Understanding Differential pH Measurement and Its Benefits
Together facing a brighter tomorrow

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Co-innovating tomorrow™
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Abstract

The significance of the differential electrode is appreciated only after a review of conventional electrodes, both in theory and practice. Obtaining successful measurements of pH was a long, evolutionary process involving various scientists. The Danish scientist, Sorenson, first defined pH. Around 1906, Cremer discovered how to manufacture glass that was capable of providing an mV potential difference. The magnitude of which depended on the acid value of the liquid in which the glass was immersed. Later, Klemensiewics proved that this potential difference within a fixed pH range followed Nernst's Law. Nernst discovered that the combination of a metal and an insoluble salt of that metal and a salt solution have a constant electrical potential. By the early 1930s, these theories had evolved to the manufacturing of successful pH electrodes.

There are different versions of differential pH available and they have significant advantages over conventional electrode designs in a variety of difficult applications. Conventional electrodes suffer from reference problems, especially when high temperatures and high pressures are involved. Seventy to eighty percent of industrial users will fully benefit from using differential sensors. An example is the cation reference. It is a hermetically sealed reference that eliminates exposure of the reference fill solution to the process, as there is no reference junction to be affected by aging, plugging or poisoning from the process. This greatly reduces maintenance problems since the reference stability of the differential sensor is then only dependent on the sodium concentration of the process. In this paper, we will discuss the different forms of differential pH, the benefits of differential pH and some common applications.
Introduction

A pH sensor measures the voltage that the pH membrane measures as a function of the pH value of the process sample. This voltage is then compared with the mV output of a reference cell that is independent on the pH value of the sensor.

In a pH measuring sensor, the reference cell is typically a metal/insoluble metal salt/salt solution combination inserted in an electrolyte solution (or gel) that is separated from the process with a liquid junction. This ensures that the electrolyte composition does not vary with process changes and therefore the mV output does not change either.

Traditionally this was electrochemically a very accurate pH measuring system when maintained properly. The reference element was Calomel: Mercury/Mercury Chloride/Saturated Potassium Chloride; extremely stable and almost no interference from process components. Mercury is now banned from the market due to its high toxicity, and Calomel based sensors are severe chemical waste. The Calomel element is now replaced by Silver/Silver Chloride/Potassium Chloride elements that are also good, but suffer from poisoning by other Halogen and Sulphide ions.

The reference element is separated from the process with a ceramic or sleeve liquid junction and the electrolyte flows out of the sensor due to pressurization of the electrolyte solution. This method prevents penetration of ions from the process into the reference cell.

Users want to measure in-line under process conditions to allow for real time pH control. The described system has disadvantages under these requirements:

1. If the process is under pressure, the reference cell must be pressurized higher.
2. If the process pressure varies and the overpressure is fixed, then electrolyte flow is not constant resulting in high electrolyte consumption at best.
3. If the temperature is high, then the flow rate is increasing.
4. The electrolyte reservoir needs to be filled and kept free of leakage (tubing) which means regular maintenance is required.

Many manufacturers have developed pH sensors with solidified reference elements. The reference element is filled with gelled or polymer electrolyte and does not require refilling. The advantages are clear:

1. Can be used in pressurized applications
2. Does not require refilling; if electrolyte is depleted, the sensor is replaced

However, the reference cell is still in open electrolytic contact with the process and the composition of the electrolyte changes over time by diffusion, so regular calibration is required. The process may contain ions that poison the reference element and these ions penetrate the element by diffusion, especially at high temperatures. Manufacturers have fixed these troublemakers by using double and triple junctions, solid polymer systems, and silver scavengers. Nevertheless, it is well known that nowadays 80-90% of all pH troubles are related to instability of the reference cells. The only solution to this is to have a true hermetically sealed reference cell.

To better understand the benefits of a differential pH sensor we need to understand how a traditional pH sensor works and how it differs from a differential pH sensor.
Understanding Differential pH Measurement and Its Benefits

Conventional vs Differential

What is absolute pH?

pH is measured with a pH sensitive electrode against a reference electrode with a stable and known electrode potential. Conventional reference electrodes supply a constant voltage that acts as a “reference line” for comparing the output of the measuring electrode. With a fixed “reference value,” conventional pH is considered an absolute measurement.

How does a conventional pH electrode work?

**Measuring Electrodes:** The measuring electrode is commonly called the glass electrode. Conventional pH measuring electrodes are constructed with a thin fragile bulb of pH sensitive glass (Cremer 1903). The glass electrode normally contains a seven buffer solution sealed from the process and develops a ± voltage proportional to the hydrogen ion concentration of the process solution. This relationship can be explained by the Herman Walter Nernst’s Formula or Law. The mathematics shows the voltage changing by 59.16 mV at 25 degrees Celsius for each decade of concentration of the hydrogen ion. Typically the isothermal point voltage is 0 mV at 7.0 pH.

The glass electrode’s performance is affected by heat and chemical attack. The inside and outside gel layers of the pH sensitive glass are affected by sterilization temperatures. The glass surface is also affected by acid and caustic attack. The outside surface may be rehydrolyzed however, the inside surface is permanently affected. The result of these process effects are reduced output span and sluggish response. A coating on the glass surface (reference junction) down in the 10 micron range will slow down response time. The normal human eye is able to detect differences in the 40 micron range.

**Reference Electrodes:** In order to complete the electrical circuit, an independent reference potential is required. The electrode providing this potential was called the reference electrode. The most common reference electrode is the silver/silver chloride potassium chloride electrode. This electrode develops a potential as a function of the concentration of potassium chloride (KCl) and is designed to allow small amounts of electrolyte to contact the process solution and complete the electrical circuit. The electrode voltage is stable so long as the electrolyte solution (KCl) is flowing and its concentration remains constant.

On-line pH measurements in fouling process solutions upset the performance balance between solution flow and junction size. Very small junctions provide an extension to reference electrode life, however they are very prone to process fouling and dictate high maintenance costs. The development of the diffusion reference electrode, which uses saturated KCl in a gel to inhibit the flow of liquid from the electrode, was a significant performance improvement. This electrode relies on the flow of KCl ions by osmosis and permits the use of a larger reference junction surface area and provides an electrode that is less prone to fouling.

The reference electrode will be affected by depletion (loss of electrolyte), fouling (surface coating) and poisoning (intrusion of the process into the electrode). The reference electrode’s voltage can be severely affected by precipitating chemicals, oily products and variations of process pressure. In each case, as the concentration gradient in the electrode changes, it will cause the reference voltage to drift. In many of these difficult environments the electrode will require significant maintenance, frequent recalibration and have a short unproductive life. It is estimated that 80-90% of all difficulties in measuring pH are caused by the electrodes. Of this 80%, problems with the reference electrode will account for 80-90% of the total electrode difficulties.

What is relative pH?

Differential pH measurement: pH is measured with a pH sensitive electrode against a second ion sensitive electrode. The reference voltage of the reference glass electrode is “process determined,” totally dependent on the amount of “cations” within the solution. It is actually a measuring electrode which measures the concentrations of salts. Thus, as salt concentrations change, so can the reference voltage.
How does a differential pH electrode work?

So how does a differential measurement work? Like with conventional pH measurement, the pH glass sensor is still used for measuring the pH relevant potential. But for generating a stable reference voltage, there are two common ways this can be done. This is where the confusion comes in between the Yokogawa way and other manufacturers.

You can use a pH sensitive electrode as reference, which is installed in a buffer solution. The idea of using a glass sensor is that now the Ag/AgCl element of reference is protected against poisoning and other problems. Or you can use an ion salt sensitive electrode as the reference, which is installed directly in the process. This is the method Yokogawa uses. This is different from the glass-in-glass. When you use a cation sensitive reference to generate the reference voltage, it is called relative pH, not absolute pH.

The sodium reference electrode is not an absolute measurement of pH, because it is not an actual reference electrode which supplies constant reference voltage. The reference voltage of the sodium reference electrode is “process determined” or dependent on the amount of all “salts” within the solution. Point in fact, it is actually a measuring electrode which “measures” or responds to the concentrations of salts. Therefore, as salt concentrations change, so will the reference voltage it generates.

When it is combined with a pH measuring electrode, we have what we call a “Differential” pH system. The system measures the concentration of sodium in the process to determine the reference voltage. Thus, the live voltage (of the cation measurement) makes the reference voltage process dependent versus being an absolute independent reference.

The differential measuring principle has significant advantages over conventional electrode designs in a variety of difficult applications. The hermetically sealed reference eliminates exposure of the reference fill solution to the process, as there is no reference junction to be affected by aging, plugging or poisoning from the process. This greatly reduces maintenance problems since the reference stability of the differential sensor is then only dependent on the sodium concentration of the process.

The benefit of using a cation reference electrode that it has NO junction. There is NO path from the process to the internal element, so NO poisoning can occur. Also, since there is NO junction, there is NO plugging or coating problems to worry about, and there is NO electrolyte depletion problem because there is NO electrolyte.
Types of Differential Technology

Glass–in-Glass Technology

An alternative reference approach is one where a “glass-in-glass” design (Figure 5) is used and may also be considered as an absolute measurement.

This design uses a standard glass electrode as the measuring electrode which generates a potential proportional to the process pH. The second glass electrode serves as the reference electrode and consists of an internal measurement electrode immersed in a stable buffer solution. The internal electrode makes electrochemical contact with the process via a salt bridge chamber (double junction) and generates a standard reference potential. Both glass electrodes have a common potential developed at the third electrode—the solution ground electrode.

This design eliminates the stability problems experienced with conventional references due to process poisoning of the reference element. However, since it utilizes a liquid junction interface with the process, this reference design will still suffer from plugging and coating problems.

Dual Enamel Technology

Dual Enamel technology is an ion specific, differential pH electrode. The electrode uses two yellow ion specific enamel bands. Each band is 1 ¾” in length and spaced 6/8” apart along the blue enamel coated 316 SS body, which has a diameter of approximately one inch (0.96”) and overall insertion length of six inches. The respective pH and sodium ion enamels are fused to the smooth enamel surface and fire polished.

The top enamel functions as the pH measuring site by reacting to Hydrogen Ions (H⁺). A positive or negative change in the activity of the H⁺ in the measured fluid results in corresponding change output of the pH enamel. The output reliability follows the Nernst Equation between the recommended range of 3 to 11 pH. Certitude is affected outside of this range. The chemical resistance of the enamel also drops off outside of this pH range and long term exposure will shorten useful life.

The bottom enamel band which measures Sodium Ions (Na⁺) provides the reference voltage. The Na⁺ enamel is a measurement band sensitive to all sodium ions. Increases or reductions in the concentration of Na⁺ (in any formulation) have a corresponding effect on the output of the sodium glass enamel (Figure 7). The reference voltage of the sodium ion electrode is not definite and predictable as is true in traditional reference electrodes. The reference voltage is determined by and is dependent on the background concentration of sodium ions in the process solution. The stability of the reference voltage is enhanced with higher concentrations of sodium ion. Conversely, low conductivity (below 5 μS) fluids lacking sufficient Na⁺ will result in unstable measurements.

A rhodium solution ground is used to eliminate stray voltages in the process solution. This is similar to the solution ground found on better conventional pH electrode systems. The resulting electrode is rugged, not affected by steam sterilization, not fouled by precipitating solids and provides unusually stable pH measurement within its operating range of 3-11 pH.
Cation Sensitive Technology

The reference portion of the cation sensor (Figure 8) is made entirely of a glass which provides a mV output corresponding to the cation concentration of the process or solution it is in. Therefore, there is no liquid junction to be coated or clogged and no path for the process to affect the electrolyte or the internal Ag/AgCl element. This means that the sensor is truly maintenance free.

It is actually a measuring electrode which measures or responds to the concentrations of salts. Therefore, as salt concentrations change, so will the reference voltage it generates. Therefore it is process dependent versus being an absolute independent reference.

This is a revolutionary solution for many of the challenges in pH applications that customers struggle with. The sensor reacts on pH changes rather than analyzing the accurate pH value. In that sense, it is best to describe the sensor as a pH control sensor rather than a pH measuring sensor.

Figure 8: SC24V Design

Figure 9: FU20-FTS Design
Understanding Differential pH Measurement and Its Benefits

Introduction to Sodium (Na⁺) Glass

pNa measurement is very similar to pH measurement. Both methods use a glass electrode in combination with a reference electrode. In a cation differential pH sensor, the reference cell is also a glass sensor that does not respond to changes in the pH value within the application range of the sensor. This means that the sensor is truly maintenance free and the output voltage of the sensor depends only on the salt concentration changes in the process.

In the past, Yokogawa developed this glass as a single pNaion sensitive electrode to measure the sodium ion concentration within a process. It was found that just as a pH measurement sensor, the analog signal to the output of the reference membrane follows the Nernst Law. However the output voltage of the salt sensitive reference membrane depends on the salt concentration of the sample. As it turns out, the pNa membrane also shows sensitivity to other cations, i.e. Li⁺, K⁺, and Ca²⁺ (Figure 10) within a process; so the use of this reference glass is not limited to only sodium ions. It can be used as salt sensitive reference in general if the concentration is high enough and consistent to generate a stable mV output reading.

In most pH control applications, the salt concentration is rather constant, so the mV output of the reference cell is constant and therefore the overall output is only dependent on the pH of the process. The graph below shows the response of the reference glass to changes in different cations concentrations. You can see that it does not matter which salt is present, because the shifts all respond similarly.

![Sensitivity reference glass for cat-ions](image)

How to read this graph:
The pH is controlled in a solution with 10 g/l Calcium Chloride (CaCl₂)
The molecular weight of CaCl₂ is 111, so the concentration of Ca²⁺ is 10/111 mol/l = 0.09. The negative logarithm of this solution is 1.045 so the voltage of this reference element is -160 mV against SCE. The output voltage of the pH sensor in pH=7 is -40 mV against SCE, so the Zero Offset (Asymmetry) of the sensor is - 120 mV.

A rule of thumb is that a change in salt concentration of +/- 25% has an effect of less than 0.1pH on the pH reading. In most pH control applications, this will not be noticed even when the salt concentration varies by 25%.
Benefits to Differential pH Measurements

The advantage of using the glass on glass differential method is that the reference electrode is a pH glass electrode installed in a buffer solution which has contact to the process via a junction. This means the inner reference element is protected by the pH glass and cannot be poisoned. So it is a double junction salt bridge design. The system also includes a close coupled encapsulated preamplifier. Some setups are available that allow for the replacement of the buffer solution and the junction so this allows for long life and long sensor to analyzer distances.

However with the cation differential reference there is NO junction, there is NO path from the process to the internal element; so NO poisoning can occur. Also since there is NO junction, there is NO plugging or coating problems to worry about and there is NO electrolyte depletion problem, because there is NO electrolyte.

This means with the cation reference we have a perfect solution to our problems, right? Well, not quite. There are always trade-offs to consider. Just like standard reference electrode designs where some designs work better in certain applications than others, no one solution solves every problem. While the cation reference does overcome problems we deal with using a standard reference, it does have a few drawbacks that must be considered to gain the best results using this style reference.

1) It is NOT a true pH measurement. The sensor is designed for pH control applications.

2) It is affected by salt concentration changes in the process.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hermetically sealed</td>
<td>No contamination of process by electrolyte</td>
</tr>
<tr>
<td>No porous junction, no diffusion</td>
<td>high stability, low maintenance</td>
</tr>
<tr>
<td>4 in 1: pH, Ref, Temp, Liquid Earth(ORP)</td>
<td>One pH application= 1 sensor, 1 cable</td>
</tr>
<tr>
<td>12 mm PG13.5</td>
<td>Compatible with most industrial holders</td>
</tr>
<tr>
<td>Wetted materials only Pt and Glass</td>
<td>High chemical resistance, sanitary</td>
</tr>
<tr>
<td>No electrolyte in contact with process</td>
<td>Universal application, no pitfalls</td>
</tr>
</tbody>
</table>
Care and Maintenance

Dual Enamel Technology

Handling: The dual enamel differential pH probes are pressure and thermal shock resistant due to the fused steel/enamel construction. The probes have a very high mechanical stability and are extremely strong. Inappropriate handling, such as hitting and scratching the probe on steel, ceramics, glass or stone may cause damage to the probe. Depending on the scope of the damage, the probe may not fail immediately but rather when the temperature changes. If a defective measuring probe remains in aqueous solutions for prolonged periods of time, enamel may flake. If sensor damage is indicated, the measuring probe must be immediately removed (within 24 hours) after an alarm message. All probes for use in the food sector are tested with a voltage of 12 kV and conditioned for five hours in steam at a temperature of 134 °C.

Storage and Hydration: The dual enamel electrode can be stored dry for an indefinite period of time at temperatures between -30 and +80 ºC. After prolonged storage or if this is a new probe from the factory, a simple steam sterilization should be performed for 15-30 minutes prior to calibration. This procedure revitalizes the probes giving it a stable reference potential. If steaming is not possible, soak the electrode for 45-60 minutes in hot water (65 to 85 °C). If steaming or a hot soak cannot be done, place the electrode in a standard pH7 buffer solution for 24 hours prior to installation. The probe must be immersed so that both measuring elements are covered with buffer.

Cleaning: The sensors can be cleaned inside the vessel or pipe. For CIP cleaning care must be taken to ensure that the permissible alkali and acids concentrations, as well as maximum temperatures and duration of cleaning time are not exceeded. Failure to follow the acceptable cleaning parameters listed below can result in increased corrosion levels of the PH18 enamels.

Acceptable CIP Cleaning Parameters

1) Steam cleaning (typical 121/124°C) no higher than 134 ° C for no longer than two hours.

2) 1.5 to 2 percent alkaline solution at a temperature (typical 50-60° C) no higher than 85° C. Maximum CIP exposure time with this solution to be no longer than 1 hour. Weaker solutions permit longer exposures.

3) 1.5% HNO3 (Nitric Acid) solution at a temperature no higher than 50° C. Maximum CIP exposure time with this solution is to be no longer than fifteen minutes. Weaker solutions permit longer exposures.

Acceptable Sterilization Methods: The electrode is resistant to the following methods of process or in-line sterilization:

1) With product
2) With steam
3) With alcoholic solutions
4) With antiseptic solutions

Calibration: The dual enamel ion specific differential pH electrode does not require a two point buffer calibration. Best results occur from a single point process calibration; which also reduces maintenance costs. The yellow pH measuring band has no internal solution and is inherently stable (in effect, fully hydrolyzed). Its output will always follow the Nernstian Formula between 3-11 pH. This removes the requirement for the second adjustment in the two point calibration method.
The yellow Na\(^+\) measuring band, however, is sensitive to changes in the background sodium ion concentration. The “zero” or reference voltage is developed by and is dependent on the background concentration of sodium ions in the process solution. This dependence mandates the process calibration method. The PH18 may be placed in the process solution without prior calibration. A key requirement to the process calibration approach is that it be done in line at the most significant process pH valve. The sample calibration sets the reference voltage based upon the Na\(^+\) concentration then present in the process. Stability occurs from this one point calibration.

The background sodium ion concentration can change up to ± 25% without causing more than 0.2 pH error, hence the operational guideline to calibrate at the most significant pH value. This guideline ensures that the reference voltage is coupled to the critical pH value. Greater shifts in Na\(^+\) concentrations may then be tolerable. Shifts greater than ± 25% can however be corrected by a new calibration. Since the resistance of the reference band is in the 100+ megohm range vs. the traditional 5-10 K ohms range of conventional reference electrodes, process coating of the electrode has a minimal effect on performance. Should large shifts in Na\(^+\) concentrations occur, the need to remove the electrode for cleaning before re-calibrating is eliminated.

The only noticeable difference in “zero” calibration is that the value of the asymmetry voltage will be higher than normally found with conventional reference electrodes. Most transmitters do not have the ability to operate with large asymmetry offset values. The Yokogawa EXA PH202 (24 VDC) and EXA PH402 (110 VAC) are therefore required. Finally the in line calibration method eliminates the normal discrepancies found in most plants when grab samples are taken at higher process temperatures and then compared to cooler lab samples. This helps improve repeatability by removing a source of measuring uncertainty.

**Cation Reference Technology**

**Storage Handling and Hydration:** The sensor should remain in the “wet pocket” when not in the process. During shipment, electrolyte in the sensor could be dislocated. To correct this, place the sensor upright for 24 hours before calibration or installation.

For best results, the sensor should be mounted with the process flowing towards the LE/ORP pin and positioned at least 15° above the horizontal plane to eliminate air bubbles in the glass bulb.

**Cleaning:** A pH sensor requires routine maintenance to keep the measuring elements clean and functioning. Because the sensor does not have an open reference junction and is hermetically sealed from the process, it does not suffer from poisoning, diffusion or fouling. This means the sensor requires very little maintenance.

In most cases cleaning with water, iso-propanol or methanol is sufficient. In other cases the measuring elements of the sensor have to be cleaned with specific solutions. Examples:

1) Deposits of limes, hydroxides or carbonates can be removed by immersing the bottom part of the sensor in a solution containing dilute hydrochloric acid (5% is recommended). Afterwards rinse the sensor with water.

2) Deposits of oil and fat can be removed with hot water with a detergent. When the results are unsatisfactory, a mild (carbonate based) abrasive can be used.

3) Protein deposits should be removed with a protein enzymatic solution; for instance - a solution containing 8.5 ml concentrated hydrochloric acid and 10 grams of pepsin in 1 liter of water. A soft toothbrush may be used to accelerate the cleaning process.

*NOTE:* Avoid cleaning with non-polar solvents like tri-chloro ethylene, toluene or hexane. The non-polar solvents will break up the gel-layer on the measuring glass elements and require that the sensor has to be soaked in water for at least 12 hours before it will function again.

**Initial Calibration:** Every SC24V includes a quality inspection certificate in the packing box. Each certificate has, under the functional test section, the zero point pH 7, which is the ASY, value and the calculated slope pH 7- pH 4 value that will be used during start-up. You can use traditional pH7 and pH4 buffers as a functional check only.
Cation Reference Technology

Place the SC24V sensor in the 7 buffer, allow the sensor to stabilize, and then place it in the pH 4 buffer. The sensor is operating properly if it responds to the pH change.

One final step is required before the sensor can be placed online. Take a process grab sample and perform a one point manual sample calibration to correct for the background salts in the process.

**NOTE:** Remember if the salt concentration changes in the process media by 25%, then a pH change of 0.2 pH could be seen that is not a true pH change but a salt concentration. If this occurs then a one point manual process calibration should be done to offset the new salt concentration.

After Initial Installation Calibration: Differential sensors having both a standard pH glass and a cation reference like the SC24V need to be calibrated to correct both the ZERO and SLOPE. However, conventional pH buffers (N.I.S.T 4.00, 6.86 and 9.18) can NOT be used because they have low strength and different values from one another (0.005-0.01 m). Therefore, when used for calibration, a slope of > 105% will be received. In order to properly perform a two-point calibration, use buffers specifically designed for cation-based references which have the same sodium level for each pH value. By using the solutions Yokogawa offers, the differential sensor will react like a traditional pH sensor. These buffer solutions have an ionic strength of 1 mol/l NaCl so they will have a theoretical zero point of 0 mV at pH 7. The Isopotential Point (ITP) of the sensor in these solutions is at 7 pH.

However because the process salt concentration will be different than the buffer concentrations, a one-point manual grab process sample calibration always has to be performed before the sensor is placed back online in the process. Follow the steps shown above for the appropriate analyzer’s Manual Process Calibration, then the ZERO point will be updated accordingly.

**NOTE:** For optimal performance, the Isopotential Point (ITP) should be updated as well. This ITP is set in the software and is typically (7+pNa).

Application Examples

**Note:** Not every application is shown) These applications represent the majority of the installation/applications by Yokogawa. If a particular application of interest is not listed, please contact Yokogawa with details of the target application.

<table>
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<tr>
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<th>Application Description</th>
<th>Which Sensor was used?</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>SC24V</td>
</tr>
<tr>
<td>Pulp and Paper</td>
<td>Stock Water</td>
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<tr>
<td></td>
<td>Pulp Stock up to 11-12%</td>
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<tr>
<td></td>
<td>Head Box</td>
<td>✓</td>
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<tr>
<td></td>
<td>Virgin Pulp</td>
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<tr>
<td></td>
<td>Bleached Pulp &amp; Discharge water</td>
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<td></td>
<td>Tall Oil (Black Liquor &amp; Soap)</td>
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<td></td>
<td>White Water</td>
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<td>Clean Pulp from Recycle Fiber</td>
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<td>Hot tomato juice</td>
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<td>Xanthan Gum</td>
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<td>De-oiler for phosphate, down stream of float: Augerous phosphate with traces of fatty acids and kerosine, blend sulfuric &amp; acid to remove fatty acids 1 kerosine</td>
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<td>Saline Solution: Oil in sand production</td>
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<td><strong>Chemical</strong></td>
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<td>Sodium Chlorate Solution</td>
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<td></td>
<td>Chlorine Dioxide &amp; Sulfuric Acid</td>
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<td>Kaolin Clay: Sodium Hydrosulphate, Sulfuric Acid</td>
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<td>Neutralization: Sulfuric Acid/Zinc Sulphate with Lime slurry</td>
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<td></td>
<td>Aluminum Nitrate Solution</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Brine Solutions</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Ethanol Distillation Column</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>De-ink Plant, Peroxide Tower</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Carboxylated Latex Reactor</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Water: Acetone in water, Ferasulfate and Iron</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Betaine (Soap) production</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Super Saturated Saline Solutions</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>SO2 Flue Gas: Fly Ash Gypsum Scrubber</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Gluten Filter Aspiration Scrubber</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Feed House Aspiration Scrubber</td>
<td>✓</td>
</tr>
</tbody>
</table>
Typical Applications: The SC24 is ideally suited for pH control applications. It is a differential pH sensor so it does not give the true pH value. Most industrial pH applications are used for process control and the operators are responsible for a stable product quality and therefore a stable pH reading. The laboratory is responsible to establish the true pH value of the product that results from the pH control.

The SC24 is the sensor used by the operators to have a reliable process control and the laboratory used off-line a traditional pH sensor to measure the true pH value. The process operators use this value to perform a process calibration for the SC24 installation to assure that both analyzers give the same value.

Probably 70-80% of all industrial users will benefit strongly from the SC24 differential sensor for their process control, but plants that operate at high temperatures, at high pressures, in nasty processes will benefit the most. The only application where the sensor cannot be used is in (ultra)pure water applications, where the salt concentration is too low.

Examples of applications where the sensor has proven to be successful are:

1) Chlorine manufacturing by electrolysis of brine
2) Bio-ethanol fermentation

Proper Applications:

When determining if the cation differential sensor can be used in a particular application, there are two main requirements that must be considered:

1) Is the process control pH value higher than the process pNa + 2?
   - It is very important to know the pNa value of the process because the operating range of SC24V differential sensor is defined as (pNa + 2) – 14 pH. The reason is the pNa cation reference cell is affected by changes in pH when the acid concentration is much higher than the salt concentration.

2) How much does the salt concentration of the process vary; or what is the conductivity of the process at 7.00 pH?
   - If the process salt concentration varies ≤ 40%, then the influence on the pH sensor will show a shift of < 0.15 pH.
   - If the salt concentration change is ≤ 25%, then the influence on the pH sensor will show a shift of only < 0.1 pH.

The concentration shift is a linear function while the pH value is a logarithmic function. This relationship is very important to understand because if the pH control needs to be maintained at ±0.1 pH, the salt concentration must not change by more than ±25%. If it does then a new process calibration must be done to account for the salt change.

Therefore, in order to determine if the cation differential sensor will work in a particular application, one of the following must be provided:

1) The minimum and maximum salt concentration values throughout the process.
2) The conductivity value of the process at a pH of 7.00. (The conductivity is measured at a pH of 7 to ensure the conductivity value is that of the cations in the process and not the influence of the acid or base in the process.

The following table can be used to assist in determining the process pNa if you know what the process conductivity is at pH 7.00.
Example 1: If the process conductivity value at 7.00 pH is 1.03 mS; then the sample would have a concentration of 500 mg/kg and a pNa of 2.08. Since the operating range of the SC24V sensor is defined as pNa + 2, this would mean the sensor would function between a pH range of 4.08-14.00.

![Table]

<table>
<thead>
<tr>
<th>mg/kg</th>
<th>mS/cm</th>
<th>pNa</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0214</td>
<td>3.778151</td>
</tr>
<tr>
<td>30</td>
<td>0.064</td>
<td>3.30103</td>
</tr>
<tr>
<td>50</td>
<td>0.106</td>
<td>3.079181</td>
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<tr>
<td>100</td>
<td>0.21</td>
<td>2.778151</td>
</tr>
<tr>
<td>300</td>
<td>0.617</td>
<td>2.30103</td>
</tr>
<tr>
<td>500</td>
<td>1.03</td>
<td>2.079181</td>
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<tr>
<td>1000</td>
<td>1.99</td>
<td>1.778151</td>
</tr>
<tr>
<td>3000</td>
<td>5.69</td>
<td>1.30103</td>
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<tr>
<td>5000</td>
<td>9.48</td>
<td>1.079181</td>
</tr>
<tr>
<td>10000</td>
<td>17.6</td>
<td>0.778151</td>
</tr>
<tr>
<td>30000</td>
<td>48.6</td>
<td>0.30103</td>
</tr>
<tr>
<td>50000</td>
<td>81.0</td>
<td>0.079181</td>
</tr>
<tr>
<td>100000</td>
<td>140.0</td>
<td>-0.22185</td>
</tr>
</tbody>
</table>

Knowing the concentration at 7.00 pH allows you to calculate the theoretically pNa of the process and the pH shift you would expect to see if the salt concentration changes. Also keep in mind that if there is a mixture of different salts, you cannot tell how much the mix will influence the reference voltage. In this situation the best practice would be to just measure the process.
Example 2: If you have a 0.2 Wt% sodium chloride (NaCl) solution and the process changes to a 0.4 Wt% solution, what would the pH shift be?

- 0.2 Wt% is 0.2 g NaCl/100 g of Water
  - This is 2 g NaCl/1000 g of Water, so approximately 2G/L
- 0.4 Wt% is 0.4 g NaCl/100 g of Water
  - This is 4 g NaCl/1000 g of Water, so approximately 4G/L
- Molecular weight of NaCl is 59.5 or 60 if you round up

So using the known equation:

\[(A-B) \times 59 \text{ mV} = \text{change in mV due to concentration change}\]

Where:

\[A = \log \left(\frac{\text{concentration before in g/L}}{\text{molecular weight of process}}\right)\]
\[B = \log \left(\frac{\text{concentration after in g/L}}{\text{molecular weight of process}}\right)\]

You can calculate A and B to be:

\[A= \log \left(\frac{2}{60}\right) = -1.477, \text{ so } pNa = 1.48\]
\[B= \log \left(\frac{4}{60}\right) = -1.176, \text{ so } pNa = 1.18\]

Therefore the expected phase shift can be calculated as:

\[(1.48-1.18) \times 59 = 18 \text{ mV} \sim \text{is approximately 0.3 pH}\]

It is very important to know the pNa value of the process because the operating range of SC24V differential sensor is defined as \((pNa + 2) - 14 \text{ pH}\). The reason is the pNa cation reference cell is affected by changes in pH when the acid concentration is much higher than the salt concentration. The following graphs show two different salt concentration samples with different pNa values. In each graph, the light blue line represents the half-cell of the cation reference and the dark blue line represents the pH half-cell. The purple line represents the mV output of the SC24 combination sensor as function of the pH. It is the dark blue line minus the light blue line (differential signal). In either graph, it can be seen that the output voltage of the cation reference cell is stable below the process \((pNa + 2)\) value.
Example 2: (con't)

In the first graph the salt concentration is 60 g/l. The pNa value is 0 and you can see that the purple line, representing the differential measuring sensor, becomes nonlinear below 2.00 pH. Therefore, the pH range in this application for SC24V is 2.00-12.00 pH.

The second graph shows a salt concentration of 6 g/l which means the pNa is 1. In this example the SC24 is only linear over 3.00-14.00 pH.
Yokogawa Solutions

Depending on installation requirements, there are a couple of different options that can be considered.

Transmitter/Analyzer

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.

Yokogawa offers two kinds of pH/ORP analyzers:

- FLXA 2-wire 24VDC pH/ORP Transmitter
- PH450G 4-wire 110 VAC pH/ORP Analyzer

Cation Reference Differential pH/ORP Electrode: SC24V

The SC24V differential pH sensor is unique to the industry, offering maintenance free operation without any reference problems. In the SC24V differential pH sensor, the reference cell is made of glass with no porous junction so no electrolyte is in contact with the process. Because the sensor integrates four functions in one – pH sensing, reference cell, temperature compensation and liquid earth (ORP) there is only one sensor and one cable to deal with. The unit is designed for 12 mm PG13.5 mounting, and is compatible with most industrial holders.

Cation Reference Differential pH/ORP Electrode: FU20-FTS

This version encompasses the benefits of the cation reference into a PVDF rugged body with a ¾” NPT. The wide body sensor (26mm diameter) holds four separate measuring elements in one unbreakable and chemical resistant PVDF body. The FU20-FTS is targeted for those applications where the cation differential reference is the best solution, but need a more durable body then a 12mm glass.
**Dual Enamel Ion Specific Differential pH Electrode: PH18**

The PH18 is composed of blue and yellow enamel. The pH glass enamel is sensitive to the hydrogen ion and the sodium glass enamel is sensitive to the sodium ion.

The high impedance values of both the measuring and reference electrodes results in the requirement of a pH transmitter with dual high impedance ($Z_{in} \geq 10^{13} \Omega$) amplifiers. The Yokogawa FLXA (24 VDC) and EXA PH450 (110 VAC) are such analyzers (unlike ISFET analyzers, these transmitters may be used with both conventional and differential glass enamel technology). The high impedance values cause the PH18 to be more impervious to measurement error from coating and fouling than conventional electrodes. Why? It's a matter of proportion. Due to the high impedance values, the significance of coating and fouling on the PH18's accuracy are negligible when compared against its impact on the small impedance valves of conventional electrodes.

The electrode exhibits lower maintenance costs. The PH18 operates without internal electrolytes. The lack of liquid fill provides the electrode with the ability to measure under severe process conditions in continuous or cycling temperatures to 140 degrees Celsius without deterioration in performance or life expectancy. There is no requirement for refilling the reference electrode.

The glazed surface of the model PH18 resists contamination, ensuring easy cleaning. The polished and nonporous enamel surface prevents encrustation. Its glossy and uniform surface assists in securing a constant heat transfer, thereby limiting both deposit formation (coating) and the adhesive strength of the coating. The model PH18 is easy to keep operational as it doesn't get as proportionately dirty as conventional electrodes and cleans up with less effort.

Labor consuming procedures to protect electrode performance or life expectancy are lessened. Removal requirements are eliminated in strong acid or strong caustic CIP (clean-in-place) solutions applications. The PH18 surface gel layer's ability to recover and to fully rehydrolyze the permits the electrode to be used in CIP processes. Placing electrodes in storage solutions, when process vessels and piping are not operational is avoided. The model PH18 may be subject to freezing temperatures in shipment or stores. Without a liquid internal fill to freeze and expand, no damage to the electrode occurs.

The normal long-term operating range of the new electrode is 3-11 pH. The mV output from the Ion Specific Differential pH Electrode fails to match the normal 59.16 mV/step change the farther the measurement exceeds the upper and lower values which limits its accuracy to this range. The chemical resistance also drops off outside of these pH values and long-term exposure will shorten useful life.

The smooth surface and solid support of the 316 SS body permit the electrode to be used in processes that are under high pressures (up to 240 PSI). Since the electrode has no porous junctions, it can be used in applications that have varying pressures with no fear of process incursion into the reference junction. These construction features also permit instantaneous temperature step changes of 130° C without damage from thermal shock.
Summary

The Differential pH is an exciting new technology and provides a giant step in solving difficult or nearly impossible process pH measurements. The cation differential pH sensors were designed for difficult applications where conventional sensors are ineffective. These include such measurements as brine solutions and applications as diverse as electrolysis processes and cheese manufacturing.

The problems experienced in these applications most often relate to the reference cell and are the result of either high diffusion potentials at the reference junction; high temperatures (often encountered in applications such as in chlorinated brine processes); and high ground-loop currents present in the pH sensor circuits. The cation differential sensors feature a sealed glass reference and does not have a liquid junction nor any electrolyte to come in contact with the process. So, the sensor does not suffer from diffusion potentials or fouling which ensures measurement stability while being virtually maintenance free.
For more information on the technologies discussed in this paper and how coal power plants can implement the devices into the process contact Yokogawa Corporation of America at the following links: