IC Controls

PH THEORY & MEASUREMENT

WHAT IS pH?

pH is a short form for the Power (p) of Hydrogen (H). pH is defined as the negative log of the hydrogen ion activity, aH^+ or the effective hydrogen ion concentration.

Mathematical Definition

$$pH = \log_{10} \frac{1}{aH^+} = -\log_{10} aH^+ \quad \text{(Theoretical)}$$

$$pH = \log_{10} \frac{1}{[H^+]} = -\log_{10} [H^+] \quad \text{(Practical)}$$

Descriptive Definition

pH is a unit of measure which describes the degree of acidity or alkalinity of a solution. Acidity is defined as the concentration of hydrogen ions $[H^+]$ in solution and alkalinity as the concentration of hydroxyl ions $[OH^-]$ in solution. As seen above the actual theoretical definition of pH is $-\log_{10} aH^+$. But, since the activity coefficient (a) for hydrogen (H^+) is 1 the practical definition for pH can then be defined as $-\log_{10} [H^+]$. Below is a chart showing the relationship between pH and the Hydrogen ion concentration.

pH MEASUREMENT TECHNIQUES

There are two ways of measuring pH. The first is a *Colorimetric Method* using color indicators to indicate the pH of the sample. There are limitations to this measurement technique. For instance, visual measurement by an operator is subject to variation. As well, this technique is done by grab sample which is not suitable for

Figure 1: Relationship between pH and Hydrogen Ion Concentration

pH = HYDROGEN ION CONCENTRATION

pH	Hydrogen Ion (H+) Moles per Liter		Hydroxyl Ion (OH-) Moles per Liter	
0	(10^0)	1	0.00000000000001	(10^{-14})
1	(10^{-1})	0.1	0.0000000000001	(10^{-13})
2	(10^{-2})	0.01	0.000000000001	(10^{-12})
3	(10^{-3})	0.001	0.00000000001	(10^{-11})
4	(10^{-4})	0.0001	0.0000000001	(10^{-10})
5	(10^{-5})	0.00001	0.000000001	(10^{-9})
6	(10^{-6})	0.000001	0.00000001	(10^{-8})
7	(10^{-7})	0.0000001	0.0000001	(10^{-7})
8	(10^{-8})	0.00000001	0.000001	(10^{-6})
9	(10^{-9})	0.000000001	0.00001	(10^{-5})
10	(10^{-10})	0.0000000001	0.0001	(10^{-4})
11	(10^{-11})	0.00000000001	0.001	(10^{-3})
12	(10^{-12})	0.000000000001	0.01	(10^{-2})
13	(10^{-13})	0.0000000000001	0.1	(10^{-1})
14	(10^{-14})	0.00000000000001	1	(10^0)

continuous on line measurement. A more effective way to measure pH in an industrial setting is the *Potentiometric Method* of pH analysis. The potentiometric method allows continuous, on-line measurement and is not subject to operator bias. Potentiometric analysis has four parts:

1) sample

2) pH sensing electrode

3) reference electrode and

4) signal amplifier/readout. When properly combined the result is accurate, representative pH readings.

pH SENSING ELECTRODE

The pH sensing electrode acts as one half of a battery whose potential varies with the hydrogen ion concentration in solution. The *Standard Glass Electrode* is commonly used in industrial applications because of its ruggedness and versatility. Finally, there are other Solid State Electrodes such as the Antimony Electrode which is a sensing element made of Antimony Hydroxide and is used in applications, like high fluoride, where glass is dissolved.

THE GLASS ELECTRODE

Since the glass electrode is still the industry standard for sensing electrodes it will be the only sensing electrode discussed. The glass electrode basically consists of four major components:

1) the glass membrane,

2) the internal buffer solution,

3) the reference wire and

4) the glass stem. Figure 2.

How Glass Electrodes Work

The glass electrode is primarily composed of alkali silicates which are comprised of Sodium, Potassium, Lithium, Silica, Oxygen and Hydrogen. All of these components are combined to form a Hydrogen ion specific sensing glass; the amount of each constituent in the glass determining its pH sensing properties.

When the glass is put into solution it undergoes a chemical reaction which forms a leached layer the surface of the glass where an ion exchange reaction takes place. In this surface layer Hydrogen ions migrate in and replace other positively charged ions such as Sodium or Potassium. This causes a Silica-Oxygen-Hydrogen bond which is essential for sensing Hydrogen ion in solution.
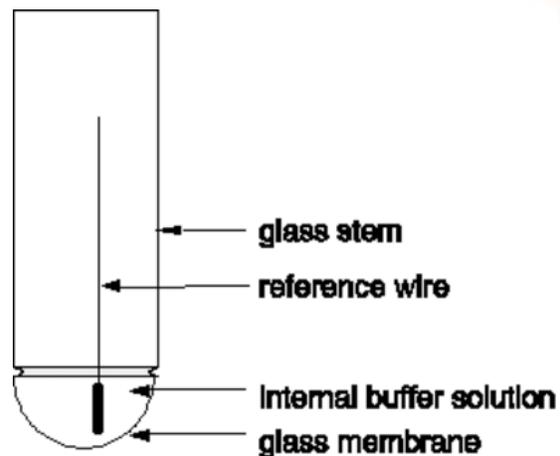

Figure 2: Glass pH Electrode

Labels: glass stem, reference wire, internal buffer solution, glass membrane

The pH glass electrode actually works on a two reference electrode basis, a reference inside the glass and a reference that is in contact with the externals of the glass. pH measurement requires measurement of the potential difference in the pH electrode system. The formation of a leached layer actually occurs on both sides of the glass membrane. The difference in potential between the two layers is called the *Phase Boundary Potential* and is the potential difference that gives the pH signal.

In the pH glass there must also be a charge transport mechanism so that a millivolt potential will be seen. In between the two leached layers there remains a glass membrane layer that does not undergo the ion exchange that occurs at the surface. In this membrane layer Potassium and Sodium, major constituents of the glass, act as the charge carriers.

For best results a *Symmetrical Cell* is set up on both sides of the glass membrane. To set up the Symmetrical cell the internal fill solution in the glass and the reference fill solution are similar in their makeup. The symmetry is important so

that the temperature curves for the two solutions are as close as possible and therefore, minimizes the temperature effect. For symmetry purposes the internal buffer is made of KCl (Potassium Chloride) solution which is the same as the reference solution.

Styles of Glass Electrodes

The basic premise behind glass pH electrodes is to have the reference and the Hydrogen Ion sensitive glass membrane in contact with the solution being monitored. The glass membrane itself is not limited to any configuration or shape; its only requirement is contact with solution. Therefore, different styles of glass electrodes have evolved to maximize pH sensing ability and extend longevity in some of the more rugged applications. Below are some of the common styles of glass presently available.
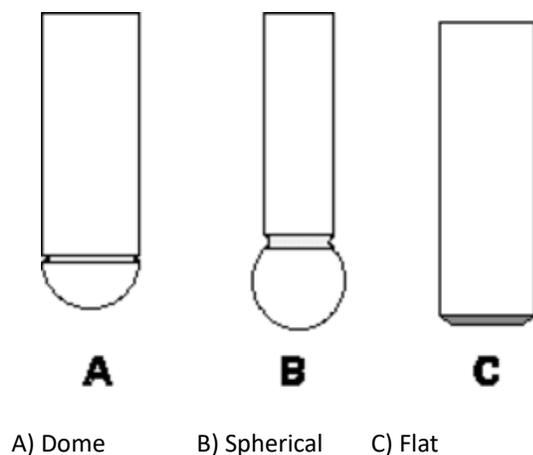

A) Dome   B) Spherical   C) Flat

Figure 3: Glass Membrane

Temperature Effect on Glass

As the charge transfer is one of the key factors in determining pH, the conductivity of the internal layer of the glass is a factor in the responsiveness of the electrode. The more conductive the glass is, the quicker the potential difference will be transferred across the membrane. Thicker, more rugged styles of glasses are slower to respond in ambient conditions than general purpose electrodes because it takes longer to transfer the charge and set up the difference between the Leached Layers.

The conductivity of the glass, which is the reciprocal of resistance, is highly temperature dependent, as seen in the following equation, where k is the conductivity and A and B are constants:

$$\log_{10} k = A + \frac{B}{T}$$

From this equation it is evident that as the temperature increases the conductivity of the glass also increases, which explains why thick glasses, which are somewhat sluggish at ambient temperatures, will be very responsive when the temperature of the sample is increased. Fig. 4, is a graph that illustrates this relationship between temperature and the conductivity of the glass for a standard glass membrane.
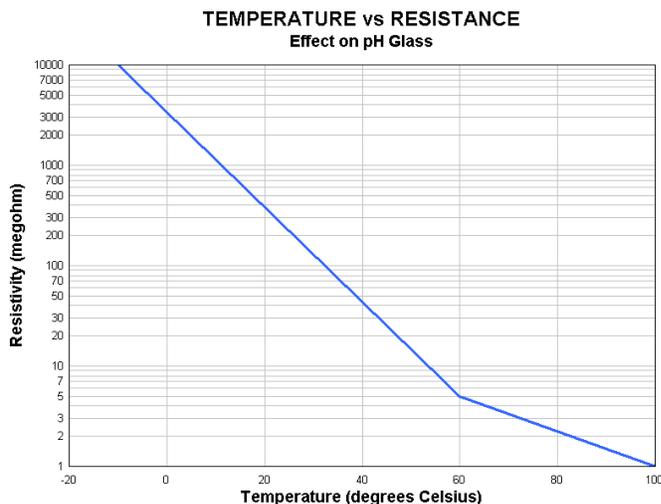

Figure 4: pH Glass Resistance vs Temperature

TEMPERATURE VS. RESISTANCE

Because of the temperature effect on the impedance of the glass, a thinner glass with a low impedance is used in ambient conditions, and a thicker more rugged glass with a higher initial impedance is used for high temperature applications.

Therefore, when selecting a glass electrode for industrial pH systems a number of different factors must be considered to maximize response and longevity of the probe in your application.

THE REFERENCE ELECTRODE

The reference electrode acts as the other half of the battery in the pH electrode. The difference in potential between the two sides of the pH glass measures the varying potential difference in the solutions due to pH. A constant reference give the glass a reference point to use

for the glass electrode to distinguish that pH relates to the process pH potentials.

As mentioned in the glass electrode section, the best results for an electrode occur when the two sides are symmetrical. Thus, a reference cell normally is comprised of a Silver wire with the tip of the wire covered in Silver Chloride. This Silver\Silver Chloride wire is submersed in a saturated KCl solution which is separated from the process by a porous junction. A diagram of a typical combination electrode with a Silver/Silver Chloride reference is seen below.
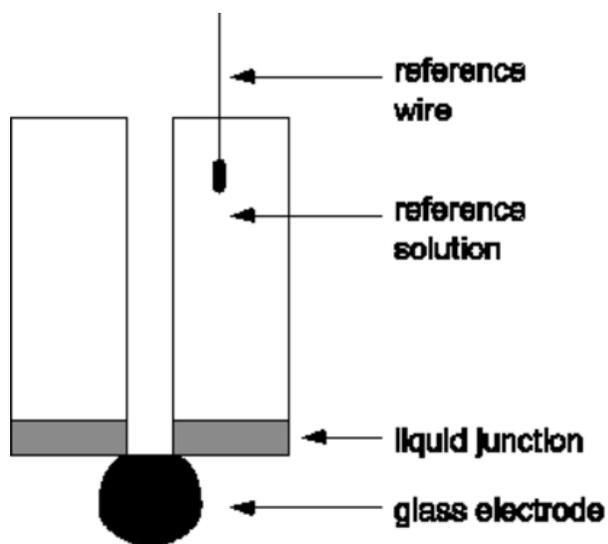

Figure 5: Combo Electrode with Ag/AgCl Reference

Like the glass electrode there are also different types of reference electrodes that can be utilized in any given pH measurement. The two common references are the *Calomel electrode* and the *Silver/Silver Chloride reference*. The Calomel electrode is not used in industrial applications for two reasons. First, the electrode tends to break down when the temperature exceeds 80 °C or 175 °F. Second, the Calomel electrode is partially comprised of Mercury which is known to be a health hazard, thus making it less user friendly than the Silver/Silver Chloride reference.

The Silver/Silver Chloride reference has a number of advantages for use in the industrial pH market. First, the temperature stability of this reference is good in applications ranging up to 105 °C (220 °F). However, when stabilizers are added to the reference, accurate pH measurements can be taken to temperatures in excess of 125 °C (260 °F). With the stability of this reference and the relative ease of manufacture into a combination electrode the Silver/Silver Chloride reference has become an IC Controls standard.

Reference Junction Impact

The Silver/Silver Chloride reference has a porous junction between the KCl reference solution and the process. This porous junction acts as a barrier to keep the reference internals and the process from readily mixing and contaminating the reference, which would render the reference useless.

Like the glass membrane, the junction can cause a noticeable potential difference in the electrode. The difference in the magnitude of this potential is small in comparison to the glass, but it is significant enough that choosing the proper junction can have an effect on the pH measurement. In considering which junction is used for an electrode the chemical compatibility of the reference junction material with the process must also be considered.

Ceramic Junctions

In the industrial pH electrode there are basically three styles of reference junctions that can be selected: ceramic, wood or porous plastic, depending on the process application. The first is the *Ceramic junction* which is very useful in high accuracy types of pH measurements because of its low junction potential. However, there are a couple of limitations with this junction. The junction usually has very little surface area in contact with the process and is prone to clogging, in dirty or oily industrial applications. As well, because of the brittle nature of ceramic, it is less shock resistant in applications where the electrode comes in contact with small solids or pieces of debris on a regular basis. For these reasons the ceramic junction is primarily used in the laboratory for grab sample purposes where high accuracy is required and the electrode will not be subject to the rigors of the process.

Wood Junctions

Another type of junction that can be used with IC Controls pH electrodes is the *Wood junction*. Wood, by its nature, allows good transport of liquid through its fibers and resists coating from most substances. These two features make the wood junction exceptional for use in applications where coating from the process can occur. IC Controls wood junctions are normally manufactured with a larger surface area which allows for better contact with the process, which is essential in the dirtier applications that try to clog the reference junction. The limitation of wood occurs in high temperature and high pH environments.

Porous Plastic

For high temperature and high pH applications a *Porous Plastic junction* is used because it is chemically resistant and is not affected by temperature in the readable temperature range of pH. Like wood, IC Controls porous plastics are manufactured with large surface areas so that good solution contact is maintained. If an application is running over 50 °C or above pH 8 continuously, a porous plastic junction may provide best results.

pH Concerns in Industry

In the industrial pH application there are a number of common problems that cause difficulties when trying to measure pH. Below is a list of some of the most common pH measurement dilemmas and how to approach them to get better results.

Slope and Offset

The slope and offset are measures of how efficient and how close to theoretically perfect the probe is.

The first step in calibration is to use pH 7 buffer to calculate the mV offset of the electrode from the theoretically perfect 0 mV. A larger mV offset is farther from a theoretically perfect electrode. pH 7 buffer is used because it simulates 0 mV thus making it the best standard to calculate the offset from this 0 mV reference point.

The next step in the calibration is to use a second buffer (usually 4 or 10). Either of these buffers gives a large enough space relative to the pH 7 buffer that a good slope

can be calculated. When calculating the slope of the electrode a good separation between the buffers is needed so that an accurate span between two points is calculated. As well, when choosing which buffers to use in calibration it is best to choose buffers that fall on both sides of the normal operating pH. By using these two buffers the slope calculation will encompass the normal pH, thus giving the most accurate pH measurement. At 25 °C the slope is 59.16 mV per pH unit and the slope is measured as a percentage of this millivoltage. When performing the two point calibration a percent value will be given in microprocessor based pH analyzers. The closer to 100% the slope is the better the efficiency and thus the performance of the electrode.

Heat Effect on Slope

At 25 °C the slope of a 100% efficient probe is 59.16 mV per pH unit with 0 mV starting at pH 7. But, as the temperature changes, so does the mV per pH unit as seen below in the graph. In fact, the slope changes 0.1984 mV per degree Celsius.

This relationship is important in determining pH. If it is not used the reading could be out a significant amount.

For example: pH is being monitored in a process at pH 4 and 60 °C. The output from the probe will be 198 mV according to the temperature mV relationship. Without temperature compensation the analyzer will see 198 mV and assume this reading is taken at 25 °C. At 25 °C, 198 mV is calculated by the pH meter at 59.16 mV per pH to be a pH of 3.64 which is off by a third of a pH unit.
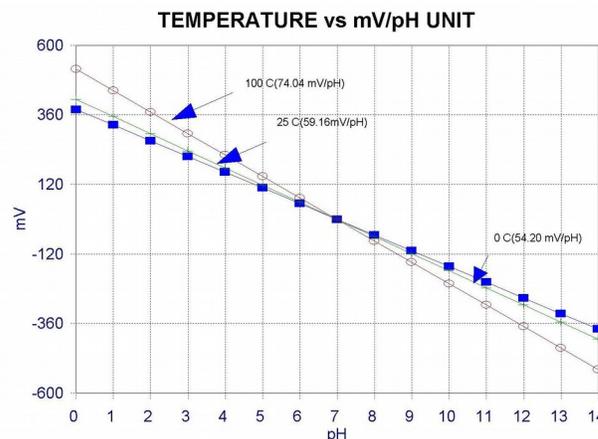

Figure 6: Temperature vs. mV/pH Unit

Therefore, it is important to ensure that temperature compensation is used in the pH probe so that accurate pH readings are given by the analyzer.

Caustic Ion Error

Another problem with pH electrodes occurs at the high end of the pH scale when the concentration of Hydrogen ions is low. In fact, high pH causes two problems. First, at high pH there is a high hydroxide (OH^-) concentration coupled with extremely low hydrogen ion which dehydrates the glass making it very sluggish in responding to pH changes.

Secondly, and more importantly, a caustic (sodium) ion error will occur if the proper glass is not used. As the pH goes up, the concentration of Hydrogen ion goes down. At the same time the concentration of Sodium ion will increase. Sodium is very close to Hydrogen in its chemical structure. As the concentration of Hydrogen ion decreases the glass will start to recognize Sodium as Hydrogen, thus giving a false, low pH reading. By using high pH glass the Sodium ion error will be negated as seen in the graph below.

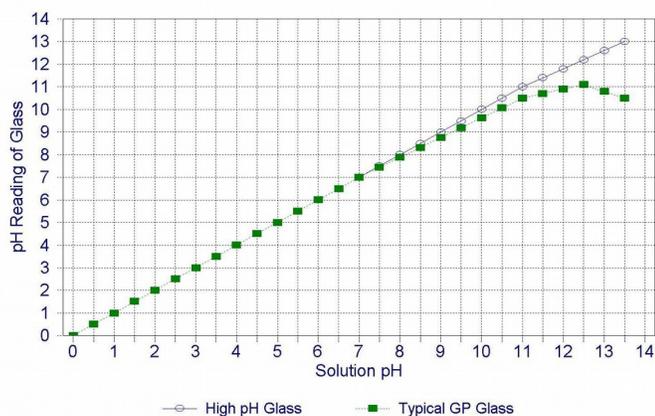**High pH Effect**
On Different Types of Glass

Figure 7: High pH Effect

This graph shows that using the proper glass can have a significant effect on the accuracy of the pH reading. One other benefit to this high pH glass is its resistance to caustic etching. Thus, using high pH glass will result in improved performance and longevity will be seen.

Coating of the Glass

In a number of applications there are constituents that will coat the glass, such as Calcium carbonate which is present in systems where lime addition is used for effluent neutralization. Coating of the glass causes poor contact between the glass itself and the process. Good contact by the electrode is essential for quick accurate response in the process. Thus, to help keep the glass clean and responsive there are a couple of procedures that can be used.
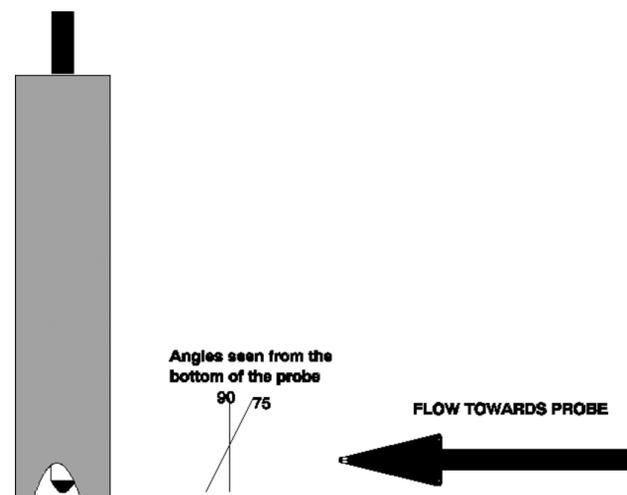

Figure 8: Electrode Flute Angles

The first is to insert the electrode with the flutes at 75° to flow, as seen in the diagram above. By inserting the probe at this angle a vortex will be created around the glass. The vortex will increase the velocity of the process around the glass and reference which will, in turn, hastens electrode response time and keeps the reference cleaner. As well, by turning the flutes to 75° the process does not directly hit the glass which will slow down the coating action. When the probe does coat, a good cleaning procedure should be used to restore the electrode back to 100%.

In the past, a Hydrochloric acid solution was used to remove scale from the tip of the electrode. Although this has been somewhat effective, a gentle scale remover will better clean the electrode. If the pH response becomes sluggish and the slope of the probe starts to get too low, an *Electrode Renew Solution* can be used. The electrode renew solution will skim off a micro-layer of the coated glass, thus

exposing a new glass surface which will exhibit better pH response.

Ground Loops

One of the more difficult problems to analyze in a pH loop is a *Ground Loop* which does not necessarily exhibit any visual signs. Unlike scaling or even Caustic ion error, which you specifically look for at high pH, a ground loop can occur at any pH under many different conditions. Fortunately, there are certain indicators that point to a ground loop problem.

First of all it is important to know that a ground loop occurs when an external charge is applied to the pH system. When analyzing for a ground loop, look for a pH offset in the process pH reading, compare it to a grab sample pH reading taken in a beaker just after the electrode has just been calibrated.

As an example , a ground loop can occur if an electrode is inserted into a pipe that is carrying a charge which is then transferred by a short to the pH probe. In a charged process the pH reference cell can act like a ground wire and current will flow through it to any ground. Therefore, to alleviate a ground loop problem an isolated reference input plus a ground wire or a solution ground is used to bleed off the residual charge, isolating the mV seen by the analyzer to the potential produced by the pH reading itself.

Reference Contamination

In different processes there are a number of different constituents that can contaminate the reference electrode. Some constituents migrate into the reference and attack the Silver\Silver Chloride reference wire causing the wire to deteriorate over time. The reference offset is a gauger of how far the deterioration of the reference electrode has progressed. If the offset from 0 mV increases the reference is becoming more contaminated. Within an offset of 1.3 pH units the electrode is still typically deemed to be good for use. Between 1.3 and 4 pH units the electrode may still be within a usable range but has deteriorated significantly. When the offset reaches 4 pH units or 240 mV the reference has been contaminated to the point where it can no longer be relied upon for use in the process.

There are two major contaminants in the industrial market, Sulfide (S=) and Cyanide (CN⁻). Sulfide is commonly found in Kraft Pulp and Paper mills. All of the different liquors in the Kraft process have a high Sulfide content and therefore, the pulp stock will have a significant amount of Sulfide as well. Cyanide, on the other hand, is typically found in mines and metal refineries. The cyanide is used as a precipitate for metal separation in flotation cells. Thus, contamination of the reference is an issue for both pH and ORP cells which are used in these processes.
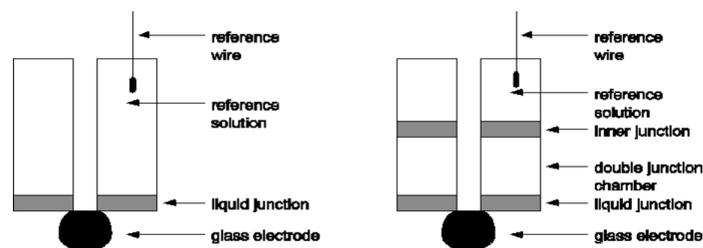

Figure 9: Single Junction vs. Double Junction

To combat reference wire contamination, double junction and/or plasticized references are used to slow down the migration of the sulfide or cyanide to the reference wire. Figure 9 is a diagram of a single junction and a double junction reference for comparison purposes.

The second junction is used to increase the path length of the contaminants to the reference wire. The longer the migration path, the longer it will take to reach the reference wire thus extending the life of the reference. The second junction also acts as a barrier which will slow the migrating ions, again extending reference life. The other contamination deterrent is the plasticized reference solution. The plasticized reference impedes ion migration as a solid as opposed to a liquid. The more solid the reference solution the longer it will take thus protecting the Silver\Silver Chloride wire.

For applications that contain Sulfide or Cyanide, a double junction plasticized reference will extend the life of the pH or ORP probe.

Chemical Compatibility with Glass

In an industrial pH steam there are usually a number of different chemicals present, some of which may not be compatible with pH glass. One of these chemicals has

already been mentioned in the *Caustic Ion Error* section which specifically addresses the problem of Hydroxide etching of the glass which will cause sluggish response.

Another chemical that causes problems is Hydrofluoric acid, which will eventually etch the glass membrane away so there is no sensing glass left. To help with longevity of the electrode, thicker glasses are used so that it will take longer to erode the sensing membrane. Be careful of the relationship between temperature and resistance of the glass. The thicker the glass the higher the resistance. Although a thicker glass is better for HF applications, the normal operating temperature of the process must be taken into consideration, as is mentioned in the *Temperature Effect on Glass* section, so that a compromise between longevity of the probe and response time is established. Tests of various glasses have shown that certain glasses resist F^- attack better and are applied for these applications.

Another chemical that should be taken into consideration is Ferric Chloride which is used in Sewage systems as a complexing agent. Ferric Chloride will attack the glass electrode at the active pH sensing sites, rendering those sites inactive. Inactive pH sensing sites on the glass will result in sluggish response to pH changes in the process. To contend with this problem, put the electrode in "Electrode Renew Solution" on a regular basis, to skim off a micro-layer of bad inactive glass leaving behind a fresh layer of glass for better pH response.

Sandblasting Due to Slurry

In mining applications there is normally a lot of grit which is traveling at a high velocity. When this grit hits the glass sensing electrode it has a "sandblasting" effect causing the glass to become pitted. This decreases the response of the electrode and wears the glass away. To help keep the glass intact the probe should be turned so the flutes are at 75° to the flow (as in the glass coating situation - See diagram). By inserting the probe at this angle a vortex will be created around the glass. The vortex will increase the velocity of the process around the glass and reference separating the grit by centrifugal force, which will also quicken the electrode response time and keep the reference cleaner by using the abrasive nature of the slurry. By turning the flutes

to 75° the process does not directly hit the glass. Keeping the glass out of the path of the sandblasting slurry which will lengthen electrode life.

Clogging of Electrode Tip

One of the major concerns in Pulp applications is clogging of the electrode tip. Pulp fibers get caught in the area around the glass, clogging the electrode. The reference and glass no longer have contact with the process and thus, proper pH measurements cannot be taken. There are two different electrode modifications to help alleviate the clogging problem including the use of a flat glass style of electrode. A flat glass surface is parallel to the flow therefore, as seen below, the glass does not come in contact with solution as well as a dome-type of glass. The best proven probe design incorporates a domed glass in with a body configuration that will not clog, while at the same time protecting the tip to the shearing action of dense pulp stock. To accommodate all of these, a pulp modified tip, shown below, was developed to ensure better contact with the solution while protecting the tip from the shearing action of the stock and clogging.
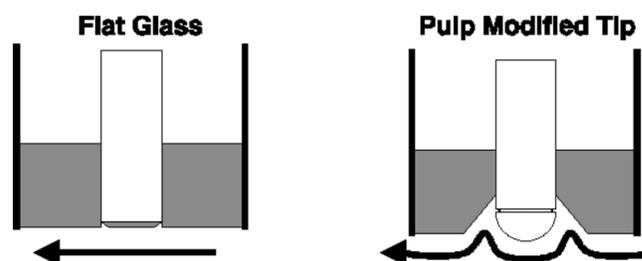

Figure 10: Flat Glass Tip vs. Pulp Modified Tip

High Purity pH

Due to the lack of conductive ions in high purity water a number of interferences occur which show up as a drifting and spiked measurement often far from the correct value. Without ions providing a conductive short circuit the pH electrode, coupled to an ultra high impedance preamp, acts as a high gain, high efficiency antenna. Escaping chloride ions from the reference cell tend to partly short the high resistance allowing the pH electrode to establish a pH output. When changes in sample flow occur, the rate at which ions are swept away is upset causing a compensating adjustment in the pH electrode. This effect is often described as sweeping away of the "ion cloud." A related

effect is the potential at the reference junction which is also affected by the number of ions and the rate of sweeping away. As sample flow increases the actual conductivity produced by the ions drops due to fewer ions left in the area of the junction. The junction, like a thermocouple, puts out a millivoltage relative to the two dissimilar conductors it is composed of. This, of course, changes if one of the conductors is changing.

A high purity pH electrode takes into account all of these effects. A stainless steel flow cell is used for shielding together with a total surround shield. Ion scarcity is compensated for by driving the cell with the analyzer power to produce an electron rich environment. Sample flow is reduced to a low, constant figure and the reference junction is modified to provide a more gradual change in the conductivity level and thereby increase potential stability. A large reservoir of KCl is supplied to provide the necessary ions and also isolate the normal AgCl component from the high purity water. Otherwise silver with low solubility precipitates, plugging the junction and cause premature failure. See the 615 pH sensor and articles in the boiler water section for more on pH measurement in low conductivity water.

Sluggish Response

One of the criteria for electrode performance is the speed of response. Thus, slow response to pH changes in the system is a concern. It is important to address some of the different factors that can cause sluggish electrode performance.

Several different causes that effect electrode performance have already been discussed in the this article; the Coating of the Glass, Sandblasting Due to Slurry, Caustic Ion Error, and the factors affecting the resistance of the glass. Yet, besides simple old age, there is one other reason for sluggish response that is important.

Sluggish response is likely to occur when an electrode is taken out of storage due to hydrolysis of the electrode membrane. The electrode is stored in salt water when shipped, which is not Hydrogen ion-rich as is best suited for the glass. To revive the electrode immerse it in a beaker of 4 buffer until the reading gets relatively close to pH 4. Rinse off the electrode and place it in pH 7 buffer until the reading gets relatively close to pH 7. Keep alternating between 4 and 7 buffer until the response time is normal.

Comparison with Lab Results

When analyzing process pH a common step in ensuring accuracy is a lab grab sample analysis. Difficulty can occur when the lab results do not correspond to the process analyzer, which is surprisingly common due to discrepancy between lab and process sample conditions.

A common lab analysis procedure is as follows: A grab sample is taken to the lab in an open container and placed on the lab bench within 10 to 15 minutes. The bench meter is calibrated within 5 minutes and a non temperature compensated pH reading is taken of the process sample. This grab sample procedure has a high potential for discrepancy between the two sample conditions.

First, the time between sample being taken and the lab pH measurement was approximately 20 minutes. In this time the sample cooled, the solution chemistry changed and thus, the pH reading at the cooler temperature will not be indicative of the pH at sample conditions. Buffer solutions have temperature curves associated with them to display how buffers are specifically designed to resist pH change.

A second problem relates to temperature compensation of the lab analyzer. As seen in the *Heat Effect on Slope* section, it is very important to have correct temperature compensation to ensure accurate pH readings.

A third point relates to contamination. The lab sample, in an open beaker, was walked through an industrial plant with contaminants in the air. The open beaker will likely pick up some of these airborne contaminants which could alter the pH of the sample.

Therefore, when noting the difference between a grab sample pH and the process pH, it is important to make sure that the grab sample is measured at the same sample conditions as the process to make sure the two readings are comparable. As the process pH electrode does not get exposed to these potential sources of error it may well be more accurate than a grab sample.

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