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Rugged, Verifiable, In-situ Oxygen Analyzers for Combustion Optimization in Sulphuric Acid Production

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Rugged, Verifiable, *In-situ* Oxygen Analyzers for Combustion Optimization in Sulphuric Acid Production

ABSTRACT

Combustion optimization in sulphur burners has always proved difficult. Extractive analyzers are prone to clogging and introduce both measurement offsets and time delays. Conventional, heated *in-situ* sensors have to be located in cooler regions of the furnace far from combustion and have similar time delays, a need for frequent calibration and are easily fouled by combustion and process by-products.

Non-heated, "high-temperature," *in-situ* oxygen analyzers have been used in this application but are fragile and require time-consuming insertion and removal processes to avoid thermal shock of the sensing element. Typical installation times can require several hours on a hot furnace. Finally, conventional non-heated analyzers do not meet zero-and-span criteria for United States EPA compliance, so a downstream unit is still required.

United Process Controls will present a new, robust, ceramic-composite analyzer that provides thermal toughness, allowing for fast insertion and removal. The new design also incorporates a focused flow system which provides zero and span capability in accordance with US EPA guidelines.

SULPHURIC ACID MANUFACTURING PROCESS

Sulphuric acid (H_2SO_4) is a strong mineral acid and the most produced industrial chemical. Major uses of H_2SO_4 include production of phosphate fertilizers, copper leaching, inorganic pigment production, petroleum refining, paper production and industrial organic chemical production. A nation’s industrial strength can be indicated by its production of sulphuric acid.

So called “wet” sulphuric acid plants are classified according to the raw materials processed in them: elemental sulphur burning, spent sulphuric acid and hydrogen sulfide burning, and metal sulfide ores and smelter gas burning.

The typical process (Fig. 1) incorporates 3 basic operations, each of which corresponds to a distinct chemical reaction. First, the sulphur in the feedstock is oxidized to produce sulphur dioxide (SO_2). The resulting SO_2 gas is cooled while passing through a waste heat recovery boiler to a process unit called a converter. In the converter the SO_2 is catalytically oxidized to sulphur trioxide (SO_3). Finally, the SO_3 is absorbed into a strong 98% sulphuric acid solution. The SO_3 combines with the water in the acid and forms more sulphuric acid.

Spent acid and/or hydrogen sulfide are also burned at elevated temperatures to provide SO_2 gas. In the case of spent acid, fuel is burned along with the spent acid in the combustion chamber to achieve the required decomposition temperature.

In any combustion reaction, oxygen and fuel are mixed to give off heat and combustion products. Typically, a fuel, such as natural gas or oil, is combined with air. Air contains only 20.9% oxygen with the remaining 79.1% consisting of nitrogen and other gases that are not required for combustion. These other components detract from the combustion process by absorbing heat, causing lower efficiency, and creating excess, undesirable emissions such as NO_x. Inaccurate control of air/fuel ratio produces quality issues with both the manufactured SO_2 precursor and H_2SO_4 final product. This can be costly to the manufacturer.

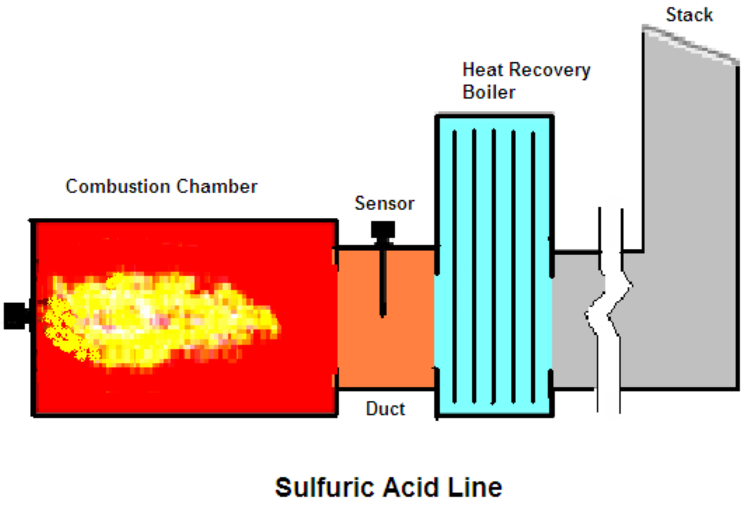

Figure 1. Typical installation location for a high-temp oxygen analyzer in the sulphuric acid production process.

Instrumenting the combustion process with oxygen-based controls can lower fuel costs, improve product quality and cut harmful emissions.

Unfortunately, this particular process is exceedingly arduous for materials used in oxygen analyzers and such systems usually have short life-expectancy and high maintenance costs.

OVERVIEW OF OXYGEN SENSOR TECHNOLOGIES

Types of sensors

The vast majority of sensors used in oxygen analyzers are electrochemical. There are light absorption sensors that operate in the blue range, but these have proved expensive and prone to signal loss owing to particulates and slag build-up on the optics.

Electrochemical cells used to detect oxygen include both solid and liquid electrolytic cells in both biased and unbiased configurations. For applications that don't require a fast response time, biased liquid electrolytic cells can be quite accurate, although somewhat difficult to set up and maintain in the field, particularly in outdoor environments. Biased, solid-electrolyte cells are uncommon owing simply to the complex construction requirements of a three-electrode electrolyte that must withstand high temperatures and remain chemically inert.

By far the most common industrial oxygen sensors are unbiased (two electrode), solid electrolytic cells. These sensors work on a specific solution to the Nernst-Einstein ion mobility equation, typically referred to as the “Nernst Equation” that relates the partial pressure of oxygen on one side of the electrolyte to the partial pressure on the other side of the electrolyte.

These sensors generate a millivoltage based on current flow from one side of the electrolyte to the other where the charge carriers are oxygen ions driven across the electrolyte because of the difference in oxygen partial pressure. The most common electrolyte used in these sensors is zirconium dioxide. Zirconium dioxide shows measurable ionic conduction above 650ºC so that these sensors can be used to measure oxygen concentrations from that temperature until the temperature where their stabilization agent (typically yttria) begins to evaporate from the lattice at about 1,600ºC. Based on a zirconium dioxide cell voltage and a measured temperature, these sensors can be used to determine oxygen levels from ppm to the percentage range in any highly kinetic or reducing process.

The chief liability of zirconium dioxide is its fragile nature. Prone to both thermal and mechanical shock, such analyzers, when made of a monolithic sensor, must be handled and heated carefully. Using small sensors brazed or cemented into steel structures has made more rugged versions, but these have serious calibration issues and obvious temperature limits owing to the steel used in their manufacture.

Wet versus dry measurements

It is common in combustion analysis to refer to either a “wet” or “dry” oxygen reading. This is, simply put, a designation as to whether the sample was conditioned – typically using some sort of dryer – before the oxygen reading was made.

A "wet" measurement is based on the assumption that the moisture content in a process gas stream is not removed and is a contributor included when the oxygen content is measured. The true *in-situ* oxygen analyzer provides a "wet" oxygen measurement.

A "dry" measurement is based on the assumption that the moisture content in a process gas stream is removed/condensed before the oxygen content is measured. Extractive type analyzers provide a "dry" oxygen measurement.

The two methods result in different levels of measured oxygen. The assumption is that this difference is due to moisture (H_2O). The dry measurement is consistently higher in oxygen percent.

Downstream versus combustion chamber measurements

The most common wet measurement analyzers are based on heated zirconium dioxide sensors. In this design a small tube or disc of zirconium dioxide is either cemented or brazed into a steel (typically 316) tube. The sensor is then heated with a resistive heater to ensure it has adequate temperature for ionic conduction.

As a result of the brazing, cementing and heating, these types of sensors introduce certain “offsets” from things like leakage of oxygen through the brazed union or cement union or poor heater calibration. As such it is critical, and often required, that these sensors be calibrated by means of flowing zero and span gases over the sensor on a regular basis (typically at least daily). This zero and span are used to find the Y-intercept and slope of the sensor's responsivity in the presence of anomalies such as leakage.

As temperatures increase these “offsets” also necessarily increase. Because the coefficient of thermal expansion for zirconium dioxide and steel can never be perfectly matched, the higher temperatures and temperature cycling lead to more and more leakage over time meaning the noise limited sensitivity also declines even if the curve can be “corrected” with a zero/span procedure.

Ultimately these designs have an upper limit of operation of either about 700ºC or 800ºC depending upon the alloys used in both the analyzer sheath and heater element. Many designs achieve high temperatures by locating the sensor's active element outside the actual process (typically in the head of the analyzer) and simply rely on a ceramic sample tube to draw process gas into the external measurement orifice. These designs are not truly *in-situ*, despite any such claims, and can readily clog in slaggy environments.

Because these heated sensors must be located in lower-temperature areas, they are typically far from the combustion process making them poor inputs for control owing to both time delays and inevitable air in-leakage that makes downstream measurements questionable.

For control applications it is far better to rely on wet measurements made as close to the combustion process as possible.

Advantages of *in-situ*, combustion zone measurements

By locating an oxygen sensor literally in the combustion zone – as close to the flame region as possible but not inside the flame since combustion in a flame is incomplete – one achieves a true measurement of excess oxygen without the artifacts of extraction, drying, in-leakage or seal leakage found in other approaches.

Since the electrolytic sensor is extremely fast and there are no plumbing/pump/duct passage delays the measurement is real-time with a step-change response time of well under 0.10 seconds. The high temperatures also serve to mitigate any slag build-up on such sensors since slag cannot form in the high-temperature, center portions of combustion zones or exit ducts from combustion zones.

These sensors make use of monolithic, tubular sensor elements that cannot “leak” like the lower-temperatures analyzers. As such they either work or they fail catastrophically when the tube cracks. This means they do not require any zero or span process to provide an accurate reading, although certain situations (such as regulatory compliance) might require such a process be performed on these analyzers.

Such measurements are, by far, the best means for controlling excess oxygen and have the added benefit of providing a simultaneous process temperature measurement for the sensor location.

Liabilities of traditional high-temp, *in-situ* analyzers

As with all things, conventional, high-temperature, *in-situ* analyzers are not perfect. Because they make use of a monolithic zirconium dioxide tube they are quite fragile. Mechanical impact can crack these tubes and any rapid changes in temperature can result in thermal shock and similar cracking.

Another liability of these analyzers is the need to verify the sensor reading or to comply with regulatory bodies that may insist on periodic “zero” and “span” calibrations. In a typical design of a high temperature sensor, a cylindrical protection sheath typically made of aluminum oxide surrounds the monolithic sensor tube. While it is possible to flood the gap between the sensor element and the protection sheath with zero and span gases, the high rate of flow in the sulphuric acid process creates enough agitation at the sensor tip that complete saturation is impossible.

Consequently, a zero and span procedure fallaciously “corrects” for an agitation process that only affects the zero and span gas; this same agitation has no impact on the process measurement. As such a “calibration” of this sort will result in a less accurate analyzer.

THE IMPROVED DESIGN

Toughness

United Process Controls sought to improve the conventional high-temperature sensor's toughness so that it would be more easily integrated into industrial processes where gingerly handling and slow temperature changes are not always possible. A number of configurations were designed and tested that used more complicated structures to use small sensors without the leakage problems associated with heated analyzers. These were not successful.

More recently a composite material was developed and tested. Instead of a traditional zirconium dioxide tube, a chemically and thermally stable composite was created that incorporated, amongst other components, aluminum oxide mixed with zirconium dioxide. The concept was to toughen the lattice at the expense of ionic conductivity. The result is a sensor that can withstand rapid changes in temperature without cracking and with only a marginal increase in the lowest operable temperature. Compared to the traditional sensor designs, which must be inserted no faster than 25 mm every 5 minutes into a hot furnace, this composite can withstand and insertion rate of 25 mm every 30 seconds. This means a typical 1 meter length sensor can be installed in just 20 minutes as compared to 3 hours and 20 minutes for a conventional design – a savings of 3 hours per installation.

The new sensor is also mechanically tougher, though detailed and quantitative destructive tests have not yet been performed.

Regulatory Compliance

In some localities an *in-situ* oxygen analyzer, coupled with a detailed knowledge of the feedstock, can be used to comply with regulatory bodies regarding emissions of NO_x so long as the analyzer can be zero and span calibrated. As mentioned before, this cannot be done with a traditional design owing to agitation at the sensor tip.

To remedy this situation a new design is used (Fig. 2) in which a closed tube with side holes allows process gas to reach the sensor element. Within the gap between the sensor tube and the protection sheath a series of small tubes are run from the head of the analyzer to the tip of the sensor tube where the active element is located. These small tubes surround the active element. By using these small tubes to introduce zero and span gases the active element can be completely saturated by the calibration gases even in very high flow rate situations. The new design meets regulatory requirements without resulting in a less accurate reading owing to a faulty zero/span procedure found in traditional designs.

CONCLUSIONS

A new ceramic composite, coupled with a new zero/span gas design, allow the latest generation of high temperature, *in-situ* oxygen analyzers to be used more easily, more reliably and in compliance with regulatory requirements for NO_x emissions monitoring in the sulphuric acid production process. Such analyzers, when used as an input to combustion and process control, have demonstrated substantial cost savings and process improvements within the industry.

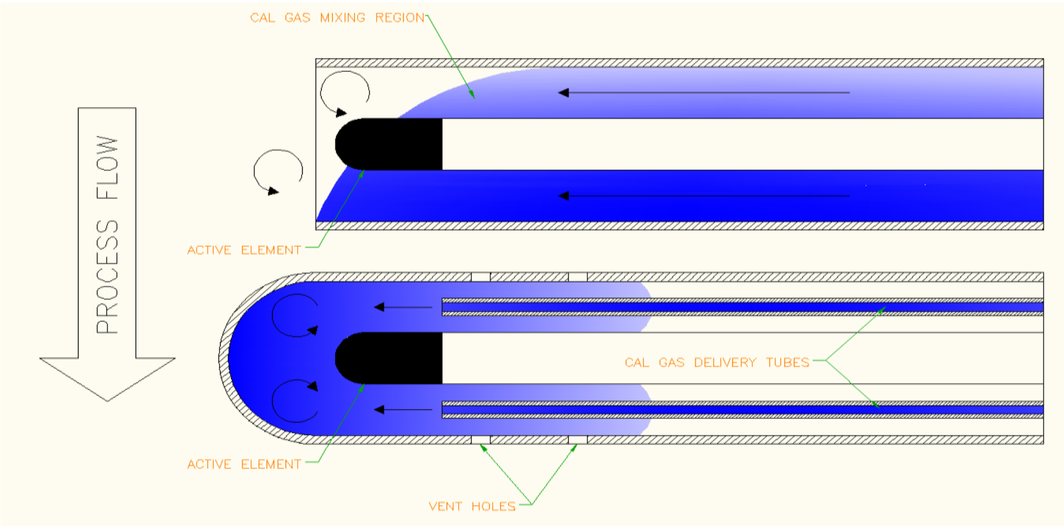

Figure 2. The new design prevents mixing of process gas and zero/span gas and allows saturation of the active element.

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