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Online pH Measurement and Control

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Abstract

The pH electrode widely used to mesure pH in an industry. pH is defined over hundreds of years ago. pH is 14 order of magnitude of hydrogen ion concentration. The industries like water treatment plants, pharmaceuticals, chemical and evvironmental protection etc. pH control plays important role. The pH measurement is highly nonlinear. The improper mechanical design, controller design, final control element selection and installation of process equipments affect control of pH. This paper describes the opportunities for the online pH control of solution. The equation of pH and control algorithms as well as effect of temperature on pH control is mentioned in this paper. An equivalent circuit of the electrode is employed to identify changes in pH unknown to most users. While controlling the pH of $CuSO_4$ Online we have regulated the flow of lime solution according to output of pH sensor.

Keywords:

pH;
pH control;
Online pH control;
$CuSO_4$ pH control;
pH control.

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1. Introduction

To measure the degree of acidity of solution, the pH meter is most commonly used in industry as well as in laboratories. pH is the measurement of Hydrogen ion concentration (H+). pH varies between 0 to 14. The acidic properties were exhibited if the pH of solution is less than value 7. Similarly, values of pH above 7 pH exhibit basic (caustic or alkaline) properties of solution. If we need to keep the solution neither acidic nor basic, we should maintain (control) the pH value to 7

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Since 7 pH is the center of the measurement scale, it is called "neutral". In 1909, pH is defined as 'negative logarithm of the hydrogen ion concentration' by the Danish Biochemist Soren Peter Lauritz Sorensen
The mathematical representation of pH is:
pH = -log (H+)
Where, (H+) is hydrogen ion concentration in mol/L [3]

2. pH Measurement

Almost all industrial processes that requires water needs to measure and control the pH value. The majority of living things depends on a proper pH value to protract life. Normal range of pH for blood between 7.35 and 7.45. The crops like wheat and corn will grow most excellent if the pH of soil in which they were planted is maintained at a most favorable level. To achieve high crop yields, farmers must condition their fields to the correct pH value. Many farmers are turning to university extensions for assistance in determining the appropriate pH value. Different pH levels were required for different crops to grow them well. In this case, one pH value (same pH value) may not fulfill demands of all crops. As we know, acid rain can be very harmful to crop yields. As the pH value of rainwater is below 7.0, hence the rainwater is naturally acidic in nature. Generally, the pH value of rain is around 5.6 but, in some areas, it increases to harmful levels between 4.0 and 5.0 due to atmospheric pollutants. Heavily industrialized areas may have the burning of fossil fuels, such as coal, releases gases into the upper atmosphere that, when combined with rain water, change composition and cause the rain water to become more acidic.

Therefore the measurement of pH in an aqueous solution becomes more important and it can be done in a variety of ways. The most common way to measure the pH level involves the use of a pH sensitive glass electrode, a reference electrode and a pH meter [2].
Alternative methods for measuring the pH value of solutions are:

Indicators:
Indicators are materials that are specially designed to change color when they are exposed to different pH values. The color of a wetted sample paper is matched to a color on a color chart to calculate the pH value. The standard pH papers are available for measuring the small pH ranges (like 3.0 to 5.5 pH, 4.5 to 7.5 pH and 6.0 to 8.0 pH), and reasonably broad pH ranges of 1.0 to 11.0.

pH Electrodes
A pH electrode assembly, or sensor, as it is sometimes referred to, consists of two primary parts:

Measuring electrode:
The measuring electrode which is used for the measurement of pH is sometimes called as the glass electrode and is also referred to as a membrane or active electrode.

Reference electrode:
The reference electrode is also referred to as a standard electrode. The pH measurement is comprised of two half-cell, or electrode, potentials.

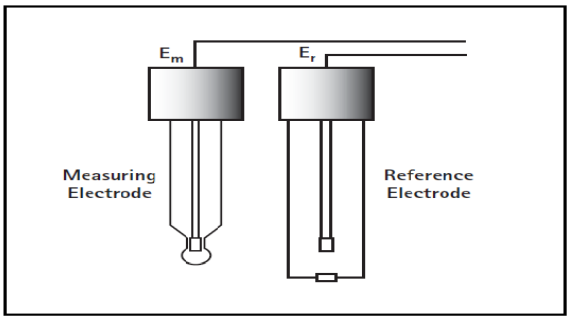

Figure 1. *Electrode Pair*

One half-cell is the pH sensitive glass measuring electrode and the other is the reference electrode. Just as the two half-cell potentials of a battery are required to complete a circuit so does a pH sensor. [5]

3. Online pH Control Mechanism

In this system we are controlling pH of $CuSO_4$. Copper sulphate/blue stone/blue vitriol/Pent hydrated cupric sulphate/CuSo4 5H20; these are the starting raw material for the production of the many of the other copper salts. Now days there are more than 100 manufacturers of CuSo4 and the world's consumption of $CuSO_4$ is around 200,000 tons per annum. Out of which it is estimated that approximately three-quarters is used in agriculture, as a fungicide.

Importance of $CuSO_4$ in Agriculture filed.

Such large amount of CuSo4 is used in agriculture field. The CuSo4 is the major contributing element in fertilizers that were used for correcting the deficiency of copper in soil.

$CuSO_4$ is used in agriculture sector mainly for:

- Preparing the Bordeaux and Burgundy mixtures.
- Controlling the fungus diseases.
- Correcting the copper deficiency in soils.
- Correcting the copper deficiency in animals.
- Stimulation of Growth for Fattening Pigs and Broiler Chickens.

Importance of CuSo4 in Industry:

$CuSO_4$ is playing an equally important role in Industry as compared to agriculture sector. It is being utilized largely in the following process in industry.

- The synthetic fiber industry.
- The metal industry as an electrolyte in copper refining.
- Electroplating industry.
- The paint industry for anti-fouling paints.
- Timber preservative industry.
- Dyeing industry.

$CuSO_4$ solution has following specifications as mentioned in the following table. These parameters need to be maintained in the desired range for the proper operation of the system. The adjustment of these parameters to the specific range is very critical task. So we are proposing the

technique so as to adjust these parameters within the desired range, according to the demand of system.

Table 1: Specification of CuSo4

Parameters	Desired Range
pH	7
Density	2.284 g / cm3
Solubility in water	316 g / L (0 °C) 2033 g / L (100 °C)
Refractive Index	1.514
Molar Mass	249.70 g / mol

To overcome conventional method of pH control following system as shown in figure is designed.

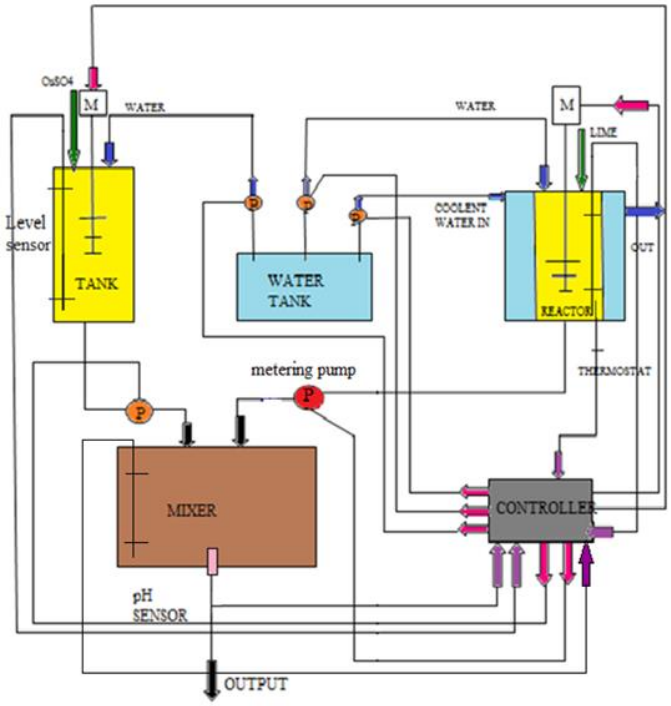

Figure 2. *Online pH control using PLC*

The system developed to control the pH of $CuSO_4$ using PLC is presented in figure 2. The online controlling of pH is more useful in all industries. This proposed system will provide automatic process for controlling the pH of $CuSO_4$ solution.

Hardware Components

- pH Sensor
- pH Transmitter
- Submersible pump
- Level Sensor
- Metering pump
- Level control unit

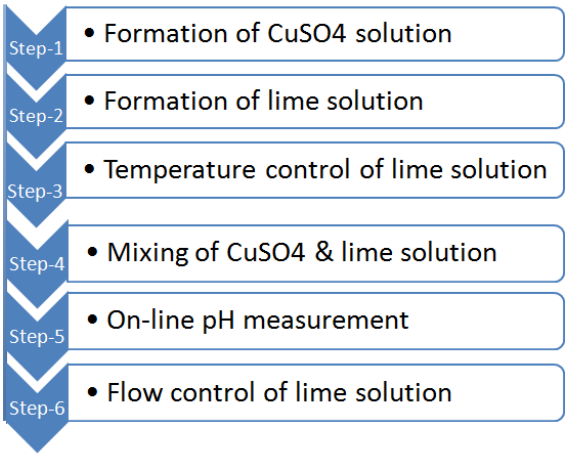

Figure 3. *pH control process*

In this section, process description is demonstrated unit wise according to the sequence of the processes.

Step-1 (Formation of $CuSO_4$)

During the first step of process, CuSo4 solution is formed by adding the solid lime in to water. The level sensor was used for continuously measuring the level of tank and the agitator motor is used for proper mixing of solution. For preparing the 10 % solution of $CuSO_4$, we have to add the 100 Gms of solid $CuSO_4$ in to the 10 liters of water. This solution is acidic in nature.

Step-2 (Formation for Lime solution)

During the second step of process, the lime solution was formed by adding the solid lime in to the water. When lime is added to water the temperature of system gets increased because of exothermic reaction. The pH is function of temperature. Therefore to control the pH, we need to control the temperature of the lime solution. Thermostat was used for measuring the temperature of lime solution. Water is passed through the reactor for cooling purpose. Here we have maintained the temperature of system below 30 Deg Celcious.

It can be seen that the slope factor of the Nernst equation contains a temperature term.

$E = E0 - 2.3(RT/nF)pH$

The effect of temperature can be compensated in many ways, while measuring the pH value. The majority of pH meters have the facility for manual or automatic temperature compensation (ATC). ATC is the use of a separate temperature probe or a temperature sensing device fitted into the pH electrode. Each measures solution temperature and the meters electronically adjust the pH reading according to the Nernst equation factor [3].

Nernst equation also given as:

$E = E0 - k.T.\ pH$

Where the k.T = slope of curve.

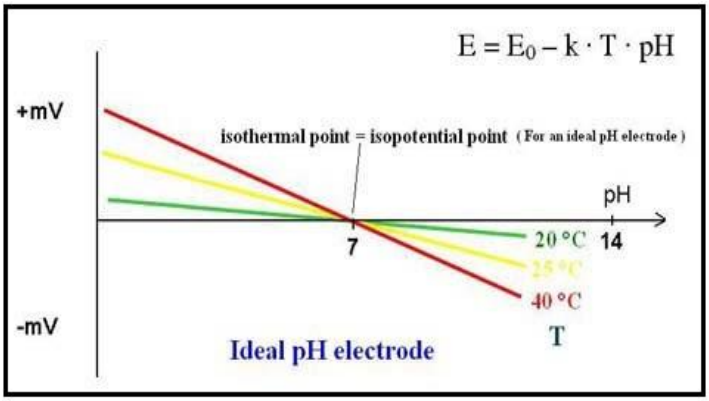

Figure 4. *Effect of Temperature on pH*

Step-3 (Mixer Unit)

Third step is one the most important step of this system; the mixer unit is used for continuous mixing of $CuSO_4$ solution and Lime solution. Here, we have to maintain the proper quantity of $CuSO_4$ solution and Lime solution so as to keep the pH value within specific range.

Step-4 (pH control loop)

During the final step i.e. during the pH control loop step specific amount of CuSO4 solution was mixed with lime solution. As soon as these two solutions were mixed the pH of the system is changed. The pH sensor will sense the changed value and give corresponding signal to the PLC and at the time controller also gives signal to metering pump. The metering pump is used to control the flow of lime solution [4]

4. Programmable Logic Controller

PLC is a digitally operating electronic apparatus. PLC mainly uses a programmable memory for the internal storage of instructions. It is most commonly used for implementing the specific functions like logic sequencing, timing, counting and arithmetic operations.

PLC and Ladder diagrams:-

1. Processor block-

Processor block is the heart of the system. All the system operations are governed by it. In fact it is the special purpose dedicated integrated chip which acts as logic solver

This unit also houses multiple memory elements. It is basically a random access memory (RAM) which provides working place for processor and a non-volatile memory mostly EPROM. The memory capacity varies with the type of the system, typical value for small version being 1 kilobyte.

2. I/O System:

INPUT MODULE-

Basically an input to PLC is the electrical signal that the switch sends. These signals are coming from process variables; the electric circuit which receives the input signal is called as input module. The basic function of this circuit is to send a low voltage signal that is usually at 5 volts to 24 volts level to the processor. The console has the status LED displaying the input status.

OUTPUT MODULE-

The signal coming out of the processor is called output signal. The electronic circuit into the module will be called output module. The source of power to energize the output load is not contained inside the output module. It only provides relay contact and user can have A.C. or D.C. source depending on the application .It may also have power MOSFETS as output devices

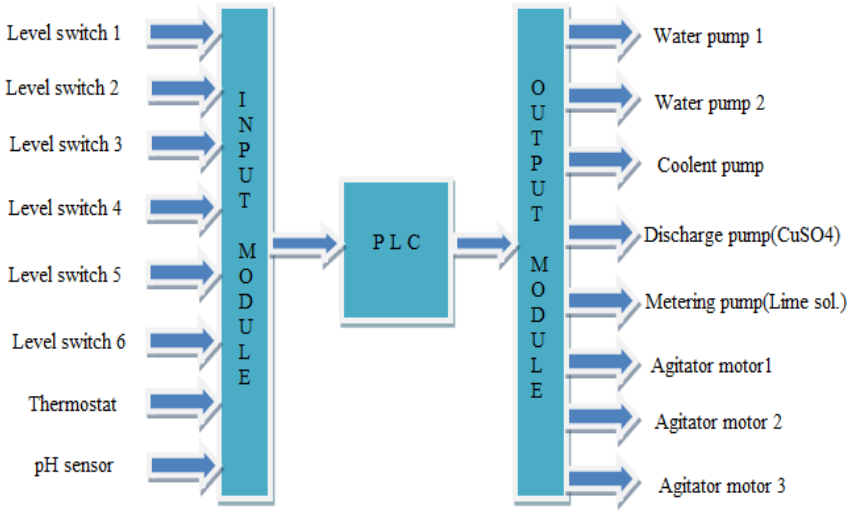

Figure 5. *PLC Interfacing*

3. Monitor or ladder:-

It is the third block which can be a hand held programmer, popularly HHP or a PC. All these blocks are connected with the processor unit via buses which carry information from one block to other.

LADDER DIAGRAMS-

Ladder diagrams are schematic representation of control logic circuit in the form of rungs of a ladder. The ladder diagram is so called because the completed diagram resembles rungs of a wooden ladder. The ladder diagram is constructed to show the sequence of the events.[9]

5. Control Algorithm

Control algorithms to control pH are given in figure 6.

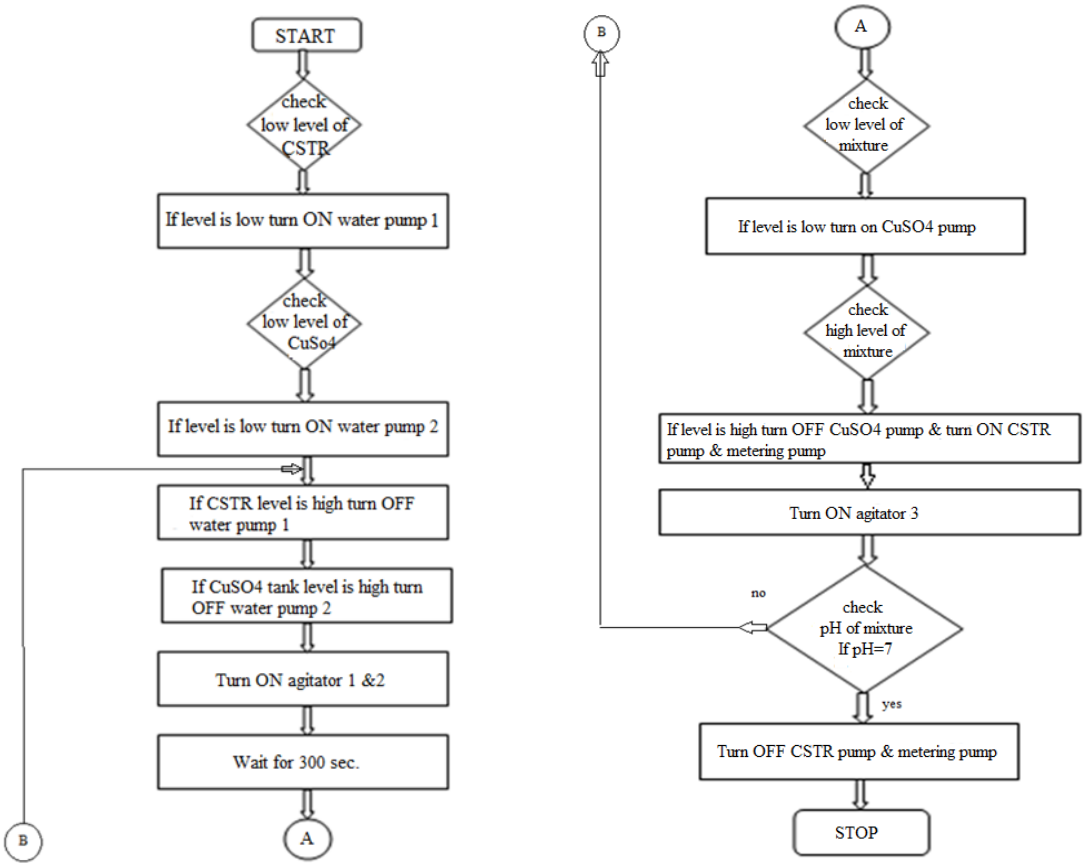

Figure 6. *Flow Chart of pH Control*

6. Results

While controlling the pH of solution we observed that, as we add the LIME solution to the $CuSO_4$ solution pH of the mixture solution changes with respect to the quantity of lime added. The approximately 7 pH in maintained by maintaining

Proper ratio of $CuSO_4$ and Lime solution.

Table 2: Results

Solution	Observed pH
$CuSO_4$	4.58
Lime Solution	11.58
Bordeaux mixture solution	7.25

Table 3: pH Electrode

Standard Buffer Sol. pH	Observed before Calibration	Observed after Calibration	Observed mA after calibration
4.01	4.05	4.02	8.59
7.01	7.05	7.01	12.01

7. Conclusion

By implementing this system we can make a process more reliable, fast, efficient & automatic, which will give better online pH control. As the process is totally automated it can be used in industries even for large applications. pH measurement is one the most important application necessary in agricultural sector here it can be used for measuring pH of Bordeaux and Burgundy mixtures.

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