Multichamber Reference Cell Ensures Measurement Accuracy Of Electrochemical Sensors

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Model S4000T is an intelligent gas sensor designed for hydrogen sulfide monitoring applications. It features long distance remote monitoring, 3-digit display, and a 4-20 mA output. Fault codes are also available for troubleshooting and redundant MODBUS communications transmits status to the control room.

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**Instrument Platform**
The 994 Integrated Instrument Platform (M2C2- Intelligent) is enclosed in a 3/16 DIN panel-mount NEMA 4/4X package, supports four advanced technology universal 1/0 ports, three networkable local/remote communication serial ports, data logging, and multiplexed signal measurement interface. Built-in process control functions include linear PID, batch, dose, monitor and manual operation, with data logging and automatic information reporting supported by an internal real-time clock-calendar.

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A supplement to IAN Instrumentation & Automation News www.ianmag.com

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The failure of the sensing elements within an electrochemical sensor is as inevitable as death and taxes. In operation, electrode elements are routinely exposed to extreme temperatures and aggressive chemicals ranging from high pH liquids like sodium or potassium hydroxide to low pH fluids like hydrochloric acid, and virtually everything in between the extremes. The instant that sensor electrodes first contact the fluid to be measured a poisoning process begins and the electrodes begin to degrade. Eventually this degradation compromises the measurement process, begins to produce inaccurate readings, and actually threatens the integrity of a continuous wet process or the quality of entire batches of materials.

To complicate matters somewhat, electrochemical sensor degradation occurs in situ, which means the entire sensor assembly must be completely removed from the process stream – often located in hazardous or physically inaccessible environments – to conduct necessary maintenance and to determine the accuracy and integrity of its readings. Unfortunately, the standard maintenance techniques employed today have a major drawback in that they can only demonstrate that the instrument is providing accurate (or inaccurate) measurements, and by how much. Without a means to detect, measure or even track the level of poisoning or contamination of the electrode as it occurs, process engineers are effectively blind to the progressive, looming death of the sensor electrode and may not even know that their process is at risk until too late.

Preemptive Maintenance Trap

In any industry with liquid processes, variations in pH, ORP or other specific process concentrations are subject to stringent specifications beyond which end products must be discarded. To ensure the accuracy of their processes, users can either perform frequent preemptive maintenance to test installed sensors or estimate the intervals when sensor electrode replacement should occur. Since most electrochemical sensors cannot be inspected and tested without removing them from a line or vessel, many process engineers prefer the frequent replacement of electrodes, regardless of their useful remaining life. This preemptive maintenance approach is costly in terms of both replacement parts and manpower, not to mention the intrusion into the process itself and the accompanying production downtime.

With electrochemical sensors used throughout the different phases of a process-from measuring the purity of influents such as water to measuring the quality of liquid ingredients comprising the final product, to monitoring effluents
such as wastewater this brute force disposable approach of wholesale sensor replacement is very expensive," says Larry Berger, a sensor design engineer for more than 25 years and president of Electro-Chemical Devices, Inc. (ECD), a Yorba Linda, CA based process instrumentation specialist. "When you consider the need to carry inventories of sometimes dozens of models of sensor electrodes that many process plants require, the real costs of sensor replacement strategies escalate even more."

Berger claims that even pre-emptive replacement is a risk, as it does not preclude the possibility that the electrode being replaced may already be malfunctioning and producing inaccurate readings. "Engineers that base electrode replacement on history and limited diagnostics can only assume they are replacing the electrode early enough to protect their processes, when what they really need is a sensor system that can alert process engineers as sensor degradation begins. Then they can manage the replacement process proactively."

"Better insight into the measurement process and control status would alleviate the frequent and needless expense of changing electrochemical sensors, as well as the risk of unwanted process variations," says Berger. "Our goal in designing our Sentinel line of electrochemical sensor/transmitter systems was to produce a sensor system with selfdiagnostics that would work in situ in real-time to monitor electrode degradation and provide a pre-pHault function to warn process engineers of impending sensor degradation."

**Tracking Sensor Deterioration**

Today’s electrochemical sensors are typically made up of two cells - a measurement cell that has specific reactivity with the specimen ion or ions to be measured, and a reference cell that is used to maintain a common electrical potential with the specimen fluid being measured and provide a stable output regardless of the specimen ion concentration. For example, in the case of a pH sensor, the specimen ion-sensing electrode can be a hydrogen ion sensitive glass bulb with a millivolt output that varies with the changes in the relative hydrogen ion concentration inside and outside of the bulb. At the same time, the reference cell in a pH sensor will exhibit an output that does not vary with the activity of the hydrogen ion.

The reference cell is the structure in which most problems can occur within an electrochemical sensor. It consists of essentially three parts: an internal element such as a metal-metal salt (e.g., Ag/AgCl, Pt/Hg2Cl2, etc), a filling solution or electrolyte, and a liquid junction through which the filling solution contacts the desired specimen to be measured. The electrolyte provides the conductive bridge to the specimen fluid and surrounds the reference element with an electrochemically stable environment. In order to obtain accurate readings, this liquid junction must be in place. In the ideal liquid junction, electrolytic contact between the reference element and specimen fluid would provide the necessary communication, yet prevent the specimen fluid from mixing with the electrolyte. However, liquid junctions cannot be perfect, and mixing will ultimately occur between the electrolyte and the specimen fluid during contact.

When the electrolyte of the reference cell mixes with the specimen fluid, the defined chemistry surrounding the reference element changes and the stable electrochemical environment deteriorates. Users of these sensors can only determine this deterioration by placing the sensor in a standard solution and comparing the results with theoretical expectations. Doing so only determines that a difference from ideal exists and a process of substitution must be performed to determine which element (ion specific, reference or instrumentation) was responsible for the discrepancy. In this world of disposables, some users find that it is cost effective to simply replace the measurement elements on a periodic basis-the preemptive maintenance trap-to eliminate the labor involved in constantly testing to determine the reliability of the measurement.
Electro-Chemical Devices has designed a new class of sensors that contain the Sentinel multi-stage electrode system. These sensors provide critical pH, ORP or Specific Ion measurements in liquids while constantly monitoring the status of all components of the sensor in operation, alerting users of approaching sensor degradation before there is a problem. This diagnostic innovation greatly enhances the reliability of the measurement by constantly monitoring the deterioration of the reference liquid junction half-cell and displaying the results on the Sentinel transmitter instrument.

In operation, the Sentinel transmitter instrument displays the degradation as it occurs in the front chamber of the multi-chambered liquid junction of the attached sensor. In monitoring the front or process chamber the diagnoses of contamination/dilution of the reference electrolyte is detected before (pre-pHault) it can actually affect the measurement. In effect, the Sentinel transmitter/sensor system provides an outer level of defense within the reference cell, giving an early warning of potential reliability problems within the inner chamber of the sensor.

To perform this pre-pHault diagnostic function, each Sentinel sensor contains an additional chamber isolating the reference half-cell from the process (as shown functionally in the accompanying figure). The potentials $e_1$, the reference half-cell and $e_2$, the measurement half-cell are shown in their controlled and predictable environments. If the two reference cell potentials - $e_1$ and $e_2$ - are equal, they cancel and are not a factor in the measurement. As mixing of the electrolyte and the specimen fluid that form the ionic bridge in the reference junction of the outer cell occurs, the interchange of material dilutes the reference cell electrolyte and the output of the outer reference half-cell varies from its nominal value. By monitoring changes in $e_1$, the Sentinel transmitter system can actually measure the poisoning and progressive degradation of the sensor through contamination, and alert an operator when the relative concentrations exceed the preset limit that compromises the accuracy of measurement.

As contamination caused by the mixing of the electrolyte and the fluid to be measured occurs in the outer reference chamber of the sensor (denoted by color change within the sensor in this diagram), the solid bar on the upper right hand side of the display grows larger until an operator-set limit is reached. At this point the bar begins to flash, alerting the operator to service the attached electrochemical sensor. Note that the degradation of the sensor is displayed to an operator without having to remove the sensor from its monitor/control function and without affecting the measurement. This innovation effectively contributes to the reliability and quality of the product or process being performed while also saving resources required to periodically remove sensors from the process for inspection and calibration.

**Improved Process Reliability...And More**

"The savings in manpower and inventory accruing from optimized sensor replacement practices, along with the enhanced reliability of process measurements, make the Sentinel sensor/transmitter system essential in any process instrumentation environment, and a virtual 'must have' for anyone responsible for quality control of the facility," says Berger. "Whether the user is employing the local display on the transmitter to monitor sensor degradation, or using the built-in 4-to-20-mA signal loop or alarm circuits to feed status information back to a remote monitoring and control system, the new Sentinel transmitter/sensor system sets a new standard for electrochemical measurement reliability in both batch and continuous process environments."

Berger noted that the Sentinel sensor family offered several other benefits to those users who are ready to experience the enhanced reliability it offers. "Each Sentinel sensor includes built-in electronics that allows process engineers to locate the transmitter up to 3 miles away from the measurement while still retaining measurement precision and accuracy and the ability to remotely monitor sensor integrity. We also offer replacement cartridges for all Sentinel sensor electrodes and liquid junctions, so when it is time to replace the degraded measurement elements, users simply plug-in a new electrode, complete with liquid junction cartridges saves time and money by lowering replacement costs and reducing inventory carrying charges," he noted.

For more information, contact **Electro-Chemical Devices**, 23665 Via Del Rio, Yorba Linda, CA 92887. 800-729-1333. www.ecdi.com