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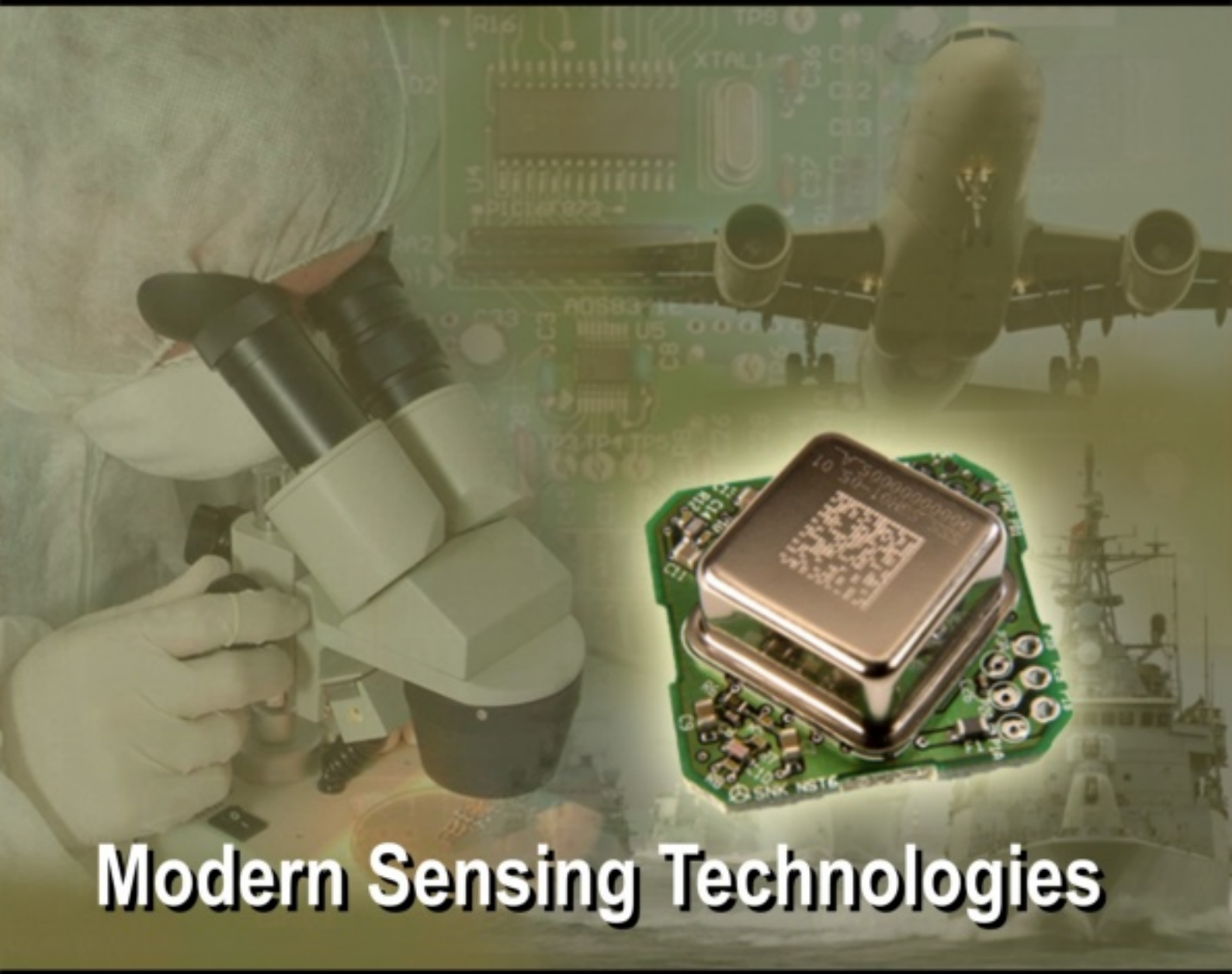

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Zirconia Oxygen Sensor for the Process Application: State-of-the-Art

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Abstract: Zirconia oxygen gas sensors are being used in increasing numbers in industrial process applications, e.g., in power industry, refining/petrochemical, kilns. Different aspects of industrial zirconia oxygen sensors especially application limits and stability are discussed in details. Special consideration is given to practical aspects of the oxygen sensor design and operation. *Copyright © 2008 IFSA.*

Keywords: High temperature sensor, Zirconia, Oxygen sensor

1. Introduction

Gas analysis with electrochemical sensors is becoming increasingly important in many fields with applications to power consumption, raw materials saving, industrial process yield improvements and pollution control [1]. Various types of solid state sensors have been initially developed for the combustion efficiency control in the automotive industry. More recently these technologies originally devised for automotive combustion have been adapted to industrial furnaces, boilers and gas turbines [2].

Zirconia oxygen sensor widely used today in different industrial applications and transportation, i.e., well known lambda sensor was first introduced in 1961 by Peters and Möbius [3] and Weissbart and Ruka (Westinghouse) [4]. One of the first zirconia oxygen sensor applications was launched in the early 1970's in steel processing control by disposable zirconia sensor analyzing oxygen in molten iron [5]. The first industrial zirconia oxygen sensor for the process gas application was developed by

Westinghouse Electric Co. and was based on robust platinum electrode and zirconia solid electrolyte technologies developed in 60th for solid oxide fuel cells (SOFC). The dominant application for the zirconia oxygen gas sensors was and still is in the internal automotive combustion engine for the controlling air/fuel ratio [6-8]. When air and gasoline are mixed together and ignited, the chemical reaction requires a certain amount of air to complete combustion. The amount of oxygen in the exhaust following combustion is a good indicator of the relative richness or leanness of the fuel mixture. Zirconia oxygen sensor or more often called lambda (λ)-sensor has been used to monitor oxygen concentration in the automotive exhaust since 70th. Influenced by common spark plug design the first zirconia sensor body was in a conical thimble shape in unheated lambda sensor (LS) introduced by Bosch in 1976 for feedback fuel control on automotive engines. Unheated zirconia O_2 sensor was only relying on the heat of the exhaust gases to reach the operating temperature of 600…900°C. The next thimble-type lambda sensor (LSH) generation was introduced by Bosch in 1982 with internal heater helping to reduce cold start emissions following by heated planar-type lambda sensor (LSF) in 1997. LSF sensor element was with platinum electrodes, zirconia solid electrolyte, insulation and heater laminated together on a single strip. The latest lambda O_2 sensor technology was based on planar design with added ability to measure the air/fuel ratio directly. Instead of switching back and forth like all previous lambda sensor designs, the new wide-band (WB) O_2 sensor produces a signal that is directly proportional to the air/fuel ratio. Like a zirconia thimble or planar-type sensor, the WB lambda sensor produces a low-voltage signal when the air/fuel ratio goes lean, and a high-voltage signal when the mixture is rich (lambda signal). But instead of switching abruptly, it produces a gradual change in the voltage that increases or decreases in proportion to the relative richness or leanness of the air/fuel ratio. At perfectly balanced air/fuel ratio 14.7:1, a wide-band zirconia O_2 sensor will produce a steady 450 mV. If the mixture goes a little richer or a little leaner, the sensor's output voltage will be only a little bit changed instead of rising or dropping dramatically. Another difference in the wide-band O_2 sensor is the heater circuit. Like a planar sensor, it is printed on the ceramic strip but the heater circuit is pulse-width modulated to maintain a consistent operating temperature of 700…800°C. The Bosch WB lambda sensor, e.g., LSU 4.9 has a response time less than 0.1 seconds to the air/fuel mixture changes, and reaches the operating temperature of 800°C within 20 seconds using its internal heater. For the precision, the integral part of WB lambda sensor oxygen pump pulls some oxygen from the exhaust into a "diffusion" gap between the two electrochemical cells. The Nernstian cell and oxygen pump are wired together in such a way that it takes a certain amount of current to maintain a fixed oxygen level in the diffusion gap. The amount of current required to maintain this balance is directly proportional to the oxygen concentration in the exhaust. This gives the engine computer the precise air/fuel measurements to meet the new emission requirements.

Another important lambda sensor development milestone was the introduction of platinum cermet electrode co-firing techniques and the so-called engobe technique for a porous protection film combined with a plasma sprayed spinel layer to form a double protection layer system [9]. Unfortunately advanced and highly reliable for automotive emission control lambda sensors are very difficult to adapt to in-situ industrial process application because of more severe process environment and sensor packaging materials issues.

2. Theoretical Background

All industrial zirconia oxygen sensors are based on an electrochemical cell with zirconia solid electrolyte (mostly yttrium stabilized zirconia, YSZ) and two platinum electrodes printed and sintered on the opposite sides of zirconia ceramics and exposed to the process and reference gases:

$$O_2(p_{O_2}, ref), Pt \mid Zirconia \mid Pt, O_2(p_{O_2}, process) \quad (1)$$

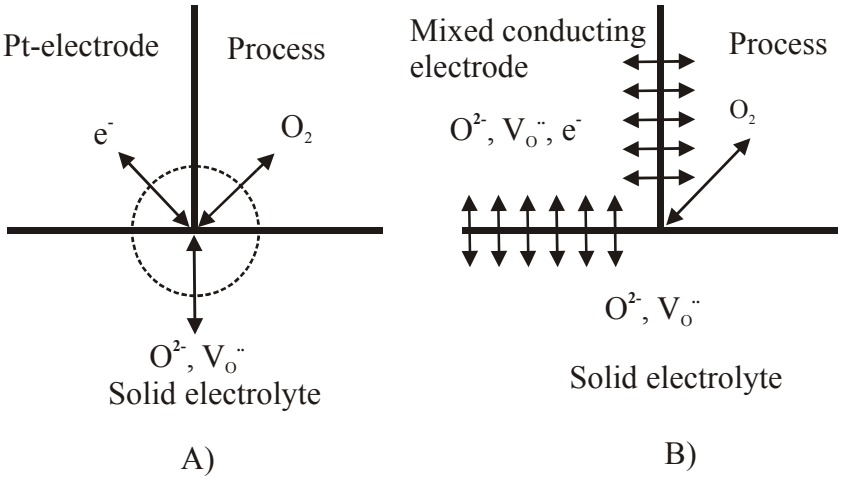
The process side is gas tight separated from the reference side using high temperature sealing and/or spacing by zirconia ceramics shape. Differential oxygen chemical potentials on the oxygen cell electrodes develop e.m.f., E, according to the Nernstian equation:

$$E = C + \frac{RT}{4F} \ln \frac{p(O_2)_{process}}{p(O_2)_{ref}} = C_1 + \frac{RT}{4F} \ln p(O_2)_{process} \quad (2)$$

with C_1= C-(RT/4F)*ln $p(O_2)_{ref}$.

C is a constant related to the thermal junctions in the probe and reference/process sides temperature and pressure mismatch. R is universal gas constant, T the process temperature in °K and F the Faraday number.

The oxygen reaction is taking place on the triple phase boundary (TPB: electrode, electrolyte, and gas) where oxygen molecules, O_2; electrons, e' ; and oxygen vacancies, $V_O^{\cdot\cdot}$; are available (Fig. 1A) and includes molecular oxygen absorption, dissociation on the electrolyte/electrode surface and final diffusion to TPB where oxygen electrochemical reaction will take place. By using mixed ionic-electronic conductive electrode or cermet electrode with electronic and ionic conductors, e.g., Pt-Zirconia, oxygen electrochemical reaction will take place in the electrode bulk and highly improve oxygen sensor performance (Fig. 1B).



$$O_2(gas) \leftrightarrow O_2(Electrolyte/Electrode)$$
$$O_2(Electrolyte/Electrode) \leftrightarrow 2O(Electrolyte/Electrode)$$
$$2O(Electrolyte/Electrode) \leftrightarrow 2O(Electrolyte/Electrode/Gas)$$
$$2O(TPB) + 4e'(Electrode) + 2V_O^{\cdot\cdot}(Electrolyte) \leftrightarrow O_O(Electrolyte)$$

Fig. 1. Oxygen sensor electrochemical reaction.

Using fixed oxygen partial pressure on the reference electrode, e.g., air with $p(O_2)$= 0.21 bar, the signal of the thermally balanced oxygen sensor will depend only on the process and/or sensor heater temperature (Fig. 2).

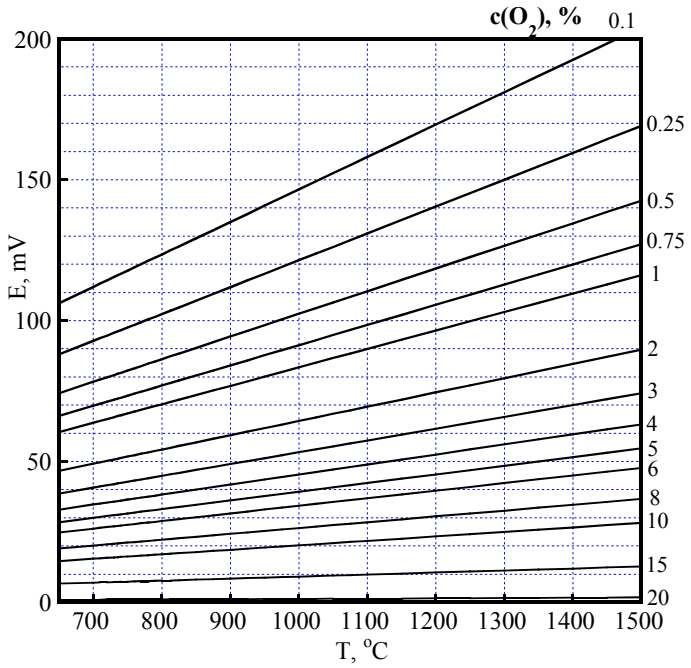


Fig. 2. Industrial zirconia oxygen sensor: temperature/concentration diagram.

Industrial zirconia oxygen sensors start to operate at elevated temperatures (>300°C) with oxide ion migration in zirconia ceramics establishing oxygen equilibrium at the process and reference electrode and zirconia electrolyte interfaces. Higher application temperature will favour sensor performance but also will highly limiting zirconia oxygen sensor packaging materials. Most industrial zirconia oxygen sensors operate at elevated temperatures around 700-800°C.

3. Oxygen Sensor Design

The industrial zirconia oxygen sensor design is based on closed end zirconia tube or disk tight sealed in supporting alumina or metallic tube (Fig. 3).

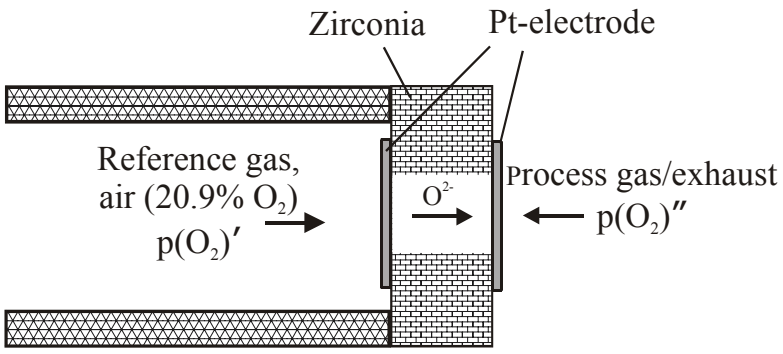


Fig. 3. Zirconia oxygen cell diagram.

Zirconia tube or "thimble" style industrial designs (Fig. 4: example ABB and Yokogawa oxygen cells) provide good performance but can be less robust because of the more complicated ceramic shape with

flange and thermal stresses across the tube. Thermal balance throughout the electrochemically active area of the zirconia cell is also not optimal.

Fig. 4. Design of industrial zirconia oxygen cells.

Disk-shape zirconia ceramics brazed into E-Brite supporting tube (Fig. 4, Rosemount) offer an advantage of much less temperature differential across the reference/process sides and reduced thermal stresses on the zirconia ceramics because of close match of thermal expansion coefficients. A special highly porous Pt-zirconia cermet electrode (Fig. 5) was developed to open TPB interface for the oxygen reaction and to improve oxygen sensor response and life time.

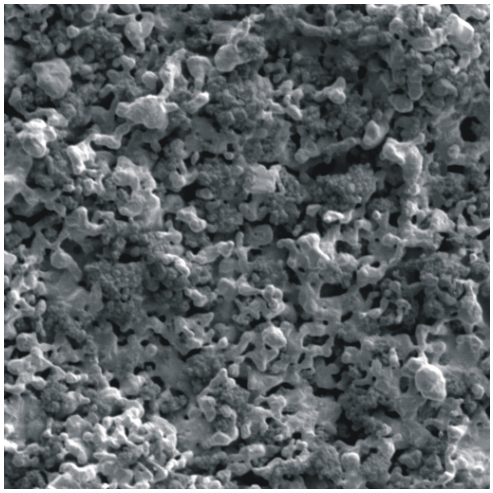


Fig. 5. SEM image of Pt-cermet process electrode.

The most preferable application of the industrial oxygen sensor would be in-situ application close to the process to measure with the presence of extreme temperatures and hazardous chemicals. Industrial zirconia oxygen probes are designed to survive in such environment for years (Figs. 6-7).

Fig. 6. ZR202G Oxygen Analyzer (Yokogawa).

Fig. 7. X-STREAM O_2 Analyzer (Rosemount Analytical).

Special protective shield, internal calibration line and reference gas line are made from special alloys like Inconel, Hastelloy or stainless steel SS 316L with excellent oxidation/corrosion resistance in severe high temperature process environment (Fig. 8).

Fig. 8. X-STREAM O_2 probe sensor assembly.

A special oxygen cell with improved thermal balance and ceramic or metallic diffusers for the high particulate applications are common options to improve Oxygen Analyzer performance (Fig. 9).

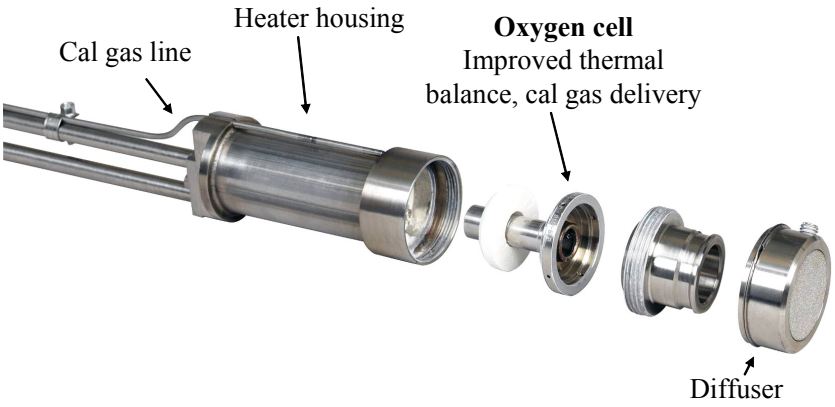


Fig. 9. X-STREAM O_2 cell assembly.

4. Combustion Process Monitoring and Control with Zirconia Oxygen Analyzers

Industrial zirconia oxygen analyzers are used for combustion monitoring and control in a wide variety of applications ranging from energy-consuming industries, such as iron and steel, electric power, oil and petrochemical, ceramics, pulp and paper, food, and textiles, to various combustion facilities, e.g., boilers or incinerators. To have perfect combustion, CO_2 should be maximized and O_2 concentration should be close to zero in the flue gas stream (Fig. 10).

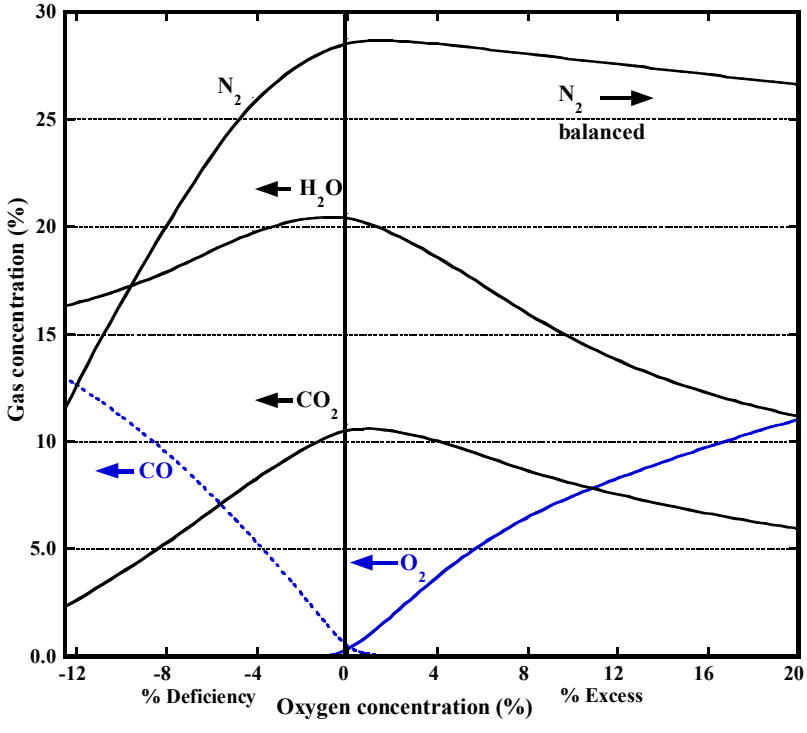


Fig. 10. Combustion gas composition diagram.

In perfect combustion, the oxygen and fuel combine in an ideal ratio producing primarily carbon dioxide, CO_2 and water, H_2O with traces of other gases like sulfur dioxide, SO_2 and nitrogen oxides, NO_x coming from fuel impurities and nitrogen oxidation (from air). This stiochiometric point with the highest efficiency and the lowest emissions will be never achieved in the real combustion because of

the not perfect fuel/air uniformity and of the fuel energy density and fuel/air flow variation. Oxidizing combustion will cause the heat loss and excessive nitrogen oxides pollution production and reducing combustion will produce a sooty emission as unburned fuel goes up the stacks will lead to a greatly reduced combustion burner life span. Since perfect combustion is not practically possible due to incomplete mixing of the fuel and air, most combustion equipment is set up to have a small percentage of oxygen excess. Typical flue gas oxygen excess concentration is ~2…3% for gas burners and ~2…6% for boilers and oil burners. The lower the flue gas temperature the higher would be the combustion efficiency (Fig. 11).

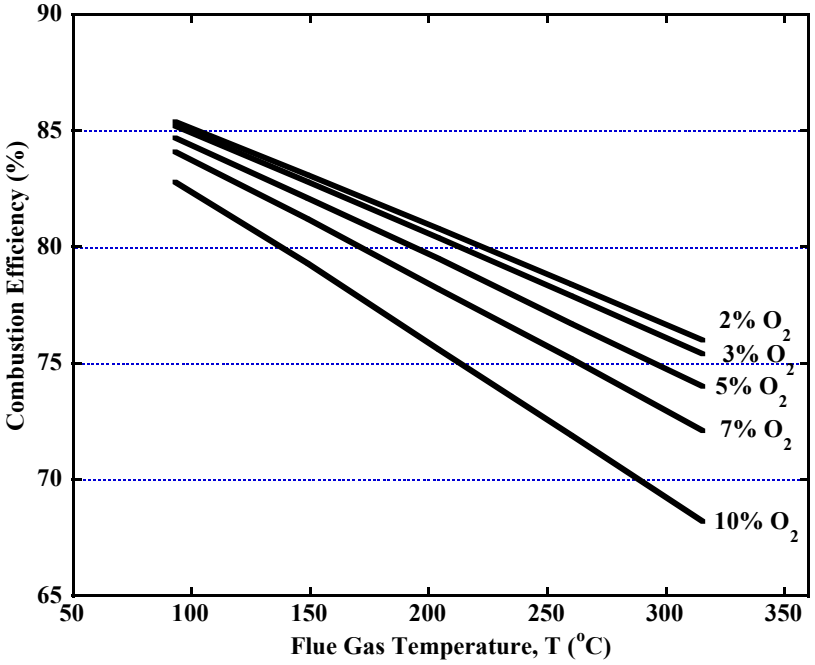


Fig. 11. Combustion efficiency dependence on the oxygen excess and flue gas temperature.

Combustion would be the most efficient between 0.75% and 2% excess oxygen. For every 1% oxygen excess reduction in combustion process depending on the process and flue gas temperature ~1-3% of fuel could be saved.

Unlike gas or oil combustion burners process flue gases from coal fired boilers contain a large quantity of dust, e.g., flying ash, sulfur and sulfur dioxide, SO_2 making in-situ O_2/CO measurements more reliable option compare to extractive system complicated by pluggage and condensation issues.

A typical oxygen control mode in coal fired Power Plant boiler is presented in Fig. 12.

While good combustion control can be accomplished with oxygen measurement alone, combustion efficiency and stability can be improved with the concurrent measurement of carbon monoxide, CO. Operation at near trace CO levels of about 100 ppm and a slight amount of excess air indicates conditions near the stoichiometric point with the highest efficiency. An example of the averaging O_2/CO concentration measurements in coal fired Power Plant boiler could be seen in Fig. 13.

Oxygen and carbon monoxide monitoring and combustion control using zirconia analyzers will also contribute to the lower nitrogen oxides, NO_x and sulfur dioxide, SO_2 emissions by allowing more complete combustion very close to the stoichiometric point using the most efficient range of 1…2 % oxygen excess.

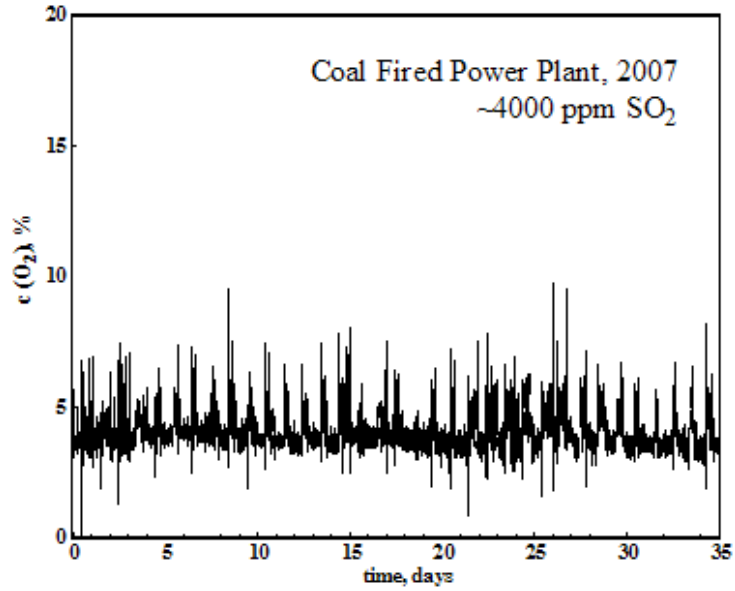


Fig. 12. Oxygen monitoring in the combustion process using X-STREAM O_2 probe.

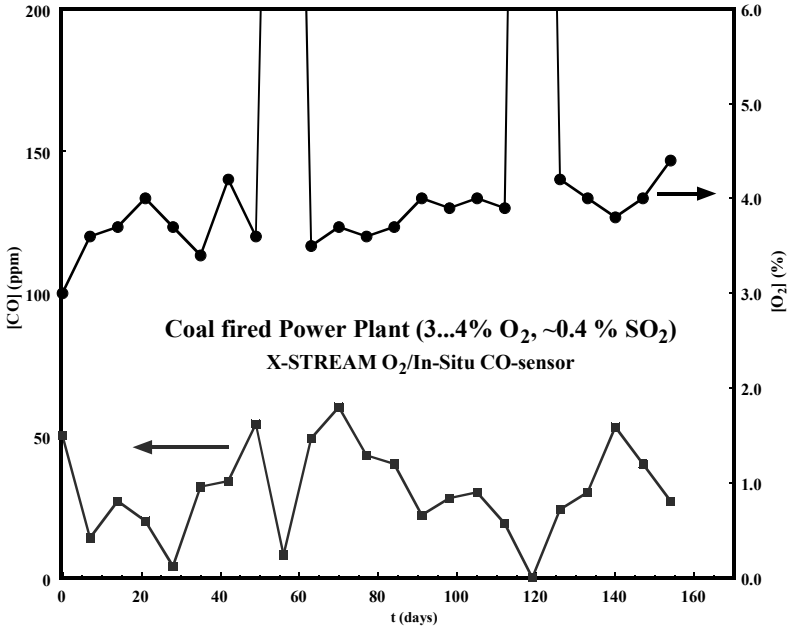


Fig. 13. O_2/CO monitoring in combustion process.

Because of the combustion process temperature variation oxygen analyzer will also see significant temperature rising and dropping during the process monitoring and control. To provide oxygen sensor reliable accuracy and signal stability in the process changing environment (especially temperature) zirconia oxygen analyzer should be thermally balanced to eliminate effect of the thermal junction points contributing to the oxygen sensor signal (up to 10 mV for some oxygen analyzers on the market) and compromising oxygen measurements, e.g., 3±1 % O_2.

Process temperature variation will have very little effect on the slope and constant of the new Rosemount Analytical X-STREAM O_2 Analyzer [10]. Error introduced by the process temperature variation between 25 and 600°C will be less than ±0.025 % O_2 (Fig. 14). This new industrial Oxygen Analyzer will provide stable and accurate oxygen measurements in a wide oxygen concentration range

except measurements in an air where slightly more significant error will be introduced by the moisture variation in air affecting oxygen partial pressure and sensor signal logarithmical dependence on the concentration (Fig. 15).

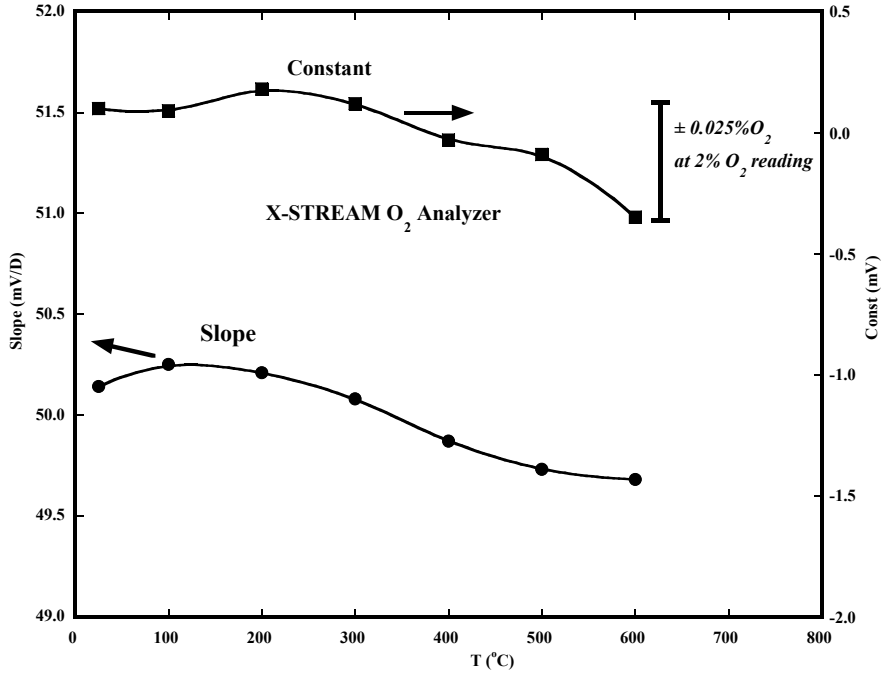


Fig. 14. Industrial oxygen sensor slope and constant dependence on the process temperature.

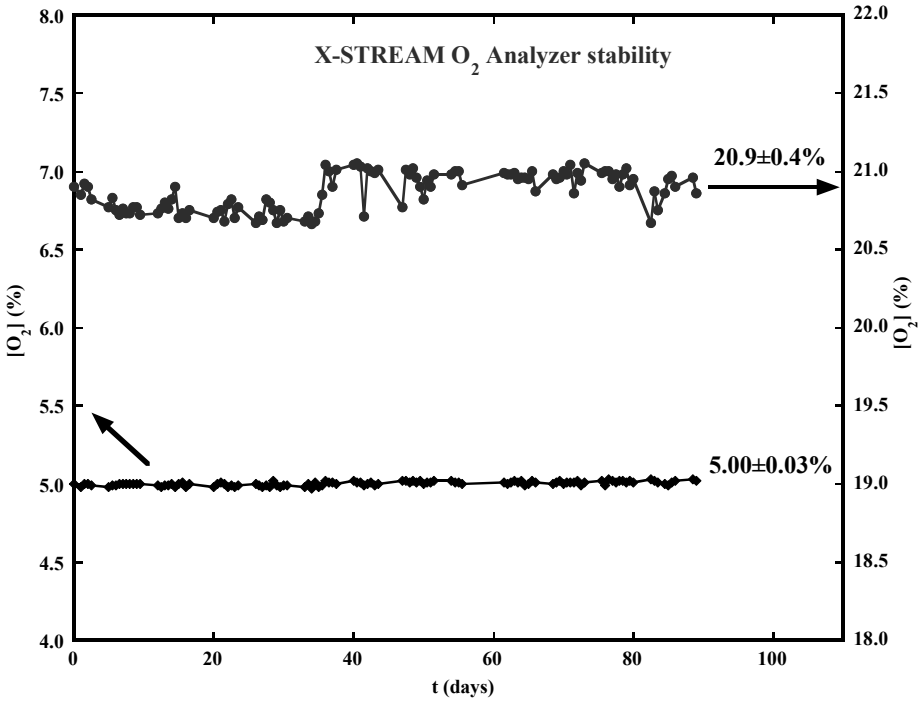


Fig. 15. Industrial zirconia oxygen sensor stability and accuracy.

Modern combustion application can be improved with real-time control. Control of combustion process could be divided in two categories: Operating Point Control (OPC) and Active Combustion Control (ACC). In active combustion control the controller output is used to modulate the flow

properties, e.g., fuel flow rate modulation. ACC has been achieved in many cases with variable degree of success in laminar flame burners and turbulent combustors. Lean premixed combustion is one of the effective approaches reducing NO_x emissions because of the lower flame temperature. Unfortunately, this approach has two major drawbacks: blowout and instability control [2]. To meet the requirements of the active combustion control strategy, the sensor system must be able to determine the states of the combustion system rapidly and accurately. Combustion instabilities usually occur with frequencies less than 500 Hz, a kHz real-time sensor response is required to provide an effective feedback control signal.

In operating point control (OPC) the fuel injection is regulated in order to maintain certain flame parameters. Unfortunately the air quantity flowing in the combustor is not known with sufficient accuracy and OPC was based on limited information of actual flame properties and estimated air mass flux. A precise adjustment of the fuel/air ratio is based on oxygen concentration measurements in flue gas using zirconia oxygen sensor signal.

More details on zirconia oxygen sensor materials, sensor performance and sensor application limits in different environment can be found in reviews and just published book [11-15].

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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