

Introduction

One of the primary applications for high purity water is for boiler feed water. The measurement of pure water pH can be one of the quickest indicators of process contamination in the production or distribution of pure water. Effective chemical treatment of the feed water is vital in maintaining the useful operating life and minimizing maintenance costs of the boiler. Boilers require pure water to reduce scaling and carryover of impurities in steam. Corrosion can occur when pH exceeds recommended limits at ranges that are dependent on metallurgies with the steam cycle.

One location for pH measurement, necessary to insure that the chemical treatment is working effectively, is after the demineralizer. At this point, the water has almost no electrolytic conductivity, making the measurement of pH difficult. In steam cycle applications, pH can be measured at several locations including after water treatment, condensate pump discharge, after polishers if used, and boiler water. The measurement of pure water can lead to a confidence that the water being used remains as pure as possible for the application.

Measurement Problems

The low conductivity and limited buffering capacity of low ionic strength pure water causes pH electrodes to drift, producing non-reproducible and inaccurate results. The common problems are large drift, unacceptable flow sensitivity and poor temperature compensation. Electrical noise and interference complicate matters further. Certain properties of pure water adversely affect that ability to obtain a reliable pH measurement. For many years it was believed these properties could not be satisfactorily overcome in order to achieve the desired measurement accuracy and reliability. The areas most affected by there pure water properties include:

- I. Reference Electrode Stability
- II. Glass Electrode Response
- III. Electrical Noise
- IV. Special T.C. Requirements

Reference Electrode

The liquid junction of the reference electrode tends to develop an appreciable diffusion potential as a result of the extremely large differences in concentration of ions between the process and the fill solution of the reference electrode.

The resulting junction potential can be as high as 20-40 millivolts (approximately 0.5 pH). Any change in this potential will show up as an erratic, drifting pH value.

It will appear that there is a change in the process pH, but this change is false since it is caused by the junction potential (Figure 1). Depletion or dilution of the reference fill solution occurs much more rapidly in high purity water, causing the reference potential to become unstable and the measurement unreliable.

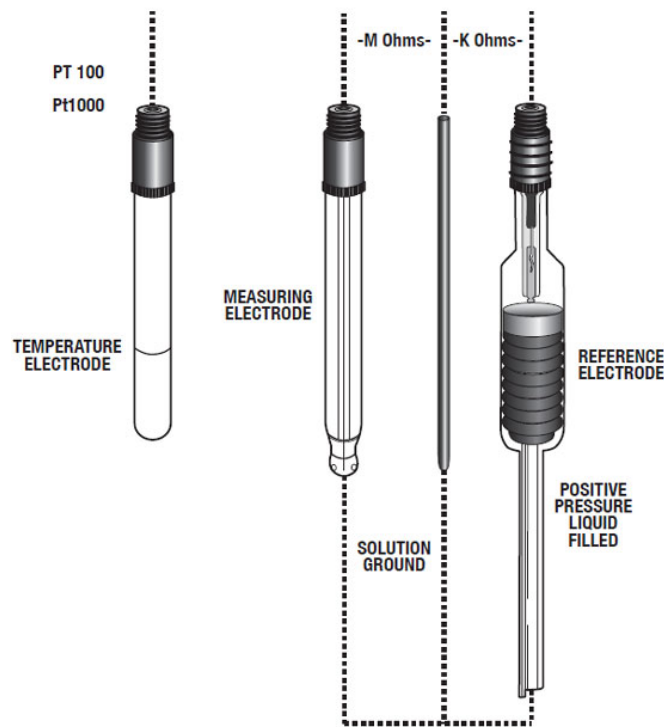


Figure 1: Typical Electrode Configuration for High Purity Water Applications

Since there are no conductive ions to speak of in high purity water, a physical path of conductive reference solution from the reference electrode to the glass electrode must be established in order for the measurement circuit to be complete. If there are no ions provided from the reference electrode (they have been depleted), there will be no stable reference from which to make the measurement.

Glass Electrode:

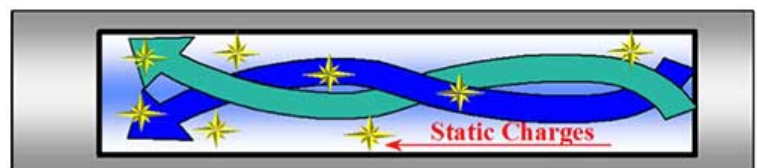
The low ion concentration of pure water appears to hinder the glass pH bulb's ability to detect hydrogen ions. This causes the electrode to have a low response speed.

It is also possible that the alkali components of the glass measurement bulb may dissolve in pure water. If a low flow rate exists in the process, the result would be a pH reading that is too high.

Electrical Noise:

Since pure water is a poor electrical conductor, it creates a static charge when flowing past nonconducting materials in the sensor. Pure water has a conductivity value of 0.055 μS (18.2 Mohm) at 25°C. This liquid resistance can lead to the formation of surface static charges. This can generate "streaming potentials" (stray currents that can mimic pH) in the solution which may cause large errors, or at least, excessive noise in the readings. A low impedance, well shielded and grounded electrode can lower these errors to a minimal value, usually less than ± 0.05 pH units. Because the electrical resistance of a typical measuring cell is so high, the electronics used to measure the cell potential are very susceptible to additional interfering factors - extraneous electrical noise pickup and hand capacitance effects. These static charges, called Streaming or Friction Potentials, are comparable to rubbing a glass rod (glass electrode) with a wool cloth (the water). This high resistance also increases the measurement loop's sensitivity to surrounding electrical noise sources. (Figure 2)

Pure Water Flowing In a Pipe



Other electrical sources such as ground loop faults and electro-treatment processes will cause the same troubles.

Figure 2: Streaming Potentials

Another problem involves the buffering capacity of pure water, which is very low. When pure water is exposed to air the absorption of carbon dioxide (CO_2) occurs causing a decrease in the pH reading. Depending on temperature and pressure, the pH of pure water may drop to as low as 6.2. Taking grab samples to a lab meter should be avoided because atmospheric CO_2 will contaminate the sample. Also, pure water temperature compensation must be taken into account.

Temperature Compensation

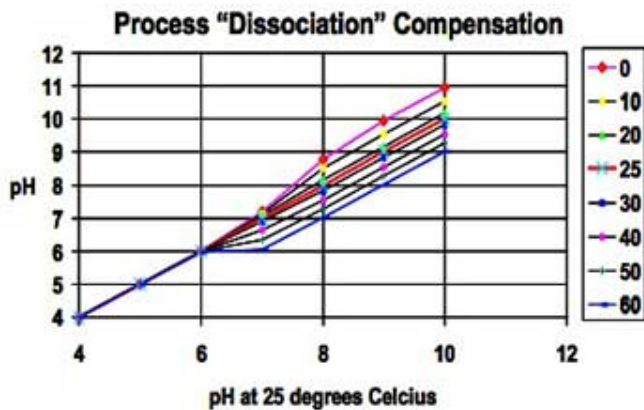
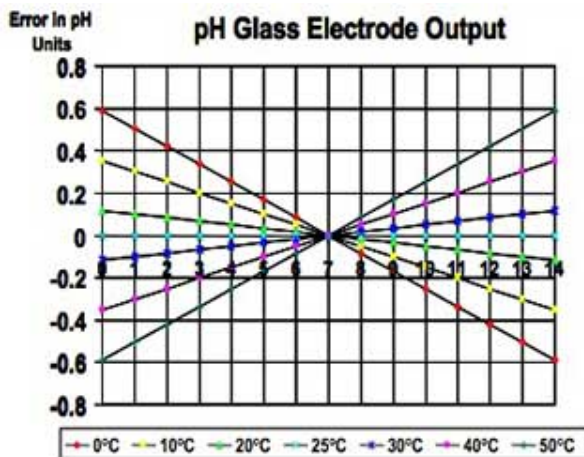


Figure 3: Two major Forms of Temperature Compensation

Temperature Compensation:

There are two major temperature effects that must be addressed in order to establish a truly accurate representation of pH in high purity water. The standard automatic temperature compensator only corrects for one of these, often referred to as the “Nernstian or electrode correction.”

Its magnitude is determined directly, using the Nernst Equation which describes that glass electrode operation which is independent of the nature of the process fluid. Simply stated, the Nernst Equation stated that as a glass electrode increases in temperature, its output voltage increases, even though the actual pH of the measured solution may remain the same. The effect is minimal at, or near a pH of 7 and increases linearly above and below a pH of 7.

The second effect is known as the “equilibrium or dissociation constant correction.” While this effect is usually much smaller in magnitude, it can become significant.

All solutions respond to changes in temperature in a specific way (dissociation constant). Depending on the solution, this response may be related to changes in pH or conductivity. The dissociation constant of pure water is 0.172 pH/10°C. This means at 50 °C pure water has a pH of 6.61, while at 0 °C it will have a value of 7.47 pH. The amount of temperature change involved and the critical nature of the measurement dictate if this effect must be compensated for or not. (Figure 3)

Many of the problems associated with high purity pH can be reduced or eliminated through careful consideration of these critical aspects of the pH measuring loop.

Solutions:

Through years of experience and innovative design, Yokogawa has developed solutions for the problems previously discussed. The high diffusion potentials of the reference electrode can be overcome by using a positive pressure style electrode. One such electrode, called the “Bellomatic,” was developed (Figure 1).

Utilizing a large refillable reservoir, the electrode provides a constant flow rate of reference electrolyte. This provides for a longer, more economical service life, than fixed reference electrodes can provide. In addition, the electrode is independent of the effects of process pressure. Therefore, the use of independent air pressure (as is used with a salt bridge) is not required.

To counter the low response speed and the effect of the alkali components of the glass electrode, special low-impedance S-glass electrodes were developed. They have a chemically resistant glass texture and very good response time due to their low impedance.

An alternative to a separate glass and reference electrode is a combination electrode with the capability to pressurize the reference portion. In addition to the benefits already stated, the close proximity of the two measuring elements helps insure electrode circuit continuity.

Noise problems resulting from ground loop potentials are addressed by the design of the pH transmitter. Many pH transmitters utilize a single-ended amplifier design. This design allows current (leakage current) to pass through the reference electrode, giving an offset in addition to shortening the useful life of the reference electrode. With the differential amplifier design, this leakage current will flow through the solution ground, not the reference. Therefore, no offset occurs and the reference electrode is not adversely affected.

To prevent the increase of static potentials a stainless steel flow chamber is recommended. Since most plastics are not completely gas tight, such a chamber will also prevent the absorption of CO₂ from the air.

For accurate pH measurement

- I. The sample temperature should preferably be in the 20 to 30° C range and remain constant.
- II. The sample must not be stagnant since errors will result
- III. Constant flow rates between 50 ml and 150 ml give the best results
- IV. Air must not be allowed into the sample stream
- V. Temperature compensation for both the Nernst potentials and the dissociation constant of pure water required.

It is also beneficial to measure pH in the smallest sample volume possible. Direct pH measurement in large volume samples such as drums or tanks and other samples with flowing or moving water tend to fluctuate and will require excessive stabilization time

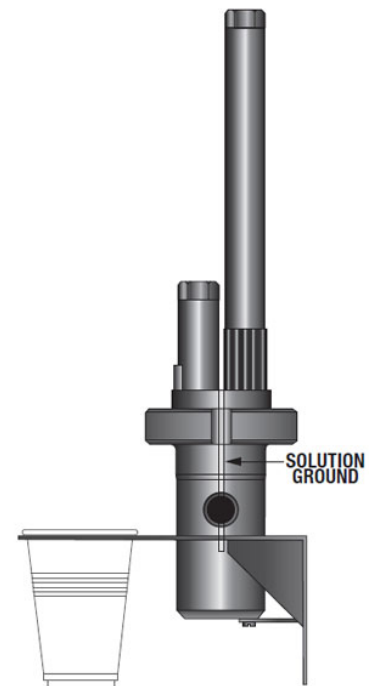


Figure 4: FF20 Configuration For High Purity

Summary

Measurement of pH in high purity water is a difficult measurement at best. In order to achieve a successful measurement, care must be taken to address the unique problems of the application.

Selecting the proper electrodes and holder will eliminate problems with reference junction potentials, slow glass electrode response and surface static charges. Selecting the proper transmitter or analyzer will eliminate ground loop problems and allow for accurate temperature compensation for both the Nernst potentials and the dissociation constant of pure water. In addition, sensor diagnostics gives the operator the ability to assure the measurement loop is functioning properly.

Yokogawa has the electrodes (Bellomatic reference and special G-glass measure electrode, or combination style); the sensor holder (model FF20/FS20 stainless steel flow through style); and the transmitter or analyzer (Models PH450G/FLXA21 with sensor diagnostics and “process temperature compensation”) to provide an accurate pH measurement in high purity water.

Where Are the Opportunities

The major players in pure water pH applications are Power Plants, however any site that has a boiler will need to monitor the pH of their feed water. Pharmaceutical applications also demand pure water where it is used as an ingredient.

Note: For additional information or assistance with there applications, please contact Yokogawa Analytical Product Marketing.

Product Recommendations Measurement System

Process Liquid Analyzer:

- 2-wire FLXA202 pH/ORP Analyzer
- 4-wire FLXA402 pH/ORP Analyzer

Sensor Selection:

Option #1: (Figure 4)



Figure 5: PH8HH Configuration for High Purity

HOLDERS

- FF20 Flow-thru assembly with individual measure, reference and temperature electrodes
- FS20 Insertion assembly with individual measure, reference and temperature electrodes

ELECTRODES

- Bellowmatic reference electrode (SR20-AC32), coupled with the shock-proof measuring electrode (SM21-AG4) and Pt1000 temperature electrode (SM60-T1)

Option #2: (Figure 5)

Holder: PH8HH Flow Thru assembly

Sensor: PH8EHP Flowing reference pH Sensor for High Purity Water

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YOKOGAWA ELECTRIC CORPORATION

World Headquarters

9-32, Nakacho 2-chome, Musashino-shi, Tokyo 180-8750, JAPAN

<http://www.yokogawa.com/an/>



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