Water Treatment for Boilers and WSC Chemistry

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PASSION FOR CHEMISTRY

Power Generating Systems

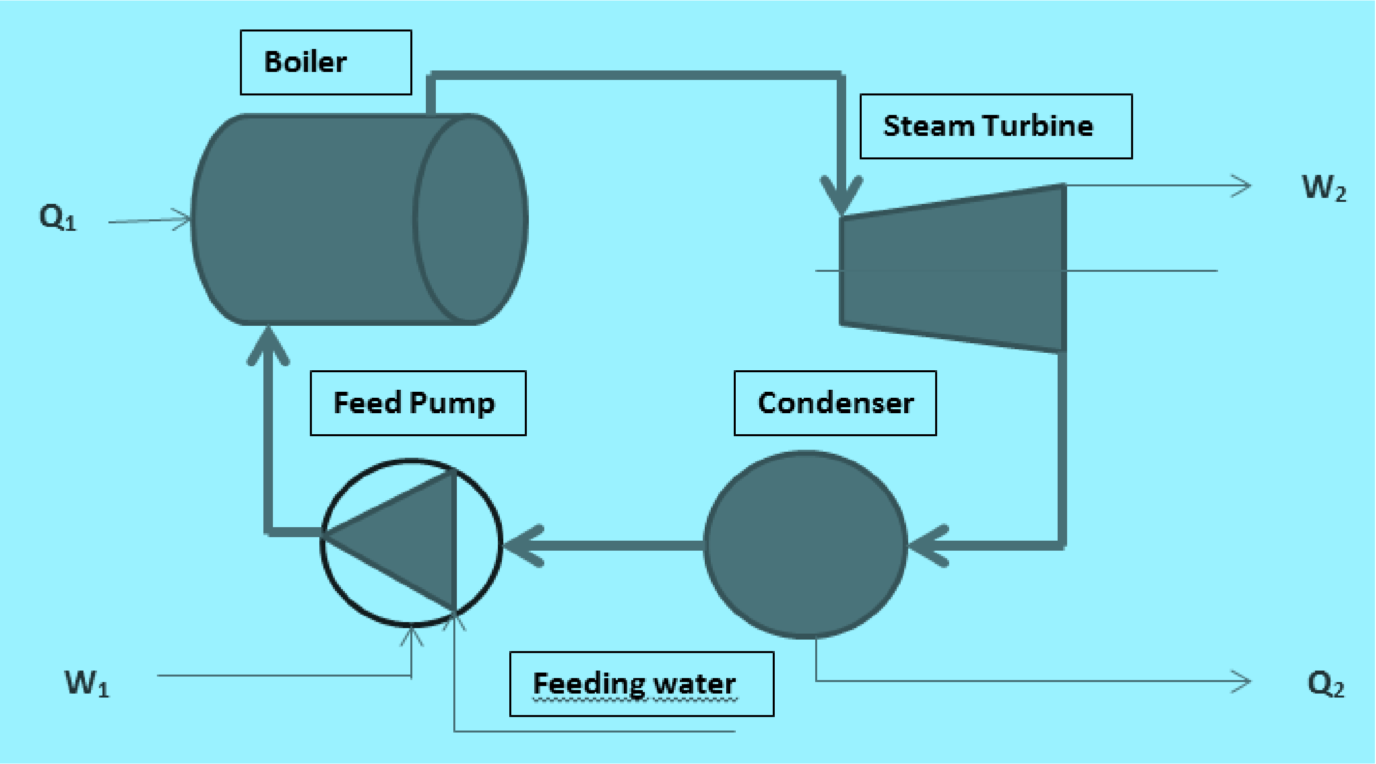
1. Heating Plants working with water at (130 – 180)°C and pressure (13 – 33) Bar
2. Heat and power plants working with water up to 600°C and pressure up to 300 Bar

- Drum boilers
- Once-through super-critical boilers

3. Combined Cycle Power Plant (CCPP) composed of:

- Gas Turbine (GT) with combustion and expansion of burnt gas in GT (operating at > 1200 °C) connected to
- Heat Recovery Steam Generator (HRST operating up to 700 °C) with steam Turbine (ST)

Power WSC



Boiler
Steam Turbine
Q1
W2
Feed Pump
Condenser
W1
Feeding water
Q2

Energy balance

<u>Balance of energy in the power transformation cycle</u>:

Input energy: $Q_1 + W_1$

Output energy: $W_2 + Q_2$

Energy Balance: $$Q_1 + W_1 = W_2 + Q_2$$

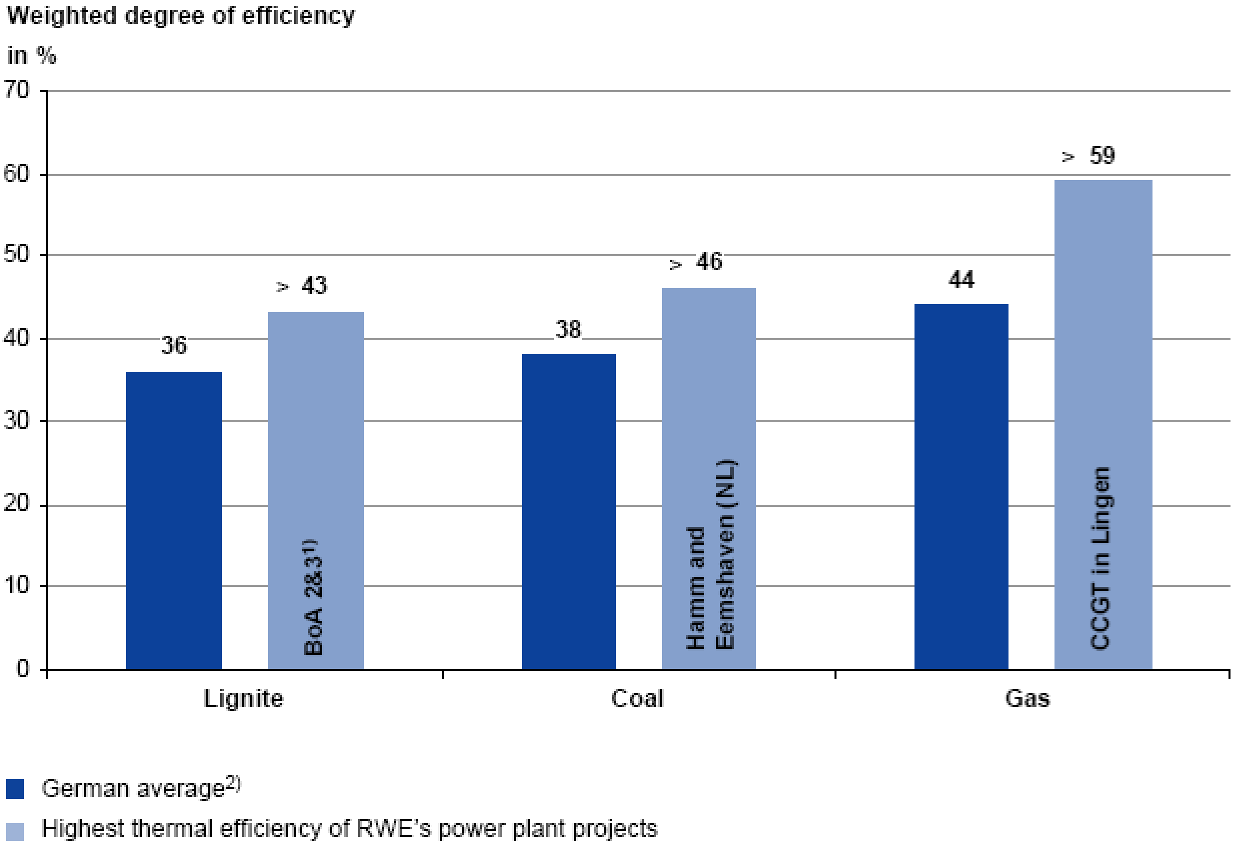
<u>W_2 - output energy enhancement:</u>

- Q_1 – temperature elevation by overheating of steam
- W_1 – operating pressure increase
- Q_2 - temperature and pressure reduction during the condensation

Efficiency of energy production

$$\eta = \frac{work\ performed}{heat\ absorbed\ from\ hot\ source}$$

$$\eta = \frac{|W_2|}{|Q_1|} = \frac{|Q_1| - |Q_2|}{|Q_1|}$$



Water treatment program for boiler systems

Water treatment = preventative maintenance program to minimize corrosion and scale in the boiler and carry over/deposits on the turbine.
Well **designed water treatment program can significantly reduce your energy, water, and maintenance costs** while **ensuring safe and reliable operation**.

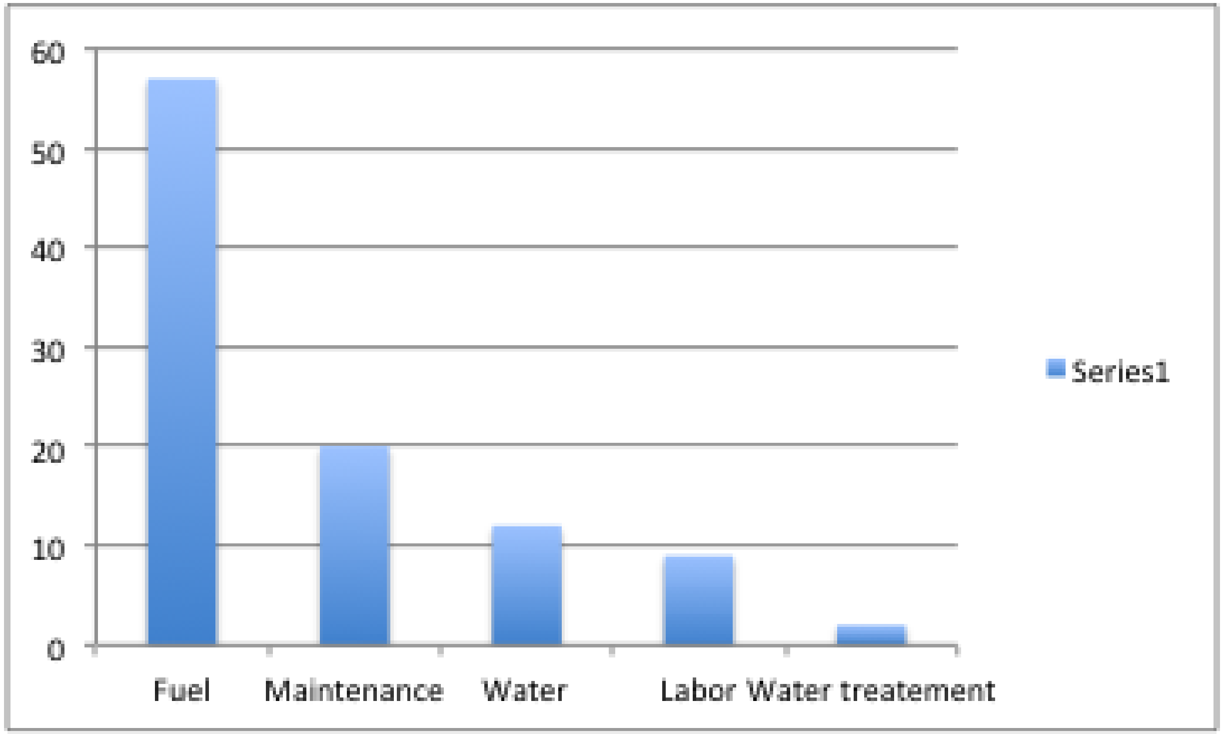
Small reductions in boiler or condenser efficiency - huge increases in operating costs.
Example:

- mere 0.8 mm of scale in a 15 tons steam/hr boiler can increase annual fuel costs by over Euro 50,000!
- mere 0.1 mm of microbiological fouling in a 3500kW chiller can increase annual electricity costs by Euro 30,000!

The high operating and maintenance costs of a poorly treated system are quickly dwarfed by the cost of production losses or an unexpected system shutdown.

Ref: Chem-Aqua, Terms and conditions 2014, http://www.chemaqua.com

Operating costs



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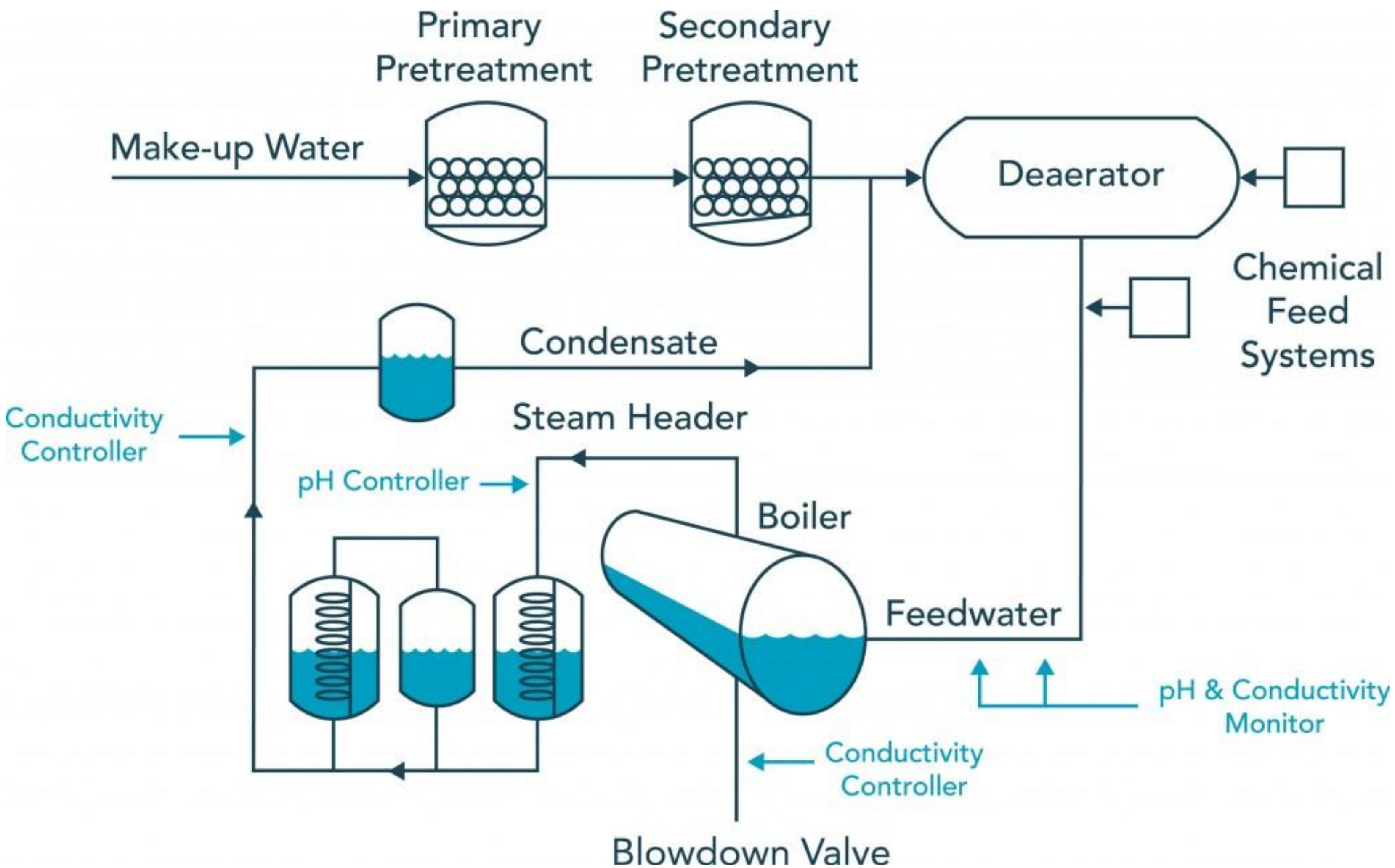
Boiler water treatment /WSC



International “EN” and VGB standards

EN 12952-12
Water-tube boilers and auxiliary installations.
Part 12. Requirements for boiler feedwater and boiler quality.

VGB Guidelines for Boiler Feedwater, Boiler Water and Steam of Steam Generators with a Permissible Operating Pressure of > 68 Bar – VGB-R 450 Le

Boiler Water Treatment for WSC

Steps of treatment:

- chemical support for magnetite or other oxide protective coating formation
- pH optimation for protection of materials against various types of corrosion
- Remove hardness and reduced scale deposits formation
- chemical scavenging of residual oxygen
- special coatings formation for metal surfaces protection

Chemicals used for the water treatment:

- sodium hydroxide,
- potassium hydroxide,
- sodium phosphate,
- ammonia and
- Hydrazine/carbohydrazide.
- Oxygen
- Various kinds of filming amines
- Dispersants in low pressure drum boilers

The Schikorr reaction

The Schikorr reaction can occur in the process of anaerobic corrosion of iron and carbon steel in the presence of steam at high T.

Anaerobic corrosion of metallic iron to give iron(II) hydroxide and hydrogen:

$3\ Fe + 6\ H_2O \rightarrow 3Fe(OH)_2 + 3H_2$ followed by the Schikorr reaction:

$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + 2\ H_2O + H_2$ give the following global reaction:

$3\ Fe + 6\ H_2O \rightarrow Fe_3O_4 + 2\ H_2O + 4\ H_2$ or

$$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4\ (\text{magnetite}) + 4\ H_2$$

WSC Chemistry Program

Phosphate pH control in the drum and feed water lines/heaters

All Volatile Treatment for pH control in the condensate

Oxygenated Treatment

Parameters for Drum boilers EN 12952-12

Parameter	Unit	Feed water with concentration of salts			Demineralised and Injection Water
Pressure	MPa	0.05 – 2.0	0.05 – 4.0	4.0 - 10	Full range
H^+ conductivity	µS cm^{-1}	-	-	-	< 0.2
pH at 25 °C ⋆		> 9.2	> 9.2	> 9.2	> 9.2
Concentration of Ca + Mg	mmol L^{-1}	<0.02	<0.01	<0.005	
Concentration of of Na + K	mg L^{-1}	-	-	-	< 0.010
Concentration of Fe	mg L^{-1}	< 0.05	< 0.03	< 0.02	< 0.020
Concentration of Cu	mg L^{-1}	< 0.02	< 0.01	< 0.003	< 0.003
Concentration of SiO_2	mg L^{-1}	-	-	-	< 0.020
Concentration of O_2	mg L^{-1}	< 0.02	< 0.02	< 0.02	< 0.1
Conc. of oil and grease	mg L^{-1}	< 1.0	< 0.5	< 0.5	< 0.5
Organic comp. TOC	mg L^{-1}			< 0.5	< 0.2

⋆) Note: for Cu alloys pH should be limited to 8.7 – 9.2

Parameters for boilers
EN 12952-12

Parameter	Unit	Demineralised and Injection water
Pressure	MPa	Full range
H^+ conductivity	$\mu S\ cm^{-1}$	< 0.2
pH at 25 C°		7.0 – 10.0
Concentration of of Na + K	$mg\ L^{-1}$	< 0.010
Concentration of Fe	$mg\ L^{-1}$	< 0.010
Concentration of Cu	$mg\ L^{-1}$	< 0.003
Concentration of SiO_2	$mg\ L^{-1}$	< 0.020
Concentration of O_2	$mg\ L^{-1}$	< 0.25
Organic comp. TOC	$mg\ L^{-1}$	< 0.2

Pretreatment of Boiler feed water

Task of feed water pretreatment is to eliminate:

a) Suspended solids

b) Colloids – substances of:
- variable submicron size
- variable charge

c) Dissolved minerals
d) TOC
e) Dissolved gases

Methods of pretreatment:

Direct separation – sedimentation, filtration, ultrafiltration or microfiltration
Coagulation and separation – ultrafiltration, nanofiltration
Clarification (coagulation + flocculation -sedimantation) – acid, neutral and alkaline
Demineralization using RO-MBX, CAX-ANEX-MBX or RO-EDI
Deaeration/Oxygen scavenging

Parameters of filtration

Method of separation	Size of particles in µm	Particles	Substances
Filtration with edge filter	< 100	macroparticles	sand, suspended substances
Filtration with granular filter	> 10		
Microfiltration	< 0.1 - 5	microparticles, macromolecules	coloids, bacteria
Ultrafiltration	< 0.05 - 0,5	macromolecules, molecules	bacteria, viruses, enzymes, pyrogenes
Nanofiltration	< 0.001 - 0.01	molecules	enzymes, pyrogenes, sugars
Reverse osmosis	<0.0001 - 0.005	ions	sugars

Clarification of boiler make-up water

Clarification is composed of:

- coagulation - elimination of charged particles
- flocculation - formation of flocs and their sedimentation
- sedimentation (settling) – separation of the flocs from water

Clarification depends upon pH value of the water – different techniques:

- Acidic clarification
- Neutral clarification
- Alkaline clarification

Acidic clarification (pH < 7)

Fe^{3+}(coagulant) + 3 HCO_3^- = $Fe(OH)_3$ + 3 CO_2 at pH 5.5 – 7.0

Neutral clarification (pH= 6 -8)

Clarification agent: coagulant + NaOH = neutral flocs

Alkaline clarification (pH >10) also removes Hardness

Fe^{3+}(coagulant) + 3 HCO_3^- = $Fe(OH)_3$ + 3 CO_2

2 CO_2 + $Ca(OH)_2$ = $Ca(HCO_3)_2$+ $Ca(OH)_2$ = 2 $CaCO_3$ + 2 H_2O

Clarification of feed water

Flocculation

- Speed of flocculation – <u>concentration of sediment</u> x <u>imput of energy</u> (mixing) x <u>time</u>
- <u>Two stages of floculation</u>
    - *perikinetics phase* (Brownian motion of particles)
    - *ortokinetics phase* (mixing or other agitation)

Sedimentation

- Separation of flocs in sediment cloud

Filtration as Polishing step

- One – component sand filters
- Multi-component sand filters

Water Softening and decarbonization

Softening - removal of Ca and Mg ions from water

IONEX

- Weak acid KATEX in H^+ form (acidic decarbonization) – removal HCO_3^-
- Strong base ANEX in Cl^- form (neutral decarbonization)

Softening with strong acid KATEX

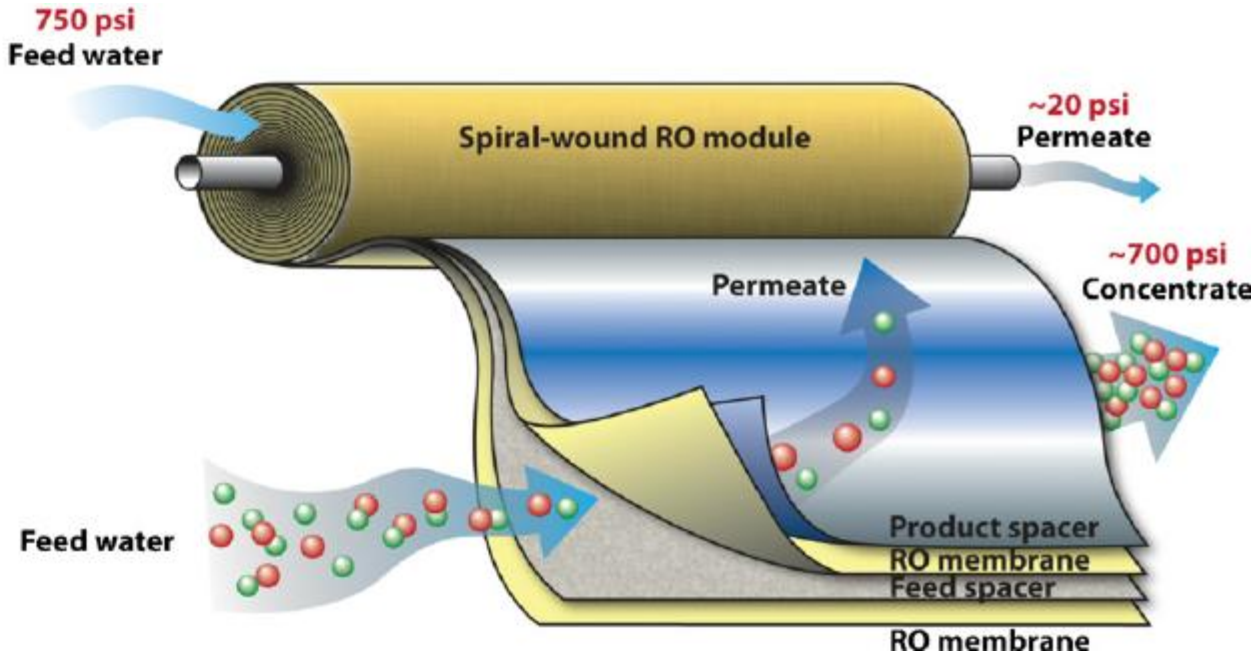
$2\ R\text{-}Na + Me^{n+} = R_2Me + 2\ Na$ *Me:* Ca^{2+}, Mg^{2+}

Decarbonization with low acidic KATEX

N R-COOH $+ Me^{n+} + n\ HCO_3^- = (R\text{-}COO)^n\ Me + n\ CO_2 + n\ H_lO$

IONEX = Ion Exchange, KATEX = Cation Exchnage, ANEX = Anion Exchange

Reverse osmosis



Usually achieves a conductivity of 5-10 Micro-Siemens/cm and needs a polishing Stage in the following step.

2'ry Treatment: Ion-ex demineralization

Ionex demineralization = Separation of soluble ionized impurities with positive or negative charges

Process - exchange of inorganic ions of water H+ and OH- in the functional groups of the resin

Types of ionex (Styrene or Acrylate):

- Weak acidic
- Strong acidic
- Weak basic
- Strong basic (type I, type II)

Strong acidic KATEX

$$n\,R\text{-}H + Me^{n+} = R_n\,Me + n\,H^+$$

Regeneration

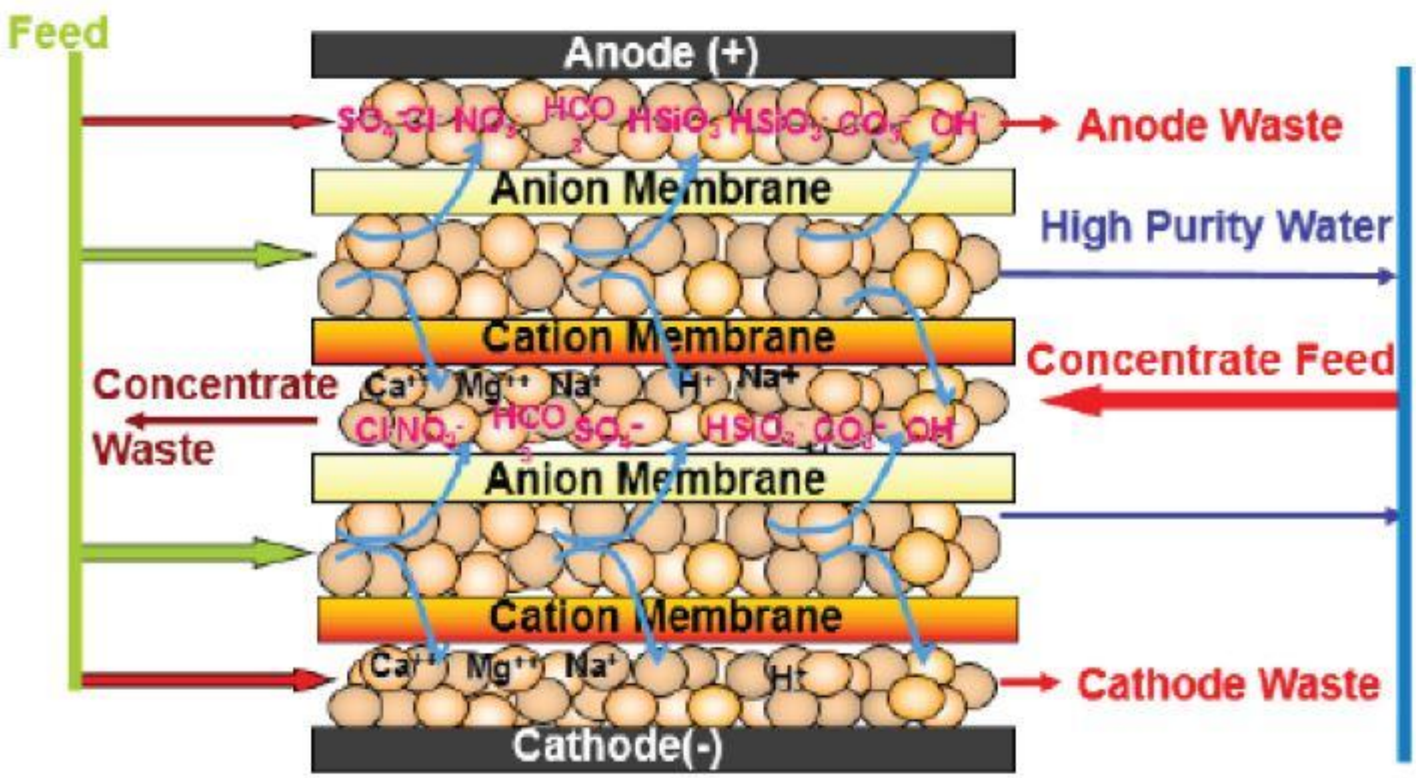
$$R_n\,Me + n\,H^+ = n\,R\text{-}H + Me^{n+}$$

Strong basic ANEX

$$n\,R\text{-}OH + H_nX = R_n\text{-}X + n\,H_20$$

Mixedbed = high acidic and high basic ionex = ultrapure quality of water

EDI - Electro De-Ionization



Counter-current EDI stack operation

https://www.youtube.com/watch?v=zTtD3CyJqM8

Oxygen Removal and Scavenging

Oxygen and non-condensable gases are removed in the Deaerator

Sometimes we also dose an Oxygen scavenger to remove traces of O_2

Sometimes we use degasifying membranes (LiquiCell)

In Oxygenated treatment, a small dose of O_2 is actually added to form a strong hematite Iron Oxide protective layer

Heat and power plants

Boilers

- HP Cylindrical boilers (HPC) with LPRH (condensate) and HPSH (feed water)
- HP once-through boilers (HPC) – used mostly for Electric Power Plants

Circulating medium – water up to 600°C and pressure up to 300 Bar

Circulating water quality:

- High water quality kept by continuous blowdown
- Steam Turbine condensate – generally not treated (only at starting phase). Treated In Super-critical boilers using Condensate Polishing step
- Return condensate – treatment (filtration, deionization by H^+catex, degassing)
- Feed-water – high quality, demineralized, low SiO_2 and salt concentration, alkalized by liquid (ammonium, amines or hydrazine)
- Make-up water (low) – demineralized and processed by degassing or vacuum pump).

Corrosion impact – mostly:

- LPRH and HPSH
- Water storage tank
- Feed-up water line
- Degasifier
- Blowdown line

Combined Cycle Power Plant (CCPP)

Boilers

- Gas Turbine (GT) with combustion and expansion of burnt gas in GT (operating at > 1200 °C) - 65% generated energy
- Heat Recovery Steam Generator (HRST operating up to 700 °C) with steam Turbine (ST) - 35% generated energy

Circulating medium –

- GT – burned gases at (900-1350)°C
- ST - water up to 700°C and pressure up to 30 MPa circulating in 3 sections: steam economizer, evaporator and superheater

Circulating water quality:

- High water quality kept by continuous blowdown and degassing
- Return condensate – treatment (filtration, deionization by H^+catex, degassing)
- Alkalization treatment – LP section -liguid and solid agents (ammonium, phosphates, NaOH)
  - - HP section – ammonium and phosphates

Corrosion impact – mostly:

- LP economizer
- LP evaporator (high flow rate of water and steam, temp. (140 – 170°C)
- Water storage tank (Feed water tank)

Boiler Layup (Conservation)

- Wet lay up with demin water, ammonia and oxygen scavengers
- Dry lay up with N2 gas
- Dry lay up with Dry air

Suppliers of Dosing Equipment

- Prominent
- Grundfos

Suppliers of Sampling Equipment and Analysers

- SWAN
- ABB
- Endress Hauser
- Siemens