

Analogue and microprocessor control of an electrochemical waste-acid treatment process

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Electrochemical cells used for effluent treatment may, in many cases, require automatic control to handle load changes in the waste discharge. Results are presented for the automatic neutralization of a simulated chloralkali waste-acid stream using hydroxyl generated by an electrochemical cell operating under current control. The performance of a simple analogue PID controller is compared with that of a modern microprocessor-based adaptive controller.

1. Introduction

Over recent years the composition of waste-water discharge has been the subject of increasing legislative control. This particularly affects the chemical processing industry in that expensive and complex plants are often needed to achieve prescribed pollution limits. One of the most important and difficult waste-water treatment problems is the neutralization of waste acid or alkali by automatic pH control. This is important for a number of reasons, both biological and chemical. For example, micro-organisms, particularly those which consume biodegradable waste compounds, thrive in the pH range 6.5 to 8.5 but die if the pH is greater than 10.5 or less than 4.3 and, also, chemicals which are stable at one pH decompose as the pH is changed to produce highly toxic gases such as HCN, H₂S, NH₃ and Cl₂.

At present pH is usually adjusted by using a control valve to regulate the flow of neutralizer and a large stirred tank to provide good mixing between the neutralizer and the waste stream and also to buffer the effect of sudden load changes. There are, however, a number of problems arising from the control of pH by this method [1], namely:

- (a) Titration characteristic: the nonlinearity and sensitivity of titration curves.
- (b) Variation of titration characteristic with effluent loading and buffering conditions.
- (c) System dead time or transportation lag: the

delay in process measurement often resulting from siting the measuring device downstream from the process.

(d) Control valve characteristics: the rangeability and sensitivity of the control valve with respect to the control signal input.

(e) Neutralization tank and control valve dynamics: the differential equations relating control signal changes to pH changes in the tank.

(f) Mixing effects and reaction dynamics.

These problems are dealt with in a number of ways, such as by using split-range valves (a small valve in parallel with a large valve) to enhance the precision of neutralizer delivery; nonlinear and/or adaptive control techniques (controller characteristics adapt to process characteristics) for problems with titration and valve characteristics; and feed-forward control for large changes in effluent flow rate or pH. However, when using this conventional neutralization technique, it is difficult to control pH within the range 5.5 to 8.5 over a wide range of inlet effluent-loading conditions and disturbances.

One major waste neutralization process in the chemical industry is pH control of the anolyte effluent from chloroalkali processes. This effluent is usually a strong brine solution (10-20% NaCl) at a pH of 2.0 to 4.0 and may also contain chlorine and some of the chemicals used to remove it. It is produced in quantities of up to several hundred cubic metres per hour, although load changes may vary enormously. The discharge is usually

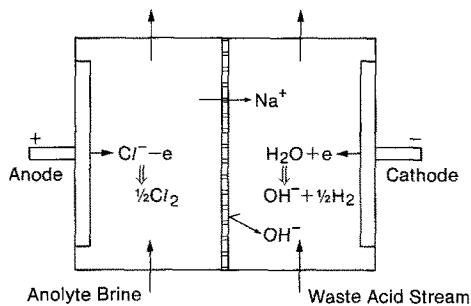
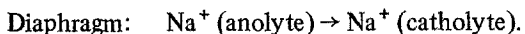
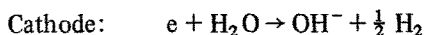


Fig. 1. Schematic diagram of the electrochemical neutralization process.

neutralized by the method already outlined and as a result suffers from the same type of control problems.

A possible alternative to the direct introduction of alkali via a control valve is to generate OH^- directly under controlled conditions by the use of an electrochemical cell [2]. The system is shown schematically in Fig. 1. A stream of waste brine is passed through the catholyte compartment of an electrochemical cell where water is electrolysed to produce OH^- and H_2 , whilst on the anolyte side of the cell the reaction may be chosen to be the production of chlorine to be returned to the main electrolyser. The overall reactions are as follows:



The cation selective membrane, in only allowing the passage of Na^+ from anolyte to catholyte, results in the current efficiency of the cathode process being very high (95.0–99.0%). By controlling the current it is possible to control almost quantitatively the amount of OH^- produced. Such a cell has a high capacity for neutralization and even at a modest current density of 100 mA cm^{-2} a 1 m^2 electrode could completely neutralize 360 m^3 of brine an hour entering at $\text{pH } 4.0$ with a power requirement of the order of 5 kW. This high throughput of the electrochemical cell produces the double advantage that mixing within the catholyte compartment is very good (Reynolds number larger than 5000) and additionally the time constant of the cell is of the order of 0.1 to

0.5 s, which is an order of magnitude less than the response time of even the pH measuring electrode. This means that by the use of an electrochemical neutralization technique some of the control problems mentioned above may be considerably reduced and in some cases entirely eliminated. For example, the control valve is replaced by an electronic power supply with almost any desired rangeability, and a resolution of a least a factor of ten better than any valve with positioner. Split ranging of power supplies, if indeed required, is also much more easily achieved than with pneumatic control equipment. In-line neutralization using an electrochemical cell eliminates the need for a neutralization tank and reagent control valve as well as considerably improving stream mixing. The problems associated with titration characteristic nonlinearity, variable buffering and system dead time are still present although, as will be shown in this paper, even conventional control (P + I + D) is now extremely effective as a result of control-loop dynamic improvements. In addition it will be shown that further improvement in the control performance may be achieved by the use of an adaptive control algorithm such that it becomes possible to regulate the pH of the brine effluent to 7.0 even under conditions of widely varying effluent loading conditions.

2. Experimental equipment

Fig. 2 shows a flow sheet of the experimental equipment used. The simulated effluent (15% NaCl) is pumped from one of the large, 500 dm^3 storage tanks via a rotameter, through the catholyte compartment of the cell and then into the

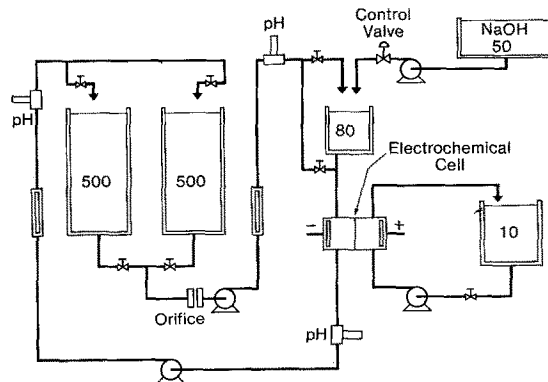


Fig. 2. Process flow sheet (capacities in dm^3).

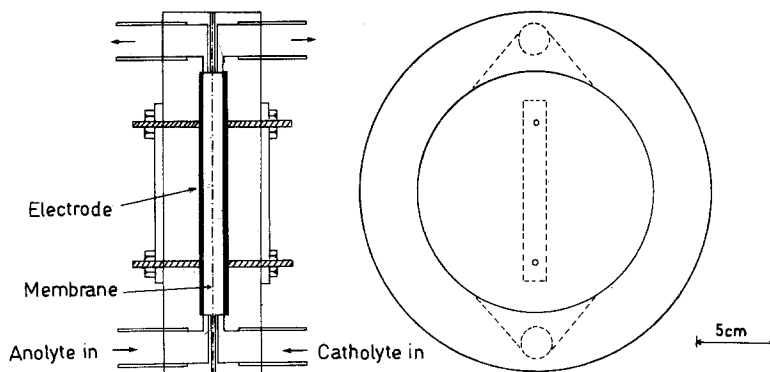


Fig. 3. The electrochemical cell.

other storage tank. By the use of a system of hand valves it is possible to quickly achieve almost any steady continuous operation. The equipment also has facilities for conventional neutralization using a reagent control valve and stirred-tank reactor. Connecting pipework is constructed from 3/4 inch PVC pipe and incorporates three pH electrodes, two after the cell and one just before it. The two electrodes sited after the cell allow the effect of dead time to be studied whilst the latter is used for feed-forward control. Current to the cell is supplied by a Farnell H30/100 power supply, operated in a constant current mode such that the current can be regulated by the means of an input control signal (1 to 5 V).

The electrochemical cell used (Fig. 3) was a simple chlorine electrolyser comprising a polypropylene frame, a DSA anode, a stainless steel cathode and a Nafion membrane. Each electrode has an area of 200 cm² and is 1 mm in thickness. The gap between the electrodes and the membrane is 0.5 cm. Electrical connection to the electrode is provided by means of screw connectors to the rear of each electrode, with two connectors to each electrode to ensure a more uniform current distribution.

3. Control policies

Although neutralization in the pilot plant as described above can be achieved by both conventional and electrochemical neutralization, this paper will only be concerned with the latter. A comparison between the two methods and their

respective dynamics will be presented in a later publication.

Two types of controller were applied to the process, firstly a conventional analogue controller and secondly a microprocessor-based adaptive controller, the self-tuning controller [3].

3.1. Analogue control

The three-term controller was a standard analogue instrument (Kent Instruments) and was tuned on-line using Zeigler-Nichols [4] settings as an initial guess. The function of the controller is to compare the pH of the effluent outlet (catholyte) with a desired (set point) pH. In response to any deviation from the set point or error signal (Er), a signal is sent to the power supply to adjust the cell current. The control action applied in this work was of proportional plus integral form. Thus the output signal produced by the controller (U_t) is given by:

$$U_t = Kc \left(Er + \frac{1}{T_I} \int_0^t Er dt \right)$$

where Kc is controller gain and T_I is integral time (seconds). For the present system control settings of $Kc = 1.1$ and $T_I = 8$ s were found to give good response over the range of input conditions discussed in the experimental results. The controller did, however, require retuning under conditions of low flow rates or when the pH electrodes were changed. The latter was caused by a change in response times, typically 2 s for a new electrode and 10 s for an electrode which had stood in the brine for several weeks. In order to avoid the need

for retuning, the self-tuning controller was applied to the process.

3.2. The self-tuning controller

The self-tuning controller is in the form of a micro-processor-based, discrete time adaptive control algorithm, in which the controller continuously identifies or 'learns' the process dynamics through controller system responses. The self-tuning control algorithm minimizes the general performance criteria:

$$J = E \{ (y_{t+k} - W_t)^2 + Q^1 (U_t)^2 \}$$

where $E \{ \}$ represents expectation, y_{t+k} represents the system output (catholyte pH) at time $t + k$, with a system time delay of k sample intervals. W_t represents the desired catholyte pH (set point), and U_t , the calculated control variable (cell current). Q^1 is a weighting function used to penalize large control actions. Setting Q^1 to zero results in the well-known minimum variance control law [5] where at every sample instant a control policy U_t is calculated to minimize the variance of the system output (catholyte pH). The control law can be shown [6] to be given by:

$$U_t = -\frac{1}{G} (Fy_t - QHU_t + HW_t)$$

where G , F and H are controller parameters (polynomials) continuously identified by a recursive parameter estimation algorithm, and Q is a general control-effort weighting function.

At each sample instant, the catholyte pH (y_t) is sampled and compared with the desired pH (W_t) to calculate a new control action (U_t) and so modify the cell current.

4. Experimental results

The process, as expected, was found to be very time dependent and nonlinear. System dynamics vary with time and the transfer functions are dependent on steady-state pH, flow rate and buffering capacity. For a nonadaptive controller, in this case a conventional three-term controller, achievement of a good response to set-point changes under different operating conditions was difficult and tuning the controller settings a very time-consuming process.

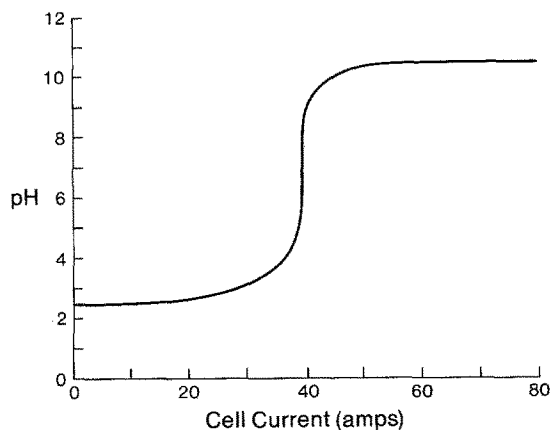


Fig. 4. pH-cell current neutralization characteristics (inlet pH = 2.40, flow = $0.333 \text{ dm}^3 \text{ s}^{-1}$).

Although the neutralization tank and valve dynamic phase shift problems are eliminated by carrying out the neutralization processes electro-chemically, the extreme nonlinearity in the neutralization characteristic is still present, as shown by Fig. 4. It should be pointed out that in all the results to be presented, the PID controller was 'on-line' tuned for the best response whilst the self-tuning controller always started with totally unknown (zero) controller parameters. (h_0 was fixed at -1 and the initial value of g_0 was chosen to be 1 .)

4.1. Set-point changes

Fig. 5 compares the controlled performance of the cell to set-point changes under both PID and self-tuning control. Here set-point demand changes to pH 8 and back to pH 7 were introduced into the controller and both regulators produced good stable control. The responses do indicate the non-

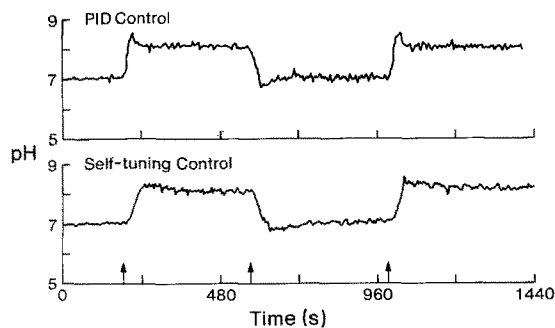


Fig. 5. Upward set-point changes.

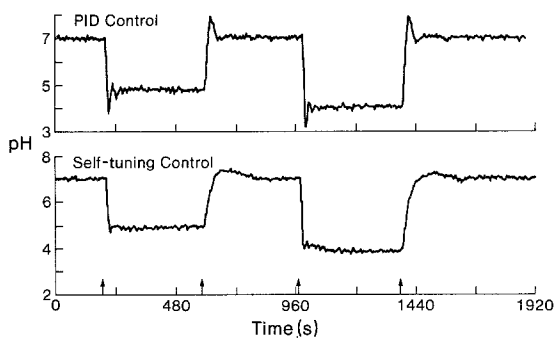


Fig. 6. Downward set-point changes.

linearity difference for positive-going and negative-going changes.

Fig. 6 shows even more dramatic set-point demand changes to pH 5 and back to pH 7, followed by a demand for pH 4 and return to pH 7. Here the performance of the self-tuning controller shows a considerable improvement over that of the well-tuned PID regulator. The different responses of the self-tuning system as time increases are due to the controller parameters converging to their correct values from their initial settings of zero as the system is progressively disturbed.

4.2. Inlet effluent load disturbances

Fig. 7 compares the regulatory control of flow-rate disturbances, $12 \text{ dm}^3 \text{ min}^{-1}$ to $20 \text{ dm}^3 \text{ min}^{-1}$ and back again, for both the PID and self-tuning

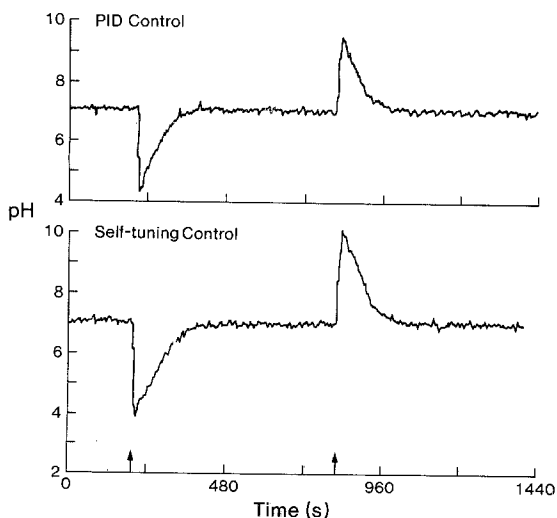


Fig. 7. Inlet effluent flow-rate disturbance.

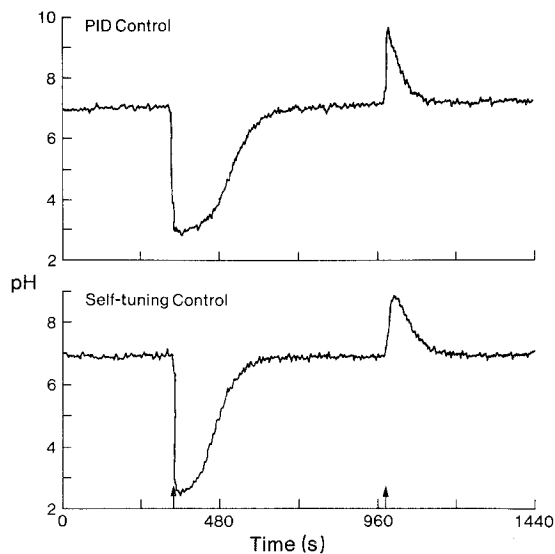


Fig. 8. Inlet effluent pH disturbance.

controller. The initial disturbance effects will always be present since both controllers rely on feedback of information and feed-forward control is not included. Again, both regulators produce quite acceptable responses.

Fig. 8 compares the performance of the two controllers for inlet disturbances in pH. Again the effect of the sudden unmeasured disturbances is immediately propagated through the cell (time constant $\approx 0.1 \text{ s}$) before the effects of the pH change are removed by regulatory action. Here the self-tuning controller tends to produce a marginally faster response than the best-tuned PID controller. Again, remarkably well-damped responses are achieved back to the pH 7 set point.

5. Conclusion

This paper has demonstrated an application of control techniques to an electrochemical process in which, although the electrochemistry is relatively simple, the control requirements are difficult. The electrochemical technique of pH control offers stable pH regulation even at the neutral point and may well be of use industrially.

The main advantage of the self-tuner over the analogue controller for this particular system is in the on-line identification of the process rather than in superior control action.

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