BECKMAN pH METERS

By P. M. HARVEY

pH is no longer just a laboratory term; its study has assumed much more than mere academic interest. It can be readily demonstrated today that in many process industries the proper control of the pH of liquids so far regarded as unimportant can have a direct and pronounced effect upon plant efficiency.

Chemical engineers and plant executives have long known about the effects of pH upon production costs and product quality, and the relation of pH to such factors as the consumption of raw chemicals and the cost of maintaining equipment. Only in recent years, however, have production men had the necessary tools to apply this laboratory knowledge and to turn it into practical, successful systems for industrial pH measurement and control. The use of pH equipment has pointed the way in numerous industries to reduced costs and a better product. The Beckman-Foxboro pH combination consists of a measuring element, called the electrode assembly, indicating amplifier and the recorder.

Electrode assemblies and indicating amplifiers are manufactured by Beckman and the recorder by Foxboro. The amplifier discussed here is the new Model W, released approximately one year ago by Beckman. Ever since 1938, when Beckman made the first industrial pH instrument, their research and design engineers have been gathering ideas for a completely new industrial pH meter. These ideas are all in the Model W. It is completely new from start to finish, and has packed into it eighteen years of experience by Beckman engineers. Let us see some of the features of the new Model W.

1. It is small and compact. It is an indicating amplifier which can be placed next to the point of measurement and can give the operator a true indication of what is going on in the process.

2. The Model W is designed to keep right on running without electronic specialists. Beckman has made it easy to service it right on the job by the operators themselves.

The circuits are all contained in three separate plug-in units. Each of these can be replaced with spares kept on hand without soldering irons—and in a matter of minutes—and by anyone, even though unfamiliar with the instrument.

Field replacement of these three units, namely, amplifier unit, preamplifier unit, and power supply unit, will put the Model W back into immediate operation. Then, the faulty component can be serviced in a shop at a more convenient time.

3. The Model W is designed for industrial use—it has rubber gaskets, which seal the door to the case, so that no corrosive gasses and dust can enter the instrument.

4. The Model W puts out zero millivolts to the recorder when the Model W needle is at mid-scale. In other words, when the recorder and Model W cover exactly the same range, the recorder will have zero input when it is in mid-scale.

5. The Model W allows the recorder to record full scale virtually for any pH range. The recorder can have the same range as the Model W amplifier, say 2 to 12. Or with a 2-12 Model W, the recorder range can be *expanded* to record a greater number of pH units, or *compressed* to record a lesser number of pH units, or *shifted* to record anywhere up or down the scale.

Let us birefly discuss pH and the Model W, to see just how this instrument works.

(The author then exhibited slides to illustrate his lecture)

pH Scale

In its simplest form, pH is the measure of acidity or alkalinity of a solution, just as the Fahrenheit scale is a measure of temperature, the pH scale is a measure of acid or alkaline strength. The pH scale ranges from 0 to 14, with 7 being the neutral point. Numbers below 7 indicate increasing acidity, while numbers above 7 indicate increasing alkalinity.

Voltage from Electrodes

If we put a pair of electrodes in a beaker of a sample solution, and if the solution is acid, a positive voltage will be developed between the electrodes, which is proportional to the pH of the solution. If the solution is alkaline, a negative voltage will be developed. This voltage is measured and amplified by the Model W and translated into pH units right on the meter dial. The exact acidity or alkalinity of any solution can thus be determined by simply inserting this pair of electrodes and reading the meter.

Voltage versus pH Graph

The relationship of voltage and pH is better explained graphically when it can be seen that there is no voltage produced between the electrodes in a pH 7 or neutral solution. At pH 6, however, there are a little less than 60 millivolts produced. As the pH numbers decrease, indicating stronger acids, the voltage increases. On the other side of the scale, alkaline solutions produce negative voltages between the electrodes.

Model W Amplifier

The voltage between the electrodes is applied to the Model W amplifier. The following points are of special interest. The power supply provides D.C. voltages for the instrument operation. The built-in electronic regulator procides constant D.C. voltages, even with line variations of plus or minus 15 per cent.

The relationship of the components of the pH measuring system was shewn diagrammatically. The amplifier produces a current between the amplifier and the ground terminal. This current is a measure of the voltage at the electrodes. The current is used to drive a direct pH reading meter on the amplifier. Also, through a resistor, the current develops the voltage necessary to drive the recorder.

Let us now see what the controls on the Model W are and what they do. First are the two controls dealing with "zero check." When the Model W is switched on, and there is no voltage input to the amplifier, the Model W meter should read pH 7. This is the "zero check" point. To make this check, we get zero voltage input by pressing the zero check button. The zero adjust control is then turned until the needle reads pH 7.

Firstly, press the button called "zero check" and observe the meter reading. Second, turn the zero adjust control until the meter reads pH 7. This sets up the amplifier and meter reference.

Adjustment for Asymmetry Potential

The second knob adjusts for asymmetry potential. To see what this means let us first consider the voltage between the electrodes. When the electrodes are immersed in a solution of pH 7, there should be no voltage between the electrodes, and the meter should read 7. If a voltage does exist between the electrodes, it is compensated by adjusting the asymmetry control. This is the process of standardisation.

This is how the asymmetry control works. With the electrodes in a buffer solution of pH 7, we should read 7 on the meter. If not, turn the asymmetry control until the current passing through the meter alters the reading to indicate the correct pH values. The feedback action of the amplifier prevents significant voltage alteration across RT.

Here is the simple set-up for standardisation. With the electrodes in a buffer of pH 7, first turn the asymmetry control to make the needle read 7. This adjustment may also be made with other buffer solution values. For example, if buffer of pH 4 is used, adjust the asymmetry control until the needle on the meter reads 4. This is a simple and fast operation.

Thermo-Compensation

One important feature of the Model W pH Meter is the thermo-compensating resistance element which is immersed in the solution along with the electrodes. The resistance of the thermo-compensator varies with the solution temperature, so that the amplifier is always giving the correct pH reading for the solution at the temperature at which it is measured.

This will serve to illustrate the necessity for the thermo-compensator. The same pH at different solution temperatures will give voltages at the electrodes which vary with the temperature. Note that for a pH of 3 at zero degrees, 200 millivolts are produced between the electrodes; but for a pH of 3 at 100 degrees, 300 millivolts are produced. Regardless of the temperature, the thermo-compensator corrects this effect of temperature on the electrodes.

Electrodes

It is well to be reminded that the key to pH measurements is the electrode pair, the glass electrode and the reference electrode. Of the two, the glass electrode, which senses the pH change, is the more important. The performance of the glass electrode depends largely on the type of glass used in the pH sensitive immersion end. Early electrodes had thin, fragile bulbs. But Beckman research engineers developed special low-resistance glass compositions for glass electrodes.

The best known electrode is the Beckman General Purpose Glass Electrode. These electrodes using this special glass can cover a temperature range from freezing to boiling, as well as almost the entire pH range. The pH sensitive glass tip is so rugged that it can withstand abrasion and even accidental impact by hard objects. It is almost universal and practically indestructable. However, for special applications such as extremely abrasive fluids encountered in the mining and particularly in the uranium industry, a special abrasion resistant glass electrode is built by Beckman, which has proved its value overseas, as well as on many uranium mines on the Rand and in the Free State.

Sodium-ion Errors

The only area not accurately covered by the General Purpose Glass Electrode, is the extreme alkaline range. As noted on this graph, all electrode glasses show some error, due to strong concentrations of sodium-ions. For accurate results even at the top of the alkaline range, Beckman research has developed special electrode glasses which are practically unaffected by these sodium-ions. Most accurate at high pH is the amber glass shown.

The most deviation from the correct pH in highly alkaline solutions is shewn by Corning 015 glass—the former standard glass electrode.

Reference Electrode

Now let us look at the reference electrode. This electrode gives a stable voltage, a voltage which *does not* change with changes in the pH of the solution. To illustrate the necessity for a reference, consider yourself in a stationary motor-car, watching a train go by. The train would be passing you at, say, 20 miles per hour. If you were riding alongside this same train in a motor-car travelling at 20 miles per hour, the train would not be passing you at all.

Just as the speed of the train depends on your reference point, so does a pH measurement depend on the reference electrode. This electrode is like the stationary motor-car—it provides a voltage which is constant and which does not depend on the pH of the solution.

Sleeve Electrode

Most common for industrial measurement is the sleeve type reference electrode. It has a moderately rapid KCl flow rate and large liquid surface contact. In cases where samples have high viscosity, the sleeve type reference electrode is especially advantageous. It is also preferred for slurries, turbid solution, oil emulsions and soap solutions.

Fibre Electrode

For some industrial installations, the fibre type reference electrode is preferred. In this electrode, electrical contact with the process solution is established by KCl solution flowing slowly through a porous fibre sealed into the immersion end of the reference electrode. The fibre electrode has a slower flow rate than the sleeve type electrode, and has no breaklable glass sleeve.

Necessity for pH Scale Accuracy

Very few people realise the important fact that a small error in a pH measurement means a large error in measuring the acidity. When you change the pH reading by 1 unit, you change the acidity 10 times. And when you change the pH of a solution by 2 pH units, the acidity changes 100 times. This comes about from the logarithmic nature of the pH scale. As the pH drops from 6 to 5, the acidity increases 10 fold; as the pH drops still further to 4, the acidity increases 100 fold. This means that the electrical components in the pH meter must be designed for accuracy if you are going to know the acid strength precisely.

On the Model W the output to the recorder is accurate to 0.02 pH, in other words, less than the thickness of the indicating needle.

Beckman manufactures two types of electrode assemblies, namely, a flow type and an immersion type assembly. These will be shown to you during the course of the afternoon. The flow type electrode assembly is porcelain enamelled in order to resist the corrosive action of the fluid to be measured.

The immersion electrodes are made in two versions, namely, one manufactured from Type 316 stainless steel and the other one in a hard rubber construction.

The Foxboro Recorder, which works in conjunction with the Beckman equipment described, is also a most modern instrument. It is the well-known Dynalog, which stands for a new conception of the electrical bridge, self-balancing type of instrument. In a sweeping departure from the conventional design, Foxboro has produced an industrial instrument that offers performance and previously unknown freedom from maintenance.

The conventionally used resistance balancing slidewire has moving, electrical contacts, which wear and limit the instrument performance unless regularly maintained. This slide wire also limits instrument accuracy and sensitivity, because it can measure resistance only step by step—from turn to turn of the coiled wire.

Foxboro dynalog instruments employ instead a very simple variable air capacitor, completely eliminating moving and rubbing contacts. The electrical capacitor varies directly with the degree of intermesh between its rotor and stator plates. It provides continuous stepless balancing and gives a precise measure of the most minute change in the measured variable. The result is extreme sensitivity of one-hundredth of 1 per cent. and high sensitivity sustained accuracy of a quarter of 1 per cent. of the scale span.

Conventionally used dry cell batteries need frequent replacement and their use generally necessitates daily manual circuit standardisation or periodic complicated automatic standardisation.

Dynalog instruments require no dry cell. They emply an electronic system with continuous and direct standardisation against a standard cell. This eliminates manual standardisation, errors which develop between standardisations and interruptions to the instrument operation for manual or automatic standardisation, especially important when on automatic control.

The conventionally used high-speed, continously rotating, circuit balancing motor, with its associated drive gears, requires periodic lubrication and maintenance. Such drives can produce high pen speed, but with the disadvantage that the higher the speed, the greater the wear. Dynalog instruments employ a powerful "dynapoise drive," which produces high pen speed, yet has only four slow moving parts, which operate practically without wear. This drive, mounted integrally with the air capacitor, balances the pull of one solenoid against that of another and moves only when the circuit is re-balancing. It can drive the pen full scale across the chart to complete balance at the new reading in normally five seconds or on high-speed instruments in one second.

The accuracy of the conventionally used mechanical balance galvanometer is limited, because it is delicate and vibration-sensitive and its movement is often hindered by dust accumulations. Galvanometers also require periodic maintenance.

Dynalog instruments employ a simple, stable, vacuum tube circuit, which is unaffected by dust and vibration, and requires no mechanical adjustment. The result is, again, greater, more dependable accuracy.

The Foxboro dynalog instrument is easy to instal. It will operate without loss of accuracy even if tilted 75 degrees from the normal vertical position, as will be shown during the demonstration. The dynalog measuring system consists of three major unit assemblies, namely, first the dynapoise drive, second the range unit, third, the amplifier.

The dynapoise drive requires no lubrication or adjustment and has no back-lash. It consists of a balancing capacitor with a cross arm, each end of which is connected to the core of a powerful solenoid. A change in the measured variable electrically unbalances the measuring circuit and causes the solenoid cores to exert an unbalanced pull on the cross arm. The range unit makes it possible to change the range of a dynalog instrument in the field by simply replacing one range unit with another one without soldering joints, without making adjustments, and without affecting instrument accuracy in any way. These dynalog range units are enclosed in compact containers which provide full protection against moisture, corrosion and mechanical damage, and a range unit for a pH recorder is simply plugged into the instrument like a vacuum tube. The amplifier units are designed and built to stand up under the strain of vibration, pulsation, dust and corrosion—conditions usually encountered in industrial service. The vacuum tubes used in dynalog amplifiers are standard—obtainable wherever tubes are sold. They are not specially selected, and normal variations in tube characteristics have no effect on instrument operation. These units are completely interchangeable and a new unit can be quickly and easily installed in case of accidental mechanical damage.

Foxboro pH dynalog instruments employ a vibrator to compare input voltage with standard cell voltage and produce a pulsating D.C. unbalance voltage for amplification.

The dynalog vibrator operates in a very high impedance circuit—a distinct advantage in that changes of as much as several thousand ohms in contact resistance can have no effect on the accuracy, speed, or sensitivity of the instrument. The vibrator unit has highly polished precious metal contacts and is oil-filled and hermetically sealed in a compact metal housing. It plugs in like a vacuum tube.

Seeing that the Beckman amplifier is of the indicating type, it is possible to mount the amplifier next to the point of measurement, thus providing the operator with an indication of the pH. The Foxboro recorder or controller can then be mounted any distance away from the amplifier, as the only connection between these two parts is standard two-core cable. All Beckman industrial electrodes have 10-feet leads and in many cases it is possible to plug these electrodes directly into the amplifier. Where it is not possible to mount the amplifier next to the point of measurement, a connector box and cable assembly should be used which is provided with four conductor shielded cable. These connector boxes and shielded cable assemblies are available in any length up to a maximum of two hundred feet.

For recording pH at several locations throughout the plant, it is possible to use a number of electrode assemblies and one amplifier only to work in conjunction with a multiple point dynalog recorder. The switch inside the multiple recorder will operate a Beckman automatic six point selector switch, which will bring into the circuit the six electrode assemblies in rotation. This Beckman automatic selector switch is equipped with an asymmetric potential adjustment for each electrode assembly.

If on the other hand, the six measuring points are too far apart, with the result that the Beckman automatic switch cannot be conveniently used, it is possible to make use of one amplifier for each electrode assembly. There is, of course, the advantage on this set-up that an indication of the pH is available at each place of measurement and can still be recorded on a common chart.

In conclusion, on behalf of my firm, I would like to express my thanks to the South African Sugar Technologists Association, for the opportunity offered me in presenting you with details of the Foxboro-Beckman pH equipment.

Dr. Douwes Dekker, the Chairman, thanked the three speakers for their most interesting papers to the Congress on the subject of pH measurement. We should be grateful for the trouble they had gone to to present descriptions of their instruments in such an interesting way. Each instrument described had some good features of its own. He hoped that the firms whose representatives had attended today now realised the necessity of obtaining spares readily.

Mr. Rault asked Mr. Toop if he had had any experience of attaching the electrodes into the inside of a tank, where juice was circulating rapidly under a pressure of 10-12 lb.

Mr. Toop replied that while he had not done this with regard to sugar juice, similar conditions in treating slimes were also measured by immersing an electrode in the tanks. Under these conditions a resistance thermometer, being in a rubber sheath, finally failed. This was overcome by fitting a metal supporting liner in the rubber sheath. He thought that trying to record pH readings under conditions where the liquid was not properly mixed, did not give correct results. In the case of a continuous process the best position for an electrode would be in the external flow.

Mr. Rault asked if there would not be a time lag with such a procedure. Certain reactions were instantaneous and a high pH had to be avoided in some cases.

Mr. Toop said that the time lag was one of the greatest importance. It was no use measuring pH at one point, which might be quite different from that further down the pipe-line.

Mr. Hardy said that by using duplicate electrodes one might easily get an error of 0.1 pH. He asked if it were possible for manufacturers to standardise their electrodes, in the same way as brix hydrometers are now standardised.

Mr. Toop pointed out that the thickness of the glass was so small that it would be impossible to standardise electrodes. If 0.1 pH was important, it was always possible to apply a buffer check and then to adjust the instrument to allow for these varying standardisations would be a simple matter.

Mr. de Kok related that during the war, when he was working for African Explosives, it was necessary for them to manufacture their own electrodes. There was quite a difference in the characteristics of one piece of glass-tubing tested at various points. So he did not think that the thickness of the glass was the chief cause in variation between two electrodes. He pointed out that it was always possible to adjust for variation between electrodes. This view was supported by Mr. Harvey.

Mr. Elysee complained that after buying pH instruments, and they went wrong, the agents were no longer interested. He hoped that the instruments to be demonstrated today would not suffer in the same way.

Mr. Bouvet said that he had a lot of trouble in Mauritius with pH controllers. He was happy to see that the makers had now gone to a lot of trouble to try to eliminate the difficulties he had experienced. He asked if frequency variations in current would not render the application of these instruments almost impossible.

Mr. de Kok replied that with his new amplification circuit such variations as normally occurred could be taken care of.

Mr. Toop pointed out that the speed at which these frequency variations occurred was of great importance. A slow change would not have any appreciable effect. He thought that any dangerous variation would be more likely to occur when current was generated by a factory itself and not when the current came from a big supply concern.

Mr. Costello asked if in removing a coating from an electrode it was not possible to severely damage it.

Mr. Harvey replied that the removal of a scale was not a difficult process.

Dr. Douwes Dekker said that in the past the sugar industry had not been very instrument-minded, but he thought that in future it would become so, and when processes were automatically controlled better results would ensue. He thought that recording instruments for temperature were increasingly used, but as far as pH recording was concerned, the situation was not satisfactory at all. He felt, however, that today had marked a great step forward.