# FLUE GAS $O_2$ ANALYZERS - ADDRESSING THE IGNITION POTENTIAL IN INDUSTRIAL BOILERS AND FURNACES


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## ABSTRACT

Zirconium Oxide ($ZrO_2$) sensing technology has been successfully used for the measurement of flue gas $O_2$ for over 4 decades, and has become one of the most ubiquitous of gas sensing technologies. The $ZrO_2$ sensing cells commonly utilized for measuring flue gas $O_2$ are typically heated to around 736-800C in order to operate, and it is wise to consider the heated sensing cell as a potential source of ignition if the gas mixtures inside a given furnace reach explosive limits. While the frequency of explosive events attributed to ZrO2 sensors appears to be very low, and these occurrences have not inhibited the sale and/or utilization of these instruments in most industries, it is again wise to consider protective measures to prevent future events.


## BACKGROUND

Zirconium Oxide ($ZrO_2$) sensing technology has been successfully used for the measurement of flue gas O2 for over 4 decades, and has become one of the most ubiquitous of gas sensing technologies. The sensing technology has migrated from large boilers and furnaces to trucks and automobiles, and even to small engines.

There are three main implementations of the $ZrO_2$ sensing technology:

Heated In Situ Probe - whereby the heated $ZrO_2$ sensing cell is placed at the end of a probe of different lengths. There is no sample system, and the flue gases diffuse into the cell area past a passive filter, or "diffusion element". This is the least expensive and lowest maintenance arrangement.

Unheated In Situ Probe - this is a similar arrangement, but without the heater. The probe must be placed in a section of the furnace where the flue gas temperatures are at least approximately 550C in order to operate. Ceramic probe materials are frequently utilized in order to endure temperature excursions to 1300 C or so. These probes will not provide flue gas $O_2$ information until the furnace has warmed up, however. Also, the ceramic materials utilized can experience a short life due to thermal stresses.

Close-Coupled Extractive Systems - these systems place the heated sensing cell outside the flue as duct, and draw a sample of flue gas into the analyzer via an educator sample pump, or "scoop tube" that directs some flow out of the flue gas duct, into the analyzer, and then back into the duct. These systems often utilize a second sensing cell to measure the combustibles in the flue gases.

The $ZrO_2$ oxygen sensing cell in the heated arrangements are typically heated to around 736-800C in order to operate, so it's wise to consider the heated $ZrO_2$ sensing cell as a potential source of ignition if the flue gas mixtures inside a give furnace reach explosive limits. While the frequency of explosive events attributed to ZrO2 sensors appears to be very low over their many decades of use, and these occurrences have not inhibited the sales of these instruments in most industries, it is again wise to consider protective measures to prevent future events.

## EXPLOSIVE EVENT

Explosive events attributed to heated analyzers have occurred in the past, but usually anecdotally. One event occurred at the Dow Chemical chemical plant in Plaquemine, La. in 2005 for which there is good investigative information, so it is instructive to review this data:

"The furnace was offline due to a plant outage caused by a power failure. The investigation of this incident determined that this mixture was ignited by an in situ zirconium oxide oxygen probe in the furnace stack. The probe was equipped with a heater to achieve the 700 C operating temperature of the element and with a flame arrestor. The probe had been placed in service in the 1990's and had functioned well with only routine preventive maintenance. When removed from the field and inspected, it was found that the threaded housing holding the flame arrestor to the probe body was loose. It was conjectured that the loose threads formed a path for flame propagation, bypassing the flame arrestor. In addition there was evidence of flame impingement on the probe body just outside the thread area. These facts led to the conclusion that the flame arrestor function was disabled by the loose threads.

During the follow-up to this incident, it was determined that the flame arrestor alone would not be an adequate protection against this scenario, even if some means were established to ensure that the arrestor function was not compromised. Other procedural, hardware, and software measures would be taken to ensure that this probe could not act as an ignition source for a flammable gas. There were follow-up actions addressing the malfunctions that led to the formation of the flammable mixture, but they are not relevant to this paper.

There was another layer of protection in the oxygen analyzer system which could have prevented this incident but failed to do so. There is a software controller which activates the probe and turns on the probe heater. This controller is programmed to lock out a probe which has lost its signal for any reason; a technician must manually override the controller to allow the probe to be activated and heat up. The probe had lost power when the plant lost power and tripped; it was initially thought that it would not have reactivated automatically. However, the software controller had lost power at the same time as the probe. When power was restored, the controller and probe were powered up simultaneously and the controller did not recognize that the probe had failed to function for some time. It allowed the probe to heat back up without any human intervention. This behavior has been confirmed by field tests."(1)

Corrective actions were noted as:

"Procedural and control changes have been made in the plant to force the deactivation of these types of oxygen probes when a furnace is taken offline. Software changes to deactivate all probes when the controller loses power are underway. In addition, Dow has recently completed a study comparing the available oxygen analyzer systems and is in the process of forming a final recommendation for a standard application. This is a complicated matter as there are pros and cons associated with each alternative and there is no solution that fits all applications."(1)

The wide publication of this report has benefitted industry, and has caused some industry organizations to address these same concerns in their publications. The American Petroleum Institute (API) has issued a revised "Recommended Practices" (RP555)for Process Analyzers , and states:

" 19.4.3 Sample Gas Ignition. Where ignition of the sample gas is possible, for instance, when a zirconia electrochemical cell at 1562 °F (850 °C) is left operating in a shutdown heater not free of fuel gas, precautions should be taken to prevent this from happening. Flash arrestors could be installed to prevent back flashing. A safety interlock system that shuts down the analyzer upon flame failure or on other conditions that could let combustible gas reach the measurement cell is a second technique available to the designer. Another option is purge gas flooding of the cell."(2)

The National Fire Protection Agency (NFPA) has also issues an Addendum to NFPA 85, NFPA 85-2012 (section No. A.6.4.2.3.4.6(2) ) :

“Analyzers could contain heated elements that exceed the autoignition temperature of some fuels. Zirconium oxide analyzers, commonly used for oxygen analysis, contain an element heated to 1300°F (704°C). This high temperature element presents a potential ignition source to unburned fuel that could be present at startup. Some analyzers are designed to protect the sampled space from the ignition source by providing flashback protection (such as flame arresters in sample gas path). Analyzers with that protection or that are not heated to autoignition temperature do not present an ignition hazard.”(3)

It should again be noted that while these recommendations are prudent, the sale of in situ oxygen analyzers by this company have not seen a dramatic downturn. The subject Chemical facility continues to utilize in situ ZrO2 analyzers, along with other technologies. Restating the report corrective actions:- “This is a complicated matter as there are pros and cons associated with each alternative, and there is no solution that fits all applications.”(1)

## INDUSTRY DISPARITIES

As mentioned in the introduction, the heated $ZrO_2$ sensing technology is pervasive, being utilized from the largest power plants to the smallest automobiles and motorcycles. Refining and Petrochemical firms have historically demanded instrumentation that will meet certain hazardous area approvals, usually based on NEC, ATEX, or IECEX standards, while other industries utilizing similar boilers and furnaces have not. Power Plants, Pulp and Paper mills, and any industrial or institutional organization utilizing steam for process or environmental reasons utilize boilers that have similar environments both inside and outside the furnaces. Ample fuel trains deliver fuel through valves and into burners and boiler furnaces, so the question can be asked, “why does the hydrocarbon processing industry require hazardous area approvals for instrumentation on furnaces, when most other industries do not”?

One difference is that most industries adhere to NFPA 85 boiler safety code. Indeed, most facilities cannot obtain insurance without NFPA adherence, including the use of flame scanners and burner management systems. Large refineries and petrochemical facilities are often self-insured, and may not adhere to NFPA code, with the possible exception of compliance in the boiler house and in process heaters utilizing forced draft operation. Many fired process heater furnaces use many smaller natural draft burners, with no automation of air control for individual burners. Light-off is often a strictly manual operation. Flame scanners are frequently not utilized for these furnaces because of the expense to outfit the many burners, and because of the difficulty of differentiating the radiation emitted from adjacent flames. These furnaces will frequently utilize pilot burners for light off that have ionic flame rods to indicate if the pilot is operating, or extinguished. From API RP 556 “These pilot burners are typically used for light-off, only, and will not provide flame stability functionality(4). This, plus the fact that individual burner air control is often in manual and not on control makes furnace balance a challenge. API RP 556 recommends multiple $O_2$ measurements in large furnaces for this reason:

"One oxygen analyzer should be provided for each heater cell. For large cells, due to non-uniformities in the firebox flue gas circulation and to facilitate balancing the burners, it is recommended to provide one analyzer for every 30 feet of firebox length."(4)

While a tube leak in a boiler is expensive and can be dangerous depending on its size and location, a tube leak in a process heater will spray a combustible feedstock into the furnace that will usually pose a significant safety issue. Flame carryover into higher sections of the furnace is typically the result, and in more than a few instances, flames have been witnessed coming out the top of the stack.

So it's understandable why the refining and petrochemical industries put more focus on ignition sources inside a furnace and its associated flue gas ductwork. The heated $ZrO_2$ sensor is one of several ignition sources that can be found in a process heater's flue gas ductwork, including thermal dispersion flow meters, and electrostatic precipitators in furnaces and CO boilers that have particulate entrained in the flue gases.

## CURRENT APPROACH BY CERTIFYING AGENCIES

Certifying agencies such as CSA and FM have traditionally treated hazardous area safety on an "entity" basis, ie. they consider each device on a stand-alone basis. Heated instruments such as the $ZrO_2$ probe have historically utilized a "flameproof" protective strategy by placing a flame arrestor ahead of all sources of gas ingress including the sensing cell, the calibration gas line, and the reference air inlet and exhaust . While the agency approval stamp makes some users confident that an approved analyzer is now safe in all conditions, this may not be the case. The capability of flame arrestors to quench an ignition is tested by the agencies, but typically only at near-ambient temperature, so there is no guarantee that the flame arrestor will work at normal flue gas temperatures. Likewise, they do not consider that the cell flame arrestor induces a significant speed of response delay, especially in in situ probe arrangements, which has safety implications to the operations personnel who use this information to safely control the furnace.

From API RP 556

"Percent oxygen measurement is a process control variable which may be used for improving heater efficiency and maintaining safe heater operation."(4), and

"Oxygen measurements are critical in applications where extremely low NOx levels are required, as this may also require operation at a very low excess oxygen condition.(4)

Again, from NFPA 85, NFPA 85-2012 (section No. (A.6.42346(2)):

"It should be noted, however, that flame arrestors may only work below a certain temperature which is usually not quantified, may not quench a flame as well once it becomes corroded and may induce a response delay that could be detrimental to the control or protection strategy. Consideration should be given to powering down the analyzers during boiler or fuel trip situations if they can exceed the autoignition temperature of the fuel being fired"(3)

Some agencies have come to understand these trade-offs, and have approved in situ probes for hazardous area approval on the ambient side of the furnace, only, with no flame arrestor protection on the inside of the furnace, for those customers who do not consider the firebox to formally be a be hazardous area.(5)

## DEFINING A HAZARDOUS AREA

The safety officer at each refining or petrochemical plant typically draws the lines to determine what he or she considers as a hazardous area, or a general purpose area. Typically, the main concern is the ambient environment around a process, as opposed to the inside of the process. A boiler or process heater furnace, however, is a process that changes state. If the burners are running, the area can be considered as "ordinary". The heated sensing cell is of little concern during this time. When the main burners are out, however, the inside of the furnace should probably be considered as potentially hazardous if fuel continues to enter the furnace, or if combustible gases migrate into a cold furnace from some adjacent source.

## A SYSTEMIC APPROACH

While certifying agencies typically treat individual instruments individually, furnace safety is best implemented on a systemic basis. A good way of approaching the safety of the heated $ZrO_2$ sensor as well as other ignition sources is a scenario analysis of the different operational modes of a furnace:

Cold Furnace- Remove power from all ignition sources inside the furnace

Light-off - Remove power from all ignition sources inside the furnace. However, many operators will not want to wait 30 minutes or so for the $O_2$ analyzer to warm up, preferring to have the measurement immediately following light-off.

From API 556- "Some oxygen analyzers, such as zirconium oxide based sensors, may be an ignition source during purge if the firebox is cold or has cooled below the fuel gas ignition temperature. This may require a safety system interlock to disconnect sensor power. Upon purge complete sensor power is restored; however, the measured process variable (oxygen) may not stabilize until the sensor warm up period is complete (15-30 minutes)."(4)

In this case, instrument air can be directed down the calibration gas line to continually purge the sensing cell with fresh air as it warms up, and until light-off. Immediately upon proof-of-flame, the purge air can be removed, and the O2 measurement is available in a few seconds.

Again from API RP 555- “Another option is purge gas flooding of the cell.(4)

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|---|---|
| Normal Operation | No action. The assumption is that the flue gases are completely burned, and inert. Ignition sources inside the furnace are of little concern as long as operators and DCS control the Oxygen and/or CO or combustibles analyzer trends to safe and efficient levels. |
| Flame-out | Establish interlocks from the flame scanners or ion flame rods of the burner management system. Remove power from the analyzer heater, or the entire analyzer system. The heated sensing cell will take a few minutes to cool to below ignition temperatures, but this is surely faster than the cooling rate of the metal and refractory around the burner. |
| Relight | This is the most dangerous scenario, as fuel is reintroduced into a hot furnace. Ignition sources inside the furnace should be left off or purged with instrument air until proof-of –flame as with initial light-off. |
| Fuel/Air ratio upset | Refining and Petrochemical facilities usually burn waste gas that cannot be sold, and the varying make-up of these gases can cause large BTU changes. Use the analyzer indications to trigger interlocks to remove power from the sensor heater (or entire system), including any other ignition sources inside the furnace, based upon a low O2 reading.<br><br>Restating API RP556- “Percent oxygen measurement is a process control variable which may be used for improving heater efficiency and maintaining safe heater operation. “(4) |

## ADDITIONAL PROTECTIVE MEASURES

Other analyzer features have been designed to enhance safety:

- Operation at a reduced heater temperature of 550C. This reduces measurement accuracy somewhat, however.

- Hybrid heaterless operation - this analyzer is heated through the furnace light-off and warm-up phase of furnace operation, but once the flue gas temperatures reach 550C at the sensing probe location, power is removed from the heater. The power can be latched off, or permitted to turn on again if the flue gas temperatures fall below 550C, at the customer's option.

- A version of in situ probe has been approved for the ambient side of a furnace, only, with no flame arrestor ahead of the hot sensing cell.(5) Again, some operators utilize the other protective measures discussed, and prefer to get a faster response measurement without the flame arrestor.

- Continued operation through furnace upsets- as opposed to the analyzer alarming, and dropping off-line.

    - Many analyzers will drop off line if the process temperatures climb above the heater setpoint. This feature turns the heater off during these excursions, and calculates the oxygen values on the fly, using the current process temperature. $O_2$ readings are maintained to 800C, 850C, 900C—all the way to the sensor failure.

    - Continued operation through reducing events – The raw MV signal from the $Z_rO_2$ sensing cell is inverse, and logarithmic, ie. it increases as the $O_2$ values decrease. The MV values continue increasing in reducing conditions when there is no free oxygen in the flue gases.

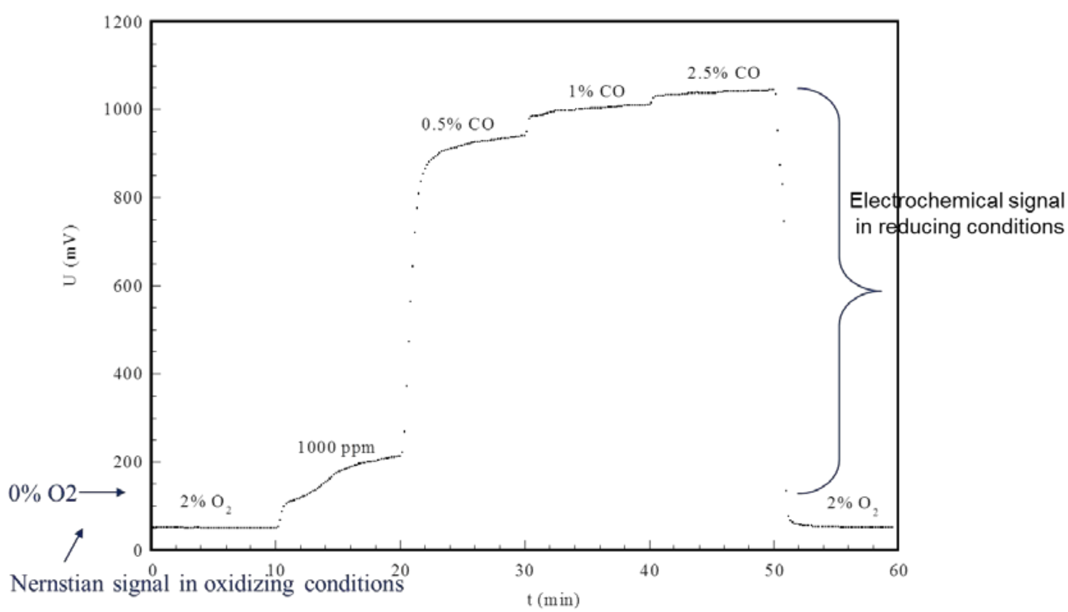


**FIGURE 1) $Z_RO_2$ CELL OUTPUT IN OXIDIZING AND REDUCING CONDITIONS.**

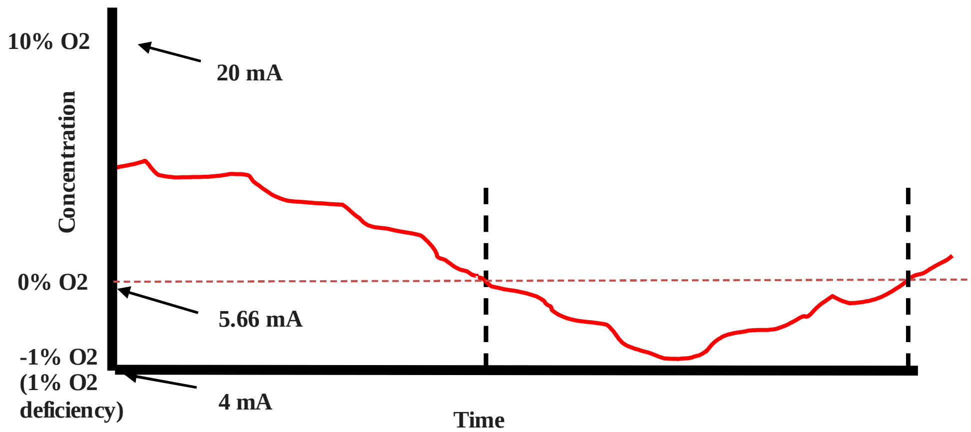


**FIGURE 2) REPRESENTATION OF A DCS TREND WITH AN ELEVATED ZERO, PERMITTING AN OXYGEN DEFICIENCY INDICATION.**

This can be implemented in the customer's DCS as an elevated zero, ie. as an oxygen-deficient indication showing up as negative $O_2$ indication.

This indicates to an operator :

1) The oxygen analyzer is still working. (Many operators immediately view a 0% $O_2$ reading as a failed analyzer.)

2) The furnace has gone into a reducing condition. Recovery can be tracked so that excessive air is not introduced during recovery

This feature is intended to provide a gross indication of the level of a reducing condition, and should not be confused with a separate CO or combustibles measurement.

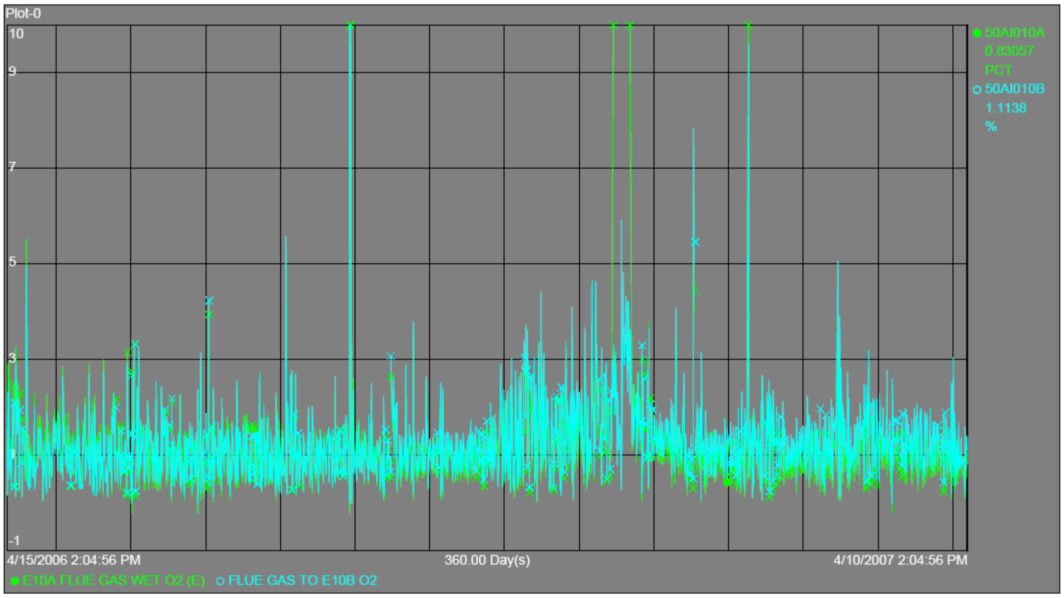


**FIG. 3) ACTUAL DCS TRENDS FROM AN FCCU REGENERATOR SHOWING OXYGEN PERIODIC OXYGEN DEFICIENT READINGS.**

# CONCLUSIONS

- The heated zirconium oxide sensor is one of the most ubiquitous gas measurements in use today, and more often than not utilized to drive an automatic control loop.
- The zirconium oxide sensor is heated, and should be considered as a potential ignition source.
- The boiler industry places a strong focus on knowing flame condition, specifying reliable burner management systems, and does not typically consider flue gases as dangerous, nor do they utilize flame arrestors to protect the flue gas ducts from a heated sensing cell.
- Although the Refining and Petrochemical industries have a strong focus on Hazardous Area Safety, they utilize many natural draft process heater furnaces that do not have

automation of individual burner air, and may not have burner management systems. Furnace light-offs are typically conducted manually.

- Certifying agencies approve flue gas analyzers as individual entities for use in hazardous areas, typically requiring the use of flame arrestors.
- It is not widely known that flame arrestors are tested at near-ambient temperatures, cannot be relied upon to work at furnace operation temperatures, and can induce a significant speed of response delay. Close-coupled extractive systems that draw a sample from the process experience much less response delay, but experience the potential for greater pluggage from particulate or condensed liquids.
- A systemic approach to addressing furnace operational scenarios permits ignition sources inside the furnace to be removed or purged during potentially explosive conditions.
- Additional analyzer features permit continued operation during furnace upset condions.

## Recommendations

- Take a systemic approach to furnace safety.
- Know your furnaces' flame condition- use flame scanners or flame rods, and automated burner management systems.
- Use interlocks to remove $ZrO_2$ analyzers as well as any other ignition sources upon flame-outs or reducing events.
- Use Instrument air purge to protect heated sensing cells during stand-by operation.

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