2024 Mary Kay O'Connor Safety & Risk Conference

Safe and Sustainable Energy Transition

In Association with ***IChemE***

October 22-24, 2024

79th Instrumentation and Automation Symposium

TEES

Texas A&M Engineering Experiment Station

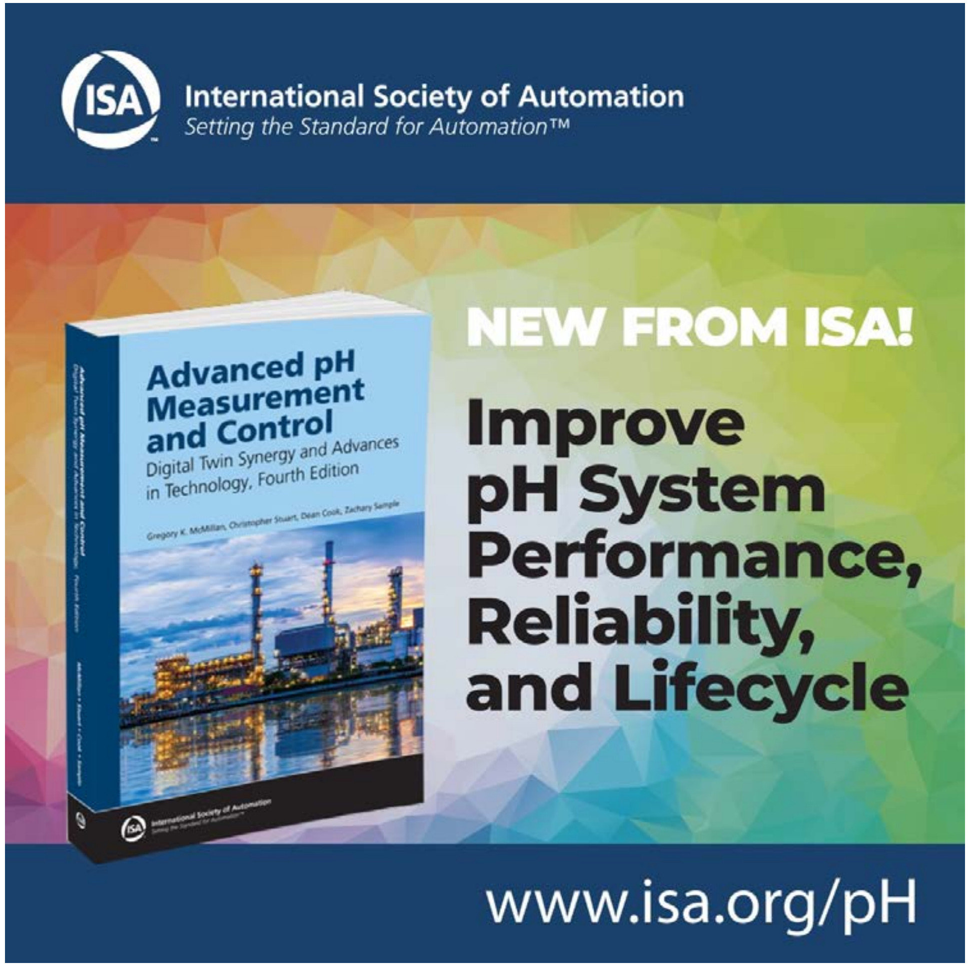
Mary Kay O'Connor
Process Safety Center

Gregory K. McMillan Speaker profile

- Retired Emerson Principal Software Engineer and Solutia Senior Fellow
- Control Magazine "Engineer of the Year" award in 1994
- Control Magazine "Automation Hall of Fame" inductee in 2001
- InTech Magazine "Most Influential Innovators" award in 2003
- International Society of Automation "Life Achievement" award in 2011
- Author of more than 20 books and 400 articles
  - https://blog.isa.org/author/greg-mcmillan
  - https://www.controlglobal.com/control-talk-column

pH Measurement Best Practices

- There have been many advances in the technology and the understanding of the trade-off in the capability of a wide spectrum of electrode technology for different process operating conditions. This knowledge can enable pH measurements to have the ability to achieve the incredible precision and rangeability of the hydrogen ion concentration that exceeds by many orders of magnitude that of any other composition measurement. Presented are insights and guidance needed for electrode selection, installation, calibration, and troubleshooting plus the advantages of middle signal selection.



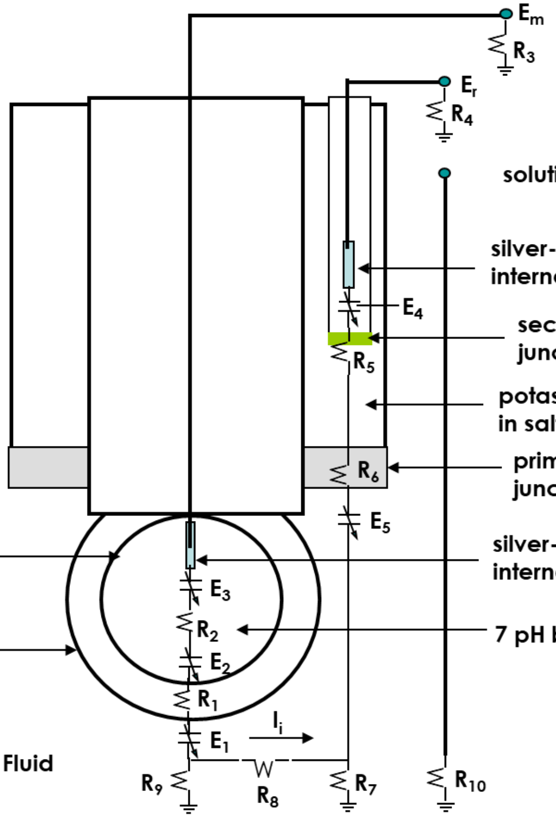
International Society of Automation
Setting the Standard for Automation™

NEW FROM ISA!

Improve pH System Performance, Reliability, and Lifecycle

www.isa.org/pH

Double Junction Combination pH Electrode



solution ground

silver-silver chloride
internal electrode

second
junction

potassium chloride (KCl) electrolyte
in salt bridge between junctions

primary
junction

silver-silver chloride
internal electrode

7 pH buffer

Measurement
becomes slow
from a loss of
active sites or
a thin coating
of outer gel

inner
gel
layer

Nernst Equation
assumes inside
and outside gel
layers identical

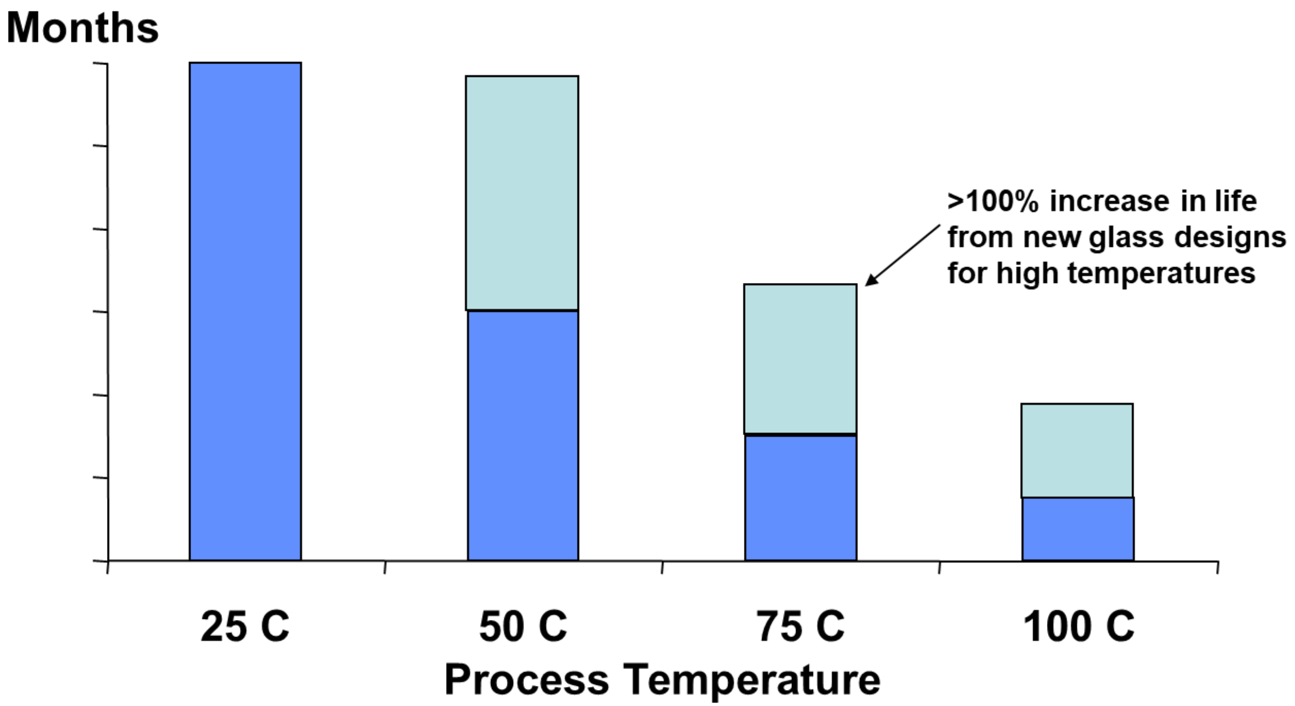
outer
gel
layer

Process Fluid

Process ions try to
migrate into porous
reference junction
while electrolyte ions
try to migrate out

High acid or base concentrations can affect glass gel layer and reference junction potential
Increase in noise or decrease in span or efficiency is indicative of glass electrode problem
Shift or drift in pH measurement is normally associated with reference electrode problem

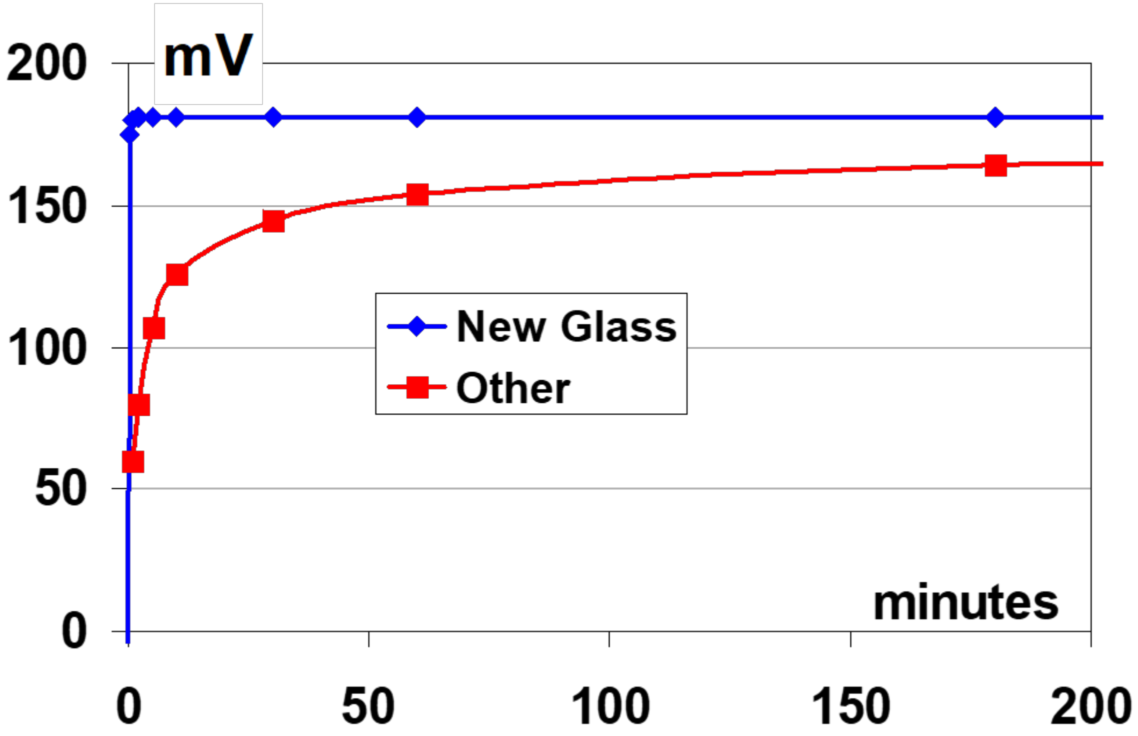
Life Depends Upon Process Conditions



>100% increase in life from new glass designs for high temperatures

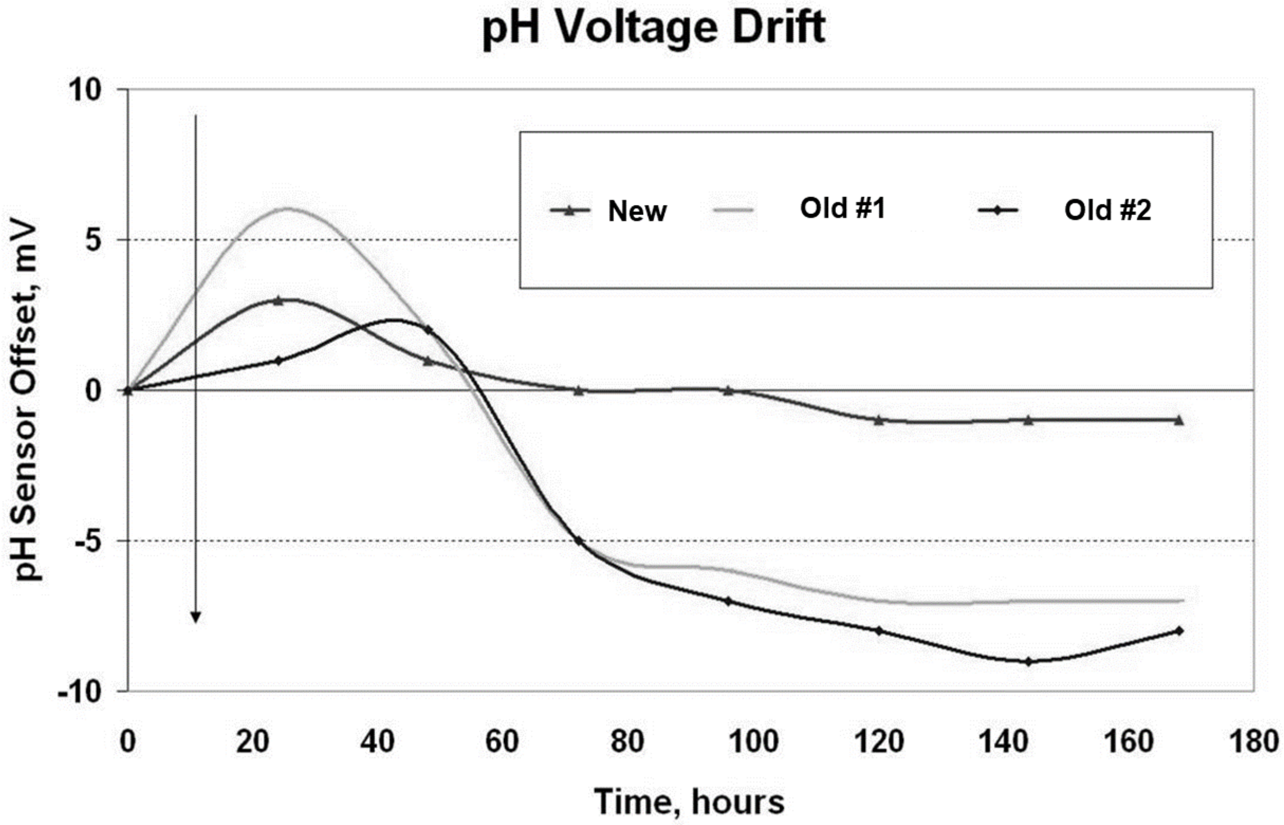
High acid or base concentrations (operation at the extremes of the titration curve) decrease life for a given temperature. A deterioration in measurement accuracy and response time often accompanies a reduction in life. Consequently pH feedforward control is unreliable and the feedforward effect and timing is way off for such cases.

New High Temperature Glass Stays Fast

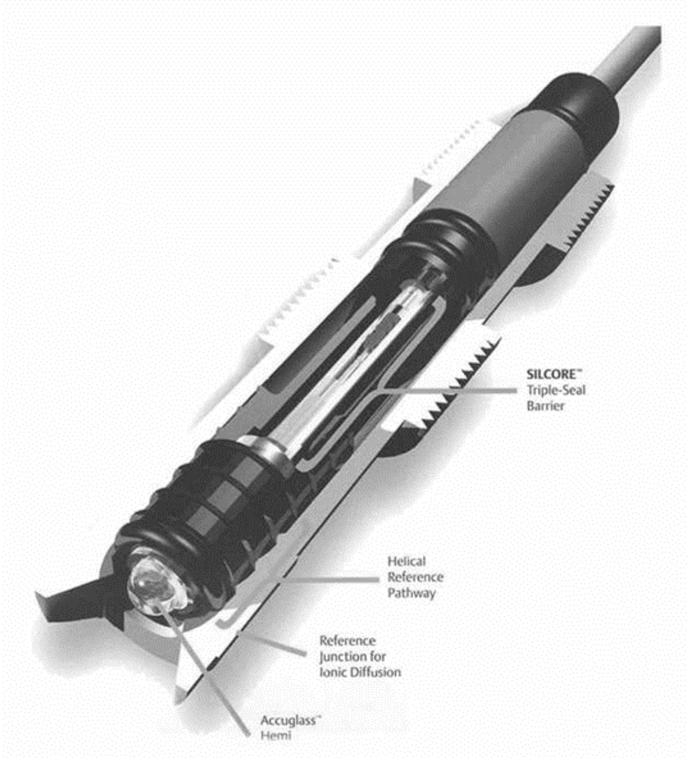


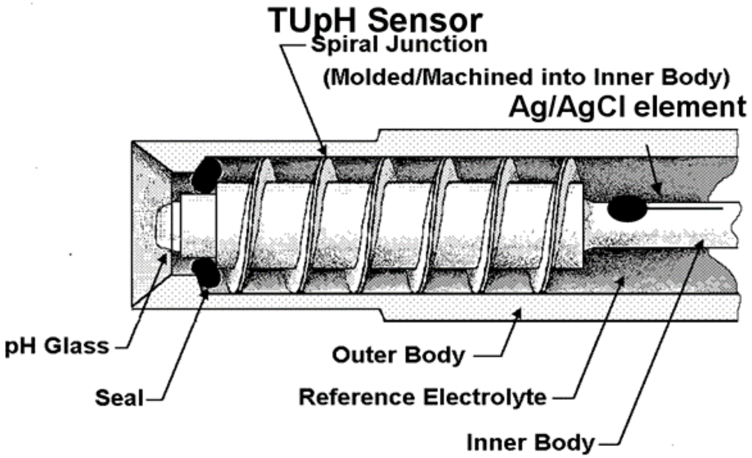
Glass electrodes get slow as they age. High temperatures cause premature aging

New Design Eliminates Drift after Sterilization



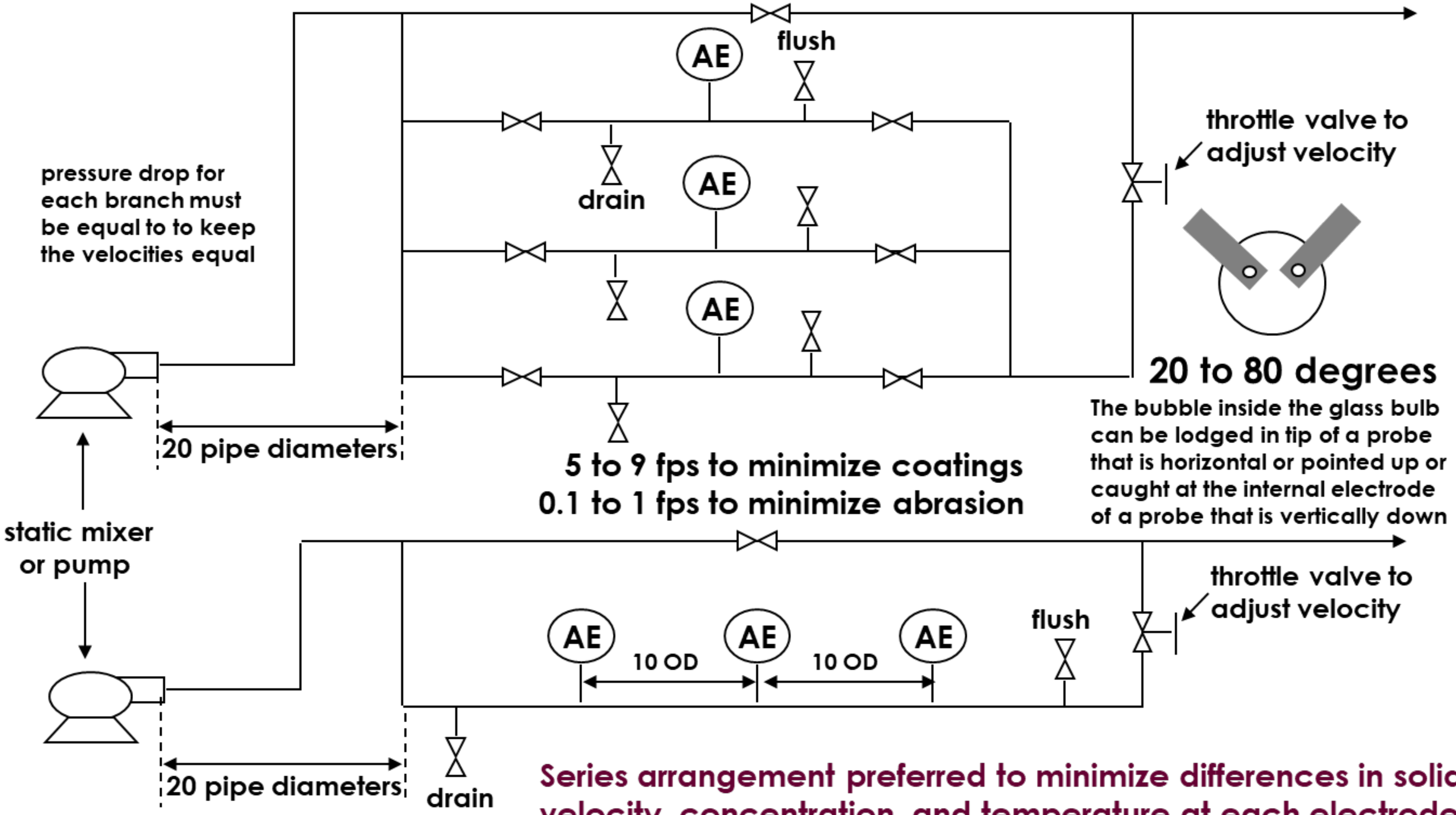
Solid Large Surface Reference Junction





Removable Reference Junction

Horizontal Piping Arrangements



pressure drop for each branch must be equal to to keep the velocities equal

throttle valve to adjust velocity

20 to 80 degrees

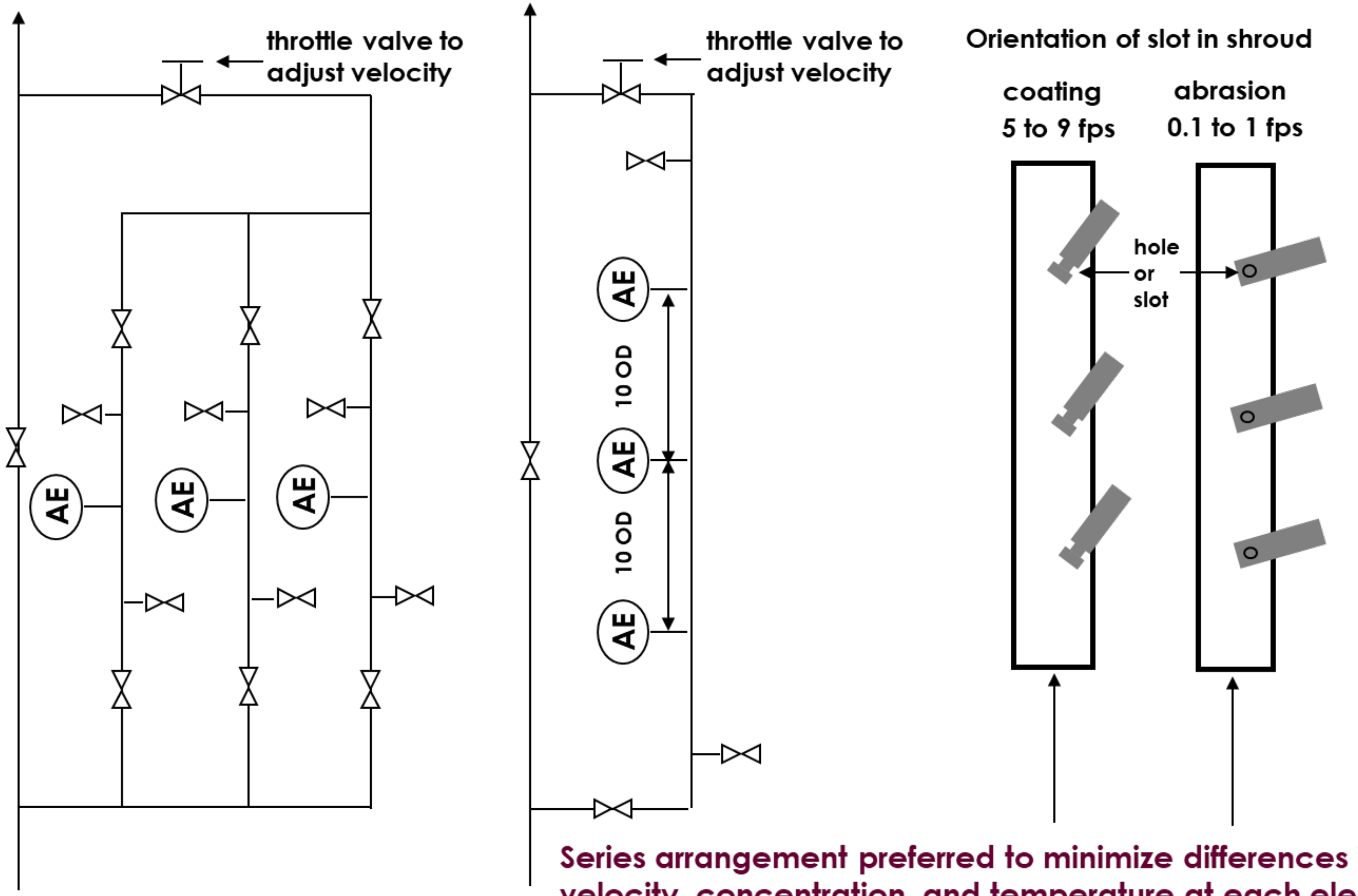
The bubble inside the glass bulb can be lodged in tip of a probe that is horizontal or pointed up or caught at the internal electrode of a probe that is vertically down

5 to 9 fps to minimize coatings
0.1 to 1 fps to minimize abrasion

throttle valve to adjust velocity

Series arrangement preferred to minimize differences in solids, velocity, concentration, and temperature at each electrode!

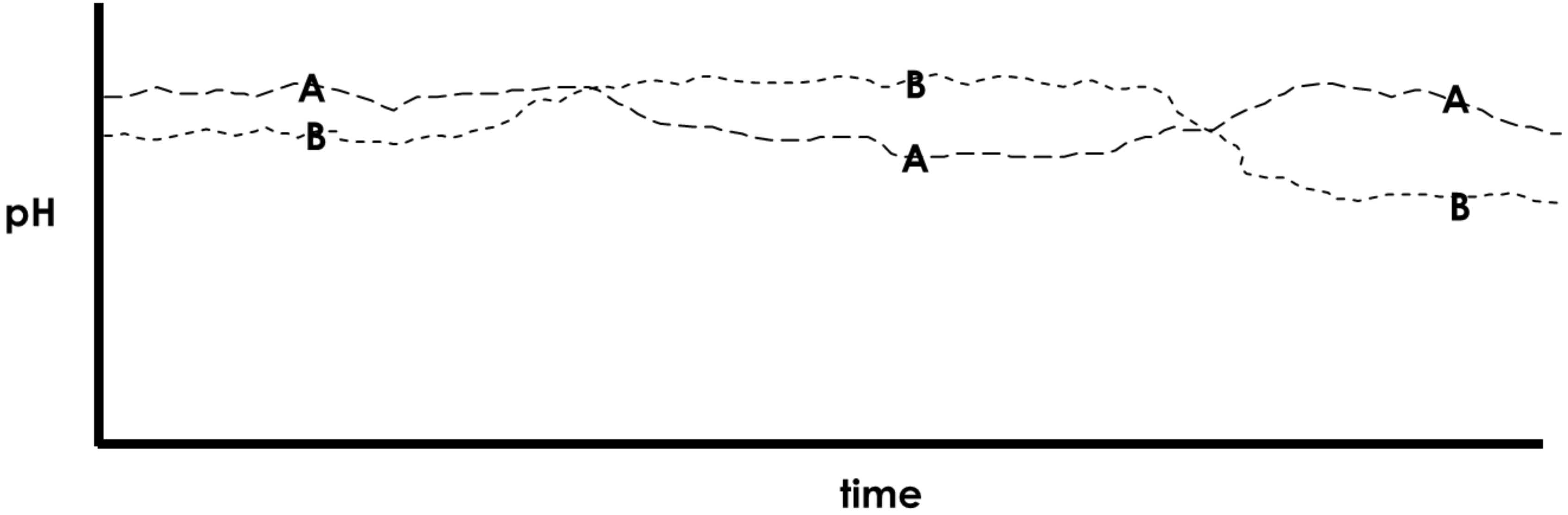
Vertical Piping Arrangements



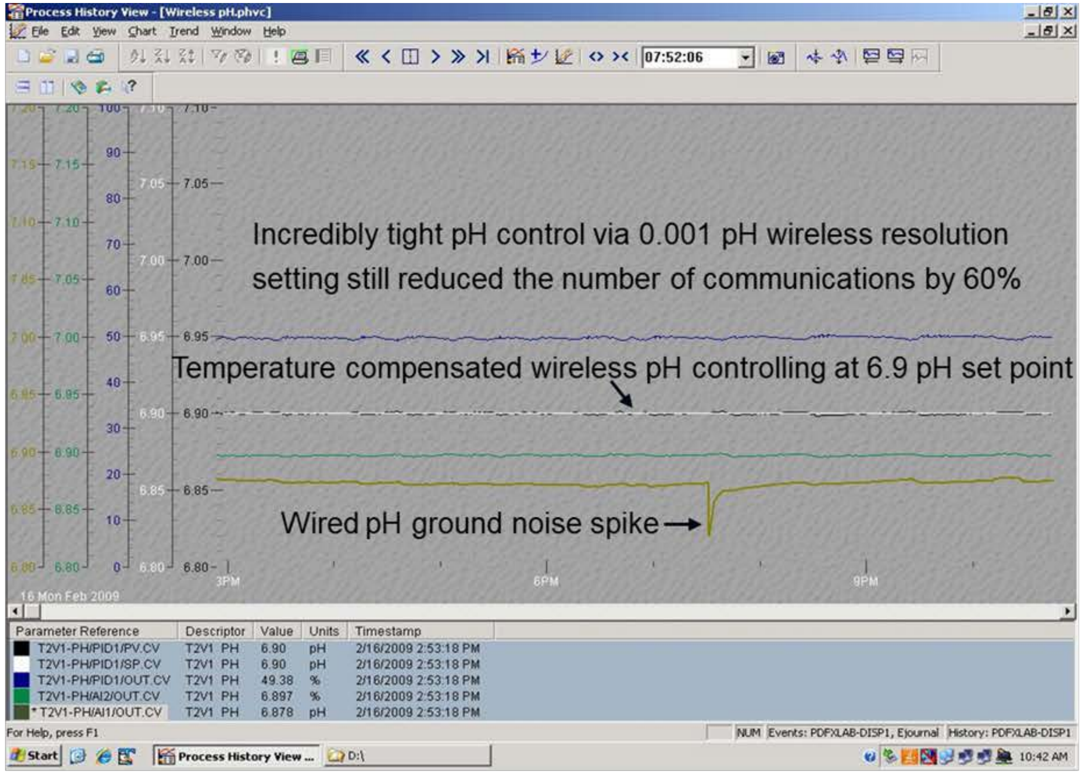
Series arrangement preferred to minimize differences in solids, velocity, concentration, and temperature at each electrode!

What is High Today may be Low Tomorrow

Most calibration adjustments chase the short term errors shown below that arise from concentration gradients from imperfect mixing, ion migration into reference junction, temperature shifts, different glass surface conditions, and fluid streaming potentials. With just two electrodes, there are more questions than answers.



Wireless pH Eliminates Ground Noise Spikes



Incredibly tight pH control via 0.001 pH wireless resolution setting still reduced the number of communications by 60%

Temperature compensated wireless pH controlling at 6.9 pH set point

Wired pH ground noise spike

	Parameter Reference	Descriptor	Value	Units	Timestamp
■	T2V1-PH/PID1/PV.CV	T2V1 PH	6.90	pH	2/16/2009 2:53:18 PM
□	T2V1-PH/PID1/SP.CV	T2V1 PH	6.90	pH	2/16/2009 2:53:18 PM
■	T2V1-PH/PID1/OUT.CV	T2V1 PH	49.38	%	2/16/2009 2:53:18 PM
🟩	T2V1-PH/AI2/OUT.CV	T2V1 PH	6.897	%	2/16/2009 2:53:18 PM
■	* T2V1-PH/AI1/OUT.CV	T2V1 PH	6.878	pH	2/16/2009 2:53:18 PM

Actual trend recording of a Single-Use-Bioreactor batch shows that a wireless transmitter did not have the noise spike seen by the wired transmitter and the wireless control of the batch is within 0.001 pH despite a reduction in the number of communications by 60% to increase battery life

Middle Signal Selection Advantages

- **Inherently ignores single measurement failure of any type including the most insidious PV failure at set point**
- **Inherently ignores slowest electrode**
- **Reduces noise and spikes particularly for steep curves**
- **Offers online diagnostics on electrode problems**
  - Slow response indicates coated measurement electrode
  - Decreased span (efficiency) indicates aged or dehydrated glass electrode
  - Drift or bias indicates coated, plugged, or contaminated reference electrode or high liquid junction potential
  - Noise indicates dehydrated measurement electrode, streaming potentials, velocity effects, ground potentials, or electromagnetic interference (EMI)
- **Facilitates online calibration of a measurement**

pH Measurement Best Practices

- Choose electrode holder materials of a construction and design that meet the requirements of worst-case corrosive and temperature operating conditions. An often-serious overlooked problem is the incompatibility of the standard O-rings and gaskets for process conditions.
- Select the best glass that will prevent an appreciable increase in drift, error, failure rate, and the 86% response time for the worst-case temperature, pH, and chemicals that can attack glass (e.g., select general-purpose, high-pH, low-pH, high-temperature, sterilizable, or Hydrogen Fluoride (HF)-resistant glass).
- Use a semispherical bulb with best glass formulation to improve accuracy and response time.

pH Measurement Best Practices

- Use the best reference design and fill that will prevent an appreciable increase in drift, error, failure rate, and the 86% response time for the worst-case temperature and composition such as low-water or pure-water solutions with low conductivity and salt and chemical concentrations that can change junction potential, plug junctions, and poison reference internals. Sulfide, bromide, iodide, and cyanide ions in the process can precipitate or complex the silver ions when diffusing into the reference.
- If the reference electrode accuracy and equilibration speed deterioration causes performance or excessive maintenance, use a pressurized flowing junction to provide the most constant reference potential and the fastest junction equilibration rate, eliminating a variable liquid junction potential, plugging, and poisoning. When inserting these electrodes in samples, ensure the junction flow rate is small and the sample size is large.

pH Measurement Best Practices

- Use double- and triple-junction to slow down the contamination rate if the slower equilibration and greater drift of the reference potential compared to the flowing junction are acceptable. Use a solid-state reference electrode to greatly reduce the effect of plugging, contamination, and poisoning if a much slower equilibration and offset of reference potential is not a problem.
- Use special electrolytes to prevent precipitation of silver salt from process contact (e.g., silver cyanide precipitate from cyanide contact with silver).
- Use a removable outer reference junction chamber to enable an electrode to be rejuvenated (reference junction and fill quickly replaced) before plugging and poisoning becomes a problem.
- If the solution conductivity is extremely low (e.g., condensate, boiler feedwater, deionized water), use a flowing junction reference electrode in a special assembly with a low sample flow, diffuser, and electrolyte reservoir.

pH Measurement Best Practices

- If a chemical attack causing premature aging from high temperature or dehydration (nonaqueous or low water concentrations) is severe, reducing electrode life to a matter of days, use an automated, retractable insertion assembly to limit sensor exposure to the process just long enough to get a periodic pH measurement with flush to clean and rejuvenate the electrode while retracted. A buffer solution can be pushed into the sensor assembly after flushing to provide an automatic calibration before reinsertion.
- If the solution conductivity is extremely low (e.g., condensate, boiler feedwater, deionized water), use a flowing junction reference electrode in an assembly with a low sample flow, diffuser, and electrolyte reservoir.
- Use a Varipol (VP) or equivalent connector to easily replace electrode by disconnecting the electrode cable, eliminating the need to twist and retract the cable through conduit and disconnect transmitter.

pH Measurement Best Practices

- Use a smart transmitter with a stored calibration record and ability to detect glass and reference problems.
- Use solution pH temperature compensation in addition to standard Nernst compensation developed in laboratory testing at process conditions.
- Test different process connections and electrodes to identify the best electrode type and location (shortest dead time and least noise/bubbles).
- Ensure the electrode is installed with the tip pointing down above a 20-degree angle to prevent bubbles residing in tip or on internal electrode.
- Ensure electrodes are always wetted (a common problem for batch operations and the startup and shutdown of all operations).

pH Measurement Best Practices

- Use middle signal selection (MSS) to eliminate a response to a single failure and reduce the effect of noise, coatings, aging, abrasion, and contamination (assuming different lengths of times each electrode is in service) to provide more intelligent diagnostics of the deviant electrode and to enable removing a single electrode for cleaning, rejuvenation, and calibration or replacement without having to put the pH control loop in manual. Only if the same electrode consistently shows poor performance is it removed. After inserting a calibrated new electrode or a cleaned and rejuvenated existing electrode, the speed and efficiency of other electrodes can be compared to quantify improvement and schedule maintenance for the other electrodes. Intelligent and less unnecessary maintenance and the faster, smoother, and more accurate response greatly reduce lifecycle costs and increases process performance benefits.

pH Measurement Best Practices

- Ensure the stream velocity and tip protective shroud design are the best for the process conditions. Use a low velocity (0.1 to 1 fps) and protect the tip from flow impingement to reduce abrasion or contamination, and a high velocity (5 to 10 fps) and sweeping action at the tip to reduce coatings.
- Ensure electrode tip extends into pipe centerline and past vessel baffles.
- Choose an electrode location free of bubbles (e.g., not near sparger ring).
- Locate electrode far enough downstream from a pump or static mixer to reduce concentration fluctuations, but with transportation delay < 6 sec.
- Put insertion electrodes in series in the same pipeline (at least 10 pipe diameters apart) rather than in parallel lines so each electrode sees the same velocity. mixing, and composition.

pH Measurement Best Practices

- Choose location free from flashing (not pump suction or valve discharge).
- Ensure the insertion electrode assembly has a ball valve and restraining strap to safely retract electrode from a pipe or vessel, preventing blowout.
- Ensure the electrode and transmitter locations are safely accessible.
- Ensure the electrode and transmitter signal connections are always dry in terms of location and type of connection seals and, if necessary, by using a dry air purge. Avoid submersion assemblies and transmitter enclosures or electrode holders that are not sealed and that have top entry of cables.
- Determine solution pH compensation by making changes to sample temperature and noting the change in solution pH caused by the changes in dissociation constants and ion activity in samples in expected pH range.

pH Measurement Best Practices

- Use an accurate RTD temperature measurement and smart transmitter process temperature compensation or input signal characterizer block to give piecewise linear fit of process pH correction vs process temperature.
- New, cleaned, and rejuvenated existing electrodes must be calibrated in fresh buffer solutions with same ionic strength and solvent as the process.
- Reference junction potential must be relatively constant (junction reached equilibrium) before new, cleaned, and rejuvenated existing electrodes are used for closed-loop control (automatically achieved by MSS).
- During calibration, the full measurement response must be achieved, and the changes in the reference junction must be negligible before an offset or slope setting is made.

pH Measurement Best Practices

- Because a 10 pH buffer solution pH is more readily changed by temperature and CO_2 absorption, a 4 pH buffer solution is generally preferred to set slope after a 7 pH buffer solution is used to set offset.
- Once an electrode is in service, the electrode is removed or the offset is adjusted only after consistent deviation of an electrode response compared to others in MSS or a representative process sample.
- Standardization is preferred over buffer calibration to account for process effects if electrode slope is still relatively OK from earlier buffer calibration.
- Samples used for standardization must be at the same temperature and composition as the process. The electrode used must be verified to be fast and accurate with the preferably field rather than lab sample pH result compared to the field pH measurement at the time the sample was taken.