

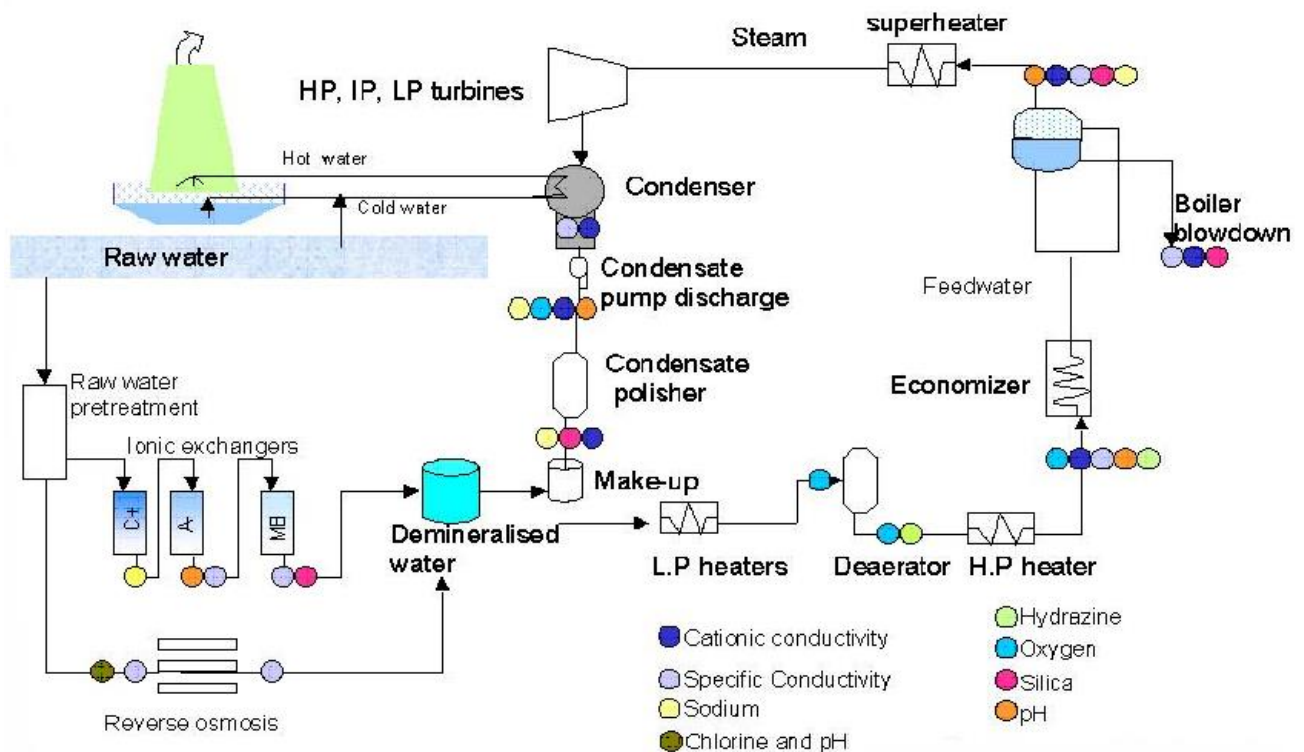
APPLICATION NOTE

STEAM GENERATION IN POWER PLANTS

Application description

Water quality within power plants is of critical importance in maintaining efficient operation and in limiting downtimes due to corrosion or preventative maintenance. The major phases and stages where water quality is measured are discussed in this application note along with the parameters measured.

Steam generation (drum boilers)



Water treatment plant

The purity of make-up water is critical in maintaining steam quality and in limiting boiler blowdown.

Raw water pre-treatment

Raw water contains organic matter, inorganic salts, bacteria which need to be removed before being purified.

Main steps:

1. Disinfection by chlorination (1-2 ppm) for preventing microbiological growth.

Parameters:

- Chlorine monitoring
- Redox can also be monitored at the raw water inlet point where oxidants (chlorine, bromine) are added (potential about 600 mV)

2. Softening by hardness removal (calcium and magnesium).

Two processes can be performed:

- Lime soda process where calcium is precipitated into carbonates and magnesium into magnesium hydroxide. These are then settled and filtered.
- Sodium cationic exchange, usually used in power because it prevents scaling (sodium ion). Calcium, magnesium and other cations (iron, aluminum) are exchanged into sodium. Conductivity is quite high at the outlet of the softening resin.

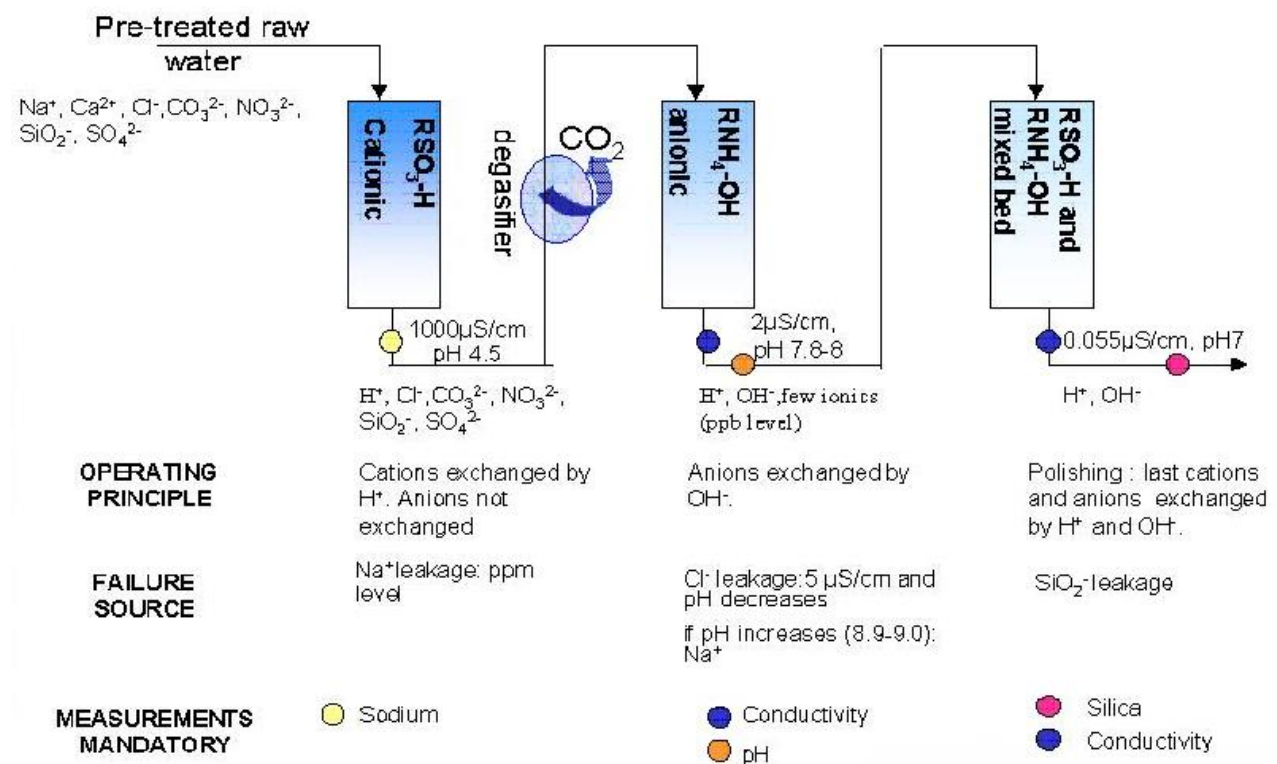
3. Dechlorination

- Carbon beds: eliminates organics and chloride. This does not offer a high performance for removing the organics and is a source of biological contamination.
- Addition of bisulphate, oxidized into sulphates (removed by anionic exchangers).

Water purification process

A demineralization plant usually consists of 2 specific ionic exchangers and by a mixed bed exchanger:

Demineralization plant



Cationic exchanger

The first ion exchanger removes all the cationic species (e.g. Ca^{2+} from CaCO_3) and exchanges them into H^+ (pH about 3-4). The H_2CO_3 is degassed before the second ionic exchanger. In case of cationic exchanger exhaustion, the first ionic leakage will be sodium because of its lower charge density.

Cationic exchangers are regenerated by HCl, H_2SO_4 : all cationic species trapped in the resin are removed and replaced by H^+ . After the completion of the regeneration, the resin is full of H^+ sites to be exchanged with cations again.

Parameters

- Sodium measurement for immediate detection of Na^+ leakage (ppb level)

Anionic exchanger

The second ion exchanger removes all the anionic species (nitrate, chloride, sulphates, silicate) and exchanges them into OH^- . Water molecules are produced (H^+ from the cationic outlet and OH^- from the anionic outlet).

Conductivity is about $2 \mu\text{S}/\text{cm}$ (because of some ppb ionic species that are not completely exchanged) and the pH is about 7.8 - 8.

In case of anionic exchanger exhaustion, the first leakage will be chloride because of its lower charge density. Anionic exchangers are regenerated by NaOH, removing all anions trapped by OH^- . When generation is completed, the resin is full of OH^- sites.

Parameters:

- Conductivity will clearly indicate ionic leakage if it reaches 5 - 6 μS . If conductivity reaches 5 - 6 μS , this is a clear indication of ionic leakage.
- pH levels also indicate leaks: If pH is about 8.9 - 9.0, this indicates sodium leaks. If pH decreases, this indicates chloride leaks.
- Therefore conductivity and pH are complementary measurements at this stage.
- Silica is sometimes monitored for diagnosing anionic bed exhaustion.

Mixed bed

For minimizing the effect of ionic leakage, a mixed bed is used for polishing demineralized water.

The mixed bed is a mixture of anion exchange and cationic exchange resin particles and allows high purity water to be produced.

Conductivity should be near $0.055 \mu\text{S}/\text{cm}$ and pH equal to 7.

Parameters:

- Conductivity is measured for ensuring the final water quality (no ionic leakage, $< 0.2 \mu\text{S}/\text{cm}$)
- pH is not so often monitored at this stage but rather at the outlet of the anionic bed.
- Silica is also measured at the outlet of the mixed bed.

Other demineralization systems use reverse osmosis with one or two stages for removing 95% of the organics as well as ionic species. Redox or chlorine can be measured before reverse osmosis to ensure the oxidant (chlorine) removal (200 mV, 20 ppb max) is complete. This protects the osmosis membrane. Conductivity is also used for monitoring the efficiency of reverse osmosis upstream and downstream.

Storage

Demineralized water is then stored before being fed into the circuitry.

Parameters:

- Conductivity: at the outlet of the storage tank, < 1 $\mu\text{S}/\text{cm}$ (CO_2 influence)

Neutralization of effluents

Without proper treatment, the effluent from the regeneration of ionic exchanger resins does not always conform to consents for discharge into the environment (river for example). The addition of a neutralizing reagent is often obligatory. pH measurement (use in the case of a 8350 probe) monitor the pH of those effluents. When it reaches the allowable limit, the effluent can be sent to the river.

Steam generation process

Operating principle

Market: All industries using steam (power plants, co-generation units)

The main concerns in power generation are the availability, reliability and life cycle of plants with one major objective: savings costs. The operating principle is based on an energy source: gas, carbon, fuel or nuclear. Water is vaporized in a boiler and steam heated which passes through a turbine, linked to an alternator, producing electricity. Steam is condensed and condensates recovered.

As circuit is principally made of carbon steel or copper alloy, corrosion and corrosion product deposition are the focal points at high temperature and pressure. The generalization of local corrosion induces stress cracking at high temperature. Any organic or inorganic impurities in the water circuitry can seriously damage the components of the boiler and turbines since water, steam, fuel and air carry over all contaminants.

Specific limits are set for the different parameters measured. Three different safety levels are usually defined:

- Above the level 1, the power plant must return to a normal level within one week.
- Above the level 2, within 24 hours.
- Above the level 3, a shutdown within few hours is mandated to avoid corrosion damage.

Due to improvements in the design of power plants, the requirements of water purity and water treatment equipment become more and more challenging.

Major source of plant failure

Main source of contaminants inleakage:

- **Make up water:** demineralization plants failure, resin fines ... Silica reduces turbine efficiency; sodium (NaOH , NaCl) corrodes boiler tubes and turbine blades. Sulfate comes from residual chemicals used for regenerating ionic exchangers.
- **Cooling water inleakage:** Introduces raw water (organic and inorganic) into the process. Inter-granular stress corrosion cracking can occur. Chloride, sulfate creates corrosion cracking in the turbine and in the boilers.
- **Air inleakage:** source of dissolved oxygen (DO) and CO_2 . DO promotes corrosion and CO_2 accelerates the attack on any copper alloy tubes (pH decreases).

Corrosion

A layer of magnetite (Fe_3O_4) protects the circuitry against corrosion which should not be removed or altered. The pH value in the process must minimize the solubility of the magnetite.

- NaOH: At low temperature, steel corrosion is inhibited by Hydroxyl alkalinity (NaOH). At high temperature, magnetite can be destroyed by high concentration of accumulated NaOH in crevices.
- Acid can produce H_2 reacting with the carbon to form methane (CH_4), weakening the metal.
- Sodium and potassium salts react with sulfur oxide and form sulphates. The molten sulphates dissolve protective oxide scale, prevent its reformation: Deposits can penetrate the metal structure of the hot section components and weaken the alloys.
- Microbiological induced corrosion is due to aerobic microbes which create anodic areas by consuming oxygen (the metal loses electrons and dissolves)

Deposits:

Calcium sulphates, calcium carbonate, silica, iron oxide can deposit on airfoils or blades and drastically reduce the power plant efficiency.

Water treatment principle:

Therefore high purity water is essential in preventing the introduction of impurities into the water circuitry. As pure water is very corrosive, conditioning is needed. This varies from plant to plant depending on the alloy used and the type of plant (pressure, pre-treatment, potential of feed water contamination).

Equilibrium phosphate treatment (trisodium phosphate) EPT: This precipitates calcium and magnesium (hardness) to avoid deposits (calcium carbonate...) on the heat exchanger. At high temperature, trisodium phosphate forms NaOH, which can corrode the circuitry.

For limiting free NaOH and reducing corrosion risks, the pH of the process should be below the curve 2.6 Na-PO₄ (congruent sodium-phosphate ratio) but above the curve 2.1 Na-PO₄ for preventing acid attack (H_3PO_4 formation).

All Volatile Treatment (AVT): Addition of ammonia, amines, morpholine, oxygen scavenger (hydrazine ...) at the condensate pump discharge.

Ammonia: It has a very volatile partition into steam and can reach high concentration in condensate. It does not prevent corrosion in the water. It has the highest neutralizing capacity (ppm CO_2 per amine). It dissolves copper: pH should be between 8.8 and 9.2, for preventing copper corrosion and remain high enough for protecting iron surfaces. If the circuitry has no copper components, the pH can be a little higher: pH 9.45 - 9.6 (2 ppm ammonia), but 2 ppm ammonia masks the presence of impurities at ppb level.

That's why the **cationic conductivity** is so important:

Cationic conductivity is a conductivity measurement after cation exchange: All cations, and therefore ammonium ions (NH_4^+), are removed and converted into Hydrogen ions (H^+). Inorganics (chloride, sulfates) and organics (acetate, formate) anions present (counter ion of cations, Cl^- , SO_4^{2-} , ...) can be easily determined because they are in their highly conductive acidic form (H^+ , Cl^- ; 2H^+ , SO_4^{2-}).

Any increase in cationic conductivity highlights anionic contamination. It indicates trend variations but does not specify which anions are present.

Specific conductivity measures all ionic species and is located before any ionic exchanger. It is always greater than cationic conductivity in power process water (not in the demineralization plant)

Amines (such as morpholine): show lower volatility than ammonia and can protect against boiler corrosion and condensate (water phases). Morpholine decomposes into acetate (acid effect) but compensates the acidity of boric acid and acetate. They can produce a filming effect avoiding water coming into contact with the circuitry.

The aim is to minimize the corrosion of iron (optimal pH about 9). **Oxygen scavengers** such as hydrazine remove dissolved oxygen and limit the risk of corrosion. 1 ppb DO produces about 80 kg rust per year. Hydrazine is decomposed into ammonia in the boiler which increases the pH and acts as protector against corrosion. Other reducers (sodium bisulfate) can be used but because of their highly corrosive decomposition (sulfur dioxide, hydrogen sulfide), they are not advised for use in plants operating at high pressure.

Sampling points and key measurements

Condensates

Condensates are the major source of contamination because they are in contact with the external source of pollution (raw water) when there are condenser tube leaks. Condensates can destroy the effectiveness of boiler water treatment, leading to damage to the boiler if they are reused without proper treatment. Condensate water is used for cooling LP turbine sprays during start up: it can cause pitting and then stress corrosion cracking. Condensate polishers are used to remove ionic impurities. In this case, the limits of water quality (cationic conductivity) are not so stringent in the condensates (before the polisher).

Parameters:

- Conductivity measurements (specific and cationic): in each hot well compartment; at the condensate pump discharge, at the inlet/outlet of condensate polisher (if any);
Specific conductivity:
Expected value: 2.5 $\mu\text{S}/\text{cm}$ to 11 $\mu\text{S}/\text{cm}$ if CCPP (LP drum and HP once through) 2 $\mu\text{S}/\text{cm}$ – 6 $\mu\text{S}/\text{cm}$ (copper alloy tube condenser), 3 $\mu\text{S}/\text{cm}$ – 11 $\mu\text{S}/\text{cm}$ (stainless steels or titanium) if drum boilers.
Cation conductivity:
Expected value < 0.2 $\mu\text{S}/\text{cm}$; level 1 < 0.5 $\mu\text{S}/\text{cm}$; level 2: 0.5 to 1 $\mu\text{S}/\text{cm}$; level 3 > 1 $\mu\text{S}/\text{cm}$
- pH measurements: condensate pump discharge, or after condensate polisher. pH would decrease if there is a brackish water ingress. pH: 8.8 to 9.3 if copper tubes condenser; 9 to 9.6 if steel.
- Sodium measurements (1 ppb): at condensate pump discharge for monitoring any sodium inleakage from condenser tubes more accurately and quickly than specific conductivity. The sodium concentration must be the same in the condenser and in the steam. If not, there is either a sodium inleakage in the condenser (sodium in condenser > sodium in steam phase), or a sodium deposit on turbine blades (sodium in steam > sodium in condenser)
- Silica measurements: for preventing as soon as possible any deposit risk (level < 20 ppb, drum boiler plants)
- Oxygen measurements: at the condensate pump for checking any condenser air inleakage. The deaerator eliminates dissolved gas (air inleakage).
- Oxygen measurements: inlet and outlet of deaerator (< 0 ppb) for checking its efficiency.

Feedwater (economizer inlet)

For optimizing the efficiency of the boiler, extending its lifespan and ensuring the steam quality, quality requirements of feed water are essential. It controls the pre-boiler corrosion risks and should an acidic condition occur, there would be rapid tube boiler damage and immediate shutdown. Feed water is also sprayed for control of steam temperature at superheated and reheated outlets.

- Conductivity measurements:
Levels are globally equivalent to those of condensates.
Specific: between 2 $\mu\text{S}/\text{cm}$ to 11 $\mu\text{S}/\text{cm}$ (drum boiler)
Degassed Cationic: it indicates all non-volatile anions (< 0.2 $\mu\text{S}/\text{cm}$)

- pH measurements:
The pH of the feed water must be greater than the pH of the boiler in the case of ammonia conditioning (volatile). If not, there are some hydroxyl ions (OH⁻) in the liquid phases of the boiler due to raw water leakage(HCO₃ into CO₂ (steam) + OH⁻ (liquid))
Iron systems: 9.3 to 9.6 pH
Iron/copper: 8.8 to 9.2 pH
- Oxygen measurements: < 20 ppb
- Silica < 20 ppb if once through steam generator (OSTG)
- Hydrazine: < 20 ppb for an accurate dosing

Boiler water

Scale formation due to hardness, silica, and corrosion product deposits can decrease the heat exchange capacity and global efficiency of the boiler. Steam quality varies with the concentration of impurities in the boiler and the potential mechanical carryover of boiler water droplets into the steam. The higher the operating pressure of the boiler, the higher the purity requirements since contaminant carryover is promoted.

The concentration of impurities after each evaporation cycles is discarded by blowdown in drum boilers (curative and preventive actions). If impurity concentrations becomes greater than its solubility (the lower the pressure, the lower the solubility), deposits may occur. Evaporation, drying of moisture and chemical reactions on surfaces, or in metal oxide can lead to deposits too.

As deposits can be very adhering, anti-scalant reagents are added to help remove them. When quality limits are exceeded, blowdowns are increased, power reduction initiated (level 1 of safety procedure) up to hot standby (level 2 of safety procedure) if measurements are far too high.

- Conductivity measurements:
Specific (Boiler):
Estimated limits depending on the steam quality
For pressure < 300 psig : < 7 mS/cm; up to 600 psig: 800/5400 μS;
at 1500 psig : < 100 μS

In low pressure boiler:
Cationic conductivity (Blowdown): < 0.8 μS/cm
Level 1 if > 0.8 μS: small condenser leaks, impurity incursions
Level 2 if > 2 μS: power reduction by 30%: sufficient flow for automatic control, impurities can be located and treated (heat exchange rate has been decreased)
Level 3 if > 7 μS/cm: immediate shutdown, steam generator corrosion
- pH measurements:
Iron systems: pH9
Copper systems: 8.6 to 9 pH
The corrosion rate of carbon steel is minimal between pH 8.5 to 9.2
Level 1: > 8 but < 8.5 or > 9.2 but < 9.4: Chemical feed, blowdown adjusted
Power reduction by 35%
Level 2 < 8 or > 9.4: hot standby
- Silica measurements (drum boiler blowdown): silica build-up in the boiler depends on the drum pressure, < 5 ppb

Main steam, reheat steam (heat recovery steam generator)

Boiler specifications do not ensure the quality of turbine steam. The solubility limits in the turbine define the feed water impurity levels. The conformance with the steam limits contributes to minimize boiler blowdowns. Steam is a good solvent at high pressure and carries over oxide, silicates, sulphates, carbonates, aluminates and chlorides, which

can corrode the turbine. Low level of impurity is mandatory; CO₂ interference must also be avoided. As water can be directly injected into the turbine for increasing the power output, its quality must obviously be under control. The gas turbine compressor can also be washed for removing fouling deposits if increased back pressure, and decreased power output are noticed.

The quality of water must conform to the following limits: 8 µS/cm and 6.5 to 7.5 pH.

- pH measurements:
Copper tube condenser: 8.8 to 9.3 pH
Stainless steel tube condenser: 9 to 9.6 pH
If CCP (LP drum and HP once through): LP main steam at boiler outlet: 9.5 to 9.9 pH
HP main steam at once through steam generator (OSTG): 9 to 9.4 pH
- Conductivity measurements:
Specific:
If CCP (LP drum and HP once through): LP main steam at boiler outlet: < 20 µS/cm
HP main steam at once through steam generator (OSTG): < 10 µS/cm
Cationic:
< 0.2 µS/cm
- Sodium measurement: < 5 ppb
- Silica measurement: < 5 ppb, deposit on turbine blades

Cooling water

Operating Principle

Cooling water uses raw water for cooling the condenser tubes and maintaining their efficiency. At the inlet of the condenser, the cooling water is quite cold, depending on the temperature of the river. After having cooled the condenser, it returns to the cooling tower at a higher temperature than that at the inlet of the condenser where it is sprayed in the cooling tower and cooled via air. Excess energy in the form of heat is evaporated through the top of the cooling tower (look at the water vapor!). As there are evaporation cycles in the cooling tower, there is a concentration effect of the water.

Concentration cycles

Depending on the construction material of the cooling systems, limits in the cycles of concentration are fixed (concentration rate of 1.2 /1.7). For this reason, blowdowns of cooling water are performed and key parameters monitored. Inductive conductivity can also be used for monitoring the concentration cycles and Alkalinity (P and M), and hardness are monitored in the largest cooling towers to evaluate the calcium carbonate precipitation risk. pH measurement must be less than the critical pH (8.3) where the calcium carbonate begins to precipitate: H₂SO₄ is injected for decreasing the TAC (total alkalinity carbonates) according to the SALE factor (depending on the TAC, calcium hardness and the ionic strength (conductivity)).

Nevertheless, if the pH level rises above 8.3 (irrespective of the SALE factor), H₂SO₄ is injected to avoid the precipitation of calcium carbonate. Sometimes, if the TAC of the raw water used is too high, the injection of H₂SO₄ does not avoid the precipitation of CaCO₃. For this reason, the volume of fresh raw water is reduced.

Microbiological induced corrosion

Raw water contains a large amount of nutrients, algae and bacteria. Algae produce oxygen and accelerate corrosion; dead algae lead to fouling, act as food for bacteria, and absorb biocides. If the biological activity in a power plant is misunderstood, the availability of the power plant can be drastically reduced. Biocides must be added to the raw water to avoid bacteria ingress in the cooling system which could rapidly damage the power plant (raw water leakage in the condenser) - this minimizes microbiological induced corrosion. If biocides are underfed, the microbiological growth can

occur and if it is overfed, it costs more money to optimize the application of biocides, redox, chlorine, and ozone can be monitored at the raw water inlet point where oxidants (chlorine and bromine) are added to kill micro-organisms.

Conductivity measurement can reliably detect 2 to 5 ppm of Sodium while Sodium measurement detects 2 to 5 ppb, that's 1000 times lower. This sensitivity allows chemists to follow trend changes before any leakage requires major immediate action. This sensitivity advantage can be converted over time to analyse the origin of the leakage and to plan either a production reduction, or even to stop production far enough in advance to avoid costly, unexpected emergency shut downs.

The analyser and installation

The analyzer requires a sample at low pressure (below 6 bar) and cooled below 40°C (104°F). Usually a sampling panel already exists for conductivity measurements and these samples can be used in parallel for the Sodium analyzer. Several local or international panel manufacturers are able to offer such systems. The Sodium analyzer sends an analogue 4-20 mA signal to the DCS:

- A trend analysis over a given rolling time period allows a 'trend warning': if the rate of raise exceeds a pre-set value of, for example, 1 ppb per hour, then a warning is given independently of the absolute actual sodium value.
- A limit from the absolute value is set according to the accepted limit level of pollution, for example, 100 ppb or 1 ppm, where the 'sodium alarm' will be activated for immediate action.
- Both warnings and alarms can be combined if the rate of increase becomes too high showing a significant problem in the near term.

Material installed

- POLYMETRON 9245 Sodium analyzer
- Polymetron Conductivity Monec 9125 with sensor 8310 (as spare wheel!)

Comments

In several pulp mills in Scandinavia, Hach Ultra is in the phase of replacing many early Sodium analysers with the new POLYMETRON 9245.

Most of these facilities, having old boilers, will be either closed or revamped with new cogeneration plants. These new modern cogeneration plants operate at a high pressure and require much higher levels of monitoring regarding the steam quality. These upgrades are linked to new demin-plants that produce high quality pure water in terms of conductivity and Sodium concentration.

This application is of interest for the pulp and paper industry (presence of white, green or black liquor), in some metal production (aluminium, zinc, all extractions using caustic solutions), in chemical plants producing or using caustic soda (sodium hypochlorite, Solvay process) as well as for the boilers located close to the sea and/or using sea or brackish water as cooling water.

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