

OPTICAL DISSOLVED OXYGEN MEASUREMENT IN POWER PLANTS

A comparison of amperometric and optical dissolved oxygen sensors in power and industrial water applications at low oxygen levels (<5ppb)

Abstract

The majority of existing dissolved oxygen analyzers use amperometric sensors. While these are renowned for their accuracy and reliability, issues encountered by users include maintenance complexity and frequency, in addition to flow dependence and calibration needs.

In more complex applications, amperometric sensors suffer from interference when measuring in the presence of high levels of hydrogen—this often results in negative readings and an unreliable measurement method. Since 2006, luminescence technology has been used in power plants. This sensor showed significant reductions in maintenance complexity and frequency but was limited by its accuracy with use generally confined to oxygenated treatment (OT) environments.

In 2009, the first luminescent oxygen sensor with sub-ppb accuracy for use in power plants was launched. In this paper, we will compare and discuss the performance of both optical and amperometric oxygen sensors in both fossil and nuclear power plant applications.

Introduction

Dissolved oxygen is one of the key parameters that must be monitored and controlled in the power industry to effectively minimize corrosion due to oxidation. Numerous guidelines exist from standards bodies on different chemistry methods that can be applied to effectively manage oxygen levels. Fossil power plant chemistries, including all-volatile treatments (AVT) for both reducing and oxidizing (AVT(R) & AVT(O)), along with oxygenated treatment (OT) allow strict control of oxygen levels to minimize corrosion [1].

In nuclear power plants (NPP), oxygen measurement is complicated somewhat both by the radioactive material in the sample and the high levels of hydrogen often found in primary cycle chemistries on pressurized water reactors (PWR) and in the balance of boiling water reactors (BWR). Differing from fossil plants using oxygen scavengers, like hydrazine in AVT(R) chemistry, nuclear power plants add hydrogen to radioactive waters to remove oxygen by recombining oxygen and hydrogen to form water. For BWR this method is called hydrogen water chemistry (HWC). In the primary side (RCS) water of a PWR hydrogen is over pressured to 2 to 3 bar. The critical nature of the hydrogen/oxygen mixture means accurate measurement accounting for any hydrogen interference is essential.

The effects of hydrogen present in water can also be seen in stator water cooling applications – the most commonly used chemistry is a low oxygen monitoring approach, with a typical range of 1-10ppb oxygen but this cooling water is generally saturated with hydrogen [2]. Again, for safety in addition to corrosion control reasons, the oxygen level must be accurately measured.

The use of LDO sensors for the measurement of oxygen is now accepted by ASTM [4]. With thousands of units in use globally, LDO measurement has been rapidly adopted by users in many industries.

Optical measurement started with the measurement of relatively high oxygen levels, with measurements at ppm level samples now widely accepted and used in process. Technology advances over the past 3 years have resulted in ppb measurement systems in the power industry; however, accurate and consistent measurement at levels below 10ppb were limited due to the accuracy and detection limits available at that time. Since 2009, accurate measurement at levels below 1ppb has now been made possible.

With the optical process for the measurement of dissolved oxygen, a measurement method has been developed that eliminates the process-related disadvantages of traditional electrochemical measurement methods, for example the progressive wear of the anodes due to the oxidation process and the decrease in electrolyte density.

Trends in Energy Management

Over the past decade a number of trends have started to gain pace within the power sector, driving a change in instrumentation requirements for operations managers and plant chemists:

- Maintenance and operations budget cuts have resulted in fewer plant personnel. This in turn has forced plant personnel to optimize even further their daily work and reduce their maintenance and calibration workload. Accompanied by the switch to inline/in-process rather than lab measurements, this puts additional time pressure on personnel.
- The cost of building new power plants spirals upwards, many operators now look to plant life-extensions as a solution to bridge gaps in production capacity at a lower investment premium. Construction cost increases are compounded by fears over the cost of new carbon capture systems often demanded on new plants. Clearly, plant extensions are only possible if the heart of any power plant, the water-steam circuit, can be well managed and maintained.
- There are a growing number of peaking plants in the power sector, especially with the advances in and environmental benefits of combined-cycle gas turbine (CCGT) peaking plants [3]. Peaking plants experience more start-up and shut-down cycles than base-load plants and each of these results in high oxygen concentrations during the start-up. This in turn leads to higher instrument maintenance of amperometric sensors for oxygen measurement, a real problem for operations managers looking for low maintenance systems.

These trends have changed the requirements in operating power plants. Starting from these trends this article analyzes the options for oxygen measurements that are precise, reliable, stable, and above all require low to zero maintenance.

Principle of Measurement

The K1100 LDO sensor consists of two major components:

- A sensor layer with the luminophore, applied on a transparent carrier material
- The sensor body with a blue LED, a photodiode as a receiving unit and an additional red LED used as a reference light source

The blue LED sends out a light pulse for the measurement. This passes through a transparent carrier material and hits the luminophore in the sensor layer. Part of the radiant energy is transferred to the luminophore as a result. The electrons in the luminophore hence move from an energetic basic state to a higher energy level. This level is exited after a very short stay via interim levels, whereby a red light is emitted.

If oxygen molecules are now present, they are in a position to take up the energy from the electrons, which are in the higher energy levels, and enable their transition into the base level without emitting radiation. This procedure is called quenching. With an increasing oxygen concentration, this process leads to a significant reduction in the emitted radiation intensity of the red light. The quenching also reduces the period the energy spends in the incited level, which leads to electrons leaving the higher energy level again faster. Both the life span and the intensity of the red emitted radiation are reduced by the presence of oxygen molecules.

The light pulse sent out by the blue LED at point in time $t=0$ hits the luminophore, which emits red light immediately afterwards. The maximum intensity and the decay time of the red radiation depend on the ambient oxygen concentration. The decay time T is defined here as the period between incitement and the

red radiation returning to 1 times the maximum intensity. To determine the oxygen concentration, the life span, T , of the red radiation is evaluated.

A constant alignment of the sensor occurs with the help of the red LED fitted in the probe. Before each measurement, this sends out a light beam of a known radiation characteristic. Changes in the measurement system are hence detected without any time delay.

System Calibration

Amperometric oxygen sensors generally require a two-point calibration – the zero point and the slope (via standards calibration sample). Optical oxygen sensors require a single-point zero-calibration. The single point calibration is used to set the zero – this is where the optical signal varies the most hence an accurate setup is essential if accurate measurement below 1ppb is required.

The big advantage of optical calibration is that no chemicals are required. The sensor can be calibrated using a pure oxygen free gas such as nitrogen or carbon-dioxide with no other liquids required for cleaning due to the sensor being electrolyte-free. The only reliable calibration method remains to expose the sensor during calibration to a known reference sample to adjust the zero-point. It is recommended that the use of a quality-50 gas as a reference zero value, giving 99.999% purity which helps ensure accuracy at sub-ppb measurement levels.

Figure 1 compares the maintenance, calibration, stabilization, and response time of an optical sensor when compared with that of an amperometric sensor. It shows that the maintenance and stabilization time of an optical sensor is 82% less than that of a typical amperometric sensor; when combined with the fact that maintenance is required 3 times less than an amperometric sensor, the operator workload can be reduced by 95%. Such time and cost savings become significant within a power plant with a multitude of oxygen sensors. This also demonstrates that optical sensor response time post-calibration, from air to reach 4ppb is 79% faster than that of a typical amperometric sensor, resulting in more system up-time and much lower operator intervention.

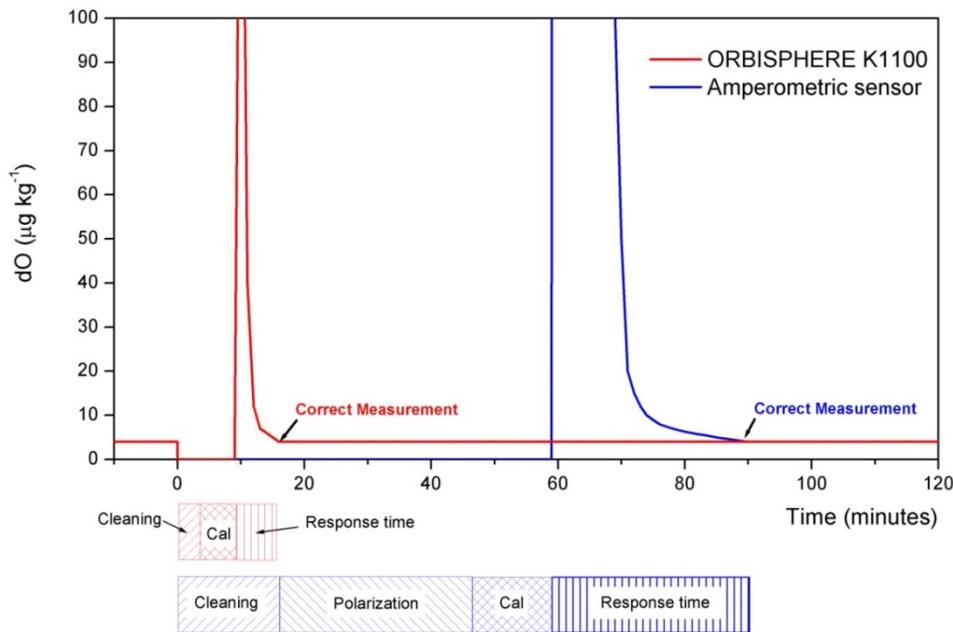


Figure 1: Maintenance, calibration, and stabilization timeline for an optical vs an amperometric sensor.

Comparative Tests and Installation

Many different tests have been performed in power plant environments globally to demonstrate the significant benefits that can be achieved by using optical oxygen sensors when compared with amperometric sensors.

Data discussed and illustrated in this paper includes that from the following installations:

1. Combined cycle power plant (gas and steam); 1000MW capacity running an AVT water chemistry.
 - a. Feed water oxygen measurement; typical values in the 0-10ppb range at temperatures of 15-25°C.
 - b. Within the AVT chemistry, Carbohydrazine and ammonia were present.
 - c. Both the Orbisphere K1100 optical sensor and the Orbisphere A1100 amperometric sensors were installed.
2. BWR Nuclear power plant; 355MW capacity running a hydrogen water chemistry (HWC).
 - a. Reactor water measurement; typical values below 1ppb during hydrogen injection (during normal operation) at temperatures of 18-23°C.
 - b. Hydrogen present in feed water at 180ppb radiation level of approximately 160Sv.

Power plants operating with AVT water chemistries typically require lower level and hence more accurate oxygen measurement than those running OT water chemistries. The oxygen levels commonly encountered within fossil power plants have been discussed in prior papers by Dooley and Shields [5]. Given such varying concentrations and water chemistries, a clear understanding of the factors impacting system performance is essential.

Stability

While some amperometric sensors can measure with an accuracy of 0.1ppb, this is balanced with a number of drawbacks:

1. Stability or drift between maintenance interventions;
2. Effort and costs associated with minimizing errors due to drift through more regular calibration and sensor maintenance.

For this reason, it is essential to consider the oxygen levels to be measured along with the constraints of time and the confidence to be placed in a system.

Sensor drift is the major cause of concern for plant operators and can result in excessive calibration and maintenance. The stability of a system directly impacts the confidence placed in it over time—a system that drifts significantly will never be trusted as the source of information in process control. With a number of systems publishing a drift of $\pm 5\%$ [7] and up to ± 2 ppb per week in the measured values [5], this leads to frequent operator intervention for calibration and a lack of trust in the system. Such drift of up to ± 2 ppb per week in applications below 5ppm is not acceptable for many operators in fossil plant chemistries.

System Performance in Hydrogen Rich Samples

As previously mentioned, NPP measurements in the PWR primary cycle, where highly precise readings are required, can be more troublesome for amperometric sensors. Often, primary cycle chemistries include high levels of hydrogen in the measurement sample; amperometric sensors can experience a negative offset

from high levels of hydrogen, at times up to 10ppb. While systems do exist to compensate for this offset [8], accurate oxygen readings are critical to plant operation in both HWC and NWC plants.

The advantage of optical technology in NPP water chemistries is that optical sensors are unaffected by high levels of hydrogen in the measurement sample; when measuring low levels of oxygen, this is a critical feature.

Table 1 compares tests of the Orbisphere K1200 optical sensor, a derivative of the K1100 for radioactive applications, to values measured by an amperometric sensor without any hydrogen compensation features in primary cycle PWR water by an independent testing group [9]. A hydrogen pressure of ~2.3bar was set with dissolved hydrogen concentrations of 3.36ppm. Values illustrated show a mean result over 5 measurement points and 4 measurement cycles. This comparison shows the negative offset experienced by amperometric sensors in the presence of hydrogen while the Orbisphere K1200 optical sensor remains unaffected by high levels of dissolved hydrogen.

	Dissolved Oxygen Readings (ppb)	
	Amperometric Sensor	K1100 Optical Sensor
Cycle 1	-3.2	1
Cycle 2	-3.2	0.2
Cycle 3	-3.5	0.3
Cycle 4	-3.5	0.9

Table 1: Comparison of the Orbisphere K1200 optical sensor and an amperometric sensor in PWR primary conditions

System Performance Under the Influence of Flow Variations

Within any power plant, the performance of any sampling system plays a role in the accuracy of most analytical systems. When flow is reduced below recommended levels, this can impact the accuracy of the measurement systems. Figure 2 shows how the performance of the Orbisphere K1100 optical sensor is independent of flow when compared with an amperometric sensor.

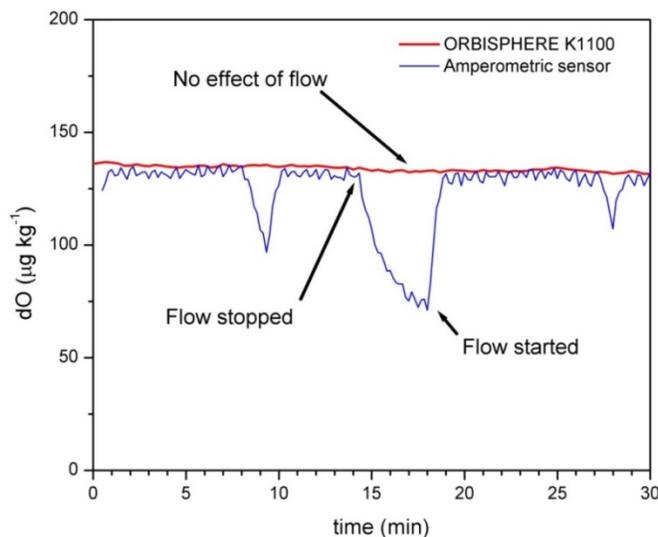


Figure 2: Comparison of an amperometric sensor with the Orbisphere K1100 experiencing variations in flow.

The optical system requires only enough flow to provide a fresh sample, while amperometric sensors have a range and minimal flow levels below which measurement errors could be encountered. For example, a flow rate that is 30% lower than a recommended minimum would likely result in an error of up to 10%.

Summary

The measurement and control of the dissolved oxygen at fossil and nuclear power plants has never been as critical as it is today. While the number of qualified service engineers has been continually reduced and continues to be reduced further, at the same time, the economic pressure on plant operators to keep the capital equipment in operation for as long as possible grows. As a result, the labor time available to the personnel for servicing the measurement technology becomes an increasingly critical factor.

With respect to its stability, the K1100 optical sensor has proven that it far exceeds the amperometric sensors with a calibration interval of 12 months without an interim intervention. Power-plant-typical flow fluctuations have no negative influence on the accuracy of optical oxygen measurements. This is a decisive advantage, as conventional amperometric sensors often tend toward results that are too low due to their attrition measurement in the case of flow fluctuations. This occurs in particular at very low flow speeds. In addition, the optical K1100 sensor did not show any cross-sensitivity in the presence of hydrogen.

The response time of the K1100, following successful calibration and return to operation upon reaching an oxygen concentration of 4ppb, was approximately 79% faster than that of the fastest amperometric sensor. The calibration and maintenance effort is lower by up to 95%.

In general, the K1100 offers all users cost-efficient and exact oxygen measurements. With a proven repeatability of ± 0.1 ppb and the possibility of measuring for a time period of 12 months without additional service intervals, calibration or personnel intervention, the K1100 LDO sets new standards in oxygen measurements within power plants.

References

- ¹Dooley, B., Shields, K.; Cycle Chemistry for Conventional Fossil Plants and Combined Cycle/HRSGs - PPChem 2004, 6(3).
- ²McInnes, D.; Stator Cooling Water Deoxygenation Control at Tarong Power Station - PPChem 2006, 8(5)
- ³Smith, Rebecca. ; Turmoil in Power Sector – Wall Street Journal – Politics, 14.01.10.
- ⁴Hach Company ; Case History: Bristol-Myers Squibb/Hach Process Luminescence DO - S-P250, 07/2004.
- ⁵Dooley, B., Shields, K. ; Cycle Chemistry for Conventional Fossil Plants and Combined Cycle/HRSGs - PPChem 2004, 6(3).
- ⁶ABB Limited ; Low and High Level Dissolved Oxygen Monitor, Model 9437 - SS/9437_7, 11/2006.
- ⁷Waltron LLC ; Dissolved Oxygen Analyzer: Aqualyzer® 9062 - 05/2009.
- ⁸Hach Company ; Orbisphere 512 Oxygen-Hydrogen Controller - 2009.
- ⁹Auener, C. ; Serco TAS Orbisphere Trial - 07/2009.

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