

Background Information on Practices to Improve the Performance of pH Electrodes

A coating of the measurement electrode typically manifests itself as a change in the speed of the pH response. A change in the condition of the external gel layer of the glass measurement electrode normally shows up as a change in slope (millivolts per pH unit) of the pH measurement. Correction is done by the slope or span calibration adjustment. Since bioprocess disturbances have such slow disturbances and tight control ranges, the measurement electrode speed or span may be less of an issue than the reference electrode stability for fermenter pH control.

Drift is normally associated with a change in the potential of the reference electrode. The job of the reference electrode is to provide a fixed potential while maintaining electrical continuity between the reference's internals and the process fluid. The internal electrolyte of the reference is in physical contact with the process fluid via its reference junction. The reference potential changes when the composition changes at the reference junction. Thus, inserting a reference into a new process fluid or changes in the process fluid itself with batch phase can result in the movement of ions within a reference electrode and its junction until the change in electrical potential opposes the further migration of ions. The result is a drift until the reference reaches equilibrium with its new environment. The reference electrode also requires time to reach equilibrium for a change in temperature but this is a factor mostly in high or low temperature chemical processes.

Process fluid is also trying to move into the reference junction. Changes in composition of the junction from coating or contamination also cause a drift. If the electrode is removed, cleaned, sterilized, and calibrated, changes made adjustment do not reflect the condition or environment of the electrode in service. If the reference is contaminated (process fluid has inside the reference) or the junction is not really clean (process fluid is trapped in the junction), then a bias adjustment will provide some compensation.

Increasing the velocity of the process fluid will reduce coating problems. How fast depends upon the process fluid. Data is rare here, but personal experience has shown that 5 feet per second has been effective. Such velocities are not normally obtainable in agitated vessels so electrodes are inserted into external recirculation lines. Since high fluid velocity can increase sensor noise or shift the signal, the velocity should be controlled by fixing the recirculation flow rate. Flat glass electrodes stay cleaner at lower velocities but the most accurate pH measurement electrode uses a spherical glass bulb. Low fluid velocities also slow the response of the electrode. In the extreme, stagnation of process fluid means that electrode is not seeing a representative portion of the process.

A reference with a flowing junction helps establish and maintains a more constant composition in and at the reference junction. Ion migration of the electrolyte is assisted and process movement into the junction is opposed by flow of electrolyte out of the junction. The result is faster equilibration and less coating and contamination problems of the reference electrode as the electrolyte flow is increased.

Smart transmitters can detect coatings and major problems with electrodes from changes in the resistance of the electrodes. A solution ground may be required, which is a good idea as well for plastic or glass lined vessels that isolate the process fluid from ground.

If two pH electrodes are used, they will always disagree and you don't know which one is best. The selection of the middle signal from three electrodes improves the accuracy, provides a basis for diagnostics, reduces the disruption from the removal of an electrode and inherently ignores a single failure of any type. An emerging possibility is the use of an online dynamic process model to provide one of the three measurements.

Since process conditions have such a significant effect and the drift of the reference is best compensated by a bias adjustment, the preferred calibration adjustment is an "in place" process standardization based on a process sample if the sample can be kept at exactly the same temperature and dissolved carbon dioxide concentration as the process. If this is not practical, then the electrode measurement furthest from the middle value should be adjusted to be closer to the middle. To avoid chasing previous calibration adjustments, only about half of the difference between the subject measurement and the sample or middle value should be used as a correction. Also, the adjustments should not be made more frequently than once a day.