

What's the Real pH Of that Stream?

Variability of fluid composition and temperature, coupled with drift and calibration issues can complicate pH determination, as this wastewater example illustrates

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The most common measure of how acidic or basic an aqueous solution has become is pH. Online (process) pH measurements provide realtime or semi-realtime insight into this important parameter, and allow operators to rapidly respond, making upstream changes in operating conditions or recipe requirements as needed. Grab samples may be periodically taken to verify online process readings, but such readings are frequently hard to reconcile with the online measurements. The resulting discrepancies often lead process operators to conclude that pH measurement is a black art, best left to chemists in dark, isolated labs.

Much of the confusion surrounding the interpretation of pH data is due to the variable nature of the liquid that is being monitored. Recognizing that there are differences in environment between the online sensor and the laboratory or portable sensor can generally help to explain most of the discrepancies — discrepancies that are commonly cited as "pH drift." But how does one decide what is the "real" pH?

Several influential factors can frustrate users of pH instrumentation, such as high temperatures, drift and calibration issues. However, guidelines (below) are available for how to control processes under varying con-

ditions. Consideration of some practical examples, such as wastewater treatment, can make the guidelines more clear.

A brief refresher on pH

pH is defined as the negative logarithm of molar concentration of hydrogen ions in a solution:

$$\text{pH} = -\log([\text{H}^+]) \quad (1)$$

A water solution is acidic or basic depending on whether there is a net excess of H^+ (acid) or OH^- (base) present. While hydrogen ions (H^+) and hydroxide ions (OH^-) generally combine to form neutral water (H_2O), small amounts of those ions are always present. The concentration of the hydrogen and hydroxide ions are related by the dissociation constant of water, K_w :

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad (2)$$

A traditional Brønsted acid is a substance that liberates H^+ when dissolved in water; a Brønsted base is an OH^- donor. Figure 1 shows that a pH of 7 is considered neutral because it contains equal amounts of both H^+ and OH^- ions. When pH is 7, $[\text{H}^+]$ is 10^{-7} , so from Equation (2), $[\text{OH}^-]$ is also 10^{-7} .

It is important to remember the logarithmic nature of pH; every pH unit corresponds to a factor of 10 in concentration. So wastewater with a

pH ⁺	Hydrogen ion (H ⁺)	Hydroxyl ion (OH ⁻)
0 Acidic	1.0	0.00000000000001
1	0.1	0.00000000000001
2	0.01	0.00000000000001
3	0.001	0.00000000000001
4	0.0001	0.00000000000001
5	0.00001	0.00000000000001
6	0.000001	0.00000000000001
7 Neutral	0.0000001	0.0000001
8	0.00000001	0.0000001
9	0.000000001	0.000001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.00000000000001	0.1
14	0.000000000000001	1.0

FIGURE 1. While the effect of H^+ content on pH is familiar concept, its inverse effect on the OH^- content due to water's equilibrium constant is often overlooked

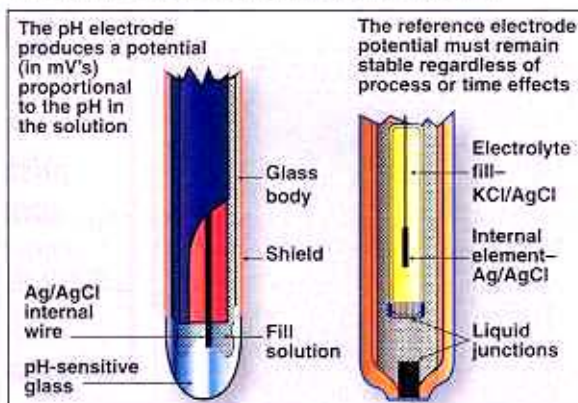


FIGURE 2. Most pH sensors contain these components

pH of 4 has 100 times the acid content of a water solution at pH 6, and will therefore need 100 times the caustic (NaOH) for neutralization.

Like pH, we can also define logarithmic terms for K_w and $[\text{OH}^-]$. If we do this, we can write another equation to bypass the scientific notation:

$$\text{pH} + \text{pOH} = \text{p}K_w \quad (3)$$

The pH sensor

A common pH sensor design, shown in Figure 2, consists of a measuring electrode (usually made of glass) and a reference electrode (typically based on silver or silver chloride). The measuring electrode produces a potential that is proportional to the pH of the solution, and the reference electrode is designed to produce a stable potential over the lifetime of the sensor. The intricacies of the pH sensor are discussed elsewhere [1, 2]; however, the output (in mV) of the pH sensor is given by the Nernst Equation:

$$E(\text{mV}) = E_0 + 2.3(RT/F) \log a\text{H}^+ \quad (4)$$

where:

E_0 = a calibration constant

$2.3(RT/F)$ = the slope, S (in mV/pH)

Note: For a related article, see Improving wastewater pH control, CE, November 1999, pp. 119-122.

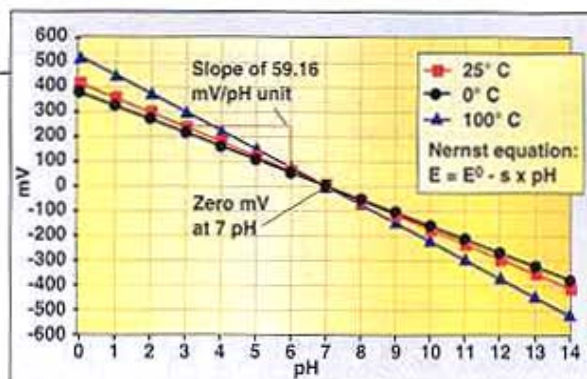


FIGURE 3. The theoretical mV response of a pH sensor is shown here

units), of the graph of E versus $\log a_{H^+}$. a_{H^+} = the activity of the hydrogen ion (which is approximated by hydrogen ion concentration, $[H^+]$, in most situations; Note: In this term, R is the gas constant, T is the absolute temperature, and F is the Faraday constant)

This produces the simple working equation used by pH analyzers:

$$(E - E_0) = -S \text{pH} \quad (5)$$

Equation (5) allows the analyzer to calculate the slope S using two different buffer solutions and then calibrate the zero offset (E_0). Although the ideal slope can be calculated from fundamental constants (RT/F), in practice the slope is always lower. The ratio of the actual slope to the ideal slope is sometimes called the efficiency of the electrode. Thus, although the ideal slope is 59.16 mV/pH unit at 25°C, typical new electrodes have values closer to 57 or 58 (96-98% efficiency).

The actual value of the slope is not very important, as long as it remains constant until the next buffer check. In practice, the slope of an electrode changes little until it nears the end of its lifetime; at that point, however, it may begin to decrease very rapidly.

The (RT/F) factor contains a temperature term (T), so the slope will be proportional to the temperature. The ideal slope varies from 54.2 mV/pH at 0°C to 74 mV/pH at 100°C (Figure 3). Nowadays, nearly all pH analyzers compensate for this variation automatically, by measuring the process temperature and using it to adjust the calculated pH reading. This automatic temperature compensation becomes very important at higher temperatures and/or extreme values of pH.

In addition to the temperature effects on the measuring electrode's slope, there are temperature effects on the reference E_0 that could also cause the calibration to shift with temperature. This secondary effect is removed by using fill solutions with specific compositions that establish the zero

and isopotential points (those at constant potential) at a convenient pH value (usually 7 for both). This means that the sensor will read 0 mV at pH 7 and will continue to read 0 mV (and 7 pH) if temperature is changed. Thus, applications that are near 7 pH may not require temperature compensation. Of course, if pH were always near 7, you might not need to measure it at all.

Process temperature effects

Now comes the tricky part. Although Equation (3) is correct, the value of pK_w actually depends on temperature. In fact, pK_w ranges from 14.9 at 0°C to 12.4 at 100°C. Higher temperatures cause more water molecules to dissociate, producing more H^+ and OH^- ions. This means that the neutral pH varies from 7.45 near 0°C to 6.2 at 100°C.

The temperature behavior of non-neutral solutions can be quite complicated, as shown in Figure 4. Generally, acidic solutions do not change their pH, but high-pH solutions take on lower pH values as the temperature rises. In basic solutions there is a net excess of OH^- , which remains present at higher temperatures and causes the pH to drop at higher temperatures. For example, a pH 10 solution at 25°C has pOH of 4 due to a pK_w of 14. At 100°C, the pK_w changes to 12.4; equal amounts of OH^- and H^+ are formed, but the concentration of H^+ goes up by a factor of 40 since there was comparatively so little present before. Thus the pH changes from 10 to 8.4 while the pOH hardly changes at all.

Wastewater neutralization

The practical effect of the behavior shown in Figure 4 is that it becomes increasingly difficult to neutralize a basic solution as temperature increases. At higher temperatures, the pH lines converge near 6.5 pH, but the amount of chemical needed to move from one line to the other remains the same as it was at the lower temperature. The batch neutralization of a caustic solution illustrates this very well. If you try to neutralize the contents of a 1,000-liter vessel full of a pH 9 solution at a temperature of 60°C,

you might think that you would need:

$$Q_{25} = 1,000 \text{ liters} \times 1 \times 10^{-5} \text{ moles/liter} = 0.01 \text{ moles acid} = 10 \text{ ml of 1 N acid}$$

where Q_{25} is the quantity of liquid needed at 25°C

However, when pH reads 9 at 60°C, the pOH is 4 (not 5), and neutralization will not occur until 100 ml of acid have been added — thus, the hot liquid requires 10 times the chemical originally expected to do the job. Furthermore, the setpoint for neutralization should be 6.5, not 7, since, if the neutralization occurred at 7 pH, the pH of the released liquid would rise to 8 once the temperature had cooled to a nominal 25°C. Some wastewater-treatment systems may not be capable of meeting their designed loads under these circumstances. This example shows both the need for accurate measurement and the need for controller tuning and equipment sizing based on differing needs at differing temperatures.

One method to improve pH control at higher temperatures is to use a pH analyzer that offers solution-temperature compensation. The simplest version of this feature allows the user to input a value for how much the pH actually changes per degree. The analyzer then adjusts the reading so that the pH displayed is the pH that would be measured if the liquid were really at a temperature of 25°C. This is mathematically equivalent to changing the isopotential point.

A setting of $-0.033 \text{ pH}/^\circ\text{C}$ works well for the curves above pH 8 in Figure 4. However, different values are needed below 8 and no correction is desired below pH 5. If this linear correction were used in the batch neutralization example, the pH would be adjusted upward by 1.15 pH units and a much closer neutralization would result. Some analyzers improve on this correction by incorporating a "high pH" setting for this kind of application and an "ultrapure pH" setting for neutral applications.

Measuring online

Measurement of pH is usually taken for granted, but there are quite a number of different effects that can show up when attempting to measure pH in

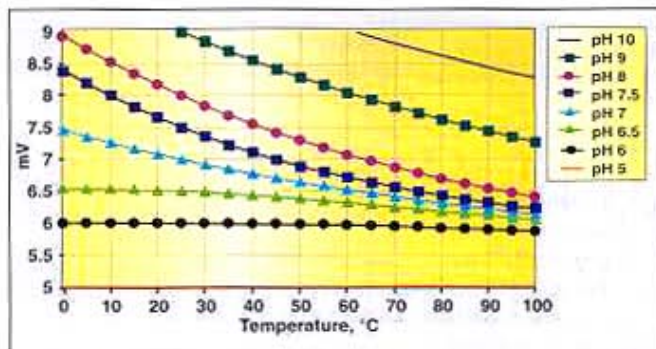


FIGURE 4. This curve shows how pH can be very temperature-dependent for some solutions

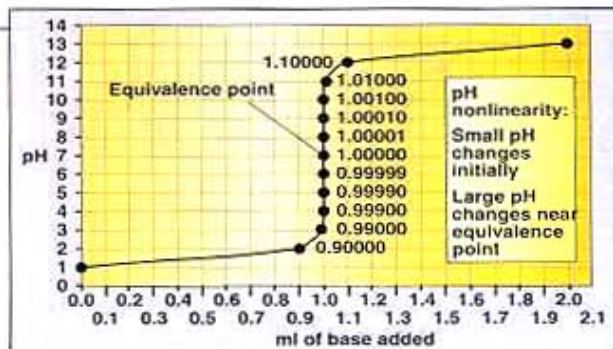


FIGURE 5. Shown here is a typical titration curve for a strong base and a strong acid

a process 24 hours a day, seven days a week. The response of a pH sensor in millivolts is actually the sum of several different potentials and is affected by several different resistances [1] that can change due to both process effects and sensor history. These effects are usually lumped together into a "standardization adjustment" that allows a single point adjustment to make the indicated reading agree with that for a grab sample. Great care must be taken to make sure that discrepancies in pH reading are not due to temperature as discussed above, since repeated adjustments of the pH reading (especially when adjustments occur in both directions) are both frustrating and counterproductive.

Although laboratory personnel may be used to reading pH to within 0.01, the field accuracy of a pH measurement is rarely better than 0.1 pH units. pH control must allow for both the measurement drift of a pH sensor and the nonlinearity of the pH titration curve. Trying to achieve 0.05 pH tolerances will likely waste chemicals due to overshoot and can cause unstable oscillatory control. Wastewater processes are usually relatively forgiving, and getting within 0.2 or even 0.5 pH of the setpoint is typically acceptable.

Neutralization control requires study of both steady-state behavior and time-dependent behavior. Whenever possible, it is best to characterize the desired chemical reaction(s) by means of a titration curve, which indicates what the expected pH will be as the process is neutralized. The titration curve in Figure 5 shows the nonlinearity of pH in that there is a very sharp change in pH around the equivalence point.

Superior pH control requires consideration of the following factors:

- **Multiple stages.** Adjusting the pH of a solution by more than 2–3 pH

units will require two stages

- **Mixing.** Static mixers (based on feedforward control, if possible) can be used for a first-stage pH adjustment, but this option will also require a well-mixed downstream tank for equalization. Many pH-control reagents are viscous and do not mix as readily as diluted solutions would. One should not try to neutralize wastewater in a pipe
- **Holdup time.** Retention time in a pH control tank should be at least 20 times the turnover time, to avoid downstream cycling
- **Feedback pH sensors.** These sensors should be located as far upstream as possible, in order to minimize deadtime. An ideal position is in a recirculation loop at the exit of a well-mixed tank
- **Valves.** Valves must be sized to throttle the largest and the smallest flows of neutralizing solution demanded. In many situations, this calls for multiple valves since no single valve has a sufficient turndown ratio. Select valves that minimize sticking and slipping. Digital valve positioners can take the guesswork out of flow control
- **pH extremes.** Some process streams are very challenging for pH control because their pH is too extreme. For instance, in applications above pH 12 or below 1, the pH sensor may not provide useful measurements long enough to be practical. In many cases, an electrical conductivity measurement can be used instead to estimate the concentration of the wastewater for rough adjustment prior to downstream processing. Conductivity is typically proportional to concentration, and is measured by robust sensors that require little maintenance (Note: The reason that conductivity meters are not always used is that

at pH 7, the conductivity difference is too small to detect when compared to that of wastewater; pH, since it's logarithmic, is much more sensitive to small amounts of acids or bases). Most vendors can supply either pH or conductivity sensors and many instruments will accept inputs from both

The pH sensor (as shown in Figure 2) is a highly accurate device that measures hydrogen ion concentration over an extremely wide range during a typical lifetime of 12 to 18 months. If the sensor gets coated, it will take longer to respond to changes, so frequent cleaning may be necessary to optimize the response time of the system. Modern sensors are designed to resist the effects of coating and may have cleaning accessories for automation. pH measurement and maintenance should be considered low-cost insurance for the prevention of metal corrosion, protection of the environment, and optimization of wastewater-treatment processes such as flocculation. ■

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