A NEW APPROACH FOR CONTINUOUS ATMOSPHERIC MONITORING OF HYDROGEN SULFIDE

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The vast majority of hydrogen sulfide monitoring systems historically use the solid state, semiconductor, metal oxide film type sensor. This type of H_2S sensor has some inherent traits which manifest themselves in the field as application problems. Examples of these application problems include lack of repeatability (span drift), partial or total loss of response with removal of power, frequent and complicated calibration requirements, desensitization with exposure to moisture and the need to subject the sensors to H_2S gas between calibrations to prevent them from "going to sleep". The following is an in-depth explanation as to how and why these problems occur along with the hows and whys behind a recommended solution.

Solid state semiconductor type H_2S sensors differ slightly in mechanical design among manufacturers but all are similar in sensing principle. This principle is the measurement of a resistance change across a heated metal oxide film. The metal oxide film, which is deposited between two electrodes, decreases in resistance as the exposed level of H_2S increases via surface adsorption.

Metal oxide film types and thicknesses vary, but all exhibit some common characteristics. One of these characteristics is their logarithmic response curve. The normal zero H_2S in air resistance across these MOx films (typically thin films) can be as high as 3-4 million ohms. This resistance normally needs to decrease to around the 100 thousand ohm region before the instrument will move off zero and full instrument scale reading can be as low as 10-15 thousand ohms. The control electronics simply take the anti-log of the sensor signal to provide a linear readout. This logarithmic nature explains why a multipoint calibration is required to set the amplifying control electronics within a specific range along this vast curve.

The descriptive phrase "going to sleep" in relation to these sensor types is a major application problem. The response characteristic of a MOx sensor based system can be detrimentally affected by the fact that there is no theoretical limit on how far the true sensor zero resistance can fall. The "going to sleep" syndrome is caused by a combination of the MOx film's high zero resistance and the effects water and the contaminants it may carry have on the film surface.

Both the susceptibility to moisture and the high zero resistance also greatly contribute to the solid state MOx type sensor's lack of repeatability. Exposure of the sensor's MOx film to water via humidity or direct washdown is one of the primary contributors to undesirable changes in the MOx film's surface which causes the system's non-repeatability.

Even brief exposures of the MOx film surface to water will cause the film's surface to change to a metal hydrate and eventually over time (as little as a couple of days) to an irreversible state of metal hydroxyl. Since this metal hydroxyl film state is insensitive to H_2S, it has, in essence, been rendered dead.

The incorporation of a heater on the solid state sensor chip is an attempt to bandaid the sensor's susceptibility to moisture. The heater prevents the settling of moisture on the MOx film by maintaining a surface chip temperature greater than 100°C. Another requirement for the heater in these sensors is their temperature-dependent rate of response. Maintaining a constant chip surface temperature is important in keeping response time and stability within an acceptable range. A sensor operating too cold will respond very slowly. A sensor operating too hot will respond very quickly but proceed to decline after peaking, thus demonstrating non-repeatability. A key in addressing the critical importance of this issue is to thermostatically control the heater to prevent surface temperature fluctuations due to environmental temperature and humidity variations.

The sensor heater and associated circuitry is a major power draw for these systems. The most efficient solid state MOx sensor-based systems will consume around 5 watts per channel, with the least efficient system consuming 15 watts. Of course, these power consumption comparisons are not "apples-for-apples", as the most efficient systems may not have a thermostatically-controlled heater.

Metal oxide film semiconductors also require the presence of oxygen to function correctly. This need is related to the surface adsorption phenomenon briefly mentioned earlier. MOx films typically exhibit high resistance values in H_2S-free air, attributable to the localizing of the film's electrons by the oxygen molecules. As H_2S is exposed to the MOx film surface, it competes for surface sites with the oxygen molecules. When the H_2S concentration increases and this surface site displacement occurs more frequently, the H_2S frees the electrons localized by the oxygen, thus decreasing the MOx film resistance and the associated sensor electrode voltage.

If oxygen is not present in the sensor environment, for example in a pure nitrogen or LNG pipeline application, the MOx film will gradually lose its normally high baseline resistance. This will be interpreted and indicated by the control circuitry as a positive response to H_2S.

It will not happen as quickly as the sensor's normal response to H_2S but it will cause a positive and ever increasing shift in the sensor's baseline. This restriction applies to calibration technique. Whether the technique is ampoules, permeation tubes or compressed gas cylinders, oxygen must be present to give an accurate calibration.

There are differences between thick and thin film MOx sensors in terms of susceptibility to moisture, response time and stability in background levels of H_2S. In general, thick film MOx sensors have a greater resistance to moisture problems but exhibit a decaying response in background levels of H_2S and are less repeatable.

From the inception of the H_2S detection industry, the solid state MOx technique was the best method available despite the above mentioned problems and limitations. However, the recent technological advances in electrochemistry have produced a technique which out-performs MOx film type sensors in reliability, repeatability, power consumption and required maintenance.

Next we shall describe this sensing technique which is not new in principle, but novel in its packaging and sensing chemistry approach. This new electrochemical technique overcomes all of the application problems inherent to the MOx film type sensors, particularly those that are applicable in the Permian Basin environments. It is an electrochemical cell supplied by Sieger Gasalarm in Tulsa, Oklahoma. It has been field tested for about four years and has completely replaced the solid state semiconductor type sensor formerly manufactured by Sieger.

The type of electrochemical cell we will discuss is classified as a fuel cell. A fuel cell operates by using a supply of chemical fuel as a source of energy. This cell should not be confused with other fuel cell types which consume cell components in their normal operation. It will consume only H_2S gas and oxygen in its normal operation. This reaction, using H_2S as the fuel being oxidized, occurs at what we term the working electrode (anode). This reaction is given below.

$$H_2S + 4H_2O \longrightarrow H_2SO_4 + 8H^+ + 8e$$

Also in the cell we have a counter electrode (cathode) where electrons generated from the working electrode reaction are recovered. These electrons are processed through external circuitry to give a current which is linearly proportional to the amount of H_2S exposed to the cell. In addition, the hydrogen ions produced from the working reaction interact with the available oxygen in the electrolyte solution at the catalyzing counter electrode to produce water. This reaction is given below.

$$8H^+ + 2O_2 + 8e \longrightarrow 4H_2O$$

Although only small currents are generated by these reactions (0.4 microAmps/ppm H_2S), the intrinsically low background current and low noise output of the cell produce an excellent sensitivity to H_2S.

As no electrolyte is consumed in these reactions, no periodic refilling of the cell with new electrolyte is necessary. As advanced mechanical design not only makes this cell exceptionally rugged, it produces a cell that is not position sensitive, which distinguishes it from other electrochemical type cells. The working and counter electrode surface areas are large, preventing saturation of the electrode catalytic sites. This helps to maintain a linear response and rapid recovery rate when exposed to significant levels of H_2S. For example, an electrochemical cell of this type recovers to less than a 3 ppm reading within 15 minutes after an exposure to 1000 ppm H_2S. Another contributing factor to the linearity and quick recovery rate is the use of an accurate and reproducible gas diffusion barrier and associated membrane which helps in controlling the volume of contaminated air diffusing to the working electrode.

Unlike MOx films, changes in humidity or direct exposure to moisture have little effect on this cell because of the reactions occurring in an aqueous medium. In theory, exposure of the cell to extended periods of dry humidity can result in the drying out of the electrolyte solution. However, this cell has been tested to a constant 10% relative humidity (RH) for up to 3 months without ill effects. In addition, once the RH increases, the cell will re-absorb any moisture that was lost during the dry spell.

The cell operates at ambient temperature without the need for a heater and the associated power consumption. This ambient temperature operation also reduces the potential for deactivation of the cell by contaminants which could coat or poison the surface of MOx films.

Ambient temperature variations from the range of -40°F to 120°F have only slight effects on the performance of this sensing system. Across this range, the cell zero could shift in the positive direction less than 3 ppm (0-100 ppm range). This shift would only occur at temperatures from 85°F to 120°F. The span or sensitivity is not affected by higher temperatures, but temperatures below freezing can cause a response shift not exceeding 5%. The above mentioned temperature variation effects on the electrochemical cell are negligible when compared to the problems these same temperature variations have on the performance of MOx film types, especially those without thermostatically controlled heaters.

The Sieger cell is manufactured to a very rigidly controlled specification and the reproducibility among cells is excellent. Direct field replacement of one cell with another without recalibration produces a response within 15% of the original. Obviously, with recalibration the replacement will respond to within our stated accuracy of less than 3% error.

The following page is a comparison regarding performance characteristics between solid state metal oxide film and electrochemical cell type sensors.

Comparison of Characteristics between Solid State MOx and Electrochemical Cell H_2S Sensors

	Solid State MOx	Sieger Electrochemical Cell
1.	Exhibits a logarithmic response curve without an absolute zero; requires 2 point calibration; causes "going to sleep" syndrome; and makes less repeatable.	The cell has a linear response curve with an absolute zero; allows one point calibration; precludes "going to sleep syndrome"; and ensures excellent repeatability.
2.	Requires a heater; exhibits response rate sensitivity to temperature and vulnerability of water adhering to and desensitizing MOx film.	A heater is not necessary as the cell is unaffected by moisture and relatively insensitive to response variations due to temperature.
3.	Requires frequent calibration; i.e., recommended at least every 3 months, but typically modified to one month.	The recommended calibration schedule is once every six months as the cell is more stable and repeatable.
4.	Requires oxygen in calibration technique, which makes calibration hardware more expensive, and the calibration procedure more complicated.	The calibration technique used is a single cylinder of H_2S in N_2 which is less costly and greatly simplifies operator interface during calibration. This cell can operate for extended periods without oxygen for calibration purposes with no noticeable shift in the cell's baseline.
5.	Demonstrates high power consumption; a minimum of 5 watts per channel or point.	The power consumption of 1.5 watts per channel is less than 1/3 the power consumed by a typical solid state semiconductor system. This benefit has particular importance with regard to solar powered installations and battery back-up considerations.
6.	Needs extended warm-up for initial commissioning or sensor replacement before calibration (some manufacturers recommend 24 hours).	The plug-in cell design does not need a lengthy warm-up time (maximum of 10 minutes) for stabilization before calibration.

A field evaluation is the most effective way to insure compliance of a system manufacturer to the performance specifications or characteristics that are important to an end user of an H_2S monitoring system. A field evaluation is more advantageous than a laboratory evaluation because it is extremely difficult, if not impossible, to duplicate all the environmental variables for a particular application in the laboratory. In addition, the desirable field operator involvement is generally not possible in a laboratory evaluation.

Testing criteria in an evaluation should be well defined. Listed below are some recommendations for evaluation testing to address key operational issues in the field.

Evaluation Site: The most obvious recommendation is to locate the evaluation system(s) at a site that is as close to, if not the same as, the environmental conditions where the purchased H_2S monitoring system(s) will be installed.

Length of Evaluation: In general, the longer the evaluation period the better. It is difficult to effectively test reliability and maintenance criteria in an evaluation period lasting less than 3 months.

Repeatability: Repeatability is an essential part in the establishment of a reliable H_2S monitoring system. In basic terms, it is how far the system span drifts from the original calibration over time, and can be evaluated by periodically exposing the sensor to the same concentration of H_2S gas without adjusting zero or span during testing period. The less repeatable a system is, the more frequent it will require re-calibration.

Calibration Ease: If a system is difficult to calibrate, it probably will not receive the proper attention after installation. The calibration hardware should be easy to operate and store and the procedure simple.

Response Time: How quickly a system responds to H_2S is important and can be measured to some degree during calibration. The presence or absence of background levels of H_2S can greatly affect the response time of some systems and should be noted.

Ambient Environmental Conditions: The effects of dust, rain and variations in temperature and humidity should be measured in terms of zero drift, span drift (repeatability) and response time.

Loss of Power: Power outages are not uncommon and their effects on a system and the manufacturer's warranty should be appraised.

Overexposure to H_2S: High concentrations of hydrogen sulfide can cause problems with some H_2S sensors. System span and zero should be checked after such exposures which can be artificially induced through a cylinder containing a high concentration of H_2S gas in nitrogen.

Local Spares and Service: Ideally, an H_2S monitoring system should require little maintenance. However, at some point, if not during initial installation and commissioning, the need for local technical assistance or system spares will arise. This is particularly true for West Texas applications.

Equipment Warranty: A system or sensor warranty is a good gauge for the true confidence a manufacturer has in its product, providing the company and product have been around longer than the stated warranty. Consideration should be given as to whether the manufacturer's stated warranty is unconditional or limited, and what, if any, those limitations are. It is also important for an end user to educate their technicians and set up a proper recording program to insure credit or replacement should a premature failure occur.

Power Consumption: A system power consumption specification as supplied by the manufacturer should be noted and confirmed during testing. Power consumption is of primary concern in applications where a battery back-up system is supplied or primary solar power is used.

Hopefully the technical discussion and specific recommendations provided with regard to H_2S monitoring systems will enable you to understand the problems experienced by the oil and gas industry in the past, and provide some solutions for resolving them in the future.