The Smart Way to pH

While pH can be challenging process measurement, advances in analysis technology are helping to save time and money for plant managers.
By *Ryo Hashimoto*.

Measurement of pH plays a vital role in virtually every major industrial processing industry, from controlling chemicals in industrial scrubbers, to measuring sulfur dioxide in sugar refineries, to optimizing coagulation in water clarification. The measurement itself is time honored. The first commercially successful pH meter was created by Arnold Beckman in the 1930s and the fundamental principles have not changed.

Fortunately for industrial plants, however, the analyzers and pH sensors *have* changed significantly and these new developments make pH analysis a far faster, easier, more reliable and longer-lasting tool in a wide range of processes, even the very challenging ones. Indeed, pH measurement has gotten smarter.

First principles

Why pH is so hard to measure is clearly understood if you look at the basics of pH control. By definition, pH is the negative logarithm of the hydrogen-ion activity in aqueous solution. This means that a solution having a pH value of four has 10 times more hydrogen ions than a solution whose pH is five. For control systems neutralizing spent acids and bases, pH value provides a control point for neutralization.

Acids and bases are either "strong" or "weak" depending on the amount of free hydrogen ions in the solution of a given concentration. For example, nitric acid is strong while acetic acid is weak. They have a very different pH value but still have the same total acidity, and therefore, each require the same amount of neutralizing base.

Titration is the popular method for determining total acidity or basicity of a solution. It is necessary in the design of a pH control system to determine the size of the final control elements, particularly the element determining the flow of reagent, and titration is the method for determining this.

An acid/base titration curve is a plot of pH versus reagent addition and graphically shows how pH changes per unit addition of reagent. It is also an indication of the degree of control obtainable. Figure 1 shows two such curves, one indicating a strong acid titrated with a strong base and the other a strong acid titrated with a weak base. Both indicate the point of greatest change per unit of reagent added called the equivalence point.

It is important for the plant engineer to notice that in the strong acid/weak base example the change per unit of reagent added is not nearly as pronounced as in the strong acid/strong base example. In addition, strong acids reacting to weak bases and vice versa produce salts that act to some degree as buffers. In general, neutralization of a strong acid with a weak base will result in better control than a strong acid/strong base combination.

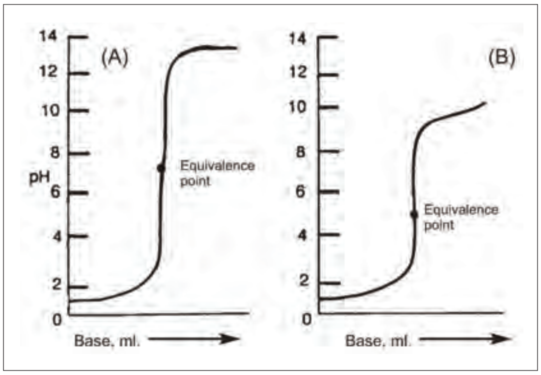

Figure 1: Curves show difference between strong acid (A) titrated with strong base, and (B) titrated with a weak base.

Design choices

A pH control system measures the pH of a solution and controls the addition of a neutralizing agent (on demand) to maintain the solution at the pH of neutrality, or within certain acceptable limits. It is, in effect, continuous titration.

At the heart of the pH control system is a pH analyzer and one or more pH sensors. The structure of the control system around these instruments, however, may be quite varied including: two-position (on/off) systems;

dual-flow one-reagent systems; two-reagent systems; and two-stage systems. To select the best system for a given application, the engineer must consider a number of factors.

Capacity is the ability of the overall system to absorb control agent without change in the process variable. In general, high capacity is favorable for effective control since it levels out abrupt changes and gives time for mixing. However, pH neutralizations are seldom high capacity since the basic nature of pH as a logarithmic function of concentration is capacity limiting.

A second important consideration is hold-up time, which is required to provide time for the neutralization reaction to go to completion. This is particularly important when a dry feed or slurry is used as the control agent since the solids must dissolve before they react. If adequate mixing and agitation do not occur, the sensing pH electrodes will detect an incorrect pH and continue to call for additional reagent after the correct amount has already been reached.

As a rule of thumb, mixing should be less than 20 percent of hold-up time, so for example, if hold-up time is 10 minutes, turnover (mixing) should occur in less than two minutes. Increasing hold-up time increases capacity.

Two final important factors in system design are transfer lag and dead time, both detrimental to effective control. Transfer lag results from the inability of the system to supply neutralizing agent instantaneously on demand. Dissolving time and poor mixing are transfer lags. Dead time is delay in any part of the system. Measuring element amplifier, signal converter, and controller lag are part of dead time. So are electrodes that do not respond rapidly to pH change because of coating.

An engineer can choose a two-position system, one in which the element controlling reagent additions is either fully open or fully closed, for control of continuous processes where waste flow rate is relatively small and hold-up time is relatively large – five minutes or more. If the flow and total acidity or basicity of the stream can vary by a factor of 10,000, then two-reagent pumps are needed. The manual valves are adjusted to give flows differing by a factor of 100 to 1,000 with high and low control points differing by one pH unit or more.

When the pH of the stream can vary from acid at one time to alkaline at another, then both acid and alkaline reagents are needed. Further if the concentrations of acid or alkali are greater than one percent, the system may tend to self-oscillate. In this situation, a two-stage method will minimize oscillations caused by overfeeding of a reagent.

When both volume and flow of spent acid or base are high, it becomes impractical to provide the relatively long hold-up time required by two-position control. This situation calls for multi-mode control in which neutralizing agent is continually added by the final control element. The amount of neutralizing agent depends upon the proportionality set up by the system and the controller. The ideal hold-up time with multi-mode control is relatively short – 30 seconds to three minutes. Beyond 10 minutes, multi-mode control may not get better results than an on/off control mode.

Technology advances

The selection of the optimum sensor(s) and analyzer for a control system is as important as its proper configuration. As can be seen above, pH measurement is not simple and furthering the problem is the fact that many, if not most applications requiring pH measurement are challenging environments involving high temperatures and/or process elements that can foul, coat or poison a pH sensor. In the past, this has resulted in the need for frequent cleaning and replacement of the pH sensor, sometimes once a day in very harsh circumstances, making the measurement costly in both equipment and time. In addition, time-consuming calibration has added significant maintenance costs to the pH analysis process. While even today there is no perfect pH sensor for every application, the technology is advancing to the point that the pH sensor is a relatively trouble-free part of the process.

One of the most significant advances in pH measurement is the advent of "smart" technology which impacts the calibration, start-up time and maintenance schedule. Historically, the only way to calibrate a pH sensor was to carry all of the calibration equipment into the field. In many facilities, this meant carrying at least two buffer solution bottles, two beakers and one rinse bottle to the various installation sites.

Then, the calibration was done on-site at a location closest to the sensor installation. So come rain or shine, sleet or snow, hot or cold weather conditions, the technician had to maintain the sensor in even the worst environmental conditions.

Smart technology changes all that. Smart pH sensors have a memory which holds calibration information, so there is no need to carry equipment to field. The sensors can be calibrated in a controlled environment such as a laboratory or maintenance shop and the calibration information is uploaded into the sensor. The sensor can then be taken to the field and installed on-site or it can be stored on shelf (keeping sensors wetted) until it's time to replace one in the field.

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Smart pH sensors have a memory which holds calibration information, so there is no need to carry special equipment out to the field.

Many of the sensors implemented with smart technology also use a special cable-to-sensor VP connector system. This allows for plug-n-play capability so that the user can plug the pre-calibrated sensors into field equipment and the sensor is ready to measure. This is especially advantageous for facilities with remote locations or multiple installations. It also gives the added benefit that the sensors can be rotated in and out of process as needed with minimal downtime. This quick and easy sensor exchange keeps the process up and running.

Another advance in pH technology is in the area of glass durability. New glass formulations and low-stress handling techniques provide exceptional resistance to thermal and caustic degradation. This translates to less breakage from thermal stress or shock and improved speed of response at near theoretical levels and minimal hysteresis for fast accurate calibrations even after months of service. In addition to the more durable glass, new sensor designs also mount the glass bulbs in protected tips that shield the glass from direct impact while in service or during calibration.

Health indications

Using the smart information that is stored in the sensor will help the user evaluate the state of the sensor's health. When operators understand how to interpret the basic information for the pH slope, glass impedance, reference offset, and reference impedance values, they gain a deeper understanding of how the information contained in the smart software can prolong sensor life.

The four main concepts for using the smart sensor information during calibration are:

- Slope Trends, which normally decrease over time
- Glass Impedance Trends, which normally increase over time
- Reference Offset Trends, which normally shift slowly over time
- Reference Impedance Trends, which normally shift slowly over time

The pH sensor slope information indicates the health of the pH sensitive glass membrane. The slope naturally decreases as the sensor ages. It also will decrease faster with elevated temperatures. Viewing the slope trends information allows users to make informed decisions. Good sensors that can be confidently used have a slope value of 54 mV/pH to 59.16 mV/pH. Bad sensors have a slope value of 48 to 50 mV/pH, which is too low and the sensor should be replaced

Glass impedance is another indicator of the pH glass health. Typical pH sensors have an impedance value of 50 to 200 Mohm; while some specialty pH glass sensors used for higher temperatures have a maximum glass impedance value of 1000 Mohm.

Viewing the glass impedance information allows users to make good decisions about the glass health, and glass impedance values trending up to 600 - 1200 Mohm may indicate one of the following issues: the glass is getting old due to high temperature exposure or normal aging – in this case, the sensor needs to be replaced soon; the sensor is not immersed in the process liquid or buffer solution; the glass is dirty and should be cleaned before installing it back into the process liquid.

Glass impedance values of less than 10 Mohm identify cracked glass, excessive exposure to high temperatures, or a high impedance short in the sensor. In any of these scenarios, the sensor should be replaced.

The reference offset indicates the health of the reference electrode. New sensors placed in pH 7 buffer solution will have an ideal output of 0 mV. An acceptable offset is 60 mV maximum. Viewing the reference offset trends allows the user to make informed decisions regarding sensor calibration or replacement.

A reference offset of less than 60 mV can be adjusted by standardizing (a one-point calibration). A reference offset of 60 mV or higher means that the reference electrode is spent or dirty, indicating that it is time to replace or recharge (refill reference) the sensor.

The reference impedance value is another indicator of the health of the reference electrode. The normal reference impedance value on a new pH sensor is between 10 and 60 Kohm. Viewing the reference impedance information allows the user to make good decisions about sensor maintenance and replacement.

A high impedance value is 140+ Kohms and indicates one of the following: the reference is coated from a dirty process liquid and needs to be cleaned; the reference junction is clogged and the sensor needs to be replaced; the reference electrolyte is depleted and the sensor needs to be replaced.

Reference challenge

Most pH measurements fail due to reference electrode problems. The most common of these are fouled or poisoned electrolytes and clogged reference junctions. New technologies in this area include improved double junction reference electrodes designed to excel in specific harsh applications.

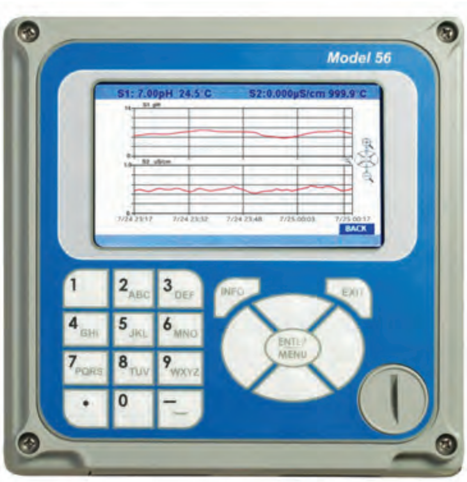
The specially designed porous liquid junctions have a large surface area to maintain a steady reference signal in dirty fouling applications. A combination of large surface area and high porosity also minimize junction potentials leading to accurate measurements without standardization.

Interestingly, some of these new designs have come full circle from the all-disposable philosophy of past years to rechargeable reference electrodes, a design feature that was commonplace over 20 years ago. These reference electrodes are designed for ease of use and optimum performance. The reference electrolyte is an inert viscous gel that is unaffected by thermal or pressure cycling. When the junction is removed, the outer reference electrolyte can be recharged using gel-filled syringes. These reference electrolytes are designed to optimize the sensor for maximum resistance to fouling in specific applications.

And the analyzer

Of course, sensor enhancements would mean little without commensurate improvements in analyzer technology. Many advances have been achieved, many of them in the area of ease-of-use which saves time and money for plant managers.

For example, Simplified Quick Start screens appear the first time the unit is powered. The instrument auto-recognizes each type of measurement board and prompts the user to configure each sensor loop in a few quick steps for immediate live readings. In addition, a complete user guide and trouble-shooting manual can be embedded in an instrument's memory and easily accessed via a single key on the keypad. Detailed instructions and troubleshooting tips are intended to provide adequate guidance to resolve most problems on site so that user manuals and offsite maintenance is eliminated.



New analyzer technology also allows for built-in data and event logger capability.

New analyzer technology also allows for built-in data and event logger capability. Extensive onboard data storage captures measurement data from the instruments channels, including such capabilities as temperature every 30 seconds for 30 days for on-screen display or local upload to a USB 2.0 memory device. Three hundred significant analyzer events can be recorded including start-up time, calibrations, hold outputs, configurations, alarms, power interruptions, faults and more. All process data and events are time/date stamped and a complete audit trail is provided without extra cost or complexity.

Of course, new analyzers are designed to work as smart devices with the smart sensors eliminating the need for field calibration. These instruments often feature a sensor to cable connector which, once wired to the analyzer, permits the sensor to be easily removed at the connector without the need for expensive reconnection of the wiring.

Besides using the USB memory device or reading the diagnostics on the instrument in the field, sensor and analyzer diagnostics can be transmitted to the host via the network using Hart communications or wirelessly using a smart wireless adapter. Using these communication protocols allows control room operators to view easy-to-read dashboard screens using the latest generation asset management system device descriptors (DDs). **CEA**

Ryo Hashimoto is Senior Business Development Manager for Instruments with Emerson Process Management, Rosemount Analytical (www.AP.EmersonProcess.com).