

High Temperature Sensor for In-Situ Process-Monitoring in Harsh Environments

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ABSTRACT

Continuously increasing emission requirements and cost pressure inevitably lead to the optimization of combustion processes. Therefore, the exhaust gas losses have to be minimized by reducing the excess air to the so called emission rim. This is a point near stoichiometry where products of incomplete combustion (e.g. CO, H₂) suddenly increase due to the lack of oxygen. Hence, a combustible gas sensing technology should be applied directly inside the exhaust pipe for realtime measurement. Harsh environmental conditions lead to the use of a robust mixed potential solid electrolyte gas sensor. High sensitivity with high time resolution, thermal, mechanical and chemical robustness enables highly dynamic in-situ control of the combustion process by positioning the high temperature sensor directly inside the flue tube. Initially developed for space application, the miniaturized high temperature sensor can ideally be used in both industrial and domestic applications through additional advantages such as low power consumption and low cost at high quantity. The paper reports the working principle, design, production of the sensor and integration into a new high temperature and corrosion resistant housing and the temperature control strategy evolved in order to compensate the influence of the high measurement gas temperatures of more than 450°C. Both results from the laboratory tests with synthetic gas and the field tests will be shown. Exemplarily, the results of a newly developed in-situ wall monitoring system for coal-fired power plants will be presented. Over a period of 5 years the field tests have been done on a 450 MW coal fired power plant and demonstrated its function and reliability. It could have been shown, that CO as sole indicator for corrosive wall conditions is sufficient. Lifetime of the monitoring system turned out to be more than 2 years. Lifetime tests are still ongoing.

INTRODUCTION

In 1993 the idea was proposed to measure the residual oxygen distribution inside an IRS plasma wind tunnel using commercially available λ -probes. These gas sensors were normally used for controlling the fuel to air ratio of car engines. The measured O₂ concentration inside a N₂ plasma plume mixing with cold O₂ gas simulates the reentry conditions into the Earth's atmosphere. This was the first use of ceramic gas sensors in such a harsh environment under plasma conditions in evacuated chambers, leading to further space applications. Based on this success, the Flux-(Phi)-Probe- Experiments FIPEX were developed in order to measure the oxygen distribution in the higher atmosphere, resulting in three flight experiments between 1996 and 1997. For the latter application, the commercially available gas sensors came out to be too large in scale and weight and their power consumption was too high. Especially, the need of

having a well known and fixed reference atmosphere was a drawback for these measurements in the higher atmosphere. Consequently, an independent development and fabrication of solid electrolyte gas sensors more capable for use in space was initiated at the IRS, leading to the FIPEX on IRDT reentry missions, where the newly developed sensor technology demonstrated its usability.

Due to its miniaturization, small power consumption and other benefits, considerable interest arose from industry for terrestrial use of the sensors in various applications, e.g. medicine, environment and vacuum technique. In 1999 the spin-off company ESCUBE was founded in order to introduce this innovative technology into the market. Finally, FIPEX has been launched on STS-122 Shuttle flight on February 7th 2008 and deployed on the COLUMBUS External Payload Facility, see Fig.1. Two out of twelve oxygen sensors were

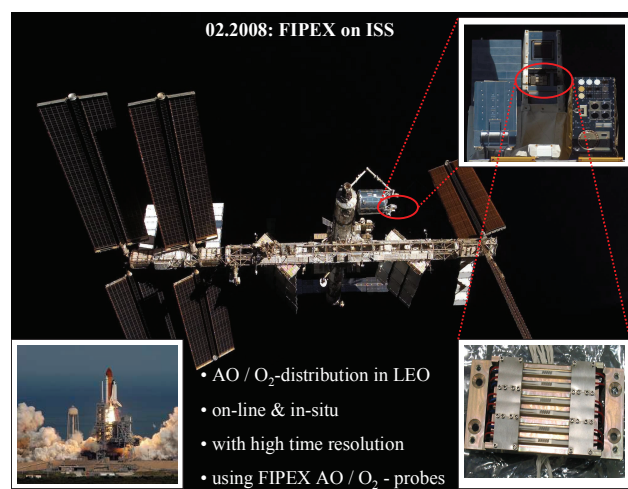


Fig.1 FIPEX on ISS measures O₂ and AO in Low Earth Orbit in-situ [credits: NASA, ILR/TU Dresden]

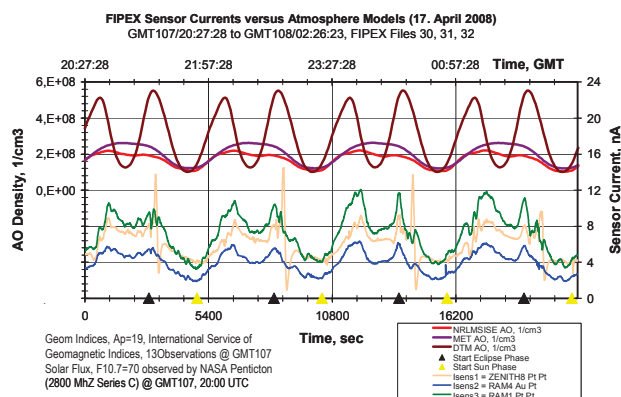


Fig.2 Data of three FIPEX sensors during four orbits compared to the prognosticated AO density of three different atmosphere models.

when continuing the orbit to higher latitudes. Some minutes before the ISS exits the local eclipse phase, the AO level reaches its minimum [1].

Based on FIPEX, and especially on the knowledge around the AO-electrode for measuring oxidizing gases the combustible gas sensor CarboSen was developed especially for combustion optimization. Its purpose is to provide a simple, low cost, time resolved in-situ process control and optimization e.g. directly in the harsh environment of a flue gas tube of gas-, oil-, or biomass-fired domestic burners. Goal is early detection of unburned gases e.g. CO, HC when reducing the excess air for more efficiency by adjusting the burner directly at the so called emission rim [2]. Such a robust solid electrolyte high temperature gas sensor will now for the first time be applied for in-situ wall monitoring of coal-fired power plants.

SOLID ELECTROLYTE HIGH TEMPERATURE GAS SENSORS

Nernstian O₂-Measurement (λ-Probe): Stabilized zirconia (ZrO₂) is a good oxygen ion conductor at temperatures between 450 °C and 950 °C. It has an excellent chemical stability. The material properties are well suited for the application as an active element in electrochemical gas sensors for the use under harsh environments. These properties originate from the yttria (Y₂O₃) as dopant. Yttria forces a defect structure with a finite concentration of octahedral voids as can be seen in **Fig.3**. These oxygen vacancies in the lattice enable an anionic O₂-diffusion through the yttria stabilized zirconia (YSZ). The electrical properties of zirconia have been studied since the last century when Nernst investigated the ionic conductivity of YSZ. The idealized electrochemical cell in **Fig.3** leads to an Electro Motive Force generated across the solid electrolyte by the passage of oxygen ions. These separated ions lead to a potential difference to be measured as sensor voltage U_S between the electrodes

$$U_S = U_0(\Delta T) + \frac{RT}{nF} \cdot \ln \frac{p_{O_2,ref}}{p_{O_2}}$$

is the universal gas constant, T the electrode temperature, n the valency of the ions involved in generating the potential (here $n=4$), F the Faraday constant, $p_{O_2,ref}$ the O₂ partial pressure in the reference chamber and p_{O_2} the O₂ pressure in the measurement chamber. The offset voltage U_0 originates from a temperature difference ΔT between the two electrodes e.g. due to forced convection, insufficient heating, asymmetric sensor geometry and catalytic combustion at one electrode. U_S is a function of the temperature T that has to be precisely controlled for an accurate measurement. The relationship is based on the assumption that the thermodynamic equilibrium exists and the kinetics of the electrode interface reactions are sufficiently fast.

Non-Nernstian CO-Measurement (CarboSen): In contrast to the Nernstian O₂-Probe, measurement signals of the Non-Nernstian CO probe do not correspond to a thermodynamic equilibrium at the electrodes and the reactions taking place are mainly kinetically controlled. Hence, the sensor temperature and its accurate control is very important (see **Fig.7**). The sensor signals of the Non-Nernstian sensor are influenced by many conditions including sensor geometry and fabrication parameters. Variation of the electrode material changes the adsorption, desorption and

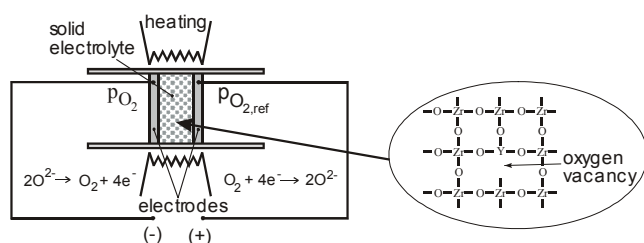


Fig.3 Classical Nernstian cell (left), structure of the YSZ solid electrolyte ceramics (right).

produced at the ESCUBE cleanroom production facilities. FIPEX is able to distinguish and measure atomic (AO) and molecular oxygen (O₂) down to 10⁻¹⁰ mbar partial pressure. Its purpose is to measure the time resolved behaviour of AO and O₂ in the upper atmosphere. Especially the flux of AO is of importance as it shows surface interactions e.g. materials erosion and solar cell degradation. Furthermore, using the atmosphere models, the prediction of total density and partial pressures in higher latitudes are insufficient.

In **Fig.2** first results show deviations of the transient behavior of AO compared to the prediction using the higher atmosphere models NRLMSISE, MET and DTM. The results prove an increase of AO after local sunrise when ISS orbits from south to the equator followed by a decrease

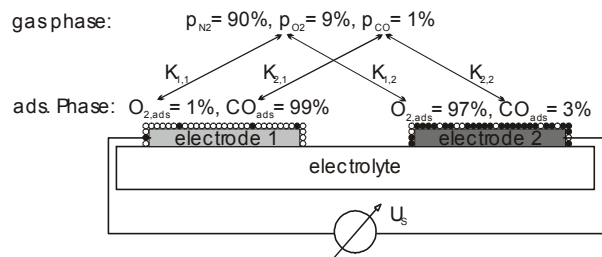


Fig.4 Non-Nernstian cell, heater structure not shown

as CO appear, different electrochemical reactions will take place simultaneously at the two different catalytically active electrodes resulting in two different electrochemical potentials. The potential difference between the electrodes finally results in the sensor signal voltage U_s between the reference and the working electrode

$$U_s = A(T) \cdot \ln c_{CO}$$

Advantageously, this results in a logarithmic type function with a temperature dependent constant $A(T)$ through origin, where the sensor signal is $U_{s,offset} = 0 \text{ mV}$ when no combustibles are present in the measurement gas. That means a physically determined and drift free origin and hence, no need for any drift or offset calibration. Since all electrodes are placed inside the measurement gas, there is no need for any reference atmosphere. As can be seen in **Fig.5**, the mixed potential sensor CarboSen is equipped with two identic measurement electrodes for redundancy and self-check reasons

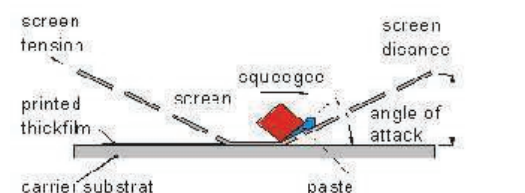
DESIGN, PRODUCTION AND INTEGRATION

Production of CarboSen: The sensitivity and the selectivity of the sensor elements are mainly influenced by geometry, materials and the way of producing the sensitive parts of the sensors which influence the surface and structure of the porous electrodes and of the functional zirconia ceramics. For production, the innovative screen printing technique was used with its advantages in high flexibility, reproducibility and possibility for producing large series of low-cost sensor elements. In combination to this, modern thin film technologies e.g. CVD or PVD is used to modify the working electrodes and plasma spray technologies could be applied in order to create different additional functional or diffusion layers e.g. on top of the measurement electrodes. In such a way sensitivity and selectivity of the CarboSen sensors can easily be varied.

In **Fig.5** the principle of the screen printing technique is shown. A viscous paste is pressed by a squeegee rubber through the openings of a fine meshed screen. The carrier substrate under the screen is coated with the paste, which is levelling down to create a closed monolithic layer with a thickness between $1 - 100 \mu\text{m}$. After leveling down, the paste has to be dried and tempered under controlled conditions inside high temperature ovens up to 1400°C . The printing has to be done under controlled clean-air conditions.

Design of CarboSen: The design of the CarboSen element is straight forward for simplicity in function, small size and projected low cost. **Fig.5** shows the CarboSen multi-layer sensor element consisting of the Pt-heater (7), Au-contact pads (5) and a protective glass layer (1) on one side of the Al_2O_3 -carrier substrate (6). On the other side, galvanically isolated there are the inner Pt-electrode (4) and two identic outer measurement electrodes (2) separated by a porous functional zirconia layer (3) and again contact pads (5) and a protective glass layer (1). The overall geometry is $20 \times 3.5 \times 0.5 \text{ mm}$, resulting in a reduced heater power of around $P_h = 2,7 \text{ W}$ at nominal sensor temperature of around $t_s \sim 600^\circ\text{C}$.

Integration of CarboSen: The tube housing for in-situ wall monitoring is shown in **Fig.6**. The INCONEL® stainless steel tube has a length of $500-1000 \text{ mm}$ and an outer diameter of 8 mm and is directly connected to the die-casting aluminum box (IP67) with integrated XC164 sensor electronics. The tube



- | Sensor layers: | |
|----------------|---|
| 1 | Glass coating |
| 2 | Measurement electrodes |
| 3 | YSZ-electrolyte ceramics |
| 4 | reference electrode |
| 5 | Au-contact pads |
| 6 | Al_2O_3 carrier substrate |
| 7 | Pt-heater coil |

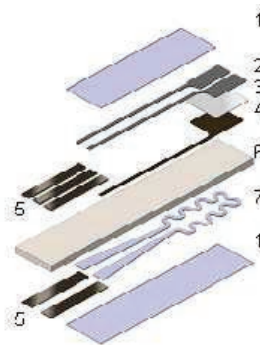


Fig.5 Design and production of the combustible gas sensor CarboSen.

catalytical reaction characteristics, leading to different sensor signals which also depend on other gases. **Fig.4** shows the principle sketch of a Non-Nernstian probe with a different surface coverage of the two electrodes corresponding to the partial pressures of the reactive gaseous components O_2 and CO in the gas phase. In practice, we apply one catalytically active Pt electrode as the ideal reference electrode and another catalytically deactivated one as the working electrode. If combustible gases such

can easily be attached to the boiler wall access pipe (see **Fig.8**). It provides a reliable fixation and positioning of the sensor element next to the boiler wall's atmosphere. The front cap with integrated sinter-filter protects the sensor element from flying ash, slag and high pressure water from the soot blower. Five Pt-wires are gap-welded to the sensor element. A high temperature fixation glass is

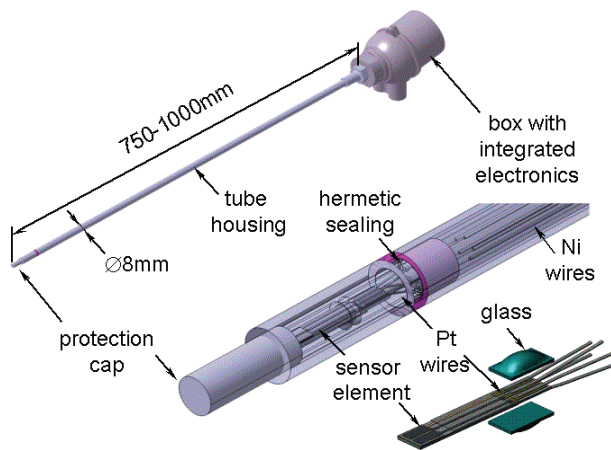


Fig.6 Integration of CarboSen into high temperature and corrosion resistant tube housing [3].

mV to industrial analogue $0/4-10\text{ mA}$ or CAN-BUS output signal. The firm- and software was especially developed, to minimize influences of the high and changing temperatures next to the combustion chamber. Therefore, a new temperature control strategy was developed based on a combined Pt-heater resistance t_f -measurement and a constant ceramic inner resistance R_{ki} -measurement, whereas $t_f = R_f/R_k = 2,6$ is the temperature factor resulting from Pt-heater cold resistance $R_{k,0^\circ\text{C}}$ at 0°C and hot-resistance $R_{h,590^\circ\text{C}}$ at nominal sensor temperature $t_s \sim 590^\circ\text{C}$ as can be seen in Fig.7, top.

RESULTS AND DISCUSSION

Temperature control of CarboSen: Fig.7, top shows that the ceramic inner resistance R_{ki} respectively the temperature factor t_f are well defined functions of the sensor temperature t_s . Hence, when adjusting t_f respectively R_{ki} and keeping the values constant, the sensor temperature should also stay constant resulting in a well defined sensor characteristics that should not be influenced from ambient temperature changes.

Fig.7, middle shows the results of the t_f/R_h -control. With increasing t_{amb} , R_{ki} increases. Since R_{ki} is the ohmic resistance of the functional ceramics between the electrodes, this means that the sensor element temperature t_s between the electrodes decreases. Hence, the sensor signal at a constant CO level of $c_{CO}=1000\text{ppm}$ in air increases from $102\text{ mV}@250^\circ\text{C}$ to $132\text{ mV}@400^\circ\text{C}$. This results in a sensor signal change of $+0,20\text{ mV/K}$.

Fig.7, bottom shows the results of the R_{ki} -control. With increasing t_{amb} , R_f/t_f as well as the sensor temperature t_s stays almost constant. In detail, the sensor signal at a constant CO concentration of $c_{CO}=1000\text{ppm}$ in synthetic air slightly decreases from $90\text{ mV}@250^\circ\text{C}$ to $84\text{ mV}@400^\circ\text{C}$. This results in a signal change of only $-0,04\text{ mV/K}$. For field tests at the power plant, the newly developed R_{ki} control was used in order to minimise the cross sensitivity measurement gas temperatures next to the boiler walls forced by varying boiler loads.

Experimental setup at the power plant: Fig.8 shows the installation of the wall monitoring system tube ($\varnothing_a = 8\text{ mm}$) into the boiler wall

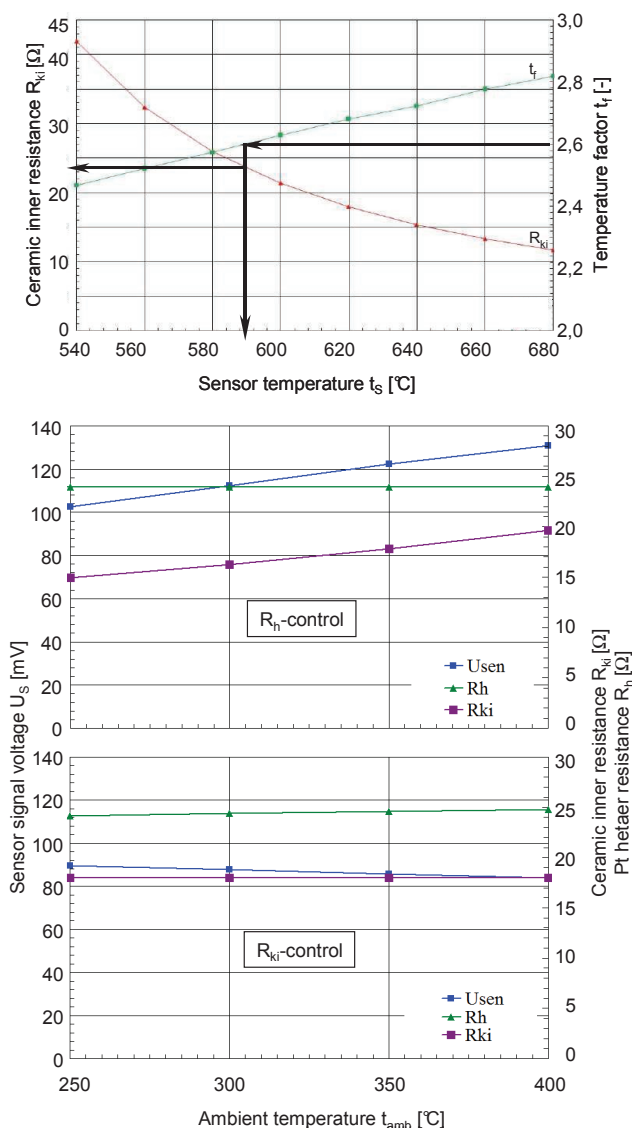


Fig.7 Different temperature control strategies [4]

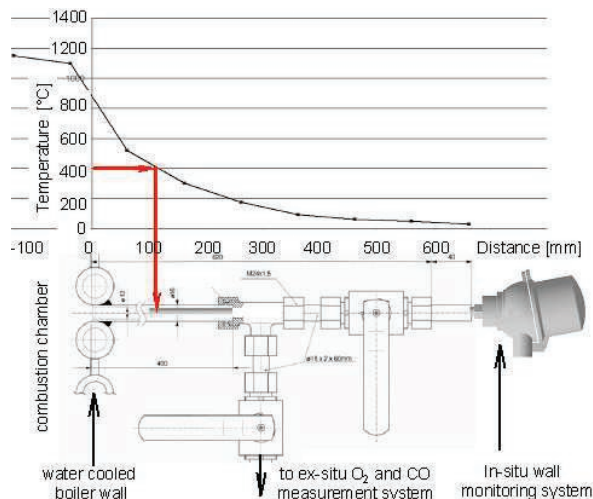


Fig.8 Installation of the wall monitoring system, temperature distribution over boiler wall access pipe and tee connector for ex-situ gas analyzer measurements [3]

sent to the measurement server. LABVIEW® was used to handle, visualize and save the data on the measurement server. All data could be handled and the system controlled via a remote-access point. It should be mentioned, that there is no need for an extractive withdrawal of gas during the final application as wall monitoring system. Natural gas exchange and diffusion processes are sufficient and yield similar results than with suction. Contrary to the suction mode, no obstruction by slug or ash was observed without suction. Finally, there is no need for tee connector or any other additional hardware installation such as pressurised gas, ejector, etc.

Experimental Results (excerpt): Fig.10a shows the typical time history of two sensor signals during changing the load of the power plant from around 450MW full load to 330MW upper respectively 230MW lower partial load and up to full load again. Both sensor signals follow the changing load resulting in a decreasing sensor signal when decreasing the load from up to 450mV@full load to around 20mV@lower partial load. During all stages, a highly dynamic sensor signal dynamic is visible. This is due to the highly dynamic combustion processes with varying combustible gases as products incomplete combustion e.g. CO, HC. Between 3:20 and 3:50 at upper partial load, the sensor signals stabilize at lower levels. This indicates a more homogenous combustion with low amounts of unburnt gases and lower levels of CO next to the boiler walls. The difference between the two sensor signals results from the different points of installation. Between 1:55 and 3:50 the sensor signal U_{S1} shows lower signal levels compared to U_{S2} indicating lower CO-loads of the boiler wall at measurement point 1 compared to higher loads at measurement point 2. From 3:50 both sensor signals approach each other at higher signal levels indicating higher CO-load for both measurement points. Data was taken without extractive measurement.

In order to quantify the CO-levels, an extractive measurement was started in parallel. Fig.10b shows the

in-situ sensor signal U_S compared to the ex-situ measurement value for CO from the gas analyzer. At the beginning, at full load of the power plant, the sensor signal level as well as the sensor dynamic was low, has indicated lower CO-levels and hence a better corrosive situation for the boiler walls compared to Fig.10a. The reason could be a combustion setting at higher levels of excess air due to e.g. better burner trim and/or changed quality of coal. Nevertheless, this would lead to a lower plant efficiency. In order to create higher CO-levels, the plant was shut down from 21:45. Accordingly, higher CO-levels and sensor dynamics can be observed, peaks occur up to 450mV@3000mg/Nm³. Fig.10c shows a close-up view where the time discrepancy of 28 s between the direct in-situ and the ex-situ measurements due to the long distance from the tee connector over tubes, pumps, filters, condensate trap to the mixing and analysing chamber. Here, no

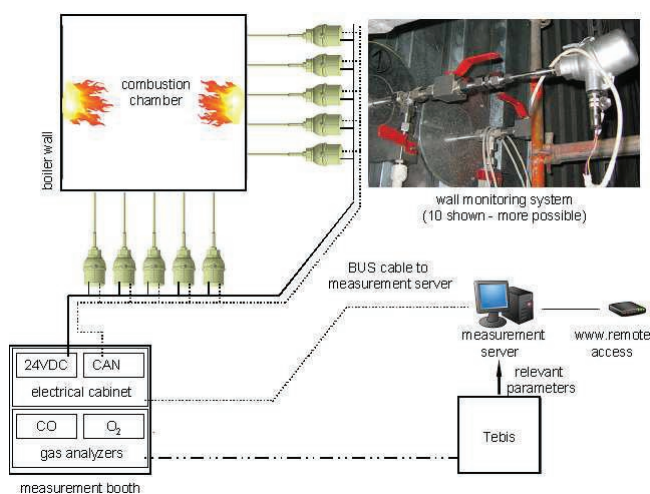


Fig.9 Sketch of the equipped boiler wall (lowest burner level at $h = 13$ m;) prepared for qualification measurement for up to 10 in-situ wall monitoring systems [3]

statistical correction was applied in order to eliminate broadening, damping and smoothening short term effects from ex-situ measurement. Despite this, after simple time correction a sensor specific calibration curve could be determined shown in **Fig.10d**. CO-concentrations stop at 3000 mg/Nm due to the end of the measuring range of the ex-situ analyzer used for gathering these data. In such a way, the CO-levels indicating a corrosive wall atmosphere could be displayed at the control room e.g. via an easy red, yellow, green signal light system.

SUMMARY AND CONCLUSIONS

A high temperature solid electrolyte Non-Nernstian mixed potential sensor was developed and successfully applied for the first time as an in-situ wall monitoring system at a 460MW coal fired power plant. 10 advanced prototype systems were installed and successfully life-time tested over a period of 24 months continuous operation. The presented measurements show a clear relation to CO as necessary, but not sufficient indicator for corrosive boiler wall conditions. Normally, $O_2 < 1\%$ as another indicator has to be taken into account. An alternative solution using additional information from the CO sensor CarboSen itself were found during this work. These results will be published soon elsewhere.

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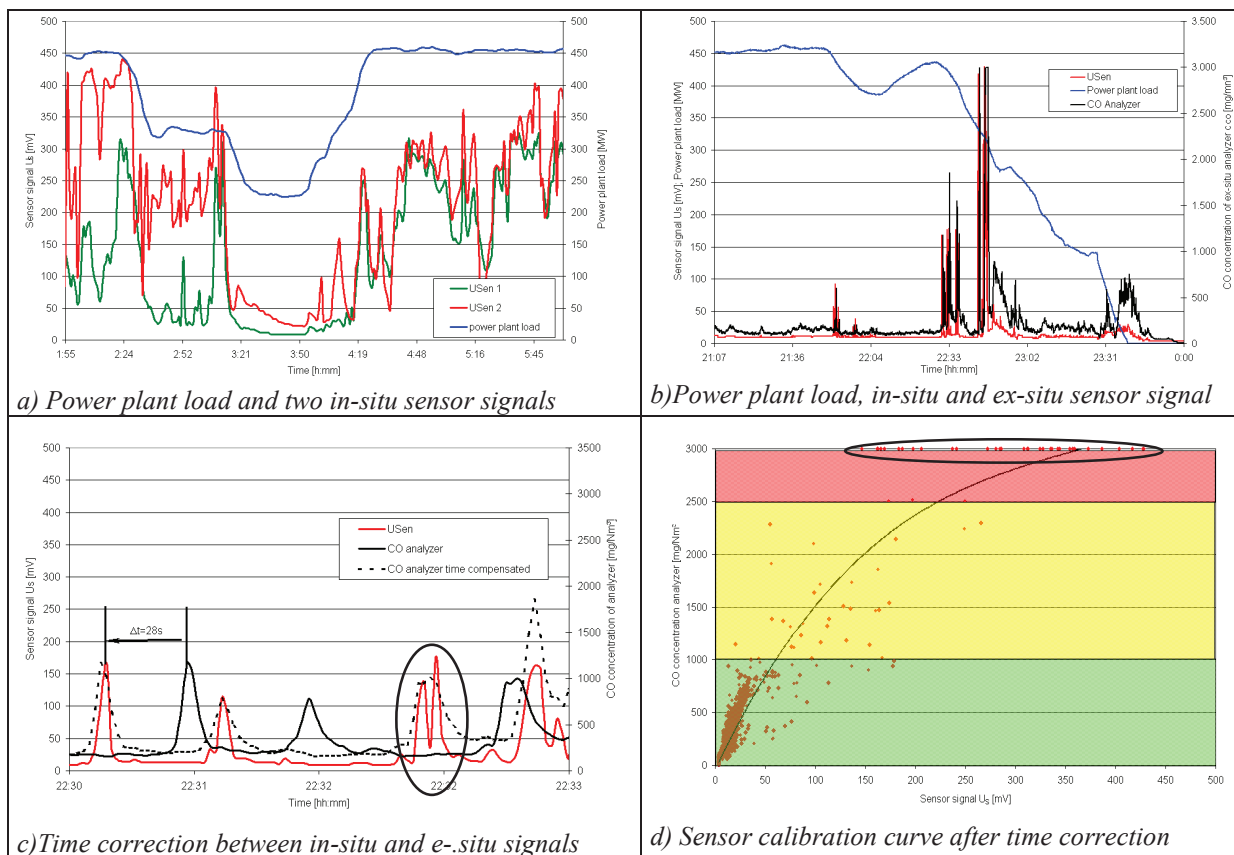


Fig.10 Histogramms of in-situ sensor signal, ex-situ references gas measurement and power plant parameter [3]