

REAL-TIME MODELLING AND SIMULATION APPLIED TO THE TREATMENT OF ELECTROPLATING WASTEWATER

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Abstract: Eco-industrial processes require high reliability control and supervision methodologies, so as to achieve the best compromise possible between the process' efficiency, safety and economy. Industries often focus on the two first objectives mainly, since they are unwilling to "experiment" not yet validated and/or complex control methodologies if safety and/or efficiency of the process may be jeopardized. This work focuses on an industrial wastewater treatment process, including a cyanides oxidation stage and a neutralization stage, applied to the surface treatment effluents. The project involved the development and validation of a model which enables to simulate various pH-control strategies as well as faults in the CSTRs.

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1. INTRODUCTION

Metal processing activities (e.g. electroplating) use huge quantities of water during their manufacturing cycles. They thus generate significant amounts of wastewater, which usually do not satisfy environmental regulations so as to be rejected directly to the receiving water. These effluents, containing mainly heavy metals and cyanides, may be either strongly alkaline and/or very acidic. Therefore they have to be treated in a dedicated wastewater treatment plant, consisting of several physical-chemical stages (Degrémont Ed., 1991).

The regulations, however, tend to be more and more strict and limitative as far as admissible quantities of rejected pollutants (metal ions, cyanides, ...) are concerned (e.g. in the coming EU-regulations: Table 1). Moreover, several stages of the treatment process imply risks for the operators' health and even for their life if not optimally controlled, Fig.1 (Szafnicki, *et al.*, 1998). For example, chemical reactions implying cyanides may produce toxic (even

lethal !) intermediary compounds, such as cyanogen chloride (CNCl) or hydrocyanic acid (HCN).

The goal of this project is to develop and validate on industrial data a real-time model enabling a better understanding of the physical and chemical processes occurring in Continuously Stirred Tank Reactors (CSTR), in order to optimize their reliability, efficiency, economy, and safety of the treatment.

Table 1 Rejection limitations (mg/L)

| Elements | 1985 | Future... |
|-------------------|------|-----------|
| Al | 5.0 | 5.0 |
| Cr ^{VI} | 0.1 | 0.1 |
| Cr ^{III} | 3.0 | ... |
| Cr total | 3.0 | 0.5 |
| Cu | 2.0 | 0.5 |
| Fe | 5.0 | 5.0 |
| Ni | 5.0 | 0.5 |
| Pb | 1.0 | 0.5 |
| Zn | 5.0 | 2.0 |
| CN ⁻ | 0.1 | 0.1 |

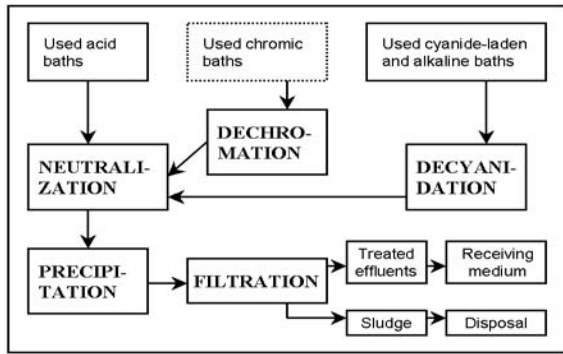


Fig. 1. General scheme of a detoxication plant

2. ABOUT pH CONTROL

2.1 Difficulty of pH control

Efficient pH control is vital for the performance (speed, efficiency) and safety of many continuous reactions; particularly during wastewater treatment. A typical pH control system consists of a set of pH electrodes, a pH transmitter, a feedback controller, a control valve, and a piece of mixing equipment. The input stream whose pH is to be adjusted is called the influent, the acid or base used to do the pH adjustment is called the reagent, and the output stream whose pH was adjusted is called the effluent (Fig.2). The control strategy appears to be relatively simple compared to that for many unit operations (Mc Millan, 1994).

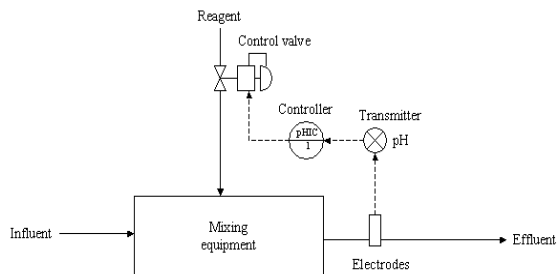


Fig. 2. A typical pH control system

$$\text{pH} = -\log_{10} [\text{H}^+] \quad (1)$$

The heart of the problem in pH control is up to the fact that the standard scale of pH 0 to 14 corresponds to $[\text{H}^+]$ measurement range of 10^0 to 10^{-14} mol/L, Eq. (1). No other type of commonly used measurement covers such a tremendous range. Also, the pH electrode can respond to changes as small as 10^{-3} pH, which means the pH measurement track changes of $5 \cdot 10^{-10}$ in hydrogen ion concentration at pH 7, which represents a very high sensitivity. Strong acid - strong base titration is thus a highly nonlinear process, Fig.3. As a consequence, it is very difficult to control precisely at $\text{pH} \in [3; 11]$.

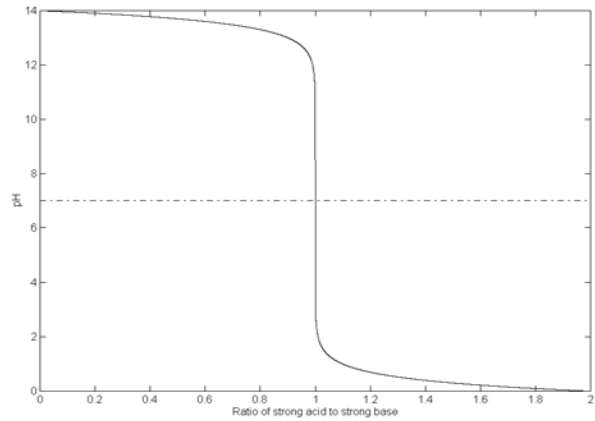


Fig. 3. Example of a strong acid - strong base titration curve.

2.2 Buffering

Some titration curves show a long portion of relatively flat slope. The addition of strong base or acid in this portion of the titration curve has little effect on the pH. This flatness is due to the buffering, which occurs for the mixture of a weak acid and a strong base salt or vice-versa. This property is thus interesting for a precise pH control. The buffering reactant is chosen in such a way that its buffer area (in the vicinity of its pKa) covers the desired pH setpoint values.

In this application, the pH setpoints are close to 9 since it corresponds to the best decyanidation conditions using H_2O_2 as well as to the optimal $\text{Me}(\text{OH})_n$ precipitation rates for Ni, Cu and Zn. Therefore buffering reactants may be considered e.g. among the following :

$\text{CO}_2 \rightarrow \text{water} = \text{weak diprotic acid with } \text{pKa}_1=6.4, \text{pKa}_2=10.3,$

or $\text{NH}_3 \rightarrow \text{water} = \text{weak base with } \text{pKa}=9.3.$

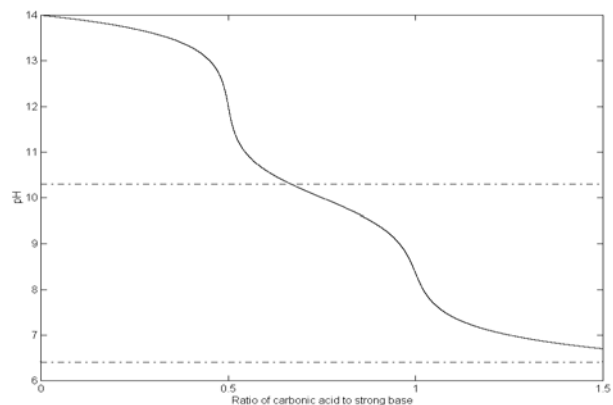


Fig. 4. CO_2 - NaOH titration curve

Carbonic acid-bicarbonate-carbonate is a commonly encountered buffer reactant, Fig.4. In this application it is being injected at 3 bar into a 50 m long mixing pipe. Equations (2) and (3) express respectively the dissociation constants for the carbonic acid-bicarbonate and the bicarbonate-

carbonate systems. The titration curve thus shows one slightly slope portion for each system.

$$ka_1 = \frac{[HCO_3^-] \cdot [H^+]}{[H_2CO_3]^*} = 10^{-6.4} \quad (2)$$

$$ka_2 = \frac{[CO_3^{2-}] \cdot [H^+]}{[HCO_3^-]} = 10^{-10.3} \quad (3)$$

Total un-ionized CO₂ in water, that is, the acidity constant is a composite constant for the analytical sum: $[H_2CO_3]^ = [CO_2]_{aq} + [H_2CO_3]$; see e.g. (Schnoor, 1996).

2.3 Buffer capacity

The buffer capacity β , also known as the buffer value, is defined as the change in normality due to the addition of dC moles of a strong base or acid divided by the change in pH as shown in Eq.(4). The buffer capacity is a measure of the ability of the solution to resist a change in pH, Fig. 5 & 6.

$$\beta = \frac{dC}{dpH} \quad (4)$$

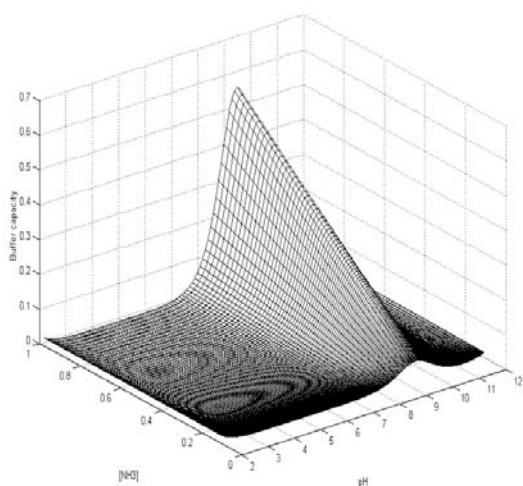


Fig. 5. Buffer capacity of NH₃/NH₄⁺ (pKa=9.3).

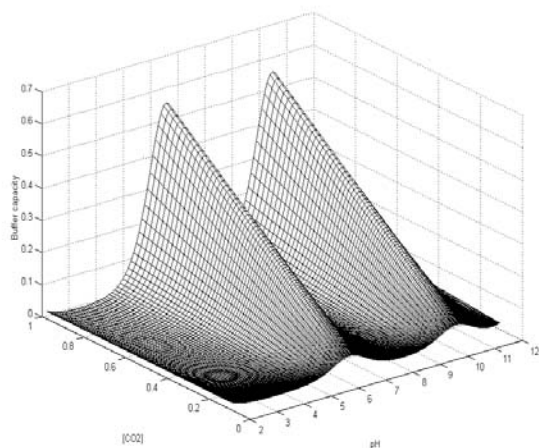


Fig. 6. Buffer capacity of CO₃²⁻/HCO₃⁻/H₂CO₃.

In both buffer regions, the concentrations of the base salt and the corresponding weak acid are very large with respect to the hydrogen ion concentration. If a strong acid (such as HCl) is added, the large concentration of base salt is quickly converted by the extra hydrogen ions to its acid form. If a strong base (such as NaOH) is added, the extra hydroxyl ions neutralize hydrogen ions but these hydrogen ions are quickly replaced by the ionisation of the acid. The buffer capacity obviously varies with the buffer's molarity as far as it depends on the quantity of molecules available for conversion. Thus the buffer capacity only depends on the pH and the weak acid's molarity, Fig. 5.

Then the addition of a buffer with a dissociation constant pKa close to the pH setpoint can greatly reduce the slope and hence the system sensitivity in the pH control band. The use of carbonic acid, whose pKa₁=6.4 and pKa₂=10.3 is thus very interesting in case of a control in the vicinity of pH 9, Fig.6.

3. CONTROL ANALYSIS

The control performances of the application (an electroplating manufacture wastewater treatment plant) have been analysed vs. efficiency, safety and economy aspects. The paper focuses on the analysis of the economical aspects, e.g. the reagents (over) consumptions as well as on the detection and comprehension of faults.

First, a global pollutant flow analysis has been performed over 9 months (Jan. – Sept. 2000). The main pollutant quantities to be treated were: 8.7 t of CN⁻ to be oxidized with H₂O₂ and 28 t of metal ions (mainly Ni⁺⁺, Cu⁺⁺, Zn⁺⁺, Sn⁺⁺, ...) to be precipitated as hydroxides by adding NaOH (50% w/w). The *theoretical* reagent consumptions, which have been calculated using the general stoichiometric reactions (e.g. CN⁻ + H₂O₂ → CNO⁻ + H₂O), were respectively: 11.4 t of H₂O₂ (35% w/w) and 75 t of NaOH (50% w/w), meanwhile the *real* consumptions were respectively: 53.4 t and 82 t. One can easily note the high level of over consumption of H₂O₂.

As a consequence, a more detailed system analysis (*via* modelling and simulation) has been performed in order to provide a better understanding of the performances of the present control system and propose, if possible, improvements for the economical aspects, i.e. a reduction of the reagents consumption (e.g. roughly: 40t of H₂O₂ at 253 Euro/t excl. VAT gives more than 10 kEuro over 9 months).

4. MODELLING

The real-time pH control of a CSTR has been modelled as a simple feedback loop (Fig.7).

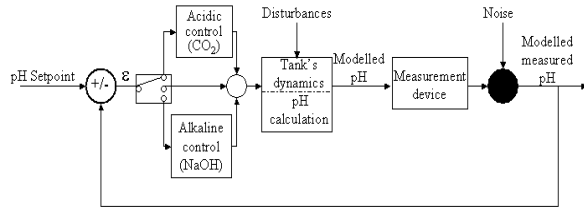


Fig. 7. General scheme of the model

4.1 Sequential proportional control

At present, different parameters on the plant (pH, ppm of H_2O_2 ...) are controlled *in situ* using sequential proportional controllers (“pH converters”) Yokogawa™ EXA pH400 (Fig.8) linked to pH-meters and dosing pumps Prominent® Vario for reagents addition. The control parameters are: Impulse Periodicities (IP); usually set to 30s, Set Points (SP) and Proportional Bands (PB).

The pH is controlled by injecting either NaOH (50% w/w) if too low or CO_2 (gaseous, at 3 bar) or H_2SO_4 (96% w/w) if too high. The dosing pumps work at “all-or-nothing” mode, at a preset reagent flow (24-120 L/h). The injection time is determined by the controllers as detailed on Fig.8.

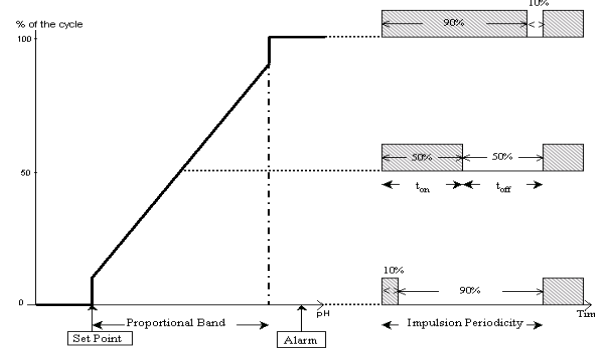


Fig. 8. Industrial controller setting scheme (Yokogawa EXA pH400)

Example:

Let $SP=9$, $PB=1$, $IP=30s$ and $pH_{measured}=9.33$ then the active part of the cycle=33%, i.e. $t_{on} = 10s$.

Up to now, the decyanidation and neutralization stages have been operating rather well, without major problems. For example, the cyanides and metal ions concentrations in the effluents have (almost) always been lower than the limitations. The controllers have thus proved to be at the same time: simple, robust and efficient.

4.2 CSTR's dynamics and pH calculation

The continuous flow process has been included in the discrete model considering small, homogeneous and perfect batches. Each batch corresponds to a perfect mixture of all the incomings (influents,

reagents) between one sampling time and the next, assuming a Zero-Order Hold (ZOH). At a sampling period $T_s=10s$, $V_{CSTR} \sim 10m^3$ and $Q_{in} \in [0,15,30]m^3/h$ one has: $dV_{max} = T_s \cdot Q_{in|max} = 0.083 m^3$ and $dV_{max}/V_{CSTR} = 0.83\%$. Therefore the hypothesis of a “sequence of small perfect batches” can be considered as a good approximation.

The pH of the different stages of the treatment plant is controlled by injections of NaOH or H_2SO_4 or CO_2 . The two first reagents are *strong base and acid*, meanwhile the CO_2 forms a *weak diprotic acid* in water solution, as described before.

The pH loop has been generally recognized as the most difficult control loop in process control (Levine, 1996). First, the response of pH to reagent addition tends to be *non linear*, which is particularly extreme for strong acid – strong base titration. Second, the *sensitivity* of pH to reagent addition in the vicinity of the equivalent point also tends to be extreme. Thus, a change of one pH unit can result from a fraction of a percent change in addition. Finally, the two previous relationships are often subject to *uncertain changes*, in particular during wastewater treatment (incoming pH variations, non homogeneous wastewater quality, varying inflow, etc.).

4.3 Measurement device

Measurement devices are interface devices and suffer from process and measurement noise as well as measurement bias. Moreover, measurement devices also have self dynamics (inertia, delays). These may be very fast but still they have to be taken into account (Katebi, *et al*, 1999).

In this study, the pH-meters have been modelled using a discrete first order transfer function with delay, as defined e.g. by Landau (1993):

$$H(z^{-1}) = \frac{b_1 z^{-1} + b_2 z^{-2}}{1 + a_1 z^{-1}} \times z^{-d} \quad (5)$$

where $b_1 = G \left(1 - e^{-\left(\frac{L-T_s}{T}\right)} \right)$ (6)

$$b_2 = G \cdot e^{-\left(\frac{T_s}{T}\right)} \cdot e^{-\left(\frac{L}{T}\right)} - 1 \quad (7)$$

$$a_1 = -e^{-\left(\frac{T_s}{T}\right)} \quad (8)$$

with T_s : sampling period;
 G : static gain;
 T : time constant;
 L : continuous delay;
 d : discrete delay.

4.4 The results

The developed real-time discrete (iterative) model made it possible to analyse the performances of the present, Yokogawa-based proportional-sequential control, in terms of its influence on the pH evolution and reagents consumption, Fig.9. The performances of the model vs. the pH measures from real industrial databases are quantified using a normed quadratic criterion:

$$Q_{\text{mod}} = 100 \cdot \sqrt{\frac{\sum_{i=1}^N [pH_{\text{mod}}(i) - pH_{\text{meas}}(i)]^2}{\sum_{i=1}^N [pH_{\text{meas}}(i)]^2}} \quad (9)$$

where Q_{mod} is the modelling criterion (in %), $pH_{\text{mod}}(i)$ and $pH_{\text{meas}}(i)$ are respectively the modelled and measured pH at the sampling point i , N is the total number of samples considered. The same kind of criterion, named Q_{set} is used to evaluate the performances of the modelled control vs. the pH setpoint by replacing $pH_{\text{meas}}(i)$ by $pH_{\text{set}}(i)$ in Eq.9.

Usually it can be considered that if $Q < 5\%$, then the control and/or modelling performances are good, if $5\% < Q < 10\%$ then they can probably be improved and if $Q > 10\%$ then there is a problem with the modelling and/or control stage.

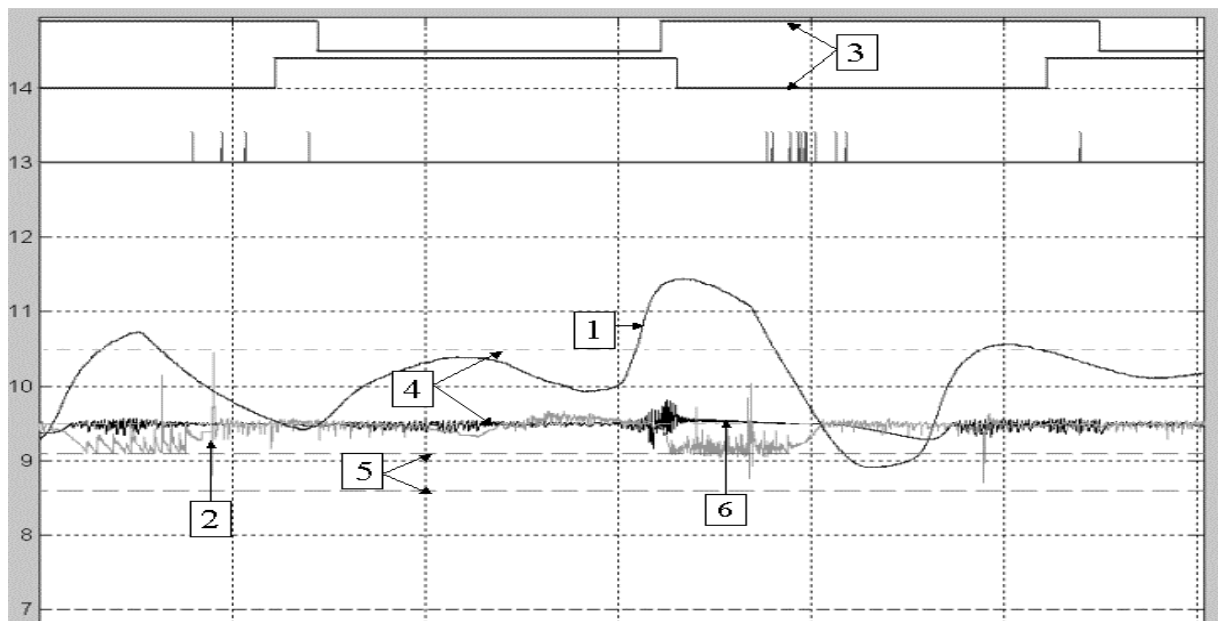


Fig. 9. Real vs. simulated data (Measured on 20/01/2000, $Q_{\text{meas}}=2\%$)

- 1 feeding (inflow) pH 2 measured decyanidation pH 3 inflow "all-or-nothing" pumps: 15 m³/h each
4 acidic reactant setpoints 5 alkaline reactant setpoints 6 modelled decyanidation pH

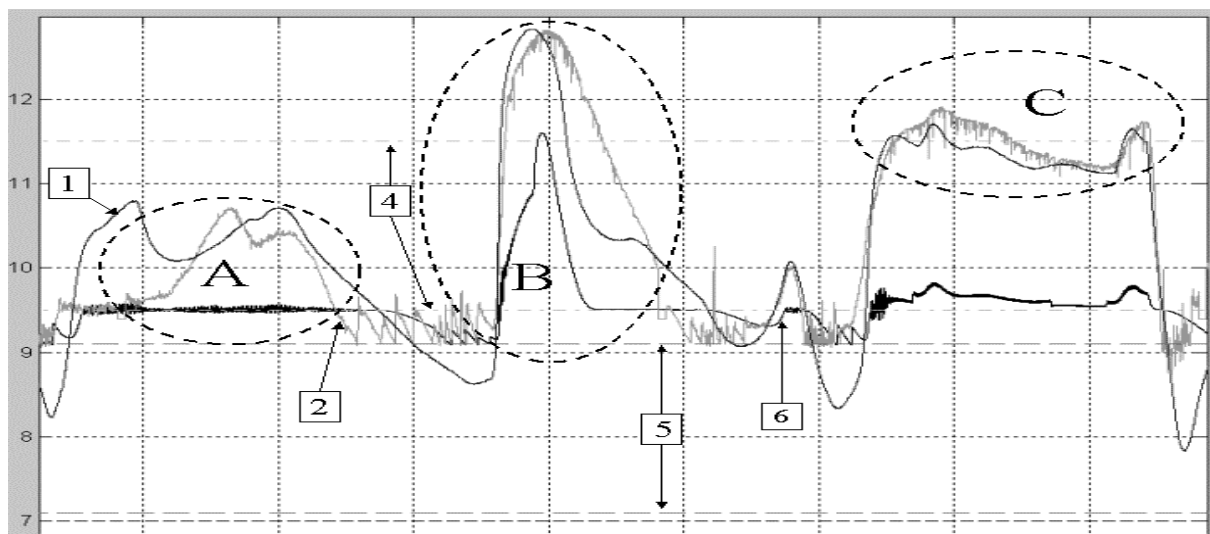


Fig. 10. Fault detections: "normal" model vs. measured data (Measures of 27/04/2000, $Q_{\text{set}}=3.5\%$)

5. SIMULATIONS

5.1 Fault detection

This project aimed at the development of a real-time discrete model of the process, enabling to simulate either its *normal* operation (i.e. being properly regulated by the reactant injection systems) or its operation in case of *faults*; e.g. a breakdown of the acid reactant injection loop.

The models have been validated on real, industrial data, so as to examine their performances. Thus, Fig. 10 presents a comparizon between a simulated pH generated by the normal model compared to the pH measured *in situ*. Three zones (A, B, C) of regulation problems (faults ?) can be noticed:

A: acidic reactant injection (CO₂) control fault: the measured pH increases whereas the modelled pH keeps to the setpoint;

B: pH control by injecting CO₂ fails when, simultaneously: the inflow pH is too high (>12) and the influx (feed) is too important (two feeding pumps running = 30 m³/h): the modelled pH increases sharply;

C: measurement devices bias detection - the measured pH is higher than the inflow pH meanwhile the CO₂ injection control failed.

Zones A & C clearly correspond to regulation faults while zone B is more "blended": it not only corresponds to a regulation fault, but also indicates the regulation limits of the CO₂ injection system, which is not able to cope with a *simultaneous* increase of the incoming pH (over 12) *and* the inflow (maximum: 30m³/h). Both, the measured and the modelled pH are far from the setpoint.

5.2 Control improvements

Subsequently to the real-time model development and validation, two directions of improvement have been considered: the readjustment (optimisation) of the present Yokogawa parameters settings (SP, PB, IP) and the introduction of discretized PI control. In fact, thanks to rather faithful simulations different scenarii could have been considered; e.g. adjustments of the Yokogawa settings, comparizon with a - theoretical - PI controller, etc. The latter is described by the following *discrete algorithm*:

$$\varepsilon(i) = pH_{set} - pH_{meas}(i-1) \quad (10)$$

$$Y_P(i) = K_P \cdot \varepsilon(i) \quad (11)$$

$$Y_I(i) = Y_I(i-1) + \varepsilon(i) \cdot K_I \quad (12)$$

$$Y_{PI}(i) = Y_P(i) + Y_I(i) \quad (13)$$

The quantity of reagent added at i is then proportional to Y_{PI} . However, if $\varepsilon < 0$ then acid is added, if $\varepsilon > 0$ then base is added. K_P and K_I are respectively the proportional and the integral coefficients.

Simulations have shown, that the introduction of a P controller could lead to a better fit to the setpoint (lower Q_{set}) while consuming somewhat less reactants (up to 10%). The PI controller would imply an even better (lower) Q_{set} , but the reactant consumption would be similar to Yokogawa.

6. CONCLUSION AND PERSPECTIVES:

Let us stress, however, that the final decision concerning the improvement solution definitely belongs to the manufacturer. Particularly, the implementation of P(I) control, although more effective in theory and simulation, would require a few significant modifications of the existing reactant injection circuit, such as the introduction of proportional injection devices (pumps and/or valves) instead of the present "all-or-nothing" equipment. Therefore, an exhaustive study of the present control system optimisation will be performed further, with the help of the simulation tool developed in this project.

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