Application Data Sheet
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Basics Of pH Control

FUNDAMENTAL CONSIDERATIONS

By definition, pH is the negative logarithm of the hydrogen-ion concentration in aqueous solution. This means that a solution having a pH value of 4 has ten times more hydrogen ions than a solution whose pH is 5. For control systems neutralizing spent acids or bases, pH value per se is of little consequence except as a control point for the neutralization.

Acids are either “strong” or “weak.” This relates to the amount of free hydrogen ions in the solution of a given concentration. Thus, nitric acid is a strong acid, since all of the nitric-acid molecules are dissociated into active hydrogen ions and nitrate ions. However, acetic acid is a weak acid. A solution of acetic acid of the same molar concentration as nitric acid would have a very different pH value, since most of the acetic acid molecules do not dissociate into hydrogen ions and acetate ions. Yet both the nitric and acetic acids have the same total acidity and, therefore, each require the same amount of neutralizing base.

Similarly, there are strong and weak bases. Sodium hydroxide is a strong base, while ammonia or soda ash are weak bases. Equal molar concentrations of these bases will all have the same capacity to neutralize a given quantity of acid.

Titration is the popular method for determining total acidity or basicity of a solution. It is necessary in the design of the pH control system to determine the size of the final control elements — particularly the element that determines the flow of reagent — and titration is the technique used to collect data for sizing.

An acid/base titration curve is a plot of pH vs. reagent addition and graphically shows how pH changes per unit addition of reagent. It also gives an indication of the degree of control obtainable. Its shape depends on such factors as the nature of the acid and base — whether strong or weak — and on concentration, particularly that of the control reagent. The point of greatest change (also called the equivalence point, or inflection point) is the point where pH changes most greatly per unit of reagent added. The equivalence point is not necessary at pH 7.0 (the neutral point of water). It depends on the acid and base being titrated.

When a strong acid is titrated with a strong base, the equivalence point is at pH 7.0, but if weak acids and bases are titrated, the equivalence point will be above or below pH 7.0. A representative curve of a strong acid (sulfuric, nitric, or hydrochloric) titrated with a strong base (caustic soda) is shown in Figure 1 (A).

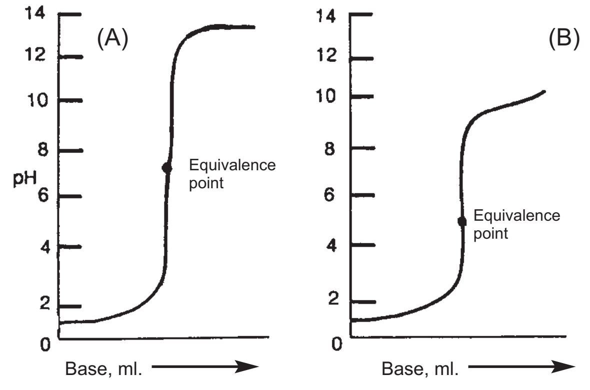


FIGURE 1. Curves show difference between strong acid (A) titrated with strong base, (B) titrated with a weak base.

Near the equivalence point, a slight deficiency or slight excess of caustic results in a change in pH of several pH units. Thus, a plant control system neutralizing spent sulfuric acid cannot expect accurate control using caustic soda as the neutralizing reagent without specifically designed equipment.

Figure 1 (B) also shows a curve of strong acid titrated with a weak base. Note that the equivalence point of a strong-acid weak-base titration is below pH 7.0. Also, the pH change per unit of base added is not nearly as pronounced as in the strong-acid strong base titration.

Furthermore, strong acids reacted with weak bases, and strong bases reacted with weak acids, produce salts that act to some degree as buffers. In general, neutralization of strong acid with a weak base, or a strong base with a weak acid, will result in better control than strong-acid strong-base neutralization.

HOW PH CONTROL SYSTEMS WORK

Basically, a pH control system measures the pH of the 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, a continuous titration.

These pH control systems are highly varied, and design depends on such factors as flow, acid or base strength or variability of strength, method of adding neutralizing agent, accuracy of control (i.e., limits to which pH must be held), and physical and other requirements. The following discussion, therefore, deals with basic designs rather than specific systems.

TWO-POSITION (ON-OFF) SYSTEMS

The two position or on-off control system is designed so that the element controlling reagent additions is always set in one of two positions, either fully open (on) or fully closed (off). Such systems are generally limited to continuous processes where waste flow rate is relatively small and residence (or hold-up) time within the control system is relatively large. Residence time is the average time a unit of volume is "held up" within the reaction vessel.

An on-off system should have a hold-up time of 5 minutes or more. With relatively large flow rates and small hold-up times, proportional control is generally used.

Mixing Must be Complete

As with other control systems, on-off control requires adequate mixing and agitation. Otherwise, the sensing pH electrodes will detect an incorrect pH and continue to call for additional reagent after the correct amount has been added. The result of insufficient mixing is excessive cycling and poor pH control.

As a rule of thumb, turnover (mixing) time should be less than 20% of holdup time. If, for example, holdup time is 10 minutes, turnover should be less than 2 minutes. The relatively wide limits of pH allowable in discharging wastes to sewage systems, plus the nature of small industrial operations with relatively small waste volumes discharging to such systems, make on-off pH control common in such operations. A representative control system is shown in Figure 2, with the type of control achieved.

If the flow and total acidity or basicity of the waste stream can vary by a factor of 10,000, then two reagent pumps will be needed (see Figure 3).

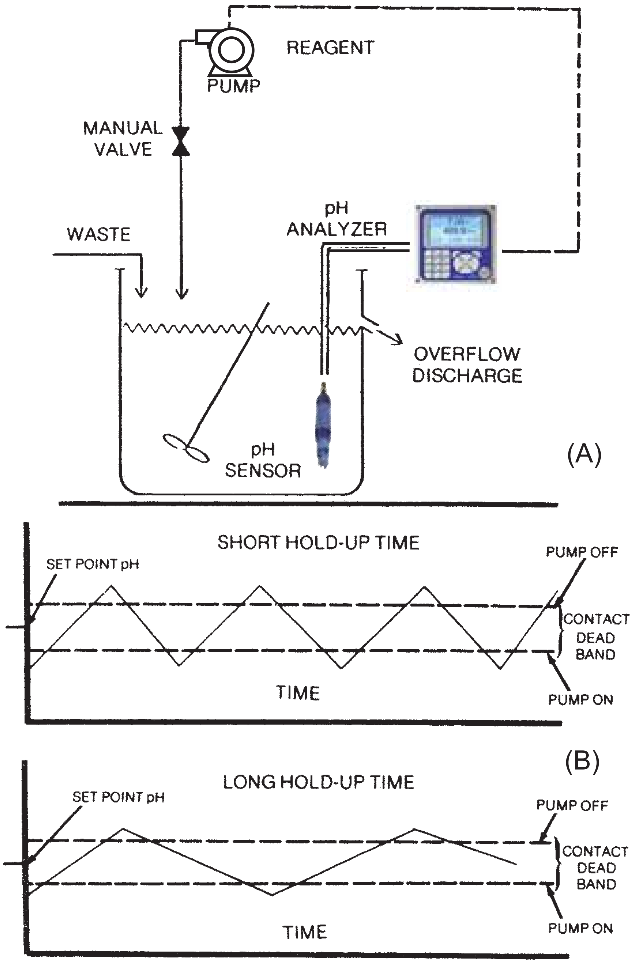


FIGURE 2. On-off method is a simple control system (A), with good control characteristics (B) when hold-up time is sufficient.

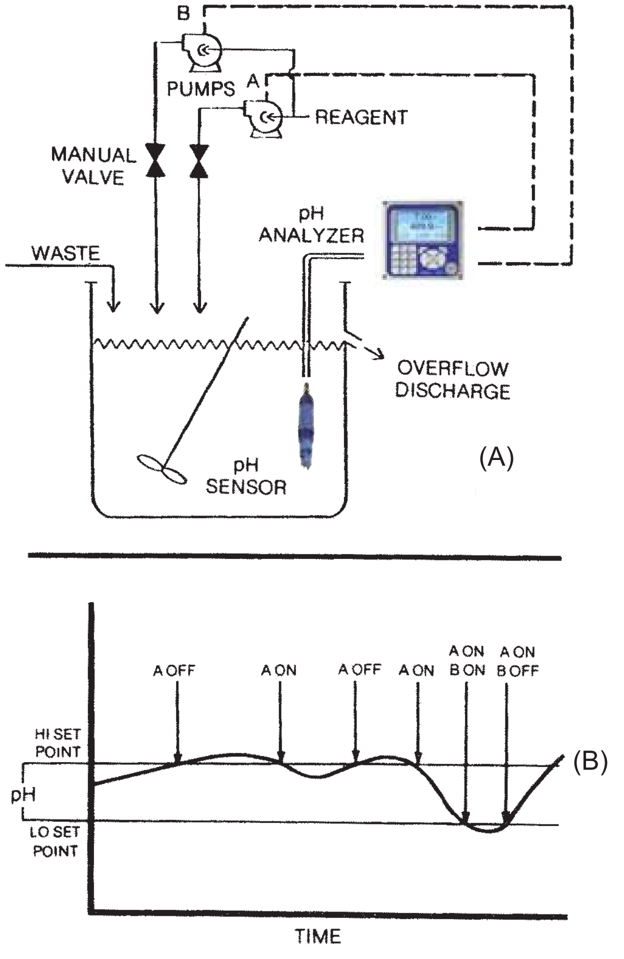


FIGURE 3. Dual-flow one-reagent control handles variable-flow situations with two pumps (A and B above).

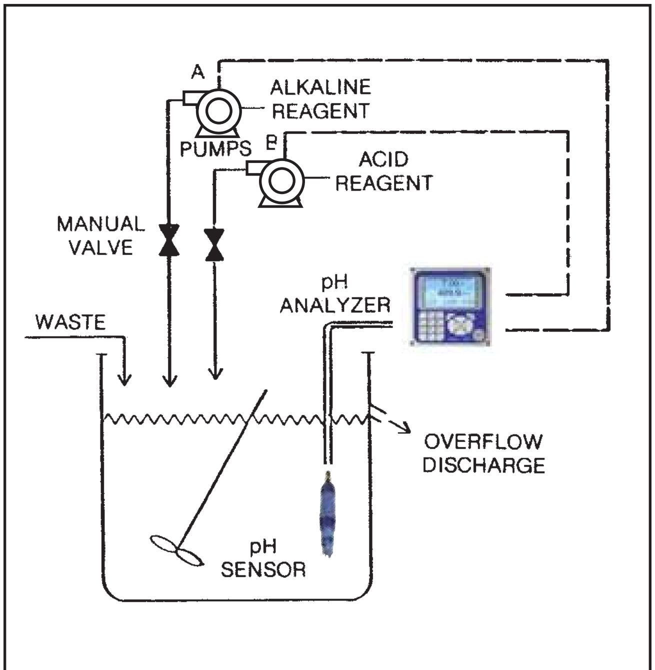


FIGURE 4. Two-reagent system for dilute wastes.

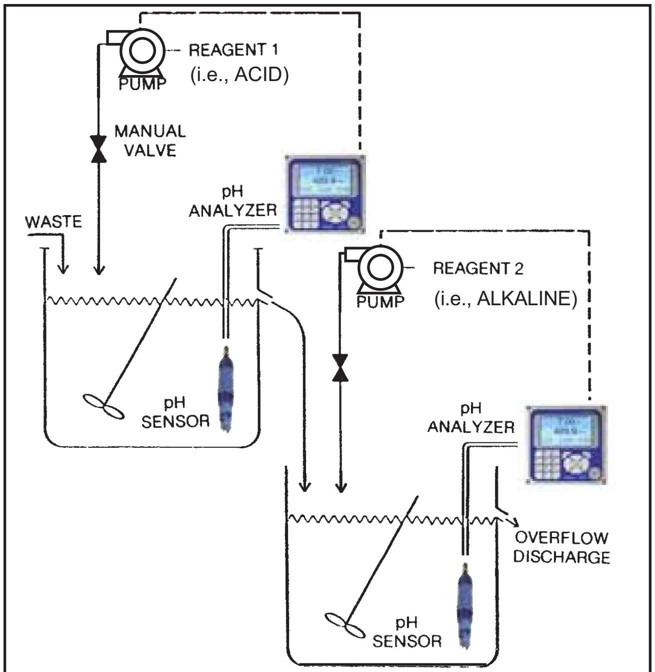


FIGURE 5. Two-stage system for concentrated wastes.

For convenience, pumps (A) and (B) may be the same size, or, for economy, one may be smaller than the other. In either case, the manual valves would be adjusted to give flows differing by a factor of from 100 to 1,000. The high and low control points should differ by 1 pH unit or more. Response of this system for an acid-waste stream is shown at the bottom of Figure 3; pump A is the larger pump.

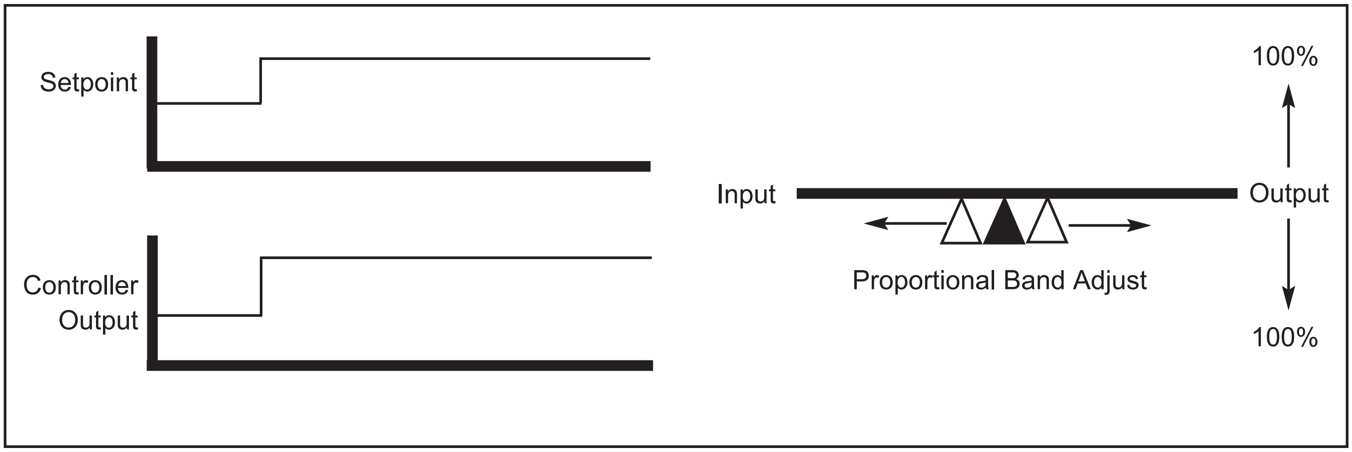
If the pH of the water stream can vary from acid at one time to alkaline at another, then both acid and alkaline reagents will be needed. Such a system is shown in Figure 4. It is ideal with dilute-acid and alkaline wastes.

If the waste contains concentrations of 1% and greater of either acid or alkali, the system shown in Figure 4 may tend to self-oscillate. For these conditions, the two-stage method shown in Figure 5 will minimize oscillations caused by overfeeding of a reagent.

Multimode Control Systems

Where 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 such systems, neutralizing agent is continually added by the final control element. The amount of neutralizing agent being added at any moment depends upon the proportionality set up by the system and the controller. Controller output and delivery of reagent are proportional to the deviation from an internal reference (setpoint). See Figure 6.

Multimode controllers for pH neutralization generally contain the control functions of proportional and integral mode (or reset). Proportional band alone is seldom, if ever, used because large load changes are common and an offset from the control point would result when one occurred. Reset advances the controller output



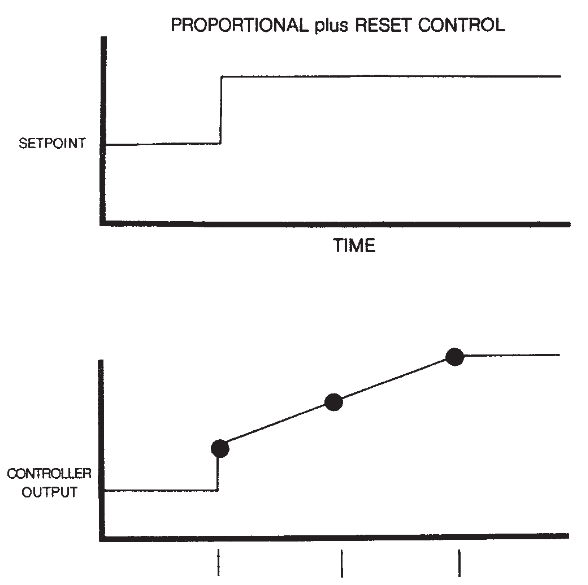


FIGURE 7.

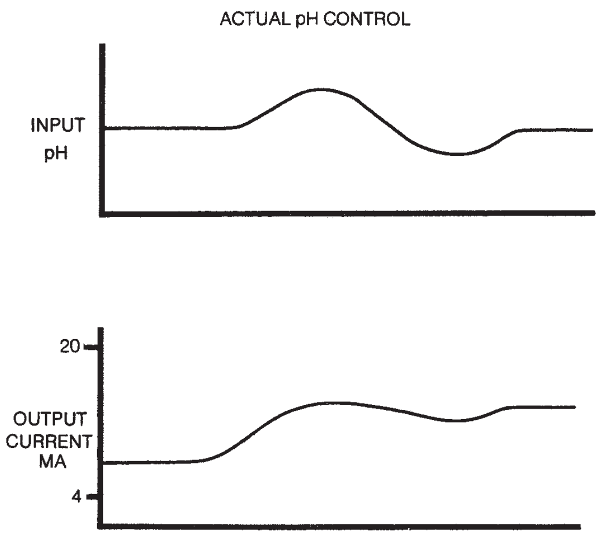


FIGURE 8.

(and control element position) by an amount determined by the magnitude and length of time of the deviation in the process variable and, thus, eliminates offset. See Figures 7 and 8.

Proportional-plus-integral mode can handle most process characteristics and is the most commonly used control pattern for pH neutralizations. Rate or derivative action, which supplies an added adjustment to the controller output determined by the rate that pH is changing, is rarely used for pH control.

Several factors are extremely important in the design of pH control systems. 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. It levels out abrupt changes and gives time for mixing (thus it tends to minimize extreme changes in the position of the final control element).

Unfortunately, pH neutralizations are seldom high capacity systems. The basic nature of pH as a logarithmic function of concentration is capacity limiting.

Also, the buffer capacity (i.e., the ability of a solution to resist change) of a given system may be zero or close to zero at the control point.

A hold-up period is required to provide time for the neutralization reaction to go to completion. This factor is extremely important, particularly where a dry feed or slurry is used as the control agent since the solids must dissolve before they react. Increasing hold-up time increases capacity.

Transfer lag and dead time are detrimental elements to effective control.Transfer lag results from the inability of the system to supply neutralizing agent instantaneously on demand. Dissolving time in the case of a dry feed or a slurry is a transfer lag. Poor mixing also results in a transfer lag. Dead time is time delay in any part of the system. Measuring element amplifier, signal converter, and controller lag are part of dead time. Electrodes that do not respond rapidly to pH change because of a coating will increase dead time.

As a rule of thumb, multi-mode control is applicable where hold-up time is relatively short, 30 seconds to 3 minutes being fairly ideal. Beyond about 10 minutes, multi-mode control may not give better results than on-off control because the gain must be reduced (i.e., the proportional band increased) and reset made to function slowly. The same degree of control can be approached by an on-off system.

Emerson Process Management

2400 Barranca Parkway
Irvine, CA 92606 USA
Tel: (949) 757-8500
Fax: (949) 474-7250

http://www.raihome.com