Inferential Model for pH Control

Uttam Ray Chaudhuri
Chemical Engineering Department, Calcutta University, 92 A.P.C Road, Calcutta 700 009, India

and

Utpal Ray Chaudhuri *
Food Technology and Bio-Chemical Engineering Department, Jadavpur University, Calcutta 700 032, India

Received: 05 October 2000; accepted: 10 May 2001

An inferential model pH control strategy based on fundamental relations for pH neutralization has been developed. The inferential model was simulated to analyze performance of the pH control scheme and then compared with an experimental acid-base neutralization system.

Introduction

Accurate pH control is an important and essential operation in many process industries like food, beverages, wastewater treatment, pharmaceutical plants, petroleum refineries, petrochemical plants and various organic and inorganic industries. Most of the traditionally used controllers are proportional integral derivative (PID) based. Generally, the wild behaviour of the pH sensor and acid-base neutralization process gives rise to complex situation to control. Several studies are reported in literature on pH control, where most of the algorithms for pH control are based on the dynamic characteristics of the process as non-linear systems. Most of the processes use a pH sensor (glass electrode) as the on-line measuring element for control. Because of the sluggishness of the dynamic process coupled with that of the sensor, feed-back control is rather difficult by the commonly employed PID controllers. Some authors studied models using hypothetical species. Adapting titration curve with the Kalman filter, state estimator were carried out for industrial applications. Strong acid equivalent (SAE) model has been developed for neutralization of mixture of acids. Due to non-linear behaviour of the neutralization process, linear control has been found to be a futile exercise, perhaps due to inherent non-linearity of the pH measurement.

Model of a pH Sensor

pH of a liquid containing H+ ions is usually measured by a glass electrode sensor which is essentially a membrane permeable to H+ ions. A concentration cell is developed across the membrane and electrically conducted through an electrode. This half-cell is then coupled with a reference cell which generates a known emf. The net voltage developed in the circuit, therefore, depends on H+ ion concentration in a sample. A silver/silver chloride electrode immersed in a gel of known pH served as reference electrode, and the base of the sensing cell containing the gel has a very thin glass membrane.

The net emf of the cell developed is given by Nernst’s equation,

\[ E = \frac{2.302 \cdot R \cdot T}{f} \cdot \log \left( \frac{H^+}{\text{common logarithm}} \right) \]  

where, \( E \) = net emf, volts, \( R \) = universal gas constant, \( T \) = absolute temperature of the cell, Kelvin, \( f \) = Faraday number, \( E_{ref} \) = emf of the reference cell, volts, \( pH = \log \left( \frac{H^+}{\text{common logarithm}} \right) \), common logarithm, to the base 10, and \( [H^+] \) = hydrogen ion concentration.

True pH of a solution, however, depends on the diffusion rate of H+ ions from sample into the cell. Let \( x \) and \( y \) be H+ ion concentrations in a sample and within the cell, respectively, then diffusion governed transfer equation across the cell membrane can be written as,

\[ V \cdot \frac{dy}{dt} = \frac{DA}{Z} \cdot (x-y), \quad \text{or} \quad \tau \cdot \frac{dy}{dt} = (x-y), \]  

where, \( V \) = volume of the cell liquid, \( A \) = area of the
Figure 1—Response of a pH transducer of time constant $\tau = 1$ s for a step change in bath pH from 1 to 7

membrane in contact with the sample, $Z = \text{thickness of the membrane}$, $D = \text{diffusivity of H}^+$ ions through the membrane, $\tau = \frac{V \cdot Z}{D \cdot A}$ is the characteristic time constant of a sensor.

Under steady state conditions, $\frac{dy}{dt} = 0$, the above equation gives,

$$ (x_0 - y_0) = 0,$$  \hspace{1cm} (3)

where $x_0$ and $y_0$ are steady state concentrations of $x$ and $y$.

Subtracting Eq. (3) from Eq. (2) gives,

$$ \tau \cdot \frac{dY}{dt} = (X - Y),$$

which, upon Laplace transformation, reduces to

$$ Y(s) \left(1 + \frac{1}{1 + \tau \cdot s}\right) = \frac{1}{X(s)},$$  \hspace{1cm} (4)

where, $Y = y - y_0$ and $X = x - x_0$, and $Y(s)$ and $X(s)$ are Laplace transforms of $Y$ and $X$ respectively. Also, $pH_0 = -\log(x)$ and $pH_y = -\log(y)$.

Response of a pH Sensor

If a step change of $A$ units in pH of a solution under study is applied then,

$$ A = pH_x - pH_y \text{ or } pH_y = A + pH_x,$$  \hspace{1cm} (5)

where $pH_i$ is the initial steady state pH. The response of the sensor due to the above change in $pH_i$ is then obtained as,

$$ pH_y = -\log\left\{Y(t) + 10^{-pH_i}\right\}.$$  \hspace{1cm} (6)

where,

$$ Y(t) = \left(10^{-pH_i} - 10^{-pH_x}\right) \left(1 - e^{-\frac{t}{\tau}}\right).$$  \hspace{1cm} (7)

Response of a pH transducer with $\tau = 1$ s is plotted in Figure 1. It is apparent from the figure that the response is too sluggish. For a step change of four units in pH of the bath, the indicated pH was found to be much lower than 6.32 per cent of the change, i.e., pH transducer is not a first order instrument. In addition to this, a dead zone also exists at the start of the response curve.

Dynamic Titration Curve

Considering a neutralization scheme as shown in Figure 2 where two streams of influents enter in a stirred tank. The effluent is drained off at the controlled pH. It is assumed that the acid (HCl) and the base (NaOH) streams, entering the tank, are well mixed at a constant temperature. The neutralization reaction in this case is written as,

$$ \text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O}$$

The charge balance is,
[H⁺] +[Na⁺] = [Cl⁻] + [OH⁻] \ldots (8)

The ionic product of water is,

K_w = [H⁺][OH⁻] \ldots (9)

Considering the flow rates of acid and base are \( F_i \) and \( F_j \) respectively at their respective acid and base concentration as \( C_i \) and \( C_j \), the material balance equations for the cations and anions of the base and acid are obtained as,

\[
\frac{d[Na^+]}{dt} = F_2 \cdot C_2 - F_1 \cdot [Na^+] \ldots (10)
\]

\[
\frac{d[Cl^-]}{dt} = F_1 \cdot C_1 - F_2 \cdot [Cl^-] \ldots (11)
\]

Combining Eqs (8 to 11), the following dynamic relation is obtained,

\[
\frac{d[H^+]}{dt} = \frac{F_1 \cdot C_1 - F_2 \cdot C_2 - F_1 \cdot [H^+] + K_w \cdot [H^+]}{1 + \frac{K_w}{[H^+]}} \ldots (12)
\]

where \( F = F_1 + F_2 \). \ldots (13)

At steady state, the time derivative term vanishes, and then solving for \([H^+]\) gives,

\[
[H^+] = \frac{(F_1 \cdot C_1 - F_2 \cdot C_2) + \sqrt{(F_1 \cdot C_1 - F_2 \cdot C_2)^2 + 4 \cdot K_w \cdot F_1 \cdot F_2}}{2 \cdot F} \ldots (13)
\]

and \( \text{pH} = -\log[H^+] \ldots (14) \)

**Inferential Control Model**

At the desired set point of pH of the solution, alkaline flow rate as triggered from the controller is as follows:

\[
F_2 = F_1 \cdot \frac{(C_1 - \beta)}{(C_2 + \beta)} \ldots (15)
\]

where \( \beta = \frac{[H^+]}{[H^+] - K_w} \ldots (16) \)

Equation (13) is then used to evaluate \([H^+]\) and hence \( \text{pH} \) as a function of time. Using the transducer and the process model equations, the dynamic pH of the mixing tank can be predicted which is utilized to determine required flow rate of the alkaline solution. Such a scheme of pH control is presented in Figure 3. A three term proportional-integral-derivative (PID) controller could be used, where the predicted pH of the mixing tank replaces the pH transducer. Such a scheme is also presented in Figure 4.

**Experimental**

In this control scheme, the flow rate of acid \((F_1)\) is measured by a glass electrode and transduced to the controller which manipulates the base flow rate \((F_2)\). Process model then evaluates pH of solution in the tank based on acid and base flow rates. Experiments were carried out at the laboratory scale consisting of a mixing vessel of 1 L capacity where two small diaphragm pumps were used for delivering acid and alkaline solutions from their respective tanks. A personal computer was connected to the controller for data acquisition and control through an RS232 interface. Based on a suitable algorithm, a control program was written in GW BASIC. The alkaline flow was manipulated by air operated valve actuated by an I/P converter. Strength of acid and alkaline solutions
were maintained at 0.1 N, with maximum allowable flow rate of 300 mL/min. The experimental scheme is shown in Figure 2.

**Results and Discussions**

The objective of the pH control scheme was to maintain the effluent at a pH of 7, for testing, by manipulating the alkali flow rate. In order to analyze the performance of the control scheme, experiments were carried out by set point disturbance. Recorded pH of the solution mix in the tank was measured against time and compared with the closed loop PID control scheme. Figures 5 to 8 show these response curves. A comparative study of the Inferential and PID control scheme is presented in Table 1. In Figure 5 pH of the solution in the tank is recorded against time when the set point is changed from the initial pH of 3 to 7. Performance of the inferential controller is like critically damped that is with zero offset. While the action of the proportional controller is quicker but with large overshoot and a positive offset, as shown in Figure 6. In Figure 7, response of the Proportional-Integral controller shows a negative offset with a large overshoot. In Figure 8, response of a Proportional-Integral-Derivative controller shows the presence of large overshoot followed by decay but with a positive offset. It is observed from these performances that the three term controller is faster than the inferential controller as obvious from the rise time from 5 to 7 s as compared to inferential controller which has the rise time of 34 s. However, there is complete absence of overshoot in the performance of inferential controller and offset is absent. In Figure 9 and 10, performance of the inferential controller are presented when the set point was disturbed from 3 to 3.2 and 13.4 respectively. These figures show that the new set point are achieved within a very small margin from the new set points. However, the perfor-
Conclusions

In this study, control of pH was carried out for strong acid and strong base neutralization system where pH changes abruptly from its initial value while approaching pH 7. Such abrupt changes in pH could not be tackled by the PID control scheme. Inferential controller, on the other hand, alleviates the situation. From the response curves, presented in different figures, it is understood that the PID control scheme could not eliminate the offsets while the inferential control system eliminated not only the offset but also had no overshoot without losing the quickness of response. Hence, a more robust control is achieved by the inferential control scheme, as detailed in the paper.

References


