

pH Measurement and Control Opportunities

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ABSTRACT

The pH electrode offers by far the widest rangeability and the greatest sensitivity of an industrial measurement. This extraordinary capability is the result of the pH relationship defined over a hundred years ago that covers 14 orders of magnitude of hydrogen ion concentration. The online measurement and control of pH is important for water, food, beverages, pharmaceuticals, specialty chemicals, and environmental protection. The extreme capability of the pH measurement and the broad spectrum of applications and process conditions create exceptional requirements for electrode design, mixing uniformity, control valve precision, deadtime minimization, nonlinearity compensation, and control strategies. pH loops are often the most challenging loops in the plant. Slight deficiencies in the mechanical, piping, process, measurement, and control system design and installation can cause the pH loop to oscillate and fail to meet objectives. This tutorial takes a holistic approach to the opportunities for the best pH control solution. The fundamental pH relationship is used to reveal how titration curves cause graphical deception. The effect of salt concentration and process temperature and hidden assumptions in the millivolt relationship are explained by simple equations. An equivalent circuit of the electrode is employed to identify changes in pH unknown to most users. The latest developments in smart instrumentation and improved electrode technology are described to address many of these problems. The advantages of installation methods, wireless measurements, and middle signal selection are offered. Common electrode symptoms and causes are summarized. Simple guidelines on mixing, control valve, and piping design and titration curves are discussed. Deadtime sources, impact, and reduction methods are detailed. The latest in low cost and small foot print equipment designs are outlined. Finally the performance improvements by smarter control techniques are explored

INTRODUCTION

Many chemical and biological processes have pH control loops. Good pH control can be important for product quality as well as environmental compliance. The pH electrode offers by far the greatest sensitivity and rangeability of any industrial process measurement in terms of the measurement of concentration (hydrogen ions). The extraordinary capability of pH as a concentration measurement poses exceptional challenges in many aspects of pH design and implementation. To realize the full

potential of this opportunity requires extraordinary performance of mixing equipment, control valves, reagent delivery systems, flow meters, control system design, and controller tuning. For pH control systems, not addressing any one of the automation and mechanical design requirements can cause the system not only to fail but to fail miserably. Besides the opportunity for keeping the pH deviations within allowable limits, there are considerable often unknown opportunities to reduce operating costs.

EXPECTATIONS AND LIMITATIONS

Key Insight 1: The pH electrode offers by far the greatest sensitivity and rangeability of any measurement. To make the most of this capability requires an incredible precision of mixing, reagent addition, and nonlinear control. pH measurement and control can be an extreme sport.

The logarithmic relationship between pH and hydrogen ion activity as seen in Equation 2 offers the ability to measure hydrogen ion concentration from 1 to 10^{-14} over the 0 to 14 pH scale range. In fact, pH measurements below 0 and above 14 are also possible, which extends the rangeability beyond 14 orders of magnitude.

$$a_H = 10^{-\text{pH}} \quad (1)$$

$$\text{pH} = -\log(a_H) \quad (2)$$

$$a_H = \gamma * c_H \quad (3)$$

Where:

a_H = hydrogen ion activity (gm-moles per liter)

c_H = hydrogen concentration (gm-moles per liter)

γ = activity coefficient (1 for dilute solutions)

pH = negative base 10 power of hydrogen ion activity

The hydrogen ion activity is the effective concentration and is a measure of the ability of the hydrogen ion to move and combine with other ions. For dilute solutions the effective and actual concentrations are equal and the activity coefficient is one. For solutions with high concentrations of ions, the crowding and presence of other charges reduces the activity coefficient to less than one and the effective concentration is less than the actual concentration. For solutions with less than 90% by weight water or more than 5% by weight salt, the pH becomes a noticeable function of water and salt besides hydrogen ion concentration. Certain salts such as NaCl also affect the millivolt potential developed by the measurement and reference electrodes. The ions from the dissociation of acids and bases also have activity coefficients that affect the charge balance and hence the pH.

The product of the hydrogen and hydroxyl ion concentrations must equal 10 raised to the minus power of the water dissociation constant (pK_w) per Equation 4 for water solutions. The pK_w and thus the actual solution pH is a function of the process temperature. The change in weak acid and weak base dissociation constants with temperature can also cause the solution pH to change. It is important to realize that the standard temperature compensator corrects for the temperature effect on the millivolt potential developed by the electrode and not for the changes in the actual solution pH with temperature. Smart transmitters have recently added the option for the user to program for the correction of the effect of temperature on the solution pH. Except for dilute strong base solutions above 7 pH, the exact relationship between temperature and solution pH is not generally available and needs to be developed from lab tests.

$$c_H * c_{OH} = 10^{-pK_w} \quad (4)$$

Where:

c_H = hydrogen ion concentration (gm-moles per liter)

c_{OH} = hydroxyl ion concentration (gm-moles per liter)

pK_w = negative base 10 power of the water dissociation constant (14.0 at 25°C)

Key Insight 2: The actual solution pH changes despite a constant hydrogen ion concentration because of changes in dissociation constants with process temperature and activity coefficients with ionic strength and water content.

At the neutral point, the concentration of hydrogen and hydroxyl ions is by definition equal. If the temperature is 25°C, the pK_w is 14.0, which means the pH is 7 and the hydrogen and hydroxyl ion concentrations are both 10^{-7} . Table 1 shows how the hydrogen and hydroxyl ion concentrations change by a factor of ten for each pH unit.

Table 1 illustrates the heart of the matter. No other type of commonly used measurement covers such a tremendous range. Also, the pH electrode can respond to changes as small as 0.01 pH, which means the pH measurement can track changes as miniscule as 0.00000005 in hydrogen ion concentration at 7 pH. No other commonly used measurement has such tremendous sensitivity. As with most things in life, you don't get something for nothing!

The rangeability and sensitivity capabilities create associated control system design problems that can seem insurmountable. It is important to realize that these problems are due to attempting a level of performance in the pH process in terms of concentration control that goes well beyond the norm. For a true strong acid and strong base control system, the reagent valve must have a rangeability greater than 1,000,000:1 for an incoming stream that varies between 0 and 6 pH and a setpoint at 7 pH. The stick-slip of the same control valve must be less than 0.00005% to control within 1 pH of the 7 pH setpoint.

How then is this possible? Such strong acid and base systems are controlled by approaching the setpoint in stages and using successively smaller precision control valves. The multiple state requirement of pH control can be visualized by comparing it to trying to sink a golf ball in the hole on a green. The distance between the tee and the green presents the rangeability requirement and the size of the hole compared to the distance represents the sensitivity requirement. For the above strong acid and strong base system, the tee would be about a million yards from the green. A hole in one is possible. Using the same large control valve at each state is like the joke about the gorilla that drives the green in one stroke but then uses his driver again and hits the ball the same distance when he tries to putt the ball in the hole.

Table 1. Hydrogen and Hydroxyl Ion Concentrations in a Water Solution at 25°C

<u>pH</u>	<u>Hydrogen Ion Concentration</u>	<u>Hydroxyl Ion Concentration</u>
0	1.0	0.00000000000001
1	0.1	0.0000000000001
2	0.01	0.00000000001
3	0.001	0.0000000001
4	0.0001	0.000000001
5	0.00001	0.00000001
6	0.000001	0.0000001
7	0.0000001	0.0000001
8	0.00000001	0.000001
9	0.000000001	0.00001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.0000000000001	0.1
14	0.00000000000001	1.0

The process gain at a given pH set point is best visualized as proportional to the slope of the titration curve. The titration curve is a plot with pH for the Y axis and the ratio of reagent to influent concentration, volume, or flow for the abscissa. For a true strong acid and base system, the process gain between 6 and 7 pH is 6 orders of magnitude larger than the process gain between 0 and 1 pH. Figure 1 shows a titration curve for a strong acid and strong base at 25°C. The curve appears to be a vertical straight line between 2 and 12 pH and symmetrical about the neutral point where the concentration of hydrogen and hydroxyl ions are equal. However, a zoom in on the straight line reveals another S-shaped titration curve as seen in Figure 1a. Successive zooms centered on 7 pH should always yield additional S-shaped curves, since the slopes is continuously changing by a factor of 10 for each pH unit deviation from 7 pH. However, most titration curves will not show this true behavior because there are not enough data points. It is quite common for there to be only a couple of data points in the neutral region where the slope is steepest even though this is the location of the set point and hence the area of greatest interest for environmental and biological systems. Also, many

users overlook or inadequately define the abscissa. For example, if process design looks at Figure 1b ignoring the X scale, the curve looks relatively harmless and they will wonder “what is the big deal?” Graphical deception is a common problem in pH systems.

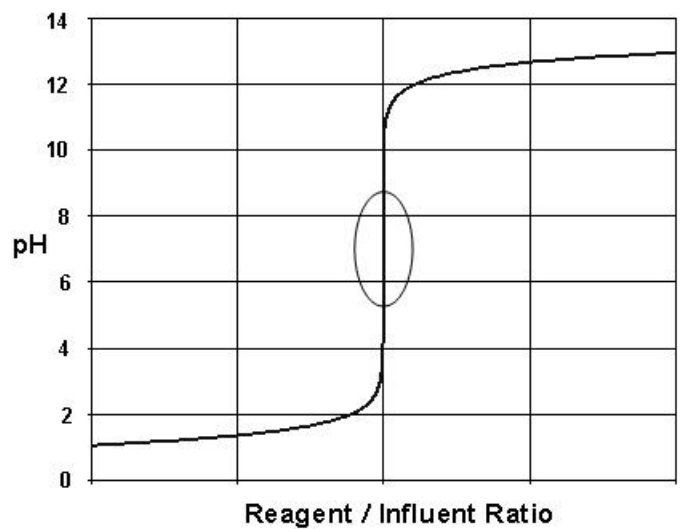


Figure 1a. Strong Acid and Base Titration Curve for the Entire Operating Range

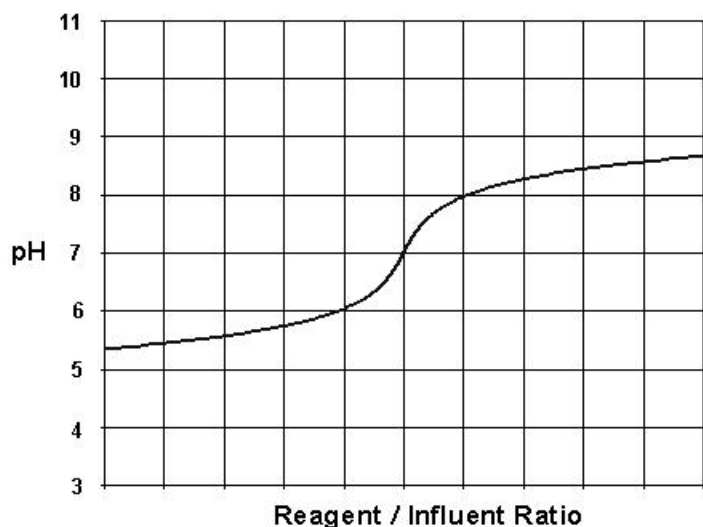


Figure 1b. Strong Acid and Base Titration Curve that zooms in on 3 to 11 pH Range

Key Insight 3: There are no straight lines in titration curve. A zoom in on any supposed line should reveal another curve if there are sufficient data points.

A titration consists of drops being added to a beaker with a fixed sample volume and composition until an end point is reached. This is similar to traditional batch pH control. If the chemist says it is too difficult to make the drops small enough during titration to add enough data points in the neutral region to see the curvature, this is a red flag. It is going to be even more difficult in the plant to adjust these small changes in dosage to hold a set point, particularly for upsets. In continuous pH control, there is a variable feed and discharge flow and a need to keep the discharge always at a set point. It is analogous to a chemist having to vary the number/size of small drops to a beaker with a hole in the bottom and a variable make up flow and composition by just looking at the pH meter.

In order for a control loop to respond equally well for all excursions along the 0 to 14 pH scale, the controller gain would have to change in an equal and opposite direction to the pH process gain so that the loop gain is constant. The use of multiple stages to limit the pH excursions to a small region around setpoint reduces the change in gain seen by the controller. The set points are incremented between the influent and desired final pH so that the distance in acid or base concentration between the influent and set point pH is reduced for each control loop.

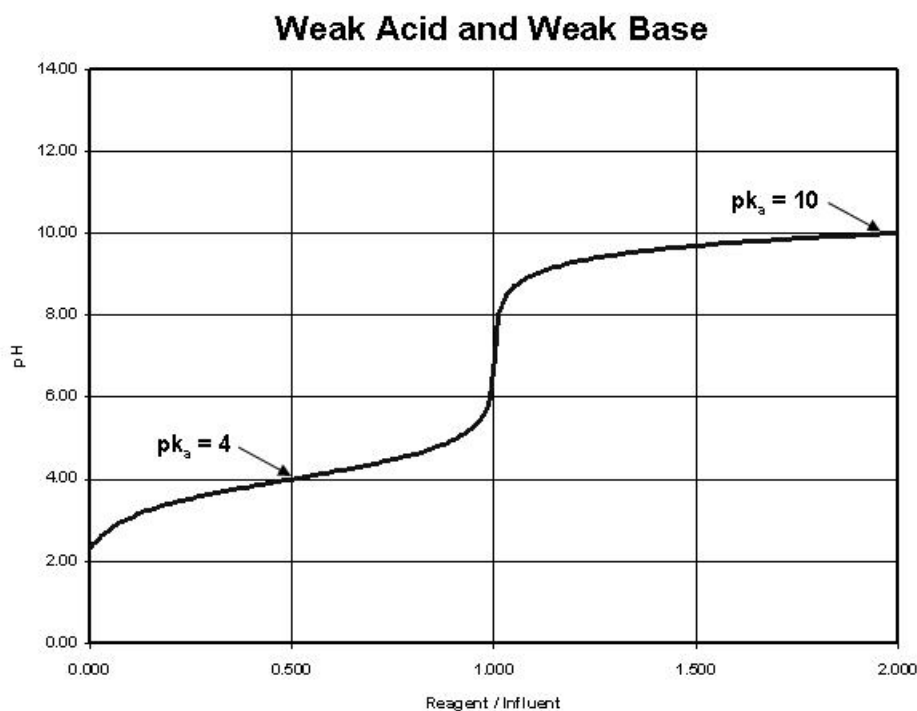


Figure 2. Weak Acid and Base Titration Curve with Flattened Areas (Plateaus) at Centered on Dissociation Constants (pK_a)

Fortunately, many pH systems have weak acids and bases that flatten out various portions of the titration curve to provide a buffering effect. The overall difficulty is reduced especially if the set point ends up residing on one of these plateaus as shown in Figure 2 for a weak acid and base. The natural buffering of surface and ground waters from carbonates can change your mood from suicidal to merely

depressed when the actual curves are compared to theoretical titration curves with pure water. Titration curves of fabricated samples will be much steeper than the titration curves of actual process samples, especially if the lab uses deionized water instead of plant water. Most process samples have dissolved carbon dioxide that provides a moderation of the titration curve slope around 6 pH from carbonic acid.

Key Insight 4: The flatness of the titration curve at the set point has the greatest effect on the tightness of pH control. The next most important effect is the distance between the influent pH and the set point.

The titration curve is the essential tool for determining the nonlinearity, sensitivity, and rangeability requirements that are important for every step from project definition through sustaining installed performance. It determines the investment required, the design details, and the expected efficiency, operability, and maintainability. Without a titration curve, you are flying blind.

Key Insight 5: The titration curve is the essential tool for every aspect of pH system design and analysis.

Rule of Thumb 1: The first step in the design of a pH system is to generate a titration curve at the process temperature with enough data points to cover the range of operation and show the curvature within the control band (absolute magnitude of the difference between the maximum and minimum allowable pH).

Table 2. Top Twelve Mistakes Made Every Day in pH System Design

1. Incorrect or missing titration curve
2. Absence of a plan to handle failures, startup, and shutdown
3. Insufficient number of stages of neutralization (inadequate rangeability and sensitivity)
4. Improper vessel geometry and agitation patterns (excessive equipment dead time)
5. Backfilled reagent dip tube (excessive reagent delivery delay)
6. Incorrect location of reagent injection point (short circuiting)
7. Gravity flow reagent (excessive reagent delivery delay)
8. Incorrect location of reagent control valve (excessive reagent delivery delay)
9. Control valve with excessive stick-slip (poor sensitivity and large limit cycle)
10. Electrodes submersed in vessel (coating and maintainability problems)
11. Electrodes located in pump suction (bubbles, clumps, and wrenches)
12. Electrodes located too far downstream (excessive measurement delay)

In order for the control system to work, special attention must be paid to the design and installation of electrodes, transmitter, controller, control valve(s), piping, and mixing equipment. A mistake in the

design or installation of any component in the loop can cause the control system to not only fail but fail miserably. The process, mechanical and instrument engineers all must be alert to special system requirements from the inception of the project. The top twelve mistakes are summarized in Table 2. Ten of these are illustrated in Figure 3, which shows the use of a horizontal tank, gravity flow reagent, and a ball valve without a positioner.

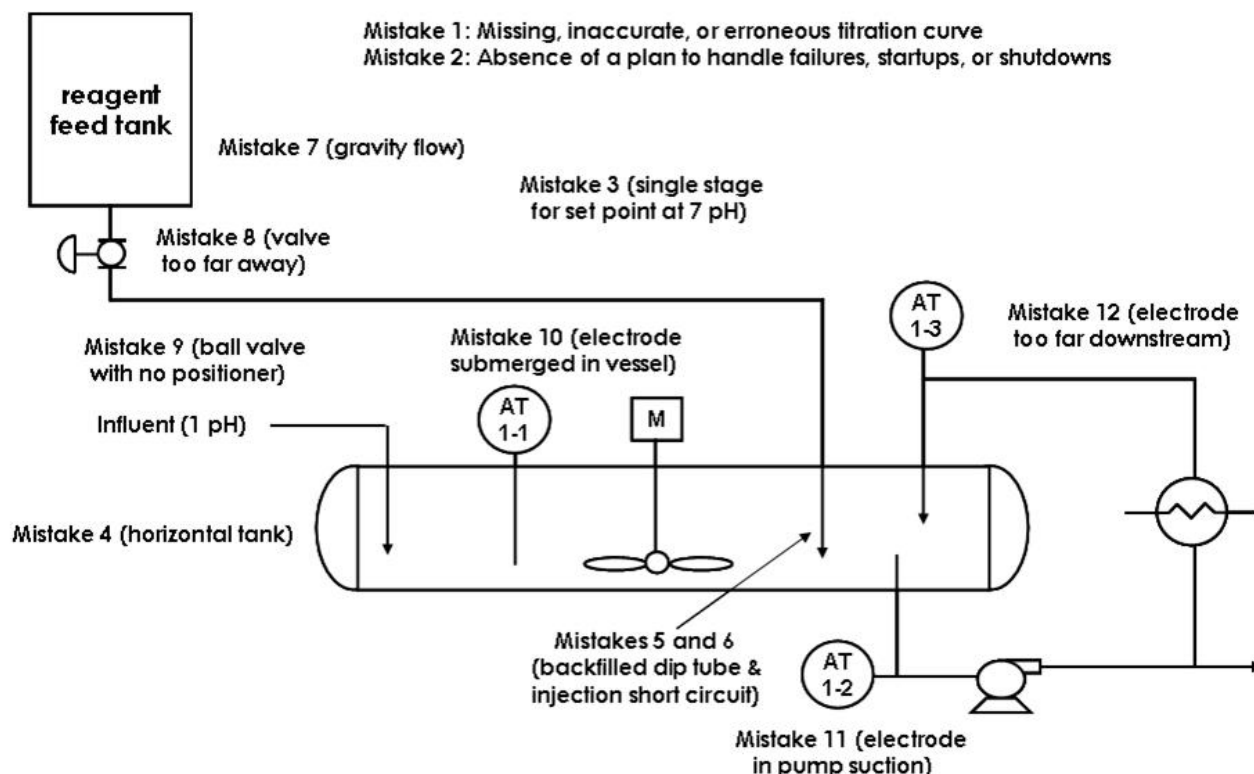


Figure 3. Examples of Mistakes Made Every Day in pH System Design

STAGE FRIGHT

With the pressure on minimizing capital costs, a project may sell themselves short on the number of stages required. The basic rule from the 1970s was that for every two pH units that the influent is away from set point requires one well mixed tank. For example, if the set point was 7 pH, one stage for an influent at 5 pH, two stages for an influent at 3 pH, and three stages for an influent at 1 pH would be recommended. The modern day version of this old rule would reduce the requirement by one stage if feedforward control or signal linearization could be effectively used or if the set point could be moved to a flatter portion of the titration curve. Today, three stages are rarely used. Even the most difficult systems are tackled by an inline system for the first stage and a well mixed vessel for the second stage with precision reagent delivery (valve resolution and threshold sensitivity better than 0.1%).

One of the most frequently missed opportunities in terms of dramatically reducing the difficulty of control and saving on reagent use is to shift the set point away from the center to the edge of a control band where the slope is flatter. While it may seem to be wrong in terms of flirting with the edge, the large oscillations from set points at the steepest point waste reagent and the sluggish tuning put you at a greater risk of going over the edge. For example, many environmental systems must keep the effluent between 2 and 12 pH to avoid its classification as RCRA hazardous waste. However, a set point at 7 pH is the wrong choice and may lead to oscillations between 2 and 12 pH. A much better choice as seen in Figure 4 would be an optimized set point of 4 pH for acidic influent and 10 pH for basic influent. You can warm up to the idea by seeing the tremendous difference at an operating point of 5 or 9 pH. You can be a hero by going into a control room and simply changing the set point to a flatter part of the curve and increasing the controller gain. Of course, the loop probably was not stable to begin with at 7 pH, so the better set point does not mean you can increase the gain by a factor of 10 per pH unit even though it might be a strong acid and base.

Rule of Thumb 2: For a set point on the steepest part of the titration curve, one stage of neutralization is needed for every two pH units away from set point. Accurate feedforward control and precise valves can eliminate one stage.

Key Insight 6: There is a huge opportunity to reduce reagent use and capital investment by simply moving the set point to a flatter part of the titration curve and closer to the influent pH.

In the 1980s it was also found you could substitute a static mixer for the first vessel by the use of an appropriate measurement filter. A static mixer is a piece of pipe baffles or tabs that sub divides the flow stream to provide radial mixing. A centrifugal pump can serve the same purpose. However, these inline mixers provide little to no back mixing or smoothing. Consequently, the process dead time is larger than the process time constant, which leads to large peak errors for fast upsets and a tendency for the loop to oscillate. Originally it was thought that the large oscillations meant you could only use inline mixers on the flat portions of curves or for large control bands. However, since the period and recovery time is fast for a well designed inline system, a judiciously applied measurement filter can allow a pH loop to control the average of the oscillations if there is sufficient volume down stream to smooth out the concentration fluctuations.

Stick-slip is the most frequent source of oscillations in pH control. For example, if the stick-slip is 0.2%, the reagent valve capacity is 1 gpm, and the influent flow is 1000 gpm, the amplitude of the oscillation in the ratio of reagent to influent flow is 0.000002 along the X axis of the titration curve. For a strong acid and base system this could translate to an oscillation of 4 to 10 pH around a 7 pH set point whenever the loop is in automatic. Moving the setpoint to a flatter part of the curve as shown in Figure 5 can drastically reduce the amplification of the limit cycle. Operations will be impressed.

Stick is the per cent change in valve signal needed to make the trim move and is thus the threshold sensitivity of the valve. Slip is the change in position, once the valve trim does move, again in per cent of the signal span. The slip in a properly designed valve is about equal to the stick and sets the resolution capability of the valve. Stick-slip is caused by friction in the packing and trim sealing surfaces. For large valves, the per cent stick-slip translates to a large error in reagent flow. Control strategies have been developed to position a large reagent valve by feedforward and valve position control to keep a small valve in a good throttle range. The manipulation of coarse and fine adjustment valves can eliminate a stage if the stick-slip of each valve is less than 0.1%.

Rule of Thumb 3: The use of a static mixer or pump as a fast inline pH system can eliminate the need for a well mixed vessel for the first stage even for a set point on the moderately steep part of a curve by the judicious use of a signal filter.

For $\tau_o > T_o$:

$$A_o = A_i * \left[\frac{T_o}{2 * \pi * \tau_o} \right] \quad [5]$$

Where:

A_o = output amplitude (pH or concentration)

A_i = input amplitude (pH or concentration)

T_o = oscillation period (minutes)

τ_o = open loop time constant (minutes)

The open loop time constant in Equation 5 is either the digital signal filter time in a Distributed Control System (DCS) for smoothing out pH oscillations and noise or the residence time for a well mixed vessel for smoothing out concentration oscillations. Equation 5 is useful for estimating the size of vessels needed to smooth out stick-slip and the size of a signal filter to keep short term pH fluctuations within the control band. For example, if the oscillation period of pH noise is 0.012 minutes, a digital filter of 0.04 minutes would reduce the noise amplitude by a factor of 20.

It is critical that filters be judiciously used because they add delay to the response to unmeasured load upsets and provide an illusion of better control by providing an attenuated version of the real world. They should only be used to help screen out transients that are so fast they will be smoothed out by a downstream volume and any response by a controller would potentially do more harm than good. It is also important to realize that there will be an offset in the actual pH of the effluent compared to the average pH signal because of measurement errors and noise and any non symmetry of the titration curve about the set point. The effect can be estimated by translation of the oscillations on the titration curve. Normally the offset is relatively small (less than 1 pH) and can be reduced by a simple bias of

the upstream set point. The use of process variable signal characterization to imbed the titration curve and create a linear reagent demand controller for the inline mixer can inherently eliminate the offset.

Key Insight 7: The average or filtered signal pH will not equal the actual pH down stream because of measurement errors and noise and the titration curve.

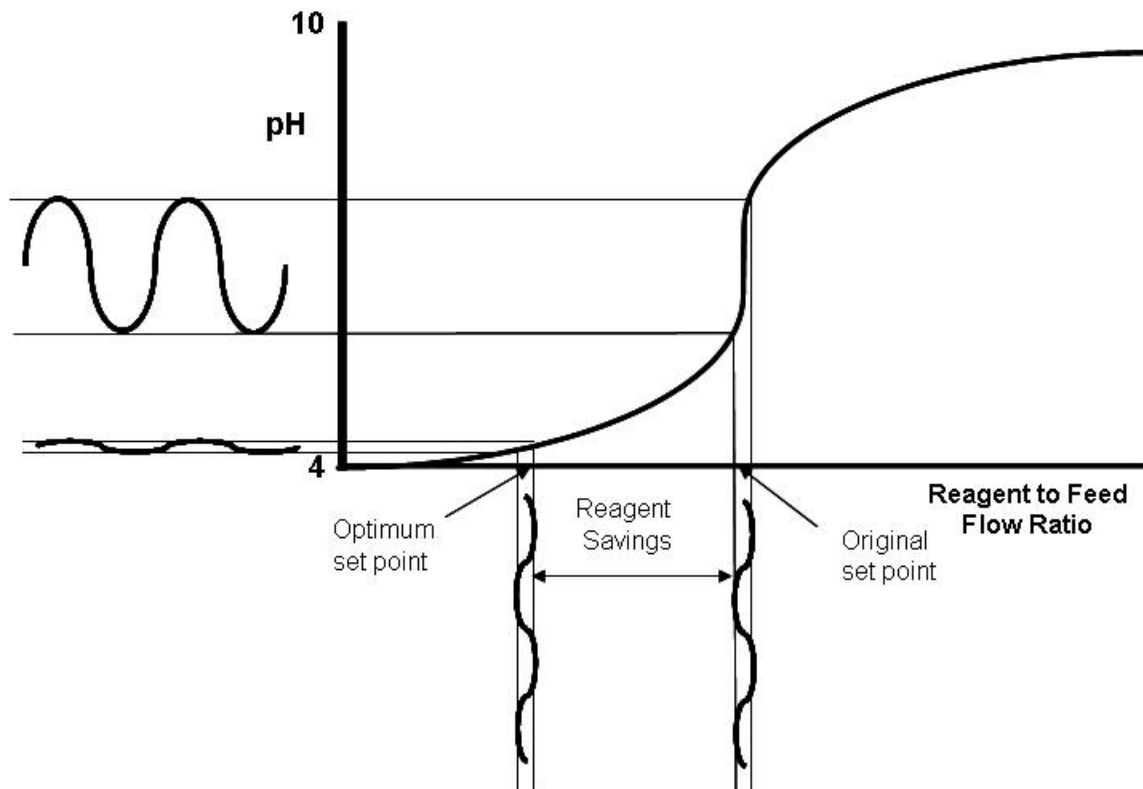


Figure 4. Movement to a Flatter Portion of the Titration Curve can Save on Reagent Use and Reduce pH Oscillation Amplitude from a Stick-Slip Limit Cycle Seen on the X Axis

In general the fastest pH control system with the largest reagent valve should be the first stage and the first line of defense to bear the brunt of an upset so that oscillations have a smaller period and can be effectively filtered out by larger down stream volumes per Equation 5. The recovery time is faster and the amount of off spec material is smaller for a fast system. The period of oscillation is proportional to the loop dead time and the integrated error is proportional to the loop dead time squared.

Another consideration is resonance of oscillations from two control loops in series. The first stage should have a total dead time from mixing and transportation delay that is at least five times faster than the next stage to minimize amplification of upsets from the resonance of in-phase oscillations. Mixing and transportation time delays are proportional to volume so this translates to a volume for the first

stage that is at least five times smaller than the volume for the second stage. A control loop may do more harm than good if the upset has a frequency that is close to its own frequency. Consequently, inline systems with pH controllers should not be put in series because they have similar delays and hence periods unless the mixers are separated by intervening volumes and the module execution time of the downstream loop is increased so the loop deadtime is 5 times larger than the upstream loop.

Rule of Thumb 4: The volume of each stage should differ by a factor of five to minimize resonance with the smallest volume first to minimize recovery time.

A typical system design would use a static mixer with a transportation delay of 0.05 minute for the first stage and a well mixed vessel with a mixing delay (turnover time) of 0.25 minutes and a minimum residence time of 5 minutes for the second stage.

While a tank for smoothing or blending requires minimal agitation, it is critical to realize that a vessel used for pH control must be well mixed with a residence time that is at least 20 times the turnover time. Anything that falls short of this is disastrous for any system with a strong acid or base because it creates large volumes of off-spec material and slow oscillations that persist downstream.

Key Insight 8: A poorly mixed tank should never be used for pH control but can be effectively used to attenuate oscillations from an upstream pH loop.

For a vessel to be classified as well mixed, the height should be less than 150% of the diameter and an axial pattern agitator should be used to provide a ratio of residence time to mixing turnover time that is greater than 20:1. The turnover time should be less than one minute and baffles should be used to improve the mixing pattern. If conventional baffles are not permissible because of the area where polymers, particles, or microbes can accumulate, special draught tubes and contoured bottoms are used to prevent dead zones.

There is a super cheap alternative for pH control. The use of a large volume with an inline pH controller around a pump in its recirculation line will provide an incredibly smooth pH from the vessel. The volume doesn't need to be particularly well mixed, just large. An educator may be sufficient. A tank salvaged from the equipment graveyard may do. The performance is achieved by blending a high recirculation flow with a much smaller influent flow and smoothing out the fast concentration oscillations from an inline system with a large volume per Equation 5. It is important that the inline system have a properly located and precise measurement and valve per Figure 5. The drawbacks to this system is the extra time required to bring the whole volume to the proper operating point on start up or for a set point change and localized high concentrations of acids and bases in the recirculation line.

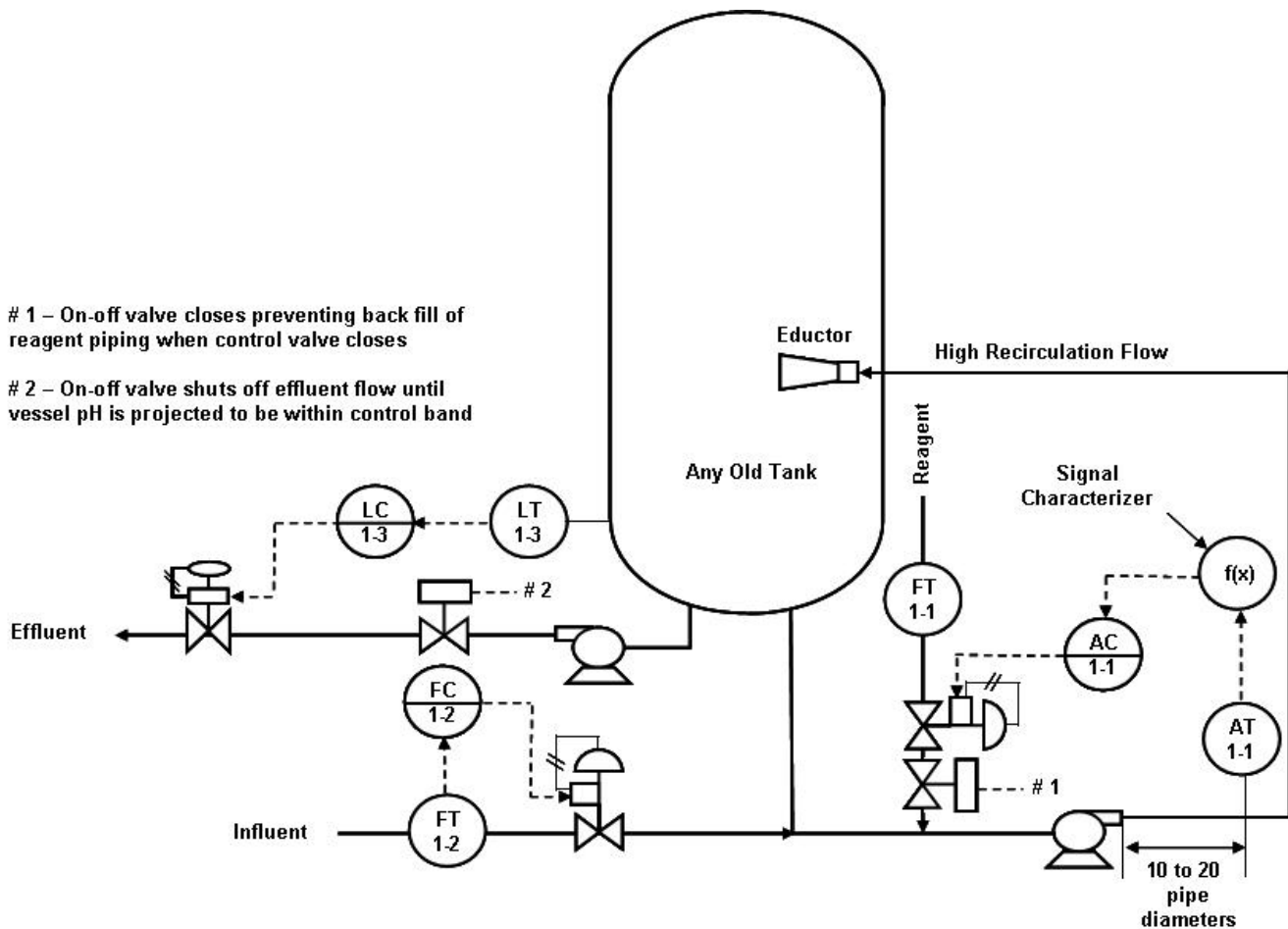


Figure 5. A Really Cheap Way to Achieve Tight pH Control of Influent Upsets

In theory, an incredibly precise valve and accurate signal characterization could enable pH control from any influent pH to any set point. Such a valve does not exist but the combination of the right valve and set point can go a long way to eliminating equipment and saving on reagent use.

SIZE MATTERS

The small valves typically used in pH control are more prone to improper sizing, irregular flow characteristics, greater stick-slip, and plugging. Here size does matter because most of these problems originate from extremely small Reynolds Numbers, clearances, and stem diameters.

Key Insight 9: Most of the problems with reagent throttling and injection stem from the extremely low flows required for pH control.

A representative titration curve with enough data points in steep sloped regions is essential for sizing a control valve and making sure the inevitable stick-slip in all control valves does not cause oscillations outside of the control band (allowable error around setpoint). Figure 6 shows how a titration curve is used to determine the capacity requirement and allowable stick-slip.

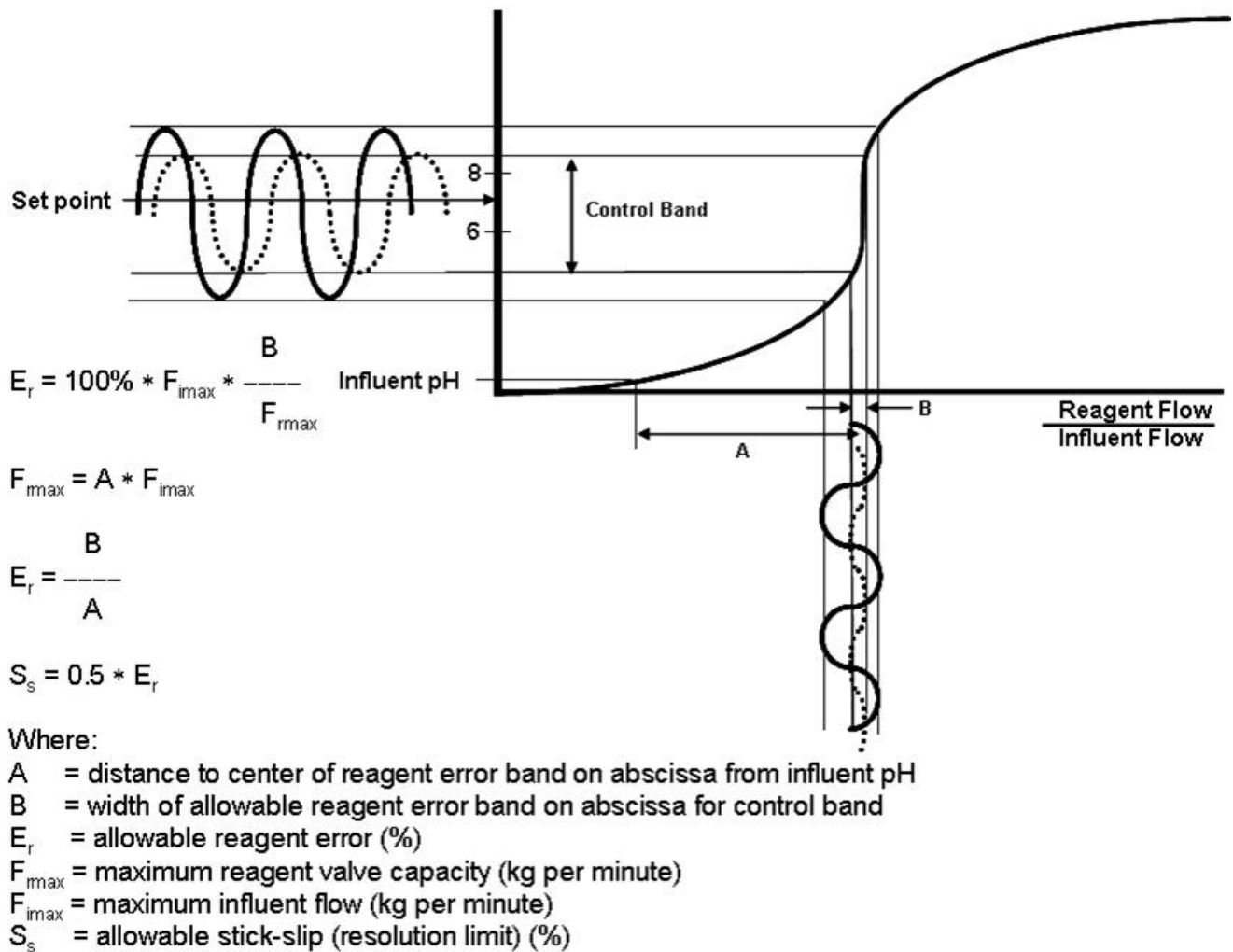


Figure 6. Required valve reagent capacity is determined by the pairing of maximum influent (feed) flow and “A” distance and the allowable valve stick-slip depends upon the B/A ratio.

For a C_v less than 0.01 or extremely viscous fluids, the valve may be operating in the laminar flow regime or in the region of transition from turbulent to laminar flow. Liquid flow moves from being approximately proportional to the square root of the pressure drop towards being proportional to the pressure drop as the flow goes from being fully turbulent to completely laminar. For anything other than a 1 psi pressure drop this can translate to an enormous sizing error. The result is often an

oversized valve that rides the seat where the high seating friction causes excessive stick-slip. Even worse is operation in the transition region where the flow for a particular valve position has poor reproducibility because normally insignificant disturbances such as microscopic changes in roughness or small vibrations can trigger a switch between turbulent and laminar flow and an erratic installed flow characteristic. Some reagents such as 98% sulfuric have a viscosity so high, starting the injection flow is like trying to get ketchup out of bottle.

Key Insight10: Most reagent valves are oversized which increases the amplitude of the oscillations from stick-slip.

Rule of Thumb 5: Make sure valve sizing calculations take in account any transition to laminar flow and viscosity correction.

If you also consider the possibility of a significant distortion of the inherent flow characteristic caused by machining tolerances that are an appreciable portion of the clearances for such tiny trim sizes, the scene is set up for an unknown and extreme nonlinearity. Tiny clearances can pose all sorts of problems because small particles and coatings cause plugging and sticking. The low flow velocities at the surface that is normally associated with laminar flow makes the likelihood of coating much greater.

Finally, tiny stems are likely to be bent from the normal handling both before and after installation. Slight deflections of the stem can cause huge amounts of stick-slip. What good is a control valve if you can't drop it or step on it?

Is the situation hopeless? Not if you go with a manufacturer who specializes in tighter machining tolerances, minimizing stick-slip, rugged stem guiding, and streamlined passages. Stay away from stems smaller than 3/8 inch and insist on getting response and flow test results. Use computer programs now available that properly deal with laminar flow and offer an installed characteristic curve for your piping and operating conditions. Even though the smart digital positioner may be larger and cost more than the valve, it is more important than ever that a digital positioner be used and properly tuned for the small actuator volume. The challenge here is for packaged platforms that are going for low bid not to get cheap where it hurts.

Rule of Thumb 6: Use precision machined industrial sliding stem (globe) valves with digital positioners tuned for the small actuator volumes to minimize stick-slip.

If there is a tendency for plugging, pulse width modulation is a solution if there are sufficient back mixed volumes to attenuate the pulses. This can also provide a linear flow characteristic and a flow large enough to be turbulent. The ratio of maximum to minimum pulse width establishes the

rangeability. The maximum pulse width and hence cycle time determine the degree of variability that needs to be filtered and the additional dead time from the pulse off time. Now stroking time can be an issue because it is desirable to have the minimum pulse be as short as possible.

Rule of Thumb 7: If the trim will plug, use pulse width modulation and set the ratio of the maximum to minimum pulse width to achieve the desired rangeability.

Reagent dilution can eliminate these valve problems associated with low flow, but can introduce large reagent concentration disturbances and transportation delays if not done properly. The requirements for precision dilution are exacting. Coriolis mass flow meters are needed for precise mass flow ratio control. A static mixer for dilution concentration control with a large volume downstream to smooth out fluctuations is needed. Conductivity or density can be used to provide inferential measurements of acid and base concentrations.

The installed characteristic of a throttled reagent valve is the inherent characteristic because the frictional loss in the piping is so small from the low flow. The pressure drop across the reagent valve is a large percentage of the system drop except for injectors with very tiny holes. Linear trims are best for vessels and equal percentage trims are best for static mixers when the pH controller directly manipulates a reagent valve instead of a reagent flow set point. As with any rule there are exceptions. The flow of acid and bases consumed by reactions can be so large that the installed characteristic of an equal percentage trim starts to resemble a linear characteristic and a linear trim starts to distort to a quick opening characteristic.

ONE IS THE LONELIEST NUMBER

The repeatability of a pH measurement on the steep part of a titration curve is rarely better than 0.1 pH if you include short and long term variability. Most of this error is caused by insufficient mixing (process noise) and fluctuations in the reference electrode potential. If you move the set point to a flat part of the curve where noise is less, the repeatability improves to 0.01 pH. Bioreactors have an extremely buffered broth offering the possibility of a 0.01 pH or better resolution. The 0.01 pH accuracy stated for electrodes is for the ideal laboratory environment and is a pipe dream for neutralization systems with strong acids and bases. Lab pH readings appear to be more consistent because the electrode is not inserted long enough for the coatings and changes in glass surface and reference junction potential to become an issue. For nasty streams, this short term immersion is duplicated in the field by the use of automatically retractable pH electrodes that are sequenced to be inserted for a couple of minutes and then soaked or calibrated for ten or more minutes.

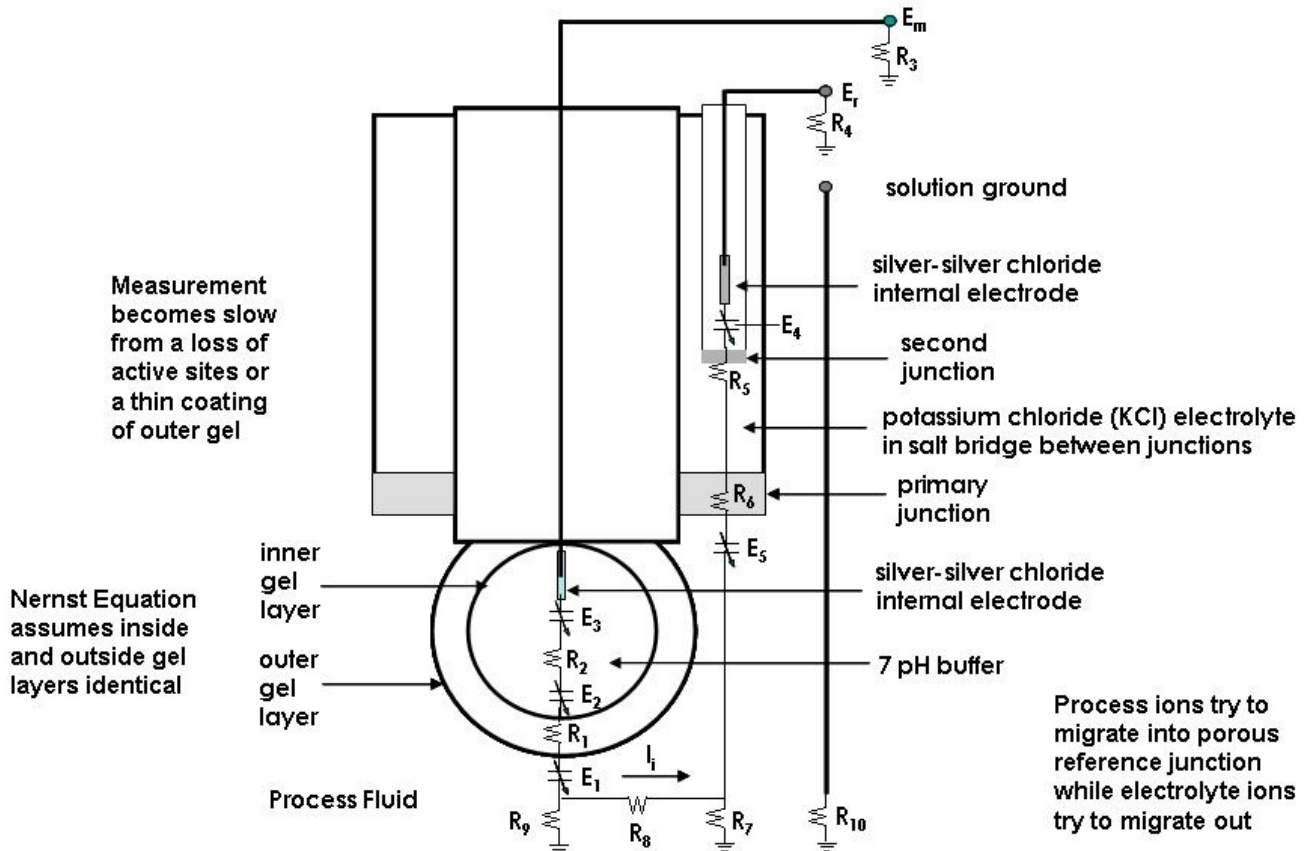


Figure 7. Measurement Electrode Depends upon a Hydrated Surface Layer and Reference Electrode Depends upon a Porous Junction for Electrical Continuity

Key Insight 11: The repeatability of commonly used electrodes is about 0.1 and 0.01pH for the steep and flat portions of a titration curve, respectively if the process is nice and the electrodes are properly selected, installed, and maintained.

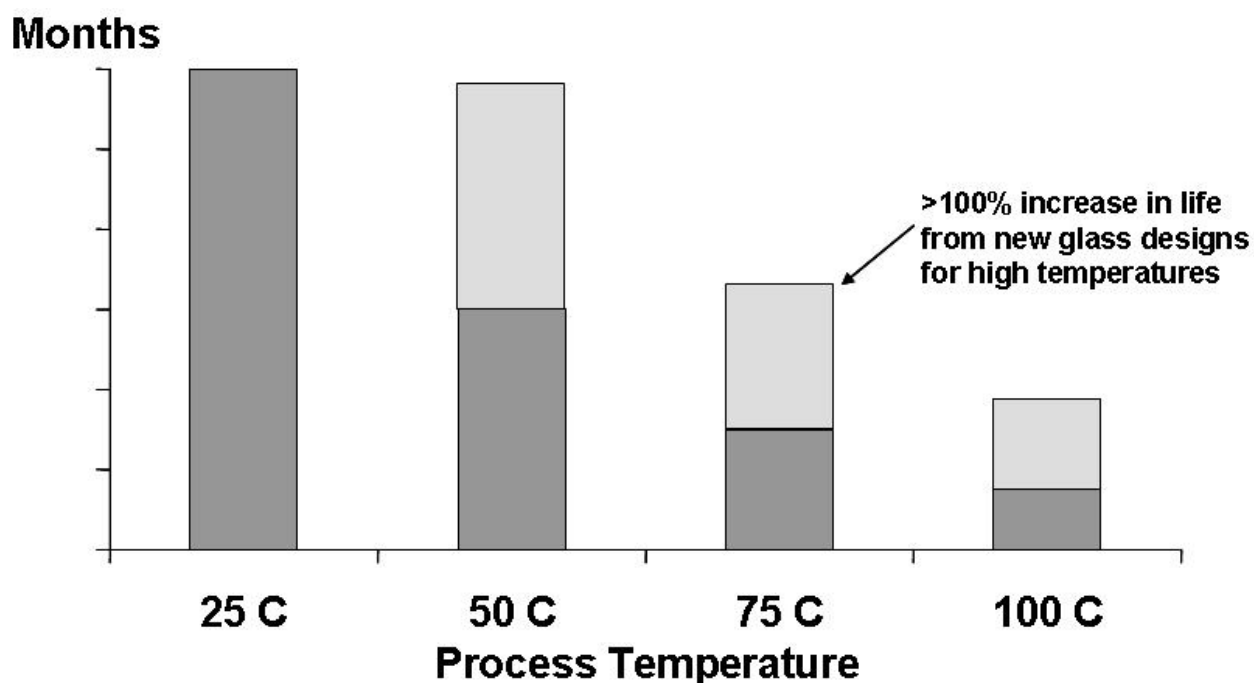
Rule of Thumb 8: When the repeatability must be better than 0.01 pH, use a pressurized flowing junction reference electrode with a reference fill solution that is compatible with the process.

Rule of Thumb 9: For really nasty process fluids that seriously shorten the life expectancy of the electrode because of chemical attack, abrasion, dehydration, or coating, use an automatically retractable and sequenced assembly to minimize the electrode's process exposure and maximize its conditioning and calibration.

The glass measurement electrode develops a potential in response to the activity of hydrogen ions at its glass surface. In theory, the hydrogen ion jumps from a hydronium ion in the aqueous solution to join

up with a water molecule in the hydrated gel layer to form a hydronium ion in the glass surface as shown in Figure 7. The reproducibility of the measurement depends upon the condition of the hydrated gel layer, which is extremely thin and fragile. For solutions with low water concentrations, non aqueous solvents, or high acid concentrations, the gel layer gets dehydrated and must be replenished by periodic soaking in water solution. Smart transmitters that measure the electrical resistance of the measurement electrode can detect severe changes in the gel layer if the resistance is corrected for the effect of glass type and temperature.

Key Insight 12: The reproducibility of a measurement electrode depends upon the condition of a thin fragile gel layer that is disrupted by abrasion, dehydration, and chemical attack.



High acid or base concentrations (operation at the extremes of the titration curve) decrease life for a given temperature. A deterioration in measurement accuracy (e.g. electrode efficiency) and response time often accompanies a reduction in life.

Figure 8. Effect of Temperature on Measurement Electrode Life in a Nice Solution

High process temperatures shorten the electrode life per Figure 8 even for nice dilute aqueous solutions. High acid and base concentrations associated with operating below 2 pH or above 10 pH can chemically attack the glass surface and reduce its efficiency and life expectancy. Special glass formulations can help and in general the higher the electrical resistance of the glass the higher the chemical resistance. Thicker glass (“ruggedized”) measurement electrodes are desirable from a stand

point of reducing breakage and resisting abrasion but the electrical resistance and the response time of these electrodes are larger and the active surface area of the dome shape is smaller. If they are used in an acidic stream that tends to dehydrate the gel layer, the problem is compounded. Low temperatures that exponentially increase the glass resistance also cause noisy erratic results for these higher resistance glasses. There is in general no glass formulation that provides an acceptable service life for hot ($> 65^{\circ}\text{C}$) relatively concentrated sodium hydroxide solutions ($> 10 \text{ pH}$).

The reference electrode is designed to provide a stable reference potential and provide an electrical path between the process and the internal electrode. To provide this electrical continuity, the reference fill must be in contact with the process, which figuratively and literally opens the reference electrode to all sorts of problems. The porous reference liquid junction shown in Figure 7 that allows the ions of the internal electrolyte to migrate and touch the process may allow process ions to migrate in the opposite direction and change the reference junction potential and eventually contaminate the internals. Pulsating pressures, high ionic strength solutions, and highly mobile ions accelerate the deterioration. A second much smaller internal junction is often used to protect the internal silver-silver chloride electrode. Particles and sticky fluids can also clog the junction. A large liquid junction surface area minimizes the clogging problem but increases the contamination problem. Solid references have large wood or plastic junctions with impregnated electrolyte ions to resist contamination. However, these junctions may be slow to reach an equilibrium potential. The most accurate and sure proof alternative is a pressurized flowing junction reference. These are not popular in the USA because they require maintaining a pressurized reservoir to replenish the fill lost out the junction. Also, a high junction flow can throw off measurements in beakers and contaminate a process. Smart transmitters can measure the junction resistance and detect clogging problems.

Key Insight 13: The reproducibility of the reference electrode depends upon its internal electrolyte ions quickly establishing and maintaining contact with the process but the process not clogging or migrating into the reference junction.

The trouble shooting of pH measurements can be confusing. Table 3 serves as a guide to finding the common cause for a given symptom.

Table 3. Symptoms and Causes

- Slow measurement
 - Coated glass, aged glass, dehydrated glass, thick glass, high temperature, low pH, low velocity
- Noisy measurement
 - Dehydrated glass, pure water, low water, low temperature, poor mixing, high velocity, EMI
- pH decreases with temperature
 - pKa or pKw decrease with temperature (missing solution temperature compensation)

- Horizontal shift to right of Isopotential point due to measurement electrode type or problem
- pH increases with temperature
 - Nernst MV decrease with temperature (missing electrode temperature compensation)
 - Horizontal shift to left of Isopotential point from electrode type or problem
- pH increases with salt or solvent concentration
 - Decrease in activity of hydrogen ion from increase in ionic strength or decrease in water content
- Constant 7 pH measurement
 - Broken glass, broken wires, protective caps still on electrodes
- Decrease in measurement range (decrease in electrode efficiency)
 - Dehydrated glass or aged glass
- Daily drift in measurement (change in electrode offset)
 - Coated reference junction
- Hourly drift in measurement
 - Slow equilibration of reference electrode
- Off-scale pH measurement
 - Poisoned reference electrode or high solvent concentration

Most electrodes in service today are combination electrodes where the reference electrode is located in a ring around the glass measurement electrode. One manufacturer offers a combination electrode whose sleeve is a plastic with immobilized electrolyte ions to form a very large reference junction area impervious to contamination. Manufacturers have developed glass formulations, reference junction, and electrode designs to deal with the spectrum of process application requirements.

Rule of Thumb 10: The measurement electrode glass type and reference electrode junction and fill must be compatible with the process composition and temperature.

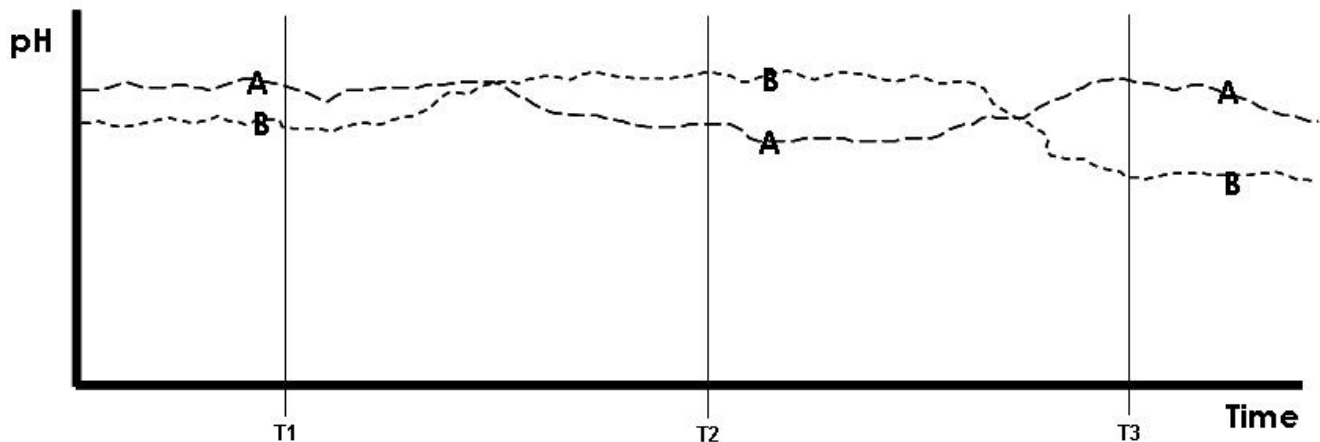
Rule of Thumb 11: Smart Transmitters should be used to continually monitor resistances to infer the condition of the glass surface and the reference junction.

Most pH systems are over calibrated while chasing sample results. If there is only one electrode, there is not much evidence to question the lab even though time, process temperature, and carbon dioxide content could explain the disagreement. Even if the sample is a representative snapshot of the process, a variety of short term errors exist particularly from seemingly insignificant concentration gradients in strong acid and strong base systems in the 4 to 10 pH region.

A second electrode will raise more questions than answers because the two electrodes will never agree because of concentration gradients, velocities, and the condition of the glass surface and reference junction. As seen in Figure 9, what is high today may be low tomorrow although long term trends may

be observable, kind of like the stock market. Except for a sluggish or noisy response, it is difficult for the operator to establish which electrode to select so suspicion and prejudice prevail. Frequent calibrations adjustments often chase short term transients and make the problem worse. The best results are often obtained by going to three electrodes and leaving them alone.

Most calibration adjustments chase the short term errors shown below that arise from concentration gradients from imperfect mixing, ion migration into reference junction, temperature shifts, different glass surface conditions, and fluid streaming potentials. With just two electrodes, there are more questions than answers.



Above shows the trend if no calibration adjustments are made. If the favorite electrode is A resulting in B pH increased at time T1, then B will be higher than shown at time T2. If B pH is decreased at time T2 then B will be more than twice as much lower than shown at time T3.

Figure 9. What is High Today may be Low Tomorrow

The addition of a third electrode and the automatic selection of the middle signal will inherently ride out a spurious signal or failure of any type from one electrode. Often, engineers think they can design a better failure strategy but in fact, all other supposedly more sophisticated strategies for failure rejection have one or more modes of failure and can do more harm than good. The middle signal selection is often a standard function block that can be readily set up in most Distributed Control Systems (DCS). Of course, if the process is truly nasty, you should not install three electrodes. You should go instead to automatically retractable and sequenced electrodes to minimize process exposure time. Table 4 summarizes the advantages of middle signal selection.

Rule of Thumb 12: Middle selection will maximize the reliability and minimize the maintenance unless the process is so nasty it causes premature electrode failure.

Finally, there is an opportunity to calculate pH online for the flat part of a titration curve if there are Coriolis flow meters to accurately measure the mass flow and density of two component mixtures or

streams with sufficiently constant acid and base concentrations. An inferential measurement or pH estimator based on an online titration or charge balance model can become a third measurement that enables middle selection. In one application it was found that the calculation was more accurate than the electrode readings because of the flatness of the titration curve. A single Coriolis flow meter on each of the influent and reagent streams could be reliable and accurate enough to replace the use of electrodes altogether for the first stage of a neutralization system, which typically is on a very flat portion of the titration curve. Coriolis meters also offer the ability to display reagent use, process efficiency, and automatically generated titration curves online. These opportunities will be explored in the chapter on control.

Key Insight 14: Coriolis flow meters can be used to replace pH electrodes in special cases and provide online displays of reagent use, process efficiency, and titration curves.

Table 4. Advantages of Middle Signal Selection

- Inherently ignores single measurement failure of any type including the most insidious failure of measurement equal to set point
- Inherently ignores slowest electrode
- Reduces noise and spikes particularly for steep curves
- Offers online diagnostics on electrode problems
 - Slow response indicates coated measurement electrode
 - Decreased span (efficiency) indicates aged or dehydrated glass electrode
 - Slow drift or bias indicates coated, plugged, or contaminated reference electrode or high liquid junction potential
 - Fast drift after installation indicates equilibration of reference electrode
 - Noise indicates dehydrated measurement electrode, streaming potentials, velocity effects, ground potentials, or EMI
- Facilitates online calibration of a measurement

ACCELERATION AND STAGNATION

The approach to the neutral point looks like an accelerating response to the pH controller and is similar to what a temperature controller experiences for a runaway condition in an exothermic reactor. The tuning rule for such temperature controllers is to minimize reset action (maximize the reset time) and maximize rate action. Reset has no sense of direction and promotes overshoot. Rate anticipates where the process is headed by looking at the rate of change of the measurement and suppresses overshoot. However, rate will amplify noise and can generally only be used for pH control on back mixed volumes where there is a large enough process lag to provide a smooth and gradual response. For operating on the flat part of the curve, the controller gain should be increased to avoid stagnation. So

for well mixed vessels, you can become famous by Friday if you simply decrease the reset setting and increase the rate setting.

Key Insight 15: The approach to the neutral point looks like a runaway response.

For inline pH systems dominated by reagent and process transportation delays and spurious readings from concentration gradients, reset should be predominantly used to provide an averaging type of control and rate should be avoided.

Rule of Thumb 13: Tune the pH controller with reset action (small reset times) for inline systems and with rate action (large rate times) for well mixed vessels.

If the titration curve is relatively fixed and known, it can be used to provide a feedforward signal. Generally this is simply flow feedforward where the reagent flow is ratioed to the influent flow and corrected by a feedback pH controller. It relies on a secondary reagent flow controller that receives a remote set point that is the flow ratio multiplied by the actual influent flow corrected by the pH controller output. If a flow meter is not available for either the influent or reagent flow, an inferential flow measurement can be calculated from the installed valve characteristic and pressure drop.

Flow feedforward is generally helpful as long as you under correct for set points on the steep portion of the titration curve. Flow feedforward is particularly important for large feed flow changes and for systems with large dead times (large reagent injection delays and vessels with less than ideal mixing). The use of pH feedforward is generally not advisable if the influent measurement is on the extremes of the titration curve where the process conditions are harsh and the flatness of the titration curve increases the reagent error from measurement error. Deterioration in the glass surface and reference potential make the measurement error larger so there is a double hit in terms of the accuracy of the feedforward signal. pH feedforward works can work well when you are going from a steep part to a flat part of the titration curve but this is rare case. New adaptive control algorithms can automatically identify the feedforward gain and dynamics from feed set point changes.

Key Insight 17: Flow feedforward is generally helpful but can waste reagent by over correction for set points on the steep portion of the titration curve.

Rule of Thumb 14: Do not use pH feedforward control if the influent pH is on the extremes of the titration curve.

For batch or continuous systems, a “head start” of the reagent valve position or reagent to influent ratio, can dramatically reduce the startup time for low pH controller gains. The “head start” logic initializes the reagent valve or ratio to what was captured as the best value from the last run or batch. The initialization of the pH controller output is held until the actual pH reading has responded and is representative of the actual operating conditions on startup.

Key Insight 18: A “head start” of reagent valve position or flow ratio can dramatically reduce the start up time for low pH controller gains.

Rule of Thumb 15: The initialization of the pH controller output on startup should be held until a representative pH measurement is available for feedback control.

There is a great tendency for pH systems to develop equal amplitude oscillations between the flat portions of the curve. People who use the ultimate oscillation method to tune a pH controller often chose a higher than actual ultimate gain because a wide range of gains create equal amplitude oscillations. Higher gains will tend to make the amplitude slightly larger but this is not perceptible and the amplitude never grows as with classic instability because the cycle is limited by the flat parts of the titration curve. The user needs to look for the start of damped oscillations to avoid confusion with the limit cycle.

Key Insight 19: A pH controller tends to cycle with equal amplitude oscillations.

Rule of Thumb 16: Do not use the ultimate oscillation method for tuning pH controllers but instead find the gain that causes damped oscillations.

For a fixed and known titration curve, there is an opportunity to linearize the process gain by signal characterization of the controlled variable. The X axis of the titration curve is scaled 0 to 100% of the operating range. Signal characterizer function blocks are then used to calculate the X axis (reagent demand) from the Y axis (pH) by entering pairs of data points. The controlled variable is now 0 to 100 % reagent demand. This strategy works particularly well if the set point is on the steep part of the curve. It avoids the pH getting hung up on the flat part of the curve. It may do more harm than good if the set point is on the bend in a curve and you must avoid at all costs getting on the steep part because it will slow down the response on the steep part. It is better in this case for the controller to see the acceleration and use rate action to kick the pH back to the flat part.

Key Insight 20: Signal characterization of the controlled variable is a powerful tool for linearization if the set point is on the steep portion of a fixed titration curve but may be counter productive to prevent excursions into the steep region for set points on the bend in the curve.

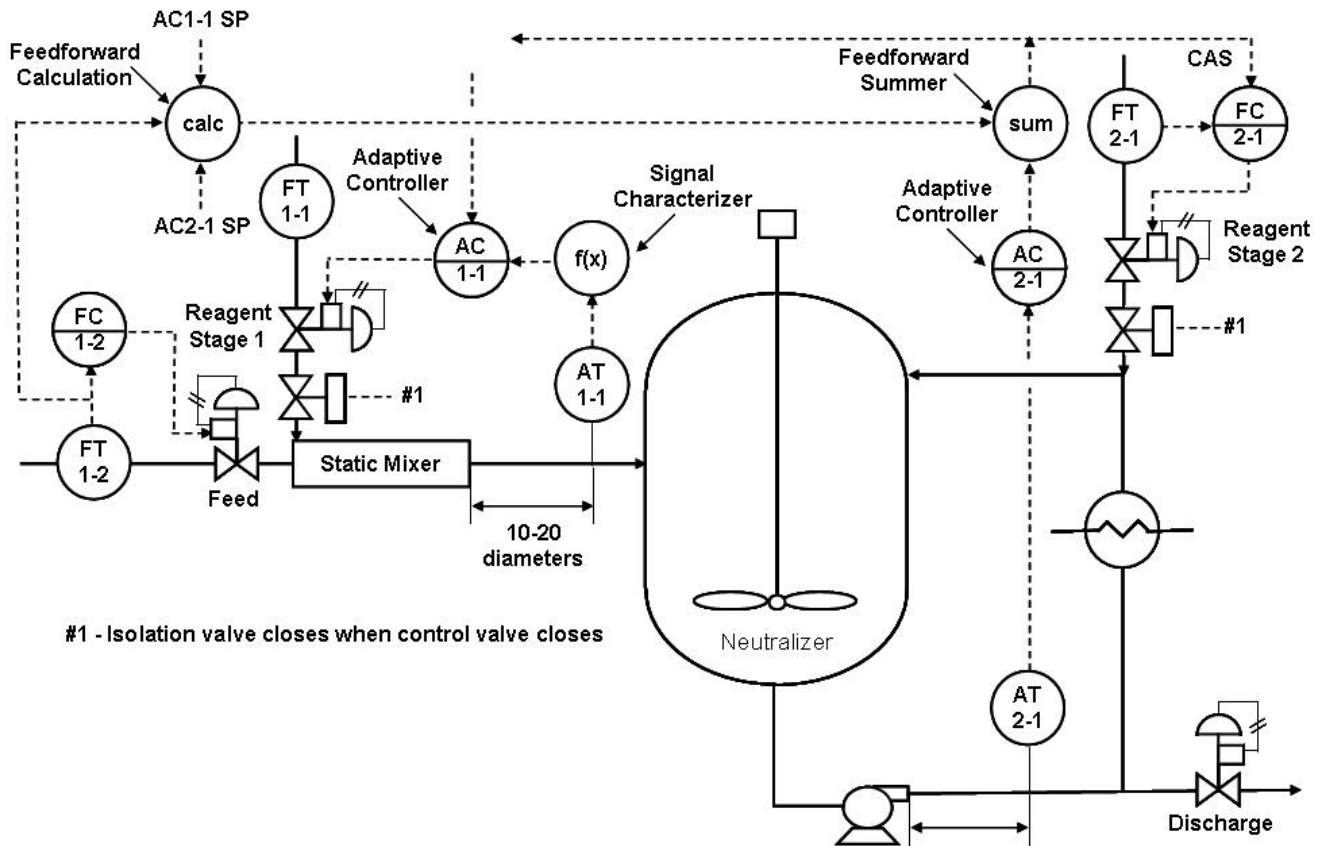


Figure 10. Advanced Control Techniques to Minimize Reagent Use

Figure 10 illustrates a myriad of advanced control techniques for a two stage system where the first stage is a static mixer and the second stage is a well mixed tank. It shows the use of signal characterization, pH and flow feedforward, adaptive control, and real time optimization of the first stage set point to minimize reagent usage. If precise reagent valves are used, this system can perform as well as the traditional system with 3 well mixed vessels in series each with their own pH loop.

If a linear trim reagent valve is not available for vessel pH control, then signal characterization of the manipulated variable can reduce the nonlinearity introduced by the valve. In this case, the signal characterizer block is on the controller output. For a static mixer where the primary disturbance is influent flow, the equal percentage characteristic where the reagent valve gain is proportional to flow compensates for the composition response gain that is inversely proportional to flow eliminating the need for signal characterization.

For a variable or unknown titration curve, an adaptive controller that will find the changes in process gain can fill in the blanks. New algorithms have been developed that can identify the process dynamics for a set point change or by automatic injection of a short step into the controller output. The combination of adaptive control with signal characterization can be a powerful “one-two punch” to eliminate the nonlinearity.

Rule of Thumb 16: The combination of adaptive control with signal characterization can be a powerful “one-two punch” to eliminate nonlinearities.

LIFE IS A BATCH

All processes have a beginning and an end. A continuous process can be thought of as a batch during start up and shutdown that can benefit from the automation of sequencing techniques and standards developed for batch operations. An important distinction between batch and continuous is that during the reaction or formation of product, the vessel discharge flow is zero for batch operations. For batch reactors where the reagent is consumed or for fed batch operations where the reagent and feeds are simultaneous, the response is self-regulating and many of the design techniques developed for continuous control and optimization apply. For more traditional batch operation where the reagent and feeds are charged sequentially, the pH response is a ramp. This integrating response has profound implications as to controller tuning and strategies. It is more critical than ever to minimize the reset action (maximize reset time) and maximize rate action to prevent overshoot. If the pH goes past the end point, the only way it can be corrected is by use of split ranged of acid and base reagents. Often there is a dead band between the closing of one valve and the opening of the other valve to prevent cross neutralization (split range gap). However, the combination of a dead band and an integrating response results in a continuous cycle even if there is no stick-slip. If you also consider that the split range point for the reagent valves is the point of greatest valve gain discontinuity and stick-slip, the oscillations from split ranged operation can significantly increase the cost of reagents and create excess salts from the cross neutralization of reagents. To prevent unnecessary crossing of the split range point, reset is turned off or reagent addition is shutoff once the pH is within an acceptable control band.

Key Insight 21: If there is no consumption of reagent in a batch, the pH response is integrating and the pH loop will oscillate across the split range point for a controller with integral action.

Most batch operations to date use mass flow meters to charge a total mass of reagent specified by a recipe. The operator may then send a sample to the lab and make some manual trim adjustments. The use of an online pH measurement and one or more of the advanced batch control strategies listed in Table 5 can reduce batch cycle time and improve consistency. If the starting pH is on relatively steep part of the curve, then a temperature corrected curve can be used to calculate the charge required based on the change in mass ratio on the X axis (item 1). However, if the pH at the start of the reagent

addition is on extremes where the conditions are harsh and the reagent ratio error is large, it is best to use a recipe number that was updated by the actual reagent used in the last best batch (item 2). A filtered and velocity limited rate of change of pH can be multiplied by the total time delay to provide a predicted pH that when compared to the desired end point can provide an anticipation need to prevent overshoot (item 3). Pulse width and amplitude modulation of the pH controller output can mimic the titration method used in the lab (item 4). Finally, inline pH control of a high recirculation flow can provide a smooth transition to the end point if the localized high reagent concentrations do not trigger side reactions, damage cells or crystals, or corrode recirculation piping and nozzles (item 5). The inline pH control set point is remotely set by a batch pH controller with its reset turned off when the batch pH approaches the end point. What works best may be a combination of an initial charge just short of the end point based on items (1) and (2) and then a combination of items (3) and (4) or (5) to make a trim adjustment.

Table 5. Advanced Batch pH Control Techniques

- (1) Automatic calculation of charge from temperature corrected titration curve
- (2) Automatic partial correction of charge based on last best batch
- (3) Automatic end point prediction and shutoff based on rate of change of pH
- (4) Pulse width and amplitude modulation of a proportional-only controller output
- (5) Cascade of batch pH to inline pH control of a high recirculation flow

INDUSTRIAL IMPORTANCE

Table 6. The Importance of pH in the Process Industry

<u>Application</u>	<u>Processes and Aspects Affected by pH</u>
Bacteriology	Microorganism growth and metabolism
Baking	Dough volume, texture, and color
Brewing	Yield of extract and sugar during mashing
Canning	Time and temperature for sterilization
Chemicals	Impurities and crystallization of salts
Cleaners	Effectiveness of removing paint and varnishes
Dyes	Yield and uniformity through intermediates
Electroplating	Nickel deposit hardness and brightness
Fermentation	Fermentation time and alien organism growth
Gelatin	Water absorption, solubility, and clarity
Pharmaceuticals	Effectiveness, stability, and body reaction
Pigments	Uniformity of composition in precipitation
Pulp and paper	Sizing, loading, coating, and foaming
Sewage	Digestion time, odors, and foaming

Sugar	Inversion of sugar and destruction of glucose
Textiles	Efficiency of most wet processes
Water treatment	Coagulation and softening processes

In the food and beverage, chemical, petrochemical, pharmaceutical, power, pulp and paper, and textile industry, pH measurement and control is important for process efficiency and product quality beside protection of the environment. Table 6 summarizes the importance of pH for various industrial applications. The number of pH loops in new plants will exponentially increase as bioprocesses move from the laboratory to plant production. The suppression of alien organisms and the yield of genetically engineered organisms are greatly dependent on tight pH measurement and control. The cost of a bad batch and contaminated equipment can be millions of dollars for high value added pharmaceuticals.

THE REAL DEAL

Table 7 summarizes the Facts of Life from a decade of pH control startups that can be best described as a “Magical Mystery Tour”.

Table 7. The Facts of Life

1. Instrumentation is frequently the source of disturbances for pH systems through reproducibility error, measurement noise, and valve stick-slip.
2. Inline pH loops will oscillate regardless of controller tuning, if the set points are on the steep parts of titration curves.
3. pH electrode submersion assemblies with unencapsulated terminations below the liquid surface will eventually have wet terminations.
4. Reagent control valves that are not close-coupled to the injection point will cause reagent delivery delays long enough to reach early retirement.
5. You need either a flow meter or a seer to diagnose reagent delivery problems.
6. Flow feedforward signals must be corrected by a pH feedback controller unless you like late night calls from operations.
7. Transportation delays to pH electrodes in analyzer houses will exceed mixing time delays to such an extent that the increasing comfort of checking electrodes is offset by a decreasing comfort in checking trend recordings.

8. Injection electrodes in recycle lines should be preferred to sample holder and submersion assemblies to reduce maintenance cost and coatings and improve response time, but not all injection electrodes are equal.
9. Large poorly mixed tanks are fine if you don't put pH control on them. Use them upstream to reduce reagent consumption or downstream to filter out oscillations. If you can't make up your mind where to use them, put them downstream.
10. Two measurements without an estimator will raise more questions than give answers.

WIRELESS

Wireless technology offers the opportunity to select the best electrode for an application. Spare wireless transmitters can be used to test electrodes in lab solutions set to mimic the concentrations and temperatures of the process. The process lab offers a controlled environment to vary the process conditions of interest and keep other conditions constant. The first through fourth variables of smart wireless transmitters can be readily made available for historization and analysis in the distributed control system (DCS). The slope, offset, and resistance of the electrodes can be studied. The accuracy and response time can be measured over an extended period of time to determine the performance and life of various electrode designs. For example, new high temperature glass formulations increase the life expectancy and prevent the deterioration of electrode response time from premature aging of the glass electrode.

Process temperature changes the dissociation constants and mobility of the ions and thus the actual solution pH and conductivity. For complex mixtures, the best way to determine the effect of process temperature is to vary the process sample temperature over the expected operating range. The change in the water dissociation constant (pK_w) with temperature causes a change in solution pH that increases as the pH approaches the pK_w . Smart wireless transmitters have the ability to configure solution temperature compensation. However, lab meters often cannot provide more than the standard temperature compensation for the electrode per the Nernst equation. Wireless transmitters could be used instead of lab meters for standardization with grab samples, the preferred method of calibration. Standardization is safer and more effective since it does not require removal of the process electrodes eliminating the associated risk of personnel exposure and damage to the glass, and disruption of the reference junction equilibrium.

pH measurements are susceptible to spikes from the start of motors and the change in speed of variable frequency drives. The fact these spikes are not observed when the electrode is connected to a laboratory meter is clue that transmitter output wiring may be a significant contributing factor to

ground loops. When a wireless pH transmitter was used on a “single use bioreactor”, the spikes in the wired transmitter left in service did not appear in the wireless transmitter trend chart in Figure 11.

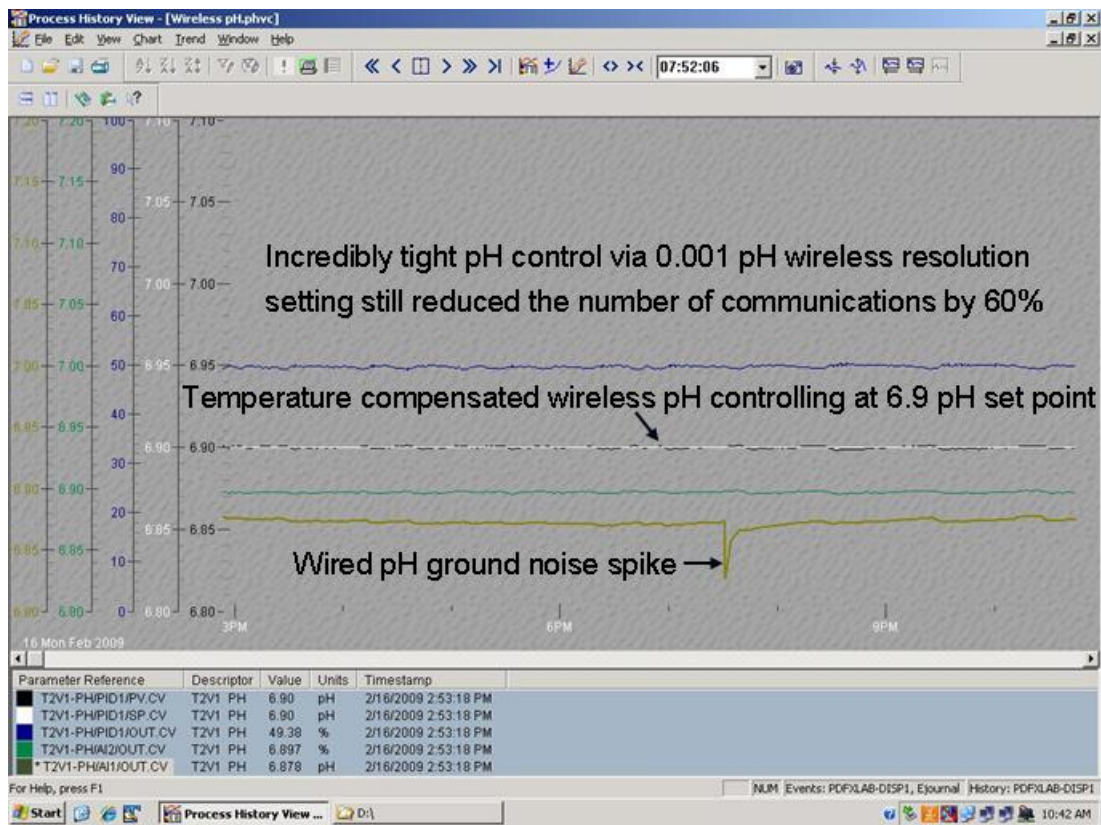


Figure 11. Spikes in Wired pH from Electrical Noise did not appear in Wireless pH Measurement

Wireless pH measurements eliminate the inevitable questions as to whether there is a problem with the wiring or terminations in troubleshooting the measurement. Also, wireless pH transmitters with automated solution temperature compensation and measurements of electrode resistance can be used to provide more intelligent grab sample calibrations that can be historized and analyzed in the DCS. Most pH systems suffer from over calibration with calibration adjustments chasing previous adjustments.

The portability of wireless conductivity and pH measurements offer the opportunity to find the best location by plant trials. If several process connections are provided, the connection that offers the most representative measurement with the least noise and deadtime can be found. Noise is minimized by finding the location with the best mixing and least bubbles. Deadtime is minimized by reducing the transportation delay and increasing the velocity at the electrode, decreasing the electrode lag and coatings that can greatly slow down the electrode response to the point of no response.

CONCLUSION

pH Measurement and Control systems offer exceptional capability with demanding requirements. New electrodes offer longer life and better accuracy. Process deadtime can be minimized by maximizing axial mixing and minimizing reagent transportation and injection delays. Precision valves and advanced control techniques can reduce the number of stages required for neutralization systems. The use of 3 electrodes with middle signal selection reduces maintenance costs by eliminating over calibration and unnecessary electrode removal besides improving measurement reliability and performance. Smart wireless transmitters eliminate ground noise spikes and offer opportunities for better electrode testing, selection, and calibration.

REFERENCES

1. *Essentials of Modern Measurements and Final Elements in the Process Industry*, ISA, 2010
2. “Opportunities for Smart Wireless pH, Conductivity Measurements”, *InTech* web exclusive, Jan-Feb, 2010 <http://bit.ly/IY6q75>
3. “pH Measurement and Control”, *Chemical Engineering*, August, 2010
4. *Process Control Case Histories*, Momentum Press, 2010
5. “The Secret Life of pH Electrodes - Parts 1 - 3”, *Control*, February - April, 2009
6. *Advanced pH Measurement and Control - 3rd Edition*, ISA, 2005