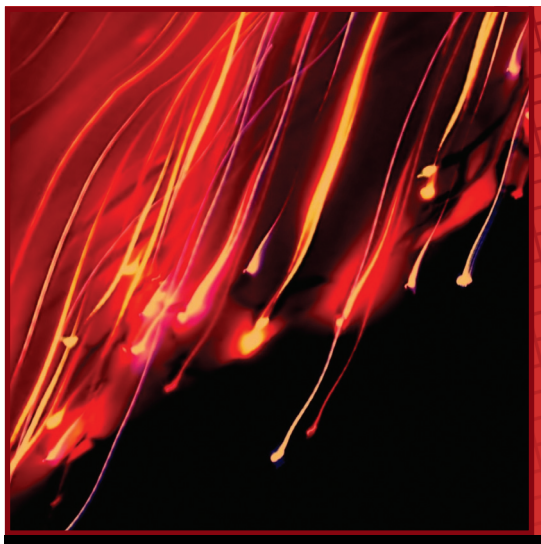

Monitoring Large Hydrogen Sulphide Releases:
Why Sensor Recovery Time Is Important

Edward Naranjo Ph.D., NPDP, Global Technical Product Manager, General Monitors
26776 Simpatica Circle, Lake Forest, California 92630 USA
Tel: +1-949-581-4464 • Email: info@generalmonitors.com • Web: www.generalmonitors.com

Hydrogen sulphide (H_2S) is a highly toxic gas and among the most common contaminants in crude oil and natural gas. Not surprisingly chemical process and petroleum facilities use H_2S gas detection systems to assure personnel are alerted to hazardous gas releases or to detect and avert large releases that could pose a significant hazard to personnel, property, the environment, or public outside the plant perimeter. To address the likelihood of such hazards, plant operators have a variety of sensor technologies at their disposal to choose from. Electrochemical sensors, solid state sensors, impregnated paper, and laser based open path detectors are among those methods used to supply early warning and initiate an appropriate automatic protective response.

With such a number of detection techniques, however, it becomes difficult to identify the one that best matches the unique requirements for each plant. All too often operators select hydrogen sulphide detectors based on sensitivity or speed of response alone, believing such instruments can mitigate minor toxic gas escapes. Unfortunately such thinking can lead to poor process safety design. The issue being the fact that fixed area gas monitors can only be deployed to maximise the likelihood a leak is detected[1]. Atmospheric conditions, especially wind direction and velocity, the proximity of the leak to the detectors, and obstructions, which may prevent the gas from reaching the sensor or traversing its path, affect detection efficiency. Additionally, the size of the release can influence the type of gas detector that best fits the characteristics of the release. Impregnated paper, for instance, is accurate at low concentrations, but not wholly suitable for detecting large gas plumes. Without such understanding, plant personnel are likely to believe that the level of protection the gas detection system offers is adequate when it is not.

One of the most common H_2S detection methods is solid state sensing. Solid state sensors consist of one or more metal oxides from the transition metals, such as tin oxide (SnO_2) or tungsten oxide (NO_3). These metal oxides are prepared and processed into a paste to form thick films or deposited as thin films through vacuum deposition onto a silica or aluminium oxide substrate. This latter process is similar to that used for fabricating semiconductors; hence the name metal oxide semiconductor (MOS) for which they are commonly known.

When exposed to gas, gas molecules react on the metal oxide surface and dissociate into charged ions or complexes that alter the resistance of the film[2]. This change is dependent on the physical properties of the metal oxide film as well as the morphology and geometric characteristics of the sensing layer and the temperature at which the reaction takes place. A heater circuit raises the temperature of the film to a range that yields optimal sensitivity and response time to the gas to be detected. Additionally, a pair of sensor electrodes or bias electrodes is imbedded into the metal oxide to measure the change in resistance. This variation of the sensor that results from the interaction of the gas molecules with the film is measured as a signal and is completely reversible. This signal is then converted to a gas concentration.

Solid state devices offer many advantages for process safety. Among these, response and recovery times are paramount for practical applications. Without fast recovery, a detector may not be able to inform whether one or several leaks have occurred in short succession or just how much gas has escaped into the atmosphere. A sense of the severity of the gas dispersal in the seconds after an accident can aid in decisions by emergency response personnel; it may help save lives before the hazard escalates or determine when it is safe for rescuers to move into an affected area. Moreover, a detector that recovers quickly can provide a time-stamped record of the incident, useful in the reconstruction of the event during an investigation.

Due in large part to such properties, solid state sensors are commonly used in petroleum and chemical process facilities. They monitor for gas releases at refineries, offshore production platforms, onshore well sites, and other locations, many of which manage process streams that contain significant quantities of H_2S. Because of their quick response and recovery, solid state sensors fit well with plants that must safeguard against large leaks in areas of high-potential release sources.

High Dosing

Solid state sensors, unlike electrochemical sensors, are resilient to repeated dosing with high concentrations of H_2S. Consider the response of four SnO_2 sensors, calibrated to 100 ppm, and exposed to 100 to 1,500 ppm by gas injection and using air as the balance gas (Figure 1). As shown, all sensors respond to the incremental concentrations of H_2S. The accuracy of sensor readings is within 10% of the applied gas, while recovery times (T_{10}) for 100 ppm and 1,500 ppm are 10 and 14 seconds, respectively.

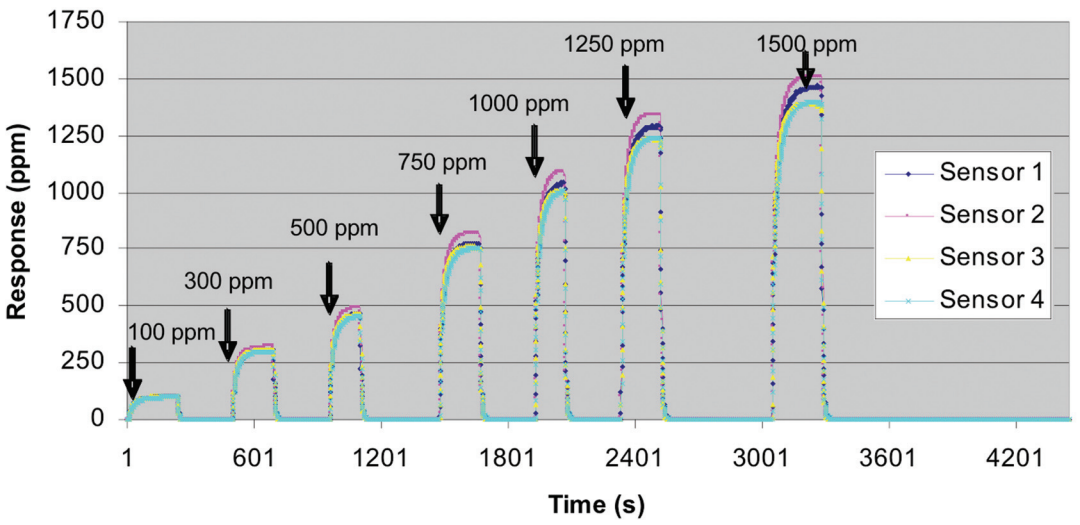

Figure 1: Response of Solid State Sensor after Calibration with 100 ppm H_2S.

Similarly, recovery does not vary greatly when SnO_2 sensors are exposed to a large concentration of H_2S for 5 minutes or 20 minutes. Table 1 illustrates the response and recovery times for sensors calibrated to 25 ppm. All sensors recovered within 70 seconds.

Exposure Duration (min)	Time (s), Response to 50% of Full Scale	Recovery Concentration (ppm)	Time (s), Recovery to 50% of Initial	Time (s), Recovery to 10% of Initial	Time (s), Recovery to 0% of Initial
5	< 2	0	10	15	40
20	< 2	0	10	30	70

Table 1: Response and Recovery Time to Exposure to 1,000 ppm H_2S.

The accuracy of the H_2S MOS detector at 25 ppm was measured 40 minutes after flooding. The difference between measured readings after 40 minutes and the initial exposure was 3 ppm or 12% of the initial reading.

Solid state sensors show good recovery properties when exposed to H_2S concentrations approaching combustible levels (LEL = 4.0% by volume). For example, when injected with 10,000 ppm H_2S (25% LEL), a commercial MOS sensor responds in less than 2 seconds with an over range or alarm indication, and upon removal of the gas, recovers to 10 ppm in approximately 31 seconds. The recovery time is not significantly different for sensors exposed for two hours or less. In contrast, an electrochemical cell exposed to 10,000 ppm H_2S takes over four hours to recover (see Figure 2). Furthermore, during the first two hours following exposure, the electrochemical sensor readings were erratic. Only after its recovery did the device display good accuracy and low baseline drift. The electrochemical cell's recovery times T_{50}, T_{10}, and T_0 are shown in Table 2.

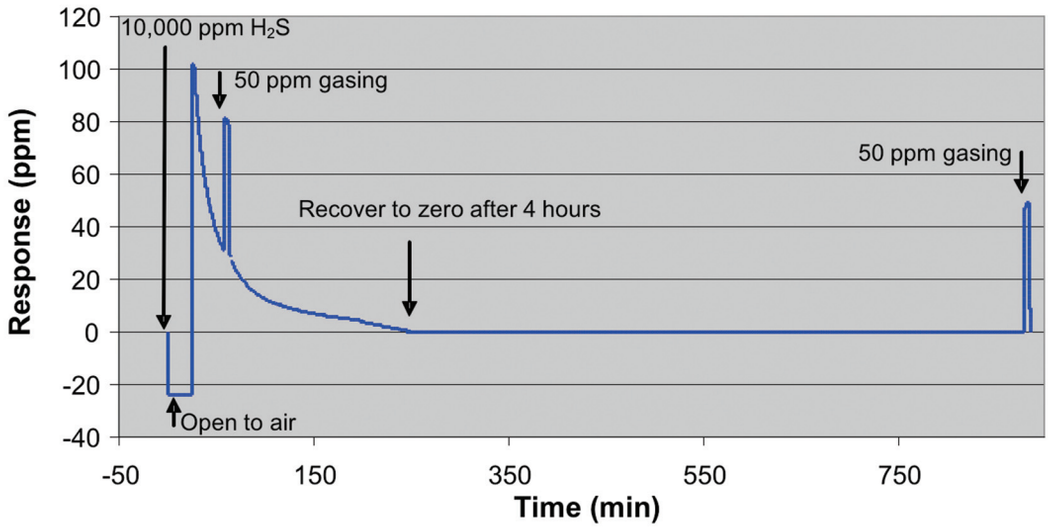

Figure 2: Response and Recovery of Electrochemical Sensor from Exposure to 10,000 ppm H_2S.

Exposure Duration (min)	Time (s), Response to 50% of Full Scale	Recovery Concentration (ppm)	Time (s), Recovery to 50% of Initial	Time (s), Recovery to 10% of Initial	Time (s), Recovery to 0% of Initial
5	< 2	0	35	105	240

Table 2: Response and Recovery Time to Exposure to 10,000 ppm H_2S.

Best Practice Applications

Response and recovery times are important considerations when selecting H_2S gas detectors. A sulphur recovery unit of an oil refinery handles large volume streams of hydrogen sulphide. In consequence, these units have fixed detection to incorporate some degree of protection. These detectors are installed along access routes, near potential leak sources, and areas where gas might accumulate. Because of high concentrations of H_2S in process streams, even small localised leaks have a high hazard potential. Both electrochemical and solid state detectors linked to an alarm system may provide the fastest approach to alert plant personnel.

Certain enhanced oil recovery operations (EOR) that use carbon dioxide (CO_2) are subject to combustible levels of H_2S. In the Zama Field in Alberta, Canada, CO_2 and H_2S are injected to increase oil production, sequester the greenhouse gas, and dispose of H_2S[3]. In CO_2 EOR facilities, H_2S detectors are placed around injection wellheads, manifolds, and compressors. Since process modules are open to the environment, detectors are primarily used to monitor potential sources with high probabilities of failure or having the potential for a large gas release. Solid state detectors are well suited to the application due to their versatility and quick recovery.

In offshore production facilities, H_2S detection is paramount. Consideration of many variables, including concentration of H_2S, process pressure, ventilation, temperature, equipment location, suggests care in selecting detectors. Indeed, electrochemical, solid state, and laser based open path detectors can be installed on the same platform to avert several release scenarios.

Conclusion

By the very scale of their operations, many industrial sites handle toxic materials at concentrations several times greater than the accepted Permissible Exposure Limit (PEL). For this reason, there is the likelihood that gas detection systems installed to safeguard personnel against hazardous releases will be exposed to large leaks. Under such circumstances, gas detection systems must respond and recover quickly.

Solid state devices are resilient to over range exposure to H_2S, and recover within half a minute to flooding at 100 times its concentration scale. Such versatility makes MOS sensors an ideal choice in many installations, where potential gas escapes may involve ranges in magnitude. The sensors are widely accepted in North America, the Middle East, and East Asia. In a survey by the Canadian Association of Petroleum Producers, researchers found fixed area MOS H_2S detectors met or exceeded expectations when monitoring for leaks at 10 and 15 ppm[5]. Other end users report H_2S fixed area detectors are installed primarily to alert operators to leaks and equipment failures in process areas that are often unoccupied.

In areas contaminated by a leak, solid state detectors' quick recovery results in greater availability of the safety system. Valves may be isolated sooner; ventilation intakes to accommodation and control quarters may be closed in time to prevent H_2S ingress; and the process for increasing ventilation to affected modules may be performed more effectively. System availability enhances safety. Fast recovery also allows for a better understanding of hazard severity and escalation, as changes in gas concentration may be monitored over time. Given such properties, the use of solid state sensors as a practical method to detect H_2S gas releases is likely to increase.

References

1. Continuous Monitoring for Hazardous Material Releases. 2009. Hoboken, New Jersey: John Wiley & Sons.
2. Korotcenkov, G. 2005. Gas Response Control through Structural and Chemical Modification of Metal Oxide Films: State of Art and Approaches. Sensors and Actuators B 107 (1): 209 – 232.
3. "Sour" Gas Streams Safe for Carbon Sequestration, DOE-Sponsored Study Shows, U.S. Department of Energy, http://www.fossil.energy.gov/news/techlines/2010/10046-PCOR_Project_Demonstrates_Importan.html. Downloaded 5 September 2012.
4. ISO 10418, Petroleum and natural gas industries – Offshore production installations – Basic surface process safety systems. 2003. Geneva, Switzerland: ISO.
5. A Feasibility Study on Responding to a Lower Hydrogen Sulfide Exposure Limit for Workers. 2009. Calgary, Alberta, Canada: Canadian Association of Petroleum Producers.