pH control of a fed batch reactor with precipitation

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ABSTRACT

In this paper, the problem of controlling the pH, in a fed batch reactor where precipitation occurs, is considered. Due to the batch nature of the production and the effects of precipitation, the control problem is rather different from the well studied cases of continuous processes, which are usually considered under the assumption of perfect solubility. To fulfill this objective on a presented laboratory reactor used to produce precipitates, a simple control strategy is proposed, which is consistent with the limitations of the apparatus. Interestingly, the reagents under consideration have well known specifications. This point is advantageously taken into account to identify a single-input–single-output model off-line. Then, based on the obtained time-varying equation, pH set point tracking is achieved by imposing linear asymptotically stable dynamics on the amount of strong acid used for neutralization. Finally, simple rules are proposed to deal with precipitation. Representative experimental results obtained on the reactor are presented to prove the relevance of the approach.

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1. Introduction

The problem considered in this paper consists in controlling the pH (classically defined as pH $= -\log_{10}(C_H)$, where C_H is the hydronium ion concentration) in a laboratory fed batch reactor operated at Institut Français du Pétrole (IFP). This reactor is used to produce precipitates. For product quality control, it is desired that the pH remains as close as possible to a prescribed set point. During a given batch, this set point is kept constant. Depending on target product, it can range from 4 to 12. In this context, the pH control problem is challenging for two reasons. On the one hand, the considered range of operating points is wide. This induces significant variations of the dynamics. On the other hand, the reactor is operated in batch mode. To address these specificities, a dedicated strategy is proposed. It relies on the following assumptions: the reagents are well known and their dissociations can be identified off-line.

The topic of pH control has attracted much attention in the literature (see, e.g., the late references [22,24,8,7,19,1,15,12,2] and the older references presented in [5] or [22]). The classic references [17,10,20] must be discarded here, because they address cases of continuous processes. Yet, they inspire the proposed strategy. Following these approaches, a static equation is derived, involving the pH and the amount of strong acid supplied to the system from the beginning of the batch. This equation holds until precipitation occurs. To the best of our knowledge, precipitation-related issues in

pH control were almost never considered before (see [21] and comments in [9]). As will appear, it is possible to account for this phenomenon in the control strategy. The reader might be interested to find connections of this work to [6] where another form of solid particles formation (crystallization) is considered.

Usually (see for instance [11,22,8,14,15,13,23]), the inlet concentrations are poorly known. To deal with this uncertainty, on-line adaptation can be used. Here, the inlet products are well known, and the various coefficients appearing in the above mentioned static equation can be efficiently estimated off-line. For that purpose, a collection of titration experiments is carried out. According to the model obtained from this process, set point tracking can be achieved by imposing a linear asymptotically stable dynamics on the amount of strong acid. This defines the strong acid flow rate, which is the control variable. Proof of asymptotic convergence is derived from a standard Lyapunov approach. Finally, precipitation is accounted for by keeping some of the control parameters to constant values, after a certain time which is experimentally evaluated.

The paper is organized as follows. In Section 2, the process under consideration is described. In Section 3, a model for equilibria is exposed. Several states are considered (volume and molar quantities for balance equations, molar concentrations). Reactions are considered as being fast when compared to mass balance dynamics. Eventually, a simple algebraic equation represents the system to be controlled. Off-line identification results are presented. In Section 4, the stabilizing control law is detailed. This feedback law is time-varying. Besides this theoretical design, practical implementation is considered. In particular, to address the issue

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Nomenclature

q_A	reactive acid molar flow rate
q_B	reactive base molar flow rate
q_u	control acid molar flow rate (control variable)
N_A	number of moles of reactive acid in the solution
C_A	molar concentration of reactive acid in the solution
C_{A0}	molar concentration of reactive acid in its storage tank
N_B	number of moles of reactive base in the solution
C_B	molar concentration of reactive base in the solution
C_{B0}	molar concentration of reactive base in its storage tank
N_u	number of moles of control acid in the solution
C_u	molar concentration of control acid in the solution
C_{u0}	molar concentration of control acid in its storage tank
F_{tot}	total feed volume flow rate
F_w	water volume flow rate
V	volume of the solution

$h_0(pH)$	function accounting for $[H_3O^+]$ and $[OH^-]$ in the main algebraic equation
$h_A(pH)$	function summarizing the dissociations of the reactive acid
$h_B(pH)$	function summarizing the dissociations of the reactive base
α	number of dissociations of the strong control acid
pH^r	pH set point
q_u^r	feedforward part of the control action
N_u^r	set point for the number of moles of control acid
χ	tuning parameter of the feedforward part for the final implementation
τ	time constant of the first order dynamics imposed on $N_u - N_u^r$
T_i	integral time for the final implementation

of precipitation, it is shown that it is sufficient to freeze the control parameters update after a pre-defined time. This bound can be conservatively chosen for sake of robustness. In Section 6, the obtained results are commented on. They illustrate the performance which can be daily observed on the reactor.

2. Process description and contribution

The process presented in Fig. 1 is used to produce precipitates of alumina sulphate ($Al_2(SO_4)_3$) and sodium metasilicate (Na_2SiO_3). Soda (NaOH) and sulphuric acid (H_2SO_4) flows are adjusted to control the pH of the mixture around a desired value. For sake of simplicity, in this paper, only the case of a control adjusting the sulphuric acid flow rate is addressed. Other setups can be considered as well using the same approach. In practice, the pH set point is kept constant during a batch. Because the pH directly impacts on

the product quality, it is desired to keep it as long as possible within ±0.2 around the prescribed set point. Our contribution is a pH controller which can be used, in batch production mode, over a wide range of operating conditions.

The process is of fed batch type. Production is scheduled as follows. At the beginning, the reactor contains a volume of water V_0. Then, a reactive acid A_0 and a reactive base B_0 feed the reactor at constant mass flow rates. Meanwhile, the control acid A_u is added. Its flow rate can be used to control the pH of the reactional mixture. Water is also added and its flow rate is set so that the total volume flow rate is kept constant during the batch.

By means of pumps, the products are fed into the reactor from separate storage tanks placed on balances. In closed-loop, the masses measured by the balances are used to control the flow rates through variations of the pumps amperages (see [3] for details). These low-level regulators are not described in this paper.
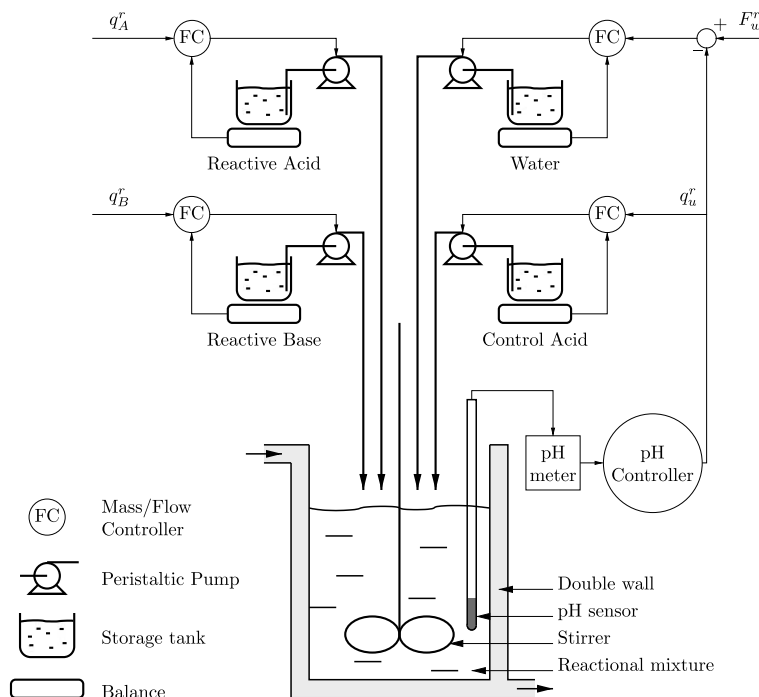

Fig. 1. Diagram of the pH regulation process. Reactive acid and reactive base are fed to a batch reactor to produce precipitates. Product quality critically depends on the pH which must be controlled with the control acid flow rate. Our main contribution is the pH controller.

Low-level controllers performance is important. It is especially true when the required flow values are small. Considering the accuracy of mass measurement, great care must be taken in the design of the flow controllers, to avoid oscillations in the flow rates, which can have a very negative impact on pH. The reader can refer to [18,16] for other experimental and theoretical illustrations of this point.

3. Modeling the pH process

The pH control problem is first addressed in the case of a solution without precipitation. The control strategy is based on the model described in this section and detailed in Appendix A. As already mentioned, modifications of the dynamics due to the precipitation cannot be neglected in the real application. However, accurately characterizing these dynamics is out of our scope, because several important modeling related issues are still largely unsolved and remain topics of on-going research. As will appear in Section 6, a rough description of the precipitation, implying only slight adaptations of the model and the controller, is sufficient to obtain good results on real batches, over the whole pH range of interest. These adaptations are detailed and discussed in Section 5.

The process under consideration involves complex dissociations, for which no accurate description of the reaction scheme is available. Moreover, the relative importance of the various ions involved are poorly known. According to [4], several tens of reactions have been identified for such mixtures of silica, alumina and strong acids and bases. However, as detailed in Appendix A, it is possible to derive a general form for equilibrium equations, from mass balance equations, the mass action law, the ionic product of water, and the electrical neutrality of the solution. The resulting model is nonlinear but also strongly time-varying, because the process is operated in batch mode.

3.1. Mass balances and equilibria

Global mass balance and partial mass balances on the control and reactive acids, and on the reactive base can be written, *for cases where no precipitation occurs*, under the form

$$\begin{cases} \frac{dV}{dt} = F_{\text{tot}} = F_w + \frac{q_A}{C_{A0}} + \frac{q_B}{C_{B0}} + \frac{q_u}{C_{u0}} \\ \frac{dN_u}{dt} = q_u \\ \frac{dN_A}{dt} = q_A \\ \frac{dN_B}{dt} = q_B \end{cases} \tag{1}$$

where

- C_{u0} (resp. C_{A0}, C_{B0}) is the concentration of the control acid A_u (resp. the reactive acid A_0, the reactive base B_0) in its storage tank;
- q_A (resp. q_B) is the reactive acid (resp. reactive base) molar flow rate. q_A and q_B are both assumed constant, because they are assumed to be perfectly controlled by low level controllers;
- q_u is the molar flow rate of control acid;
- F_w is the water volume flow rate. It is adjusted according to q_u variations so that the total volume flow rate F_{tot} remains constant

$$F_w = F_{\text{tot}} - \frac{q_A}{C_{A0}} - \frac{q_B}{C_{B0}} - \frac{q_u}{C_{u0}}$$

- N_A is the total number of moles of reactive acid and corresponds to a concentration C_A;
- N_u is the total number of moles of control acid and corresponds to a concentration C_u;
- N_B is the total number of moles of reactive base and corresponds to a concentration C_B.

In the general case, assuming that reactions reach their equilibrium instantly, the implicit equation linking pH to C_A, C_B, and C_u depends nonlinearly on C_A and C_B. In the case of a production of precipitates of alumina sulphate and sodium metasilicate using soda and sulphuric acid, it was reported in the literature (see [4]) that, among the identified reactions, most of them consist in gaining or loosing a single proton. Under this hypothesis, and after some computations reported in Appendix A, the following equilibrium relation is obtained:

$$h_0(\text{pH}) + h_A(\text{pH})C_A + h_B(\text{pH})C_B - \alpha C_u = 0 \tag{2}$$

where $h_0(\text{pH}) = (10^{-\text{pH}} - \frac{K_e}{10^{-\text{pH}}})$, $K_e = 10^{-14}$, and $\alpha = 2$ is the number of dissociations of the strong control acid. Finally, h_A and h_B are nonlinear functions whose expressions (see again Appendix A for details) involve the successive acidity constants of the reactive acids and the electric charge of the ions obtained through their dissociation processes.

The validity of this simplifying assumption is demonstrated in the next subsection.

3.2. Identification of $h_A(\text{pH})$ and $h_B(\text{pH})$

An interesting property of Eq. (2) is that the functions h_A and h_B can be easily identified off-line through distinct titration experiments.

To identify $h_A(\text{pH})$, titrations by soda (NaOH) of the reactive acid are carried out for various concentrations C_A. In these titrations, $C_B = C_u = 0$, and Eq. (2) becomes

$$h_0(\text{pH}) + h_A(\text{pH})C_A + C_{\text{NaOH}} = 0$$

This last equality is used to express $h_A(\text{pH})$ from the total reactive acid concentration, the soda concentration, and the measured pH. Experiments are carried out with different initial concentrations of reactive acid. Fig. 2 represents the curves obtained for five titrations. For these, the initial concentration of reactive acid varies from 0.01 to 0.44 g/ml. If $g_A(\text{pH}, C_A) \approx h_A(\text{pH})C_A$, defined in Appendix A, really was a linear function of C_A, the curves would be identical for all the considered initial concentrations (up to measurement accuracy). In our case, they match closely. Experimental values can be interpolated to obtain an analytical expression for $h_A(\text{pH})$ (bold black in the figure). For pH $\in [4.5, 10]$, the experimental values lie within the interval $\pm 3\%$ of $h_A(\text{pH})$.

A similar method has been used to identify h_B. However, the reactive base titration by the sulphuric acid (strong acid) can form gels, for some pH and concentration values. These make the obtained pH measurements from the probe meaningless. Instead, titrations were obtained as follows: the strong acid is titrated by the reactive base. In this case, $C_A = 0$. Eq. (2) becomes
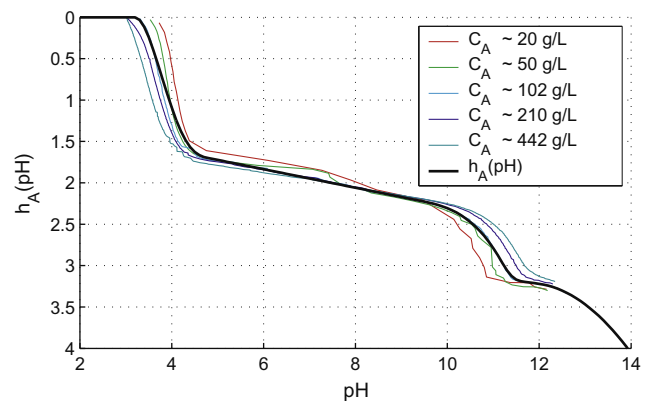

Fig. 2. Experimental identification of $h_A(\text{pH})$.

$$h_0(\text{pH}) + h_B(\text{pH})C_B - \alpha C_u = 0$$

Fig. 3 represents the curves for five titrations, when the final concentration of reactive base C_B varies from 0.04 to 0.3 g/ml. Once again, the linearity assumption does not hold strictly, but the function $h_B(\text{pH})$, obtained by interpolating the experimental data, accurately approximates them for pH $\in [4, 10]$. Whenever possible (i.e. in the absence of gel), reactive base titrations by the sulphuric acid were performed. The results strongly agree with those obtained through titration by the reactive base.

4. Control design

4.1. Theoretical design

Let us denote

$$h(\text{pH}, t) = (h_0(\text{pH})V(t) + h_A(\text{pH})N_A(t) + h_B(\text{pH})N_B(t))/\alpha \qquad (3)$$

where α is a known constant and h_0, h_A and h_B are known or experimentally derived functions (see Section 3). Then, Eq. (2) can be rewritten $N_u = h(\text{pH}, t)$. Using (1), the implicit input–output dynamical system giving the pH (output) in terms of q_u (input) is

$$\begin{cases} \frac{dV}{dt} = F_{\text{tot}} \\ \frac{dN_u}{dt} = q_u \\ \frac{dN_A}{dt} = q_A \\ \frac{dN_B}{dt} = q_B \\ 0 = h(\text{pH}, t) - N_u \end{cases} \qquad (4)$$

where F_{tot}, q_A, and q_B are constant.

Assuming that N_A and N_B have some given values over time, a set point N_u^r for N_u can be computed such that (2) holds for pH = pH^r, where pH^r is a given (constant) pH set point

$$N_u^r = h(\text{pH}^r, t) \qquad (5)$$

Conversely, if $N_u = N_u^r$, then pH = pH^r, because the function defined by Eq. (5) is one to one (it is continuous and strictly monotonic) with respect to pH^r.

This shows that the pH control is, in fact, a regulation problem for the quantity of strong acid. It is proposed to control the number of moles of strong acid by imposing an asymptotically stable first order dynamics (similarly to e.g. [22])

$$\frac{d(N_u - N_u^r)}{dt} = -\frac{1}{\tau}(N_u - N_u^r)$$

Since $dN_u/dt = q_u$, this leads to

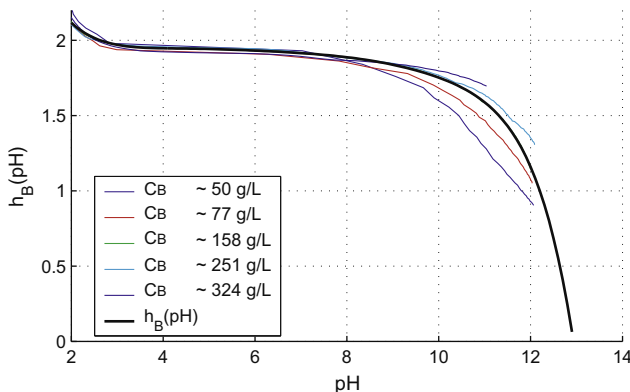$$q_u = \frac{dN_u^r}{dt} - \frac{1}{\tau}(N_u - N_u^r)$$

Fig. 3. Experimental identification of $h_B(\text{pH})$.

where (because pH^r is constant)

$$q_u^r = \frac{dN_u^r}{dt} = (h_0(\text{pH}^r)F_{\text{tot}} + h_A(\text{pH}^r)q_A + h_B(\text{pH}^r)q_B)/\alpha \qquad (6)$$

Proposition 1. *Applied to system (4), the control law*

$$q_u = q_u^r - (N_u - N_u^r)/\tau \qquad (7)$$

guarantees global exponential convergence of pH *towards the constant value* pH^r.

Proof. The proof follows along the lines of Lyapunov's first method. Yet, one should notice that the system under consideration is time-varying, so standard theorems fail here. Fortunately, it is possible to directly derive uniform (with respect to t) exponential stability for this one dimensional problem. Let us denote

$$\begin{cases} \phi(\text{pH}, t) = \left(\frac{\partial h_0}{\partial \text{pH}}(\text{pH})V(t) + \frac{\partial h_A}{\partial \text{pH}}(\text{pH})N_A(t) + \frac{\partial h_B}{\partial \text{pH}}(\text{pH})N_B(t)\right)/\alpha \\ \qquad = \frac{\partial h}{\partial \text{pH}}(\text{pH}, t) \\ \psi(\text{pH}, t) = (h_0(\text{pH})F_{\text{tot}} + h_A(\text{pH})q_A + h_B(\text{pH})q_B)/\alpha = \frac{\partial h}{\partial t}(\text{pH}, t) \end{cases}$$

Differentiating the last equation of (4) leads to

$$\frac{d\text{pH}}{dt} = -\frac{\psi(\text{pH}, t)}{\phi(\text{pH}, t)} + \frac{q_u}{\phi(\text{pH}, t)}$$

Yet, q_u (defined in (7)) can be written as

$$q_u = \psi(\text{pH}^r, t) - \frac{1}{\tau}(h(\text{pH}, t) - h(\text{pH}^r, t))$$

For constant pH^r,

$$\frac{d(\text{pH} - \text{pH}^r)}{dt} = -\frac{1}{\phi(\text{pH}, t)}((\psi(\text{pH}, t) - \psi(\text{pH}^r, t)) + \frac{1}{\tau}(h(\text{pH}, t) - h(\text{pH}^r, t))) \qquad (8)$$

Picking up the positive error function

$$\mathscr{V}(\text{pH}) = \frac{1}{2}(\text{pH} - \text{pH}^r)^2,$$

the following equation is derived:

$$\frac{d\mathscr{V}}{dt} = -\frac{1}{\phi(\text{pH}, t)}((\psi(\text{pH}, t) - \psi(\text{pH}^r, t)) + \frac{1}{\tau}(h(\text{pH}, t) - h(\text{pH}^r, t))) \\ \times (\text{pH} - \text{pH}^r)$$

From the intermediate value theorem applied on the scalar function

$$\text{pH} \mapsto k_t(\text{pH}) = \psi(\text{pH}, t) + \frac{1}{\tau}h(\text{pH}, t),$$

there must exist pH$^0(t)$, with pH$^0(t) \in [\text{pH}, \text{pH}^r]$ or pH$^0(t) \in [\text{pH}^r, \text{pH}]$, such that

$$\frac{d(\text{pH} - \text{pH}^r)}{dt} = -\frac{1}{\phi(\text{pH}, t)}\left(\frac{\partial \psi}{\partial \text{pH}}(\text{pH}^0(t), t) + \frac{1}{\tau}\frac{\partial h}{\partial \text{pH}}(\text{pH}^0(t), t)\right) \\ \times (\text{pH} - \text{pH}^r)$$

Yet, from the definition of h_0, h_A and h_B (see Figs. 2 and 3 for pH$^0 \in [4, 12]$), there exists $\phi_{\max} < 0$ such that, for all t, $\phi(\text{pH}^0(t), t) < \phi_{\max} < 0$. Moreover,

$$\partial \psi / \partial \text{pH} \leqslant 0 \qquad (9)$$

and ϕ can be uniformly bounded in time

$$\phi_{\min} \leqslant \phi \leqslant \phi_{\max} < 0 \qquad (10)$$

Then,

$$\frac{d\mathscr{V}}{dt} \leqslant -\frac{2\phi_{\max}}{\tau\phi_{\min}}\mathscr{V}$$

So, $\mathscr{V}$ exponentially converges towards 0. In particular, $\lim_{t\to\infty}\mathrm{pH} = \mathrm{pH}^r$. $\quad\square$

4.2. Practical implementation

To implement (7) on the actual process, the following points need to be addressed:

- The flow rates F_{tot}, q_A, q_B appearing in q_u^r (Eq. (6)) are not measured but indirectly controlled about known setpoints using mass measurements. Neglecting the fast and stable flow variables dynamics, these values for the flow rates are replaced by their set points.
- The total volume V is not directly measured. In practice, it is estimated from densities and mass measurements.
- For the strong acid, no flow rate controller is used. The relationship between the pump amperage and the flow rate has been identified. A constant gain is used to transform the computed flow rate set point into a pump amperage. This gives the fastest possible action on the pH.

These points, and the unavoidable errors on h_A and h_B, are sources of inaccuracies. They could lead to biases. For sake of robustness, an integral term is added, and the computed feedforward action q_u^r is only partially used. Finally, the control is implemented under the following form:

$$\begin{cases} q_u = \chi q_u^r - \frac{1}{\tau}(h(\mathrm{pH},t) - h(\mathrm{pH}^r,t) + \frac{1}{T_i}\int_0^t (h(\mathrm{pH},s) - h(\mathrm{pH}^r,s))ds) \\ q_u^r = (h_0(\mathrm{pH}^r)F_{\mathrm{tot}}^r + h_A(\mathrm{pH}^r)q_A^r + h_B(\mathrm{pH}^r)q_B^r)/\alpha \\ h(\mathrm{pH},t) = (h_0(\mathrm{pH})V + h_A(\mathrm{pH})N_A + h_B(\mathrm{pH})N_B)/\alpha \end{cases}$$
$$(11)$$

where

- χ is the applied fraction of the computed feedforward term q_u^r: $0 \leqslant \chi \leqslant 1$, $\chi = 0.8$ is used;
- T_i is the integral time;
- F_{tot}^r (resp. q_A^r, q_B^r) is the set point for the total flow rate (resp. the reactive acid flow rate, the reactive base flow rate);
- V is an estimate of the liquid volume in the reactor;
- N_A and N_B are indirectly measured.

5. Dealing with precipitation

The acid-basic reactions produce particles which precipitate. The obtained precipitate is uniformly distributed in the reactor. It is produced only when the reagents are sufficiently concentrated in the reaction medium (i.e. there exists a critical concentration), provided a zero charge precursor is present. Precipitation is a poorly known phenomenon in the case under consideration, and it is difficult to derive an accurate model for. A simple way to take it into account is to consider that, after a given time $\bar{t}$, all the added reagents precipitate. A tentative explanation of this limiting effect on a particular case is provided in Appendix B. Furthermore, it is assumed that the equivalent volume of the precipitate is very small compared to the total volume. This assumption is not very strong, as the precipitate represents between 0.5% and 5% of the total volume.

These assumptions simply imply that, from $\bar{t}$, the values of the concentrations C_A and C_B, used in (5) (see (3)) and in (11) to define

the quantities N_A and N_B, can be "frozen". Certainly, a remaining question is the definition of $\bar{t}$. In Appendix B, this time is implicitly defined as the time when the concentrations reach a given level. In practice, this level might be difficult to compute and it has been decided to set $\bar{t}$ at the average of values found on several experiments.

As will be demonstrated by practical results, this is a relatively robust strategy. When the freezing occurs too early, the pH simply takes more time to reach its set point; when it occurs too late, the pH begins to oscillate, because too large gains are used. This very simple approach provides good performances. Therefore it is not necessary to investigate methods to identify $\bar{t}$ on-line from existing measurements, though solutions could be considered, e.g. torque variations of the stirrer (only for cases with large variations of the viscosity), or maybe changes of the output of the temperature controller.

Now is discussed the closed-loop behavior of the system when precipitation occurs and when the above mentioned "freezing" strategy of the concentrations is considered in the control computations.

5.1. A closed-loop analysis in the presence of precipitation

For sake of simplicity (extension to cases of simultaneous precipitations follows along the same lines) it is assumed that only A precipitates at a known time $\bar{t}$. Due to the precipitation of A, it is considered that

$$C_A(t) \approx C_A(\bar{t})g(\mathrm{pH})$$

for all $t \geqslant \bar{t}$. Such an equation can be obtained from the dissociation scheme of A. An example is given in Appendix B.

Under this last assumption, the equilibrium relation (2) is replaced by the following:

$$h_0(\mathrm{pH}) + h_A(\mathrm{pH})C_A(\bar{t})g(\mathrm{pH}) + h_B(\mathrm{pH})C_B - \alpha C_u = 0 \qquad (12)$$

Following the approach proposed in the proof of Proposition 1, define

$$h'(\mathrm{pH},t) = (h_0(\mathrm{pH})V(t) + h_A(\mathrm{pH})V(t)C_A(\bar{t})g(\mathrm{pH}) \\ + h_B(\mathrm{pH})V(t)C_B(t))/\alpha \qquad (13)$$

By freezing the parameters of the control law (7), as already proposed, the following feedback is obtained:

$$q_u = \psi'(\mathrm{pH}^r,t) - \frac{h'(\mathrm{pH},t) - h(\mathrm{pH}^r,t,\bar{t})}{\tau}$$

where $\phi'(\mathrm{pH},t) = \frac{\partial h'}{\partial \mathrm{pH}}(\mathrm{pH},t)$ and $\psi'(\mathrm{pH},t) = \frac{\partial h'}{\partial t}(\mathrm{pH})$.

The closed-loop behavior of the system is defined by the following equation which is obtained by differentiating (12) with respect to time:

$$\frac{d(\mathrm{pH} - \mathrm{pH}^r)}{dt} = -\frac{1}{\phi'(\mathrm{pH},t)}((\psi'(\mathrm{pH},t) - \psi'(\mathrm{pH}^r,t)) + \frac{1}{\tau}(h'(\mathrm{pH},t) \\ - h'(\mathrm{pH}^r,t)))$$

This equation is precisely Eq. (8) where ψ and ϕ have been replaced with ψ' and ϕ', respectively. Provided that bounds similar to (9) and (10) can be obtained, either numerically or analytically, closed-loop stability is guaranteed by existence of the Lyapunov function $V = \frac{1}{2}(\mathrm{pH} - \mathrm{pH}^r)^2$. This is the case when $h_A(\mathrm{pH})g(\mathrm{pH})$ is a decreasing function. A simple illustrative example is proposed in Appendix B.

6. Practical results

Fig. 4 shows a typical result obtained by a standard PI controller working in the neutralization zone. This is a very challenging zone.
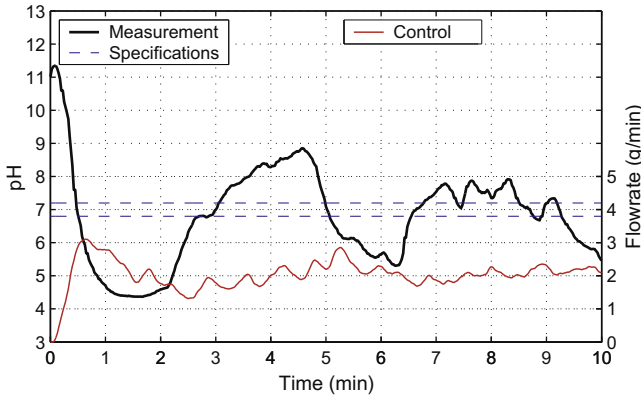
Fig. 4. Typical results obtained with a standard PI in the neutralization zone.
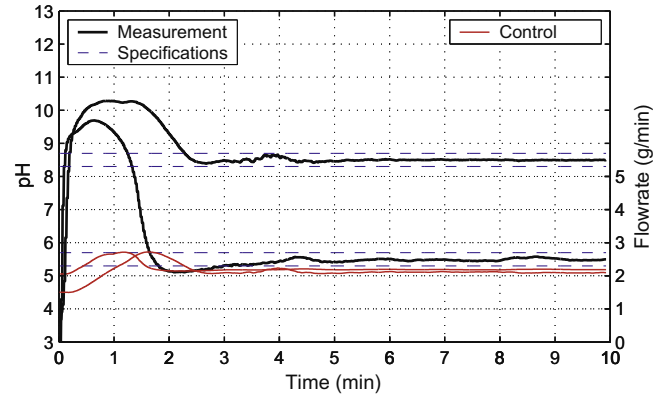
The situation is far better outside this zone, but simple controllers cannot cope with the whole range of interest without refined tuning methods. Fig. 5 shows the application of our controller (11) on the process when precipitation is not taken into account. Clearly, although slow and biased, the behavior is almost acceptable up to $t = 4$ min, but then oscillations become very important. They are due to precipitation.

Using partial feedforward ($\chi = 0.8$), the results of Fig. 6 are obtained for pH^r 7. These results are good, even if the transient may seem a bit long. It is due to the operating mode and is indeed very difficult to shorten. In fact, the pumps dealing with reactive acid

Fig. 5. Oscillations inevitably occur when the precipitation is not taken into account in the closed-loop control strategy.

Fig. 6. Control at pH 7.

Fig. 7. Control at pH 5.5 and pH 8.5.

and base are started first, but not simultaneously. Over a short period, they operate in open loop (with pre-defined amperages). When mass measurements become usable to estimate flows, the flow control loops are closed, while first computations of q_u occur (feedforward χq_u^c alone first, for a few seconds, then (11)). pH has time to escape towards a value corresponding to the pH of the mixture of the reactive acid and base, and it takes some time to get back to the desired set point. In some cases, the transient is shorter when $\chi = 1$, but in others, due to the model uncertainties, using $\chi = 1$ makes pH drop far below the set point, and it is then very long to reach admissible values. The choice $\chi = 0.8$ is a good compromise between robustness and duration of the transient, as shown on the typical results of Fig. 7, obtained for various set points.
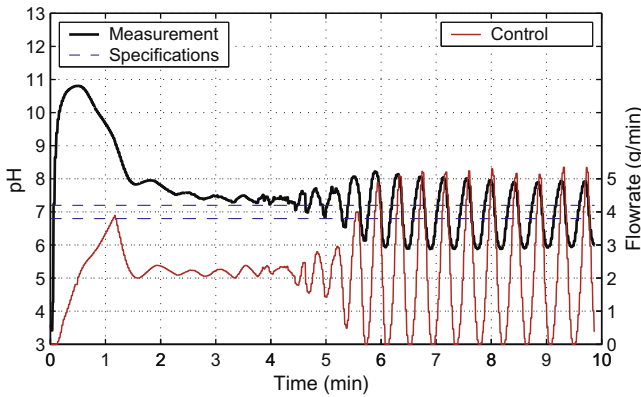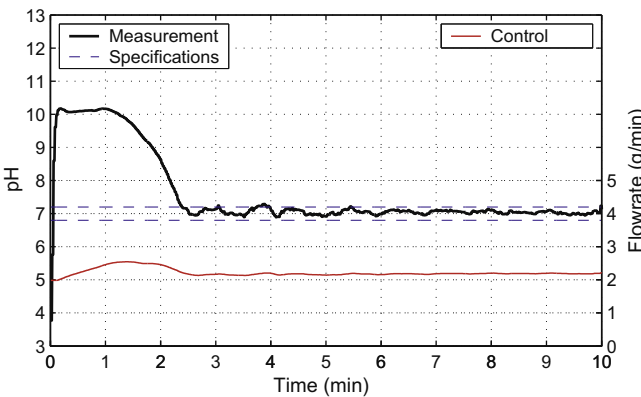
7. Conclusion

In this paper, an approach to control the pH in a fed batch reactor has been presented. The case of neutralization by a strong acid is described. It should be noted that other acids could be used, through a $h_u(\text{pH})$ function instead of the constant α used throughout the paper. On the real process, this approach has been successfully extended, to cope with neutralization by soda, or simultaneously by soda and sulphuric acid. End users, deeply involved in the developments, now daily use the controller and report sustainable good performances. The presented controllers have been in service since September 2006.
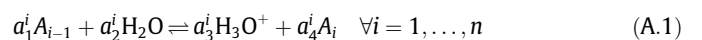
Appendix A. Modeling details

Let us consider N_A and N_B in Eq. (1), page 5:

- N_A is the total number of moles of reactive acid. The molecule A_0 is dissociated to produce ions that are further dissociated. This set of n reactions involving n ions A_i is denoted

$$a_1^i A_{i-1} + a_2^i H_2O \rightleftharpoons a_3^i H_3O^+ + a_4^i A_i \quad \forall i = 1, \ldots, n \tag{A.1}$$

For instance, H_2SO_4 gives HSO_4^- then SO_4^{2-}; HCl gives Cl^-. A negative electric charge q_i^- is associated to each A_i. Define N_A by

$$N_A = \sum_{i=0}^{n} z_i^A N_{A_i} \tag{A.2}$$

Once an atom/ion has been chosen as the reference in A_0 (as SO_4^{2-} in the H_2SO_4 example), z_i^A stands for the occurrence of this reference in N_{A_i}. This relation is derived from principles of conservation applied to atoms in A_0. Most cases found in the literature concern exchanges of only one proton by reaction. Then, the stoichiometric coefficients are equal to 1, as well as z_i^A for any i.

- N_B is the total number of moles of reactive base. m possible dissociations from B_0 are considered

$$b_1^i B_{i-1} + b_2^i H_2O \rightleftharpoons b_3^i OH^- + b_4^i B_i \quad \forall i = 1, \ldots, m \tag{A.3}$$
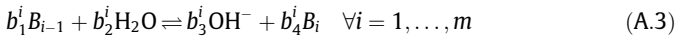
Each B_i has a positive electric charge q_i^+. N_B is being defined, for ad hoc z_i^B, by

$$N_B = \sum_{i=0}^{m} z_i^B N_{B_i} \tag{A.4}$$

A.1. Equilibria

An algebraic equation is obtained from the electrical neutrality of the solution, considering that all the reactions are fast, compared to the mass balances. Equivalently, reactions are considered at equilibrium.

When the electrolytes are weak, they are only partially dissociated. It is assumed that the concentrations involved are small enough to consider that the mixture is an ideal solution. Under this hypothesis (anyway a reasonable hypothesis for control purposes), the activities of the species can be expressed by their molar concentrations. For reactions (A.1) and (A.3), the acidity constants (that implicitly depend upon temperature) are

$$K_a^i = \frac{C_H^{a_3^i} C_{A_i}^{a_4^i}}{C_{A_{i-1}}^{a_1^i}} \quad \text{and} \quad K_b^i = \frac{C_H^{b_3^i} C_{B_{i-1}}^{b_1^i}}{C_{B_i}^{b_4^i}} \tag{A.5}$$

For the control acid, considered as a strong electrolyte, the dissociation is complete, so that $C_u = C_{A_u^\alpha}$, where α is the number of dissociations from A_u, and A_u^α is the ion resulting from these dissociations. For water, $K_e = C_H C_{OH^-}$.

Electrical neutrality of the solution writes, using the previous equation

$$C_H + \sum_{i=1}^{m} q_i^+ C_{B_i} = \frac{K_e}{C_H} + \sum_{i=1}^{n} q_i^- C_{A_i} + \alpha C_{A_u^\alpha} \tag{A.6}$$

Eqs. (A.2) and (A.4) can be equivalently expressed in terms of concentrations. Then, in Eqs. (A.2), (A.5) can be used, sequentially, to express C_{A_i} as a function of K_a^i, $C_{A_{i-1}}$ and C_H ($i = n, \ldots, 1$). Through these computations, each C_{A_k} (k from 1 to n) appears as a function of C_A, C_H and K_a^j ($j = 1, \ldots, k$). These can be used in (A.6) to formally substitute $-\sum_{i=1}^{n} q_i^- C_{A_i}$ with a function of C_H and C_A or, equivalently, a function of pH and C_A, denoted $g_A(pH, C_A)$. Similarly, Eqs. (A.4) and (A.5) can be used to substitute $\sum_{i=1}^{m} q_i^+ C_{B_i}$ with $g_B(pH, C_B)$ in (A.6). Finally, electrical neutrality allows us to derive the sought after equilibrium relation

$$h_0(pH) + g_A(pH, C_A) + g_B(pH, C_B) - \alpha C_u = 0,$$

with

$$h_0(C_H) = \left(10^{-pH} - \frac{K_e}{10^{-pH}}\right)$$

A.2. Assuming unitary stoichiometric coefficients

In the general case (i.e. $a_j^i \neq 1$), $g_A(pH, C_A)$ cannot be expressed as a product of C_A by a function depending only on pH. There is a similar obstruction for $g_B(pH, C_B)$. However, in almost all works reported in the literature, i.e. in most practical cases, it is assumed that the stoichiometric coefficients are equal to 1 (all the reactions consist in gaining or loosing a single proton). Then, the equation for electrical neutrality can be simplified as

$$h_0(pH) + h_A(pH)C_A + h_B(pH)C_B - \alpha C_u = 0$$

Appendix B. A model for precipitation

A simple model is proposed for the precipitation process occurring in the reactor. For that purpose the notations already used before are considered. From the control perspective presented in this paper, a particular phenomenon, observed in practice, is stressed: once a critical value is reached, concentrations become close to a limit value which depends on the current pH.

Consider the simple case of a product A decomposing into two ions A_1 and A_2 and into a precursor A_3. This last product may precipitate.

The reaction scheme is

$$A \rightarrow A_3$$
$$A_3 + H_2O \leftrightarrow A_2 + H_3O^+$$
$$A_2 + H_2O \leftrightarrow A_1 + H_3O^+$$
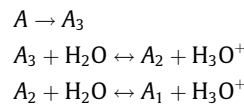
The reaction equilibria are given by the following constants:

$$k_i = \frac{C_{A_i} C_H}{C_{A_{i+1}}}, \qquad i \in \{1, 2\}$$

A balance gives

$$C_A = C_{A_3}\left(1 + \frac{k_1 k_2}{C_H^2} + \frac{k_2}{C_H}\right)$$

The precursor A_3 can precipitate. This occurs once C_{A_3} reaches a critical value noted $\bar{C}_{A_3}$. Then the exceeding A_3 precipitates into a solid product A_s by the extra reaction

$$A_3 \rightarrow A_s$$

The reaction rate of this phenomenon is generally modeled as proportional to $C_{A_3} - \bar{C}_{A_3}$. It is very high compared to the feed flow rate. In fact, the following typical set of ordinary differential equations can be written, where $\epsilon > 0$ is a small positive parameter that stresses the slow-fast decomposition of these dynamics

$$\begin{cases} \epsilon \dot{N}_A = \epsilon q_A - \frac{N_A}{V}\left(1 + \frac{k_1 k_2}{C_H^2} + \frac{k_2}{C_H}\right)^{-1} + \bar{C}_{A_3} \\ \epsilon \dot{N}_{A_s} = \frac{N_A}{V}\left(1 + \frac{k_1 k_2}{C_H^2} + \frac{k_2}{C_H}\right)^{-1} - \bar{C}_{A_3} \\ \dot{V} = q + q_A \end{cases} \tag{B.1}$$

The limit case $\epsilon = 0$ can be obtained by a singular perturbation analysis. The reduced dynamics is simply

$$C_A \approx \bar{C}_{A_3}\left(1 + \frac{k_1 k_2}{C_H^2} + \frac{k_2}{C_H}\right)$$

Define $\bar{t}$ the time when precipitation occurs. Denote $f(pH)$ (resp. $\bar{f}$) the value of

$$1 + \frac{k_1 k_2}{C_H^2} + \frac{k_2}{C_H}$$

at time t (resp. $\bar{t}$). For $t \geqslant \bar{t}$, the following approximation holds:

$$C_A(t) \approx \bar{C}_A(\bar{t})g(\text{pH})$$

where $g(\text{pH}) = f(\text{pH})/\bar{f}$.

This relation has been obtained for the presented simple example reaction scheme. Yet, extensions can be considered. The key point of the above analysis is that the amount of the precursor A_3 in the reactor cannot go above a certain limit. Due to the equilibrium, this affects the other concentrations through equations which are pH dependent.

Depending on the values of k_1 and k_2, an interval can be defined such that $g(\text{pH})$ remains sufficiently close to a constant such that the decreasingness of the product $h_A(\text{pH})g(\text{pH})$, which stems for the decreasingness of $h_A(\text{pH})$, holds. This is a sufficient condition for the stability of the closed-loop controller proposed in Section 4.

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