OLD PROBLEMS, NEW SOLUTIONS IN pH SENSOR DESIGN

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Introduction

Dairy processors have been measuring pH for a long, long time. It's a basic measurement of milk quality — a verification of freshness at the farm, at the point of transfer to the dairy, and throughout the processes that produce everything from bottled milk, to yogurt, cheeses, and other products. Rapid and accurate pH measurement is essential for safe and efficient continuous and batch processing, from the measurement and addition of ingredients, to process timing, and the maximization of product yield. It's also a vital measure in maintaining process cleanliness in a manner that minimizes the use of water, cleaning solution, labor time, and other resources.

Maintaining a high level of confidence in process-wide pH measurement is essential for efficient production, but it's never been particularly easy or inexpensive. Measuring pH has always been a maintenance and inventory-intensive process because, with a few recent exceptions, the design and technology of most pH sensors has changed little for a long, long time.

The fundamental element in process-wide pH measurement continues to be the 12-mm pH sensor, a product that was developed and proven in laboratories decades ago. Most of these still feature the same basic attributes as they did a generation or more ago:

- A 12-mm glass body.
- A domed measurement electrode, containing a silver/silver chloride half cell.
- A silver/silver chloride reference electrode.
- A temperature compensation sensor.
- A reference junction that establishes a conductive path between the measured fluid and the reference electrode.

Sensors that utilize this basic design continue to serve today because they're essential to process performance. But key characteristics of their aging, laboratory-inspired designs pose growing obstacles of time, effort and cost to process operators. This paper will examine three key concerns — sensor fragility and breakage, the lack of sensor diagnostics, and the sources of reference electrode failures — and discuss new thinking in pH sensor design, aimed at creating 3-A Sanitary compliant pH measurement solutions that better fit with the current needs of food, beverage, and dairy process operators.

Problem 1: Losses due to fragility and breakage

Typical glass-body, dome-type pH sensors aren't very durable. Their design, which was optimized in a lab, was never really toughened or ruggedized to meet the needs of process operation personnel who have to install, remove, clean, rebuild, and calibrate these fragile instruments regularly without breaking them. Handling damage and breakage problems are significant enough that in some processing facilities, special training in glass handling has become mandatory to reduce losses and their associated costs.

Glass body pH sensors are widely used today in food, beverage, and dairy operations because they are non-reactive, easy to clean, and because they make a relatively good external container for electrode elements that are bathed in liquid or gel electrolyte. But glass bodies aren't strictly needed for many food, beverage, or dairy applications. Foxboro found that pH sensor bodies made of PEEK (Polyetheretherketone) met requirements for most applications while providing superior durability and breakage resistance.

There is one place — the measurement electrode itself — where a glass material is essential for proper performance. Electrode glass is specially formulated from silica and other ingredients that give the glass selectivity properties that are essential to sensing hydrogen ions from the measured fluid that are needed to read its pH level. This specialty glass remains a relatively fragile element, though it is somewhat less likely to break when encased in a plastic outer body.

The shape of the measurement electrode also factors into sensor durability. Most pH sensors utilize dome-shaped measurement glass, which protrudes outward into the process flow from the base of the sensor and therefore, remains vulnerable to damage in handling or from aggressive process flows. A more durable alternative is a ruggedized "flat" electrode that is built to remain essentially flush with the base of the sensor body. However, adoption of flat sensors was at one time, limited due to the non-availability of ruggedized, high-temperature pH sensitive glass. Extensive research by Foxboro was successful in developing a proprietary glass formulation for flat electrodes (Figure 1) that is rated for use at temperatures up to 125°C (257°F). This innovation, together with advanced flat electrode technology that rivals the pH measurement range and speed of domed electrodes, now makes flat ruggedized electrodes ideal for use in food, beverage, and dairy applications.

Figure 1. Improving pH sensor durability demands innovations to reduce the risk of breakage while preserving the cleanability, selectivity, and performance associated with glass bodies and dome-style glass electrodes. The Foxboro PH12 family of 3-A Sanitary compliant pH sensors incorporates a durable PEEK body with a specially engineered, ruggedized flat-glass electrode.

Problem 2: Limited sensor diagnostics impede preventive maintenance

The trend for corporations to maximize process yields while minimizing labor costs has led process operators to run with leaner staffs, more automation, and to emphasize the use of predictive and preventive maintenance strategies. But implementing these strategies in the case of pH measurement has been challenging for many operators. Until recently, they had to choose whether the benefits of preventive maintenance would outweigh the incremental costs of equipping their pH sensors with the additional features needed to enable comprehensive diagnostics. Traditionally, this has involved ordering sensors equipped with an optional solution ground, typically made of platinum — an expensive proposition. The alternative, also expensive, was to burden process personnel with maintaining troublesome pH sensors through a time-consuming process of removal, testing, calibration and reinstallation to make up for the lack of sensor-based diagnostics.

Solution grounding is essential to pH sensor diagnostics because it provides a reference point — a stable ground — against which an array of diagnostic measurements can be made to check the integrity of other sensor elements. For example:

- Detecting an increase in the resistance of the reference electrode often indicates that it has become coated, or is fouling, and needs to be removed and cleaned to prevent measurements from becoming unstable or sluggish.
- A drop in the resistance of the measurement glass indicates a loss of integrity, possibly due to breakage, while increased resistance indicates that the glass is wearing out, losing its ability to easily sense the ions needed for accurate pH measurement.

When a solution ground is available, these diagnostic signals are readily obtainable for reference on a transmitter. Guesswork is eliminated, because the source and likely cause of pH sensor faults are identified. With real-time sensor status information available, preventive maintenance can be effectively implemented, with personnel labor focused only on the sensors that definitely require attention.

Product developers at Foxboro who recognized the value of solution grounding — and the diagnostic capabilities it enabled — also recognized that its typical implementation through the use of expensive metal electrodes was not cost-effective for widespread use. So, they sought and ultimately developed a simpler and far less expensive way to accomplish solution grounding, using a conductive, carbon-impregnated plastic called Kynar®. This cost-saving innovation made it possible for Foxboro to offer a solution ground and advanced diagnostics as a standard feature on the entire PH12 pH sensor family (Figure 2).

Figure 2. Comprehensive pH sensor diagnostics requires a stable solution ground, but traditional grounding methods are prohibitively expensive for widespread use in sanitary applications. Development of an inexpensive solution ground using electrically conductive, carbon-impregnated Kynar plastic, solved the problem. This cutaway view shows how the Foxboro PH12 family of pH sensors uses a standard Kynar solution ground (at bottom, in blue), to protect fast-response Resistance Temperature Detection (RTD) circuitry (near bottom, in red) and make solution grounding — plus comprehensive pH sensor diagnostics — affordable for every application.

Problem 3: Reference electrode degradation and fouling

Inherent to the design of every pH sensor is a structure called a "reference junction." Though these may vary in design and appearance, every reference junction balances two vital tasks: First, it provides a path for electrical continuity — a doorway or "diaphragm" of sorts — from the reference electrode, through the exterior reference junction and into the measured fluid. Second, it contains a protective layer of electrolyte gel that slows the "poisoning" of the silver/silver chloride reference element by outside ions while minimizing the formation of silver ion precipitates that can accumulate and clog the external reference junction. Obviously, poisoning the electrode shortens the life of the sensor, while clogging necessitates that the sensor be removed for cleaning and recalibration.

By definition, this is a complicated balancing act and some reference junction designs do a much better job of extending reference electrode life and minimizing precipitation and clogging than others. After evaluating a series of promising designs, Foxboro engineers developed a unique variation of the double junction reference. The Foxboro design, which is used in the PH12 family of pH sensors, uses an exterior ceramic reference junction to provide the electrical continuity with the measured fluid, but is carefully sized to balance electrical signal strength with minimal consumption of the electrolyte gel surrounding the reference electrode.

As the measured fluid makes contact with the reference electrolyte and ions pass through it, some of those ions react with silver ions that are present in the potassium chloride reference gel, forming a precipitate that can eventually accumulate on and clog the external ceramic reference junction, slowing measurement performance, increasing sensor instability, and necessitating sensor removal and cleaning.

To provide maximum isolation and life of the electrode and prevent the presence of silver ions that lead to precipitate formation and clogging, Foxboro adds an additional level of electrode containment by encasing the reference electrode in an ion barrier material called Nafion®. Nafion keeps the silver ions contained in the inner reference electrode so they cannot reach the external junction and cause maintenance problems.

The results of improved reference junction design in Foxboro's PH12 sensor family is a significant improvement in electrode protection and longer electrode life, reduced consumption and fouling of electrolytic reference gel, and reduced precipitate formation. The result is a 3-A Sanitary compliant sensor that offers greater stability over a longer life.

Figure 3. This cutaway view of the Foxboro PH12 sensor shows the unique, long-life design of its double junction solution reference.

At bottom, the sensor's exterior ceramic reference junction (just right of the glass electrode) makes contact with the process solution. An electrical path is created between the porous junction and the internal silver/silver chloride reference electrode, which is housed in the section highlighted in blue (detail close-up at right).

To provide maximum isolation for the reference electrode, prevent the presence of silver ions in the electrolyte, prolong the life of the electrolyte gel, and prevent "clogging" of the ceramic reference junction below, Foxboro engineers encase the reference electrode and electrolyte gel in a tubular ion barrier made of Nafion.

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Applications

Accurate pH measurement is a vital, ongoing part of every food, beverage, and dairy production process, essential to evaluating the quality of milk at every stage from farm to market. Ideally, fresh milk has a pH between 6.5 and 6.7. Because fresh milk is so rich in nutrients like lactose, naturally occurring bacteria can multiply rapidly if milk is improperly handled or stored. The result is elevated levels of lactic acid that lower pH. Milk pH values below 6.5 indicate that considerable acid has been produced, causing deterioration of the product.

Accurate pH measurement is also critical in the fermentation processes by which pasteurized milk or milk products are processed into cream, butter, cheese, or yogurt. In yogurt production, for example, the pH level of a batch can change rapidly once a culture is introduced and the process of fermentation begins to build up higher levels of lactic acid. In a yogurt culture that has been heated to incubation temperature — about 43 to 46°C — pH levels can drop rapidly, moving from 6.7 to 4.5 in as little as 30 minutes. Process operators must precisely monitor falling pH levels, because when the optimum level is reached (typically 4.3-4.5 pH) the entire yogurt batch must be cooled rapidly to halt fermentation and retain optimum yogurt quality.

Conclusion

Overall, the design improvements adopted by Foxboro in its latest generation of 3-A Sanitary compliant pH measurement devices not only address common and costly pH measurement challenges, but do so through cost-saving innovations — such as the use of plastics to replace glass and metals — that improve sensor durability and ruggedness while reducing acquisition costs. Similar innovations in the Foxboro PH12 family of sensors support standard solution grounding and improved diagnostics that reduce longer term maintenance and ownership costs.

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