

pH-neutralization: integrated process and control design[☆]

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Abstract

The paper addresses control related design issues for neutralization plants. Mainly for control reasons, the neutralization is usually performed in several steps (mixing tanks) with gradual change in the concentration. The aim is to give recommendations for issues like tank sizes and number of tanks. Assuming strong acids and bases, we derive linearized relationships from the disturbance variables (e.g. inlet concentration and flow rate) to the output (outlet concentration), including the scaled disturbance gain, k_d . With local PI or PID control in each tank, we recommend to use identical tanks with total volume V_{tot} , where we give V_{tot} as a function of k_d , the time delay in each tank θ , the flow rate q , and the number of tanks n . For $k_d \gg 1$, which is common in pH-neutralization, this gives $V_{\text{tot}} = 2qn\theta k_d^{1/n}$.

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1. Introduction

The pH-neutralization of acids or bases has significant industrial importance. The aim of the process is to change the pH in the inlet flow, the *influent* (disturbance, d), by addition of a *reagent* (manipulated variable, u) so that the outflow or *effluent* has a certain pH. This is illustrated in Fig. 1 as a simple mixing, but normally it takes place in one or more tanks or basins, see Fig. 3. Examples of areas where pH control processes are in extensive use are water treatment plants, many chemical processes, metal-finishing operations, production of pharmaceuticals and biological processes. In spite of this, there is little theoretical basis for designing such systems, and heuristic guidelines are used in most cases.

Textbooks on pH control include (Shinskey, 1973) and (McMillan, 1984). General process control textbooks, such as (Shinskey, 1996; Balchen & Mummé, 1988), have sections on pH control. A critical review on design and con-

trol of neutralization processes which emphasizes chemical waste water treatment is given by Walsh (1993).

Our starting point is that the tanks are installed primarily for dynamic and control purposes. In our paper, process design methods using control theory are proposed. We focus on the neutralization of *strong* acids or bases, which usually is performed in several steps. The objective is to find methods to obtain the total required volume for a given number of tanks, and discuss whether they should be identical or not. Design of surge (buffer) tanks is generalized to other processes in (Faanes & Skogestad, 2003). Clearly, the required tank size depends on the effectiveness of the control system, and especially with more than one tank there are many possibilities with respect to instrumentation and control structure design. This is discussed in (Faanes & Skogestad, 1999).

Section 2 motivates the problem. Since time delays are important design limitations, Section 3 contains a discussion on delays. From the models presented in Section 4, in Section 5 we follow Skogestad (1996) and derive a simple formula for the required tank volume, denoted V_0 . In Section 6, the validity of the simple formula for V_0 is checked numerically, and improved rules for sizing are proposed. Whether equal tanks is best or not is discussed in Section 7. Discussions on measurement noise, feedforward control and the pH set-point to each tank are found in Section 8. The main conclusions are summarized in Section 9.

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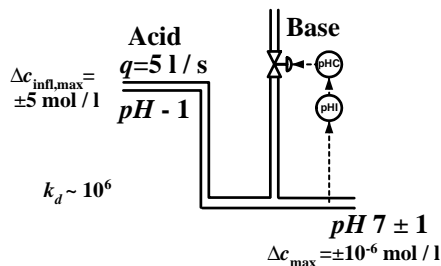


Fig. 1. Neutralization of strong acid with strong base (no tank).

2. Motivating example

We use a simple neutralization process to illustrate the ideas.

Example 1. We want to neutralize 5 l/s of a strong acid (disturbance) of $\text{pH} = -1$ ($c_{\text{H}^+, \text{infl}} = 10 \text{ mol/l}$) using a strong base (input) with $\text{pH} = 15$ to obtain a product of $\text{pH} = 7 \pm 1$ ($10^{-8} \text{ mol/l} < c_{\text{H}^+} < 10^{-6} \text{ mol/l}$).

We present a model for the process in Section 4, and we find that it is convenient to work with the excess H^+ -concentration, $c = c_{\text{H}^+} - c_{\text{OH}^-}$ (mol/l). In terms of this variable, the product specification is $c = 0 \text{ mol/l}$, and the variation requirement $\pm 1 \text{ pH}$ corresponds to a concentration deviation $\Delta c_{\text{max}} = \pm 10^{-6} \text{ mol/l}$. We assume that the maximum expected disturbance is $\Delta c_{\text{in, max}} = \pm 5 \text{ mol/l}$, corresponding to a pH variation from -0.70 to -1.18 .

We first try to simply mix the acid and base, as illustrated in Fig. 1 (no tank). The outlet concentration is measured (or calculated from a pH measurement), and the base addition is adjusted by a feedback PI-controller assuming a time delay of 10 s in the feedback loop. A step disturbance in the inlet concentration of 5 l/mol, results in an immediate increase in the product of 2.5 mol/l (to $\text{pH} -0.4$), since the total flow is half the acid flow. After a while the PI controller brings the pH back to 7, but for a period of about 700 s the product is far outside its limits. This can be seen from the simulation in Fig. 2 (solid line).

This is clearly not acceptable, so, next, we install one mixing tank to dampen the disturbances. For a tank with residence time τ , the response is (for the case with no control):

$$c(t) = 2.5(1 - e^{-t/\tau}) \quad (1)$$

Now the pH of the product does not respond immediately, and provided τ is sufficiently large, the controller can counteract the disturbance before the pH has crossed its limit of 6. Solving for $c(t) = 10^{-6}$, we get

$$t \approx 4 \times 10^{-7} \tau \quad (2)$$

For example, $\tau = 1000 \text{ s}$ gives $t = 4 \times 10^{-4} \text{ s}$, that is, for a tank with residence time of 1000 s the pH goes outside its limits after 0.4 ms. However, no control system can respond this fast. With a time delay of 10 s (typical value), the feedback controller needs at least $t = 10 \text{ s}$ to counteract

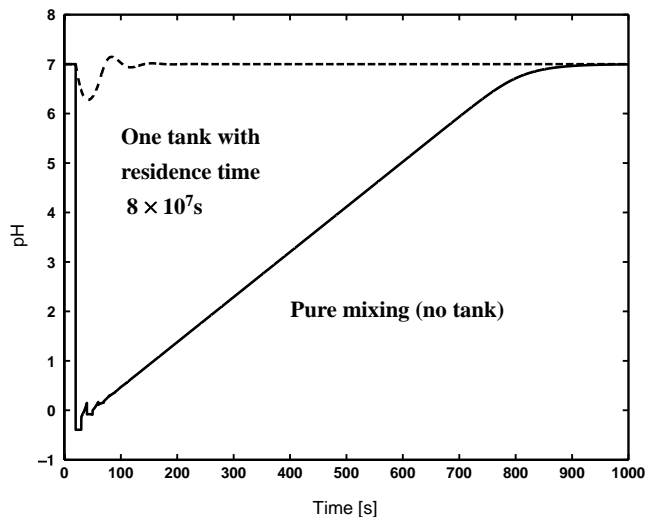


Fig. 2. Mixing capacity is required to dampen the disturbance. Closed-loop responses in outlet pH to a step change in inlet acid concentration from 10 to 15 mol/l with time delay of 10 s in the PI-control loop. (Controller: PI with k_d tuning.)

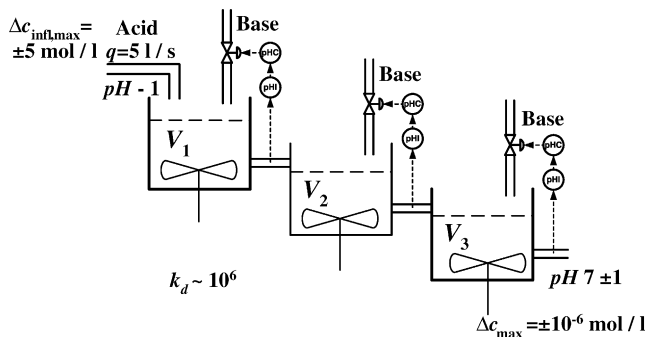


Fig. 3. Neutralization in three stages.

the disturbance, which gives a minimum required residence time of $\tau = 10/4 \times 10^{-7} \text{ s} = 2.5 \times 10^7 \text{ s}$. In practice, a larger tank is required, and in Fig. 2 we also show the closed-loop response for the case with $\tau = 8 \times 10^7 \text{ s}$ (dashed line). With a flowrate of 10 l/s this corresponds to a tank size of 800 000 m^3 . This is of course unrealistic, but in Section 5 we will see that the total tank size can be reduced considerably by adding several tanks in series as illustrated in Fig. 3.

3. Time delays

Time delays provide fundamental limitations on the achievable response time, and thereby directly influence the required volumes. The delays may result from transport delays or from approximations of higher order responses for mixing or reaction processes and from the instrumentation. For pH control processes, the delays arise from

1. Transport of species into and through the tank, in which the mixing delay is included (θ_p)

2. Transport of the solution to the measurement and approximation of measurement dynamics (θ_m)
3. Approximation of actuator and valve dynamics (θ_v)
4. Transport of the solution to the next tank (θ_n)

In this paper, we mainly consider local feedback control, and the total effective delay is the sum of the contributions from the process and instrumentation $\theta = \theta_p + \theta_m + \theta_v$. If the influent (disturbance) and the reagent addition (manipulated variable) are placed close, they will have about the same delay θ_p , but for feedback control only the delay for manipulated variables matters.

Both the volume and the mixing speed determine the mixing delay, which is the most important contribution to θ_p . If the volume is increased, then the mixing speed is also usually increased and these two effects are opposing. Walsh (1993) carried out calculations for one mixer type and found $\theta_p \sim V^{0.07}$. Since the exponent of 0.07 is close to zero he concludes that θ_p is constant (typically about 7 s), independent of the tank size. On the other hand, Shinskey (1973, 1996) assumes that the overall delay θ is proportional to the tank volume (this is not stated explicitly, but he assumes that the ultimate or natural period of oscillation, which here is 4θ , varies proportionally with the volume). In this paper, we mainly follow Walsh and assume that the overall effective delay is $\theta = 10$ s in each tank.

4. Model

The model is derived in Appendix A. pH-control involving strong acids and bases is usually considered as a strongly “nonlinear” process. However, if we look at the underlying model written in terms of the excess H^+ concentration $c = c_{H^+} - c_{OH^-}$:

$$\frac{d(cV)}{dt} = c_{infl}q_{infl} + c_{reag}q_{reag} - cq \quad (3)$$

then we find that it is linear in composition c (the overall model is bilinear due to the product of flow rate (q) and concentration (c)). The fact that the excess concentration will vary over many orders of magnitude (e.g. we want $|c| < 10^{-6}$ mol/l to obtain $6 < \text{pH} < 8$, whereas $c = 1$ mol/l for a strong acid with $\text{pH} = 0$), shows the strong sensitivity of the process to disturbances (with $k_d \gg 1$; see below), but has nothing to do with non-linearity in a mathematical sense.

In Appendix A, we have derived a Laplace transformed linearized scaled model for the process illustrated in Fig. 4:

$$y(s) = G(s)u(s) + G_d(s)d(s) \quad (4)$$

where $y = \Delta c/c_{max}$ is a scaled value of the effluent excess concentration, $u = \Delta q_{reag,u}/q_{reag,u,max}$ is a scaled value of the reagent flow rate, and $d = (\Delta c_{infl}/c_{infl,max}, \Delta q_{infl}/q_{infl,max}, \Delta c_{reag}/c_{reag,max}, \Delta q_{reag,d}/q_{reag,d,max})^T$ is a disturbance vector. The subscripts max denote the maximum tolerated (y), possible (u) or expected (d) variation; see also

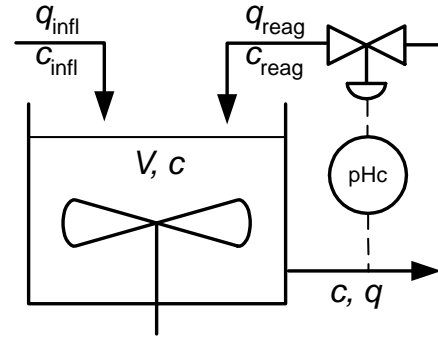


Fig. 4. Neutralization tank with pH control.

Table 1. Note that we have included a reagent flow rate, $q_{reag,d}$, as a disturbance, since it may also have uncontrolled variations due to, e.g. inaccuracies in the valve or upstream pressure variations. G is the transfer function from the control input, and G_d a vector of transfer functions from the disturbances. Normally, it is convenient to consider the effect of one disturbance at a time, so from now on we consider d as a scalar and G_d as a (scalar) transfer function. The reason for the scaling is to make it easier to state criteria for sufficient dampening, and we scale the model so that the output, control input and the expected disturbances all shall lie between -1 and 1 .

For a single tank, the transfer functions $G(s)$ and $G_d(s)$ are represented as

$$G(s) = \frac{k}{\tau s + 1} e^{-\theta s}, \quad G_d(s) = \frac{k_d}{\tau s + 1} e^{-\theta s} \quad (5)$$

where τ is the nominal residence time in the tank ($\tau = V^*/q^*$, where V^* is the nominal volume and q^* the total flow rate), and θ is effective time delay, due to mixing, measurement and valve dynamics (see Section 3).

In Appendix A.2, we derive a linear model for a series of n tanks. Neglecting reagent disturbances (except in the first tank) and changes in outlet flow-rates of each tank, we obtain for any disturbance entering in the first tank,

$$G_d(s) = \frac{k_d}{((\tau_h/n)s + 1)^n} e^{-n\theta s} \quad (6)$$

where τ_h is the total residence time V_{tot}/q . V_{tot} is the total volume and q is the flow rate through the tanks, and we here assume $\theta_1 = \dots = \theta_n = \theta$.

Table 1
Steady-state gain for different disturbances

	Concentration disturbance	Flow disturbance
Influent	$k_{d,infl,c} = \frac{c_{infl,max} q_{infl}^*}{c_{max} q^*}$	$k_{d,infl,q} = \frac{c_{infl}^* - c^*}{c_{max}} \frac{q_{infl,max}}{q^*}$
Reagent	$k_{d,reag,c} = \frac{c_{reag,max} q_{reag}^*}{c_{max} q^*}$	$k_{d,reag,q} = \frac{c_{reag}^* - c^*}{c_{max}} \frac{q_{reag,d,max}}{q^*}$

Superscript symbol (*) denotes nominal values, and subscript max denotes maximum tolerated (c_{max}) or expected (the other variables) variation. $q_{reag,d,max}$ is maximal expected uncontrolled variation in reagent flow.

With the above-mentioned scalings, the gain from the control input is (Appendix A.1)

$$k = \frac{c_{\text{reag}}^* - c^*}{c_{\text{max}}} \frac{q_{\text{reag},u,\text{max}}}{q^*} \quad (7)$$

while k_d for various disturbances is given in Table 1. We will assume that $k_d \gg 1$ (typically k_d is 10^3 or larger for pH systems).

Example 1 (continued from Section 2). We consider the influent disturbances. Nominally, $q_{\text{infl}}^*/q^* = 0.5$ (acid flow rate is half the total flow rate), $c_{\text{max}} = 10^{-6}$, $c^* = 0$ mol/l, and $c_{\text{infl},d,\text{max}} = 5$ mol/l (maximum inlet concentration variation). This gives $k_{d,\text{infl},c} = (5/10^{-6}) \times 0.5 = 2.5 \times 10^6$ (as found earlier).

Furthermore, $q_{\text{infl},d,\text{max}}/q^* = 0.5 \times 0.5$ (maximum variation in acid flow rate is $\pm 50\%$) so $k_{d,\text{infl},q} = (10/10^{-6})0.5 \times 0.5 = 2.5 \times 10^6$.

5. A simple formula for the volume and number of tanks

The motivating example in Section 2 showed that the control system is able to reject disturbances at low frequencies (including at steady state), but we need design modifications to take care of high-frequency variations. Based on (Skogestad, 1996) a method for tank design using this basic understanding is presented.

The basic control structure is local control in each tank, as illustrated in Fig. 3 (flowsheet) and Fig. 5 (block diagram). We assume no reference changes ($r_1 = r_2 = \dots = 0$), and the closed-loop response of each tank then becomes

$$y_i(s) = \frac{1}{1 + G_i(s)K_i(s)} G_{d_i}(s)d_i(s) = S_i(s)G_{d_i}(s)d_i(s) \quad (8)$$

where $d_1 = d$, and for $i > 1$, $d_i = y_{i-1}$. $S_i(s)$ is the sensitivity function for tank i . Combining this into one transfer function from the external disturbance d to the final output

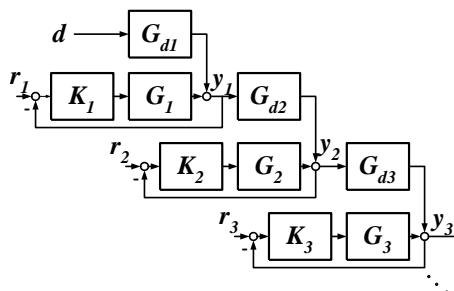


Fig. 5. Block diagram corresponding to Fig. 3 with local control in each tank.

y leads to

$$\begin{aligned} y(s) &= \left(\prod_{i=1}^n S_i(s)G_{d_i}(s) \right) d(s) \\ &= \left(\prod_{i=1}^n S_i(s) \right) \left(\prod_{i=1}^n G_{d_i}(s) \right) d(s) \end{aligned} \quad (9)$$

$$y(s) = S(s)G_d(s)d(s) \quad (10)$$

where $S(s) = \prod_{i=1}^n S_i(s)$. The factorization of S is possible since the tanks are SISO systems.

We assume that the variables (y and d) have been scaled such that for disturbance rejection the performance requirement is to have $|y| \leq 1$ for all $|d| \leq 1$ at all frequencies, or equivalently

$$|S(j\omega)G_d(j\omega)| \leq 1, \quad \forall \omega \quad (11)$$

Combining (11) and the scaled model of G_d in (6) yields an expression for the required total volume with n equal tanks:

$$V_{\text{tot}} \geq \frac{qn}{\omega} \sqrt{(k_d|S(j\omega)|)^{2/n} - 1}, \quad \forall \omega \quad (12)$$

Assuming $(k_d|S(j\omega)|)^{2/n} \gg 1$ (since $k_d \gg 1$ and the design is most critical at frequencies, where $|S|$ is close to 1) this may be simplified to

$$V_{\text{tot}} \geq qnk_d^{1/n} \frac{|S(j\omega)|^{1/n}}{\omega}, \quad \forall \omega \quad (13)$$

We see that $|S(j\omega)|$ enters into the expression in the power of $1/n$. This is because G_d is of the same order as S . This gives the important insight that a “resonance” peak in $|S|$, due to several tanks in series, will *not* be an important issue. Specifically, if the tanks are identical and the controllers are tuned equally, the expression is

$$V_{\text{tot}} \geq qnk_d^{1/n} \frac{|S_i(j\omega)|}{\omega}, \quad \forall \omega \quad (14)$$

where S_i is the sensitivity function for each locally controlled tank. This condition must be satisfied at any frequency ω and in particular at the bandwidth frequency ω_B , here defined as the lowest frequency for which $|S(j\omega_B)| = 1$. This gives the minimum requirement (Skogestad, 1996)

$$V_{\text{tot}} \geq \frac{qn}{\omega_B} \sqrt{k_d^{2/n} - 1} \quad (15)$$

Since $|G_d(j\omega)|$ decreases as ω increases, this volume guarantees that

$$|G_d(j\omega)| \leq 1, \quad \forall \omega \geq \omega_B \quad (16)$$

In words, the tank must dampen the disturbances at high frequencies where control is not effective. With only feedback control, the bandwidth ω_B (up to which feedback control is effective), is limited by the delay, θ , and from (Skogestad & Postlethwaite, 1996, p.174) we have $\omega_B \leq 1/\theta$ (the exact value depends on the controller tuning), which gives

$$V_{\text{tot}} > V_0 \quad (17)$$

Table 2
Total tank volume, V_0 from (18)

Number of tanks, n	Total volume V_0 [m ³]
1	250000
2	316
3	40.7
4	15.9
5	9.51

Data: $q = 0.01$ m³/s, $k_d = 2.5 \times 10^6$ and $\theta = 10$ s.

where (Skogestad, 1996)

$$V_0(n) \stackrel{\text{def}}{=} qn\theta \sqrt{k_d^{2/n} - 1} \quad (18)$$

is a “reference value” we will compare with throughout the paper. For $k_d \gg 1$, we have

$$V_0 \approx qn\theta k_d^{1/n} \quad (19)$$

(19) gives the important insight that the required volume in each tank, V_0/n , is proportional to the total flow rate, q , the time delay in each tank, θ , and the disturbance gain k_d raised to the power $1/n$. Table 2 gives V_0 as a function of n for Example 1. With one tank the size of a supertanker (250 000 m³) is required (as we got in the motivating example). The minimum total volume is obtained with 18 tanks (Skogestad, 1996), but the reduction in size levels off at about three to four tanks, and taking cost into account one would probably choose three or four tanks. For example, Walsh (1993) found the following formula for the capital cost in £ of a stirred tank reactor

$$C = 20\,000 + 2000V^{0.7} \quad (20)$$

From this we obtain the following total cost for $n = 1, \dots, 5$ in £1000: 12 000, 180, 97, 101, 120, i.e. lowest cost is for three tanks.

Remark 1. Conditions (15) and (17) are derived for a particular frequency ω_B and other frequencies may be worse. However, we will see that $|SG_d|$ is “flat” around the frequency ω_B if the controller tuning is not too aggressive, and ω_B is close to the worst frequency in many cases.

Remark 2. In (6), we neglected the variation in the outlet flow rate from each tank. The outlet flow rate is determined by the level controller (see (A.21) and (A.22)). With more than one tank and a different pH in each tank, a feed flow rate variation (disturbance) into the first tank will give a parallel effect in the downstream concentration variations since both the inlet flow rate and inlet concentration will vary. Also variations in the reactant flow rate will influence the level and thereby outlet flow rate. Perfect level control is worst since then outlet flow rate equals inlet flow rate. With averaging level control (surge tank), the outlet flow variations are dampened, but extra volume is required also for this,

which is not taken into account in the analysis presented in this paper.

6. Validation of the simple formula: improved sizing

In (18), we followed Skogestad (1996) and derived the approximate value V_0 for the total volume. This is a lower bound on V_{tot} due to the following two errors:

- (E1) The assumed bandwidth $\omega_B = 1/\theta$ is too high if we use standard controllers (e.g. PI or PID).
 (E2) The maximum of $|S(j\omega)G_d(j\omega)|$ occurs at another frequency than ω_B .

In this section, we compute numerically the necessary volume V_{tot} when these two errors are removed. We assume first sinusoidal disturbances, and later step changes. Each tank (labeled i) is assumed to be controlled with a PI or PID controller with gain K_{c_i} , integral time τ_{I_i} and for PID derivative time τ_{D_i} :

$$c_{i,\text{PID}} = K_{c_i} \frac{(\tau_{I_i}s + 1)(\tau_{D_i}s + 1)}{\tau_{I_i}s(0.1\tau_{D_i}s + 1)} \quad (21)$$

(cascade form of the PID controller). We consider four different controller tuning rules for PI and PID controllers: Ziegler–Nichols, IMC, SIMC and optimal tuning.

For the case with Ziegler–Nichols, IMC or SIMC tunings the controller parameters are fully determined by the process parameters k , τ and θ , and an optimization problem for finding the minimum required tank volumes may be formulated as:

$$V_{\text{tot,opt}} = \min_{V_1, \dots, V_n} \sum_{i=1}^n V_i \quad (22)$$

subject to

$$|S(j\omega_k)G_d(j\omega_k)| \leq 1, \quad \forall \omega_k \in \Omega \quad (23)$$

$$S \text{ is stable} \quad (24)$$

To get a finite number of constraints, we define a vector Ω containing a number of frequencies ω_k covering the relevant frequency range (from 10^{-3} to 10^3 rad/s). It is assumed that if the constraints are fulfilled for the frequencies in Ω , they are fulfilled for all frequencies. The stability requirement is that the real part of the poles of $S(s)$ are negative. The poles are calculated using a 3rd order Padé approximation for the time delays in $G(s)$, but this is not critical since the stability constraint is never active at the optimum.

Ziegler and Nichols (1942) tunings are based on the ultimate gain K_u and ultimate period P_u . For our process, the resulting PI controller has gain $K_c = 0.45K_u \approx 0.71\tau/(k\theta)$ and integral time $\tau_I = P_u/1.2 \approx 3.3\theta$. The corresponding “ideal” PID tunings are: $K'_c = 0.6K_u \approx 0.94\tau/(k\theta)$, $\tau'_I = P_u/2 = 2\theta$ and $\tau'_D = P_u/8 = 0.5\theta$, which correspond to $K_c = K'_c/2 \approx 0.47\tau/(k\theta)$ and $\tau_I = \tau_D = \theta$ for our cascade controller.

The IMC-tunings derived by Rivera, Morari, & Skogestad (1986) have a single tuning parameter ε which we select according to the recommendations for a first order process with delay as $\varepsilon = 1.7\theta$ for PI control and $\varepsilon = 0.8\theta$ for PID control. We get a PI controller with gain $K_c = 0.558\tau/(k\theta)$ and integral time $\tau_I = \tau$. For the cascade form IMC-PID controller, we get $K_c = 0.77\tau/(k\theta)$, $\tau_I = \tau$ and $\tau_D = 0.5\theta$.

However, the IMC tuning is for set-point tracking, and for “slow processes” with $\tau \gg \theta$ this gives a very slow settling for disturbances. Skogestad (2003) therefore suggests to use $\tau_I = \min(\tau, 8\theta)$ which for our process gives $\tau_I = 8\theta$. The controller gain is $K_c = 0.5\tau/(k\theta)$. We denote this tuning SIMC PI. For a SIMC-PID controller (on cascade form), the gain and integral time are left unchanged, and we have chosen to set the derivative time τ_D to 0.5θ .

For optimal tunings, the controller parameters are optimized simultaneously with the volumes:

$$V_{\text{tot,opt}} = \min_{V_1, \dots, V_n, K_{c1}, \dots, K_{cn}, \tau_{I1}, \dots, \tau_{In}} \sum_{i=1}^n V_i \quad (25)$$

subject to

$$|S(j\omega_k)G_d(j\omega_k)| \leq 1, \quad \forall \omega_k \in \Omega \quad (26)$$

$$|S_i(j\omega_k)| \leq M_S, \quad \forall \omega_k \in \Omega, i = 1, \dots, n \quad (27)$$

$$S \text{ is stable} \quad (28)$$

To assure a robust tuning, a limit, $M_S = S_{\text{max}} \leq 2$, is put on the peak of the gain of the individual sensitivity functions $|S_i|$. (For PID control we also let $\tau_{D1}, \dots, \tau_{Dn}$ vary in the optimization.)

In the following, we apply this numerical approach to the process in Example 1. For n multiple tanks in series, k_d is distributed equally between the tanks, so that for tank i we get $k_{d,i} = (k_d)^{1/n}$. The results for the four different controllers (ZN, IMC, SIMC and optimal) are given in Table 3 for PI control and in Table 4 for PID control.

The optimal controller PI-tunings (last column in Table 3) give a large integral time, so that we in effect have obtained P-control with $K_c k\theta/\tau$ equal to 0.63 (one tank), 0.71 and 0.56 (two tanks), 0.38 and twice 0.71 (three tanks) and 0.31 and three times 0.71 (four tanks). The optimal PID-tuning (last column in Table 4) also gave a large integral time (PD control) with $K_c = 0.8\tau/(k\theta)$ and derivate time $\tau_D = 0.4\theta$ for all tanks.

Table 3

PI controllers: volume requirements V_{tot} obtained from (22) (for Ziegler–Nichols, IMC, SIMC) and from (25) (optimal tuning)

n	ZN	IMC	SIMC	Optimized
1	3.16 V_0 (1)	1.81 V_0 (1)	2.48 V_0 (1)	1.78 V_0 (1)
2	3.16 V_0 (2)	1.81 V_0 (2)	2.48 V_0 (2)	1.77 V_0 (2)
3	3.14 V_0 (3)	1.81 V_0 (3)	2.46 V_0 (3)	1.73 V_0 (3)
4	3.09 V_0 (4)	1.81 V_0 (4)	2.42 V_0 (4)	1.68 V_0 (4)

Data: $k_d = 2.5 \times 10^6$, $\theta = 10$ s.

Table 4

PID controllers: volume requirements V_{tot} obtained from (22) (for Ziegler–Nichols, IMC, SIMC) and from (25) (optimal tuning)

n	ZN	IMC	SIMC	Optimized
1	2.31 V_0 (1)	1.30 V_0 (1)	2.15 V_0 (1)	1.22 V_0 (1)
2	2.31 V_0 (2)	1.30 V_0 (2)	2.15 V_0 (2)	1.22 V_0 (2)
3	2.29 V_0 (3)	1.29 V_0 (3)	2.14 V_0 (3)	1.21 V_0 (3)
4	2.25 V_0 (4)	1.28 V_0 (4)	2.10 V_0 (4)	1.19 V_0 (4)

Data: $k_d = 2.5 \times 10^6$, $\theta = 10$ s.

From Tables 3 and 4 we find that the “correction factor”, f on V_0

$$V_{\text{tot}} = fV_0 \quad (29)$$

is in the range $f = 1.2$ – 3.2 . The correction factor is independent of the number of tanks in most cases, which is plausible since the combination of (14) and (19) gives

$$V_{\text{tot}} > \frac{|S_i(j\omega)|}{\theta\omega} V_0 \quad (30)$$

where $|S_i|/\omega\theta$ is close to independent of the number of tanks involved. To see this, insert the tuning rules into the controller transfer function and calculate $|S_i(j\omega)|$. For the IMC tuning $|S_i(j\omega)|$ depends only on $\theta\omega$, so that when it is scaled with $\theta\omega$ it will independent of the process parameters. $|S_i|$ for ZN and SIMC depends on τ , but only for low frequencies (when $\tau\omega$ is small compared to 1). For up to three tanks, $|S_i|$ only depends on $\theta\omega$ at the relevant frequencies. Recall, however, that this analysis is not exact since (30) is an approximation.

Frequency-plots for three tanks with PI control are given in Fig. 6. In all four cases, the bandwidth ω_B is lower than $1/\theta$ (error E1). ω_B is the worst frequency, with exception of the Ziegler–Nichols tunings (which due to the high peak in $|S(j\omega)|$ give error E2). The optimal controller makes $|S(j\omega)G_d(j\omega)|$ constant for a wide frequency range.

Next consider in Fig. 7(a) the response to a step disturbance in inlet concentration (d) for the different controller tunings and tank volumes for the case with three tanks in series. As stated before, the optimal PI controller is actually a P controller, and the controller with IMC tuning also has a “slow” integral action and this is observed by the slow settling. We see that for the other two tunings, and especially for the Ziegler–Nichols tuning, the frequency domain result is conservative when considering the step response. This is because the peak in $|SG_d|$ is sharp so that $|S(j\omega)G_d(j\omega)|$ exceeds 1 only for a relatively narrow frequency range, and this peak has only a moderate effect on the step response. This means that we can reduce the required tank volume if step disturbances are the main concern. For the step response we find that a total tank size of $1.9V_0$ keeps the output within ± 1 for PI controllers tuned both with Ziegler–Nichols and SIMC. For PID control we find that $1.5V_0$ and $1.6V_0$ are necessary for these two tuning rules (1–4 tanks).

In conclusion, for PI control we recommend to select tanks with size $V_{\text{tot}} \approx 2V_0$, whereas with PID control $V_{\text{tot}} \approx$

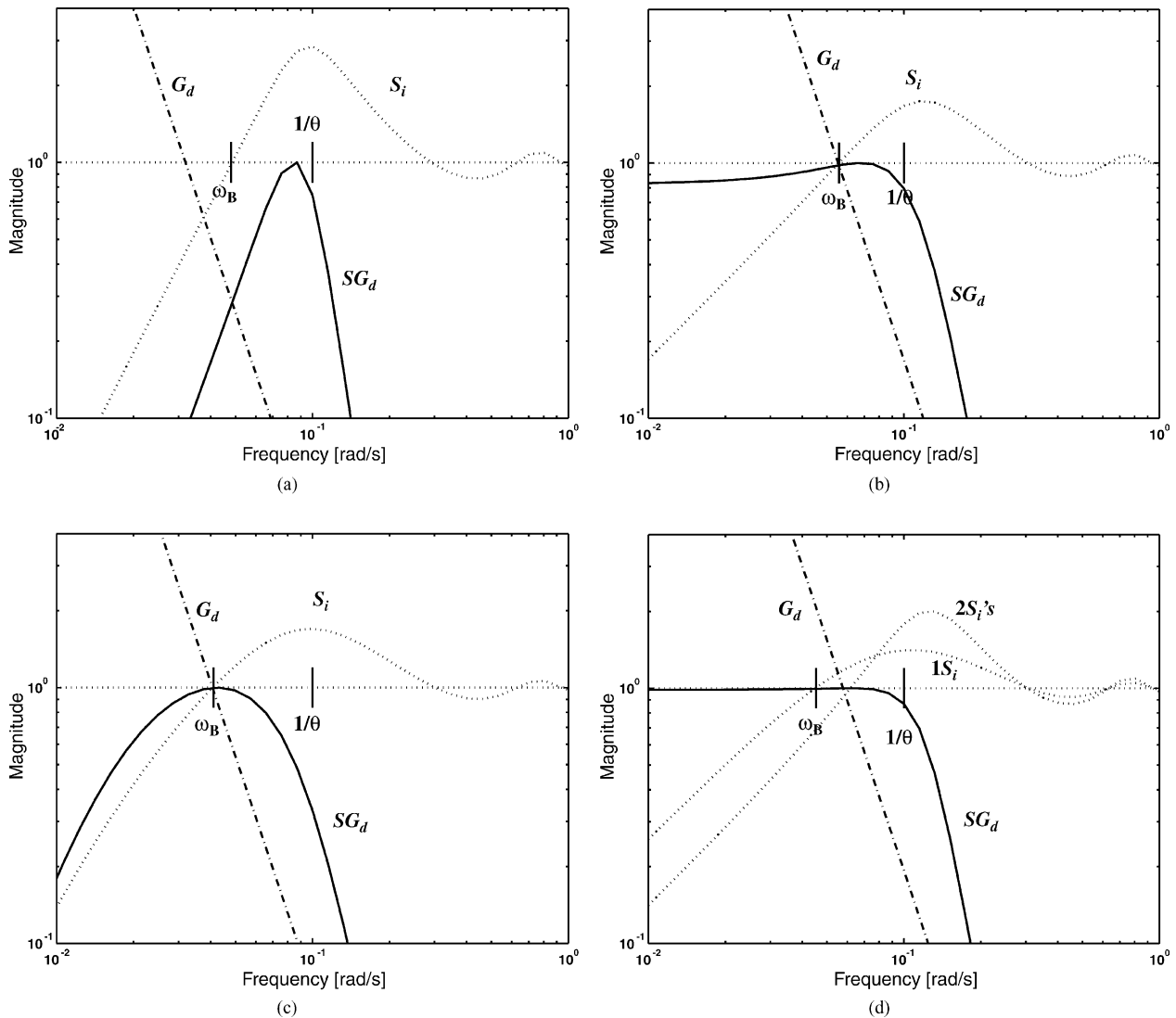


Fig. 6. Frequency–magnitude plots corresponding to results for PI control of three tanks in Table 3. (a) ZN settings; (b) IMC settings; (c) SIMC settings; (d) Optimal PI settings.

$1.6V_0$ is sufficient. These recommendations are confirmed in Fig. 7(b) where we use $V_{tot} = 2V_0$, and we see that after a unit disturbance step the output is within ± 1 .

Remark 1. We have specified that in each tank $k_i = 2k_{d,i}$, where $k_{d,i}$ is the (open loop) disturbance gain in each tank, but the results are independent of this choice, since the controller gains are adjusted relative to the inverse of k_i .

Remark 2. The sensitivity functions, $S_i(j\omega)$, are independent of the pH set-points in each tank (see Remark 1). $G_d(j\omega)$ is determined by its time constants and delays, which are independent of the pH-values, and its steady state overall gain, k_d . k_d is defined by the inlet and outlet pH. The fundamental requirement (11), and thereby the results of this and the previous section, are therefore independent of the pH set-points in intermediate tanks.

7. Equal or different tanks?

In all the above optimizations (Tables 3 and 4), we allowed for different tank sizes, but in all cases we found that equal tanks were optimal. This is partly because we assumed a constant delay of 10 s in each tank, independent of tank size.

This confirms the findings of Walsh (1993) who carried out calculations showing that equal tanks is cost optimal with fixed delay. We present here a derivation that confirms this. We assume that the cost of a tank of volume V is proportional to V^x , where x is a scaling factor. To minimize the total cost we then must minimize

$$\min_{V_1, \dots, V_n} (V_1^x + V_2^x + \dots + V_n^x) \tag{31}$$

which provided the flow rate through all tanks are equal (which is true for example if most of the reagent is added

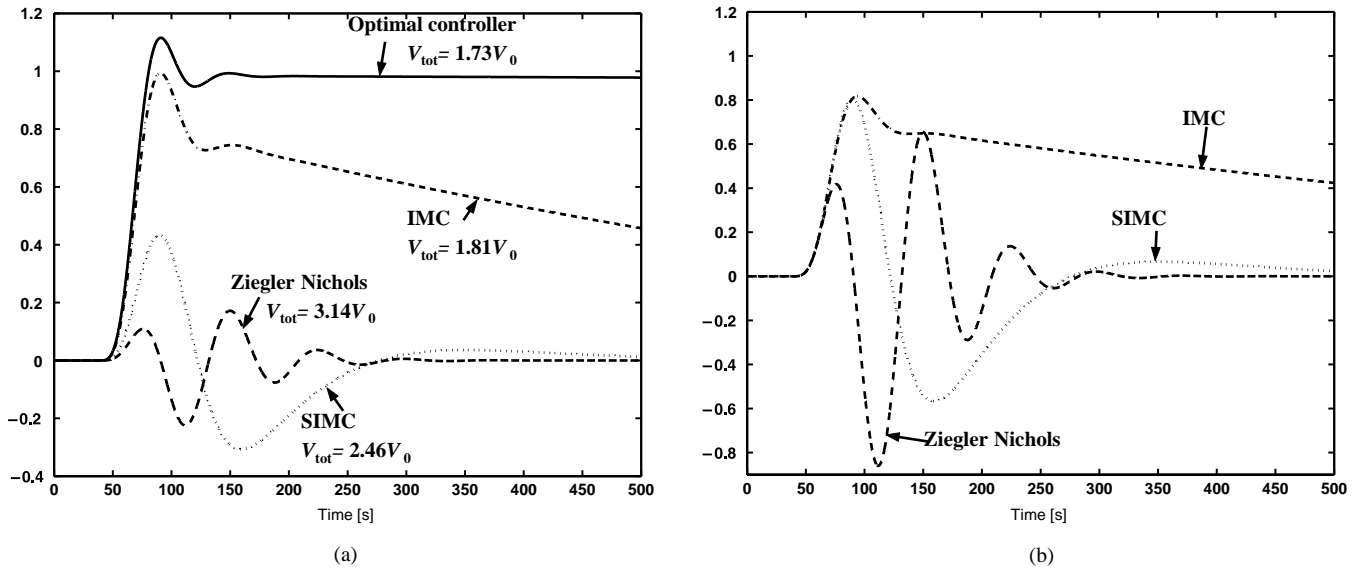


Fig. 7. Response to step disturbance in c_{infl} for three tanks using PI-control. (a) Volumes and tunings from Table 3; (b) equal tanks with $V_{tot} = 2V_0$ ($V_1 = V_2 = V_3 = V_{tot}/3$).

into the first tank), is equivalent to

$$\min_{\tau_1, \dots, \tau_n} (\tau_1^x + \tau_2^x + \dots + \tau_n^x) \quad (32)$$

This cost optimization is constrained by the demand for disturbance rejection (11). The expression for $G_d(s)$ for arbitrary sized tanks is:

$$G_d(s) = \frac{k_d e^{-(\theta_1 + \dots + \theta_n)s}}{(\tau_1 s + 1) \dots (\tau_n s + 1)} \quad (33)$$

Combining (33) with the inequality (11) yields

$$((\tau_1 \omega)^2 + 1) \dots ((\tau_n \omega)^2 + 1) - (|S(j\omega)|k_d)^2 \geq 0 \quad (34)$$

which constrains the optimization in (32). We assume again that the peak in $|SG_d|$ occurs at the frequency ω_B , where $|S| = 1$. (34) then simplifies to

$$((\tau_1 \omega_B)^2 + 1) \dots ((\tau_n \omega_B)^2 + 1) - k_d^2 \geq 0 \quad (35)$$

and it can easily be proved (e.g. using Lagrange multipliers, see Appendix C) that equal tanks minimizes cost.

This result contradicts Shinsky (1973, 1996) who assumed that the delay varies proportionally with the volume, and found that the first tank should be about one fourth of the second. McMillan (1984) also claims that the tanks should have different volume. Let us check this numerically. We assume a minimum fixed delay of 5 s and let $\theta(V) = (\alpha V + 5)$ s. To get consistency with our previous results with constant delay of 10 s, we let $\theta = 10$ s for $V = V_{tot}/n$, where V_{tot} is the total volume required with constant delay (see the final column of Table 3). The results of the optimization with PI control are presented in Table 5. We see that in this case it is indeed optimal with different sizes, with a ratio of about 1.5 between largest and smallest tank. However, if we with the

same expression for θ , require equal tanks and equal controller tunings in each tank, the incremental volume is only 14% or less for up to 4 tanks (see the last column in Table 5).

With a smaller fixed part in $\theta(V)$, the differences in size are larger. For example with a fixed delay of only 1 s we get a optimal ratio of up to 7.7 (for three tanks). However, if we allow for PID-controllers the ratio is only 1.5.

These numerical results seem to indicate that our proof in (35), which allows for different delays in each tank, is wrong. In the proof, we assumed that $|S| = 1$ at the frequency where $|SG_d|$ has its peak. This will hold for a complex controller, where due to the constraint (26) we expect $|SG_d|$ to remain flat over a large frequency region, but not necessarily for a simple controller, like PI. The frequency plots for the resulting PI-controllers in Table 5 confirm this.

In conclusion, it is optimal, in terms of minimizing cost, to have identical tanks with identical controllers, provided there are no restrictions on the controller. With PI-control there may be a small benefit in having different volumes, but this benefit is most likely too small to offset the practical advantages of having identical units. This agrees with the observations of Proudfoot (1983) from 6 neutralization plants with two or three tank in series. In all cases, equal tanks had been chosen.

Table 5
Optimal PI design with volume dependent delay: $\theta = (\alpha V + 5)s$

n	Volume each tank	V_{tot}	Volume ratio	V_{tot} increase with equal tanks (%)
2	217, 326	544	1.50	+4
3	18.4, 18.4, 30.7	67.6	1.67	+9
4	5.36, 5.36, 5.36, 9.14	25.2	1.71	+14

8. Discussion

8.1. Measurement noise and errors

In this paper, we have focused on the effect of disturbances. Another source of control errors is errors and noise in the measurements. Normally, the accuracy of pH instruments is considerable better than the requirement for the pH variation, which we as an example has given as ± 1 pH units in the present paper. However, due to impurities, the measured value may drift during operation. In one of Norsk Hydro's fertilizer plants, the probes are cleaned and recalibrated once a week, and during this period the pH measurement may drift up to 1 pH unit. This drifting is, however, very slow compared to the process, and will not influence the dynamic results from this paper, except that the controller cannot make the pH more correct than its measurement.

The worst error type is steady-state offset in the measurement of the product. This can lead to a product outside its specifications, and can only be avoided by regular calibration (possibly helped by data reconciliation).

Measurement errors in upstream tanks may lead to disturbances at later stages, since the controller using this measurement will compensate for what it believe to be a change in the concentration. Such errors can be handled at later stages.

To study the effects of measurement errors in the setting of this paper, one must convert the expected errors in the pH measurement to a corresponding error in the scaled concentration variable, y . Tools for such conversion is provided in [Appendix B](#). Often the error in y becomes larger than the pH error (as seen in the example of [Appendix B](#)).

The conclusion is that small and slowly appearing measurement errors do not cause problems, provided frequent maintenance is performed, whereas higher frequency variation with amplitude close to allowed pH variation must be converted into variation in y and treated as disturbances.

8.2. Feedforward elements

In this section, we discuss the implications for the tank size of introducing feedforward control. Feedforward from an influent pH measurement is difficult since an accurate transition from pH to concentration is needed. An indication of this is that Shinskey removed the section "Feedforward control of pH" in his fourth edition (compare ([Shinskey, 1988](#)) with ([Shinskey, 1996](#))). Feedforward from the influent flow rate is easier, and [McMillan \(1984\)](#) states that one tank may be saved with effective feedforward from influent flow rate and pH.

[Skogestad \(1996\)](#) show for an example with three tanks that use of a feedforward controller that reduced the disturbance by 80%, reduced the required total volume from 40.7 to 23.8 m³.

Previous work has considered feedforward from external disturbances. We will in the following analyze the situation

Table 6

The volume requirement with feedforward from each tank to next assuming that the feedforward reduces the disturbance by 80% ($r = 0.2$) and with perfect feedforward control ($r = 0$)

No. of tanks	80% reduction	Perfect feedforward control
1	V_0	V_0
2	$0.45V_0$	0
3	$0.34V_0$	0
4	$0.30V_0$	0
5	$0.27V_0$	0
∞	$0.20V_0$	0

V_0 is given by (18).

with n tanks in series and "feedforward" to downstream tanks from upstream measurements. In this way no extra measurements are required. As is discussed in ([Faanes & Skogestad, 1999](#)), a multivariable controller may give this kind of feedforward action. We assume no feedforward to the first tank, and assume that the feedforward controllers reduce the disturbance to each of the next $n - 1$ tanks by a factor of r_j , $j = 1, \dots, n - 1$ (where hopefully $r_j < 1$). The effective gain from an inlet disturbance to the concentration in the last tank then becomes

$$k_d^{\text{FF}} = k_d \prod_{j=1}^{n-1} r_j \quad (36)$$

To calculate the required volumes for this case, we insert (36) into (18), and get

$$V_0^{\text{FF}} = qn\theta \sqrt{\left(k_d \prod_{j=1}^{n-1} r_j\right)^{2/n} - 1} \quad (37)$$

If $r_1 = \dots = r_{n-1} = r$, (19) and (37) yield:

$$V_0^{\text{FF}} \approx V_0 r^{(n-1/n)} \quad (38)$$

For example, if each feedforward effect reduces the disturbance by 80% ($r = 0.20$), we get $V_0^{\text{FF}}/V_0 = 1$ (1 tank), $= 0.45$ (2 tanks), etc.; see [Table 6](#) for more details.

To have perfect feedforward from one tank to another one need, in addition to a perfect model, an invertible process. With a delay in the measurement or a larger delay for the control input than for the disturbance, this is not possible. Feedforward and multivariable controllers may actually benefit from transportation delay as will be illustrated in the following example.

Example 2. We have three tanks with (at least) measurement of pH in tank 1 and reagent addition in at least tank 3. The transport delay is 5 s in each tank, and the measurement delay is also 5 s (or less). If an upset occurs in tank 1 at time 0 s, the upset reaches tank 2 at time 5 s and tank 3 at 10 s. It is "discovered" in the measurement in tank 1 at time 10 s or before (the sum of the transport delay and the measurement delay). With a multivariable controller or a feedforward controller from tank 1 to 3, action can be taken in tank 3 at the

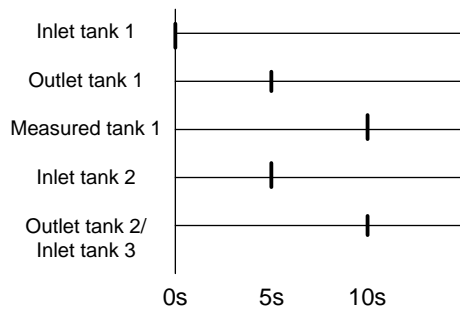


Fig. 8. With three tanks in series, an upset entering tank 1 reaches tank 3 at the same time the upset is seen in the measurement of tank 1. We assume the measurement and transport delays are equal.

same time the upset reaches the tank. For control of tank 2, however, the measurement in tank 1 will show the upset 5 s too late. The example is illustrated in Fig. 8.

From the feedback analysis in the previous sections, the smaller the total time delay the better. Example 2 shows, however, that if feedforward or multivariable control is used, one may benefit from a transport delay in intermediate tanks that is not shorter than the measurement delays. One should always seek to minimize the measurement delay.

8.3. pH set-points in each tank

We have already noted that the analysis in the previous sections is *independent* of the pH set-point in each tank (Remark 2, Section 6). Here we discuss some issues concerning the set-points or equivalently the distribution of reagent addition between the tanks.

For some processes, e.g. in fertilizer plants, the pH in intermediate tanks is important to prevent undesired reactions. Such requirements given by the chemistry of the process stream shall be considered first.

Next, instead of adjusting the set-points directly, one may use the set-points in upstream tanks to slowly adjust the valves in downstream tanks to ideal resting positions. But also in this case, one must have an idea of the pH levels in the tanks when designing the valves.

Whenever possible, we prefer to add only one kind of reagent, for example only base, to save equipment (see Fig. 3). To be able to adjust the pH in both directions as we have assumed, one then needs a certain nominal flow of reagent in each tank. This implies that the pH nominally needs to be different in each tank.

On the other hand, equal set-points in each tank minimizes the effect of flow rate variations. In addition, more reagent is added early in the process, so that reagent disturbances enter early.

One common solution is to distribute the pH set-points so that the disturbance gain is equal in each tank. In this way, one may keep the pH within $\pm\delta$, where δ is the same in each tank.

In conclusion, it is preferable to choose the set points as close as possible, but such that we never get negative reagent flow.

9. Conclusions

Buffer and surge tanks are primarily installed to smoothen disturbances that cannot be handled by the control system. With this as basis, control theory has been used to find the required number of tanks and tank volumes. We recommend identical tank sizes with a total volume of $2V_0$, where V_0 is given in (18) as a function of the overall disturbance gain, k_d , time delay θ in each tank, the flow rate q and number of tanks n . The disturbance gain k_d can be computed from Table 1. Typically, the mixing and measurement delay θ is about 10 s or larger.

Acknowledgements

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Appendix A. Modelling

A.1. Single tank

We first consider one single tank with volume V , see Fig. 4. Let c_{H^+} (mol/l) denote the concentration of H^+ -ions, c_{OH^-} (mol/l) denote the OH^- concentration, and q denote flow rate. Let further subscript infl denote influent, subscript reagent denote reagent and no subscript denote the outlet stream. Material balances for H^+ and OH^- yield:

$$\frac{d}{dt}(Vc_{H^+}) = c_{H^+,infl}q_{infl} + c_{H^+,reagent}q_{reagent} - c_{H^+}q + rV \quad (A.1)$$

$$\frac{d}{dt}(Vc_{OH^-}) = c_{OH^-,infl}q_{infl} + c_{OH^-,reagent}q_{reagent} - c_{OH^-}q + rV \quad (A.2)$$

where r (mol/(sl)) is the rate of the reaction $H_2O = H^+ + OH^-$. For strong, i.e. completely dissociated, acids and bases this is the only reaction in which H^+ and OH^- participate, since the ionization reaction already has taken place (for weak acids and bases, also the ionization reaction must be included in the model). r can be eliminated from the equations by taking the difference. In this way, we get a model for the excess of acid, i.e. the difference between the concentration of H^+ and OH^- ions (Skogestad, 1996):

$$c = c_{H^+} - c_{OH^-} \quad (A.3)$$

The component balance is then given by

$$\frac{d}{dt}(cV) = c_{infl}q_{infl} + c_{reagent}q_{reagent} - cq \quad (A.4)$$

Making use of the total material balance ($dV/dt = q_{\text{infl}} + q_{\text{reag}} - q$) the component balance simplifies to

$$\frac{d}{dt}c = \frac{1}{V} \{ (c_{\text{infl}} - c)q_{\text{infl}} + (c_{\text{reag}} - c)q_{\text{reag}} \} \quad (\text{A.5})$$

Linearization of (A.5) around a steady-state nominal point (denoted with an asterisk) and Laplace transformation yields:

$$c(s) = \frac{1}{(V^*/q^*)s + 1} \left\{ \frac{q_{\text{infl}}^*}{q^*} c_{\text{infl}}(s) + \frac{c_{\text{infl}}^* - c^*}{q^*} q_{\text{infl}}(s) + \frac{q_{\text{reag}}^*}{q^*} c_{\text{reag}}(s) + \frac{c_{\text{reag}}^* - c^*}{q^*} q_{\text{reag}}(s) \right\} \quad (\text{A.6})$$

where $q^* = q_{\text{infl}}^* + q_{\text{reag}}^*$ (steady-state mass balance) and the Laplace variables c , c_{infl} , q_{infl} , c_{reag} , and q_{reag} now denotes deviations from their nominal point. Note that the dynamics of V have no effect on the linearized quality response.

The nominal excess acid concentration are found from the nominal pH values:

$$c^* = (10^{-\text{pH}} - 10^{-14+\text{pH}}) \text{ mol/l} \quad (\text{A.7})$$

The composition balance is used to obtain the nominal reagent flow rate.

The reagent flow rate, q_{reag} , may be divided into $q_{\text{reag},u}$ which is determined by the controller, and a disturbance term, $q_{\text{reag},d}$, which is due to leakages and other uncertainties in the dosing equipment. Thus $q_{\text{reag}}(s) = q_{\text{reag},u}(s) + q_{\text{reag},d}(s)$.

We introduce scaled variables, where subscript max denotes maximum allowed or expected variation:

$$y = \frac{c}{c_{\text{max}}} \quad (\text{A.8})$$

$$d_{\text{infl},c}(s) = \frac{c_{\text{infl}}(s)}{c_{\text{infl},\text{max}}}, \quad d_{\text{infl},q}(s) = \frac{q_{\text{infl}}(s)}{q_{\text{infl},\text{max}}} \quad (\text{A.9})$$

$$d_{\text{reag},c}(s) = \frac{c_{\text{reag}}(s)}{c_{\text{reag},\text{max}}}, \quad d_{\text{reag},d,q}(s) = \frac{q_{\text{reag},d}(s)}{q_{\text{reag},d,\text{max}}} \quad (\text{A.10})$$

$$u(s) = \frac{q_{\text{reag},u}(s)}{q_{\text{reag},u,\text{max}}} \quad (\text{A.11})$$

Thus y , $d_{\text{infl},c}$, $d_{\text{infl},q}$, $d_{\text{reag},c}$, $d_{\text{reag},d,q}$ and u all shall stay within ± 1 .

We obtain

$$y(s) = \frac{1}{(V^*/q^*)s + 1} \left\{ \frac{c_{\text{infl},\text{max}}}{c_{\text{max}}} \frac{q_{\text{infl}}^*}{q^*} d_{\text{infl},c}(s) + \frac{c_{\text{infl}}^* - c^*}{c_{\text{max}}} \frac{q_{\text{infl},\text{max}}}{q^*} d_{\text{infl},q}(s) + \frac{c_{\text{reag},\text{max}}}{c_{\text{max}}} \frac{q_{\text{reag}}^*}{q^*} d_{\text{reag},c}(s) + \frac{c_{\text{reag}}^* - c^*}{c_{\text{max}}} \frac{q_{\text{reag},d,\text{max}}}{q^*} d_{\text{reag},d,q}(s) + \frac{c_{\text{reag}}^* - c^*}{c_{\text{max}}} \frac{q_{\text{reag},u,\text{max}}}{q^*} u(s) \right\} \quad (\text{A.12})$$

The scaling factor c_{max} is found from the given allowed variation in pH ($\pm \delta \text{pH}$):

$$c_{\text{max}}^- = (10^{-(\text{pH}-\delta \text{pH})} - 10^{-14+\text{pH}-\delta \text{pH}}) - c^* \quad (\text{A.13})$$

$$c_{\text{max}}^+ = c^* - (10^{-(\text{pH}+\delta \text{pH})} - 10^{-14+\text{pH}+\delta \text{pH}}) \quad (\text{A.14})$$

$$c_{\text{max}} = \min(c_{\text{max}}^-, c_{\text{max}}^+) \quad (\text{A.15})$$

If we consider one disturbance at a time, the model is on the form

$$y(s) = G(s)u(s) + G_d(s)d(s) \quad (\text{A.16})$$

$$G(s) = \frac{k}{\tau s + 1}, \quad G_d(s) = \frac{k_d}{\tau s + 1} \quad (\text{A.17})$$

where $k = (c_{\text{reag}}^* - c^*/c_{\text{max}})(q_{\text{reag},u,\text{max}}/q^*)$ and k_d for different disturbances are given by Table 1.

A.2. Linear model for multiple tank in series

We will now extend the model to include n tank in series, and label the tanks $i = 1, \dots, n$. For the first tank we get the same expression as for the single tank (A.12) (except for the labeling):

$$y_1(s) = \frac{1}{(V_1^*/q_1^*)s + 1} \left\{ \frac{c_{\text{infl},\text{max}}}{c_{1,\text{max}}} \frac{q_{\text{infl}}^*}{q_1^*} d_{\text{infl},c}(s) + \frac{c_{\text{infl}}^* - c_1^*}{c_{1,\text{max}}} \frac{q_{\text{infl},\text{max}}}{q_1^*} d_{\text{infl},q}(s) + \frac{c_{\text{reag},1,\text{max}}}{c_{1,\text{max}}} \frac{q_{\text{reag},1}^*}{q_1^*} d_{\text{reag},1,c}(s) + \frac{c_{\text{reag},1}^* - c_1^*}{c_{1,\text{max}}} \frac{q_{\text{reag},d,1,\text{max}}}{q_1^*} d_{\text{reag},d,1,q}(s) + \frac{c_{\text{reag},1}^* - c_1^*}{c_{1,\text{max}}} \frac{q_{\text{reag},u,1,\text{max}}}{q_1^*} u_1(s) \right\} \quad (\text{A.18})$$

For the following tanks, the inflow is equal to the outflow from previous tank, so that

$$y_i(s) = \frac{1}{(V_i^*/q_i^*)s + 1} \left\{ \frac{c_{i-1,\text{max}}}{c_{i,\text{max}}} \frac{q_{i-1}^*}{q_i^*} y_{i-1}(s) + \frac{c_{i-1}^* - c_i^*}{c_{i,\text{max}}} \frac{1}{q_i^*} q_{i-1}(s) + \frac{c_{\text{reag},i,\text{max}}}{c_{i,\text{max}}} \frac{q_{\text{reag},i}^*}{q_i^*} d_{\text{reag},i,c}(s) + \frac{c_{\text{reag},i}^* - c_i^*}{c_{i,\text{max}}} \frac{q_{\text{reag},d,i,\text{max}}}{q_i^*} d_{\text{reag},d,i,q}(s) + \frac{c_{\text{reag},i}^* - c_i^*}{c_{i,\text{max}}} \frac{q_{\text{reag},u,i,\text{max}}}{q_i^*} u_i(s) \right\} \quad (\text{A.19})$$

$q_{i-1}(s)$ is the deviation from nominal value for the flow rate from previous tank and is determined by the level controller

$$c_{\max} = \min(|c(\text{pH}^* + \delta\text{pH}) - c(\text{pH}^*)|, |c(\text{pH}^*) - c(\text{pH}^* - \delta\text{pH})|) \\ = \begin{cases} -(c(\text{pH}^* + \delta\text{pH}) - c(\text{pH}^*)), & \text{pH}^* \leq 7 \\ -(c(\text{pH}^*) - c(\text{pH}^* - \delta\text{pH})), & \text{pH}^* \geq 7 \end{cases} \quad (\text{B.5})$$

(B.4) and (B.5) yield for the error in the scaled variable, Δy :

$$\Delta y = \begin{cases} -\frac{c(\text{pH} + \Delta\text{pH}^m) - c(\text{pH})}{c(\text{pH}^* + \delta\text{pH}) - c(\text{pH}^*)}, & \text{pH}^* \leq 7 \\ -\frac{c(\text{pH} + \Delta\text{pH}^m) - c(\text{pH})}{c(\text{pH}^*) - c(\text{pH}^* - \delta\text{pH})}, & \text{pH}^* \geq 7 \end{cases} \quad (\text{B.6})$$

(B.6) can be used to find Δy corresponding to a pH measurement error or noise of ΔpH^m .

We will now consider some special cases. As in the paper, we specify $\delta\text{pH} = 1$, and let the actual value equal the nominal value. We consider first $\text{pH} = \text{pH}^* < 7$. Then

$$\Delta y = -\frac{c(\text{pH}^* + \Delta\text{pH}^m) - c(\text{pH}^*)}{c(\text{pH}^* + 1) - c(\text{pH}^*)} \\ = -\frac{(10^{-\Delta\text{pH}^m} - 1)10^{-\text{pH}^*} - (10^{\Delta\text{pH}^m} - 1)10^{-14+\text{pH}^*}}{-0.9 \times 10^{-\text{pH}^*} - 9 \times 10^{-14+\text{pH}^*}} \quad (\text{B.7})$$

For $\text{pH} = \text{pH}^* \geq 7$ we obtain

$$\Delta y = -\frac{c(\text{pH}^* + \Delta\text{pH}^m) - c(\text{pH}^*)}{c(\text{pH}^*) - c(\text{pH}^* - 1)} \\ = -\frac{(10^{-\Delta\text{pH}^m} - 1)10^{-\text{pH}^*} - (10^{\Delta\text{pH}^m} - 1)10^{-14+\text{pH}^*}}{-9 \times 10^{-\text{pH}^*} - 0.9 \times 10^{-14+\text{pH}^*}}$$

For $\text{pH}^* < 6$ we get $\Delta y \approx (10^{-\Delta\text{pH}^m} - 1)/0.9$ (since then $10^{-\text{pH}^*} \gg 10^{-14+\text{pH}^*}$) and for $\text{pH}^* > 8$ we get $\Delta y \approx -(10^{\Delta\text{pH}^m} - 1)/0.9$ (since then $10^{-14+\text{pH}^*} \gg 10^{-\text{pH}^*}$). This yields the following simple formula (when $\delta\text{pH} = 1$):

$$|\Delta y| = \frac{10^{|\Delta\text{pH}^m|} - 1}{0.9}, \quad \text{pH} = \text{pH}^* < 6 \text{ or } \text{pH} = \text{pH}^* > 8 \quad (\text{B.8})$$

Example 3. We have made a model of a neutralization process (as described in Appendix A) and have chosen $\text{pH}^* = 5$ and $\delta\text{pH} = 1$. The pH measurement may have a measurement noise of ± 0.05 pH units, and we want to determine the corresponding noise in the scaled concentration variable y . We consider an actual pH value equal to the nominal, and since $\text{pH} = \text{pH}^* < 6$, we can use (B.8): $|\Delta y|_{\max} = (10^{0.05} - 1)/0.9 = 0.14$.

Appendix C. On the optimization problem (32) subject to (35)

Here we prove that the solution to

$$\min_{\tau_1, \dots, \tau_n} (\tau_1^x + \tau_2^x + \dots + \tau_n^x) \\ \text{subject to} \\ ((\tau_1\omega_B)^2 + 1) \cdots ((\tau_n\omega_B)^2 + 1) \geq k_d^2 \quad (\text{C.1})$$

is to have $\tau_1 = \tau_2 = \dots = \tau_n$. The solution will not be at an interior point so we take the limiting of the constraint. We introduce $\alpha_i = \tau_i\omega_B$, and get the following optimization problem with the same solution as the original:

$$\min_{\alpha_1, \dots, \alpha_n} \alpha_1^x + \alpha_2^x + \dots + \alpha_n^x \\ \text{subject to} \quad (\text{C.2})$$

$$\prod_{i=1}^n (\alpha_i^2 + 1) - k_d^2 = 0$$

The Lagrange function, \mathcal{L} , for this problem is, denoting the Lagrange multiplier λ :

$$\mathcal{L} = \alpha_1^x + \alpha_2^x + \dots + \alpha_n^x + \lambda \left\{ \prod_{i=1}^n (\alpha_i^2 + 1) - k_d^2 \right\}, \\ i = 1, \dots, n \quad (\text{C.3})$$

and in the constrained optimum we have

$$\frac{\partial \mathcal{L}}{\partial \alpha_i} = x\alpha_i^{x-1} + \frac{2\alpha_i\lambda}{(\alpha_i^2 + 1)} \prod_{j=1}^n (\alpha_j^2 + 1) = 0 \quad (\text{C.4})$$

This implies, using the constraint, that

$$x\alpha_i^{x-1} + \frac{2\alpha_i\lambda}{(\alpha_i^2 + 1)} k_d^2 = 0, \quad i = 1, \dots, n \quad (\text{C.5})$$

In Eq. (C.5), x , k_d and λ are independent of the index i , and the value of α_i is therefore the same for all i 's. So $\alpha_1 = \dots = \alpha_n$, which implies that $\tau_1 = \tau_2 = \dots = \tau_n$.

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