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ALGORITMS FOR *pH* CONTROL

A.J. Niemi
Helsinki University of Technology
Finland

P.K. Jutila
Helsinki University of Technology
Finland

ABSTRACT

The acidity of solutions containing both weak and strong constituents simultaneously are discussed and algorithms for their control by feedback and feedforward are suggested.

RESUMEN

Se discute la acidez de soluciones que poseen simultaneamente constituyentes débiles y fuertes , y se sugieren algoritmos para su control por retro alimentación y alimentación progresiva.

1. INTRODUCTION

Automatic control of acidity in industry followed closely to the development and implementation of controls for such physical process variables like temperature, pressure, flow, etc. Instruments for the continuous measurement of acidity through *pH* and for control of the feed of chemical agents were made available and construction of control loops was readily accomplished by similar methods. However, the *pH* control was often observed particularly difficult, and combinations of conventional feedback and feedforward loops and other cascaded controls are fairly generally applied, in order to reach more satisfactory results.

Although the nonlinear dependence of the *pH* on the hydrogen ion concentration and the laws of formation of these ions by dissociation have long been known, the quantitative physical and chemical approach has only recently been applied to studies of control. Related models have been used for simulation [1], and for studies of optimal control [2] and stability [3, 4].

More lately, practical linear feedback and feedforward control algorithms were suggested by the present authors and applied to the control of a continuous flow process in laboratory [5, 6]. These algorithms are theoretically correct in the control of solutions of strong, fully dissociated acids and bases and in feedforward control of a weak, buffering acid (base) with a strong, fully dissociated base (acid). The present paper discusses the acidity of solutions which contain both weak and strong constituents simultaneously, and suggests algorithms for their control by feedback and feedforward.

2. *pH* OF AQUEOUS SOLUTIONS

Dissociation of the water (H_2O) molecule to the hydrogen (H^+) and hydroxyl (OH^-) ions is a very fast and reversible process. The dependence of the ion concentrations on each other is unambiguously expressed by the value of the ion product K_w. The concentrations can be used instead of the activities with a good accuracy especially for dilute solutions. Only isothermal systems shall be studied, and the value of the ion product at 25°C is given below.

$$K_w = a_H \cdot a_{OH^-} \approx C^+C^- \approx 10^{14} (mole/litre)^2 \qquad (1)$$

Dissolved acids produce H^+ ions and bases OH^- ions by dissociation. Since the liquid is electrically neutral, the Equation (2) which consists of the concentrations of all ions present must be valid at any point.

$$C^+ - \frac{K_w}{C^+} + C_B - C_A + \sum_{i=1}^{n} \frac{K_{bi}\, C_{\beta i}\, C^+}{K_w + K_{bi}\, C^+} - \sum_{j=1}^{n} \frac{K_{aj}\, C_{\alpha j}}{K_{aj} + C^+} = 0 \qquad (2)$$

$$K_{aj} = \frac{C^+ C^-_{aj}}{C_{aj}} \qquad K_{bi} = \frac{C^- C^+_{bi}}{C_{bi}} \qquad (3)$$

$$C_{\alpha j} = C_{aj} + C^-_{aj} \qquad C_{\beta i} = C_{bi} + C^+_{bi}$$

The first and 2nd term of Eq. (2) are the above concentrations C^+ and C^- (1). A strong, i.e. fully dissociated base produces positive cations in a concentration which is equal to the total concentration of the base at the point under inspection (3rd term), and a strong acid negative anions in a concentration equal to the total concentration of the acid (4th term). The concentration of the cation of a weak, i.e. partly dissociated base is represented by a member of the 5th term and the concentration of the anion of a weak acid by a member of the 6th term. The last two terms are easily derived with the aid of the dissociation equilibria (3). Only chemicals showing a single step of dissociation under the process conditions are being considered.

The acidity of a solution is easily measured by means of a *pH* meter or transmitter. This produces a voltage which is linearly dependent on the *pH* value of the solution, but the dependence of the latter on concentration is highly nonlinear.

$$pH = -\log_{10}\left[a_{H^+} / (mole/litre)\right] \tag{4}$$

$$\approx -\log_{10}\left[C^+ / (mole/litre)\right]$$

3. CONTROL OF *pH* IN SOLUTIONS OF STRONG ACIDS AND BASES [5]

If only strong acids and bases are present, the two last terms in Equations (2) are eliminated. The two first terms are equivalent to the difference of the concentrations of the H^+ and OH^- ions, and this difference depends linearly on the concentrations of the strong bases and acids, and linearly and unambiguously on their difference.

In a continuous flow system, the concentration of a chemical at any point depends linearly on its concentration at the inlet point (5). Thus the total process consisting of both the flow and mixing and the dissociation is linear, if the concentration of a chemical at the feed is considered the input variable and the difference of the H^+ and OH^- ion concentrations the output variable.

$$c_k(t) = \int_{-\infty}^{t} c_{k,feed}(\theta)\, g(t-\theta)\, d\theta \tag{5}$$

$$k = B, A, \beta i, \alpha j$$

Since pH, C^+, $C^+ - C^-$ and $C_A - C_B$ depend unambiguously on each other (4, 1, 2), the measured pH value can be converted by computation to the corresponding value of $C^{+} - C^{-} = C$ or of $C_A - C_B$. Thus the output of the linear process can be detected by a *pH* measurement and subsequent computational conversion. The variable C was brought as the input data to a standard linear control algorithm, in order to produce a completely linear feedback control loop, Fig. 1 [5]. Since the set point is normally given as a *pH* value, this must also be converted to the desired ion concentration difference C_{ref} before the introduction to the loop. It is seen that the operation and stability of the resulting loop are equivalent to the case of the pure concentration process in the same vessel, i.e. to the case of a pure flow and mixing in the absence of the dissociation reactions.

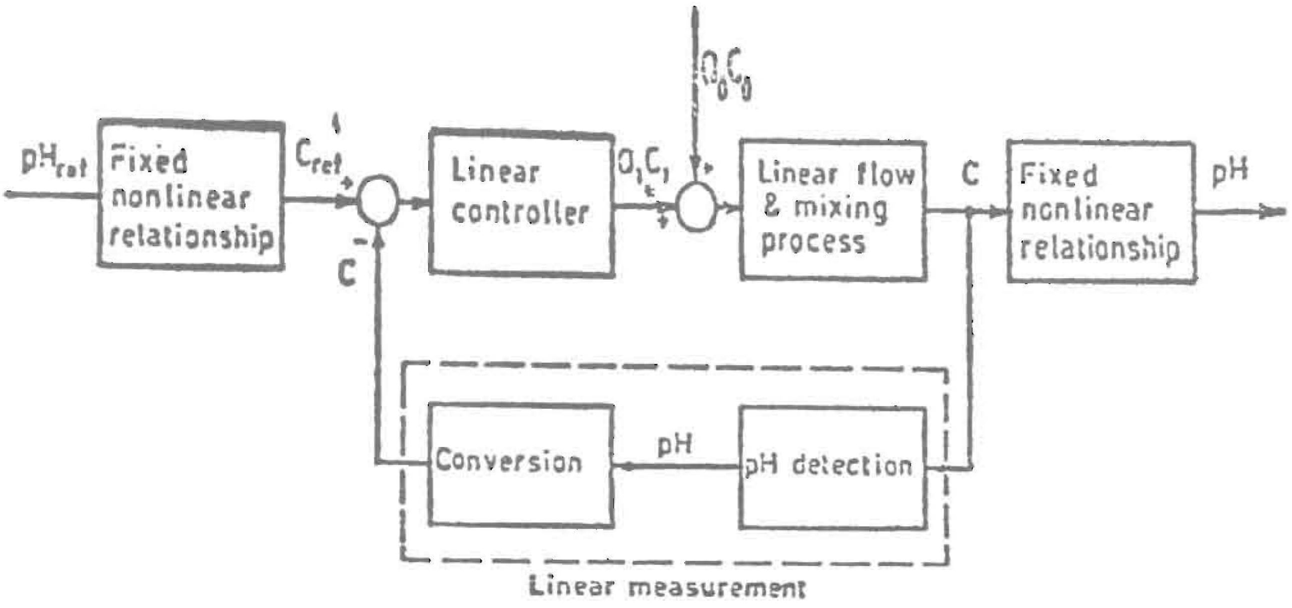

Fig. 1. *pH* control with linear feedback loop; strong chemicals.

The described linear control was compared, theoretically and experimentally, with the conventional nonlinear control in which the control deviation is formed as a difference of *pH*-valued quantities and fed into a linear controller. The block diagram of the latter control loop is obtained if the conversions of the primary reference variable and of the detected *pH* are left out in Fig. 1, and the corresponding pH variables brought directly to the comparator. It turned out that the gain of the conventional loop decreases with the increase of the control deviation resulting in a slow control and in a difficulty to reach a satisfactory control for both large and small disturbances.

If a feedforward control is based, without conversions, on the *pH* value measured in the feed pipe, and the controller tuned for small disturbances, the results are almost worthless at large disturbances. When the above concentrations and concentration differences are applied after appropriate conversions, the control is theoretically correct, and the accuracy of the operation is limited substantially only by the finite accuracy of the meters and actuators [5].

4. CONTROL OF *pH* IN SOLUTIONS OF WEAK ACIDS AND BASES

If the solution contains weak acids and bases, the equilibria (3) must be considered and members of the two last terms in Eq. (2) included in the model as needed. A $(\nu+2)$nd order polynomial results, where ν is the number of weak constituents. E.g. for the case of one weak acid and one or more strong base this is $(i = 0\ ,\ j = 1\ ,\ C_A = 0)$:

$$C^{+3} + (C_B + K_a)C^{+2} + (K_a C_B - K_a C_\alpha - K_w)C^{+} - K_a K_w = 0 \tag{6}$$

If the Equation (5) is written separately for the strong base B and weak acid α, these equations together with Eq. (6) form a complete model of the system. For the special case of a continuous flow stirred tank reactor the state equations (7) can be written instead of the integrals (5).

$$\begin{aligned} \dot{C}_\alpha &= q_0 C_{\alpha 0} - (q_0 + q_1) C_\alpha \\ \dot{C}_B &= q_1 C_{B1} - (q_0 + q_1) C_B \end{aligned} \tag{7}$$

This model (5, 7) was derived in Ref. [7] for the case of acetic acid and sodium hydroxide. The above equations show that pH measurement alone is insufficient for an unambiguous description of the state of the process. An inspection of the Eq. (2) shows that in this case no such unambiguous function of C^+ exists which would depend linearly on the concentration of the control agent B.

One reason to practical difficulties met in feedback control of liquids having a complex composition, by means of one pH measurement only, is obviously the nonlinear influence of the disturbance variable (C_α). High value of C_α implies a low process gain dC^+/dC_B and vice versa. When C_α varies and information of the variation is missing, the loop must be tuned for the worst case, and the control is less efficient under other conditions.

An additional independent measurement of the concentration of a compound or ion is needed for an accurate description of the state of the system. All other concentrations can then easily be calculated by means of the Eqs. (3, 6, 4).

The concentration of the cation of the strong base B which, for the complete dissociation, is equal to the total concentration of B will be considered in the following as an example of such second measured variable. A realization of the measurement is achieved by means of an ion selective electrode. If e.g. a solution of potassium hydroxide is used for control, the K^+ detector followed by a linear amplifier provides the negative logarithm pK of C_B.

$$pK = -\log_{10}[C_B / (mole/litre)] \tag{8}$$

If the raw feed stream is a solution of a weak acid, like acetic acid, a control algorithm based on two measurements can now be constructed (Fig. 2). The outputs pH and pK of the sensors are converted to C^+ (4) and C_B (8) values (#1, #2, #3, #4). The total concentration C_α of the weak acid is obtained by means of Eq. (6), (#5).

If C_α and the desired value C^+_{ref} (#6) of the acidity are now introduced in Eq. (6), that concentration $C_{B ref}$ of the base can be calculated which in the presence of the disturbance C_α would produce

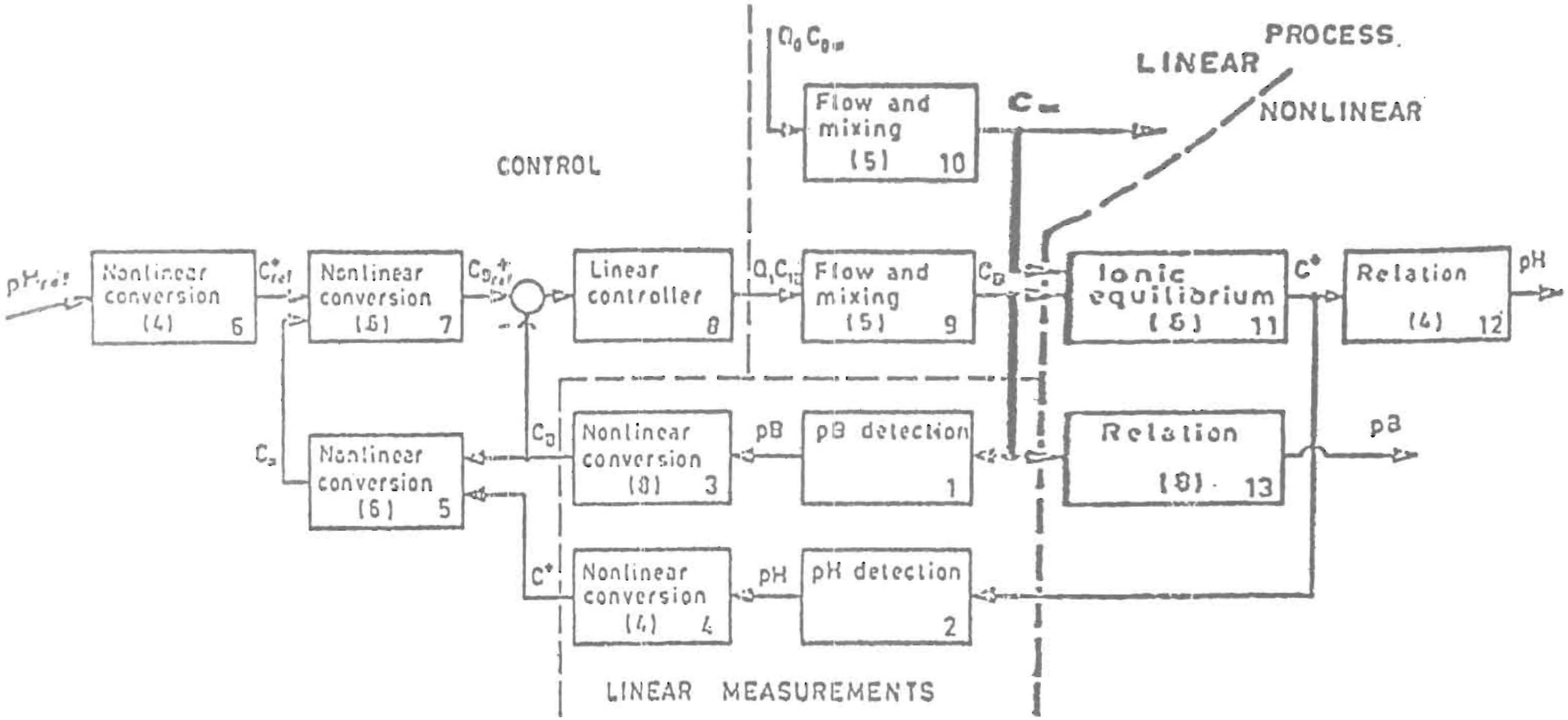

Fig. 2. *pH* control by means of two measured concentration variables.

the desired $pH = pH_{ref}$ (#7). By introducing C_{Bref} as the set point and C_B as the feedback to a linear controller (#8), a linear loop is obtained for the control of C_B by manipulation of the feed flow $Q_1 C_{1B}$ of the base. (The changes of the control flow Q_1 are assumed small in regard to the total flow $Q_0 + Q_1$). The final controlled variable pH (#12) or C^+ (#11) depends on the controlled loop output C_B (#9) and on the independent disturbance C_α at the process outlet (#10). The process pB is related only to the former output (#13).

The control scheme seems to include two closed loops, but only one really exists. The process block #11 yields C^+, with C_α and C_B as the inputs, and assuming correct measurements and conversions, the block #5 with inputs C^+ and C_B reproduces the momentary value of the disturbance variable C_α irrespective of the values of C^+ and C_B. If the process model is considered complete and correct and any other disturbances absent, the outer loop is therefore equivalent to an open loop feedforward compensation of the disturbance. This compensation is completely linear, because the block #7 represents a linear dependence of C_{Bref} on C_α (6), although the dependence on C^+_{ref} is nonlinear.

The remaining feedback loop is linear which makes the design of the control function (#8) and the stability studies easy. A comparison with the case of Fig. 1 shows that the loop controls a pure concentration process, viz. that of the strong base B, while being preceded by an open loop disturbance compensation.

Operation of the algorithm was illustrated by simulation. The continuous flow system model was that of Fig. 3; the same model was used earlier for simulation of pH control in solutions of strong ac-

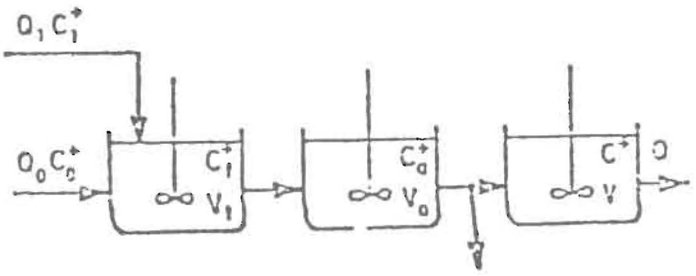

Fig. 3. Continuous flow system.

ids and bases [5] . The liquid volumes of the vessels were set constant. Q is the constant sample flow through the 3rd vessel (measuring chamber) . The values of the parameters and the steady state values (sub-index s) of the variables are : $C^+_{1s} = 10^{-12}$ *mole/litre* ($pH = 12$), $C^+_{0s} = 10^{-4}$ *mole/litre* ($pH = 4$), $Q_{0s}/V_f = 1\ min^{-1}$, $Q_{1s}/V_f = 0.067\ min^{-1}$, $Q_s/V = 10\ min^{-1}$, $V_a/V_f = 0.25$, $C^+_{ref} = C^+_{fs} = C^+_{as} = C^+_s = 10^{-7}$ *mole/litre* ($pH = 7$) . The control flow was limited between *0...0.1 litre/min*, and the inertia of the actuator was neglected.

Fig. 4 shows the response under the described control , when *pH*

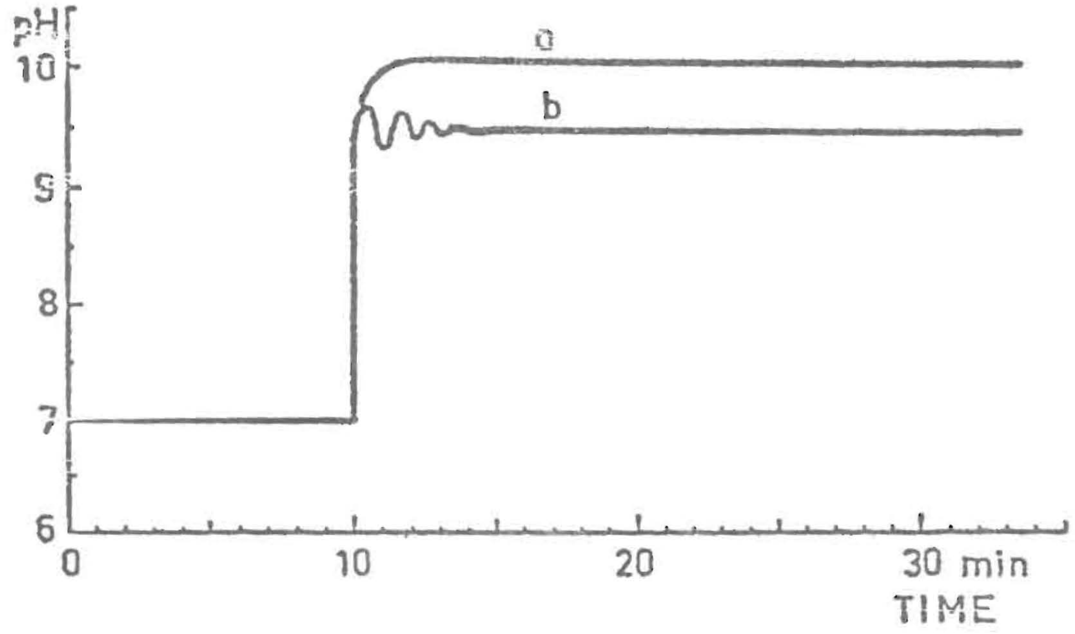

Fig. 4. Simulated step responses of systems with proportional control based on a) one measured *pH* value (nonlinear), b) arrangement of Fig. 2.

of the feed stream (acetic acid solution) changes stepwise from *4* to *4.2* at the time $t = 10\ min$. The other step response in the same picture was obtained for the same disturbance , when the simulation was based on the conventional pH control by means of one pH measurement only . For the process of Fig. 2 this implied the deletion of one measurement (blocks #1 and #3), and of the conversions (#4, #5, #6, #7), and the connection of the *pH* signal from block #2 and of the primary reference pH_{ref} to the comparator.

In both cases a proportional controller algorithm only was applied in order to illustrate better the basic behaviour of the system, and the controller gain was set to 50% of that at the stability limit. The straightforward *pH* control results in a greater permanent deviation than the control of Fig. 2 which corresponds to the simulated and experimental results in the case of strong compounds [6]. The non-oscillating output of the nonlinear *pH* control corresponds also now to a gain which decreases with the distance from the reference value.

The responses in Fig. 5 were obtained, when the proportional control was expanded to proportional and integral control, and the

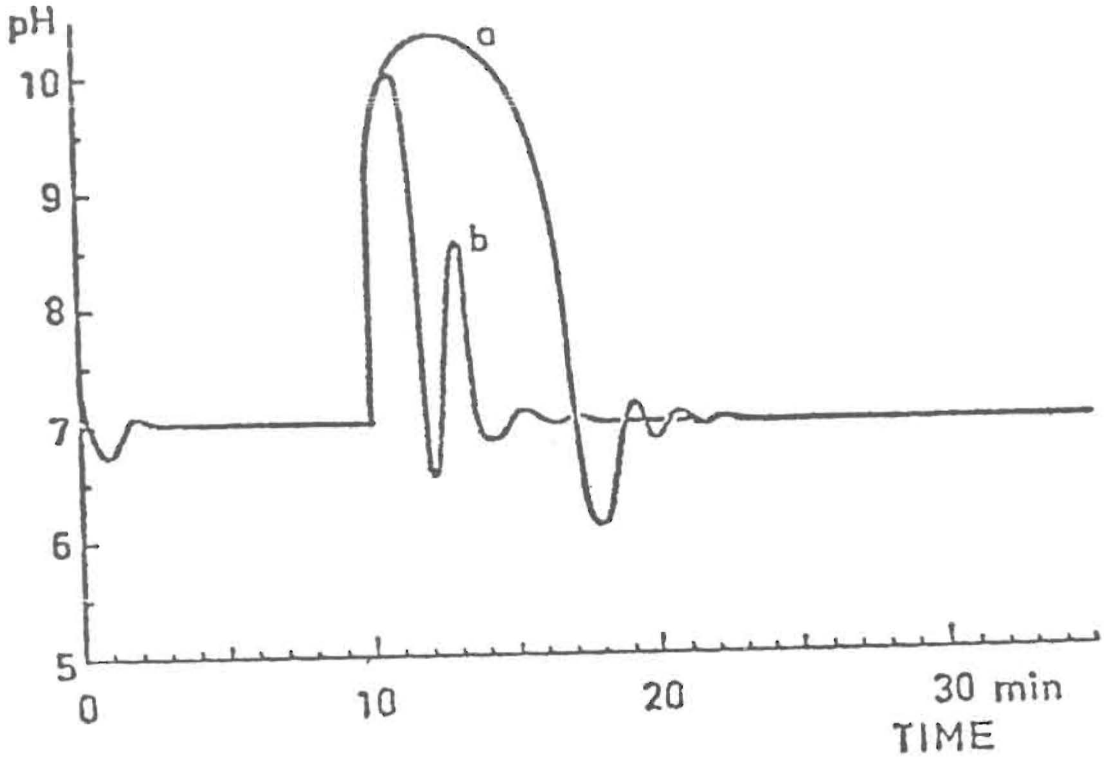

Fig. 5. Simulated step responses with proportional and integral control. Cases a) and b) of Fig. 4.

values of the parameters were chosen , by an evaluation of a set of simulated responses by eye . It is seen that the output of the process controlled by the concentration control returns to the reference point faster than in the case of *pH* control which implies a greater deviation and a slower return. Oscillations at the reference point limit the selection of the parameter values in both cases.

Another system in which the weak acid solution (C_{α}) is controlled with a weak base (C_B instead of C_B) was submitted to a similar theoretical study . Although the output relationship was now a 4th order polynomial, a block diagram could be constructed which did not differ much of Fig. 2 . Also now the control could be based on one *pH* and one ion selective measurement, and it consisted, in principle, of a linear feedback loop and of a linear open loop compensation of the disturbance.

A computer controlled continuous flow system was constructed in the authors' laboratory , in order to test algorithms for *pH* control in solutions of strong compounds [5, 6] . It is now being provided with an independent second concentration measurement for tests with weak compounds.

In feedforward control , the *pH* control of the raw feed is measured and used in control of the feed of another chemical agent . Since the control chemical is not contained in the process flow at the point of measurement, the recognition of the variables affecting the acidity is generally easier than in feedback control . The case of a weak acid solution as the raw feed stream and a strong base solution as the controlling agent was studied, and a linear *pH* control algorithm was derived in terms of concentrations of the constituents . Experiments showed that the method worked much better than a control which, without conversions, was based on the measured *pH* only [5].

If an ion selective measurement , together with a *pH* measurement , is located in the process feed channel , a mixed feed consisting of a weak and a strong compound can be analysed and the results used for feedforward control by means of a separate feed of a strong compound , in order to reach the desired pH at the meeting point of the two feeds at the process inlet. The analysis procedure for C_B and C_α is essentially the same as that by blocks #1...#5 in Fig. 2 reproducing, by means of pH_{ref}, the required total concentration of the strong compound(s) (#7). This concentration is then produced by means of an additional, controlled feed of the strong compound. The procedure can be extended to the case of a mixture of a weak acid and a weak base as the raw feed, and one of the weak compounds or a strong compound as the controlling agent.

5. CONCLUSIONS

The conventional feedback control of solutions of strong acids and bases is nonlinear, but by means of a suitable conversion of the measured pH value a theoretically correct feedback control with linear closed loop can be established. An additional, independent concentration measurement is needed in the case of weak compounds. By appropriate conversions and despite of the nonlinear output relationship, the linear feedback loop results also in the latter case, augmented with a linear open loop compensation of the disturbance variable. These results are applicable to the control of processes with arbitrary flow patterns.

By similar efforts, a linear feedforward control can be established for the same process and even for somewhat more complicated cases. Both control methods can be superimposed for the control of the system through the same actuator. While the described control methods are theoretically correct, it is expected that they can be applied, e.g. in the industry and environment, to control of liquids showing buffering effects which can be adequately modelled by weak compounds with suitably chosen values of the dissociation factor.

LIST OF SYMBOLS

C^+	H^+ ion concentration
C^-	OH^- ion concentration
C_A	concentration of strong acid
C_B	concentration of strong base
C_α	concentration of weak acid
C_β	concentration of weak base
C_a	concentration of undissociated acid
C_b	concentration of undissociated base
C_a^-	concentration of weak anion
C_b^+	concentration of weak cation
C	$= C^+ - C^-$
$g(t)$	residence time distribution (weighting function)
K_a	dissociation constant of weak (acetic) acid
K_w	ion product of water
Q	volumetric flow
q_i	$= Q_i/V$ (V volume)
$0, 1$	as subindices of variables refer to process feed and control, respectively

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