Luminescent Oxygen Sensor to Monitor Power Plant Water and Steam Cycles

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ABSTRACT

The majority of existing dissolved oxygen analyzers use polarographic sensors. These are well recognized for their accuracy and reliability, but maintenance complexity and frequency, as well as flow dependence and calibration needs are among the issues encountered by users. A new oxygen sensor has been developed based on luminescent technology. The main advantages of luminescent technology over electrochemical cells are the operator independence of the calibration, the low flow requirement, the absence of flow dependence, and of course the drastic reduction of the maintenance activities. The application of luminescent technology to accurately measure low ppb oxygen concentrations is demonstrated based on laboratory and field experience in both all-volatile treatment (AVT) and oxygenated treatment (OT) environments.

INTRODUCTION

Dissolved oxygen is recognized as being a key parameter to be monitored in the power plant cycle chemistry by most of the guidelines including EPRI, VGB, and more recently by the European Guideline EN12952-12:2003. Common chemistry types requiring tight oxygen control include reducing all-volatile treatment (AVT(R)), oxidizing all-volatile treatment (AVT(O)), and oxygenated treatment (OT) [1–3]. OT chemistry is gaining in popularity as it prevents flow accelerated corrosion (FAC) and the iron content in the feedwater is typically as low as 0.5 µg · kg⁻¹. EPRI benchmarking shows that the most reliable and best performing units in the world operate on OT or AVT(O) [1]. In presence of oxygen, the pores in the magnetite protective layer are blocked with low-solubility ferric oxide hydrate (FeOOH) and/or ferric oxide (Fe₂O₃, hematite). Hematite also covers the magnetite layer. In this way, the lowest possible iron concentration in the feedwater is reached. Typical oxygen levels in the feedwater are ≤ 5 µg · kg⁻¹ for AVT(R) in units with mixed metallurgy, 1–10 µg · kg⁻¹ for AVT(R) in units with all-ferrous metallurgy, < 10 µg · kg⁻¹ in units operated on AVT(O), and 30 to 150 µg · kg⁻¹ for OT chemistry.

Choosing the most adapted chemistry and knowing what the expected oxygen levels are is the first challenge. The second challenge is to monitor the dissolved oxygen and maintain the oxygen analysers. In a recent paper E. Maughan described the common problems with existing on-line instrumentation and key criteria to be considered to improve these [4]. Of course reliability, accuracy and minimum maintenance are reported among the most important features, but flow dependence and calibration are also identified as sources of problems related to on-line analysis and oxygen measurement in particular. An additional in depth study focuses on dissolved oxygen measurement and clearly highlights the limitations and problems of currently used electro-chemical (EC) sensors [5]. Despite their recognized reliability and accuracy the available membrane covered electro-chemical cells have some drawbacks.

The Clark cell requires regular maintenance due to the consumption of the electrolyte which enters in the oxidation-reduction reaction and the coating of the anode by the by-products of the reaction (silver halides). For all EC cells the use of chemicals or at least of caustic electrolyte is necessary in the maintenance procedure. In general the exposure of EC sensors to high oxygen levels reduces the maintenance interval. Next to the fragility of the membrane itself, temperature and pressure changes can affect the thickness of the electrolyte layer between the membrane and the cathode and therefore affect the accuracy of the measurement over time. The flow is critical to maintain an accurate oxygen reading with an EC sensor. A minimum flow is required to reach a steady-state diffusion controlled electro-chemical reaction in the cell (typically around 200 ml · min⁻¹). Below this flow rate, the measurement is drastically influenced by the flow. Depending on the construction of the sensor and its flow cell, very high flow can also affect the measurement through a mechanical effect on the membrane and the electrolyte thickness over the cathode.

In the range of interest for power plant chemists (0 µg · kg⁻¹ to about 8 000 µg · kg⁻¹ in air) EC sensors have a linear response to oxygen concentration. Even though no oxygen means no chemical reaction and no signal, most of the sensors require a regular calibration of the zero due to either sensor or electronics drift. The slope can be calibrated using a sample of known concentration, the most accurate and simple sample being air. In most cases zero or air calibration require the sensor to be taken out of the
cell and exposed to the calibration sample. The slope calibration can be automatically performed using a Faraday cell which produces oxygen by means of water electrolysis. This method relies on external influences: the accuracy of the water flow during the electrolysis process, a constant sample concentration during the procedure, and the presence of oxygen scavengers which can react with the produced oxygen if a single addition of oxygen is performed. Another commonly used automatic procedure is to drain the flow cell and expose the sensor to air, unfortunately the presence of micro drops of water on the membrane can lead to a completely wrong calibration.

Is oxygen monitoring using luminescent technology, a solution? Many substances can be quantitatively analyzed optically by measuring induced color changes on a specific indicator. A well known application is the simple, single-use pH strip where a cellulose paper is soaked with an acid-base dye. As indicators exist for numerous species, many applications of optical chemical and biochemical sensors have been published in the literature [6,7].

The challenge was to apply this new technology to measure oxygen in the range of interest for power plant chemists. This paper describes how luminescent technology works, how it can be used to monitor low levels of oxygen and the advantages it brings that overcome some of the drawbacks of EC sensors.

**GENERAL PRINCIPLE OF OPERATION**

Optical sensing of oxygen originates from the work of Kautsky [8] in 1939 where he demonstrated that oxygen can dynamically quench the fluorescence of an indicator (decrease the quantum yield). This principle has been reported in various fields of application such as monitoring aquatic biology in waste water [9], tests for blood gas analysis [10] and cell culture monitoring [11-12]. The method is now recognized by ASTM [13] for the measurement of oxygen in water. Compared to classical oxygen detection using electrochemical sensors, luminescent technology offers several advantages such as no oxygen consumption, independence from sample flow velocity, no electrolyte and low maintenance.

Optical sensing of oxygen is based on the measurement of the red fluorescence of a dye/indicator illuminated with a blue light as shown in Figure 1.

The dye fluorescence is quenched by the presence of oxygen. The oxygen concentration can be calculated by

![Figure 1: Principle of optical oxygen detection using fluorescent dye.](image1)

![Figure 2: a) Fluorescence intensity decay time as a function of oxygen concentration; b) Phase-shift of modulated signals.](image2)
measuring the decay time of the fluorescence intensity as shown by Figure 2a. The higher the oxygen concentration is, the shorter the decay time will be. By modulating the excitation, the decay time is transformed into a phase-shift of the modulated fluorescence signal, which is independent of fluorescent intensity and thus of potential aging (Figure 2b).

The oxygen partial pressure \( pO_2 \) is then linked to the corresponding phase-shift measurement \( \Phi \) to build the sensor calibration curve (Figure 3). This curve is described by the Stern-Volmer equation, Eq. (1), where \( K_{sv} \) is the indicator quenching constant (in mbar\(^{-1}\)) representing the quenching efficiency of the oxygen and thus the sensor sensitivity, \( f_0 \) is a constant and \( \Phi_0 \) is the phase-shift at zero oxygen representing the unquenched fluorescence decay time of the dye. The calibration curve thus relies on two parameters: the phase-shift at zero oxygen and the luminescent spot sensitivity, \( K_{sv} \). The dissolved oxygen concentration is then calculated with Henry’s law using the water solubility curve as a function of the temperature.

\[
pO_2 = \frac{(\Phi_0 - \Phi)}{K_{sv} \left( \Phi - \Phi_0(1 - f_0) \right)}
\]  

\( pO_2 \) = RESOLUTION OPTICAL SENSOR TO MONITOR DISSOLVED OXYGEN

System Description

The measuring system consists of four key components. First, a specific sensitive luminescent spot has been developed to reach ppb resolution (Figure 4). This exchangeable spot is fixed on an optical fiber probe connected to the measuring electronics. In the instrument, a high resolution digital phase meter is integrated together with the optoelectronics component (excitation light and light detection device). Finally, a flow chamber equipped with a solenoid valve is connected to the sample line. The role of the solenoid valve is to switch from the measurement sample to the calibration sample at user programmable intervals to either verify or calibrate the system. The calibration procedure is therefore completely automatic and operator independent.

Installation and Maintenance Requirements

As for any other oxygen analyser, great attention must be paid to avoid oxygen intake in the sample line between the process and the analyser. Once connected to the line a first manual calibration is advised before setting-up the automatic calibration. In contrast to EC sensors, no cleaning of the sensor is necessary and no time is wasted to wait for the polarisation of the sensor; the luminescent sensor is ready to measure immediately. This luminescent technology requires no chemical reaction, no membrane, therefore the maintenance interval is not influenced by the oxygen level in the sample. The active spot is expected to

![Figure 3: Stern-Volmer calibration curve.](image)

![Figure 4: Luminescent sensor (left), mounted in the flow chamber (right).](image)
need replacement every 18 months. Therefore the only regular maintenance activity is the annual replacement of the active spot and its o-ring, this simple operation takes no more than 2 minutes.

Calibration Procedure

Calibration of optical oxygen sensors usually requires 2 parameters; the phase-shift \( \Phi_{0} \) at dissolved oxygen, dO = 0 µg · kg\(^{-1}\), and the luminescent spot sensitivity, \( K_{sv} \) [mbar\(^{-1}\)]. The reproducibility of the luminescent spots relies on a carefully designed manufacturing process. In addition statistical tests have shown that the stability over time of the luminescent spot was such that the \( K_{sv} \) parameter would not vary and can be factory calibrated. Consequently, the sensor only needs an adjustment of the phase-shift (\( \Phi_{0} \)) at zero oxygen. This is achieved by exposing the luminescent spot to pure nitrogen. The software verifies that the phase-shift is within a satisfactory range and most important that the standard deviation over 30 measurement points is inferior to 1 µg · kg\(^{-1}\), this is usually achieved in less than 8 min. Another big advantage of the gas phase calibration is the possibility to use certified and traceable gas standards. Accumulated experience in laboratory and field tests shows the need for a calibration every 3 months in the range from 0 to 600 µg · kg\(^{-1}\). A standard calibration gas bottle (1 L, 34 bar) allows a monthly calibration during its validity period of 3 years.

Accuracy Comparison between Optical and EC Sensors

Extensive laboratory tests were performed to verify the accuracy and reproducibility of the optical sensors. Three luminescent sensors were calibrated using the above procedure and a reference EC sensor (Orbisphere) was air calibrated. All sensors were then exposed to variable oxygen concentrations and temperature conditions. Figure 5 shows a comparison between the optical sensors and one EC sensor over a dO range from 0 to 600 µg · kg\(^{-1}\) and temperatures from 18 °C to 34 °C. Within the entire sample temperature range of the experiment depicted in Figure 5, all sensors exhibit an accuracy of \( \pm 2 \) µg · kg\(^{-1}\) + 2.5 %.

Monitoring an OT Chemistry

\( \text{Figure 6} \) shows a record of a power OT process over 10 days with one point collected every 0.5 h. Note that with such a gap between two data points the observed noise originates from the process. It can be seen that at the beginning of day 5, the average concentration increases up to about 140 µg · kg\(^{-1}\). One might first question the reliability and accuracy of the oxygen analyser. In this case an automatic calibration was scheduled in the afternoon of day 5. After the calibration the signal went back to values around 140 µg · kg\(^{-1}\) confirming the validity of the observed trend.

Monitoring an AVT Chemistry

In order to verify the limits of the luminescent sensor and to evaluate its capacity to track process changes at low oxygen concentrations, we have used a luminescent system to monitor an AVT chemistry (\( \text{Figure 7} \)). While it is agreed that the \( \pm 2 \) µg · kg\(^{-1}\) accuracy as measured in the laboratory is not good enough to determine if the water contains 6 µg · kg\(^{-1}\) or 8 µg · kg\(^{-1}\), the luminescent sensor (in red) could perfectly follow all concentration and temperature changes and can be efficiently used to confirm that the oxygen level is below 10 µg · kg\(^{-1}\) rather than above 15 µg · kg\(^{-1}\). Figure 7 shows the capacity of the luminescent sensor to monitor the difference between full-load day times (dO around 8 µg · kg\(^{-1}\)) and night times (dO = 30–40 µg · kg\(^{-1}\)). Note that the period between day 2 and 4 corresponds to a weekend. Similar results were obtained on another unit working shifts where the sample regularly reached > 4 000 µg · kg\(^{-1}\) of oxygen during shutdowns. Thanks to its intrinsic response time < 1 minute, the luminescent sensor could accurately follow the changes from full load day times to night times as well as the shutdown and startup periods.

CONCLUSION

The use of luminescent technology brings significant improvements in terms of frequency and complexity of maintenance compared with other technologies. Furthermore no particular attention has to be paid to the sample flow, and abnormally high oxygen levels have no influence on the maintenance frequency. The simplification of the maintenance and sensor preparation combined with the automation of the single point calibration renders the accuracy of the system literally operator independent.

Whereas the Clark cell is probably still the best choice for nuclear applications and process monitoring requiring high accuracy at low level, luminescent technology appears as the best solution for OT process monitoring and a very good compromise of accuracy, reliability, and maintenance requirements for plants running AVT and working shifts with frequent contact with high oxygen containing samples.

REFERENCES

Figure 5:
Laboratory comparison between three optical sensors and an EC sensor.

Figure 6:
Monitoring of dO level in OT process.

Figure 7:
Monitoring of dO level in AVT process over 10 days, comparison between an EC sensor and an optical sensor.
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