Application Report

Power: No 5

Calculated pH using Cationic Conductivity Measurements in Power Plants

Introduction

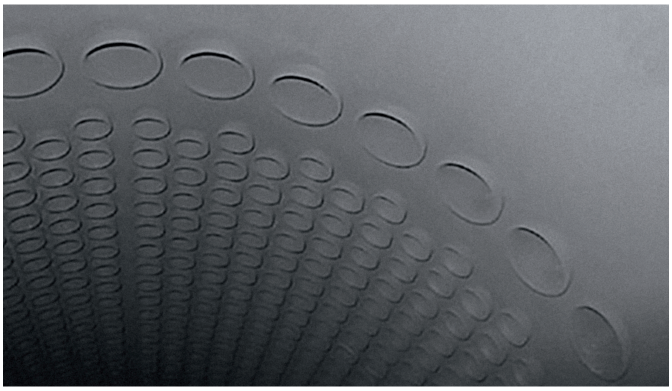
Measurement of pH in pure water found in power plants is a challenge for conventional pH electrodes. On the other side, calculated pH measurements with a dual conductivity setup provides a highly reliable measurement, and can be more accurate than a conventional pH electrode.

This report describes the challenges of pH measurements, how calculated pH works as well as the benefits of calculated pH and cationic conductivity measurements. Finally a solution is presented.

Water chemistry and pH

As recommended by organisations like the VGB (European technical association for power and heat generation) and EPRI (electric power research institute, U.S.A.), **corrosion control** is assessed by oxygen concentrations in combination with pH and purity of the water system. High purity of the water allows increased concentrations of oxygen and decreased pH, which result in better protection of steel pipes.

If high purity of the water is not achievable, then the protection must rely on higher pH at low oxygen concentrations. **Therefore pH is a key parameter to keep the water of the plant in a specific regime: AVT, OT, etc.**



A stable magnetite layer inside a boiler (Fe_3O_4 with a dull black or gray appearance)

A pH measurement challenge

Although the pH technology is widely extended, the measurement in pure water, is a challenge for conventional pH electrodes:

- Potential between electrodes is affected by high purity water properties that makes the pH measurement unstable and difficult.
- The very low ionic content of the high purity water makes the pH glass less sensitive; it will also cause the measuring electrode to wear out faster, increasing replacement frequency.
- The reference junction develops interfering electrical potentials.
- Interfering static charges are generated on the sensor surfaces and the measurement becomes highly noise sensitive.

Additionally, grab samples for pH do not provide real-time data and are not accurate.

Due to the above mentioned reasons the calculated pH solution has gained attractiveness.

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Calculated pH, how does it work?

1. The conductivity is measured before the cationic resin. It is mainly driven by ammonia and NaCl.
   Cond1 = cond NH_3 + cond NaCl
2. Cations are exchanged with the H^+ ions of the resin. The resin, having a greater affinity for the cations, releases the H^+ ions while grabbing the cations. The released H^+ ions form acids with the remaining anions in the water.
3. Conductivity is measured after the resin, where the main contributor is HCl.
   Cond2 = cond HCl
4. By calculation, the contribution of NaCl in Cond1 is taken away, and the unknown cond NH_3 remains.
5. The relation of a pure ammonia (NH_3) solution and its conductivity is well known. The final formula gives a direct relation between the logarithm of Cond1, Cond2 and the pH of an equivalent solution of ammonia:
   $pH = \log [Cond1 - (Cond2 / 3)] + 8.6$

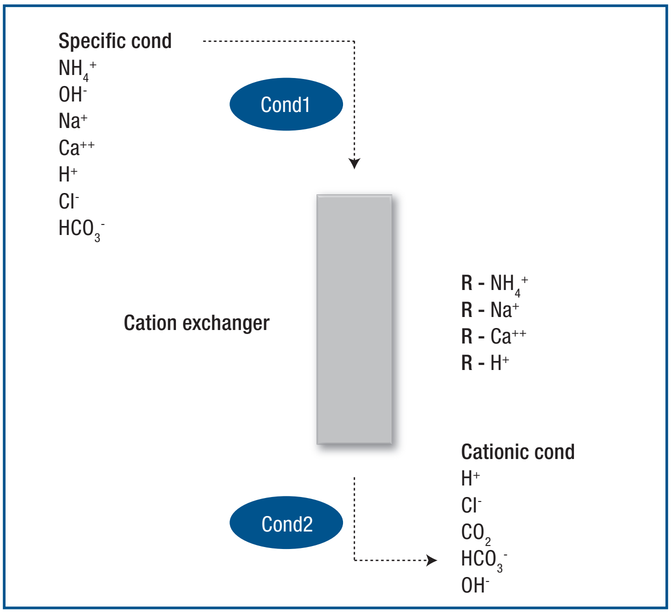
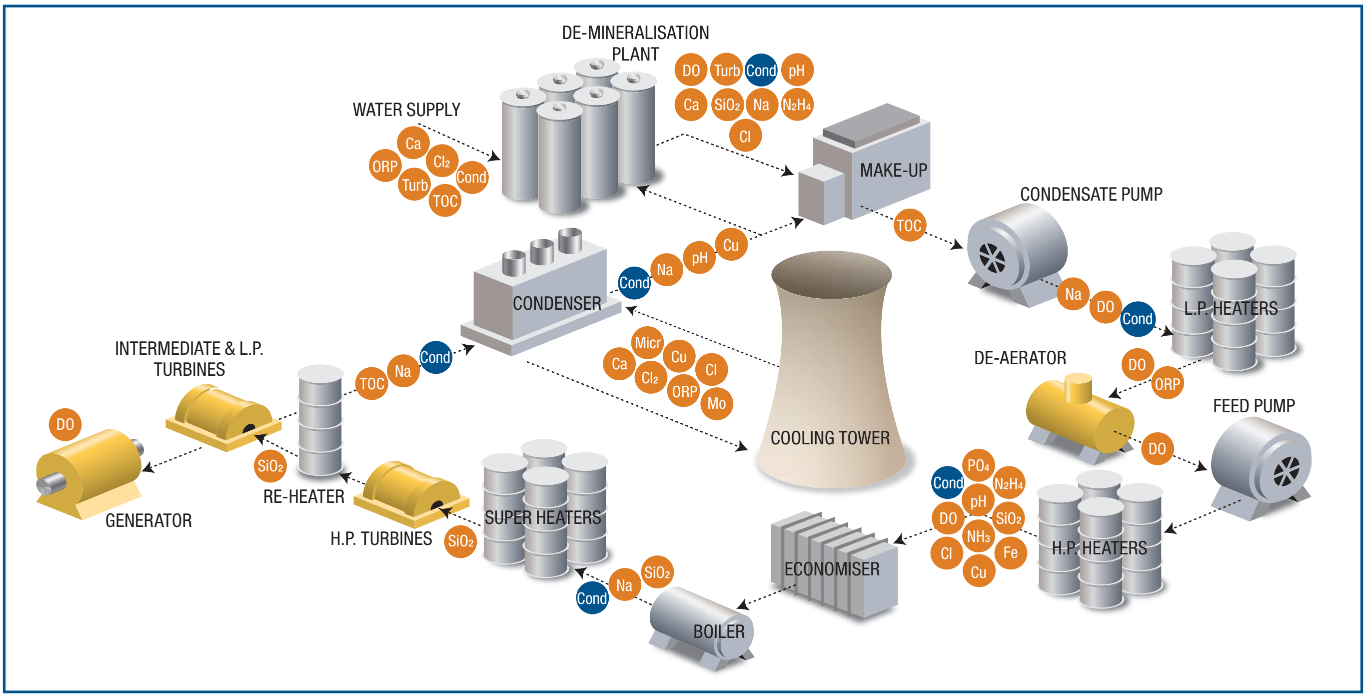


Fig. 1: Ions before and after the cationic resin

For a valid pH calculation, the following sample specifications should be met:

- pH value should be between 7.5 and 10.5
- Phosphate concentration below 0.5 mg/L
- The conditioning of the boiler feed water should be alkaline-based of only one alkaline reagent: ammonia or sodium hydroxide
- Below pH value 8, the concentration of impurities must be small when compared to the alkaline reagent

The POLYMETRON 9523 calculated pH analyser has a system alarm which is activated when the pH calculation is outside the valid limits (NH_3: 7<pH<10, NaOH: 7<pH<10.7).



Locations for calculated pH monitoring

Benefits of calculated pH measurements

- Accurate pH value is provided without the constraints typically associated with conventional glass electrodes in low conductivity applications
- Conductivity sensors are very stable over time and do not require extensive maintenance like pH electrodes
- Under normal water chemistry conditions the algorithm gives long term reliable results
- Higher sensitivity and linear response. For example, a change of only 0.3 pH represents a two-fold (100 %) change in both concentration and conductivity in cycle chemistry ranges. Linear response of conductivity with changing concentration gives a higher pH sensitivity than what is achieved with the logarithmic response of traditional pH electrodes.

Cationic conductivity

The conductivity measurement after a cationic resin (see Fig.1) provides the cationic conductivity (or acid conductivity), an additional parameter of importance for the power plant chemist.

Measuring conductivity after a cationic resin **enhances the sensitivity to contaminants** in two ways:

1. Ammonia and amines, which are present as oxygen scavengers and give very high conductivity values, are removed. Enabling the exclusive measurement of impurities in the sample.
2. The cation resin converts low conductive mineral ions such as Na^+, Ca^{++} and Mg^{++} to an acid form with a high conductive hydrogen ion H^+. As the acid form has three to six times the conductivity of the corresponding salts, the process is much more sensitive in measuring impurities than a standard conductivity measurement.

Grab samples analysis is not possible, as the conductivity measurement will get interferences from the CO_2 present in the air. Thus the cation exchange column can be seen as a “conductivity amplifier” for minerals and organic acid contaminants (acetates and formates).

Cation conductivity is recommended as the key parameter in continuous monitoring of steam. It has also been proved to be the **decisive criterion allowing to start the steam turbine** (at values lower than 0.2 µS/cm), especially for peak load plants requiring short start up times.

Benefits of cationic conductivity measurements

Simplicity and Reliability

Conductivity probes are the simplest probes used in water chemistry analysis. No reactive or complex sampling devices are used leading to minimal maintenance costs and highly reliable measurements.

A winning combination

The measurement of cationic conductivity offers a good combination of trace contaminants detection with the simplicity, reliability and low price of conductivity sensors.

The solution: POLYMETRON 9523 Calculated pH Analyser

All-in-one panel analyser or single transmitter version available
The panel version is the preferred quick installation and "turn-key" solution that is ready for use. A single transmitter can also be supplied for easy integration in any power plant sampling panel.

Cost effective analysis compared with traditional pH electrodes
With standard water chemistry conditions found on power plants the calculated pH analyser provides a more stable measurement and requires no maintenance, unlike typical pH electrodes.

Provides calculated pH and cationic (acid) conductivity
The cationic conductivity is provided after the cationic resin. This is an efficient way to track low contamination in the water loop and is a key parameter for startup conditions on peak load plants.

Quick visualisation of sample flow and resin exhaustion
The transparent flow chamber allows a quick visual control of flow conditions. The same applies for the cartridge which visualises the indicator dye change showing the resin exhaustion over the time.

System configuration

The POLYMETRON 9523 calculated pH analyser is shipped on a complete panel that contains all necessary parts to perform the analysis: controller, probes, cables, flow cell and installation hardware. The system is configured according to VGB standard VGB-S-006-00-2012-09-EN

Ensure flawless operation with flexible service contracts

Whether a power plant operates 24 hours a day, 7 days a week or comes online to meet peak demand, there are unique challenges to monitoring the water quality in the steam cycle and waste water at your facility.

Hach Lange Service can help you with your maintenance and support challenges ensuring flawless operation and reliable results.

HACH LANGE offers flexible service contracts to fit your needs and including the option to extend the warranty for up to 5 years!

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