pH ELECTRODE PERFORMANCE

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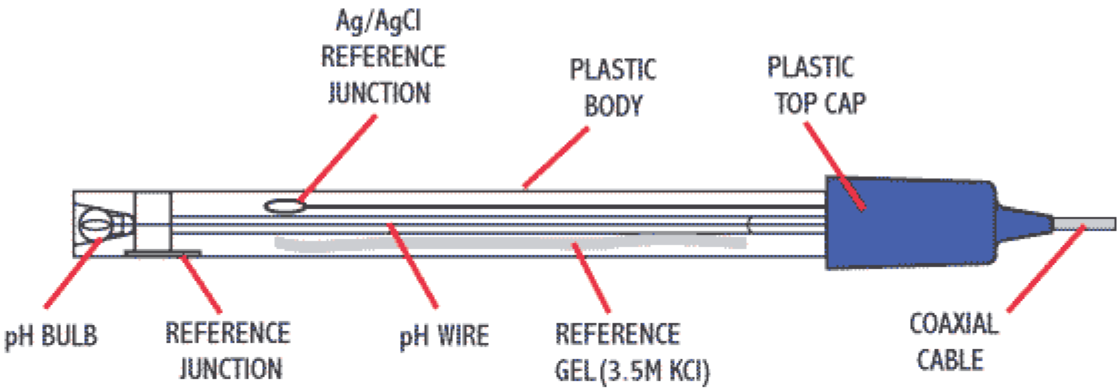
Preface

The purpose of this article is educational. The intent is to provide a practical explanation and general understanding of how to evaluate the performance of both new and used pH electrodes. Also discussed are some of the many factors which can affect pH electrode performance and to aid the reader in understanding what they may be able to do to increase performance and service life.

pH Electrodes

pH electrodes are electrochemical sensors used by many industries but are of particular importance to the water and wastewater industry. The sensor itself is similar to a battery. It generates a voltage output and has a useful service and shelf life. While there are many types of pH electrodes used in field, lab and process environments, we will concentrate on a basic design for this article.

Basic Construction of a pH electrode Fig 1



OFFSET - Theoretically, when placed in 7.00 buffer at 25°C a pH electrode produces zero millivolts which the pH meter reads as 7.00 pH. The difference between these perfect readings and the electrode's actual reading is called the offset error.

SPAN - A perfect pH electrode, at 25°C produces 59.12mV per pH unit. The difference between this perfect reading and the electrode's actual reading is called the span error.

These theoretical values are not always achieved, even with brand new electrodes. New pH electrode performance specifications should meet the following criteria:

TYPICAL SPECIFICATION - Offset: 7.00 +/- 0.2 pH (+/- 12mV) SPAN: Better than 95% of theory; i.e. between 56.2 and 59.2 mV

Normal Aging

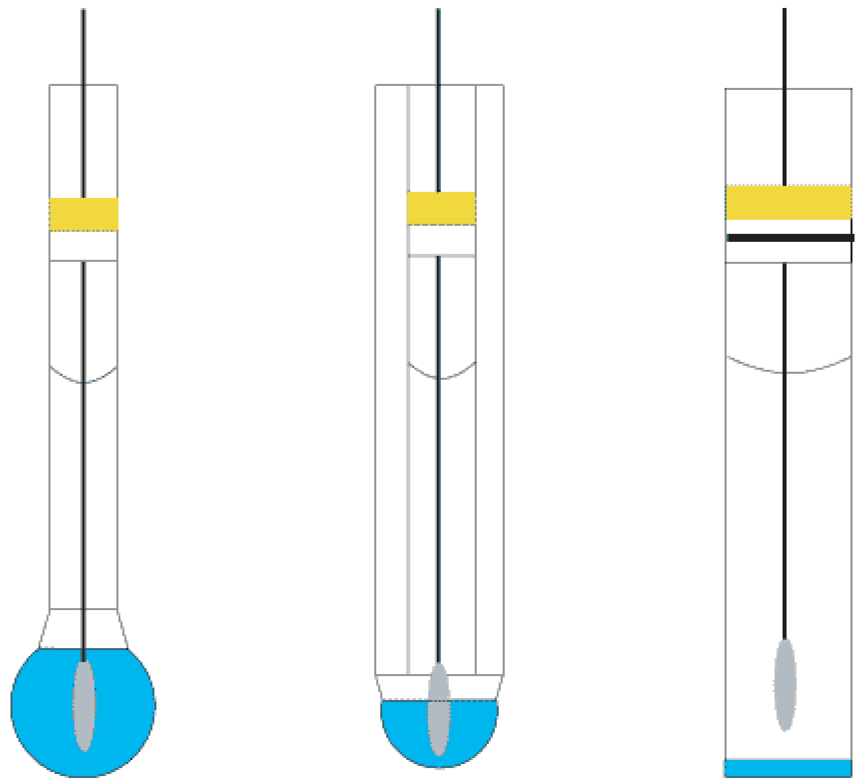
As electrodes are used or stored for long periods they will experience some shifts in these new electrode specifications. OFFSETS will change and SPAN error will increase; i.e., the span will become shorter. By using the calibration controls these errors can be corrected. If an electrode is able to be calibrated and it is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

As described later in this article, an electrode's response time becomes longer as it ages. Even though the electrode can be calibrated, sluggish response can limit its life. Also, certain application conditions, elevated temperatures, for example, will cause electrodes to have shorter service lives.

Speed of Response

An electrode's speed of response is affected by several things; mainly, by the impedance (resistance) of the pH glass measuring surface and the condition of this surface. The type of pH responsive glass used and the size, shape and thickness of its surface all affect impedance characteristics. When selecting pH electrodes there are tradeoffs to consider. Here is a comparison of the three most common shapes:

Shapes of pH measuring Surfaces Fig 2



SPHERICAL BULB **HEMI-SPHERICAL BULB** **FLAT pH GLASS**

A spherical shaped bulb will provide 95% response in less than one second. It has low impedance and fast response but is relatively fragile. pH electrodes with spherical shaped surfaces are designed so that the bulb is recessed inside the electrode body. Such designs protect the glass bulb against breakage.

A hemispherical shaped bulb is a stronger shape mechanically and, as a result, it has a higher impedance and slightly slower response. These shapes are often used in a fully exposed manner.

A flat measuring surface is the most durable of all the shapes. It makes good sample contact, is easily cleaned, is very strong mechanically but has the highest impedance and the slowest speed of response-95% in less than 5 seconds.

Coatings can mimic a sluggish speed response problem; therefore a used pH glass measuring surface should be cleaned before assuming that the electrode is no longer functional. Normally, the electrode may be cleaned with whatever chemical the coating material is soluble in provided the chemical will not attack the electrode's materials of construction. The glass surface should never be cleaned in a manner that would scratch the glass surface. Scratches will result in a slow response and shorter working life. When wiping the surface always use clean, non abrasive materials and cloths.

Effects of Temperature

The impedance issue previously discussed is also a factor when measuring samples at temperatures other than 25°C. For every 10°C decrease in temperature the glass impedance will increase about 2.5 times. Therefore a spherical electrode (which has lower impedance) will offer better speed of response in lower temperatures than a flat electrode will.

Use of electrodes in elevated temperatures will cause pH electrodes to experience shorted service life than if used at ambient temperature. High temperatures accelerate both the natural aging of pH glass and chemical attack of the glass. These factors can cause impedance to increase and the surface to loose its ability to respond to hydrogen ion activity (which is what a pH electrode actually measures!).

High and Low pH Measurements

Very strong acidic or caustic solutions will accelerate aging of a pH electrode leading to shorter service life. Some of these solutions will actually etch the pH glass surface with a resulting loss of response to hydrogen ions. There are special formulations of glass which are available from some manufacturers to resist this degradation.

Low Ionic Strength Measurements

pH measurement in low ionic or low conductivity solutions may create several problems for standard pH electrodes. Typical difficulties include:

- Slow sluggish or drifting readings
- Unrepeatable readings
- Premature electrode failure

Special design electrodes have been developed and are often used in low ionic strength applications. They may feature:

Reference junctions- the porous material that contacts the sample- are made of porous materials so that there is a very large surface area where the junction contacts the sample.

The reference junction is peripheral; that is, it surrounds the glass stem onto which the pH bulb is blown. This design minimizes streaming current effects which can generate spurious reference junction potentials.

The built-in reference electrode is a double junction design. The inner chamber contains the usual high (3.0M or higher) salt concentration solutions or gels so that stable outputs are generated. The outer chamber, which contacts the sample through the porous reference junction, is filled with a low ionic solution or gel. This lower ionic strength material more closely matches that of the sample and further reduces spurious potentials.

Single vs. Double Junction References

For many applications, a single junction reference electrode is satisfactory. However, if samples contain proteins, sulfides, heavy metals or any other material which interacts with silver ions, unwanted side reactions may occur. These reactions can lead to erroneous reference signals or to precipitation at the reference junction leading to a short service life.

A double junction reference design affords a barrier of protection to combat the above interactions. When in doubt about using single or double junction designs, the safest approach is to use the double junction; they can be used anywhere a single junction design can be used. Conversely, single junction designs should not be used where double junction designs are needed. In most process applications, it is recommended to use double junction electrodes.

Electrical Ground Problems

When a pH system is unstable, erratic, has short electrode service life or the offset drifts, the most common problem is an electrical ground loop in the system, particularly if the tank and/or pipes are plastic. To verify this problem, remove the electrode and calibrate it in a known buffer in a beaker. Pull a sample of the solution from the process and verify meter reads sample correctly.

Electrical Ground Problem Fig 3

ELECTRODE CALIBRATES **THEN** **ELECTRODE READS HIGH**

IN BUFFER AND READS **OR OUT OF RANGE IN ROCESS**

SAMPLE OUTSIDE OF PROCESS

The sources of the ground loop could be any mixer motor, pump, conductivity probe, or other electrically powered device in the media with the pH electrode.

POSSIBLE SOLUTIONS

1. Check to see if any voltage producing sensor such as a conductivity or amperometric sensor is in the same solution or the meter to which they are attached is sharing same ground with your pH meter or controller. Power down that device and verify if the pH instrument is reading correctly.
2. Try placing a large (12 or 14 AWG) copper wire into the media and the other end to the meter or controller ground terminal to draw the ground loop away from the pH electrode.
3. Disconnect all devices connected to meter or controller. This includes all pumps, alarms, outputs, etc. If the problem solves, re-connect 1 item at a time to isolate the problem device.
4. A pH electrode with an internal differential amplifier and solution ground may provide a solution if all else fails. There are electrodes available with internal batteries, solution

grounds and differential amplifiers which will hook directly to your existing meter even though it was not designed to use this technology.

Storage / Shelf Life

Since pH electrodes have limited lives, it is important to keep one or more spare electrodes available for replacement. An important aspect of the performance of any spare pH electrode is that it will it work when you need it. Electrodes supplied in soaker storage bottles with special soaker solutions have longer shelf lives than those supplied dry, with small caps or dry stored after use. The special solution in soaker bottles provides an environment that maintains pH glass hydration in an acidic environment as well as keeping the reference junction wet and communicating. If the original solution is no longer available, the following are acceptable storage medias for pH electrodes in order of preference:

- 4.00 pH Buffer

- 7.00 pH Buffer

Note: Never store a pH electrode in de-ionized water. De- ionized water is only for rinsing.

Conclusion

I hope this article provided you with some insight into pH electrodes and the real world issues pertaining to their use and performance. Similar to batteries, they will have a useful service life and will require replacement. Understanding application use effects and the causes can assist you in the use, expense and performance of your pH operating system.

ABOUT THE AUTHOR

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