

pH Measurements in a Power Plant

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Summary: The measurement of pH is vital to a number of applications within a power plant. The purpose of this paper is to provide an overview of each application and its associated problems so that users have a better understanding of how to successfully measure pH.

Introduction

pH is a critical measurement to power plants worldwide. The types of applications that utilize pH vary widely. A strong understanding of pH measurement basics is required to successfully measure and control these applications. The most common applications include the plant makeup water (including reverse osmosis pretreatment and ion exchanger effluent), scrubbers, cooling towers, condensate/feedwater, and waste water treatment. Each application possesses a unique set of characteristics that can require special considerations in order to achieve accurate and efficient pH measurement. Concerns such as the mounting location, process flowrate and pressure, pH range, temperature, contaminant level, chemical composition, and probe type must be evaluated in order to properly measure pH in each application.

Power Plant Applications

All large power plants, whether nuclear or fossil-based, share similar pH-based applications, such as makeup water, condensate/feedwater, and wastewater. There are also some pH applications, such as scrubbers or cooling water, which may not be present at each power plant.

Some samples present little challenge for pH measurements. Samples that are highly buffered or that change pH gradually over time and can be easily characterized by a representative grab sample present little challenge for pH measurement. Unfortunately, this is not the case with many of the samples in a power plant. The water streams of interest are frequently difficult to sample representatively. Some are lightly buffered with very little ionic strength.

Others are very high in solids and/or scaling rates, which makes them very abrasive and subject to rapid pH changes. All of these different types of samples require the highest accuracy possible in a pH measurement.

Makeup Water from Ion Exchangers – A parameter that is widely monitored in makeup water is pH. Properly applied, the pH measurement can either be very useful in either predicting the end of a run or indicating resin performance problems.¹ Improperly applied, this measurement can be frustrating and of little value to the analyst.

pH is generally considered to be one of the most common water quality parameters which is measured in most power plants. When it is applied to the high purity water on a mixed bed effluent with a standard pH probe, the result is often a frustratingly unstable measurement that is not of much value. In recent years, EPRI water chemistry guidelines have recognized the realities of the pH measurement process and the difficulties measuring mixed bed effluent pH, and it is no longer a recommended pH monitoring point.² Despite this fact, many plants continue to utilize on-line pH analyzers or grab samples to monitor the mixed bed effluent pH.

The major problem with monitoring pH on the effluent of a mixed bed demineralizer is the purity of the water, typically less than 0.3 $\mu\text{S}/\text{cm}$, and often much closer to the theoretically pure conductivity level for water, 0.055 $\mu\text{S}/\text{cm}$. The same issues occur when attempting to monitor the effluent of a condensate polisher. When the conductivity is very low (less than 1.0 $\mu\text{S}/\text{cm}$), a pH measurement can be somewhat useful for telling the type of contaminant (acid or base), but the actual pH will not usually vary much. For example, the maximum possible pH variance at 0.3 $\mu\text{S}/\text{cm}$ would be 6.1 to 8.0 pH, which is well within any makeup guidelines.³ As the conductivity drops to even smaller values, the need for a pH measurement diminishes.

A better and more meaningful pH measurement on a traditional demineralizer system (cation/anion twin bed followed by a mixed bed) will be realized by moving the on-line pH meter from the mixed bed effluent to the anion bed effluent. The conductivity at this point in the system is typically 1 to 10 $\mu\text{S}/\text{cm}$, which is sufficient for a stable pH measurement with many high quality electrodes. A probe specifically designed for high purity water usage is highly recommended for this application.

The anion effluent pH will normally be greater than 8.0 because there is always a certain amount of sodium leakage from the cation bed. If the cation bed begins to exhaust, the sodium throw will increase and the pH will rise to above 10. If the anion bed begins to exhaust, the pH will drop to less than 7 as the silica leakage increases and chloride and sulfate begin to leak from the bed. Used in this way, a pH measurement can be used to track demineralizer problems before the twin bed exhausts and significantly contaminates the mixed bed or demineralized water storage tanks.

Makeup Water from Reverse Osmosis – Reverse osmosis (RO) membranes are currently in use in many power plants.

They are typically utilized prior to the cation/anion beds or mixed bed within the demineralizer system. The control of pH in the RO feed water is critical for a number of reasons. The RO membranes have specific pH operating ranges that must be maintained or membrane damage could result. Cellulose acetate membranes deteriorate by hydrolysis at pH levels less than 4 or more than 6. Non-cellulose membranes typically have a much wider pH range, such as 2 to 11 pH for thin film composites or 4 to 9 pH for polyamides.⁴

Another reason for controlling the pH of RO feed is to control scaling. Polyamide membranes typically do not deteriorate, but their performance may be severely reduced by scaling, typically due to carbonates. Scaling of various dissolved solids which may be present is highly pH dependent, and therefore pH control is vital.

pH control is critical when a biocide is fed to control biological growth, which can contaminate or deteriorate the RO membrane. This is often the case with cellulose acetate RO membranes. A strong oxidant, such as chlorine or bromine, is often used, and both are less powerful at higher pH ranges.⁴

Control of pH in an RO feed is typically the easiest application for pH probes in a power plant. There is little potential for coating the probe since the probe is usually mounted in a side-stream pipe, where there is a constant flowrate of water, which prevents any fouling from occurring. Dissolved and suspended solids are typically found in moderate concentrations, so there is little potential for abrasion or etching of a pH electrode. The pH range will typically be within 5 to 9 pH. A combination pH probe that is specifically designed for long term accuracy and reliability is recommended for this type of pH control, due to the potential for damage to the RO membrane or degradation of process water.

Scrubbers – In a typical wet flue gas desulfurization (scrubber), flue gases containing sulfur dioxide enter the absorber and come in contact with a sorbent liquid (typically lime or limestone, although magnesium oxide is also used). The optimal pH control range is typically between 6.5 to 7.0 pH when lime is used, and 5.6 to 5.7 pH when limestone is used. Maintaining the optimal range is critical for promoting efficient flue gas scrubbing as well as for minimizing calcium carbonate precipitation, which can clog the scrubber.

This application can be quite difficult for pH probes, since the application involves a high concentration of solids. These solids can easily build up on electrodes, requiring excessive maintenance and replacement of probes. The probes can either be immersed in the absorber tank or mounted in the recirculation line. The scrubber pH tends to be easier to control when the probe is in the tank, but the probe will require cleaning more often due to the lack of flow in the tank. Mounting in the recirculation line (immediately after the inlet or outlet pump) will help ensure a longer probe life with less cleanings, but the pH can be more difficult to control. A fouling-resistant probe, such as a flat-glass electrode, should be considered to minimize coating/fouling.

Cooling Towers – pH is an important part of most cooling tower systems in use today. The system pH affects corrosion, scaling, and microbiological growth. The range is typically somewhere between 7 and 9 pH, depending upon the makeup water characteristics and the type of system metallurgy. Often the pH in cooling towers is controlled by acid addition, which is typically controlled by an automated control loop with pH feedback. Controlling the pH is usually not very difficult.

Cooling water can present a small challenge to any pH probe, due to the high solids content and varied chemical background (including pH-adjusting reagents, corrosion/scaling inhibitors, and microbiological control agents). If the probe is immersed into the cooling tower basin, there will be some potential for coating due to the high solids content, but little potential for abrasion or etching. However, it is recommended that the probe be located in the circulation line after the circulation pump. In that case, the high solids content can provide some potential for etching or abrasion, but little potential for coating. While this may shorten electrode life slightly, it will certainly reduce maintenance time necessary for cleaning and calibrating the probe. A basic combination probe designed for long-term stability and abrasion resistance is highly recommended for this application.

In cold or hot lime softening of a partial cooling water stream, the application is scale inducive, due to the nature of the technology. Lime softening enhances the precipitation of hardness and alkalinity, providing a difficult measurement for pH probes due to scale growth. Probe inspection and cleaning should be carried out on a regular basis in this type of an application.

Condensate / Feedwater -- In a power plant, the cycle water samples are typically the most highly monitored and conditioned samples due to the critical nature of corrosion control in the plant. High importance is placed upon the pH of the water in this system. Proper control of the pH in the feedwater cycle is critical to minimize the corrosivity of the water to the system components. Corrosion will lower plant efficiency and increase maintenance costs. Low pH excursions can cause hydrogen damage and high pH can lead to caustic gouging or ammonia attack, all of which can lead to system destruction and endanger personnel. Under normal circumstances, the pH control ranges are narrow, typically from 8.8 to 9.8 on All-Volatile Treatment (AVT) or Phosphate, and 9.6 to 9.9 with Alternate Amine Treatment. The pH range is somewhat lower for Oxygenated Water Treatment (OT) in once-through boilers -- 7.0 to 8.8 pH. The narrow ranges and critical nature of the water's pH make accuracy and stability highly important.

The conductivity of the water in the condensate/feedwater cycle is very low -- less than 10 $\mu\text{S}/\text{cm}$ on AVT, Phosphate, or Alternate Amine, while less than 2 $\mu\text{S}/\text{cm}$ for OT. This low conductivity water presents problems like those in the low conductivity water of the demineralizer effluent.

Because the accuracy and stability of the pH measurement in this application is so critical, but also so difficult to achieve, many chemists, chemical engineers and instrumentation technicians become very frustrated with the excess of time required to maintain the online pH probes. Grab samples in water with low conductivity are inherently difficult, which can cause further aggravation. Fortunately, recent advances have produced probes that can measure in low conductivity with both accuracy and stability. Utilizing a probe type that is specifically designed for high purity water is highly recommended. In addition, some software programs and analyzers offer equations which can check the pH accuracy with a specific/cation conductivity comparison as well.^{5,6}

Wastewater -- The pH measurement concerns in waste water or bottom ash service are quite different than those in high purity water. Wastewater or bottom ash streams typically have high levels of dissolved solids and significant amounts of suspended solids, so probe fouling and scaling can be problems. The pH in these samples can experience large swings from low to high and back again depending on what is being processed at the time.

The installations are typically outdoors so it is important that the probe and pre-amp assembly be weather tight. In addition, these applications tend to have pH probes in immersion service rather than separate flowing samples. Some applications employ side stream samples but these typically have problems obtaining a representative sample of the measurement. Immersion service requires a probe that is well sealed against water intrusion. Any water that gets into the connection between the probe and the preamp will cause an immediate malfunction of the pH signal. A combination probe designed to have minimal fouling and good chemical resistance is recommended for this application.

Measurement Recommendations

Accurate measurement in the many varied pH applications throughout a power plant can be a daunting task, especially due to the many details which must be properly understood and applied. However, many of these details are not well documented, and thus cannot be applied or taken into account, and bad measurements are the direct result of that problem.

High Purity Water -- Water of low conductivity presents a special challenge to pH probes. When the low conductivity of the water (thus a high resistance) is coupled with varying sample flow rates, significant changes in the reference junction potential can occur, causing significant errors.

Low conductivity water will also cause the measuring electrode to wear out much faster, increasing replacement frequency. Streaming potentials can cause fluctuations in the electrical circuit made up by the measuring and reference electrode, resulting in a pH error. Other stray voltages within the system can cause measurement problems, and are often very difficult to isolate or remove. In addition, sample temperature changes can cause actual pH changes in the water which are not compensated by the typical electrode temperature compensation within the pH meter, adding further confusion to the measurement.

There are a number of steps that can be taken to ensure an accurate and stable measurement. Pressurized/ flowing junction reference probes are vital for high purity water. The added ionic strength that the reference electrolyte provides to the sample will decrease the high sample resistance. The pressurized reference electrolyte will minimize reference junction potential changes. A well-designed flow chamber can minimize flow changes to the system, also stabilizing the reference junction potential. Accurate solution temperature compensation (different from the standard electrode temperature compensation) is provided with many new instruments to offset the temperature-based pH fluctuations that can occur.

Probe Fouling – Fouling of pH probes is common in most of the pH applications in a power plant, but especially in wastewater, scrubber or cooling water applications. Many types of dissolved (iron, amines, copper) and suspended solids (flyash, silt) can quickly clog the reference junction and/or coat the measuring electrode. Iron fouling is also very prevalent in water streams that are not operating under steady state. Another potential cause of pH probe fouling is oil. Any oil present will usually cause probe fouling, and can often be much more difficult to remove than iron.

Normally a quick wipe with a clean cloth is sufficient to clear up solids fouling. Some organic solvents have been shown to work in limited application. Immersing the probe tip with a 1 N HCl solution for 30 to 60 seconds has also proven to be effective in cleaning stubborn deposits. Often soaking the probe in hot water or spraying distilled water on the probe can help to remove oil fouling. Microbiological fouling can typically be removed with either hot water and soap or a mild biocide, such as dilute hydrogen peroxide.

On sample lines that have a large amount of iron, particularly those on cycling units, wiping out any iron in the sampling chamber is a good practice.

Another consideration for side stream samples that experience high levels of dissolved solids is the use of an in-line filter. The use of in-line filters requires balancing small size and limited capacity against large filters that may mask spikes due to their volume retention.

If the pH probe is used in an application where suspended solids are an issue, erosion may be an important consideration. Locating the probe in the proper configuration can minimize these problems. In general, locating the probe in a pipeline where the process velocity is high (3-10 feet per second) will minimize oil or solids fouling, but will promote erosion. Likewise, a probe located in a low or no velocity installation, such as that of a tank or lagoon, will experience almost no erosion but can have significant problems with fouling. The optimal location and flowrate may vary from site to site, depending upon maintenance funds, probe type used, available mountings, etc.

Backpressure on pH Cell – Some sample lines are configured with a positive backpressure on the sample outlet (i.e. flow meter after the probe or a drain line that is above the pH sample chamber). The backpressure causes sample diffusion into the reference at a very rapid rate. Even a small amount of backpressure on a pH sample probe can yield unacceptable results with a gel filled probe. It is often critical to use a pressurized junction pH reference electrode in these applications. This problem is often overlooked with many pH installations.

Loss of Sample Flow – Maintaining a sample flow and preventing probes from drying out are two important things to consider. All probes, especially those that utilize flowing junction reference electrodes, need a flow to prevent excessive buildup of electrolyte in the sample chamber and on the electrode. These probes will read much more accurately when there is some flow, however small it may be.

If probes are allowed to run dry, two main problems could result. One such problem could be that the reference electrolyte could dry out, requiring electrolyte replacement or even a new probe. A second problem would be if minerals, salts, or other contaminants would dry out on the measuring and reference electrodes. The coating that forms can often be difficult to remove, and the probe can be damaged in the process. Often soaking in the probe in hot water for a long period of time can help, but not always.

One improvement that has proved useful on pH analyzers on sample lines that can lose flow or potentially run dry is to install a three-way sample valve to switch to an alternative source when the sample loses flow. If this is impractical, the use of a loop seal can be effective.

On-line pH Measurement Validation

One of the most important aspects of on-line pH measurement is making the analyst, operator, or user of the data from the pH measurement comfortable with the accuracy of the measurement. Good decisions require good data. The user of the data must feel confident with the pH meter and probe.

Traditionally, pH measurements have been validated by grab samples, but these measurements can suffer from a number of problems. To combat this, many locations use flowing grab samples which are typically much more accurate than static grab samples.

Another technique that has been used to validate on-line pH readings is to use two online pH meters, each reading in parallel. This allows the precision of the pH measurement to be checked. Very close agreement within 0.2 pH units, and often within 0.1 pH units, is possible with this technique. If a reference on-line pH meter has been calibrated to a known standard solution, it can be used to assess the accuracy of the pH measurement. This “floating verification instrument” technique requires a good deal of time and planning and it requires effort to setup an on-going program. Properly applied it can be used to generate statistics which show the performance of pH analyzers over time and allows operators to build confidence in the on-line measurements. This technique can also be very useful in troubleshooting situations, especially if there is a question whether a pH variation is process-related or instrument-related.

Calibration – A proper understanding of calibration and grab sample techniques are vital to accurate pH measurements. Many users misunderstand the pH calibration process, which can lead to bad habits and poor results. Since there are a number of places where a user can find basic information on calibration and pH measurements, this paper will attempt to provide information which is more specifically directed toward the power plant chemist/engineer/technician.^{3,7-9}

As pH electrodes age and become contaminated or damaged by the process, the voltages produced at a given pH will change. This requires that a standardization (zero, or offset) and slope (span) be done on a periodic basis.

The actual frequency and methods utilized for calibration will differ depending upon the application, probe type, and requirements utilized by the particular chemistry lab. One good practice is trending the calibration parameters (offset and slope) for each online pH analyzer. Many of the modern pH analyzers provide these parameters, and trending of them can be used to identify a set of pH probes that are questionable. The slope percentage and offset pH/voltage are important to utilize in keeping track of changes in probe performance. Large offset values normally indicate problems with the reference electrode, while low slope values indicate measuring electrode problems. It should be noted that the slope diagnostics are determined in highly conductive buffers, and most electrodes will show good values for these parameters when new. However, this is no guarantee of applicability for a given measurement point.

The traditional method of calibration is the two-point calibration. The first point of the calibration will usually be required due to voltage changes in the reference electrode, while the second point of the calibration deals with the changes in the measuring electrode's output with pH changes. The measuring electrode's characteristics will usually change far less often than the reference electrode's do, so the second point of the calibration is not required as often. Taking this fact into account, a single point calibration can be done more often than a two-point calibration. However, this should be done with caution, especially in high purity water, since it can mask other pH problems. Both the two-point and single point calibrations can be easily misapplied, depending upon the application.

One of the best ways of doing a single point calibration is actually to do a “trim”, where the probe remains in the process. In the case of a trim calibration, the pH of the process is determined either by a properly done grab sample with a high quality, two-point-calibrated pH electrode system, or else by another on-line pH meter (floating verification instrument) which has just been two-point calibrated. A two-point calibration must be done occasionally to ensure accuracy of the measuring electrode as well, but utilizing the trim method above can yield excellent accuracy with much less maintenance cost. However, this method should only be utilized by technicians or chemists who have a good understanding of pH measurements and the characteristics of the water in the various sampling points, since there is a high potential for error. There are many published articles which provide more detail on properly applying calibration techniques to the most difficult application, water of low conductance.^{3,10-12}

Buffers – When a two-point calibration is done, care should be taken that high quality buffer solutions are utilized, and that these are replaced on a periodic basis. Buffer solutions that are NIST traceable are readily available and generally considered to be quite accurate. Some buffers, such as the 10, do not last nearly as long as the other buffers do. This is due to the reaction of the buffer with carbon dioxide in the air, forming carbonic acid. It has been observed that the 10 buffer can drop as much as 0.1 pH per day when exposed to the air. Using a 9 or 9.18 buffer can help prevent some of these problems.

Reference Electrodes – A good reference electrode can mean the difference between an accurate, stable pH reading and a calibration-intensive, non-trustworthy reading. Proper care of reference electrodes is important to maintain the accuracy and stability of the measurement. A good practice prior to performing the periodic two-point calibration is to discard the solution in “flowing” reference probe and refill it. When the reference solution is emptied from the probe, a check can be made to ensure that the solution is not bound up by air bubbles (if a gravity feed electrode is used), or that the bellows are not hung up inside the probe (if a bellows-type reference electrode is used). The reference solution in a laboratory meter should be changed on a regular basis as well.

Note that many electrodes, such as most gel-filled types, do not have changeable reference solution, since they are “throw-away” probes. These electrodes typically will experience more drift than their “flowing” counterparts, and should be replaced or cleaned once they begin to significantly drift away from the actual pH on a daily basis. A good maintenance practice for gel or flowing reference electrodes is to buff the liquid junction with emery paper prior to a recalibration to ensure the junction is clear. This practice can be helpful to reduce fouling effects, especially those from iron oxides.

Grab Samples – It seems that there is no area where secret rituals and smoke/mirrors are more ardently practiced than in pH analysis of grab samples. The expectation is that some level of agreement between the on-line and the grab sample can be obtained to ‘validate’ the on-line measurement. It seems that each person has his own method of ensuring that the grab and the in-line pH agree. The following is a list of some methods that have been brought to the authors’ attention:

- Shake the first sample vigorously around the probe, discard that sample and then collect a fresh sample to measure.

- Don't shake the second sample at all, or you will introduce carbon dioxide, which will affect the pH.
- Use a flowing grab sample instead of a static one when possible with high purity water.
- Take the first stable number (use an auto-lock feature to stabilize the reading).
- Store the laboratory probe between analyses in KCl storage solution, buffer, city water, DI water, or the last sample taken.
- Buffer the lab electrode at least every week, but preferably every day, shift, or between readings.
- Throw the buffer out each week, day, shift, or between each calibration
- Never throw the buffer out.
- Rinse off the probe either between samples or between buffers.
- An on-line probe only needs calibration once a year.
- If samples must be obtained from a remote location, collect only full bottles and cap tightly.
- Analyze as close in time to collection as possible.
- Analyze samples that are as close to 25 C as possible. Cool samples in an ice or water bath if necessary. (If hotter samples must be analyzed, recognize that most grab pH meters have temperature compensation for the probe but not for the solution.)
- Check the level of reference solution in electrode regularly, and change it periodically
- Use a double junction, combination, or flowing junction reference electrode

Note: The tips that the authors feel are legitimate and applicable are underlined.

Grab Samples of Very Pure Water -- Obtaining an accurate pH measurement in a grab sample of very pure water is very difficult. If the conductivity is less than 0.3 $\mu\text{S}/\text{cm}$, it is typically fruitless to attempt this. There are occasions when a grab sample of pure water may need to be made, and there are several things that should be kept in mind. The diffusion rate of carbon dioxide from the atmosphere into a pure water sample is inversely proportional to the conductivity (the purer the sample the quicker it gets contaminated).

Water which is absolutely pure ($0.055 \mu\text{S}/\text{cm}$) can increase in conductivity by 0.8 to $1.5 \mu\text{S}/\text{cm}$ when fully equilibrated with air (assuming a concentration of 350 to 1000 ppm of carbon dioxide).¹³ Flowing grab samples are much better but still subject to contamination that can greatly affect the measured pH.

Flowing grab samples should be performed on samples with a fairly low flow rate, and flow from the bottom up should be used.

Some chemists advocate the addition of an Ionic Strength Adjuster (ISA) to low conductivity samples to stabilize the pH measurement. Typically ISA powders or liquids consist of neutral salts that raise conductivity so that the measuring probe can better sense the pH of the solution. The authors do not recommend this practice as it is not only poor analytical technique, but it also contaminates the sample and the actual affects of the ISA on the pH of that particular sample are not known.

Conclusions

Properly measuring pH in the variety of power plant pH application can be quite a challenge. To successfully achieve the accuracy and stability required by these applications, a full understanding of each application, the various probe types available, and the many pitfalls to the measurements (both in the on-line process and the laboratory) is required. However, the measurement of pH is not the mystic art that many people believe it to be, nor is it as simple or troublefree as others might believe. It is the authors' hope that this paper will be useful to the many plant chemists and technicians who are frustrated on a continual basis with the process of obtaining a good pH measurement.

More Information

For more information on pH Measurements, visit www.honeywellprocess.com, or contact your Honeywell account manager.

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