pH-NEUTRALIZATION: INTEGRATED PROCESS AND CONTROL DESIGN

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Abstract: The paper adresses control related design issues for neutralization plants. Mainly for control reasons, the neutralization is usually performed in several steps with gradual change in the concentration. The aim is to give recommendations for issues like tank sizes and number of tanks.

Keywords: Process control, pH control, Processs design, PID control

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 *reactant* (manipulated variable, u) so that the outflow or *effluent* has a certain pH. Normally this is taking place in one or more tanks or basins, see Figure 1 for a case with one tank. 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. Our starting point is that the tanks are installed primarily for dynamic and control purposes. But nevertheless, theory for dynamic systems and control systems has hardly been used for process design.

Textbooks on pH control are (Shinskey, 1973) and (McMillan, 1984), while the process control textbooks (Shinskey, 1996) and (Balchen and Mummé, 1988) have sections on pH control. A critical review on design and control of neutralization processes which emphasizes chemical waste water treatment is given by Walsh (1993).

In this 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. Since time delays are important design limitations, section 2 contains a discussion on delays. From the models presented in section 3, a basis for the choice of the number of tanks and their total volume is discussed in section 4. In section 5 improved rules for sizing for different controller tunings are proposed. Whether equal tanks is best or not is discussed in section 6. For processes with more that one tank, the pH set-point in each tank has to be decided (section 7).

2. 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 rise 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_t)

In this paper we mainly consider local feedback control, and the effective delays is the sum of the contribution from the process and instrumentation $\theta = \theta_p + \theta_m + \theta_v$. If the influent (disturbance) and the reactant

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addition (manipulated variable) are placed close, they will have about the same delay θ_p. 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) carries out a calculation for one mixer type leading to $\theta_p \sim V^{0.07}$ and concludes that θ_p typically is about $7s$ 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 is here 4θ, varies proportionally with the volume). In this paper, we follow Walsh and assume that the overall effective delay is $\theta = 10s$ in each tank.

3. MODEL

The required number and size of mixing tanks for neutralization is related to the resulting operability. The task of the tank(s) is to smoothen the disturbances to the extent that the control system can handle the remaining variations and keep the effluent concentration within certain limits. The tank(s) handle high frequency variations, while the control system has to take care of the low frequency region. Based on (Skogestad, 1996) a method for tank design using this basic understanding is presented.

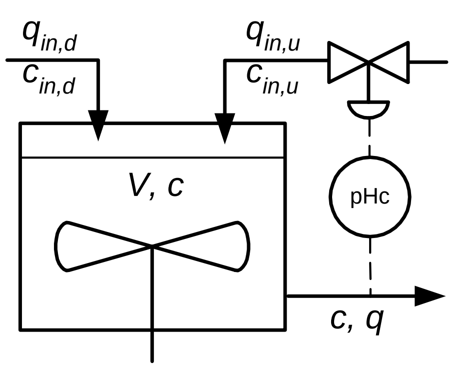

Fig. 1. Neutralization tank with pH control

pH-control involving strong acids and bases is usually considered as a strongly "nonlinear" process. However, if we look at the underlying model

$$\frac{d\,(cV)}{dt} = c_{in,d}q_{in,d} + c_{in,u}q_{in,u} - cq \qquad (1)$$

written in terms of the excess H^+ concentration $c = c_{H^+} - c_{OH^-}$, then we find that it is linear (strictly speaking, it is bilinear with a product of flow (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 have $6 < pH < 8$, whereas $c = 1 mol/l$ for a strong acid with $pH = 0$), shows the strong sensitivity of the process to disturbances (with $k_d \gg 1$; see below), and has nothing to do with non-linearity in a mathematical sense. By linearizing the bilinear terms (cq) we obtain the transfer function model in terms of derivation variables

$$y(s) = g(s)u(s) + g_d(s)d(s) \qquad (2)$$

where $y(s)$ is the effluent excess concentration, $u(s)$ is the reactant flow, and $d(s)$ is the disturbance, either the influent flow, $q_{in,d}$, or (excess) concentration, $c_{in,d}$. g and g_d are the transfer functions from the control input and the disturbance, respectively. To make it easier to state criteria for sufficient dampening, the model is scaled so that the output, control input and the expected disturbances shall lie between -1 and 1.

For a tank labeled i, the transfer functions $g_i(s)$ and $g_{d_i}(s)$ are represented as

$$g_i(s) = \frac{k_i}{\tau_i s + 1} e^{-\theta_i s} \; g_{d_i}(s) = \frac{k_{d_i}}{\tau_i s + 1} e^{-\theta_i s} \qquad (3)$$

where τ_i is the residence time in the tank and θ_i is effective time delay, due to mixing, measurement and valve dynamics. For n equally sized tanks we obtain

$$g_d(s) = \frac{k_d}{(\frac{\tau_h}{n} s + 1)^n} e^{-n\theta s} \qquad (4)$$

where τ_h is the total residence time V_{tot}/q. V_{tot} is the total volume and q is the flow through the tanks, and we here assume $\theta_1 = \ldots = \theta_n = \theta$. With the above-mentioned scalings, the gain for a flow disturbance in the influent becomes

$$k_d = \frac{c^*_{in,d} - c^*}{c_{\max}} \frac{q_{in,d_{\max}}}{q^*} \qquad (5)$$

where $*$ denotes nominal values. $q_{in,d_{\max}}$ is maximal expected variation in the inlet flow, and $c_{\max}$ is the maximum allowed variation in the excess H^+ concentration, c. We will assume that $k_d \gg 1$ (typically k_d is 10^3 or larger for pH systems).

Example: Consider neutralization of a strong acid with $pH = -1$ ($c^*_{in,d} = 10 - 10^{-15}$) using a strong base with $pH = 15$ as reactant. We want to make a product with $pH = 7 \pm 1$, i.e. $c_{\max} = 10^{-6}$ and $c^* = 0 mol/l$. The nominal acid flow is 50% of the total flow, and if we assume the maximum variation in acid flow is $\pm 50\%$, then $q_{in,d_{\max}}/q^* = 0.5 \cdot 0.5$. Thus $k_d = \frac{10}{10^{-6}} 0.5 \cdot 0.5 = 2.5 \cdot 10^6$.

4. THE VOLUME AND NUMBER OF TANKS

The basic control structure is local control in each tank, as illustrated in Figure 1. We assume no reference changes ($r = 0$), and the closed-loop response of each tank then becomes

$$\begin{aligned} y_i(s) &= \frac{1}{1 + g_i(s)c_i(s)} g_{d_i}(s) d_i(s) \\ &= S_i(s)\, g_{d_i}(s)\, d_i(s) \end{aligned} \qquad (6)$$

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

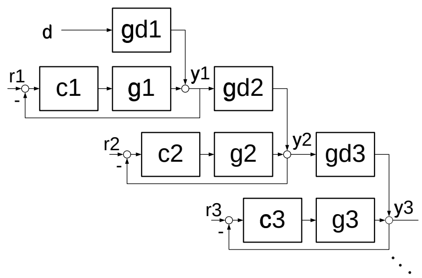

Fig. 2. Local control in each tank.

one transfer function from the external disturbance d to the final output y leads to

$$y(s) = \left(\prod_{i=1}^{n} S_i(s)\, g_{d_i}(s)\right) d(s)$$
$$= \left(\prod_{i=1}^{n} S_i(s)\right)\left(\prod_{i=1}^{n} g_{d_i}(s)\right) d(s) \qquad (7)$$

$$y(s) = S(s) g_d(s)\, d(s) \qquad (8)$$

where S is defined by $S(s) = \prod_{i=1}^{n} S_i(s)$. The factorization is possible since the tanks are SISO systems. If instead only one controller is used, which takes the measurement in last tank and manipulates the control input of the first tank, the same expression as (8) would result, although S is different.

Due to scaling of the variables, the product quality constraint gives the following requirement for the process and control system:

$$|S(j\omega) g_d(j\omega)| \le 1; \quad \forall\omega \qquad (9)$$

Combining (9) and (4) yields an expression for the total volume with n equal tanks:

$$V_{tot} \ge \frac{qn}{\omega}\sqrt{(k_d\,|S(j\omega)|)^{2/n} - 1}; \quad \forall\omega \qquad (10)$$

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

$$V_{tot} \ge qnk_d^{1/n}\frac{|S(j\omega)|^{1/n}}{\omega}; \quad \forall\omega \qquad (11)$$

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 controllers are equally tuned, the expression is

$$V_{tot} \ge qnk_d^{1/n}\frac{|S_i(j\omega)|}{\omega}; \quad \forall\omega \qquad (12)$$

where S_i is the sensitivity function for each locally controlled tank. The smallest volume fulfilling (12) depends on the controller tuning and the "worst" frequency. A reasonable assumption is that the limiting value is not far away from the lowest frequency, ω_B, for which $|S(j\omega_B)| = 1$. (Note that other sightly different definitions of ω_B are in use.) We will see that $|Sg_d|$ is "flat" around the frequency ω_B if the controller tuning is not too aggressive. We insert $|S(j\omega_B)| = 1$ into (10), and obtain

$$V_{tot} \ge \frac{qn}{\omega_B}\sqrt{k_d^{2/n} - 1} \qquad (13)$$

for a given value of ω_B. This equation is given by Skogestad (1996). Since $|g_d(j\omega)|$ decreases as ω increases, this volume guarantees that

$$|g_d(j\omega)| \le 1; \forall\omega \ge \omega_B \qquad (14)$$

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. Skogestad and Postlethwaite (1996, p.174), state that for practical purposes $\omega_B \le 1/\theta$ (the exact value depends on the controller tuning), which gives (Skogestad, 1996):

$$V_{tot} > V_0 \stackrel{def}{=} qn\theta\sqrt{k_d^{2/n} - 1} \qquad (15)$$

which we will use as a reference throughout the paper. For $k_d \gg 1$, (15) simplifies to

$$V_0 \approx qn\theta k_d^{1/n} \qquad (16)$$

(16) gives the important insight that the volume in each tank, V_0/n, is proportional to the total flow, q, the time delay in each tank, θ, and the disturbance gain k_d raised to the power $1/n$. Table 1 shows V_0 for the example. With one tank the size of a supertanker ($250,000m^3$) is required. The minimum total volume is obtained with 18 tanks (Skogestad, 1996), but the reduction in size levels off at about 3-4 tanks, and taking cost into account one would probably choose 3 or 4 tanks.

Table 1. Total tank volume, V_0, with $q = 0.01m^3/s$, $k_d = 2.5 \times 10^6$ and $\theta = 10s$.

Number of tanks, n	Total volume V_0 $[m^3]$
1	250,000
2	316
3	40.7
4	9.51
5	6.96

Remark: With more than one tank and different pH in each tank, a feed flow variation (disturbance) into the first tank will give a "double" effect in the downstream concentration variations: Both inlet flow rate and inlet concentration will vary. The flow rate variations may be dampened with slow level control, but extra volume is required also for this, which is not taken into account in the analysis presented in this paper.

5. IMPROVED SIZING

In (15) we derived the reference 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. Each tank 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}. We consider three different controller tuning rules for PI and PID controllers: Ziegler-Nichols, IMC and optimal tuning.

The optimization problem for the case with Ziegler-Nichols or IMC tunings may be formulated as:

$$V_{tot,opt} = \min_{V_1,\dots V_n} \sum_{i=1}^{n} V_i \quad (17)$$

subject to

$$|S(j\omega_k) g_d(j\omega_k)| \leq 1; \;\; \forall \omega_k \in \Omega \quad (18)$$

$$S \text{ is stable} \quad (19)$$

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). 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 the ultimate period P_u, and give for our process a PI controller gain of $K_c = 0.45K_u \approx 0.71\tau/(k\theta)$ and integral time $\tau_I = P_u/1.2 \approx 3.3\theta$. For PID controllers, the tuning rules are: $K_c = 0.6K_u \approx 0.94\tau/(k\theta)$, $\tau_I = P_u/2 = 2\theta$ and $\tau_D = P_u/8 = 0.5\theta$.

The IMC-tunings derived by Rivera *et al.* (1986) have a single tuning parameter τ_c (denoted ε in the original paper) which we select to get a robust tuning. For a first order process with delay, we get a PI controller with gain $K_c = 0.5\tau/(k\theta)$ and integral time $\tau_I = \tau$. However, this tuning is for set-point tracking, and for "slow processes" with $\tau \gg \theta$ this gives a very slow settling for disturbances. Skogestad (1999) therefore suggests to use $\tau_I = \min(\tau, 8\theta)$ which for our process gives $\tau_I = 8\theta$. For a cascade form IMC-PID controller, the gain and integral time are left unchanged, and the derivative time τ_D is set to 0.5θ.

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

$$V_{tot,opt} = \min_{V_1,\dots V_n, K_{c_1},\dots K_{c_n}, \tau_{I_1},\dots,\tau_{I_n}} \sum_{i=1}^{n} V_i \quad (20)$$

subject to

$$|S(j\omega_k) g_d(j\omega_k)| \leq 1; \;\; \forall \omega_k \in \Omega \quad (21)$$

$$|S_i(j\omega_k)| \leq S_{\max}; \;\; \forall \omega_k \in \Omega; \; i = 1,\dots,n \quad (22)$$

$$S \text{ is stable} \quad (23)$$

For PID we also let $\tau_{D_1},\dots,\tau_{D_n}$ vary in the optimization. To assure a robust tuning, a limit, $S_{\max} = 2$, is put on the peak of the gain of the individual sensitivity functions $|S_i|$.

The results for the three different controllers (ZN, IMC and optimal) are compared in table 2 for PI controllers and in table 3 for PID controllers. The "correction factor" on V_0 is in the range 1.2 to 3.2. The correction factor is independent of the number of tanks in most cases, which is plausible since the combination of (12) and (15) gives

$$V_{tot} > \frac{|S_i(j\omega)|}{\theta\omega} V_0 \quad (24)$$

where $|S_i|/\omega$ and θ are independent of the number of tanks involved. Frequency-plots for 3 tanks with PI control are given in Figures 3 (ZN), 4 (IMC-2) and 5 (optimal). For the IMC based PI-tuning the deviation from V_0 is because the bandwidth is not $1/\theta$ (error E1, see Figure 4), whereas for the Ziegler-Nichols tuning both the errors E1 and E2 occur, see Figure 3.

Table 2. PI controllers: Volume requirements V_{tot} relative to V_0 from (15) for Ziegler-Nichols, IMC and optimal tuning. (Data: $k_d = 2.5 \times 10^6$, $\theta = 10s$.)

n	ZN-PI	IMC-PI1 $\tau_I = \tau$	IMC-PI2 $\tau_I = 8\theta$	Optimized PI
1	$3.16V_0$	$2.00V_0$	$2.48V_0$	$1.78V_0$
2	$3.16V_0$	$2.00V_0$	$2.48V_0$	$1.77V_0$
3	$3.14V_0$	$2.00V_0$	$2.46V_0$	$1.73V_0$
4	$3.09V_0$	$2.00V_0$	$2.42V_0$	$1.68V_0$

Table 3. PID controllers: Volume requirements V_{tot} relative to V_0 from (15) for Ziegler-Nichols, IMC and optimal tuning. (Data: $k_d = 2.5 \times 10^6$, $\theta = 10s$.)

n	ZN-PID	IMC-PID1 $\tau_I = \tau$	IMC-PID2 $\tau_I = 8\theta$	Optimized PID
1	$1.98V_0$	$2.00V_0$	$2.15V_0$	$1.71V_0$
2	$1.98V_0$	$2.00V_0$	$2.15V_0$	$1.22V_0$
3	$1.97V_0$	$1.99V_0$	$2.14V_0$	$1.21V_0$
4	$1.94V_0$	$1.96V_0$	$2.10V_0$	$1.34V_0$

A response to a step disturbance in inlet concentration (d) is shown in Figure 6 for the different controller tunings. We see that the optimal PI controller is actually a P controller and the IMC controller with $\tau_I = \tau$ also has a "slow" integral action. We see that for the other two tunings, and especially for the Ziegler-Nichols tuning, the 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. On the other hand, for the optimal tuning and IMC with $\tau_I = \tau$, $|SG_d|$ remains at its maximum value of 1 for several decades. For the step response we find by adjusting the volume that a total tank size of $1.9V_0$ keeps the output within ± 1 for PI controllers tuned both with Ziegler-Nichols and IMC-2 (with $\tau_I = 8\theta$). For PID control we find that $1.3V_0$ and $1.6V_0$ are necessary for

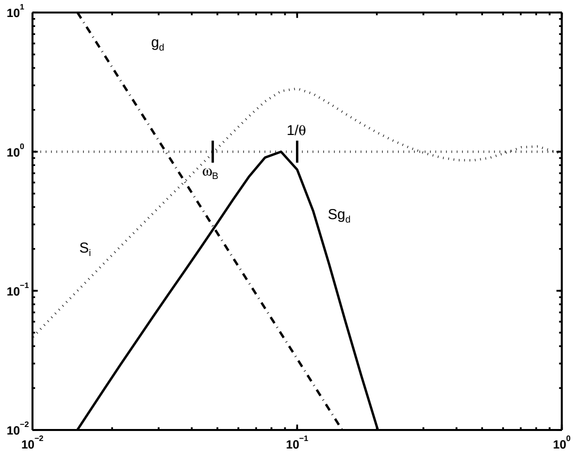

Fig. 3. For ZN-PI tuning, ω_B is not the worst frequency. This is due to the high peak in $|S(j\omega)|$. $V_{tot} = 3.14V_0$ is needed to obtain $|S(j\omega)\, g_d(j\omega)| \leq 1$ for all ω.

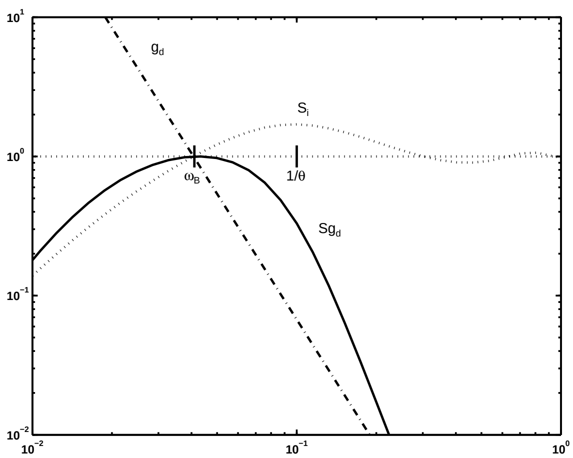

Fig. 4. For IMC-PI with $k_c = 0.5\tau/k\theta$, $\tau_I = 8\theta$: ω_B is approximately the worst frequency. $V_{tot} = 2.46V_0$ is needed to obtain $|S(j\omega)\, g_d(j\omega)| \leq 1$ for all ω.

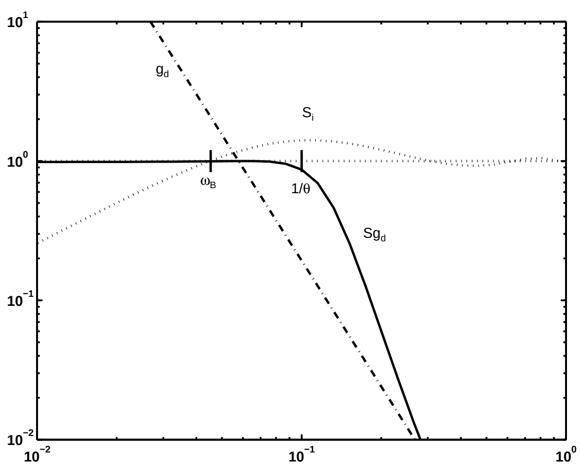

Fig. 5. Frequency response with optimal PI-tuning, $V_{tot} = 1.73V_0$.

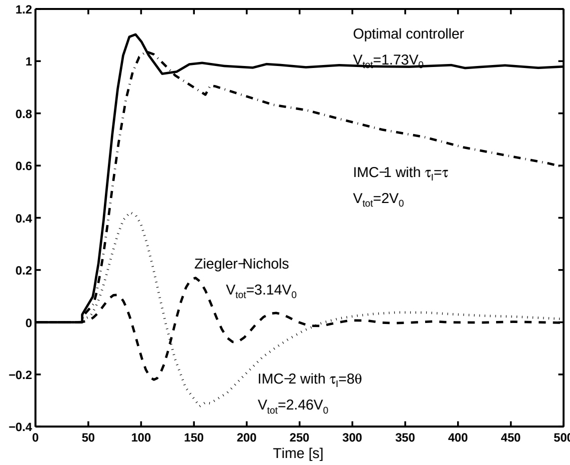

Fig. 6. The response of a disturbance step for different PI controller tunings (for 3 tanks).

these two tuning rules. In conclusion, for PI control we should select tanks with size $V_{tot} \approx 2V_0$, while if PID control is possible $V_{tot} \approx 1.6V_0$ is sufficient.

6. DISCUSSION ON EQUAL SIZED TANKS

In all the above optimizations (Tables 2 and 3) we allowed for different tank sizes, but in all cases we found that equal tanks were optimal. This is mainly because we assumed a constant delay of 10 seconds 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 give here a different derivation which confirms this. The cost function for a fixed number of tanks is equivalent to the sum of a given power of the volumes (plus a constant bias):

$$\min_{V_1,\dots,V_n} \left(V_1^x + V_2^x + \cdots + V_n^x\right) \qquad (25)$$

which is equivalent to

$$\min_{\tau_1,\dots,\tau_n} \left(\tau_1^x + \tau_2^x + \cdots + \tau_n^x\right) \qquad (26)$$

if the flow through all the tanks is assumed to be the same. The cost optimization is constrained by the demand for disturbance rejection (9). The expression for $g_d(s)$ for arbitrary sized tanks is:

$$g_d(s) = \frac{k_d e^{-(\theta_1 + \cdots + \theta_n)s}}{(\tau_1 s + 1)\cdots(\tau_n s + 1)} \qquad (27)$$

Combining (27) with the inequality (9) yields

$$\left((\tau_1\omega)^2 + 1\right)\cdots\left((\tau_n\omega)^2 + 1\right) - \left(|S(j\omega)|\, k_d\right)^2 > 0 \qquad (28)$$

which constraints the optimization in (26). We assume again that the peak in $|Sg_d|$ occurs at the frequency ω_B where $|S| = 1$. (28) then simplifies to

$$\left((\tau_1\omega_B)^2 + 1\right)\cdots\left((\tau_n\omega_B)^2 + 1\right) - k_d^2 > 0 \qquad (29)$$

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

As stated earlier, Shinskey (1973, 1996) assumes that the delay varies proportionally with the volume, and then derives that the first tank should be about one forth of the second, and also McMillan (1984) claims that the tanks should have different volume. To study the effect of Shinskeys assumption, we assume a minimum fixed delay of $5s$ and let $\theta(V) = (\alpha V + 5)$s To compare it with the constant delay of $10s$, we let $\theta(V_{tot}/n) = 10$ where V_{tot} is the total volume required with constant delay (see the final column of table 2). The results of the optimization PI control are presented in table 4. We see that in this case it is optimal with different sizes with a ratio of about 1.5 between largest and smallest tank.

Table 4. Optimal design with volume dependent delay: $\theta = (\alpha V + 5)\,s$.

n	Volume each tank	V_{tot}	Ratio
2	217, 326	544	1.50
3	18.4, 30.7, 18.4	67.5	1.67
4	4.37, 4.37, 4.37, 6.32	19.4	1.45

Of course with a smaller fixed part, the differences in size is larger. For example with a fixed delay of only $1s$ we get a ratio of 3.1. However, if we allow for PID-controllers the ratio is only 1.5. These numerical results seem to indicate that our proof for equal tank sizes, which actually applies also with 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 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 4 confirm this). In conclusion, we believe that it is always optimal, in terms of minimizing the volume, to have identical tanks, provided there is no restriction on the controller. With PI-control there may be a small theoretical benefit by having different volumes, but this benefit is most likely too small to offset the practical advantages of having identical units.

7. pH SET-POINTS IN EACH TANK

The analyses in previous sections are independent of the pH set-point in each tank. Here we will outline some issues concerning the set-points or equivalently the distribution of reactant addition between the tanks. Different pH set points in two subsequent tanks requires that reactant addition is available in the second tank. In this case, one would normally only be able to change the pH in one direction, so that a certain set-point difference is needed. For some processes e.g. in fertilizer plants, the pH in intermediate tanks is important to prevent certain reactions.

In stead 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.

The more equal the set-points in each tank is, the smaller is the effect from flow variations. In addition, more reactant is added early in the process, so that reactant disturbances enter early. One possible compromise would be 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 ± 1 in each tank. An important factor is of course available reactant valves.

8. CONCLUSION

Buffer tanks are primarily installed to smoothen disturbances which cannot be handled by the control system. With this as basis, control theory has been used to find the number of tanks and tank volumes. We recommend identical tank sizes with a total volume of $2V_0$ where V_0 is given by (15). The disturbance gain k_d can be computed from (5). Typically, the mixing and measurement delay θ is about 10s or larger.

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