Dissolved Oxygen Measurement in Power Plants

Introduction

Dissolved oxygen is a prime contributor to corrosion in power plant steam cycles and is affected by a number of design and chemistry related parameters. These include cycling versus base-load operation, drum versus once-through boiler design, feed water system metallurgy, phosphate versus all volatile treatment, and operating pressures. This report describes main locations for the dissolved oxygen measurement, in combination with different water chemistry regimes in water loops.

Water chemistry and Dissolved Oxygen

As recommended by organisations such as the VGB (European technical association for power and heat generation) and EPRI (Electric Power Research Institute, U.S.A.), assessment of oxygen concentrations has to be made in combination with pH and purity of the water system. The high purity of the water allows increased concentrations of oxygen and decreased pH, which results in a better protection of steel pipes. This improvement is generated by the oxidation of the magnetite protective layer to hematite. Hematite shows a lower solubility with a much finer crystalline structure, it seals the porous magnetite structure.

If high purity water is not achievable, then the protection must rely on increased pH at low oxygen concentrations. However, very low oxygen concentration is only achievable by the addition of strong reducing agents (oxygen scavengers), which should be carefully considered.

According to the water chemistry applied in the plant, oxygen should be either maintained at low concentrations (AVT) or kept within a specific range (OT).

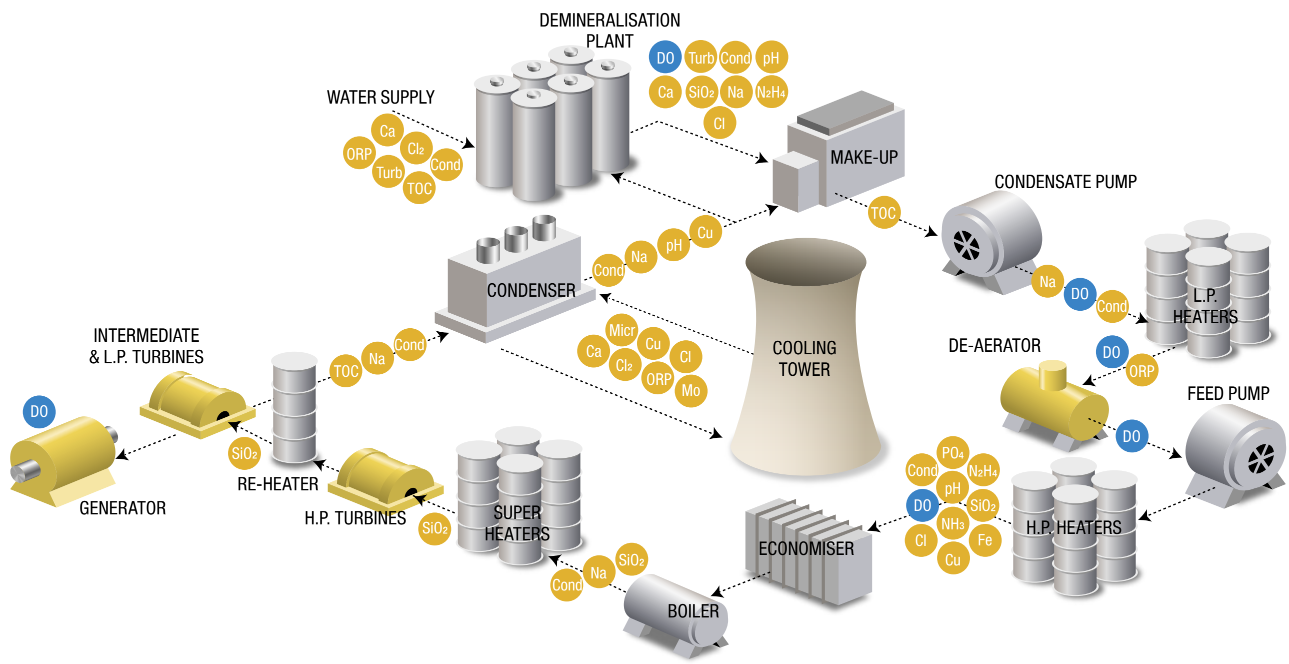
Plants using oxygenated treatment (OT) typically operate with boiler feed water oxygen concentrations between 50 and 200 ppb, and therefore oxygen instruments should be selected on the basis of a prolonged service life. In this situation, the new luminescent oxygen sensor technology (LDO) fully covers this requirement with up to one year of continuous operation without sensor service.

On the other hand, power plants practicing the "all volatile treatment" (AVT) type of water chemistry with high-pressure steam cycles typically maintain boiler feed water dissolved oxygen concentrations under 5 ppb and condensate concentrations under 20 ppb.

Thus, oxygen measuring instruments require high sensitivity. For this scenario, LDO type sensors can be used in most cases but electrochemical sensors remain the reference, below 1 ppb oxygen concentrations.

The different water chemistry regimes and their acronyms:

- **AVT:** Conditioning regime in which only volatile alkalising agents are added to the feedwater.
- **AVT(R):** Reducing conditions (added reducing agent) recommended for units with copper alloys.
- **AVT(O):** Oxidizing conditions (residual oxygen present). Applicable only to units with all-ferrous metallurgy.
- **OT:** Conditioning regime in which alkalising agents and oxygen are added to the feedwater. It is only suitable for units with all-ferrous metallurgy and high purity feedwater.



Locations for dissolved oxygen measurement

Continuous analysis of dissolved oxygen is normally made on the boiler feed water, de-aerator outlet, and condensate discharge.

Oxygen sensors mounted on a panel in the water steam cycle

Dissolved Oxygen measurement in generator stator coolant

Water chemistry in stator coolant is different from the main water loop because the major cause of problems in stator cooling systems is not the corrosion itself, but rather deposit accumulation in critical areas.

Dissolved oxygen and pH drive different water treatment regimes, with different effects on copper oxide generation and release.

Low oxygen conc. (<10 ppb) and neutral pH	High oxygen conc. (>2000 ppb) and neutral pH
Low oxygen conc. (<10 ppb) and alkaline pH (8-9)	High oxygen conc. (>2000 ppb) and alkaline pH (8-9)

Only three of the four possible stator cooling water treatment options are viable. (M&M Engineering)

Four stator cooling water treatment options:

- **Low oxygen concentration, neutral pH option.** This treatment is found in about 50% of the stator cooling systems. A thin layer of passive cuprous oxide protects the copper tubes.
- **Low oxygen concentration, higher pH option.** Increasing the pH of the stator water to 8 - 9 significantly reduces the corrosive response during oxygen transitions.
- **High oxygen concentration, neutral pH option.** The goal is to maintain a high dissolved oxygen level in the cooling water at all times. It is estimated that 40% of water-based stator cooling systems operate with these parameters. In this regime, CuO is formed on the copper which will tightly adhere to the surface and create a passive layer on the metal. This layer tends to be thicker than the Cu_2O formed under low-oxygen conditions.
- **High oxygen concentration, high pH option.** This is not recommended because it increases the likelihood of bar clip corrosion.

Typical installation

The picture on the right shows a standard Orbisphere panel. The sample enters in the centre of the flow chamber via a three way valve. This valve allows the interruption of the sample flow and also purging of the inlet line. All lines are connected with Swagelok® fittings to avoid any risk of air entrance. A flowmeter with a regulator valve is placed after the flow chamber. There are several reasons for this configuration:

- If the water sample contains a high concentration of some other dissolved gas, for example Hydrogen (H_2) in Pressurised Water Reactor (PWR) coolant water, then it keeps the pressure in the sample and prevents degassing before measurement.
- Another reason is to avoid any risk of air contamination which can be generated by deterioration of the flowmeter, and in particular by deterioration of the gasket of the regulator valve.

The sensor should be mounted vertically above inlet valve and flow chamber as shown in the picture. In this position, any gas bubbles entering the chamber are quickly swept past the sensor and out through the exit port.

Careful attention to sampling system design will help avoid common sampling problems. A typical sampling related problem is disagreement between the on-line analyser and a portable device.

This problem is most often generated by a sample line leak which “doses” the lines with continuous amounts of oxygen. A typical indicator of this is a decrease of the oxygen reading when increasing the sample flow.

Orbisphere sampling panel

Calibration and validation of online oxygen devices

Modern portable devices such as the Orbisphere 3100 Oxygen Analyser can be used as online calibration or validation tools. The portable device is first calibrated against a traceable standard in the lab and is then used as a mobile reference throughout the plant. Because online analysers have direct calibration functions, the calibration will take just few seconds with the portable unit connected at the same sampling location. In this scenario the traceability and link to external official standards is fully covered.

The LDO technology for dissolved oxygen measurement has the benefit of long term stability, even when the measuring device is in stand-by mode. Weeks or months without operation do not affect the metrological properties of this working reference.

The Orbisphere 3655 Portable Oxygen Analyser, with an electrochemical sensor, is the absolute reference for levels below 5 ppb with a sensor residual going down to 0.1 ppb.

Portable Oxygen Analysers Orbisphere 3100 and 3655

The solution from Hach: Orbisphere K1100 Sensor

One calibration per year
Traditional electrochemical sensors display significant drift after only a few months, demanding regular re-calibration & substantial operator time. Due to its luminescent technology, the Orbisphere K1100 sensor is designed for minimal drift, resulting in it being the most stable sensor with the longest calibration interval in the industry.

No membranes = 2 minutes of maintenance
With no membranes to replace, no electrolyte solution to replenish and no hazardous chemicals required, the K1100 sensor is virtually maintenance-free requiring only two minutes of maintenance per year.

Low cost of retrofit
The K1100 sensor is compatible with Orbisphere 28 mm flow chambers previously used with electrochemical sensors, thus eliminating the need for engineering changes to weld, add, and test new connections, an ideal retrofit.

A new level of confidence
No warm-up time is required for the LDO, which provides a strong benefit for peak load plants requiring a quick response time from the whole instrumentation. The frequency of measurement is configurable to achieve unsurpassed long periods without calibration required.

Orbisphere K1100 Online Oxygen Sensor and Orbisphere 410 Controller

References
[1] Dooley, R. B. Power Plant Chemistry 2002, 4(6), 320.
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[3] Dunand, F. et al.; LDO sensor to monitor power plant water and team cycles – PPChem 2006, 8(10).
[4] Optische Sauerstoffmessung in Kraftwerken, VGB Powertech, p119-124, 9, 2012

Ensure continuous 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® Service can help you with your maintenance and support challenges ensuring flawless operation and reliable results.

Hach offers flexible service contracts to fit your needs, including the option to extend the warranty for up to 5 years!

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