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pH Neutralization Process as a Benchmark for Testing Nonlinear Controllers

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This work outlines the pH neutralization process as a benchmark for nonlinear control design. The typical industrial conditions for this class of process are analyzed in order to elaborate a proposal for laboratory equipment that closely resembles a real system and also furnishes an excellent test bench for verifying new control strategies. This equipment has been installed at National University of San Juan, Argentina. The control problem, namely, the benchmark, with all of its operating restrictions is presented for real applications. The benchmark representation capability is discussed. The final goal is to define a pH region where the model has a good representation capability for industrial acid mixtures. Several experiments conducted at the laboratory assembly demonstrate the effectiveness of the proposed benchmark. Finally, a PID controller is presented as a reference for comparing the performance of tested nonlinear controllers.

Introduction

The pH neutralization process, a frequent stage in chemical processes as a part of wastewater treatments, has been largely regarded as a very difficult control problem. The complexity of this process is increased when, instead of a single acid, the wastewater presents a combination of acids (a more realistic condition). Nevertheless, various successful examples of new control strategies have been presented in the literature,[1–5] but the problem has not been totally solved. Some proposals were tested only for a simulated process, while others were tested on an experimental test bench, either at the laboratory scale or at a pilot plant. However, a main problem arises in the lack of congruency and uniformity with respect to operating conditions, constraints, applied perturbations, and ability to reproduce industrial processes. A significant generalization among these examples could be realized only through some effort, and then, only a blurred view of typical industrial processes could be attained. The typical alternative for overcoming this is to state a benchmark problem that allows for comparative studies of different control strategies. Benchmarks are regularly used in other scientific areas, although in the process control area only a few benchmarks are available.[6] Particularly, the literature shows no benchmark available on pH neutralization control, even though many related works have been reported in this field.

It is important to note that a benchmark formulation is more than a mathematical model or laboratory assembly. A benchmark for nonlinear control design includes a mathematical model, a laboratory assembly, a set of conditions for the process operation, a set of explicit requirements for the controlled process, an index for evaluating the controller performance, and a set of

testing signals to be applied during the tests. Additionally, the mathematical model must be validated with the laboratory assembly. A desirable condition is that the laboratory equipment also be validated with an industrial real plant. In this paper, such conditions are fulfilled, an average neutralization process at industrial plants is taken and scaled to a process conducive to laboratory equipment, and finally, such an assembly is validated in regard to a proposed mathematical model. All of these stated benchmark foundations are taken directly from previous papers,[3,7,8] with application of the modifications required to present a formal benchmark for the real pH neutralization process. Such modifications were applied after an extensive revision of current neutralization plants installed in several countries. Despite their nonstandard operating conditions, the previous works were used to formulate a benchmark problem. A scheme of a well-stated benchmark problem can be defined as simple, credible, self-contained, and clear.[6]

2. Process Definition and Modeling

The proposed process is the pH neutralization of industrial wastewater that will be considered to always be in the acid region. The process takes place in a continuous stirred tank of constant volume V. Both the outflow pipe arrangement and the low level changes obtained by design constraints permit constant-volume operation. The wastewater stream is divided into two hypothetical streams: a strong acid solution (stream 1 with flow rate q_1) and a buffer salt solution (stream 2 with flow rate q_2, smaller than q_1). This fact facilitates model formulation and permits broadening of the operating conditions to maintain a representation of the real situation where n acids (strong and weaks) are in aqueous solution.[1,7] The control action should regulate a third stream, a strong base aqueous solution (stream 3 with flow rate q_3). A schematic representation of the proposed process is presented in Figure 1. The proposed experimental assembly (currently installed at National

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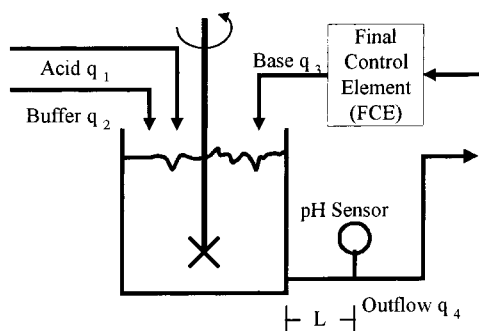
Figure 1. Test bench as defined from benchmark.

University of San Juan, Argentina) has the following particularities, all regarding the selection of process equipment: (1) three metering pumps for solution dosage, with each pump commanded through a 4−20 mA signal; (2) one propeller-type agitator with a 0.5-hp electrical motor; (3) two digital pH sensors with 4−20 mA transmitters, 0.01 pH precision, and local pH indication; (4) one level sensor operated by hydrostatic pressure; (5) one analog−digital/digital−analog board and one PC for the data acquisition system; and (6) an acid tank (90 L), base tank (70 L), salt tank (8 L), and reactor tank with 20 L of effective volume.

2.1. Modeling of Instrumentation. A convenient situation would be if we could have industrial final control elements (FCEs) and pH sensors that give immediate responses. For the pH sensor, this feature is approximately available in stock industrial instruments (pH response times of less than 1 s for 90% of total interval). However, for typical FCEs at industrial sites, a short response time becomes economically prohibitive, especially at wastewater treatment plants. As in other works,[1,7,9] this condition allows us to consider the sensor dynamic response to be negligible and to model the FCE dynamics as a first-order system with an input restriction, such as

$$q_{3R}(s) = \frac{1}{T_{FCE}s + 1}q_{3C}(s)$$
$$0 \leq q_{3C}(k) \leq q_{3CMAX}, \forall k \geq 0 \quad (1)$$

where T_{FCE} is the time constant for the FCE, q_{3R} is the real flow rate to the tank, q_{3CMAX} is the maximum flow rate as calculated by the controller, q_{3C} is the applied control flow rate, and k is the sampling period.

2.2. Modeling of Hydraulic Behavior. Under ideal conditions, mixing effects are negligible, so each liquid portion coming into the tank will be immediately homogenized. Obtaining these ideal conditions is very expensive for industrial-scale tanks, and only under special design circumstances can this high cost be justified. Therefore, to produce the operating conditions for a typical neutralization plant, a mixing time delay in the mixing−reaction tank must be considered (θ_{MIX}). The other important hydraulic behavior in the system is the liquid transport through the output pipeline where the pH sensor is installed. Normally, this pipe is long enough that a significant time elapses between a tank pH change and its respective detection at the sensor location. This design condition is applied in order to avoid sensor shocks and noise in the measured pH. To incorporate this operating condition in the system model, a transport time delay in the outlet pipeline must be considered (θ_{TTE}). These two time delays can be

grouped into a single value denoted by $\theta_{pH} = \theta_{MIX} + \theta_{TTE}$ and computed by

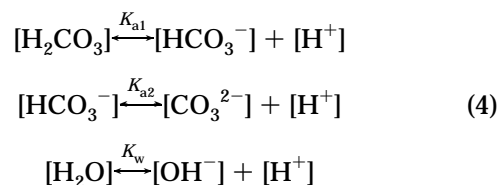$$\theta_{pH} = \frac{1}{q_4}\left\{[C_{MIX}V] + \left[L\left(\frac{\pi}{4}\right)D_p^2\right]\right\} \quad (2)$$

where C_{MIX} is the system agitation constant, q_4 is the outflow rate, and D_p is the outlet pipe diameter.

It should be noted that C_{MIX} can be approximated by one of the following set of constant values, related to tank size:[10] 0.09 for large tanks ($V \approx 50$ m^3); 0.05 for medium-size tanks ($V \approx 10$ m^3), and 0.01 for small tanks ($V \approx 0.1$ m^3). Obviously, a more precise calculation must consider C_{MIX} as a complex function of the agitation system characteristics.[11,12] This fact is irrelevant for stating the benchmark, but it is indispensable for designing the agitation system. Finally, taking the previous discussion into account, the indicated pH value (used for control purposes) is calculated by the expression

$$pH_S(t) = pH_R(t - \theta_{pH}) \quad (3)$$

Here, pH_S is the pH value shown at the sensor panel, and pH_R is the real pH value in the tank.

2.3. Modeling of the Chemical Reactions. The core of the process stated here as a benchmark is constituted by the chemical reactions that take place in the neutralization tank when the streams are stirred together. Despite the diversity of acid−base reactions that can be found at industrial neutralization processes, the present benchmark uses a weak acid−strong base reaction under buffered conditions. The assumed reagents of that reaction are carbonic acid (H$_2$CO$_3$) as the weak acid, sodium hydroxide (NaOH) as the strong base, and sodium bicarbonate(NaHCO$_3$) as the conjugate salt of the acid. In particular, the last reagent gives the buffer effect to the system. If the ionic dissociation of the water as the solvent is included, the following ionic species interactions take place:

$$[H_2CO_3] \xrightarrow{K_{a1}} [HCO_3^-] + [H^+]$$

$$[HCO_3^-] \xrightarrow{K_{a2}} [CO_3^{2-}] + [H^+] \quad (4)$$

$$[H_2O] \xrightarrow{K_w} [OH^-] + [H^+]$$

To enhance the representation properties of this particular chemical system with respect to real neutralization processes at industrial sites, the following special implementation for the laboratory test bench is proposed.[8] The typical industrial effluent stream assumed to have acidic characteristics is divided into two streams in the laboratory test-bench implementation and in the simulated system. The first is an aqueous solution of a strong acid (HNO$_3$, nitric acid) that produces H$^+$ ions. The second stream is an aqueous solution of a conjugated salt of a weak acid (NaHCO$_3$), which provides buffer ions. Such a choice of streams allows the benchmark to represent a wider set of neutralization processes when compared to previous related works that use a simple weak acid−strong base system.[3,9] By completing the description of the system dissociation reactions, the strong characteristic of the base and acid reagents used for the laboratory test

bench and simulated process allow us to consider both reagents as being totally dissociated before they enter the tank.

For modeling the chemical reactions, a general and systematic approximation called reaction invariants will be used.[13] This method is very useful for obtaining dynamic models for a process in which fast acid–base reactions take place. Reaction invariants or transparent species are inert with respect to the chemical reaction progress. In other words, they neither form compounds nor are destroyed during these chemical reactions. One interesting feature of reaction invariants is that they can be used directly as weighed quantities for pH calculations when two or more aqueous solutions with different concentrations and chemical species are mixed. Therefore, a more general problem statement is available for treating problems with unknown inlet stream characteristics using hypothetical acids and bases in a given proportion.[14] Normally, reaction invariant concentrations are taken as system states. Because there is only one weak acid (H_2CO_3) in the proposed benchmark, two reaction invariants are stated for each system stream ($i = 1, ..., 4$).[1,7]

$$W_{ai} = [H^+]_i - [OH^-]_i - [HCO_3^-]_i - 2[CO_3^{2-}]_i$$
$$W_{bi} = [H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{2-}]_i \quad (5)$$

As can be seen from the above formulation, reaction invariants W_{ai} are quantities related to the electron system charge, whereas the W_{bi} represent the concentration of the conjugated salt negative ion (carbonate CO_3^{2-}).[8] By using W_{ai} and W_{bi}, it is possible to calculate the pH value for any process stream ($i = 1, ..., 4$). Because the system output is the pH of the effluent stream q_4, the following potential function and pH definitions applied to K_{ai} and $[H^+]$ are used:

$$pK_{ai} = -\log_{10}(K_{ai}) \qquad pH = -\log_{10}[H^+] \quad (6)$$

An implicit output function between pH and reaction invariants is

$$W_{a4} = -W_{b4}\left(\frac{1 + 2 \times 10^{(pH-pK_{a2})}}{1 + 10^{(pK_{a1}-pH)} + 10^{(pH-pK_{a2})}}\right) + 10^{-pH} - 10^{(pH-14)} \quad (7)$$

Next, the states of the system will be assumed to be equal to these two reaction invariants: $x_1 = W_{a4}$, and $x_2 = W_{b4}$.

2.4. Modeling of Mass Balance. By combining mass balance on each of the ionic species in the system, the following differential equations were found for the outlet stream reaction invariants:

$$V\left(\frac{dW_{a4}}{dt}\right) = q_1(W_{a1} - W_{a4}) + q_2(W_{a2} - W_{a4}) + q_3(W_{a3} - W_{a4}) \quad (8)$$

$$V\left(\frac{dW_{b4}}{dt}\right) = q_1(W_{b1} - W_{b4}) + q_2(W_{b2} - W_{b4}) + q_3(W_{b3} - W_{b4}) \quad (9)$$

Two further interesting points about the reaction invariant arise. First, reaction invariants are independent of the reaction progresses, in contrast to the high dependence of the pH value with respect to the same

Table 1. Industrial Assembly and Laboratory Test Bench under Nominal Stable-State (NSS) Conditions

parameter	industry	laboratory
volume V	14 m³	0.02 m³
diameter	2.612 m	0.294 m
acid type	mix	strong (HNO_3)
K_{a1}	–	4.47×10^{-7}
K_{a2}	–	5.62×10^{-11}
K_W	1.0×10^{-14}	1.0×10^{-14}
$q_{1\,NSS}$	0.01166 m³/s	1.666×10^{-5} m³/s
T_{RESA}	1200 s	1200 s
$W_{a1} = [HNO_3]$	–	0.01 M
$W_{b1} = $ Cte	–	0 M
buffer type	–	$NaHCO_3$
$q_{2\,NSS}$	–	5.5×10^{-7} m³/s
$[NaHCO_3]$	–	0.1 M
$W_{a2} = $ Cte	–	- 0.1 M
$W_{b2} = $ Cte	–	0.1 M
base type	NaOH	NaOH
$q_{3\,NSS}$	5.83×10^{-3} m³/s	7.81×10^{-6} m³/s
molar comp. of base	~0.025 NaOH and 3.5×10^{-4} NaHCO₃	~0.025 NaOH and 3.5×10^{-4} NaHCO₃
$W_{a3} = $ Cte	–	−0.02535 M
$W_{b3} = $ Cte	–	0.00035 M
q_{3CMAX}	–	2.4×10^{-5} m³/s
$q_{4\,NSS}$	~1050 10^{-5} m³/s	2.5×10^{-5} m³/s
$W_{a4\,NSS}$	–	−0.0018862 M
$W_{b4\,NSS}$	–	0.0023067 M
L	2.0 m	0.446 m
D_p	0.15 m (~5 in.)	0.012m (~0.5 in.)
θ_{TTE}	2 s	2 s
C_{MIX}	0.05	0.01
θ_{MIX}	40 s	8 s
θ_{pH}	42 s	10 s
T_{EFC}	10 s	10 s

system variable. Second, there is no easy and direct way to measure the invariants' values from the process. Therefore, these values must be estimated through other measurable process variables. Note that, if the present pH value is known, only one of the reaction invariants needs to be estimated, and then the other can be computed through eq 7.

2.5. Operation Intervals and General Model Statement. The goal of the present work is to propose a benchmark that resembles, as closely as possible, the real neutralization processes at typical industrial conditions. This constitutes both its main contribution and its departure point from previous works, which furnish a starting set of constraints for the laboratory implementation.[1,7] Thus, it is crucial to define a set of operation intervals that allows the model to reproduce the above conditions but at a laboratory test-bench scale.

Currently, most industrial arrangements for pH neutralization of wastewater are designed with the aim of reducing space and saving costs.[11,12] It is also known that, with a proper choice of liquid agitation conditions, homogenization of the liquid is facilitated, chemical reaction is promoted, and noise in the pH measurements is reduced.[2] Obviously, this high agitation level is attained at a lower cost by using smaller tanks. As a consequence of the above facts, an increasing number of industrial facilities now tend to use smaller cylindrical tanks ($V = 10-20$ m³) with short residence times ($T_{RESA} \approx 20$ min) for input streams.

Following our objective, average data, which approximate true plant values, were needed. This called for a collaborative effort with process engineers who added their expertise to our knowledge, which resulted, among other things, in an average reference process at the industrial scale and a laboratory test-bench assembly. Table 1 shows the nominal stable-state (NSS)

conditions for pH = 7.0 in both the average reference industrial process and the proposed laboratory test-bench equipment. This set of data and eqs 1, 3, and 7–9 enable us to follow the time evolution of the output stream pH. Moreover, to facilitate the simulation and control tasks, a possible state space representation for the pH neutralization benchmark was introduced, regarding its variables at nominal stable state

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = \begin{bmatrix} -50(q_1 + q_2 + u) & 0 \\ 0 & -50(q_1 + q_2 + u) \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} + \mathbf{B}u + \mathbf{P}\mathbf{w}^T$$

$$\mathbf{x}^T = [W_{a4} \quad W_{b4}] \qquad \mathbf{w} = [q_1 \quad q_2] \qquad u = q_3$$

$$\mathbf{B} = \begin{bmatrix} -1.0175 \\ 0.0175 \end{bmatrix} \qquad \mathbf{P} = \begin{bmatrix} 50\,W_{a1} & -5 \\ 0 & 5 \end{bmatrix} \qquad (10)$$

where W_{a4} and W_{b4} are the reaction invariants, q_1 is the acid flow rate, q_2 is the buffer flow rate, u is the base flow rate, W_{a1} is the acid concentration, and the output y is calculated from eq 7.

3. Benchmark Statement

On the basis of the above discussion, in this section, a nonlinear control design problem is proposed as a benchmark based on the nonlinear interactions of chemical species in a continuously stirred tank reactor. The objective is to regulate the pH of the effluent (q_4) equal to or very close to neutrality (pH = 7.0) by manipulating the base flow rate (q_3). The general approach from this benchmark assumes as unknown perturbations the acid flow rate (q_1), the buffer flow rate (q_2), and the acid concentration (W_{a1}). To decrease installation costs, only two measured variables are available for this most general case: the effluent pH and the base flow rate (control action).[1,12] If the proposed control strategy requires other measured variables or the assumption that some variables have constant values, this can always be done with the aim of good performance at low cost that fulfills the following criteria.

3.1. Closed-Loop Stability and Good Perturbation Rejection. System stability must be guaranteed for closed-loop operation under the particular conditions and perturbations stated by the benchmark. In previous works, extensive discussions have been presented about the internal stability of the model used in the benchmark[15] and the controllability of the process.[16] The benchmark states two classes of perturbation, variable steps and periodic sinusoidal waves, that closely duplicate industrial systems with a mother pipe line receiving wastewater from various process equipment. The particular conditions for choosing such perturbations are as follows:

Variable Step Perturbation. This condition is typically found whenever the effluent pipeline is short or has a small diameter or there is no flow softener tank before the neutralization tank. Despite the abrupt variable changes, this type of perturbation is frequently found at industrial facilities with such a low-cost equipment array.[12]

Periodic Sinusoidal Waves. This perturbation arises whenever a flow softener tank is placed before the neutralization tank or when the effluent pipeline has both sufficient diameter and length to perform as a softener tank. In both cases, typical homogenization and
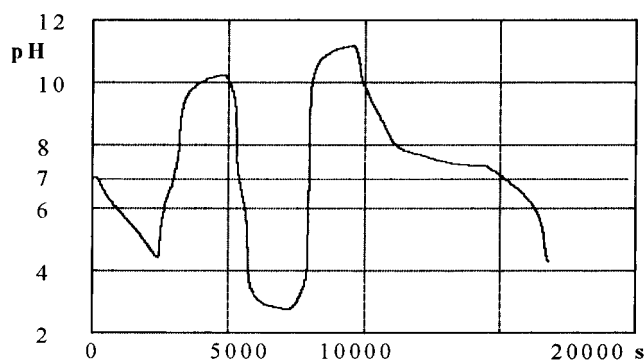

Figure 2. Open loop response to test 1.

Table 2. Test 1: Steps q_1 with Different Value Buffer

time (min)	q_1	W_{a1} (M)	q_2
5	$1.3q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$
40	$0.7q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$
80	$1.3q_{1\,\text{NSS}}$	0.01	$0.05q_{2\,\text{NSS}}$
120	$0.7q_{1\,\text{NSS}}$	0.01	$0.05q_{2\,\text{NSS}}$
160	$q_{1\,\text{NSS}}$	0.01	$2.5q_{2\,\text{NSS}}$

Table 3. Test 2: Steps W_{a1} with/without Buffer

time (min)	q_1	W_{a1} (M)	q_2
5	$q_{1\,\text{NSS}}$	0.015	$q_{2\,\text{NSS}}$
40	$q_{1\,\text{NSS}}$	0.005	$q_{2\,\text{NSS}}$
80	$q_{1\,\text{NSS}}$	0.015	$0.05q_{2\,\text{NSS}}$
120	$q_{1\,\text{NSS}}$	0.005	$0.05q_{2\,\text{NSS}}$
160	$q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$

Table 4. Test 3: Sine Wave q_1 with/without Buffer

time (min)	q_1	W_{a1} (M)	q_2
5	$\sin(xx)$	0.01	$q_{2\,\text{NSS}}$
80	$q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$
160	$\sin(xx)$	0.01	$0.05q_{2\,\text{NSS}}$
240	$q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$

Table 5. Test 4: Sine Wave W_{a1} with/without Buffer

time (min)	q_1	W_{a1} (M)	q_2
5	$q_{1\,\text{NSS}}$	$\sin(xx)$	$q_{2\,\text{NSS}}$
80	$q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$
160	$q_{1\,\text{NSS}}$	$\sin(xx)$	$0.05q_{2\,\text{NSS}}$
240	$q_{1\,\text{NSS}}$	0.01	$q_{2\,\text{NSS}}$

dilution effects are well represented by sine waves of constant period and amplitude. The benchmark postulates a sine wave ($\sin(xx)$ in the tables) with a 30-min period, based on the natural time response of industrial transportation pipelines.[2,10]

Tables 2–5 show the proposed benchmark perturbation plan for testing any control strategy for pH neutralization problems. All tests begin at NSS conditions, and each test is applied as a whole. The open-loop responses of the process to tests 1 and 4 are presented in Figures 2 and 3.

3.2. Reasonable Control Action and Performance Index. Based on environmental and economic objectives, the control policy must use the least number of sensors and FCEs and minimize the consumption of the neutralization reactant. However, the designer is free to choose other constraints. For example, the FCE rate of change can be limited in order to augment its useful life. To unify the performance evaluation for tested controllers, the benchmark states an index for
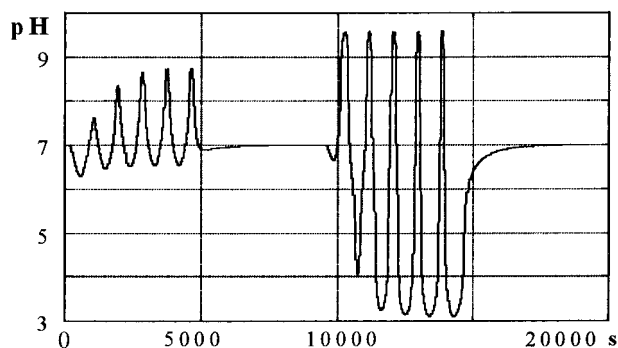
Figure 3. Open loop response to test 4.

evaluation of controller performance

$$FC = a_1 \sum |y_{ref} - y| + a_2 \, \mathbf{Max}(|y_{ref} - y|) + a_3 \\ (N_{POB}/N_{MPOB}) \quad \textbf{(11)}$$

where FC is the cost function of the tested controller, a_i are the scaling coefficients, y_{ref} is the set-point value, y is the process output (pH), N_{POB} is the number of points out of a band around the neutrality point, and N_{MPOB} is the maximum number of points out of the previously described band.

4. Benchmark Representation Capability

The representation capability is a very important characteristic of any particular process model, especially when that model is used for a benchmark formulation.[6] Two aspects should be considered in order to determine the benchmark representation capability. The first is the inlet stream characterization starting from the particular weak acids contained in this stream. The other is the internal effect of that inlet stream on the reactor behavior (output pH). Benchmark formulation shows that the model inherits the effect of dissociation constants of the acids forming the input stream. As a consequence, the analysis done by the model over the input stream provides sufficient information about internal system behavior.

4.1. Limit Plots for the Benchmark Proposal. Equations 7 and 10, stated as a process model in the benchmark, show that the principal characteristics of any inlet stream are pH and W_a. Therefore, any current condition for an inlet stream is represented in its titration plot by a point.[14] The nonlinear pH changes caused by W_a mutations can be followed over the titration plot provided that the current anion concentration is a known constant. If this anion concentration changes, the pH variations must be followed by jumping among the titration plots associated with the particular anion concentrations. Thus, the titration plot of the inlet stream contains all of the necessary information to characterize the behavior of the neutralization reactor.[13] Then, the exact region limited by the extreme titration plots for the benchmark last anion (carbonic, CO_3^{3-}) can be determined.

The two limit conditions, which generate the pair of border plots, are extremes among all the possible last anion concentrations. For both conditions, $q_3 = 0.5q_{1NSS}$ will be taken. For the maximum anion concentration, the flows are $q_1 = 0.7q_{1NSS}$ and $q_2 = 4q_{2\,NSS}$. For the minimum anion concentration, the system resembles a strong acid neutralization process with flows $q_1 = 1.3q_{1NSS}$ and $q_2 = 0$. In Figure 4, this region of interest,
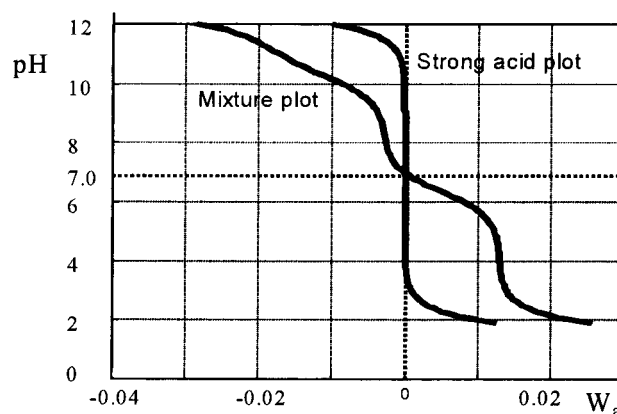

Figure 4. Carbonic system region (CSR).

delimited by the benchmark proposal (carbonic system) titration plots is presented. Henceforth this region will be called the carbonic system region (CSR). The CSR borders are a strong acid titration plot and a weak−strong acid mixture titration plot.

Finally, it should be noted that two open limits exist in the CSR: below pH 2.0 and above pH 12.0. By using an acceptable control system, a high pH value has little probability of occurrence,[12] so the above zone is rejected. On the other hand, a high weak-acid concentration at any lower crossing point (pH < 2.0), allows us to consider an economical acid recovery rather than neutralization and discharge.

4.2. Representation Capability Analysis. Following the procedure stated by Gutafsson,[14] it was possible to calculate a minimum inlet stream concentration for mono- and diprotic acids.[16] In both groups of weak acids, the worst case occurs when the pK_a equals 8.0. The minimum anion concentrations in the inlet stream, $c = 0.0025$ M, is associated with a diprotic acid with $K_{a1} = 10^{-7}$ and $K_{a2} = 10^{-8}$. This input stream has a pH of 4.80. In addition, $c = 0.0043$ M (the maximum of the minimum anion concentrations) occurs for a group of weak acids. In particular, for one acid of this set ($K_{a1} = 10^{-1}$, $K_{a2} = 10^{-8}$), a solution with a pH value of 2.38 is obtained. Between these pH limits will range all of the pH values for possible solutions with inferior concentrations. As can be seen, this is a typical interval for the minimum pH of the inlet stream at anindustrial neutralization plants. This fact can be extended to a pair of triprotic acids, phosphoric and citric, based on their minimum inlet stream concentrations found following a similar procedure.[12]

Looking for a general CSR characterization, the minimum concentration of the anion in the input stream can be taken as a coarse upper limit. In this case, it is possible to postulate that any weak-acid solution with concentration less than 0.0025 M will have a good representation through the postulated benchmark. As a summary, it can be affirmed that the carbonic system represents a great variety of industrial acids mixture in their characteristics previous to the reactor and in their reactive behavior in the reactor.

5. Experimental Results

A group of experimental tests was conducted at the laboratory assembly previously described. Here, a group of tests is presented that demonstrates the representation capability of the benchmark and a closed-loop response using a PID controller. To test the two
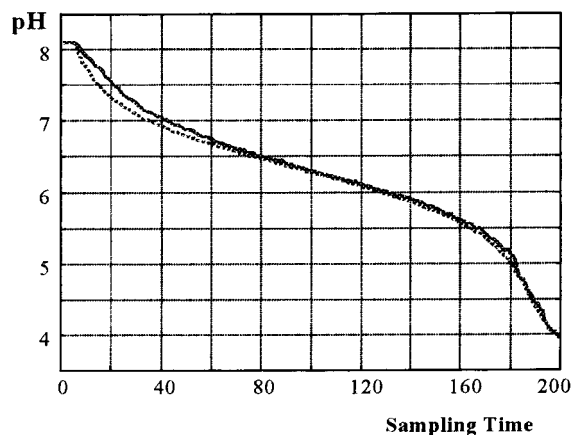
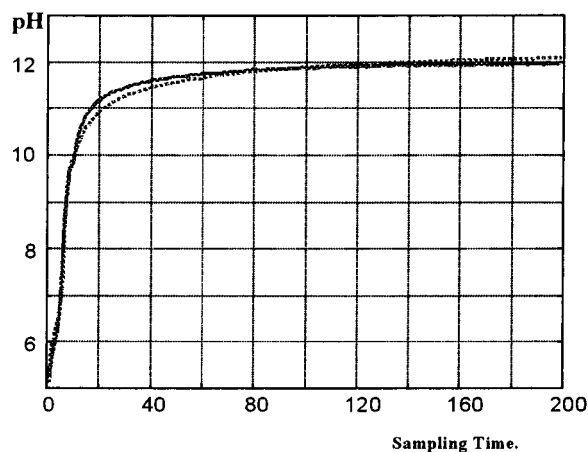**Figure 5.** Flow rate of acid from 0.0 to 1.3 mL/s.

Figure 6. Flow rate of base from 0.0 to 9.7 mL/s.

Figure 7. Flow rate of acid from 0.0 to 17.8 mL/s.

Figure 8. Flow rate of salt from 0.0 to 1.3 mL/s.

principal dynamics of the process, chemical reaction and hydraulic behavior, the experiments were divided into two classes. The first class of tests explores the chemical reaction dynamic by applying strong step changes in the concentration and flow rate of the acid stream and in the flow rate of the base stream. The second class of tests explores the hydraulic behavior of the process by means of slight step changes in the flow rates of the acid stream and buffer stream. In the following, the tests are presented as they were performed in the plant. When a flow rate was changed, the other streams were maintained closed. In all figures, a continuous line represents the real plant response, and a dashed line the model simulation. The process response when the flow rate of acid (0.01 mol/L) was change from 0.0 to 1.3 mL/s is presented in Figure 5. Figure 6 shows the response when the base flow rate (0.02 mol/L) was changed from 0.0 to 9.7 mL/s. The response when the acid flow rate was change from 0.0 to 17.8 mL/s is presented in Figure 7, and the response when the salt (0.1 mol/L) flow rate was change from 0.0 to 1.3 mL/s is shown in Figure 8.

As can be seen from these figures, the model represents adequately the process dynamics, as was stated in the benchmark formulation (eqs 7 and 10). The slight difference in salt concentration in the solvent (water from the city resource) is one particularity that was found in the laboratory bench. Such a situation was compensated in the benchmark formulation by means of a constant value in the salt concentration. Nevertheless, as can be seen in Figure 7, the basic nature of the salt present in the solvent alters the form of the process
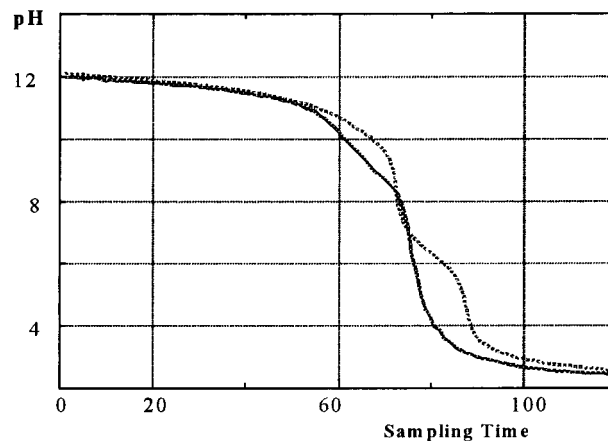
response. In regard to this fact, the previously discussed representation capability of the benchmark guarantees that form changes in the response curve will be covered. Additionally, the approximation capacity of the proposed model is adequate for testing nonlinear controllers.[16]

Whenever the classical PID control strategy is applied to the pH neutralization problem, its poor performance readily appears, fundamentally because of the nonlinear characteristics of this process.[11,12] Nevertheless, the PID control strategy gives a good initial reference point for comparisons with other control proposals. Previous works have demonstrated the low performance of the controller when a derivative mode is used, because of process delays.[1,8] As a result of these observations, the benchmark proposes to use the following PI controller that was tuned for load changes, first through the Ziegler−Nichols procedure with a criterion for minimal integral error and then through a proof and error method for fine-tuning:[8] $K_C = 2.0 \times 10^{-6}$ m³/seg. $T_I = 100$ s. These are the proposed values for the PI reference controller in the present benchmark. Figures 9 and 10 show the PI controller response in simulations for tests 1 and 4 stated in section 3. Finally, Figure 11 presents the PI controller response to the first part of test 1, directly applied to the laboratory assembly. As can be seen, the real response is similar to the simulated response given in Figure 9. In summary, the process model and the benchmark statements represent the principal dynamic characteristics of the neutralization process. Therefore, the benchmark is a good tool for testing new control strategies.
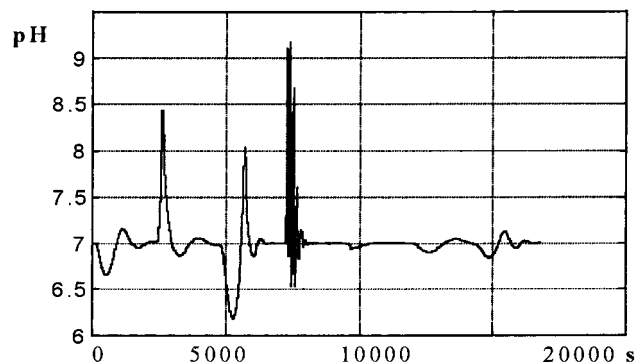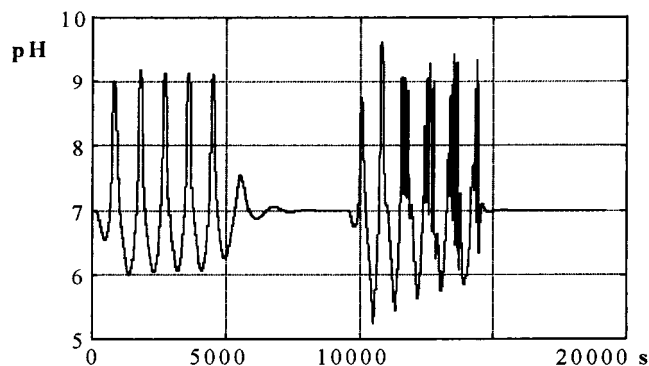
Figure 9. Simulated PI response to test 1.

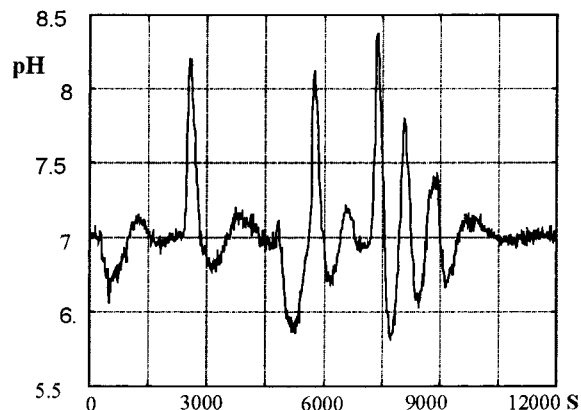**Figure 10.** PI response to test 4.

Figure 11. Laboratory PI response to first part of test 1.

Conclusions

The pH neutralization process was stated as a benchmark for nonlinear control system design. The representation capability of the benchmark was discussed, and limit values for the acid concentration were presented. A laboratory test bench was postulated, assembled, and tested at the control process laboratory in the Instituto de Automática, Facultad de Ingeniería, Universidad Nacional de San Juan, Argentina. The attained results demonstrate the applicability of the benchmark and its good performance as a representation of the real process conditions.

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