



In situ measurements of O₂ and CO eq. in cement kilns

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Abstract. The simultaneous in situ measurement of O_2 and COeq. in cement kilns is a great challenge due to the high process temperatures and high dust load. The standard method for measurement for flue gas in cement kilns is extractive. Extractive measurements have a higher response time due to the flue gas conditioning including the length of heated extraction lines for electrochemical or optical analysis. This delayed response is not optimal for fast process control.

A probe was developed for this purpose in which the in situ solid electrolyte oxygen sensor and an in situ CO eq. mixed potential sensor are implemented. Due to the high temperatures, the probe is cooled by a water–coolant mixture. In order to prevent deposits of raw material forming and sintering on the probe, it rotates 90° in programmable intervals. In addition, an automated probe plunger pneumatically removes plugging at the probe flue gas entrance, also in programmable intervals. These self-cleaning functions allow the probe to continually stay in the process for combustion optimisation (low excess O₂ and CO) and enable the plant operator to measure additional process-related gas components (NO, SO₂, HCl etc.) and optimise the SNCR (selective non-catalytic reduction) for NO_x reduction. Combustion air supply can be adapted very quickly due to the in situ sensors, which has been demonstrated by a CEMTEC[®] probe over years (Märker Cement Harburg, 2017).

1 Introduction

Combustion control in cement kilns is an enormous challenge as real-time data of the O₂ and COeq. gas concentrations are necessary. In a typical cement kiln, various fuels with different calorific values are used, resulting in flue gas with varying compositions. The optimal fuel/air ratio varies depending on the fuel in use. Coal, gas or oil are the most common fuels used at the kiln burner. Besides these fuels, domestic and industrial waste consisting of a variety of materials is burnt. For optimal combustion, excess O₂ and COeq. should be kept at a minimum. For this purpose only solid electrolyte sensors are suited as they are stable enough to withstand the harsh process conditions and exhibit a fast response in milliseconds. In order to measure under these circumstances, a water-cooled probe was developed which can be installed as near as possible to the kiln burner. Usually oxygen sensors based on the Nernst principle are utilised. While the application of oxygen sensors for this process is

common, CO eq. sensors are not usually implemented for this purpose.

2 Set-up of the gas probe

The CEMTEC system consists mainly of the probe itself (1), a compressed air tank (3), a re-cooler for the cooling water (4), a coolant control cabinet (5), a local control box (2) and a programmable logic controller (PLC) cabinet (6) – see the CEMTEC[®] system overview in Fig. 1.

Inserted in the process, the probe oscillates 90° to prevent deposits of raw material forming and sintering on the probe surface, to prevent the probe from sticking and to ensure homogeneous heat distribution. The plunger/filter tube removes plugging at the probe's flue gas entrance and pulverises any internal deposits which are then removed during purging. The O₂ and CO eq. sensors are situated at the back of the probe tube and measure in situ. Additionally, dust-free sample gas is extracted through the probe's sintered metal filter, through the heated sample lines to an analyser cabinet



Figure 1. Overview of the CEMTEC gas analysing system with air/coolant re-cooler.



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



Figure 3. Sensor response of the COe MXP sensor.

for downstream measurement of other gas components necessary for process control.

The probe is cooled by a coolant (water–glycol mixture) which in turn is cooled by an air–water re-cooler. A threeway valve provides a constant coolant return temperature of 85 °C. Once a day the probe is retracted and re-inserted into the process to ensure that the probe can retract automatically in case emergency retraction is necessary. All PLC-controlled drives of the CEMTEC[®] probe system are completely pneumatically operated, namely, probe rotation, plunger movement and probe insertion/retraction. 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.

3 Sensor principles

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

$$U_{\rm eq} = \frac{\rm RT}{4F} \ln(\frac{p_{O_2}''}{p_{O_2}'}).$$
 (1)

- U_{eq} cell potential
- R universal gas constant
- T temperature
- F Faraday constant
- p_{O_2} " O₂ partial pressure reference air
- $p_{O_2}' O_2$ partial pressure process gas

With air as a reference the volume concentration of oxygen is obtained by Eq. (2) (Guth, 2012):

$$p'_{O_2}/\text{vol}\% = 20.69 \cdot \exp\left[-46.42(U_{eq}/\text{mV})/(T/K)\right].$$
 (2)

The operating temperature of the solid electrolyte cell was fixed at 800 $^{\circ}$ C.

For the measurements of gas components such as carbon monoxide (CO) or hydrocarbons (C_xH_y) in non-equilibrated gas phases, kinetically determined sensors are used. Depending on the electrode material, the gas components do



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

not equilibrate on the measuring electrode at temperatures <700 °C. Thus gas components, which are not thermodynamically stable, are electrochemically active. In CO and O₂ containing gas, at least two electrode reactions can take place: electrochemical reduction of oxygen and the electrochemical oxidation of carbon monoxide. The measured open circuit voltage does not obey the Nernst 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) (Guth and Zosel, 2004; Shuk et al., 2008):

$$U_{\rm mix} = U_0 - A \cdot \ln(\varphi_{\rm CO}). \tag{3}$$

- $U_{\rm mix}$ mixed potential
- U₀ offset voltage
- A material- and temperature-dependent constant
- $\varphi_{\rm CO}$ CO concentration

The mixed potential sensor in thick film technology was developed for measurement of CO in flue gases of combustion chambers. The top view of the sensor which has the size 9.5×3.5 mm is shown in Fig. 2. For the CO-sensitive electrode, a mixture of different oxides is used. The choice of electrode materials diminishes the cross-sensitivity to hydrogen and hydrocarbons. Nevertheless, certain cross-sensitivities cannot be avoided. Therefore, the concentration of CO is expressed in CO eq., which means CO and equivalent. The specific mixture of oxides allows a wide measuring range of CO eq. The operating temperature of the mixed potential sensor was adjusted to 700 °C. The sensor response is shown in Fig. 3.

The high sensitivity and fast response are evident whereby a sensor signal of 80 mV per 1000 ppm COCO is reached. The calibration of the COeq. sensors is carried out under simulated process conditions. Offset, span and slope are determined during the calibration process which enables higher accuracy under process conditions.

4 Results and discussion

The results of gas analysis, which was carried out in a cement plant, are shown in Fig. 4. It is clear to see that the sensor response is fast enough to control the process optimally.

A high oxygen concentration corresponds to a low carbon monoxide concentration and vice versa. The measured O_2 and COeq. 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, resulting in excessive fuel use due to more combustion air being heated than required for the combustion process. If the O₂ value is too low and there is a very high CO content, the combustion is sub-optimal as the oxidation process is incomplete. In addition, high CO concentrations will result in destruction of the refractory lining in the kiln and kiln inlet chamber due to CO corrosion. 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 concluded that the results of the probe measurements are very convincing and, when compared to extractive measurements of the same flue gas, are also plausible. Maintenance consists of purging the sample line twice a year as well as a general maintenance in the analyser cabinet with calibration of the analysers for NO and SO₂. The CEMTEC probe has a yearly maintenance interval. No loss in sensor performance was observed over this 2-year period (Märker Cement Harburg, 2017). This analysing technique also helps to meet the emission limits of NO_x and NH₃, as can be seen in Fig. 4.

Data availability. The data that support the findings of this study are not publicly available.

Competing interests. The authors declare that they have no conflict of interest.

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