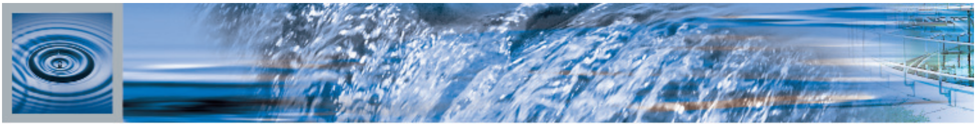
The ABB Guide to Fast pH Measurement



Used for a host of applications across a variety of industries, getting the best from pH equipment requires consideration of a range of factors to achieve optimum efficiency and cost effectiveness.

The measurement and control of pH – the degree of alkalinity or acidity of a liquid or solution – is instrumental in many processes throughout industry.

In basic terms, pH is a measurement of the relative amount of hydrogen and hydroxyl ions in an aqueous solution using measuring and reference electrodes with an analysis and display unit for calculating and displaying pH readings. These systems may be stand alone 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.

Maximizing **pH** performance

1. Choosing the right equipment to meet the application:

- **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 90ºC or higher, making them suitable for heavy process applications in the pulp and paper, pharmaceutical and chemical industries.

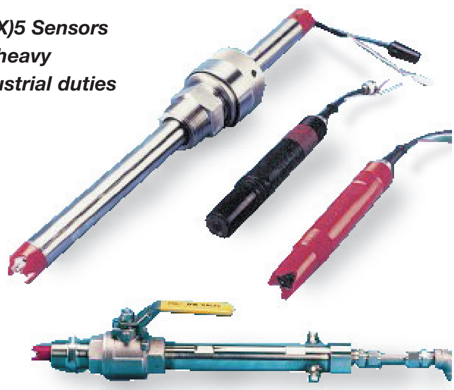
- **Low temperature glass**
  Sensors made from low temperature glass provide the best speed of response for measuring pH in applications with temperatures from 15ºC down to below zero. They are ideal for use in municipal and industrial wastewater applications, particularly in cold climates.

- **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 90º 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 140ºC 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.

AP300 Sensors ideal for industrial applications

TB(X)5 Sensors for heavy industrial duties



Maximizing **pH** performance

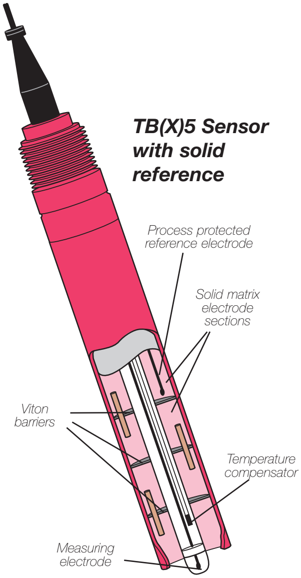
- **Reference type**

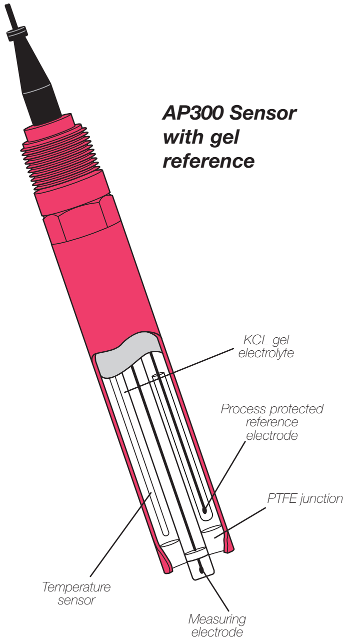
a) Solid and gel reference

While for most applications a simple gelled reference is appropriate, solid reference electrodes provide additional protection for very poisonous applications. Both types of sensors offer excellent low maintenance by slowing the ingress of 'poisons' in the sample process liquid that could attack and destroy the sensor reference electrode.

A gel filled electrode of the design shown slows the spread of poisoning because of the inherent properties of the gel and, in this case, protects the reference electrode in a glass tube sealed at the process side. This protects the reference from poisoning until the poison has reached the top of the glass tube and travelled back down inside to the reference electrode at the bottom. Retaining the reference elecrode's proximity to the measuring electrode and temperature sensor ensures a fast and accurate response to temperature variations.

Solid electrode sensors (KCL impregnated wood) provide additional protection in 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.

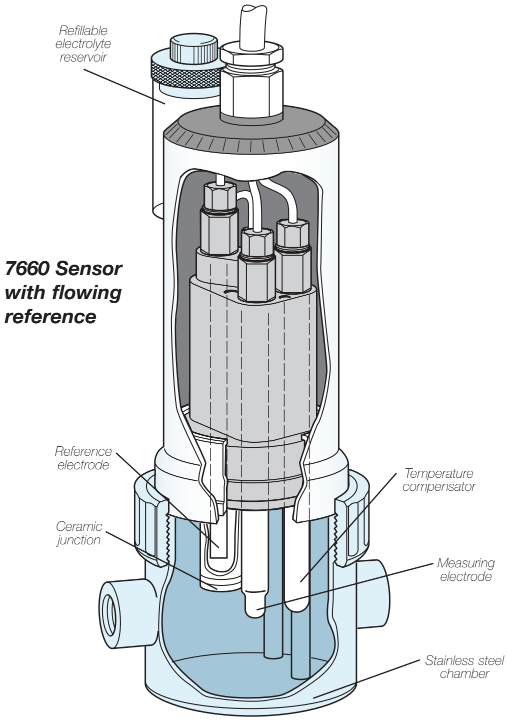




b) Flowing reference

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.



2. Install for easy access

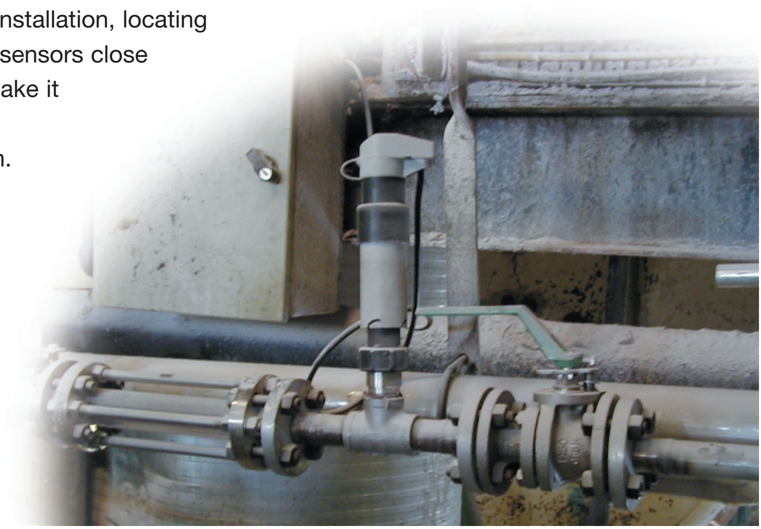
Installing your pH sensor where it can be easily accessed will reduce the effort required whenever calibration, checking or occasional replacement is needed.

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.



Maximizing **pH** performance

3. Watch out for air

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.

4. Do you really need to calibrate?

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.

AP200 Sensor essential in chemical processes

5. Configure buffer tables

All pH systems should always be calibrated before use. This requires the pH measurement cell to be calibrated with a solution with a traceable, 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. 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).

4pH Potassium Hydrogen Phthalate ($KHC_8H_4O_4$)											
ºC	0	10	20	25	30	40	50	60	70	80	90
pH	**4.00**	**4.00**	**4.00**	**4.01**	**4.01**	**4.03**	**4.05**	**4.08**	**4.12**	**4.16**	**4.21**

7pH Di-Sodium Hydrogen Phosphate and Potassium Dihydrogen Phosphate (Na_2HPO_4 and NaH_2PO_4)											
ºC	0	10	20	25	30	40	50	60	70	80	90
pH	**7.11**	**7.06**	**7.01**	**7.00**	**6.98**	**6.97**	**6.97**	**6.97**	**6.99**	**7.03**	**7.08**

9pH Sodium Tetraborate ($Na_2B_4O_7$)											
ºC	0	10	20	25	30	40	50	60	70	80	90
pH	**9.48**	**9.35**	**9.23**	**9.18**	**9.13**	**9.05**	**8.98**	**8.93**	**8.90**	**8.88**	**8.84**

Typical Buffer Tables

6. 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.

7. 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.

7660 Sensor with in-line stainless steel chamber

8. Make a sample and process log sheet

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 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 table below.

Date	Time	Sample pH		Correction Factor	Corrected sample pH	Process pH Sensor	
		pH	°C	-0.029 pH/°C	pH	pH	°C
2-8	08.00	11.35	52°C	-0.67	10.68	10.67	75°C
	10.00	10.94	62°C	-0.29	10.65	10.63	72°C
	12.00	11.66	46°C	-0.90	10.76	10.67	77°C
	14.00	11.23	56°C	-0.52	10.71	10.69	74°C
	16.00	11.44	51°C	-0.73	10.72	10.71	76°C
Apparent sensor error ~ 0.66PH				*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.

9. 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.

10. Summary

These easy to follow guidelines should help you measure pH accurately and keep your sensors in good working order, thereby reducing costs while maintaining product quality. 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.

PB/pHguide–EN

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