Choosing the Right Electrode

pH Electrodes in the know

Choosing the right equipment?

Every application is different and has its own difficulties; knowing potential nuisances of an application helps to ensure that the proper electrodes are selected from the beginning. A pH sensor has four components: a measuring electrode, a reference electrode, a temperature electrode and a solution ground/liquid earth. Each of these electrodes serves a purpose; however, the measuring and reference are the most critical. There are different versions of each electrode to combat known difficulties in various pH applications.

Measuring electrode **-** The correct selection of a glass electrode for a particular application can only be made if details of the components of the measuring loop and their significant properties are known. Example, in pure water to counter the low response speed and the effect of the alkali components on the glass electrode, a low-impedance glass is recommended. There are different versions of pH measuring glass available on the market and the following points should be considered when selecting the proper glass electrode:

- selection of the glass membrane (sensitivity of the glass electrode (mV/pH))
- chemical resistance of the glass membrane

pH sensitive glass has the particular property that alkali metal ions present in the texture of the glass are exchanged with H^+ ions of the liquid.

What is the benefit of using heavy-duty glass?

Heavy Duty Glass is the description of pH sensors that feature a wall thickness of the sensitive glass membrane of approximately 1 mm. All customers who consider pH sensors as fragile will benefit from this feature. Also applications corrosive to Glass like hot alkaline solutions with high salt content or processes with risk of HF (Fluoride containing waters at low pH) will benefit from heavy duty features.

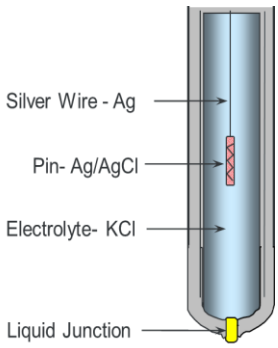


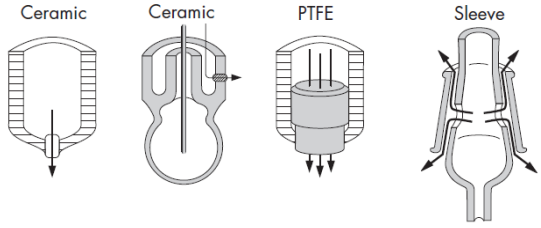
Figure 4: Reference Electrode

Reference electrode **-** The reference electrode is the most important piece in the measurement setup besides a liquid earth/ solution ground element. The purpose of the reference electrode is to provide a constant reference voltage as well as completing the pH measuring circuit. In order to have electrochemical continuity between the measuring electrode and the reference electrode a liquid junction/diaphragm is required.
The reference system may be poisoned by the penetration of "unwanted ions" in the salt solution. To overcome this problem an eletrolyte and diaphragm is used to connect the metal/metal salt with the process liquid (see fig.4).

A constant flow of electrolyte from the reference electrode prevents poisoning of the electrolyte around the reference pin. The KCl can be liquid or Gel. In Gels, the KCl will diffuse out of the junction. Gels do not require (cannot) be refilled and diffuse at a slower rate. If liquid, the KCl will diffuse and flow out of the junction (this is what is called a flowing reference) solving some problems we'll discuss in a moment.

Along with different types of KCl solution there are also different types of junctions that can be used:

- Ceramic
- Porous Teflon
- Glass sleeve capillary element



The Reference electrode is the weakest link in the measurement system being the problem in 80-90% of all applications.

- Typical modes of Reference Failure
  - Plugging
  - Fouling
  - Poisoning
  - KCl Depletion
  - Pressure Spikes (causing pumping of KCl out of the electrode)

What is electrode replacement expectancy?

Typical Applications - Expect to replace (3) Reference Electrodes for every (1) Measuring.
Harsh Applications - Expect to Replace (10) Reference Electrodes for every (1) Measuring.
Minimum Life expectancy - Junction Poisoning

- Symptoms to be aware of:
  - Severe discoloring (turning brown or black in color) of the Junction
  - Discoloration is not removed with cleaning

However, knowing the process allows you to select the right reference system for the process. Each electrode has their own advantages and were made to solve particular issue.

When should we use a flowing reference?
In pure water for example, because of the low conductive properties of high purity water, a flowing reference is needed. The purpose of the flowing reference is to release just enough ions to carry the measurement signal and to complete the measurement circuit. With a standard nonflowing reference the internal KCl solution will be depleted causing a short sensor life.

Flowing references are very useful in applications that have a high potential for plugging of the junction. If you use a sensor where the KCL is always flowing out (see fig.6) of the sensor, as long as the reservoir is full then the only potential for process ingress is if the process pressure exceeds the pressure applied to the KCl chamber.

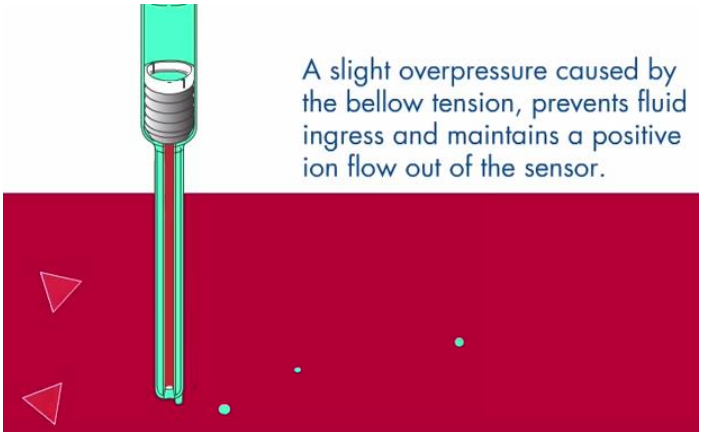


Figure 6: Flowing Reference Electrode (Bellomatic, SR20-AC32)

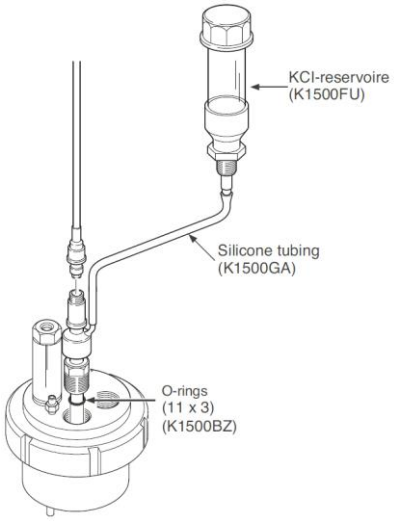


Figure 7: KCl reservoir installation example

When should we use salt bridge over flowing reference?

Flowing reference cell and salt bridge have the same purpose: to prevent diffusion through the junction and fouling of the sensor. Sometimes a salt bridge is easy to retrofit existing installation where you experience sensor troubles. You keep the same reference sensor but place it inside the KCl chamber of the salt bridge.

If the process reacts with KCL or cannot be contaminated with KCl you can use a salt bridge filled with another solution like NaNO3. In high temperature applications the maintenance may be even less with a salt bridge because the reference cell is under reference conditions. Refilling of the large reservoir is easy and does not need to be done frequently.

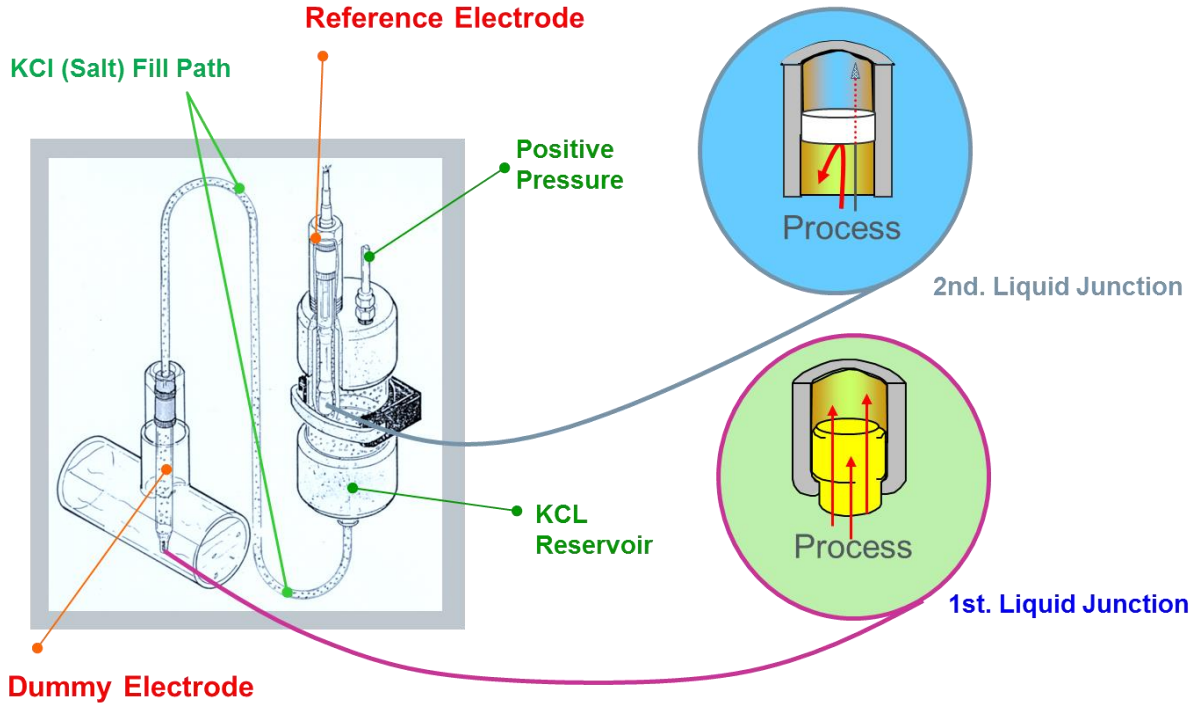


Figure 8: Salt Bridge Installation

Liquid Earth/ Solution Ground - To counter the effects of noise (static charge) it is essential that the equipment setup include a liquid earth/solution ground.

Temperature electrode - To ensure accurate temperature compensation it is recommended that the pH system include a built in temperature electrode.

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Quick Reference Sensor Selection:

The following chart can be used as a quick reference guide for some of the most commonly used Yokogawa sensors.

UNIQUE pH Sensor	FEATURES	WHERE TO USE IT
PH87/97 "Hot Tap"	♦ Simple design and rugged construction ♦ Integral J-Box for easy wiring ♦ Anti-Blowout guard ♦ Optional Solid-State reference system ♦ "Hot-tap" applications with ball valve ♦ Titanium sheath for chemical protection ♦ Adjustable insertion lengths ♦ Cost effective, long life ♦ Built-in solution ground	♦ Process that requires retractable assembly ♦ Process that contains slurry, abrasives, or pulp stock ♦ Process that may poison the reference requires Solid-State reference option
FU20	♦ Easy removal of sensor without twisting cable ♦ Pressure rating up to 145 psi ♦ Integral Pt1000 temperature element for enhanced accuracy ♦ Simple maintenance by comprehensive design ♦ Ion trap designed for sensor life extension and acts as a double junction	♦ All applications where quick removal of the sensor and no compromise in safety is needed
FU24	♦ Easy removal of sensor without twisting cable ♦ Pressure rating up to 145 psi ♦ Integral Pt1000 temperature element for enhanced accuracy ♦ Automatic compensation for changes in process pressure ♦ Simple maintenance by comprehensive design ♦ Ion trap designed for sensor life extension and acts as a double junction	♦ For harsh chemical applications were large temperature/pressure variations results in early depletion of KCl and poison the reference ♦ Harsh pH applications were an all-in-one style body is desired ♦ Extremely clean water ♦ Extremely dirty, coating process ♦ Upside down or 360° mounting is needed ♦ All applications where quick removal of the sensor and no compromise in safety is needed ♦ Process that is prone to see pressure and temperature changes

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UNIQUE pH Sensor	FEATURES	WHERE TO USE IT
Heavy Duty/ High Temp.	♦ Glass 15 times thicker than regular sensors ♦ "L Glass" for use in Temps. >130ºC and high pH ♦ Metal foil screening ♦ Maximum pressure: 1000kPa (10 bar) ♦ Bulb membrane for general purpose ♦ Dome shaped membrane for "Heavy Duty" applications	♦ Process with solids or abrasives ♦ High temperature process ♦ Pocess with pH > 12
SR20-AC32 Bellomatic	♦ Automatic compensation for changes in process pressure ♦ Constant, positive flow of KCl ♦ Large electrolyte reservoir	♦ Extremely clean water ♦ Extremely dirty, coating process ♦ Process with poisonous ions ♦ Applications that see pressure changes ♦ Where probe life up to 3 years is desired
SC25	♦ Sterilizable pH sensor ♦ Heavy duty glass for higher temperature and alkaline applications up to 130°C. ♦ Can be used in low conductivity (>10µS)	♦ Process that is prone to pressure spikes ♦ Process that may poison the reference ♦ Mono and Tri ethylene glycol (meg/teg) ♦ All-in-one 12mm design (pH/Ref/Temp/LE)
PH18	♦ Sterilizable pH sensor ♦ All enamel construction ♦ No reference electrode or junction ♦ Easy installation and commissioning ♦ No routine maintenance ♦ Flexible installation options ♦ 140ºC, 15 bar (284ºF, 214 psi)	♦ Process where KCL is forbidden ♦ 'Process containing a low water content ♦ High process temperature and pressure ♦ Process with rapid pressure/temperature changes ♦ Fermentation processes ♦ Dairy product manufacture
pNa (SM23-AN4 or FU20-FTS)	♦ Sodium reference electrode ♦ No reference junction ♦ No electrolyte ♦ 120°C	♦ Process where KCL is forbidden ♦ Applications with high and stable salt concentrations ♦ Brine applications ♦ Fermentation processes ♦ Electrolysis processes ♦ Cheese manufacturing