on amount of hardness
- Predominant reactions take place in FW
- Low to Medium Pressure Units



Most metals have six reactive coordination sites. EDTA can effectively tie into each coordination site and produce a stable complex



MONITORING AND CONTROL

Knowing where you stand is more than half the battle

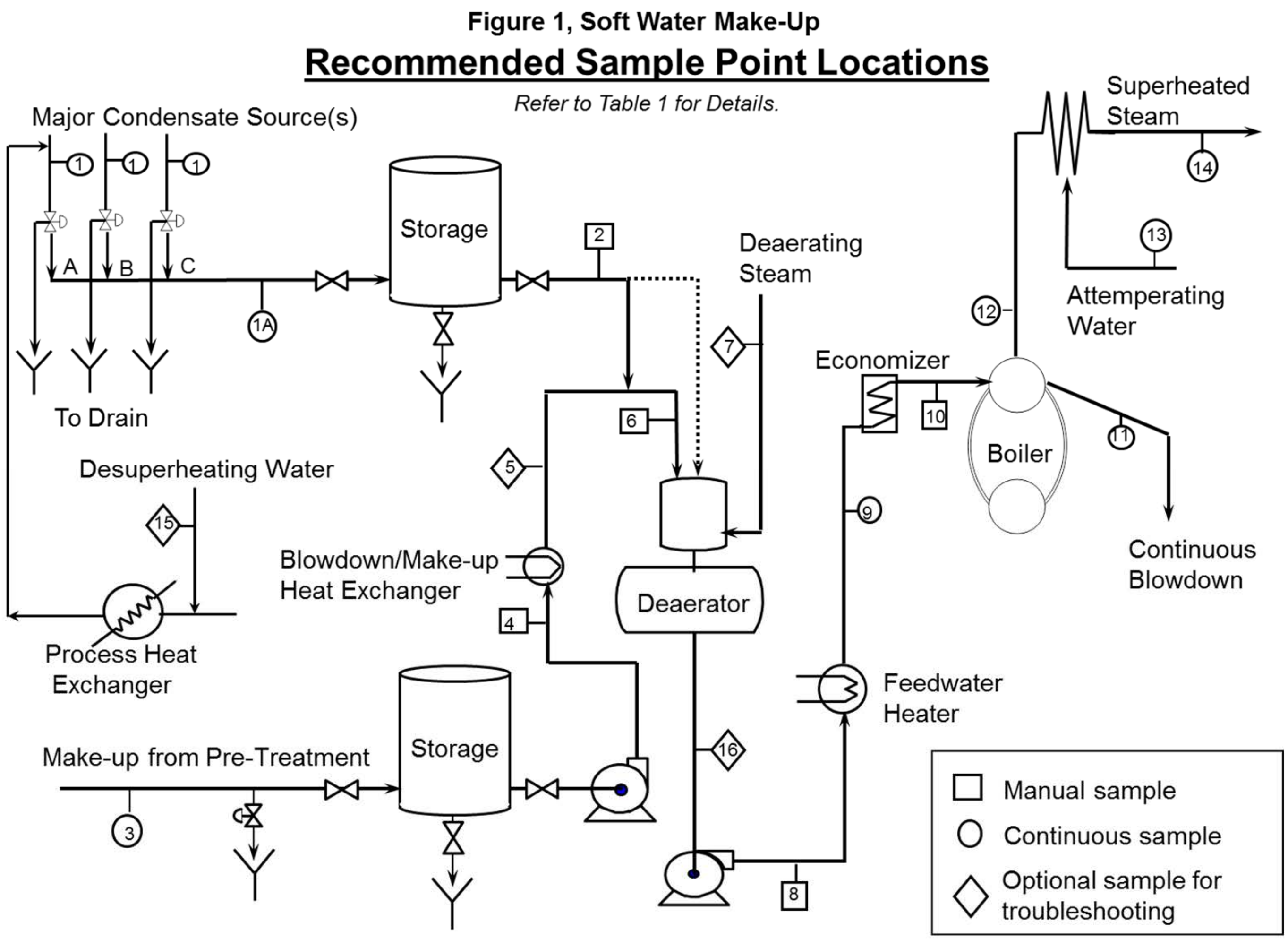
ASME Water Chemistry Limits (Water Tube Boilers)

Drum Operating Pressure (psig)	0-300	301-450	451-600	601-750	751-900	901-1000	1001-1500	1501-2000
Feedwater								
Dissolved oxygen ppm (mg/L) 0_2	< 0.007	< 0.007	<0.007	<0.007	<0.007	< 0.007	<0.007	<0.007
Total iron ppm (mg/L) Fe	≤0.1	≤0.05	≤0.03	≤0.025	≤0.02	≤0.02	≤0.01	≤0.01
Total copper ppm (mg/L) Cu	≤0.05	≤0.025	≤0.02	≤0.02	≤0.015	≤0.01	≤0.01	≤0.01
Total hardness ppm (mg/L)	≤0.3	≤0.3	≤0.2	≤0.2	≤0.1	≤0.05	ND	ND
pH @ 25℃	8.8-10.5	8.8-10.5	8.8-10.5	8.8-10.0	8.8-10.0	8.8-9.6	8.8-9.6	8.8-9.6
Chemicals for preboiler system protection	NS	NS	NS	NS	NS	VAM	VAM	VAM
Nonvolatile TOC ppm (mg/L)	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Oily matter ppm (mg/L)	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Boiler Water								
Silica ppm (mg/L) SiO_2	≤150	≤90	≤40	≤30	≤20	≤8	≤2	≤1
Emergency Minimum Boiler Water pH	8	8	8	8	8	8	8	8
Total alkalinity ppm (mg/L)	<700	<600	<500	<50	<50	<50	NS	NS
Specific conductance µmhos/cm (µS/cm) @ 25℃ without neutralization	1100	900	800	300	200	200	≤150	≤80
	(higher specific conductivity values are allowed carryover tests confirm compliance with required steam purity)							

ASME Water Chemistry Limits (Fire Tube Boilers)

Drum Operating Pressure	0-300 psig 0-2.07 MPa
Feedwater	
Dissolved oxygen ppm (mg/l) O_2 - measured before chemical oxygen scavenger addition	<0.007
Total iron ppm (mg/l) Fe	<0.1
Total copper ppm (mg/l) Cu	<0.05
Total hardness ppm (mg/l)	<1.0
pH @ 25℃	8.3-10.5
Nonvolatile TOC ppm (mg/l) C	<10
Oily matter ppm (mg/l)	<1
Boiler Water	
Silica ppm (mg/l) $Si0_2$	<150
Total alkalinity ppm (mg/l)	<700
Free OH-alkalinity, ppm (mg/L)	NS
Specific conductance µmhos/cm (µS/cm) @ 25℃ without neutralization	< 7000

Sample Locations

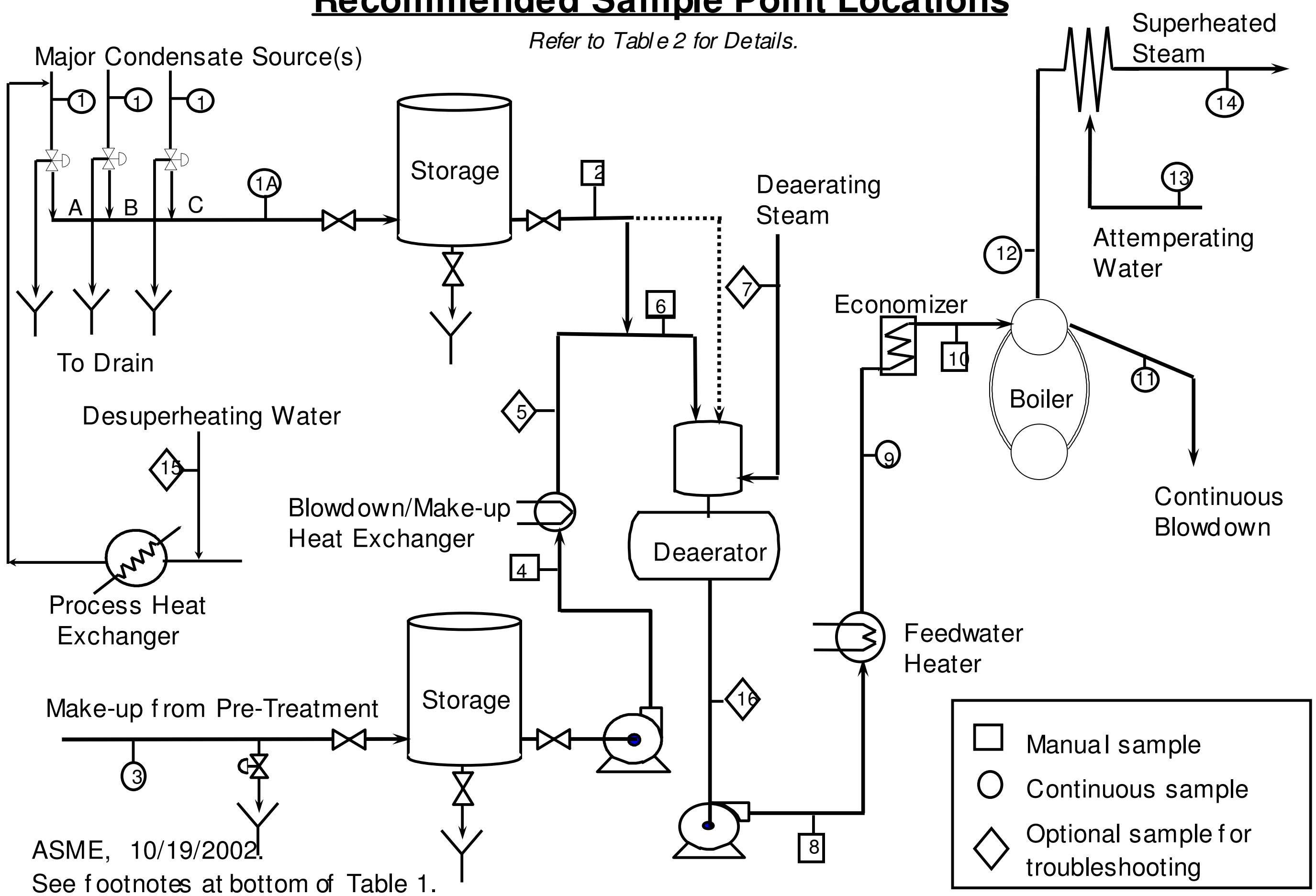


Sample Locations

Figure 2, High Purity Make-Up

Recommended Sample Point Locations

Refer to Table 2 for Details.

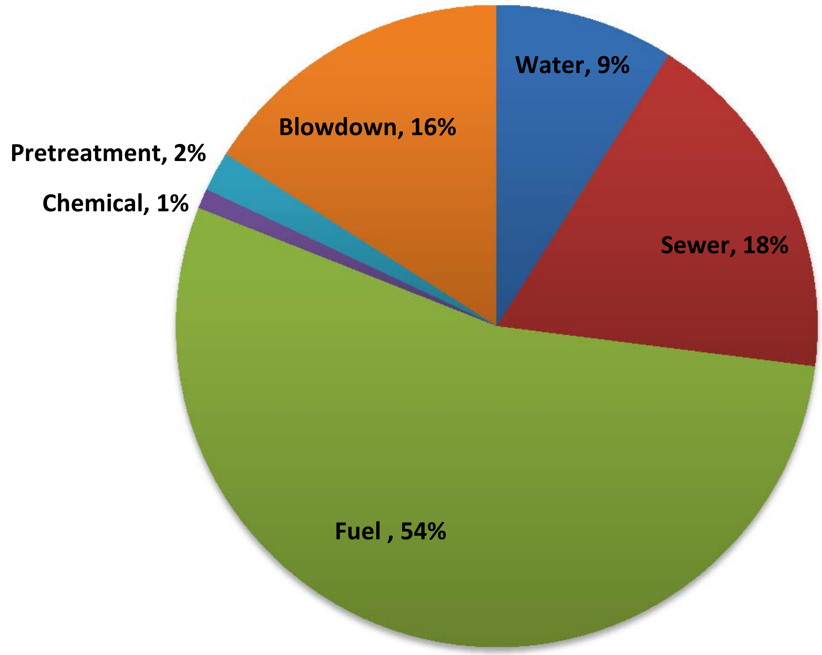


ASME, 10/19/2002.
See footnotes at bottom of Table 1.

The Value of Condensate can be Substantial

- Value can be broken down into the following:
  - Water cost
  - Sewer cost
  - Fuel cost
  - Chemical cost
  - Pretreatment cost
  - Blowdown cost

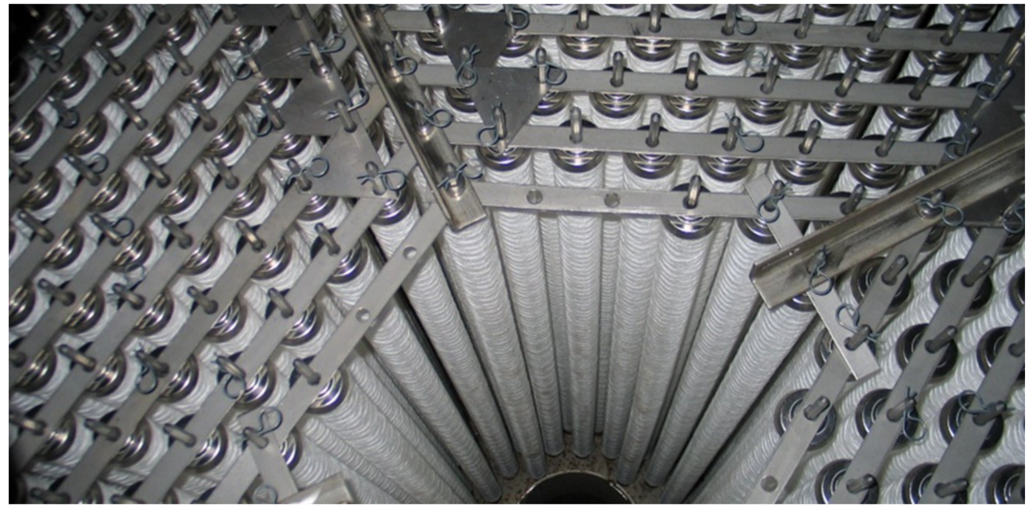
- Additional benefits of:
  - Improving FW quality
  - Increasing Cycles
  - Reducing WW



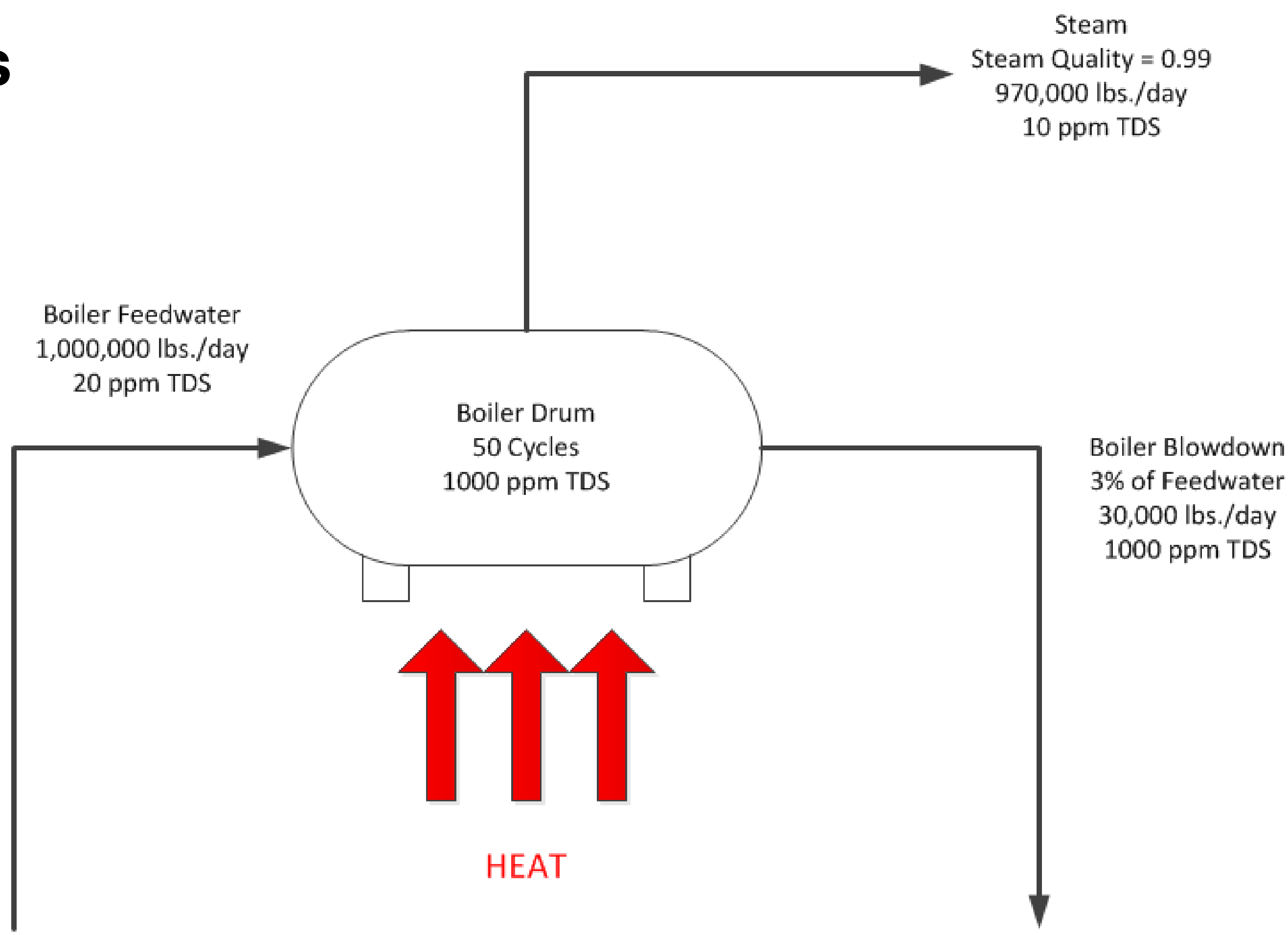
Range $10 to $25 per 1000 gallons of condensate recovered

Types of Condensate Treatment Systems

- Deep Bed Condensate Polishers
- Pre-coat Condensate Polishers
- Condensate Filters
- Chemical Injection



Boiler Cycles and Percent Blowdown



Blowdown Control

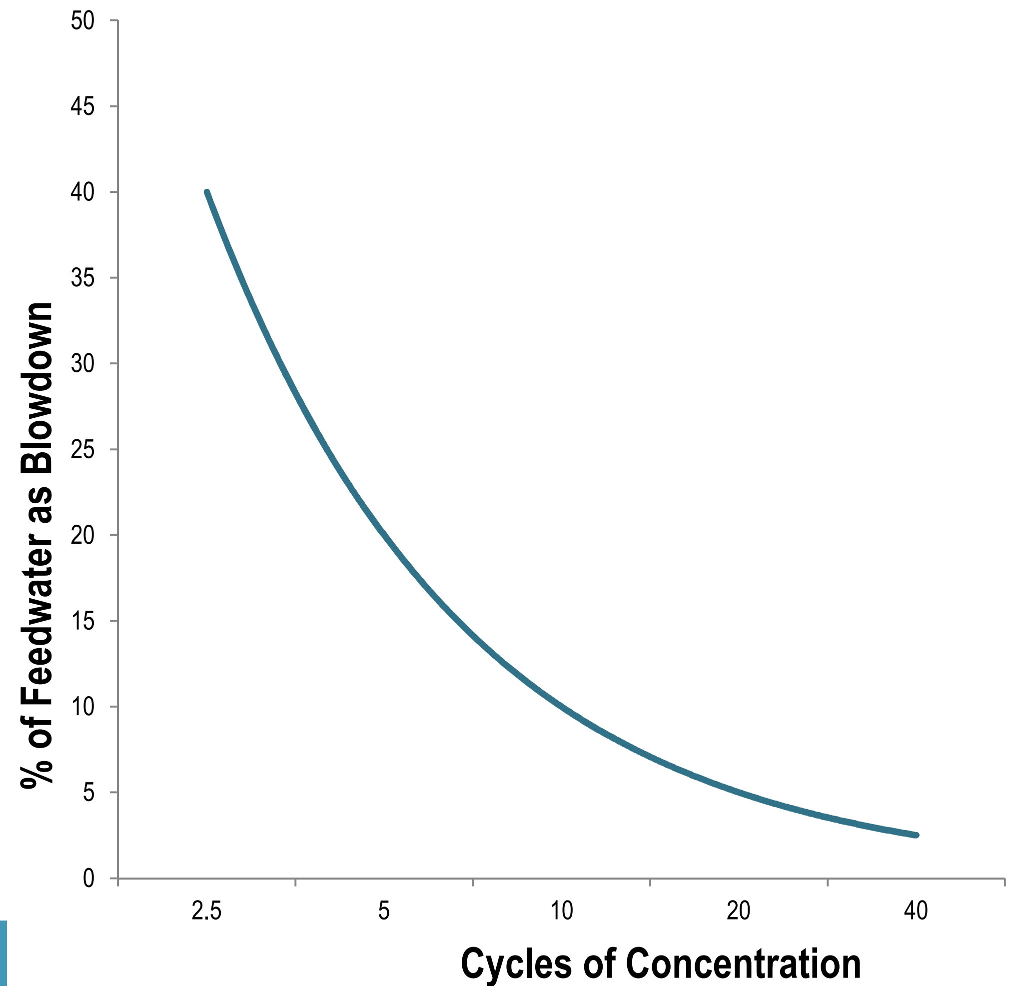
Can Save Water and Energy and $:

- Increase 5 to 10 cycles saves 10%
- Increase 20 to 40 cycles saves 2.5%

Savings in:

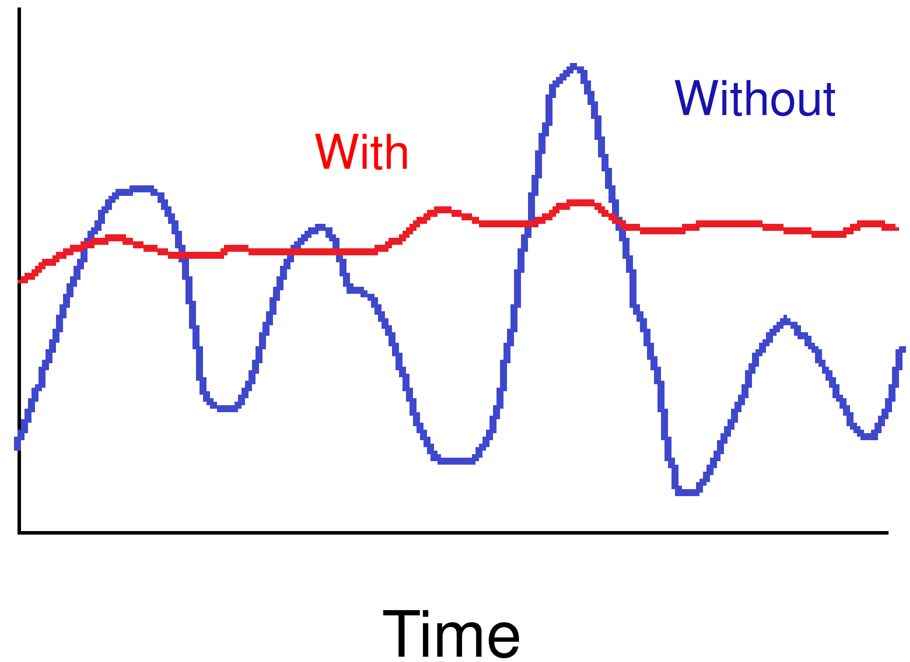
- Water cost
- Sewer cost
- Fuel cost
- Chemical cost
- Pretreatment cost

Range $10 to $25 per 1000 gallons



Blowdown Control

- Minimizing chemistry swings in the boiler
- Typically based on conductivity
- Starts with good makeup quality
- Monitor and test appropriate parameters relative to treatment program
- Maintain chemical feed dosage rates
- Prevent over-cycling boiler
- Use automation where practical



To Summarize:

Successful Program include 4 parts:

- Minimize contaminants entering system through makeup water pretreatment
- Use best internal treatment program for your system
- Controlling cycles of concentration and recovering condensate can save dollars
- Monitoring is a crucial component of control