pH-CONTROL USING A HEURISTIC MODEL:

A PILOT SCALE DEMONSTRATION

by

MEHUL MAHADEV DESAI, B.S.Ch.E.

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CHAPTER 1

INTRODUCTION

Chemical process control has been dominated by linear control theory and technology over the last few decades. However, the use of linear system techniques is quite limiting, since a significant portion of the chemical processes are inherently nonlinear. Recent advances in computer software and hardware have paved the way for the development of advanced nonlinear control methods and algorithms. Though linear systems have the advantage of computational simplicity, in many instances it may not be prudent to use them, especially for severely nonlinear processes. This has led to the rapid development of nonlinear control methods during the last ten years.

To some extent, every process is nonlinear. Some nonlinear effects are mild and can be handled fairly well by conventional linear control methods. However, some nonlinearities can be extremely severe and controlling such processes would entail the usage of information inherent in the process itself. Thus sprang the concept of nonlinear process model based control, which despite its lack of simplicity, is positively and surely seen as an emerging technology, offering more efficient control than the conventional linear approaches.

Exothermic reactions and pH processes are two good examples of extremely nonlinear processes. Also noted for notorious nonlinearities are high purity distillation columns and various bioprocesses.

One way of evading a nonlinear problem is to suitably modify the process so that the nonlinear effects can be reduced or perhaps even be eliminated. This has been shown to be true for flow control routines where equal percentage valve characteristics sufficiently linearize the process. There have also been instances wherein a complex process with nonlinear elements and constraints has been effectively controlled using a PID controller with a variable gain. But, there still remains a class of problems for which linear control technology is ineffective and the only recourse is a nonlinear algorithm.

pH control is without doubt one of the most difficult control problems of today. It has been well-documented that the pH process is extremely nonlinear and conventional PID or even advanced linear control techniques have not been able to satisfactorily solve this problem. However, pH control is industrially very important with wide ranging applications like wastewater neutralization, ore floatation, cooling tower water treatment, boiler feed water treatment, beverage manufacturing, acid pickling and etching, metal treating and finishing, pulp and paper manufacturing, chemical scrubbing and several others. Of these, industrial wastewater control

is the most important, demanding and difficult problem. Lately with more stringent governmental regulations and their stricter enforcement, a lot of time, money and research effort have been invested into this problem.

Wastewater pH control is replete with difficulties. Firstly, the pH response to the addition of a reagent (titration curve) is a highly nonlinear classic "S" shaped curve and the process gain changes drastically as we move along it. Secondly, the wastewater composition is constantly changing, typically being an unpredictable mixture of substances with widely differing properties. Owing to this, an advanced prediction of the titration curve is not possible. Finally, in the neutralization and equivalence regions, the process is very sensitive to small changes and disturbances.

Wastewater effluent discharged from a chemical plant is typically required to be in the pH range 6.0 to 9.0. This work details an attempt to refine and demonstrate an effective solution to the pH control problem. This work on pH control is based on the dual reagent injection approach, which involves splitting of the reagent stream and its sequential addition to the process influent in two separate portions. This method for pH control was patented by Riggs and Rhinehart (U.S. Patent #4,940,551). Excellent control has been achieved for acidic as well as alkaline streams at neutrality (pH=7.0), on a real time experimental system. The methods developed cannot only be applied to wastewater neutralization but also

used equally well for other pH control situations. A detailed description of the laboratory scale pH control experimental system and the experimental procedures involved is given in Chapter 2.

CHAPTER 2

EXPERIMENTAL SYSTEM AND ITS ANCILLARIES

The true test to determine the performance of any new algorithm is its successful implementation on a real time experimental system. Computer simulation and theoretical grounding are no doubt important; but it is the experimental component that lends credibility to the efficacy of an effervescing technology. An experimental system presents all the ingredients of what is to be expected in reality, like noise on the measured variables, drift, transportation lags and delays, deadtime, sensor inaccuracies, calibration errors, etc.

The experimental set-up used for this project is a laboratory scale on-line control scheme with a dual reagent injection strategy, as shown in Figure 2.1. This unit is designed to be compact and portable so that the technology can be tested at an industrial site. The concept of dual reagent injection has been patented by Riggs and Rhinehart (U.S. Patent #4,940,551, July 1990). The experimental system has been divided into separate components and each one is described in detail.

2.1 Influent and Reagent Flow System

Typically, wastewater from different sections in a chemical plant is combined into one stream and sent for further treatment and discharge. The tanks T1, T2 and T3 in Figure 2.1 represent the manufacturing plant containing different effluent streams (either acid or base) at different concentrations. Each tank is mounted 1.5 meters above the pumps and has a capacity of 30 gallons (114 liter) and is connected by a 1/2 inch (1.27 cm) stainless steel tubing and a rotameter. The three tubes, one from each rotameter, then join together in a cross to form a single process line which connects to pump P1 and the three pH sensors before finally emptying into a waste drum. Tank T4, which is also of 30 gallon (114 liter) capacity, supplies the reagent necessary to affect neutralization. The reagent tank is connected to another 1/2 inch (1.27 cm) stainless steel tubing that connects to pump P3 and joins the main process line after the first pH probe. There is a tubing connection between the reagent line and the main process line with a two-port three-way manual valve at the center. To allow either reagent or wastewater splitting, there is another 1/2 inch tubing emerging from this valve which passes through pump P2 and empties into the main process line just after the second pH probe. The three-way valve can direct flow through this tubing from either the reagent line or the process line.

Figure 2.1: In-Line pH Controller Experimental Set-up.

2.1.1 Metering Pumps

There are three positive displacement gear pumps labeled P1, P2 and P3 on Figure 2.1. These pumps are manufactured by Micropump Corporation (Model 211/56C). The pump motor is a 1/3 h.p. (249 W), 3450 rpm permanent magnet motor, manufactured by Pacific Scientific (Model SRF3616-4574-7-56BC). These pumps can deliver a continuous non-pulsating flow with a maximum capacity of 5.5 lit/min. It may be pointed out that very high flow rates or very low flow rates are not delivered controllably by the pumps. For best results, it is desirable to operate the pumps in an intermediate flow range, something between 1 lit/min. to 4.5 lit/min.

It was decided to adopt the following nomenclature for the metering pumps. Pump P1 which pumps the contrived plant effluent stream (the stream whose pH needs to be controlled) from tanks T1, T2 and T3 is called the influent pump. Pumps P2 and P3 which pump the reagent from tank T4, injecting it sequentially into the process line are called reagent pumps. It is to be noted that pump P2 can also be used to pump the influent by simply altering the knob position of the three-way valve. But, in our experiments we have not looked at the merits and demerits of influent splitting. Hence, it was decided to call pump P3 as the major reagent pump since it almost always delivers more than half of the total reagent flow. Likewise pump P2 is called the minor reagent pump.

Henceforth pumps P2 and P3 will be referred to as minor and major reagent pumps, respectively.

2.1.2 Pump Speed Controllers

These are the three 250D series variable speed DC controllers labeled as D1, D2 and D3 on Figure 2.1. They output a power voltage to the motor and thereby adjust flow from pumps P1, P2 and P3, respectively. These controllers are manufactured by Dart Controls Incorporation (Model no. 253D-200E). D1 has the "-5A" option arrangement, while D2 and D3 have the "-7A" option arrangement for receiving a 4-20 mA current signal. The "-7A" option has additional features, in the sense that it can be used in the auto as well as manual modes while the "-5A" has the auto option only. There is no difference between the two options as far as our purpose is concerned since we only need the auto mode. D1 just happens to retain the earlier version. The reader may wish to consult the Dart Controls 250D series variable speed control instruction manual for further information.

The D/A convertor board sends a 4-20 mA signal to each speed controller. Based on this current signal, the controller linearly adjusts the armature voltage thus regulating the pump speed and hence the flow rate. The relationship between the input current signal from the D/A board and the flow rate delivered by the pump is more or less linear. Hence the pump calibration equation, which is a plot

of the current in mA against the flow rate in lit/min., is a straight line.

2.1.3. In-Line Mixers

There are two static mixers in the process line, one each after every reagent injection point. They are labeled as M1 and M2 on Figure 2.1. After a reagent injection, the two streams have to be thoroughly mixed before the next pH reading is sampled, as this information is vital to the model and needs to be extremely accurate. Improper mixing will result in an inaccurate pH reading and cause the model to envision a titration curve which is different from that of the actual process. This could lead to incorrect control action. Hence the system has to be designed in such a way that enough residence time is provided for proper mixing and reaction completion. Acid-base neutralization reactions are almost instantaneous and hence reaction residence time may not be an issue. The mixing component has to be very carefully attended to. This is accomplished by the Kenics static mixer manufactured by Chemineer Incorporated (Model 1-KME-PVC-4).

The Kenics mixer which provides in-line continuous mixing, has no moving parts, requires no external power and no maintenance. The unit comprises a number of alternated short elements of right and left handed helices. It provides two simultaneous mixing actions, namely, flow division and radial mixing thus resulting in near plug flow characteristics. More

details are available from the manual on Kenics static mixers published by Chemineer, Inc.

2.1.4. Water Filters

There are two candle filters: one on the process line and the other on the reagent line just before the pumps. They are labeled as F1 and F2 on Figure 2.1. The filters remove undissolved particles from the streams to prevent clogging or fouling of the downstream equipment. Periodic cleaning or replacement of filter candles is essential for assurance of a continuous non-pulsating flow from the pumps.

2.2 pH Sensing and Transmission

The device that accomplishes the pH sensing/transmission consists of two parts which are:

- (1) pH sensor which measures the pH of the stream;
- (2) pH transducer which displays the measured pH and also relays the information to the computer.

The three pH probes are labeled as pH1, pH2 and pH3 on Figure 2.1 and their corresponding transducers will be designated as pHIT1, pHIT2 and pHIT3. The three pH sensors (Model FU25) and the three pH transducers (Model EXA pH400) are manufactured by Yokogawa Corporation.

All pH measurement systems are based on the principle of an electrochemical cell in which two electrodes are placed in a charge conducting solution called the electrolyte. An

electric potential develops between the electrodes. To measure pH, one electrode is constructed from a specially formulated glass membrane that responds to hydrogen ions by an exchange of mobile ions within the membrane structure.

The pH transducer receives the mV signal developed by the pH sensor and converts this signal into pH units for display. It further transmits the measured pH information to the computer work station in the form of a mA signal. The output from the transducer is a non-isolated 4-20 mA range analog signal which is equivalent to 0-14 pH units. For further information on the pH sensors and transducers and their calibration, the reader is advised to consult their respective manuals published by Signet Scientific.

2.3 Data Acquisition Hardware

Analyses of measured information and control decisions are made at the local work-station which is a Packard Bell PB286 12 MHz personal computer. The computer can accept and send only digital signals. The measured variables from the transducers (1-5 V) and the inputs to the speed controllers (4-20 mA) need to be analog signals. Thus for computer interfacing and control, all the analog input signals have to be converted into their digital equivalents and the digital output signals converted into their analog forms.

The former is accomplished by the analog-to-digital (A/D) convertor board, while the latter is accomplished by the

analog convertor (D/A) board. The circuitry for the data acquisition hardware is shown on Figure 2.2.

2.3.1 A/D Conversion

The A/D convertor board called DASH-8 is manufactured by Metrabyte Corporation. It is an 8-channel 12-bit high speed convertor, with an A/D conversion time of approximately 25-35 microseconds. DASH-8 requires eight consecutive address locations in the I/O space and this address is set by the Base Address D.I.P. switch to be on a 8-bit boundary anywhere in the P.C. decoded I/O space. Some I/O addresses are reserved for internal functioning and other peripheral devices. So, to provide flexibility in avoiding conflict with these devices, DASH-8's address locations have to be set by a Base Address. The Base Address for the DASH-8 board used in our experiment has been set to &H300 or 300 hex (decimal number 768). This address is not shared by any other peripherals. The DASH-8 board will now occupy the address locations &H300-&H307. Thus there are 8 analog input channels on DASH-8. The channels are single ended, i.e., they share a common (low level) ground.

The full-scale input of each channel is -5V to +5V corresponding to a digital number between -2047 to +2047. The output from the pH transducer, which is an analog signal of 4-20 mA corresponding to 0-14 pH units, has to be converted into a voltage signal for acceptance by the A/D board. Since the maximum current is 20 mA and the maximum input range is 5V, a

Figure 2.2: A/D and D/A Circuitry.

250 Ω shunt resistor is added in the loop. This converts the 4-20 mA signal into a 1-5 V signal, to be input to the A/D board. It is to be noted that the pH transmitter outputs are non-isolated signals, and the A/D channels share a common ground. Hence using a resistor alone is not sufficient. Therefore, a signal conditioner with an operational amplifier is inserted into this loop to change the non-isolated current signal into an isolated voltage difference. The A/D convertor board converts this 1-5V analog input into a digital number between 0-2047 decimal range, corresponding to 0-14 pH units. The function of the A/D board is controlled by the I/O driver routine DAS8.BIN, provided by the manufacturer Metrabyte Corporation. The A/D conversion software is explained in Appendix A. For more details on A/D conversion, the reader is advised to read the DASH-8 manual provided by Metrabyte Corporation.

2.3.2 D/A Conversion

The control action from the computer is a digital signal in the range 0-4095 decimal, which has to be converted into an analog 4-20 mA current signal. This is done by the D/A convertor board called DAC-02, also manufactured by Metrabyte Corporation. The DAC-02 is a 2 channel board, i.e., it can accept only two digital signals. It is a double buffered 12 bit convertor. The data supplied to the D/A board is 12 bits, which is broken into 2 consecutive bytes. The first byte

called the low byte is the least significant byte, comprising the four least significant bits of data. The second byte called the high byte is the most significant one and contains the most significant 8 bits of data. The least significant byte is written first and is stored in an intermediate register in the D/A. When the most significant byte is written, its data is added to the stored least significant data. This process is called double buffering.

The DAC-02 board also requires 8 consecutive addresses in the I/O address space. The I/O address locations are again set by the Base Address switch such that the addresses do not conflict with those of other peripheral boards. One signal conversion and transmission set requires four address locations. The four address locations are used for reference input, bipolar output, unipolar output and 4-20 mA output. Hence only two signal conversions can take place on one D/A board which means that only two speed controllers can be operated from one D/A board. Since there are three pumps and three speed controllers, two separate D/A boards have been used.

The Base Address for the first DAC-02 board has been set to &H330 (decimal number 816). The DAC-02 board will now occupy the address locations &H330-&H337 in I/O space. The address locations &H330 and &H331 are used for the major reagent pump P3 and its speed controller D3, while the locations &H332 and &H333 are used for the influent pump P1

and its corresponding speed controller D1. The Base Address for the second DAC-02 board has been set to &H370 (decimal number 880). The address locations &H372 and &H373 are used for the minor reagent pump P2 and its corresponding speed controller D2. D/A conversion software is explained in Appendix A. The reader is advised to consult the DAC-02 manual published by Metrabyte Corporation, for further details.

2.4 Preparation of Experimental Solutions

Neutralization and control of acidic as well as alkaline streams have been demonstrated. Hence both acidic and basic solutions were used as effluent as well as reagents. Acid wastewater characteristics were simulated and tested by preparing solutions of sulfuric acid, oxalic acid, acetic acid, acetic acid buffered with sodium acetate, phosphoric acid, hydrochloric acid and others. Basic wastewater characteristics were simulated and tested on prepared solutions of sodium hydroxide, ammonium hydroxide, ammonium hydroxide buffered with ammonium chloride, sodium carbonate and others. The acid reagent used for neutralizing basic solutions was sulfuric acid (strong acid) and the alkaline reagent used for neutralizing acidic solutions was sodium hydroxide (strong base). All solutions were prepared in the concentration range .01-.03 Normal, which is an approximate concentration range for many industrial waste streams.

However, the results can be easily extrapolated to higher or lower concentrations.

The acidic solutions were prepared in Lubbock city tap water which contains dissolved salts, such as bicarbonates and sulfates of several metal ions. The pH of Lubbock water is about 8.2. This implies that the acid solution prepared in Lubbock water will not be a pure acid solution but a complex mixture of the acid, unknown salts and free bases. Since industrial wastewater is also such a multicomponent unknown mixture, our prepared acidic solutions would represent an appropriate simulation of the same.

The alkaline solutions were prepared in deionized water rather than Lubbock city water due to the propensity of bases to induce precipitation in Lubbock water. Such precipitation is detrimental to our experimental set-up, because it can clog up the tubes, valves, filters and even degrade the performance of the gear pumps. During the design of an industrial system, this fact has to be borne in mind and a proper selection of equipment, especially filters, must be made. Hence this special preparation of alkaline solutions must be viewed only as a limitation of our experimental system to handle precipitation and not as a drawback in our control technology.

2.4.1 Calculation Procedures for Solution Preparations

This section lists some formulae and methods useful for calculation procedures, during the preparation of experimental solutions. This procedure is adopted from Natarajan (1993).

Many acids and bases are available in the form of their highly concentrated solutions in conventional glass bottles. The label on the bottle usually lists all relevant information like density, specific gravity, normality, weight percent, purity, etc. To prepare a dilute solution in the tank, one needs to know the volume of the concentrated liquid contained in the bottle, that has to be added. A formula such as the one given below can be used.

$$N = \frac{d_s \times V_s \times x}{E \times V}, \quad (2.1)$$

where, N : Required normality of the dilute solution,

d_s : Density of the concentrated solution in gm/ml,

V_s : Volume of the concentrated solution in ml,

x : Weight fraction of the component,

E : Equivalent weight of the component in
gm/gm equivalents,

V : Volume of the prepared dilute solution in liters.

Suppose it is required to calculate the volume of 98% concentrated sulfuric acid needed to prepare 60 liters of .02N sulfuric acid solution. Then Equation (2.1) yields:

$$V_s = \frac{.02 \times 49 \times 60}{1.836 \times .98} = 32.68 \text{ ml.}$$

The calculations need not be very accurate since the model does not know the influent concentration anyway and estimates it on-line as an adjustable parameter. This method is very useful when the normality of the concentrated solution is not specified on the bottle label.

If the normality of the concentrated solution is also known, then a simple rule can be used, which is:

$$N_A = \frac{N_B \times V_B}{V_A}, \quad (2.2)$$

where, N_A : Normality of the dilute solution,

N_B : Normality of the concentrated solution,

V_A : Volume of the dilute solution in ml,

V_B : Volume of the concentrated solution in ml.

The volume of concentrated ammonium hydroxide solution (normality 14.8) required to prepare 50 liters of 0.02N dilute solution of the same is given by Equation (2.2):

$$V_B = \frac{.02 \times 50000}{14.8} = 67.57 \text{ ml.}$$

Some reagents and usually all salts are available in the form of pellets or powders. In that case, we need to know the weight of the sample required to prepare a dilute solution.

The basic definition of normality can be used as:

$$N = \frac{W}{E \times V}, \quad (2.3)$$

where, N: Normality of the dilute solution,

W: Weight of the sample in gm,

E: Equivalent weight of the component in
gm/gm equivalents,

V: Volume of the dilute solution in liters.

For instance, the quantity of sodium hydroxide pellets required to make a .02N 50 liter solution is calculated from Equation (2.3):

$$W = .02 \times 40 \times 50 = 40 \text{ gms.}$$

An important fact has to be borne in mind while performing calculations for the preparation of phosphoric acid solution. Phosphoric acid is a triprotic acid with two of its dissociations below pH 7. The third dissociation occurs close to pH 12. Although, the equivalent weight of phosphoric acid is defined as its molecular weight divided by three, which is the number of replaceable hydrogen ions, only two hydrogen ions have been replaced up to neutrality. Hence, the volume of 85% concentrated phosphoric acid required to prepare 40 liters of 0.025N phosphoric acid solution is given from Equation (2.1) as:

$$V_s = \frac{0.025 \times 40 \times \frac{98}{2}}{0.85 \times 1.7} = 33.9 \text{ ml.}$$

2.5 Improvements over the Earlier Experimental System

Some modifications were made on the equipment set up worked upon by Natarajan (1993). They are detailed as follows:

(1) The three pH sensors (Model MK-712) manufactured by Signet Scientific Company were replaced by Model FU25 pH sensors manufactured by Yokogawa Corporation.

(2) The three pH transducers (Model MK 710A-3) manufactured by Signet Scientific Company were replaced by Model EXA pH400 pH transducers manufactured by Yokogawa Corporation.

2.6 Experimental Procedure

The general procedure and format common to all the experimental runs, is described here. Most of the control runs are for a period of about 20-25 minutes. For most of the experiments, the controller is tested for two disturbances within a run. The acidic and basic solutions prepared have concentrations in the range 0.015N to 0.025N. The concentration of salts used are in the range 0.01M to 0.02M. This is typical of industrial wastewaters found in practice. The reagent used to neutralize acidic streams is NaOH and that used to neutralize basic streams is H_2SO_4 . The reagent concentration used in all the experiments is 0.02N. For most of the runs, the influent flow rate is kept constant at 3 liters/min. Since the concentration of the influents range

from 0.015N to 0.025N, the total reagent flow rates (manipulated variable) will range from about 2 lit/min to 4.5 lit/min. Keeping in mind that one reagent pump delivers about 70% of the total reagent flow and the other pump the remainder 30%, the flow rates will be well within the controllable range of the metering pumps.

The steps during an experimental control run are in general as follows:

- (1) Open the reagent tank valve. Run the major reagent pump till a continuous non-pulsating flow is obtained at the end of the line. Stop the major pump and run the minor reagent pump till a continuous non-pulsating flow is obtained at the end of the line. This will ensure that the air bubbles are removed and the reagent line is flushed and filled with the reagent only and not water or any other liquid.

- (2) Open the valves on the influent tanks. Start the influent pump and run the two different test solutions through the process line, one at a time. This should be done until a continuous non-pulsating flow is seen at the end of the line, so that the air bubbles are expelled. The process line should be flushed with each test solution until all three pH readings are roughly the same, i.e., at steady-state. This would ensure that all parts of the process line are flushed and filled with the solutions to be used and not water or any other liquid. The solution to be subjected to the controller auto start-up routine should be the last to flush the process

line. All this is necessary to facilitate an easy automatic controller start-up.

(3) Load the controller program onto the quickBASIC environment along with the library routine DAS8 as QB/L DAS8 CONTROLPROGRAM.BAS and run it from the menu. This program can also be run directly from the DOS prompt, if an execution file has already been created.

(4) Simulate disturbances by opening and closing tank valves. After completion of the experiment, flush the process line with Lubbock city tap water.

The following experimental procedure is used for giving ramp upsets on our system. Two influent solutions differing in type and concentration are prepared and stored in two different influent tanks. Our set-up now has a separate pump to transfer liquid from one tank to the other continuously. So, a ramp upset is simulated by continuously transferring liquid from one tank to the other at a constant rate such that the type and concentration of the original liquid changes slowly and continuously.

CHAPTER 3

HEURISTIC MODELING

One of the most important things in nonlinear model based control is the development of a model, which represents the translation of the physical information contained in the process in to a mathematical form. Even when linear control techniques are used, a model can lend itself to simulation studies of the process.

A model can never be an exact representation of the process because it would have to be the same process or its replica in order to accomplish that. A model should be adequate enough to cover all the essential features of the process so that there is very little mismatch between itself and the process. Also a concurrent objective should be to keep it as simple as possible. The use of unnecessary complex nonlinear equations that might lead to problems of stability, convergence or require excessive computing time, should be avoided at all costs. Hence process modeling is no easy job, for one needs to be cognizant of all the requirements and endeavor to balance the opposing issues as efficiently as possible.

Our attempt at mathematically representing the pH process has been to develop a heuristic model. The titration curve which is a plot of the pH against the reagent to influent ratio, is the most vital piece of information as far as pH

control is concerned. Hence mimicking the most important characteristics of the titration curve would be the most logical place to start.

It is possible to analytically generate a titration curve for a single acid-single base system, provided the concentrations and dissociation constants are known. For a mixture of acids and bases, this task, although possible, will be simply monumental, requiring a lot of computer time. Hence for pH control, it is impractical to analytically model the titration curve by accounting for all the species present and all the reactions taking place.

Anyway, such a detailed model is not really called for. It is enough if we have a model that can mimic the salient features of the process like gain at the setpoint $\text{pH}=7.0$ and the inherent nonlinearity.

Examples of some nonlinear model based pH controllers for the traditional large tank process have been described by Henson and Seborg (1993), Burtusiak et al. (1989), Wright and Kravaris (1991) and Parrish and Brosilow (1988). The success of the model-based approach in control of crude product qualities is described by Friedman (1994).

3.1 Previous Work on the Same Experimental System

Choi and Rhinehart (1987, 1988) were the first to develop a model to describe the pH system. They modeled the acidic wastewater stream as a single fictitious acid described by two

parameters, which were the acid concentration and acid dissociation constant. The two parameter model obtained from only two data points (pH-ratio pairs) could not always effectively describe the salient features of the process. The dual-base injection scheme came into being with the collaboration between Riggs and Rhinehart and was explored when Williams (1989, 1990) took over this project. The third point provided needed information on the intermediate behavior. The earlier two parameters were retained but they were now determined from three data pairs using a least squares parameterization technique. Mahuli (1991, 1992), who worked on this project after Williams, incorporated a three-parameter nonlinear model. He described the acidic wastewater stream by two models. One was the Monoprotic Acid Plus Common-ion Salt (MACS) model, which handled streams whose inlet pH was greater than 3.5. The common-ion salt allowed for better description of buffered mixtures. The other was Monoprotic Acid Dihydroxyl Base (MADB) model, which handled streams whose inlet pH was less than 3.5. This model described buffering in the basic region. Mahuli's parameterization method required the solution to three nonlinear equations. Natarajan (1993, 1994), who worked on the project after Mahuli, found that by suitably tailoring and restructuring the model equations, the complicated nonlinear equations could in fact be reduced to three linear equations in three unknowns. Besides refining the models for acidic

wastewater control, Natarajan also developed analogous models for alkaline streams. He also incorporated into his model the concept of ubiquitous acid.

3.2 Development of Heuristic Model/Control Law

A typical acid influent would have a titration curve of the nature shown in Figure 3.1. A titration curve is the steady-state relationship of process response to manipulated action.

From Figure 3.1, we define s_1 as the slope between points 1 and 2.

$$s_1 = \frac{pH_2 - pH_1}{R_1} . \quad (3.1)$$

Similarly, s_2 is defined as,

$$s_2 = \frac{pH_3 - pH_2}{R_2 - R_1} , \quad (3.2)$$

where, R_1 is the ratio of $F_{\text{reagent}}/F_{\text{wastewater}}$ corresponding to the 1st base addition (80%) while R_2 is the ratio of $F_{\text{reagent}}/F_{\text{wastewater}}$ corresponding to 1st+2nd base additions (100%). pH_1 , pH_2 , pH_3 are the pH-measurement values. As can be seen from the Figure 2.1, the pH_3 value is not yet equal to 7. Since the objective is to maintain the pH of the acid at 7, in a primitive approach we can project s_2 up to $pH=7$ to give the new desired steady-state value of R_2 .

Figure 3.1 : Typical Titration Curve

$$S_2 = \frac{7 - pH_3}{R_{2new} - R_{2old}} . \quad (3.3)$$

Rearranging,

$$R_{2new} = R_{2old} + \frac{7 - pH_3}{S_2} . \quad (3.4)$$

The basic control law then becomes,

$$R_{2new} = R_{2old} + \Delta R_2 , \quad (3.5)$$

which is very similar to the standard velocity mode algorithm.

This equation means that if the pH of the acid is to be brought to 7 then R_{2new} is the desired ratio of the base to acid flow rate. However, there are some problems associated with this approach.

First, when a change of ΔR_2 is made, the influence is not measured instantaneously. There are fluid transport delays, and both sensor and final control element lags associated with the system. Equation (3.5), however, duplicates the control action at each sampling. The first modification is to reduce ΔR_2 by the number of the samplings in the transient.

Using ,

$$\begin{aligned} T &= \text{sampling period (.5 secs),} \\ F_{\text{Total}} &= \text{total flow rate (reagent + process} \\ &\quad \text{water),} \\ V &= \text{pipe volume from } R_1 \text{ rejection to } pH_3, \\ \tau &= \text{sensor lag time (1 sec),} \\ \theta &= \text{transport delay time (= } V/F_{\text{Total}} \text{),} \end{aligned}$$

3τ = sensor effective response time,
 $(3\tau+\theta)/T$ = number of samplings passed before the
control action is completely expressed.

The basic control equation becomes,

$$R_{2new} = R_{2old} + f \frac{7 - pH_3}{s_2}. \quad (3.6)$$

where

$$f = \frac{T}{3\tau + \frac{V}{F_A + F_B}}.$$

Second, the control action assumes that s_2 is constant to the setpoint. If not, then the process is nonlinear and the above linear projection should be modified. We will use s_1 and s_2 to indicate whether the process is linear or not.

If $s_2/s_1 \gg 1$, then we have a strong (fully dissociated) dominant component in the process water and a very small change has to be made to ΔR_2 . If $s_2/s_1 = 1$, then we have a buffered and/or weak dominant component and a small change is required. If $s_2/s_1 \ll 1$, then there may be an intermediate dissociation, a plateau and again a very small change in ΔR_2 is required so that s_2 does not extrapolate well beyond the plateau.

The control law then becomes

$$R_{2new} = R_{2old} + f \alpha \frac{7 - pH_3}{s_2}, \quad (3.7)$$

where α depends on the s_1 to s_2 comparison and accounts for the type change in the influent. For example, if the type of the influent mixture changes, the value of s_2/s_1 will change. Thus, the value of α is decided based on the new s_2/s_1 value. The functionality of α with s_2/s_1 will be as shown in Figure 3.2. The numerical break point values were initially chosen by experience and then subsequently fine tuned to those shown, i.e., 1/8, 1/16, 0.5, 2 by experimental trials. These are purely heuristic values.

Third, either because of the characteristic nature of an acid or a ramp type of disturbance, the offset may persist on one side of the pH setpoint. If this offset persists for an increasing amount of time, more aggressive action is called for. Here the symbol β is the ΔR_2 multiplier that will account for the extra aggressive action to be used. The value of β is decided based on the number of samplings for which an offset persists without crossing pH_{sp} . The term "f" was previously defined as the number of samplings until control action can be measured. Now we define "sum" as the number of samples when pH_3 is continuously on one side of pH_{sp} .

Define, $RN = sum * f$, where RN is the number of transients for which an offset has persisted. The functionality of β with RN is as given in Figure 3.3. This, too, is purely experiential.

By experience it was also decided that as soon as the value of pH_3 would increase beyond $pH=8$, the value of sum

Figure 3.2 : Functionality of Alpha versus s_2/s_1

Figure 3.3 : Functionality of Beta versus RN

would be reset to a value such that $RN=3$ and β would start increasing linearly with RN . Also, to prevent pH excursions and overcompensations, it was decided to reset the value of sum to 0 when pH_3 decreased below $pH=8$. This ensured that the controller did not take too aggressive an action when the pH was well on its way to being controlled.

Thus, the control law now becomes

$$R_{2new}=R_{2old}+f\alpha\beta\frac{7-pH_3}{s_2}. \quad (3.8)$$

Thus we can write this equation as

$$R_{2new}=R_{2old}+fu, \quad (3.9)$$

where

$$u=\alpha\beta\frac{7-pH_3}{s_2}.$$

Fourth, there exists a possibility that pH_3 may be very much lower than pH_{sp} (in case of a major disturbance). In such an event, an even more aggressive action is called for. In such a case, we increase R_2 by 10%, if $pH_3 < 5$.

Thus, if $pH_3 < 5$, then

$$R_{2new}=R_{2old}+0.1R_{2old}f. \quad (3.10)$$

Fifth, there also exists a possibility that pH_2 may be very high. In that case we decrease the value of R_2 by 10%, if $pH_2 > 8$. Thus, if $pH_2 > 8$, then

$$R_{2new}=R_{2old}-0.1R_{2old}f. \quad (3.11)$$

Thus, it can be seen that after considerations of various possibilities, we have three different control laws. For normal operation ($pH_2 < 8$ and $pH_3 > 5$), use Equation (3.9). If $pH_2 > 8$, use Equation (3.10). If $pH_3 < 5$, use Equation (3.11). However, it is possible to combine all three equations to give a general equation of the type,

$$R_{2new}=R_{2old}+f\delta\epsilon u, \quad (3.12)$$

where $u = (7-pH_3)\alpha\beta /s_2$ if $pH_3 > 5$ and $pH_2 < 8$ otherwise, $u = 1$. Further, $\delta = 0.1 R_{2old}$ when $pH_3 < 5$ otherwise, $\delta = 1$. And, $\epsilon = -0.1 R_{2old}$ when $pH_2 > 8$ otherwise, $\epsilon = 1$.

Sixth and finally, we introduce another parameter, γ , which we will call the operator's tuning parameter. This is just a provision for the on-line manual adjustment of the value of ΔR_2 if the control seems to be either too aggressive or too sluggish. Currently, γ has a value of 1.

Thus, the complete heuristic-model-based control law would be

$$R_{2new}=R_{2old}+fu\delta\epsilon\gamma. \quad (3.13)$$

3.3 Caustic Wastewater neutralization

A duplicate but complementary logic can be developed for the acidic neutralization of the caustic influent.

3.4 Standard Fuzzy Logic Implementation

Based on the above logic, standard Fuzzy Logic Control has also been demonstrated on this experimental system (Parekh et al., 1994). The results of the standard fuzzy logic control were exactly the same as those for the heuristic model based control presented here.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the actual control results obtained with the heuristic model based pH controller. The experimental runs were conducted on the laboratory scale set-up described in Chapter 2. Control performance for a wide variety of acidic as well as alkaline streams have been investigated. This has been done for different types of disturbances that occur in practice, especially for the worst case conditions. Also, the results obtained from tests performed on actual industrial wastewater samples supplied by a chemical plant, have been presented. The controller has been installed at the Heating and Cooling Plant #1 at Texas Tech University, to withdraw wastewater from the waste pit during the regeneration of the ion-exchange system. Results of the controller working in an industrial setting are also presented.

4.1 Results for Step Upsets

A step change is a sudden and instantaneous change; theoretically a change that occurs within zero time. A perfect step change is only an ideality. Step changes are given on our system by opening or closing feed storage tank valves. The time required to open and close valves, the transport delay associated with the flow of influent from the

tank to the pH probes and time constant of mixing in the water filter, all make the supposedly instant change to occur over a period of 25 to 30 seconds.

A step change is the most severe of the upsets. The controller performance for step changes in the type of the influent as well as concentration, has been explored. The "type" of the influent is based on two characteristics; mainly the gain of the titration curve at neutrality and the inlet pH. Step changes can be made only in concentration or only in type of influent, but these would be a subset of the type-plus-concentration step change. Therefore, the results obtained for type-plus-concentration changes have been presented here.

The type-plus-concentration step changes are the most difficult control tasks for any pH control scheme. These can be considered to be the ultimate test of the controller performance. The controller has to not only respond to the concentration change by changing the manipulated input, but also intelligently adapt itself to a change in the gain characteristics (type) of the system.

The results of five different experimental runs involving type-plus-concentration step changes are presented. Unless stated otherwise, the runs are co-intuitive which means that a stronger influent requires more reagent for neutralization than a weaker one. The control interval is of 0.5 seconds. The reagent used for acidic neutralization runs is 0.02N NaOH

and that used for basic neutralization runs is 0.02N H_2SO_4 , unless stated otherwise.

4.1.1 Moderately Strong Acid to Buffered Strong Acid and Back

The buffered system used in this case is a mixture of 0.02N acetic acid and 0.015M sodium acetate. The moderately strong acid is 0.025 N oxalic acid. Figure 4.1 shows a typical control result. Up to 180 seconds, the influent was a moderately strong acid, which is characterized by a low inlet pH and a high gain at neutrality. At about 180 seconds, the influent was switched to a buffered mixture which is characterized by a high inlet pH and a low gain at neutrality. At about 460 seconds, the influent is again switched back to the strong acid. As can be seen from Figure 4.1, the controller does a fair job at keeping the pH at the setpoint when the system is subjected to the 2 disturbances. The change in the gain at neutrality is indicated by the change in the $\text{pH}_3 - \text{pH}_2$ value, when a change is made in type and concentration of the influent.

The reagent flow rate is illustrated in Figure 4.2. The plot of β (beta) and RN versus time and that of α (alpha) and s_2/s_1 versus time are illustrated in Figures 4.3 and 4.4, respectively. As can be seen from Figure 4.4, α does not vary at all and remains constant at .0625 since the value of s_2/s_1 does not go below 2.4. As explained earlier β is a function

Figure 4.1 : Response to step upsets from moderately strong acid to buffered system and back. pH versus Time

Figure 4.2 : Response to step upset from moderately strong acid to buffered system and back. Base Flow Rate versus Time.

Figure 4.3 : Response to step upsets from moderately strong acid to buffered system and back. Beta and RN versus Time.

Figure 4.4 : Response to step upsets from moderately strong acid to buffered system and back. Alpha and s2/s1 versus Time.

of RN where $RN = f * \text{sum}$. It should be noted here that pH_3 neither decreases below $pH=5$ nor does pH_2 increase beyond $pH=8$. Thus, the values of δ and ϵ are maintained at 1.

4.1.2 Weak Acid to Triprotic Acid and Back

The weak acid is 0.025N acetic acid and the multiprotic acid is 0.02N phosphoric acid. Figure 4.5 illustrates a counter-intuitive change. Up to 170 seconds, the influent was a weak acid which is characterized by a moderate gain at neutrality and a high inlet pH. At 170 seconds, the influent was switched to a multiprotic strong acid which has a very low gain at neutrality. Since the inlet pH decreased, it would imply a more concentrated acid which would require a base increase. Yet as seen in Figure 4.6, the base flow rate decreased. This is because the weak acid (having a higher inlet pH) had a higher concentration than the strong acid (having a lower inlet pH). A ratio or a feedforward controller would have taken an opposite control action from that required. On the other hand, the heuristic-model-based controller tracks the changes in the pH and also changes the reagent flow rate correctly and in the right direction. At about 450 seconds, the influent pH is switched back to the concentrated weak acid. The pH excursions at this time is because the excess base pushed the system to a higher pH. The β and RN versus time plot and α and s_2/s_1 versus time plot are

Figure 4.5 : Response to step upset from weak acid to triprotic acid and back. pH versus Time.

Figure 4.6 : Response to step upset from weak acid to triprotic acid and back. Base Flow Rate versus Time.

Figure 4.7 : Response to step upset from weak acid to triprotic acid and back. Beta and RN versus Time.

Figure 4.8 : Response to step upset from weak acid to triprotic acid and back. Alpha and s_2/s_1 versus Time.

illustrated in Figures 4.7 and 4.8, respectively. Here too the pH_3 does not go below $pH=5$ and pH_2 does not go above $pH=8$. Thereby δ and ϵ are maintained at 1.

4.1.3 Strong Acid to Triprotic Acid and Back

The strong acid is 0.02N sulfuric acid while the triprotic acid is 0.025N phosphoric acid. Figure 4.9 illustrates, perhaps, the most extreme type of change possible. Up to 185 seconds, the influent is a dilute strong acid which is characterized by a low inlet pH and a very high gain at neutrality. At 185 secs, the influent was switched to a concentrated multiprotic strong acid characterized by a slightly higher inlet pH and an extremely low gain at neutrality. At about 470 seconds, the influent was switched back to the dilute strong acid. As can be seen from Figure 4.9, when the first change was made, the pH_3 value deviates only slightly from $pH=7$. As can be seen from Figure 4.9 when the influent is a strong acid the difference between pH_2 and pH_3 is high. This is indicative of a high gain system. On the other hand, when the influent is a multiprotic strong acid, the difference between pH_2 and pH_3 is not high which in turn is indicative of a low gain system. The reagent flow rate, shown in Figure 4.10, increases in such a way that the pH_3 value hardly deviates from the setpoint $pH=7$. However, when the second change is made back to the dilute strong acid, a pH excursion results due to the fact that the base flow rate

Figure 4.9 : Response to step upset from strong acid to triprotic acid and back. pH versus Time.

Figure 4.10 : Response to step upset from strong acid to triprotic acid and back. Base Flow Rate versus Time.

Figure 4.11 : Response to step upset from strong acid to triprotic acid and back. Beta and RN versus Time.

Figure 4.5 : Response to step upset from weak acid to triprotic acid and back. pH versus Time.

decreases slightly more than it should have. The controller immediately "realizes" the overcompensation and increases the base flow rate to the desired value. Figure 4.11 shows the plot of β and RN versus time while Figure 4.12 shows the plot of α and s_2/s_1 versus time.

4.1.4 Weak Acid to Buffered Acid System and Back

In this case, the weak acid used is 0.023N acetic acid, and the buffered acid system is a mixture of 0.02N acetic acid and 0.015M sodium acetate. The control results are shown in Figures 4.13, 4.14, 4.15 and 4.16. Figure 4.13 is the plot of the three pH values versus time. Figure 4.14 shows the response of the manipulated variable, which is the base flow rate. Figure 4.15 shows the plot of β and RN versus time, while Figure 4.16 shows the plot of α and s_2/s_1 versus time. Up to 190 seconds, the influent was a weak acid which is characterized by a high inlet pH and a moderate gain at neutrality. At 190 seconds, the influent was switched to a buffered system which has a higher inlet pH and a very low gain at neutrality. In about 100 seconds, the controller brings the effluent pH back to the setpoint of 7. The minor pH excursion is due to the slight undercompensation of the controller. At about 450 seconds, the influent is switched back to the weak acid system. The control is excellent and

Figure 4.7 : Response to step upset from weak acid to triprotic acid and back. Beta and RN versus Time.

Figure 4.14 : Response to step upsets from weak acid system to buffered system and back. Base Flow Rate versus Time.

Figure 4.15 : Response to step upset from weak acid system to buffered system and back. Beta and RN versus Time.

Figure 4.16 : Response to step upsets from weak acid system to buffered system and back. Alpha and s2/s1 versus Time.

for most part within ± 0.1 units of pH 7. Also the pH 6-9 range is hardly violated. The manipulated variable changes by about 20% on either side.

4.1.5 Strong Base System to Buffered Base System and Back

The buffered system used in this case is a mixture of 0.018N ammonium hydroxide and 0.015M ammonium chloride. The strong base is in the form of a 0.027N solution of sodium hydroxide. The start-up is performed with the strong system. At about 180 seconds a step change is made to the buffered system and this change is reversed at 480 seconds. This again is an extremely severe type-plus-concentration change on the alkaline side. The inlet pH changes by about 2.5 units and the reagent (acid) flow rate, as seen in Figure 4.18, changes by almost 50%. The setpoint gain change is also drastic, going from a high gain system for a strong base to a low gain system for a buffered system. Figure 4.17 shows the three pH values plotted versus time. The effluent pH strays outside the pH 6-9 range for about 50 seconds when the first disturbance is made. As a result of this ϵ is triggered. During the second disturbance, the effluent pH strays outside the pH 6-9 range only for about 20-25 seconds and thus δ is triggered. This is indeed excellent control for such an extreme change. The plot of β and RN versus time is given by

Figure 4.17 : Response to step upsets from strong base to buffered system and back. pH versus Time.

Figure 4.18 : Response to step upsets from strong base to buffered system and back. Base Flow Rate versus Time.

Figure 4.19 : Response to step upsets from strong base to buffered system and back. Beta and RN versus Time.

Figure 4.20 : Response to step upsets from strong base to buffered system and back. Alpha and s2/s1 versus Time.

Figure 4.19 while the plot of α and s_2/s_1 versus time is given by Figure 4.20.

4.2 Results of Ramp Tests

A ramp change is a less severe upset than a step change. It is a slow but continuous change in the influent to the process, unlike the step disturbance which is a sudden change. While not as instantaneously severe, the control problem associated with a ramp is the sustained offset in process variable as the feedback controller tries to catch up. A ramp disturbance is the most common form of upset occurring in an industrial setting. Sudden and drastic step changes occur very seldom, because the wastewater neutralization facilities are usually far downstream and in-line blending smears upstream events. Disturbances in industrial pH can be caused by changes in production throughput, batch operations and environmental changes like rain water.

The controller performance for ramp disturbances in the type-plus-concentration of the influent is presented here.

4.2.1 Weak Acid to Strong Acid

The weak acid is 0.025N acetic acid and the strong acid is 0.02N sulfuric acid. Figure 4.21 illustrates a counter-intuitive ramp change from a concentrated weak acid to a dilute strong acid. The ramp change is given over a period of 900 seconds. Despite the continuous disturbance on the system

Figure 4.21 : Response to ramp upset from weak acid to strong acid. pH versus Time.

Figure 4.22 : Response to ramp upset from weak acid to strong acid. Base Flow Rate versus Time.

Figure 4.23 : Response to ramp upset from weak acid to strong acid. Beta and RN versus Time.

Figure 4.24 : Response to ramp upset from weak acid to strong acid. Alpha and s2/s1 versus Time.

the controller maintains the value of the effluent pH between pH=6.8 and pH=7.8. The base flow rate illustrated in Figure 4.22 is a constantly decreasing manipulated variable. Plots of β and RN versus time and α and s_2/s_1 versus time are shown in Figures 4.23 and 4.24, respectively. α in this case remains constant at 0.0625, since the ratio of the slopes remains above 2.5.

4.2.2 Buffered Acid System to Strong Acid System

The strong acid is a 0.025N sulfuric acid and the buffered system is a mixture of 0.02N acetic acid and 0.015M sodium acetate. This is a co-intuitive change. Start-up is performed with the buffered system, which is ramped to the strong acid system over a period of 1000 seconds. Figure 4.25 shows the responses of the three pH values versus time. The control is excellent and the outlet pH always stays within the pH 6-9 range. In fact, the pH never goes beyond ± 0.5 units of the setpoint. The base flow rate shown in Figure 4.26 is a constantly increasing manipulated variable. β and RN versus time is shown in Figure 4.27, while α and s_2/s_1 versus time is shown in Figure 4.28.

4.2.3 Buffered Base System to Strong Base

The buffered system is a mixture of 0.025N ammonium hydroxide and 0.015M ammonium chloride while the strong base

Figure 4.25 : Response to ramp upset from buffered system to strong acid. pH versus Time.

Figure 4.26 : Response to ramp upset from buffered system to strong acid. Base Flow Rate versus Time.

Figure 4.27 : Response to ramp upset from buffered system to strong acid. Beta and RN versus Time.

Figure 4.28 : Response to ramp upset from buffered system to strong acid. Alpha and s2/s1 versus Time.

is a 0.012N solution of sodium hydroxide. Figure 4.29 shows the the three pH values versus time for the ramp-change. The ramp change is made from a concentrated buffered mixture to a dilute strong base (counter-intuitive). The base flow rate (Figure 4.30), shows that the buffered mixture is more than twice concentrated than the dilute strong base. In spite of the extreme nature of the change, the controller maintains the pH of the effluent mixture between pH=6 and pH=7. The average effluent pH over the total period of experimentation would be about 6.5 which is well within standard discharge limits of 6 to 9. Figure 4.31 illustrates the behavior of β and RN versus time, while Figure 4.32 illustrates the behavior of α and s_2/s_1 versus time.

4.3 Control Results Obtained on Actual Industrial Wastewater

So far we have discussed control results involving laboratory prepared experimental solutions that were used to simulate industrial wastewater characteristics. This section presents the control results obtained on actual industrial wastewater supplied to us by a chemical company. Also our controller has been installed at the Heating and Cooling Plant #1 at Texas Tech University, to withdraw wastewater from the waste pit during the regeneration of the ion-exchange system. This section also presents control results obtained in an industrial setting.

Figure 4.29 : Response to ramp upset from buffered system to strong base. pH versus Time.

Figure 4.30 : Response to ramp upset from buffered system to strong base. Base Flow Rate versus Time.

Figure 4.31 : Response to ramp upset from buffered system to strong base. Beta and RN versus Time.

Figure 4.32 : Response to ramp upset from buffered system to strong base. Alpha and s2/s1 versus Time.

4.3.1 Control results obtained on wastewater samples

A leading chemical company supplied us with two of their wastewater solutions, representative of their highest and lowest pH values. The wastewaters are acidic comprising a mixture of acids like acetic, propionic and several others.

The wastewater solutions are about five to six times as concentrated as our conventionally prepared laboratory solutions. Thus reagent NaOH was prepared of concentration 0.1N, so that the reagent flow rates will be in the controllable range of the metering pumps. The pH of sample A is about 2.9 and that of sample B is about 1.4. Sample B seems to have a slightly steeper gain at neutrality than sample A.

The start-up is performed with sample A. At about 150 seconds, a step change is made to sample B. This happens to be only a type change and not a type-plus-concentration change, because the concentrations of the two samples are almost the same even though the pH was one unit different. The inlet pH decreases by about 1.5 units. The reverse step change back to sample A is administered at about 435 seconds. Figure 4.33 shows the response of the three pH values with time. The control is extremely good, with the pH_3 staying within the ± 0.5 units of the setpoint for most part of the run. Figure 4.34 shows the plot of the base flow rate versus

Figure 4.33 : Response to step upsets from type A to type B wastewater and back. pH versus Time.

Figure 4.34 : Response to step upsets from type A to type B wastewater and back. Base Flow Rate versus Time.

Figure 4.35 : Response to step upsets from type A to type B wastewater and back. Beta and RN versus Time.

Figure 4.36 : Response to step upsets from type A to type B wastewater and back. Alpha and s2/s1 versus Time.

time. Figure 4.35 shows the plot of β and RN versus time while the plot of α and s_2/s_1 is illustrated by Figure 4.36.

4.3.2 Control results in actual Industrial Setting for acidic Influent

The ion exchange regeneration procedure at Texas Tech Heating and Cooling Plant #1 results in generation of an acidic influent. We used our laboratory in-line system to neutralize this acidic influent. Figure 4.37 shows the pH values versus time. The line marked pHsp is the setpoint for the controlled pH. During the automated start-up period (0 to 200 seconds) the controller increased the ratio to about 2.1 to hold the effluent pH at the setpoint of 7. pH(4) represents the pH after downstream mixing blends the pH(3) material. Ideally, pH(4) should equal pH(3) but something (calibration differences, downstream CO₂ adsorption, slow hydrolysis reactions, imperfect mixing prior to pH(3), etc.) makes it less than pH(3) during the 1000 to 2700 second period. It can be seen that pH(3) tracks the setpoint really well and that the value of pH(4) was successfully moved to 7. During the 2700 to 4000 second period, a sequence of step changes in the setpoint for pH(3) were made. The controller could move and hold the process at the setpoint values of 5, 7 and 9. This indicates that the controller has wider pH control applicability than simply neutralization.

Figure 4.37 : pH versus Time. Beta Site Test Results. Ion Exchange Regeneration. Acidic Influent.

**Figure 4.38 : Ratio of Reagent to Influent Flow versus Time.
Beta Site Test Results. Ion Exchange Regeneration.
Acidic Influent**

At 4000 seconds, we created our first unmeasured disturbance by dumping some concentrated NaOH into the reagent tank. After a temporary excursion, the controller returned the pH to the setpoint. Figure 4.38 shows the reagent to the acid flow ratio versus time. The manipulated variable dropped 25%. Then at 4800 seconds, we created a second disturbance by continuously diluting the reagent. While the manipulated variable increased by 22% during the 4800 to 5800 second ramp period, pH(3) was held slightly off setpoint (characteristic of a ramp disturbance).

4.3.3 Control results in actual Industrial Setting for caustic Influent

Figure 4.39 shows the pH values versus time for a caustic influent. The controller took about 500 seconds to bring the effluent pH to the setpoint. The variability of pH(3) between a pH of 6 and 9 indicates that the system is highly nonlinear and even small changes in reagent flow rate can bring about big changes in the pH. On the whole, it can be seen that pH(3) tracks the setpoint of 7 really well. At about 1400 seconds, an unplanned disturbance hits the system and the controller does well to bring pH(3) back to the setpoint. Step changes are made in the setpoint from a pH of 7 to 5.5 at 2100 seconds and from 5.5 to 8.5 at 2800 seconds. The controller is seen to track these setpoint changes really well. Figure 4.40 shows the plot of reagent flow rate versus time.

Figure 4.39 : pH versus Time. Beta Site Test Results. Ion Exchange Regeneration. Caustic Influent.

**Figure 4.40 : Ratio of Reagent to Influent Flow versus Time.
Beta Site Test Results. Ion Exchange Regeneration.
Caustic Influent.**

CHAPTER 5

DYNAMIC SIMULATOR

5.1 Description of the Dynamic Process Simulator

Choi et al. (1993) offered a dynamic simulator for pH-Control studies. This simulator was used as a basis for the development of a dynamic process simulator that mimics the experimental system described in Chapter 2. The dynamic simulator is based on the same assumptions, restrictions, electrochemistry and mixing dynamics as proposed by Choi et al. (1993). These assumptions are:

- (1) The mixing/reaction process is isothermal.
- (2) The salts dissociate completely.
- (3) The salt ion concentrations do not exceed their solubility product and there are no precipitates.
- (4) The activity coefficients of all components are unity.
- (5) The ionic reactions are instantaneous, in relation to other dynamic effects.
- (6) Third step dissociations of triprotic acids and trihydroxyl bases are unimportant.
- (7) Dissolved gases are unimportant.
- (8) Interactions are limited to water, four acids, four bases and eight common ion salts.

To calculate the pH, one must know the total H^+ ion concentration in the system.

The H^+ ion concentration is obtained by the summation of the dissociated amounts of strong and weak acids and strong and weak bases.

The process model has been derived by Choi et al. (1993) based on a series of equilibrium statements of the multicomponent system. They are equilibrium relations which can be restated as a set of nonlinear algebraic relations. If one assumes the total hydrogen ion concentration (or equivalently the pH) and inserts it into the water equilibrium relation the total hydroxyl ion concentration becomes known. Then the remaining 8 equations reduce to a set of 8 linear equations. This set of 8 linear equations can be solved by using a linear equation solver LINPAC obtained from Riggs (1988). Using the solution of the linear set of equations, one can calculate the total hydrogen concentration. By comparing the initial guessed and the calculated values of H^+ ion concentration, the search will continue until the gap is reduced to 0.0001 pH units. The bisection method is used for the pH search.

The sequence of steps in which the current process simulator operates is as follows.

- (1) Composition drift is added to the influent compositions to express non-stationary influent behaviour. Also drift is added to the influent flow rate.
- (2) Using the model definition proposed by Choi et al. (1993) to calculate the pH of the influent process stream.

- (3) Sensor lag, calibration drift and noise are added to the deterministically calculated pH to obtain measured influent pH, i.e., P1.
- (4) After the 1st reagent injection, the concentration of the influent species and reagent species are delayed in order to account for the transport delay to the second pH sensor.
- (5) Solving the mass transfer equations using the delayed concentration values to determine new "active" zone concentration.
- (6) Using the model definition proposed by Choi et al. (1993) to calculate the pH after the first reagent injection.
- (7) Sensor lag, calibration drift and noise are added to the deterministically calculated pH to obtain the measured intermediate pH, i.e., P2.
- (8) After the second reagent injection, the concentration of the species in the process stream are delayed in order to account for the transport delay to the third pH sensor.
- (9) Solving the mass transfer equations using the delayed concentration values to determine the new "active" zone concentration.
- (10) Using the model definition proposed by Choi et al. (1993) to calculate the pH after 2nd reagent injection.
- (11) Sensor lag, calibration drift and noise are added to the deterministically calculated pH to obtain the effluent pH, i.e., P3.

5.2 Simulator Results

5.2.1 Open Loop results

Figure 5.1 shows the open-loop response of the dynamic simulator to step changes in influent concentration and in reagent flow rate. In the beginning, the entire pipeline is filled with water and all pH readings, i.e., pH1, pH2, pH3, are 7. At about 50 seconds, the acidic influent enters the system and pH1 drops almost immediately to a pH of 3, which happens to be the pH of the influent. Initially, the influent stream contains 0.005 mol/lit of a diprotic weak acid, 0.005 mol/lit of a monoprotic weak acid and 0.0005 mol/lit of a diprotic strong acid. At the flowrate of 60 lit/min, the transportation delay between pH1 sensor and pH2 sensor is about 10 seconds and the transportation delay between pH2 sensor and pH3 sensor is about 80-85 seconds. The transportation delay can be very clearly seen in the Figure 5.1, where pH1 drops to pH of 3 first, followed by pH2 and then by pH3.

At about 500 seconds, a step change is given in the influent concentration. Of a monoprotic strong acid, 0.005 mol/lit is added to the influent stream. Again, pH1 is the first to drop to a pH of 2.1, followed by pH2 and then by pH3.

At about 1500 seconds, 0.25 lit/min of reagent is added to the system. The reagent is a monovalent strong base having a concentration of 3 mol/lit. This reagent stream is split in to two parts as shown in Figure 2.1. The first injection is

Figure 5.1 : Open Loop Response of Dynamic Simulator
pH versus Time.

Figure 5.2 : Open Loop Response of Dynamic Simulator
Reagent and Influent Flow versus Time.

80% of the total reagent and the second injection is the remaining 20%. After a transportation delay of about 5 seconds, pH2 starts increasing. Since 20% of the reagent is being added at the second injection point, pH3 starts increasing and reaches a pH of about 2.4 after a transportation delay of 5 seconds from the second injection point. After 70-75 seconds of transportation delay, pH3 starts increasing rapidly since by now it has seen all the reagent that had been added.

5.2.2 Control results

Figure 5.3 shows the control results on the dynamic simulator. The initial influent character is the same as described in the previous section. Also, the reagent is a monovalent strong base having a concentration of 3 mol/lit. A ramp change in the influent flow is made from 600 lit/min to 60 lit/min in the time period from 400 seconds to 800 seconds. This ramp change can be very clearly seen in the Figure 5.5. The control is so good that hardly any deviations from the setpoint can be seen. At 1500 seconds, a step change in the concentration is made. The concentration of the diprotic weak acid is reduced from 0.005 mol/lit to 0.0005 mol/lit. In about 200 seconds, the controller brings the effluent pH back to 7. The severity of the step upset is indicated in Figure 5.4, where the ratio of the reagent to the influent flow is seen to drop by 50%.

Figure 5.3 : Control Results on Dynamic Simulator
pH versus Time.

Figure 5.4 : Control Results on Dynamic Simulator
Ratio of Reagent to Influent Flow versus
Time.

**Figure 5.5 : Control Results on Dynamic Simulator
Reagent and Influent flow versus Time**

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The difficult problem of pH control has been successfully solved using the heuristic-model-based-control algorithm. This technique has been applied to achieve excellent control results at neutrality for various acidic as well as alkaline streams. The experiments were conducted on our laboratory scale set-up, using the dual-reagent injection scheme. The pH controller has been tested for a wide variety of upsets and disturbances, on both acidic and alkaline streams. This testing has been done on laboratory prepared solutions, actual industrial wastewater solutions as well as in an actual industrial setting.

The controller was tested for step upsets in type-plus-concentration, for both acidic and basic streams. The "type" upsets included very drastic neutrality gain-changes, ranging from a flat gain for buffered systems to extremely steep ones found in the case of strong acids and bases. This represents the worst kind of upset; a rarity as far as an industrial pH control setting is concerned. The controller performance was outstanding. The outlet pH was brought back to within ± 0.2 unit of 7.0 in 60 to 70 seconds following a drastic step upset, for most of the runs. The pH 6-9 limits were violated for very short times, in most cases for about 15 to 20 seconds

immediately after a drastic step upset. The pH controller was also tested for type-plus-concentration ramp disturbances, on both acidic as well as alkaline streams. These are more common in an industrial situation. The results were so good that the outlet pH never violated the pH 6-9 range, throughout the ramp.

The experimental set-up was taken to an actual industrial site where the controller was successfully implemented on acidic as well as on alkaline streams. The success of this controller is exhibited in the fact that it has been successfully implemented, on a commercial scale version of the laboratory set-up in a leading chemical refinery in West Texas.

The development of a dynamic process simulator that mimics the experimental system was found to be particularly useful when the heuristic-model-based-controller is to be applied on a commercial scale. The dynamic process simulator can serve to simulate the industrial wastewater on which the controller has to be applied. This controller can be fine tuned for the commercial application without actually going on the industrial setting, thereby making the commercial application much less difficult.

6.2 Recommendations

The heuristic-model-based-controller has been applied on a commercial scale at one industrial site. The next step

would be the testing of this controller at a variety of industrial sites, like refineries, power plants, food processing plants, pharmaceutical set-ups and many other applications. For commercial application, the first step would be to gain as much information about the industrial wastewater as possible and simulate that on the dynamic process simulator. After that, the controller should be fine-tuned for that specific commercial application before it is applied on an actual industrial setup.

Currently, the pH control equipment design can handle only one kind of influent, either acidic or basic. In an industrial pH control situation, one may encounter a sudden switch from an acidic influent to a basic influent. To deal with such cases, some hardware and software modifications have to be made.

Another idea that can be investigated is of a triple-reagent injection scheme instead of a dual reagent injection scheme. These 3 injections may be tried in various permutations to achieve better control results. This idea can be investigated with the aid of the dynamic process simulator.

A schematic arrangement as the one shown in Figure 6.1 could yield better performance than our present one. The outlet pH (pH_3) will always be bracketed between pH_1 and pH_2 and this can facilitate more accurate model parameter evaluation. In this arrangement, there will only be two transport delays to account for, as against four in our

present one. One will be the deadtime between pH1 probe (or pH2 probe) and the pH3 probe and the other will be the deadtime between either reagent injection point and the pH3 probe. However, this arrangement will require an additional pump.

Another step ahead is to investigate and compare performances of neural networks and fuzzy logic with regard to pH control.

Figure 6.1 : Recommended strategy for improving the current In-Line pH Control Scheme

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APPENDIX
DATA ACQUISITION SOFTWARE

A.1 A/D Conversion

The functions of the A/D convertor board are controlled by a machine language I/O driver routine DAS8.BIN. The driver can select multiplexer channels, set scan limits, perform software commanded A/D conversions, interrupt driven conversions and scans, set and read timer counter, measure frequency and period etc. thus performing a variety of functions. To run the controller program from the Quick Basic menu, it has to be loaded together with the DAS8 routine as: QB/L DAS8 CONTROLPROGRAM.BAS. For our application three functions are to be used:

1. Initialize the DASH-8 and input the Base Address.
2. Set up multiplexer channel low and high scan limits.
3. Perform a single A/D conversion, return data and increment multiplexer address.

The software code for the A/D conversion is as follows:
C Mode 0 is the initialization mode by which you acquaint the routine with the I/O location or Base Address. The initialization need be done only once at the beginning of the program. Any errors will be indicated by a non zero value of the error flag (FLAG%).

MD% = 0

BASADR% = &H300

```

FLAG% = 0

CALL DAS8 (MD%, VARPTR(BASADR%), FLAG%)

IF (FLAG% <> 0) THEN

PRINT "ERROR IN INITIALIZATION"

END IF

```

C Mode 1 is for setting multiplexer channel scan limits. The channels are numbered 0 through 7. We require only three out of the eight channels. LT%(0) sets the lower limit and LT%(1) sets the upper limit. Non zero value of FLAG%, indicates an error.

```

MD% = 1

FLAG% = 0

LT%(0) = 0

LT%(1) = 2

CALL DAS8 (MD%, VARPTR(LT%(0)), FLAG%)

IF (FLAG% <> 0) THEN

PRINT "ERROR IN SETTING SCAN LIMITS"

END IF

```

C Mode 4 performs the actual A/D conversion and increments the multiplexer address. The digital numbers 0-2047 are stored in A%(I), corresponding to 0-14 pH units. Error is again indicated by a non zero error flag.

```

LL% = 0

UL% = 2

MD% = 4

FLAG% = 0

```

```

FOR I = LL% TO UL% STEP 1
CALL DAS8 (MD%, VARPTR(A%(I)), FLAG%)
IF (A%(I) < 0) THEN
A%(I) = 0
END IF
NEXT I

```

C The digital numbers have to be converted into normal pH units for the controller to understand them. This is done by a calibrated linear relationship between the pH displayed on the transmitter and it's equivalent digital number.

```

PH(1) = A1 * A%(1) + B1
PH(2) = A2 * A%(2) + B2
PH(3) = A3 * A%(3) + B3

```

A.2 D/A Conversion

There are two D/A convertor boards (DAC-02). The first DAC-02 board, whose Base Address has been set to &H330, sends signals to the influent pump (P1) and the major reagent pump (P3). The Base Address for the second D/A board has been set to &H370, and it sends a signal to the minor reagent pump (P2). Only a simple manufacturer provided code is required to run the D/A boards. Given below is the program code for the influent pump P1.

C The linear calibration equation converts flow rate into analog current.

```

CURRENT = A * FLOWRATE + B

```

C Make sure signal does go out of bounds.

```
IF (CURRENT < 0) THEN
CURRENT = 0
ELSE
IF (CURRENT > 20) THEN
CURRENT = 20
END IF
```

C Generate the digital input.

```
D = 204.75 * CURRENT
```

C Generate high byte and low byte.

```
DH% = INT(D/16)
DL% = D - 16 * DH%
DL% = 16 * DL%
```

C Perform the D/A conversion and output the signals.

```
OUT &H332, DL%
OUT &H333, DH%
```

It may be reiterated that the address locations &H330 and &H331 are used for the major reagent pump, &H332 and &H333 are used for the influent pump and &H372 and &H373 are used for the minor reagent pump.

APPENDIX B
DIFFICULTIES IN pH CONTROL

pH control is without doubt one of the most difficult control problems of today. Some of the difficulties in pH control are

- (1) Extremely nonlinear "s" shaped titration curve with process gain changes of 10^4 to 1.
- (2) Unknown and nonstationary composition of the influent. This may result in a shift in the titration curve (Figure B.1), a change in the influent pH (Figure B.2) or a change in the process gain at neutrality (Figure B.3).
- (3) Extreme process sensitivity at neutrality.

Ratio of Reagent to Influent Flow

Figure B.1 : Shift of the titration curve due to change in concentration

Figure B.2 : Change in Influent pH due to change in type of influent.

Figure B.3 : Change in Gain at neutrality