White Paper

INGOLD
Leading Process Analytics

Three Reasons
to Measure pH In-Line

Continuous measurement of process pH has long been an established method in fermentation and other biochemical processes, but adoption has lagged behind in the chemical industries. As a measurement often frowned upon, many process engineers and technology owners rely instead on laboratory analyses of process samples. Their lives could be so much easier, for the three reasons explained in this white paper.

Reason 1:
Real-time pH measurement allows better control
Of all analytical process parameters, pH is by far the most important and most widely used for process control – or is it? pH is a critical parameter in many aspects of production, from setting the conditions for a reaction to happen, to the management of the reaction's process quality, and from sustaining process equipment integrity to avoiding environmental pollution and health hazards. And yet pH is not well understood. This is largely due to its logarithmic nature.

The fact that increasing or decreasing pH by one unit implies a tenfold difference in acid or alkali strength to the previous unit is not well grasped, let alone the fact that one would have to actually add ten times the amount of acid or alkali to change the pH of a solution by one unit (and only if the solution is not buffering, in which case even more reagent would be required).

Although it provides the input for process control, pH instrumentation often has a bad reputation due to its

METTLER TOLEDO

perceived need for high maintenance efforts in harsh process conditions. Because of this, process control strategists often ignore the installed pH instrument or decide to remove it completely and find other ways to control the process; none of which is as efficient or reliable as in-line measurement.

Most of the distrust towards process pH sensors finds its root cause in a misunderstanding of the implications of not measuring continuously. When properly implemented, using the real-time measurements from in-line pH instrumentation can be one of the most cost-effective and efficient ways to control key parts of processes.

Reason 2:
Off-line pH measurement is subject to temperature influences

Contrary to physical parameters that, due to their nature, cannot be measured off-line in a lab, off-line too often seems to be the preferred way for many analytical process variables. pH values are important in so many areas in and around the process that the sheer number of grab samples required to efficiently run a process would take too much time to analyze. Combined with the dynamics of processes, continuous or otherwise, lab results would never be available in time to allow proper process control.

One of the most impactful variables that can be influenced by the grab-sample testing of pH, is sample temperature. Samples taken from hot processes usually have cooled substantially by the time they are measured. And there is a common misconception between both process engineers and laboratory personnel in that they believe this will not be an issue because their lab pH meters are temperature compensated. It is very important to note that temperature compensation in a pH probe does not cancel out temperature differences between process and lab samples.

The reason why a good pH probe is equipped with a temperature sensor is because its output is both pH and temperature dependent. A pH probe generates a mV potential proportional to the pH of a solution. With a glass electrode a pH sensor outputs 59.2 mV per pH unit at 25 °C. At different temperatures the output changes,

$$E = E_0 + 2.3\,\frac{RT}{nF} \times \log\,[a_{H+}]$$

E = measured potential
E_0 = constant
R = gas constant
T = temperature in Kelvin
n = ionic charge
F = Faraday constant

Figure 1. The output potential of a pH electrode as a function of hydrogen ion activity and temperature of a solution

even if the solution pH remains constant. Only at neutral pH 7 will the sensor show a steady 0 mV at all temperatures. The temperature dependency of a pH electrode's output is clearly demonstrated in the Nernst Equation (Fig. 1).

What no pH probe can ever compensate for is the temperature/pH correlation or behavior of a specific solution, as it is a characteristic property of each medium. So depending on the solution, pH changes related to temperature may be large or small. Therefore, no pH sensor is capable of identifying what the pH of a hot process solution was when measuring in the cold sample, and vice versa. This frequently leads to frustration with in-line pH sensors, as although the measurement difference is due to the change in temperature of both solutions (assuming both sensors are operating correctly), the in-line measurement is usually blamed for being inaccurate. As a result, the pH measurement from the lab sample tends to be used to control the process.

As mentioned above, a discrepancy of a single pH unit implies tenfold the acidity or ten times the amount of chemical reagents required to control the process as needed. Relying on the lab pH measurement may not only pose a significant cost issue because of excessive chemical consumption, it may also create the conditions for severe equipment corrosion and/or adversely affect the process and product quality.

Another influence temperature has on pH is on the pH scale itself. That pH is measured on a scale of 0 … 14 is common knowledge. What is not so well understood is that the scale is applicable only at the standard temperature of 25 °C. At higher temperatures things change, and at roughly 125 °C the pH scale would actually be 0 … 12. This means that neutral pH is now at pH 6 and pH 7 would be alkaline! High temperatures are not uncommon in chemical processes such as in fertilizer production. In these cases, cold sample pH will differ substantially from the hot process value, leading to a different interpretation and therefore the very real risk of incorrect running of the process.

Reason 3:
Advances in real-time diagnostics have extended sensor lifetime and reduced maintenance

While there are a lot of good reasons for measuring pH in-line, the concerns that many processes engineers have for transitioning from off- to in-line are not completely without merit. Any general purpose pH sensor will fail rapidly in the demanding applications common to the chemical process industries and mining operations.

Finding the probes that are fit for the applications has always been a challenge. When selecting a sensor all process conditions need to be considered, not only temperature, pressure and flow but also the composition of the process medium, including characteristics such as abrasiveness and chemistry. The reference side of a pH sensor is vulnerable to poisoning by sulfide compounds and oxidant species in the medium. Hydrocarbons also have a great influence on the performance and longevity of a probe.

Decades of experience in the process industries have allowed METTLER TOLEDO to gain vast process know-how and identify industry-specific pain points. The range of pH sensors in the METTLER TOLEDO portfolio has been developed to cover the widest spectrum and the most severe applications. But even with the right sensor, there are still challenges for process engineers to overcome.

The amount of maintenance needed to keep sensors clean, accurate and in service has always been a concern. Ensuring a stable, reliable signal without interference has been another. As a result, process engineers usually only install in-line pH measurement if no alternative means to process control are found.

To resolve this, METTLER TOLEDO developed Intelligent Sensor Management (ISM®), a powerful and unique digital technology integrated into analytical sensors. ISM boosts the measurement performance and reliability of the instrument to a level far exceeding traditional analog probes.

Digital signal ensures reliability

In a traditional analog system, the transmitter has the task of calculating a solution's pH from the millivolt output of the attached pH sensor and a resistance thermometer. ISM sensors, on the other hand, calculate the pH value internally and output it as a digital signal. Shifting the calculation to the sensor and digitizing the output signal ensures 100 % signal integrity and provides a major improvement in both reliability and accuracy.

Outside influences such as moisture or electromagnetic fields no longer affect or corrupt sensor signals (a frequent issue with analog technology). Using ISM, the transmitter's role is reduced to its basic functionalities: to convert, to transmit and to be the human-machine interface.

Predictive diagnostics improve maintenance strategies

ISM probes also runs continuous performance diagnostics. Sophisticated sensor-specific algorithms keep track of process conditions, sensor glass membrane and reference status, and use the data to forecast when sensor calibration, cleaning or replacement should be performed. This enables implementation of a true predictive maintenance program, ensuring probes are kept in top condition and avoiding use when one is no longer reliable.

ISM also counters the tedious cleaning and calibration activities in the field that analog sensors require. Using iSense™ calibration software, maintenance becomes an easy and guided procedure. Further, ISM sensors can be conveniently calibrated in the maintenance shop. They retain their calibration settings and will immediately start measuring once (re)installed in the field. As the actual calibration process requires just a matter of minutes, maintenance time is typically reduced by a factor of ten.

Conclusion

In-line pH measurement is, by design, a far more reliable approach to process control compared with testing grab samples. The perceived drawbacks of in-line measurement can easily be overcome by proper engineering of the measurement point and selecting the right sensor for the right application based on process conditions and composition of the process medium. High pH sensor maintenance requirements and its complexity are eliminated with ISM sensors that allow for fully predictable maintenance and easy off-line calibration in the workshop.

ISM pH sensors

▶ **www.mt.com/ISM-chem**

ISM is a registered trademark of the METTLER TOLEDO Group in Switzerland, Brazil, USA, China, European Union, South Korea, Russia and Singapore.
iSense is a trademark of the METTLER TOLEDO Group.

iSense calibration software

www.mt.com/pro
For more information

METTLER TOLEDO Group
Process Analytics

Local contact: www.mt.com/pro-MOs

Rev. A. MarCom Urdorf, CH. PA5001en