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In situ Measurements of O_2 and CO in Cement Kilns

O. Driesner[1], F. Gumprecht[1], Ulrich Guth[2]
[1] ENOTEC GmbH, Höhere Birken 6, 51709 Marienheide, Germany
[2] Technische Universität Dresden, 01062 Dresden, Germany
olga.driesner@enotec.de

Abstract

The in situ measurements of O_2 and CO simultaneously in cement kilns is a great challenge due to the high temperature of the process and the dust load. A probe is developed for this purpose consisting of a water cooled tube in which are located the solid electrolyte oxygen sensor and a CO mixed potential sensor. In order to prevent the deposition and sintering of raw material the probe rotates 90 ° in certain intervals. Beside coal, gas or oil also municipal waste is used as a fuel. Due to the varying fuel, the demand of oxygen is also changing. The combustion air supply has to adapt very fast in such a way that a minimum in CO concentration is reached and simultaneously the NOx emission can be limited. This was demonstrated by a CEMTEC® probe over years.

Key words: In situ measurement, O_2, CO gas sensors, solid electrolyte, cement kiln

Introduction

The control of the combustion in cement kiln is an enormous challenge because real time data on the gas concentration of O_2 and CO are necessary. In typical cement kilns different fuels with different caloric values are used. Mostly the main kiln burner fuel is coal, gas or oil. Beside these domestic and industrial waste consisting of variety of materials is burnt. The combustion should be at a minimum excess of oxygen and a minimum of CO as well. For this purpose only solid electrolyte sensors are suited which are stable enough to withstand the harsh condition respecting temperature, flue gas composition and high dust load. Solid electrolyte sensors exhibit a fast response in milli-seconds. Hence a direct probe cannot be inserted into the rotary kiln. In order to measure under these circumstances a water cooled probe was developed that can be installed near as possible in the process close to the burner. Usually oxygen sensors based on Nernst' concentration cell are utilized. While the application of oxygen sensors is state of the art, CO sensors are not so common for that purpose. Both gas concentrations have to be measured in order to meet the requirements respecting the NO_x emission given by law. It is the aim of this contribution to show the results of application of both sensors during the operation in a cement kiln.

Setup of the gas probe

The probe system mainly consists of the probe tube itself, compressed air tank, re-cooler for the cooling water, coolant control cabinet, local control box and PLC cabinet. As the probe is inserted, it rotates 90° and the plunger is activated to remove deposits at the tube flue gas entrance. Beside that inside the probe installed O2 and CO sensor sample gas can be supplied to an analyzer cabinet. The overview of the CEMTEC® system is given in Fig. 1.

Inserted in the process, the probe tube is cooled by coolant (water-glycol mixture) and is cooled by the air/water re-cooler. A 3-way valve provides a constant coolant return temperature of 85 °C. In order to prevent the probe from caking stuck in the kiln inlet, the probe rotates 90 ° in adjustable intervals. Once a day the probe is retracted and re-inserted into the process to ensure that the probe can extract automatically in case emergency retraction is necessary. Sample gas is extracted by the probe from the kiln inlet through its internal sintered metal filter. Deposits on the inner filter tube and at the sample gas inlet are removed by regular plunger movement. Plunger movement means that the internal filter tube with plunger is regularly driven back and forth by pneumatic pistons. The sample gas is extracted through the heated sample gas line for sample gas conditioning and further to the gas analyzers cabinet which can have additional analyzers.

All drives of the CEMTEC® probe system are completely pneumatically operated, namely probe rotation, plunger movements and probe drive. A sufficiently large compressed air buffer tank is used as an "energy reserve" for an

emergency retraction should the main voltage or plant air fail and is controlled by a PLC with a backup battery.

Sensor principles

Oxygen is measured by the well-known solid electrolyte cell using platinum electrodes on yttria stabilized zirconia (YSZ). The concentration can be calculated according to the Nernst's equation:

$$U_{eq} = \frac{RT}{4F} \ln \frac{p''_{O_2}}{p'_{O_2}} \quad (1)$$

With air as a reference the volume concentration of oxygen is obtained by eq. (2) [1]:

$$\varphi_{O_2} / vol\% = 20.69 \cdot \exp\left[-46.42 (U_{eq} / mV) / (T / K)\right] \quad (2)$$

The operating temperature of the solid electrolyte cell was fixed at 800 °C.

For the measuring of gas components like carbon monoxide (CO) or hydrocarbons (HC) in non equilibrated gas phases kinetically determined sensors are used. Depending on the electrode material, the gas components do not equilibrate on the measuring electrode at temperatures < 700 °C. Thus gas components, which are not thermodynamically stable, are electrochemically active. In CO and O_2 containing gas at least two electrode reactions can take place: The electrochemical reduction of oxygen and the electrochemical oxidation of carbon monoxide. The measured open circuit voltage does not obey the Nernst's equation. Therefore such electrode behaviour is often referred to non-Nernstian electrodes (or *mixed potential sensors*). The cell voltage U_{mix} depends logarithmically on the concentrations according to eq. (3) [2, 3]:

$$U_{mix} = U_0 - A \ln(\varphi_{CO}) \quad (3)$$

The mixed potential sensor in thick film technology was developed for measurement of CO in oxygen containing flue gases of combustion chambers. The top view on the sensor which has the size 9.5 x 3.5 mm² is shown in Fig. 2. As CO sensitive electrode a mixture of different oxides is used. The choice of electrode material diminish the cross sensitivity vs. hydrogen and hydro carbons. Nevertheless, a certain cross sensitivity cannot be avoided. Therefore, the concentration of CO is expressed in COe, that means CO equivalents. According to the measuring range a certain mixtures of oxides are used. The operating temperature of the mixed potential sensor was adjusted at 700 °C. The sensor response of three different prepared sensors is shown in Fig. 3 Similar to the solid electrolyte oxygen sensors which can be calibrated with known test gas mixtures, these mixed potential sensors have to be calibrated at the same time with the same test gas mixtures in order to generate the sensor function.

Results and Discussion

The results of gas analysis are shown in Fig. 4. It is clearly to see that the sensor response is fast enough to control the process according to the optimal conditions. A high value in oxygen concentration corresponds with a low carbon monoxide concentration and vice versa. The measured O_2 and CO values at the kiln inlet enable the operator to adjust the combustion air quantity accordingly. If the O_2 value is too high, the ID fan must draw more flue gas through the furnace system than necessary. If the O_2 value is too low and there is a very high CO content, the combustion is sub-optimal. Here, the operator can make appropriate changes to the settings, either to the burner or to the ID fan to achieve the best possible combustion. After 2 years of operation, it can be concerned that the results of the probe measurements are very convincing and when compared to other measurements in the kiln process control system, also plausible. The maintenance consists in purging the sample line twice a year, as well as a general maintenance in the analyzer cabinet with calibration of the other analyzers for NO and SO_2. No lost in sensor performance was observed over that time [3]. This analysing techniques help to meet the requirements on emission of NO_x and NH_3 given by law.

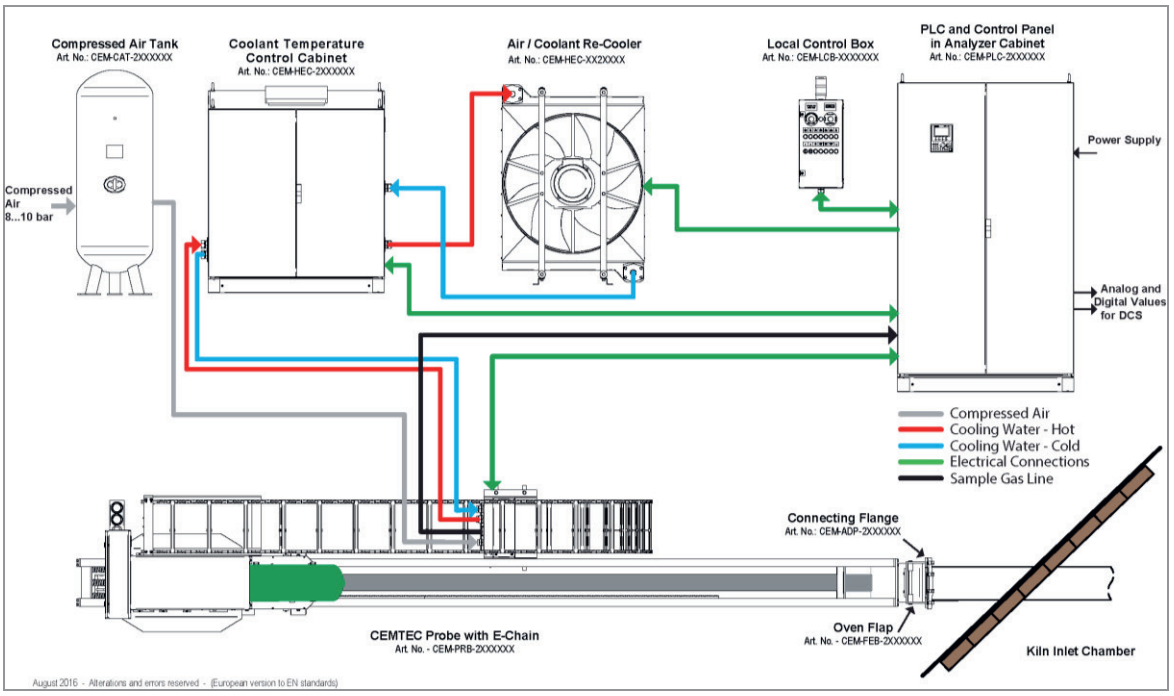

Fig.1.Schematic overview of the CEMTEC gas analyzing system with air/coolant re-cooler

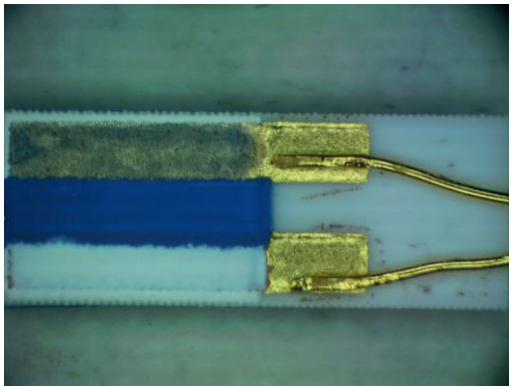

Fig. 2 Top view on mixed potential sensor, electrodes are printed on YSZ electrolyte, contacts made of gold

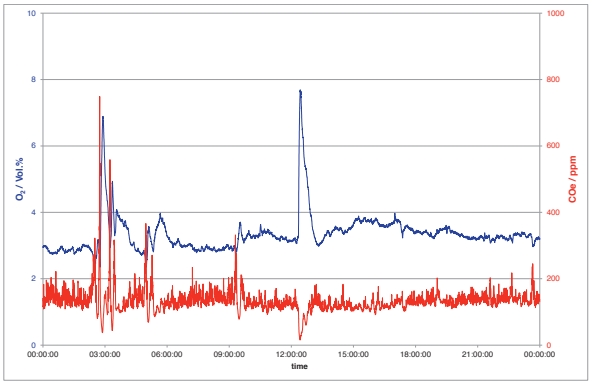

Fig. 4. Oxygen and CO concentrations from the kiln inlet over a full day (upper curve oxygen, the lower one CO)

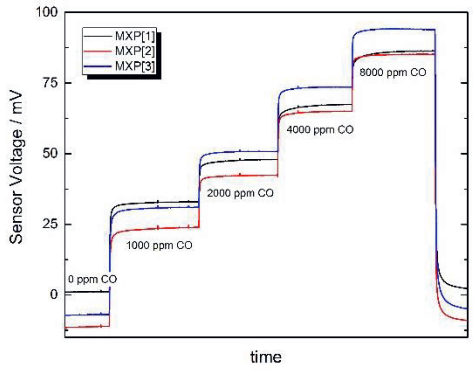

Fig. 3 Sensor response of three different COe-sensors MXP [1-3]

References

[1] U. Guth
Gas sensors, 2nd Ed. Springer 2012, 400-402 in: Electrochemical Dictionary ed. by A.J. Bard, G. Inzelt, F. Scholz

[2] U. Guth, J. Zosel
Electrochemical solid electrolyte gas sensors – hydrocarbon and NO_x analysis in exhaust gases, Ionics 10, 366-377 (2004)

[3] P. Shuk, E. Bailey, J. Zosel, U. Guth
New advanced in situ carbon monoxide sensor for the process application
Ionics 15, 131-138 (2009)

[4] Märker Cement Harburg, User Report
In: Global Cement Magazine May 2017