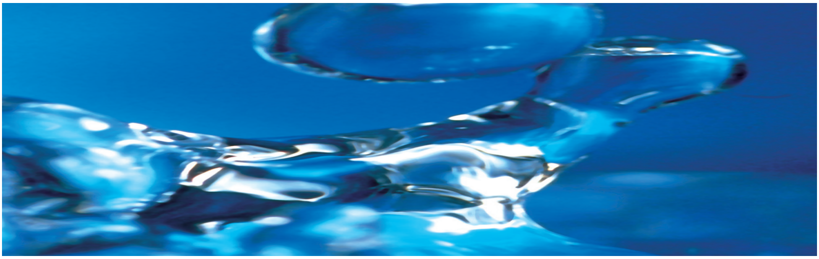
The easy guide to pH measurement



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Introduction

pH measurement equipment is used for a host of applications across a variety of industries. Getting the best from this equipment requires consideration of a range of factors to achieve optimum efficiency and cost effectiveness. Mike Modla, Product Manager, ABB Limited, offers a selection of tips on how to get the best performance from your pH equipment.

The measurement and control of pH – the degree of alkalinity or acidity of a liquid or solution – is instrumental in many processes throughout industry. It covers a diverse range of applications, from checking and maintaining product quality in the chemical, pharmaceutical, food and beverage industries through to helping water industry users ensure they meet regulatory limits for acidity and alkalinity when discharging water.

In basic terms, pH is a measurement of the relative amount of hydrogen and hydroxide ions in an aqueous solution. It is an electrochemical measurement using measuring and reference electrodes and an analysis and display unit for calculating and displaying pH readings. These systems may be standalone or form part of a more sophisticated control system to ensure that pH is maintained at a certain level.

The aggressive nature of many pH measurement applications means that periodic maintenance and checking are required as a matter of good practice to ensure continued accuracy. This should be understood when specifying a pH system.

Keeping a pH system in good working order requires additional expenditure, for example on buffer solutions to help recalibrate the sensor electrodes.

The following is a collection of hints that can help you to optimise the performance of your pH monitoring systems.

There's no such thing as a 'universal' sensor suitable for measuring everything, be it pressure, flow, humidity or pH. Instead, where pH is concerned, a range of versions is available, which varies according to the applications concerned. Some examples of the typical variations on offer include:

- High temperature glass

High temperature applications can degrade general purpose pH sensors. In particular, premature ageing of the sensor glass can reduce both the accuracy of the sensor and its overall service life. The solution is to use sensors made from specially formulated high temperature glass. These sensors are ideal where the process temperature is 90°C or higher, making them suitable for heavy process applications in the pulp and paper, pharmaceutical and chemical industries.

- Low temperature glass

Sensors made from low temperature glass provide the best speed of response for measuring pH in applications with temperatures from 15°C down to below zero. They are ideal for use in municipal and industrial wastewater applications, particularly in cold climates.

- Flat profile glass

Flat profile glass sensors offer a self-cleansing solution for applications such as in the pulp and paper industry where high levels of particles are present which could foul the sensor. However, they are only able to self-cleanse if mounted in line at an angle of 90° to a uni-directional fast flow, making them unsuitable for dip-type measurement applications with varying, multidirectional flow.

- Bulb glass

Bulb glass sensors are the prime choice for any application up to 140°C and 10 bar g. Their robust construction makes them suitable for in-line, dip and retractor type installations in a variety of industries, from municipal through to heavy duty chemical processing.

Reference type

Solid reference

While for many applications a simple gelled reference is adequate, solid reference electrodes provide additional protection. These types of sensors offer excellent low maintenance by preventing the ingress of 'poisons' in the sample process liquid that could attack and destroy the sensor reference electrode. A solid gel or potassium chloride (KCl) impregnated wood provides a barrier preventing contact between the sample liquid and the reference electrode, reducing the risk of contamination and greatly prolonging sensor life.

Solid electrode sensors are ideal for most industrial and municipal waste water applications, where high levels of sulphides are present that could contaminate the reference electrode of a standard pH sensor. They are also ideal for use in pressurised environments such as tanks and pipelines. Their one main drawback, however, is their limited life in pure waters. For that a flowing reference electrode is recommended.

Flowing reference

Flowing reference electrodes are the best choice wherever pH monitoring is required for high purity water applications, such as steam-raising for power plants or for use in semiconductor manufacture. The inherently aggressive nature of high purity water applications with their low ion concentration can quickly leach away the potassium chloride filling solution in solid electrode sensors, rendering them ineffective.

Flowing reference sensors overcome this problem by using a liquid filling which flows to the areas depleted by attack. A separate liquid-filled reservoir also enables the sensor to self-fill. Provided that this reservoir is periodically topped up, a flowing reference sensor can continue to operate indefinitely.

Install for easy access

Installing your pH sensor where it can be easily accessed will reduce the effort required whenever calibration, checking or occasional replacement is needed.

pH sensors can be installed and operated in several ways, each offering their own set of advantages and disadvantages.

For an immersion-type installation, keeping the dip-tube shorter than two metres will make calibration and replacement a lot easier. A flow cell in a bypass line, where the sample is diverted from the main line, offers many advantages. If mounted at ground level, the bypass provides easy access to the sensor, as well as helping to minimise cable lengths. Constructing a bypass can, however, add to the cost of installation.

A final alternative is to use a 'hot-tap retractor', mounted directly into the process line. As well as enabling measurements to be performed virtually anywhere, this method also allows self-cleaning flat glass sensors to be used to best effect, greatly reducing fouling even in high consistency pulp & paper lines.

For any method of installation, locating the transmitter and sensors close to each other will make it easier to check and calibrate the system.

Exposure to air can dry out pH glass and form crystalline deposits at the reference junction, dramatically reducing the sensor's service life. For this reason, sensors should never be installed at the top of a pipe, as a half-empty pipe will not permit direct contact with the process. To avoid the sensor drying out, it should always be mounted where it is constantly wetted. A good idea is to install the sensor in a u-bend, which will ensure that a sample is always captured even if the line goes dry.

The frequency of calibration really depends on whether you think there is any need for adjustments. In many cases, adjustments are unnecessary if there is a difference of less than 0.2 pH between a sample measurement and the process pH meter.

All pH systems should always be calibrated before use. This requires the pH measurement cell to be calibrated with a solution with a known pH value. However, calibration does have its own peculiarities, being affected by a range of different factors, of which temperature is the most important. Just because the buffer bottle says 9.18 pH doesn't mean it actually is! Remember, unless the buffer is maintained at an ambient temperature of 25°C, its pH will vary. At 0°C, for example, its pH will rise to 9.46.

To compensate, make sure you've set the instrument to the buffers you're actually going to use. Most modern pH meters will have built-in buffer and temperature tables and will be able to automatically compensate for temperature variations. To ensure an identical measurement standard, these tables are based on values developed by national standards laboratories such as BSI (British Standards Institute), DIN (Deutsche Institute für Normung) or NIST (National Institute of Standards and Technology).

Be wary of lab measurements

Beware of variations in laboratory samples when comparing with the process. Neutral or mild alkali, high-purity waters, for instance, will dissolve CO_2 from the air on the way to the lab, resulting in a drop in pH. Ideally, these types of sample should be transported in a sealed polyethylene container. Better still, the measurement should be made as near as possible to the process.

The pH of laboratory grab samples can also be affected by variations in temperature caused by the sample cooling on the way to the laboratory.

Beware also of taking pH measurements from processes where chemical reactions are taking place. In a scrubber using lime for pH control, for example, if a sample is taken early in the process its pH could differ from the value of an in-line sample taken later on. This occurs because the measurements have been made at different stages in the reaction process.

Make sure the sensor is adjusted for temperature

In-line sensors measure at up to 140°C so may need time to cool to calibration temperature. This could take quite a while unless using a fast acting temperature sensor with balanced pH and reference electrodes offering similar temperature responses, such as ABB's new AP120 sensor. If you're unsure, it is always advisable to wait before attempting a calibration.

Consider a grab sample calibration

Calibration is achieved by using two different pH standards or buffers or by comparison to a grab sample. In most applications, calibrating using the first method is fine and will present no difficulties. However, in some processes, relying solely on buffers can result in incorrect readings.

Consequently, buffer calibration should only be a starting point, followed by one-point grab sample calibrations. In this type of calibration, the sensor is allowed to acclimatise to the process and a sample is measured with a high quality lab sensor, with the resulting value being used to calibrate the process pH meter.

Over recent years, changes have occurred in chemical usage. Factors such as the introduction of new process techniques, environmental legislation and a general trend towards increased process temperatures have resulted in some users seeing discrepancies in pH values from the real process compared to laboratory and historic sample values. An example is laboratory samples from pulp & paper mills, which are often based on temperatures some 5 to 50°C lower than the actual process temperature. One method of tracing the cause of such variations is to make a note of the sample and process temperatures, as illustrated in the below table.

Date	Time	Sample pH		Correction Factor	Corrected sample pH	Process pH Sensor	
		pH	ºC	–0.029 pH/ºC	pH	pH	ºC
2–8	08:00	11.35	52ºC	–0.67	10.68	10.67	75ºC
	10:00	10.94	62ºC	–0.29	10.65	10.63	72ºC
	12:00	11.66	46ºC	–0.90	10.76	10.73	77ºC
	14:00	11.23	56ºC	–0.52	10.71	10.69	74ºC
	16:00	11.44	51ºC	–0.73	10.72	10.71	76ºC
Apparent sensor error ~ 0.66 pH				**Actual sensor error ~ 0.02 pH**			

In the example shown, logging the change with temperature reveals a correction factor of –0.029 pH per °C, which needs to be entered into the meter's solution temperature compensation facility.

Clean the sensor regularly

Up to half of industrial pH applications benefit from some sort of cleaning regime. The simplest way to ensure reduced contamination is to use a flat glass sensor, the benefits of which were outlined earlier.

This type of sensor needs cleaning much less often. In pulp stock applications, for instance, changing from a bulb to a flat glass sensor could extend periods from every three days to every third week.

The requirement for manual cleaning can be further reduced by using sensors with an automatic cleaning capability. These sensors use a jet wash system comprised of a cleaning solution, which is controlled by the pH transmitter. The type of cleaning solution used depends on the conditions of the application. In many cases, ordinary water will be sufficient. For crystalline deposits, carbonates, metal hydroxides, cyanides and heavy biological coatings, a mild acid may be required, whereas an alkaline detergent or a water soluble solvent, such as alcohol, would be sufficient for grease and oils.

Failure to regularly clean a sensor can result in excessive fouling, reduced accuracy and a shortened service life. If a chalky film is seen on the sensor glass, the sensor should be wiped down with a clean cloth and some distilled water. If the film remains, a more astringent cleaning solution, such as isopropyl alcohol, should be used.

These easy to follow guidelines should help you measure pH accurately and keep your sensors in good working order, thereby reducing costs while increasing yields, maintaining product quality and reducing emissions. Although pH sensors and monitoring systems themselves are not complex, their successful use requires their performance to be monitored, as well as a commitment to proper and regular maintenance.

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