

Opportunities for smart wireless pH, conductivity measurements

Smart wireless transmitters integrate lab and plant data to improve conductivity and pH electrode performance and decrease maintenance costs

FAST FORWARD

Spare transmitters can be put to work in labs to determine sensor design, detail inferential measurements, quantify solution temperature correction, provide multivariate models for predictive diagnostics, and increase calibration efficiency.

The best location for the pH measurement installation has the maximum mixing, optimum velocity, and minimum transportation delay. Smart wireless conductivity and pH transmitters offer the portability, communication, solution temperature correction, and auxiliary variables needed for a more intelligent installation and use of lab and plant data.

By Greg McMillan, Robert Montgomery, and Teresa Wang

Conductivity and pH are critical measurements in many industrial processes to control the concentration of acids, bases, ions, and solvents. In most cases, the measurement is temperature compensated per a standard equation and used as the controlled variable. There are new opportunities for inferential measurements, solution temperature correction, efficient calibration, noise minimization, location optimization, and predictive maintenance by taking advantage of smart features and wireless communication.

Inferential measurements

Conductivity and pH electrodes offer flexible low cost and reliable methods of online composition analysis. The connectivity, intelligence, and portability of new wireless conductivity and pH measurements increase the potential for successful applications of online inferential measurements to improve process performance. An example of increasing importance is the use of these measurements for CO₂ reducing emissions.

The University of Texas (UT) Pickle Research Campus has a pilot plant with an industrial DCS that is an ideal setup for research and development of processes and control systems to reduce emissions from swing boilers that are added to meet increasing demand. For example, the optimization of an absorber for CO₂ capture and a column for solvent recovery are critical for an efficient process. The emission load varies considerably as the swing boilers startup and shutdown and move to and from peak

demands every day. The column and absorber are continually subjected to a rapidly changing load. Control and optimization is more challenging due to lack of steady state operation. Inferential measurement from conductivity and pH are expected to play a key role in control and optimization by providing fast online feedback measurements of CO₂ loading and solvent concentration.

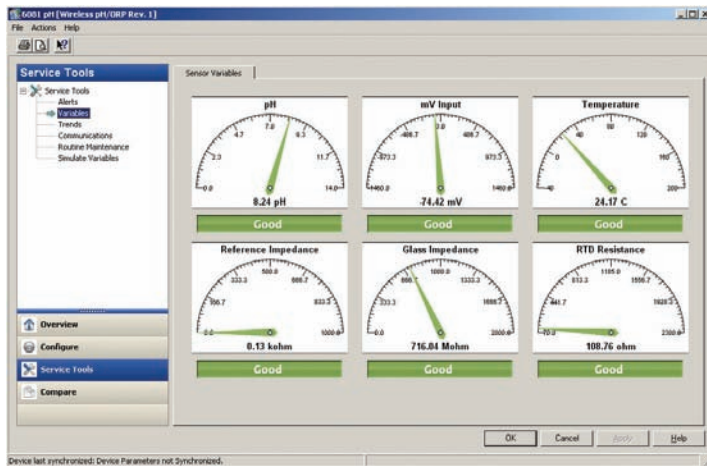
In the UT lab that supports the pilot plant, solvent concentration and loading are being varied, and the conductivity and pH are being measured and communicated to the DCS in the control room.



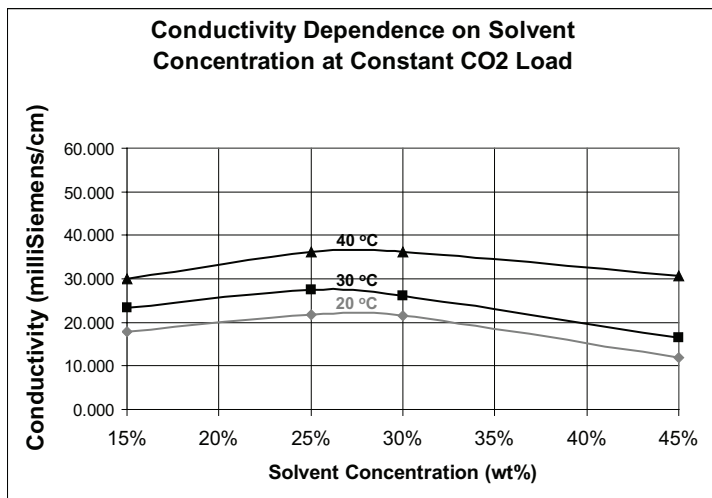
Wireless conductivity and pH lab setup

The availability of the primary process variable (pH), and the auxiliary variables (milliVolts, temperature, reference impedance, glass impedance, and RTD resistance) for a smart wireless pH transmitter, facilitates the monitoring of sensor performance besides developing relationships for solution temperature compensation, solvent concentration, and CO₂ loading. For some solvents, particularly at higher temperatures, it is expected the measurement electrode efficiency will decrease, and the reference electrode offset will increase. There are an increasing variety of electrodes especially designed to minimize these errors by advancements in pH sensor technology. By the use of wireless lab tests, the long term

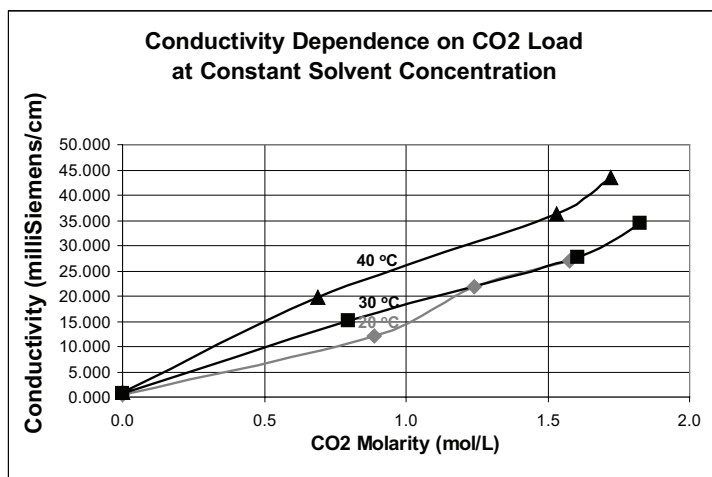
performance capability of various electrode designs can be evaluated, and the best electrode for the application selected and monitored. During initial tests in the UT lab, it was found a new high temperature pH electrode offered good performance and life expectancy. Subsequently, the non-linearity and sensitivity of conductivity and pH for inferential measurements was quantified at particular process conditions.



Variables monitored and communicated by a smart wireless pH transmitter



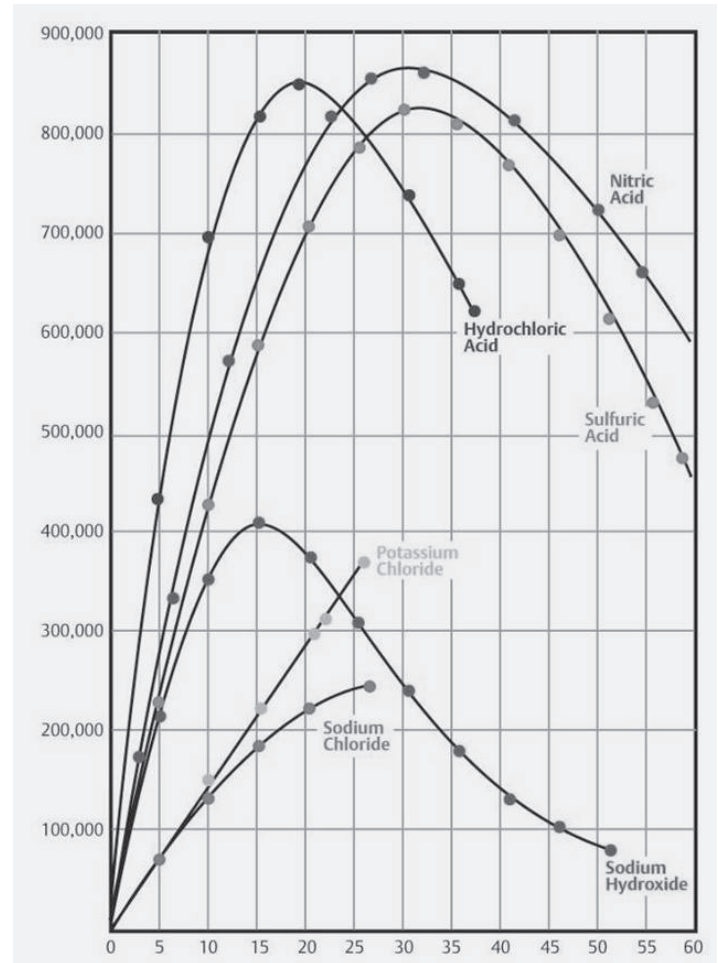
Effect of solvent concentration on conductivity



Effect of CO2 loading on conductivity

Conductivity measures the concentration and mobility of ionic species. Temperature and solvent concentration can affect the mobility and concentration of ions in solution. UT lab test data show conductivity in the operating range of 25% to 30% by weight solvent is relatively unaffected by solvent concentration but shows good sensitivity to CO₂ loading.

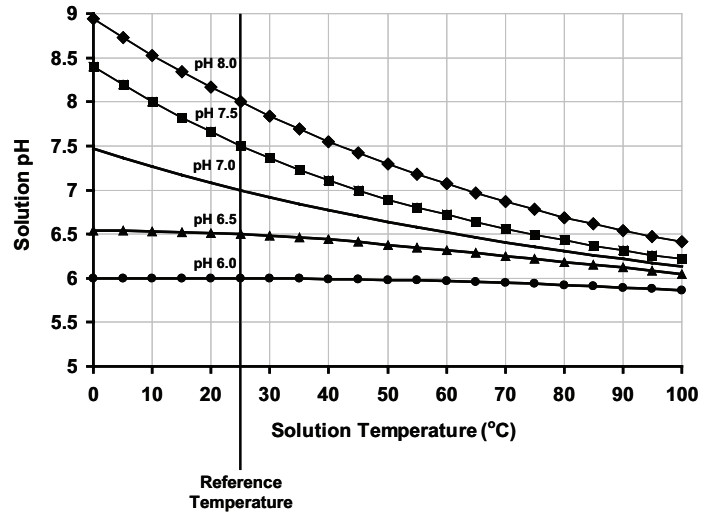
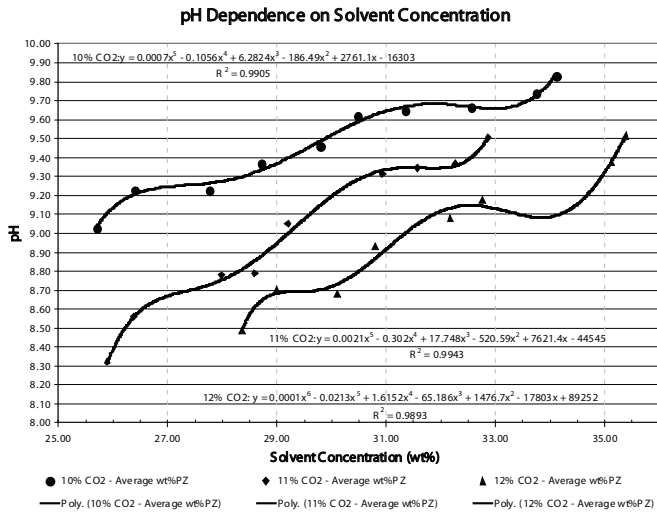
In general, plots of conductivity versus ion concentration will increase from zero concentration to a maximum (peak or hump) as the number of ions in solution increases. The conductivity then falls off to the right of the maximum as the ions get crowded and start to interact or associate (group) reducing the ion mobility. Some components, such as sulfuric acid, may have a secondary peak or hump at very high concentrations. For inferential measurement of concentration, the operating point should never cross a peak or hump since it causes a reversal of signal direction and process gain.



Effect of various ion concentrations on conductivity

pH measures the activity of the hydrogen ion, which can be simplified to a hydrogen concentration multiplied by an activity coefficient that is 1.0 for water solutions of low ionic strength. An increase in solvent concentration increases the pH by a decrease in the activity coefficient and a decrease in the hydrogen ion concentration from a decrease in the water dissociation constant.

The UT lab test data for pH showed good sensitivity and a nonlinearity that could be fitted by a polynomial. In future tests, the effect of operating temperature will be explored and additional relationships developed. Neural networks that are part of the DCS advanced control toolkit will be used with inputs of conductivity, pH, and temperature to develop a more accurate prediction of solvent concentration and CO₂ loading.



Effect of solvent concentration on pH

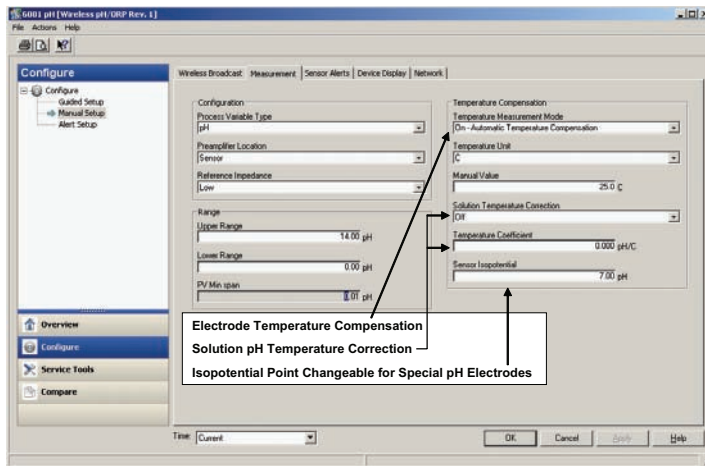
There is a broader spectrum of opportunities for improving the performance of conductivity and pH measurements in all types of applications by the use of wireless lab and field transmitters.

Solution temperature correction

The standard temperature compensation in pH measurement corrects for the change in milliVolts per pH unit generated by the glass electrode as defined by the Nernst equation. Most users do not realize the actual pH of the solution changes with temperature that is not corrected by the standard temperature compensation. Solution temperature correction in smart transmitters should be added for many applications. The pH meters found in most labs to date have manual or automatic electrode temperature compensation but no customized solution temperature correction.

Effect of temperature on solution pH. This shows how the changes in the water dissociation constant with temperature affects the pH for five solutions that had a pH = 6.0, 6.5, 7.0, 7.5, and 8.0 at the reference temperature of 25°C. Higher pH solutions were not plotted because they are off-scale at low temperatures.

For strong acid and base solutions at moderate temperatures, the effect of the water dissociation constant in the basic region is often approximated as -0.033 pH/°C. Lab tests where the pH and temperature of the sample are varied to cover the operating range are required to quantify the effect of weak acid and base dissociation constants on solution pH. Smart wireless pH transmitters allow the user to develop, document, and integrate the solution temperature compensation results from lab tests. Note the standard temperature compensation should be turned on to eliminate the effect of temperature on the milliVolts generated by the electrode.



Configuration of solution pH temperature correction

The change in solution pH with temperature is the result of changes in the dissociation constants with temperature. The change in the water dissociation constant is rather well defined, but the effect of temperature on acid and base dissociation constants that does exist is often in proprietary data bases especially when the acids or bases are key reactants or products. The effect of temperature on solution pH increases as the pH approaches the dissociation constant. For strong acids and bases, the dissociation constants are beyond the 0 to 14 pH scale, so the primary effect is the water dissociation constant that is 14 pH at 25°C. Consequently, the effect of temperature is greatest for highly basic solutions.

There is no standard temperature compensation for conductivity sensors since the signal generated for a given solution conductivity does not change with temperature. However, solution conductivity increases with temperature from increases in the mobility of ions. For solutions with a conductivity above 10 microSiemens/cm, the temperature dependence can be approximated as linear. Fresh water has a temperature dependence of about 2.0% per °C. For common acid, base, and salt solutions, the temperature coefficients typically fall in the following ranges:

- Acids: 1.0 - 1.6% per °C
- Bases: 1.8 - 2.2% per °C
- Salts: 2.2 - 3.0% per °C

The conductivity of solutions less than 10 microSiemens/cm are highly susceptible to contamination by trace contaminants in containers and by CO₂ in air. For the very low conductivities seen in demineralized and de-ionized water, the relationship is highly nonlinear because in addition to an increase in the mobility of the hydrogen ion with temperature, there is an increase in the hydrogen ion concentration from an increase in the water dissociation constant. The conductivity now depends more on the conductivity of water. For streams with very low water concentrations (e.g. less than 10%), the relationship is also highly nonlinear due to changes in dissociations constants.

For a specific application, the relationship between temperature and conductivity should be identified from lab tests. A smart wireless lab measurement enables the data to be historized and the resulting configured solution temperature compensation to be tested.

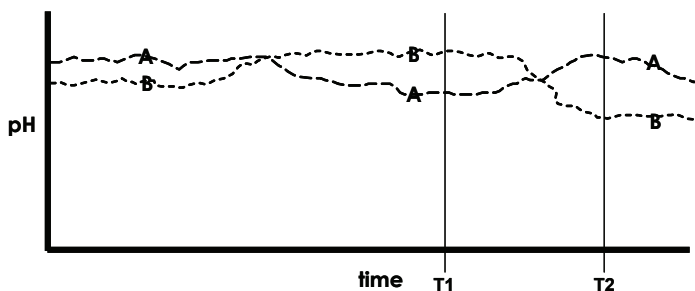
Efficient calibration

Smart conductivity and pH transmitters offer automatic calibration by the use of standard solutions (buffer solutions for pH) or grab samples. Before installation, standard solutions are used to set the slope (efficiency) (milliVolts/pH) and offset (milliVolts) of pH transmitters and the cell constant (1/cm) of conductivity transmitters. Different types of buffer solutions and their temperature dependence can be selected. The pH transmitter will then automatically recognize the buffer solution pH when the electrode is immersed and has reached its final reading. The insertion of the pH electrode into the second buffer then results in an automatic slope and offset adjustment. For conductivity transmitters, waving the sensor in air should result in a zero conductivity indication. Insertion into standard solution then results in an automatic adjustment of the cell constant.

Grab sample calibrations eliminate the need to remove the sensor from its process connection for a buffer calibration. There can be performance advantages of a correctly done grab sample calibration for difficult and demanding processes, such as chemical and biochemical reactions. For pH electrodes, the time for the reference electrode to equilibrate (reference junction to stabilize) is significant for non-flowing junction reference electrodes upon re-installation in high ionic strength process streams. For solid references in reactors, reference equilibration times of hours to days have been observed. The solution pH also changes with ion concentration from changes in the activity coefficient in high ionic strength streams. Sometimes high ionic strength buffers are used to help duplicate the process conditions, but the match is usually not good enough to provide the accuracy needed for many chemical reactions. For biochemical processes, pH electrodes removed must be sterilized. The pH electrode may drift for days after sterilization. Removal of an electrode after a batch has started is typically not permitted because of the excessive risk of contamination. For these and many other practical reasons, grab sample calibrations are used for pH electrodes used in industrial processes. Buffer calibrations are usually only done when the electrode slope (efficiency) has decreased due to age or non-aqueous solvent concentrations. Even here, for tight pH typically achieved in chemical and biochemical reactions, the excursions from set point are so small that an error introduced by slope is usually smaller than the offset error.

The process sample is normally measured with a lab meter and a lab electrode. A wireless pH transmitter and industrial electrode for the lab measurement enables the use of a solution pH correction, an electrode design optimized for process conditions, and improved calibration practices.

The historization of the data by the communication to the DCS of the wireless lab results facilitates a more efficient calibration. In difficult applications, pH transmitters are often over calibrated. Redundant electrodes will rarely ever agree except in highly buffered streams due to concentration gradients from imperfect mixing. If a calibration adjustment was made at time T1, the error at time T2 would be worse for both electrodes. A best practice would only make an offset adjustment based on whether the error between the lab and process measurement is

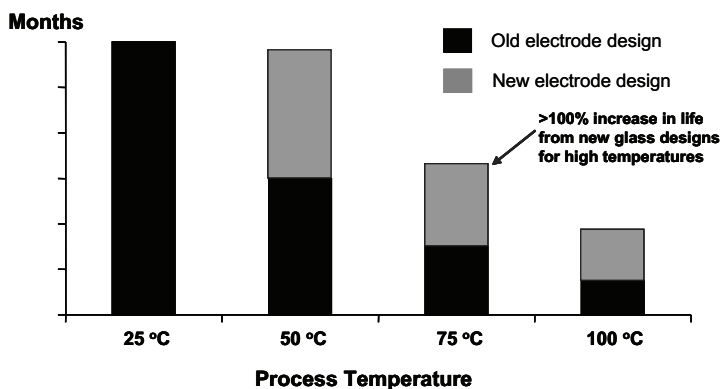


Short-term pH excursions that result in over calibration

consistently of the same sign and the error is significant or increasing. The magnitude and slope of a filtered error could be used. More proficient statistical techniques could be developed from lab and field data historized in the DCS.

Location optimization

The best location for pH and conductivity sensors is a representative point in the process with sufficient mixing, reasonable fluid velocity, moderated process conditions, and least transportation delay. For strong acids and bases, the mixing requirements are extraordinary. The distance between the outlet of a static mixer and the electrodes often needs to be increased to 20 or more pipe diameters to reduce measurement noise from concentration fluctuations. For applications with sticky fluids or particles, fluid velocity needs to be in the 5 to 7 feet per second range to prevent coating and plugging of the electrodes. Locations with pulsating pressures or



Effect of temperature on life expectancy of pH electrodes

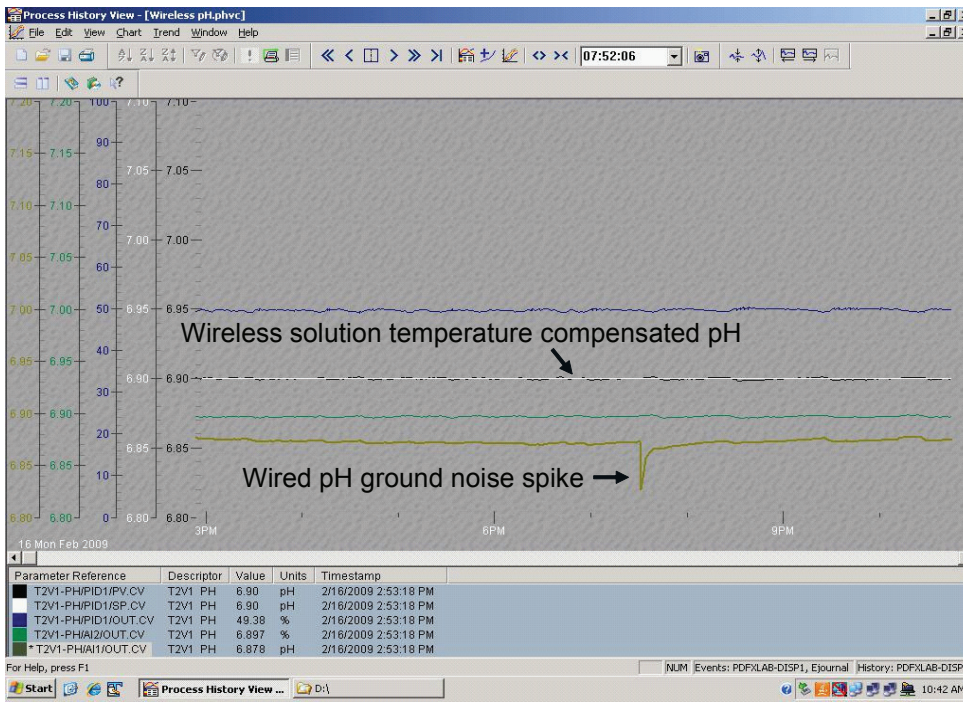
continually fluctuating temperatures need to be avoided to prevent contamination and poisoning of the reference electrode. High temperatures accelerate the aging process. For example, the life of many electrodes is reduced from 12 months at 25°C to three months at 75°C, primarily due to premature aging of the glass and the breakdown of internal structures. New measurement electrode designs can double the life expectancy at high temperatures, but whenever possible high temperatures should be avoided.

Finally, the volume between the point at where reagents are mixed into the process and where the sensor is installed divided by the flow between these points is the transportation delay. The deadtime from this delay limits control loop performance. The best integrated absolute error for a disturbance is proportional to the total loop deadtime squared. The location of pH and conductivity sensors in sample times or in recirculation lines downstream of heat exchangers causes a significant degradation in control loop performance from the transportation delay. The portability of wireless transmitters allows the user to find the best location that will minimize errors, noise, coatings, contamination, maintenance, and delays.

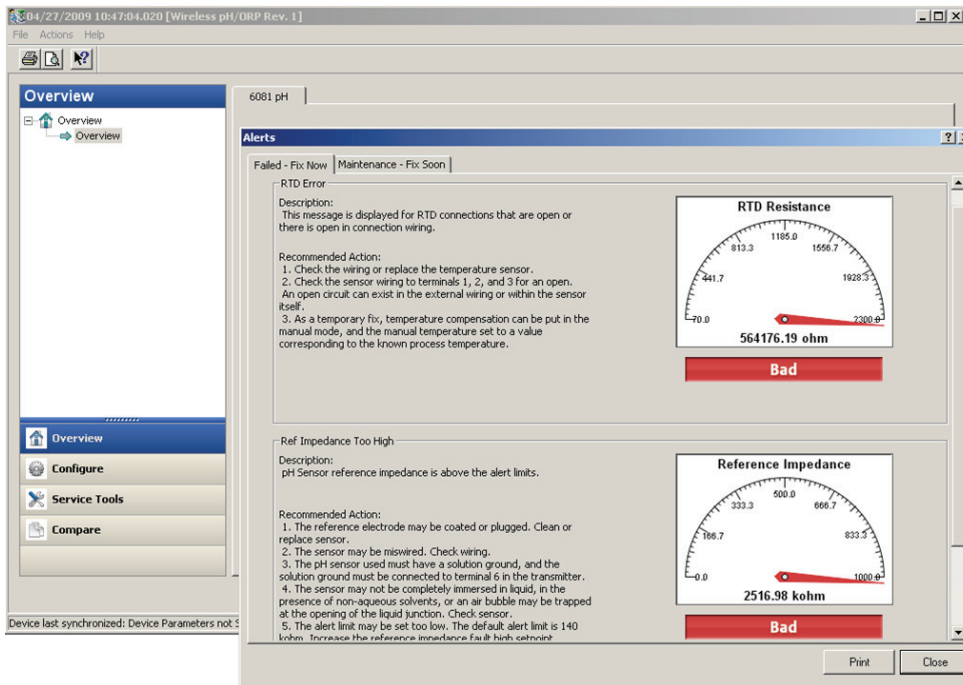
Noise minimization

Spikes in pH measurements are common due to electromagnetic interference (EMI) picked up on the transmitter output or by the electrodes from the operation of motors and variable speed drives. Often the EMI noise disappears when a lab meter is connected showing the source or ground loop is associated with transmitter signal wiring. Wireless pH transmitters can eliminate most of the problems.

While the problem with noise on conductivity measurements is generally less, variable speed drives are notorious for inducing noise on all types of measurements with conductivity being no exception. Wireless transmitters



Elimination of ground noise spike by wireless pH transmitter—how a spike appeared in a wired transmitter output but not in the wireless transmitter output for electrodes installed in the same bioreactor.



Example of built-in diagnostic messages for RTD resistance and reference impedance

eliminate this concern and the inevitable questions about the signal wiring whenever there is a problem.

Predictive maintenance

The use of wireless lab and field pH and conductivity measurements offers the opportunity to use new data analytic tools in the DCS. Since in difficult process applications, significant electrode coating, plugging, and

aging can occur in a matter of days or weeks, a wireless lab pH measurement in a process sample that duplicates operating conditions and redundant smart pH field pH measurements creates interesting opportunities for predictive maintenance on when to clean or replace electrodes.

Randy Reiss who has worked on DCS tools for the statistical analysis of batch processes offers the following perspective on prospective possibilities for smart pH measurements.

“With the auxiliary variables, such as measurement impedance, reference impedance, and temperature, you could analyze multiple sensors in one model and be able to detect individual sensor failures quicker and more accurately. I think this will also add to the overall analysis. Using more of the raw data gives the analysis better insight, in the form of more dimensions, as to what is going on in the process. What will be interesting is to see how the auxiliary measurements relationships react as the process changes, even during normal operation. I think this is a really good marriage of analytics and advanced sensors technology.”

“The sensor manufacturer could actually produce a model for a particular sensor and run a simplified principal component analysis (PCA) within the transmitter to detect a failure. The model and online algorithm can be stripped down to a very few lines of code since there are just a few variables and dynamic time warping or time delay compensation is not needed. If manufacturers presently use just individual univariate statistical (mean and standard deviation) monitoring, then a multivariate analysis (e.g. PCA) would detect a failure sooner. We have seen the benefits of multivariate versus univariate analysis for early process fault detection. The results may also give the manufacturer better insight into how their sensors are failing. The PCA can provide them with a profile of the auxiliary measurements relations when a failure occurs which can serve as a fingerprint for a particular failure mode.”

Since many process conditions that affect electrode performance are unique to a particular product that the electrode manufacturer does not know or cannot duplicate, it may be useful for the user to develop the PCA models from smart lab and field measurements by the use of data analytic tools becoming available in the DCS.

In conclusion, wireless pH and conductivity transmitters in the lab and the field offer a much more intelligent and integrated use of data that makes the most of the ability of the lab to develop process relationships and explore the effect of process conditions and prolonged exposure on sensors. The result can be better performance of pH, conductivity, and inferential measurements and less maintenance from longer life expectancies and fewer cleanings and calibrations.

ABOUT THE AUTHORS

Greg McMillan is a principle consultant with CDI Process & Industrial in residence at Emerson Process Management. Robert Montgomery is a technical assistant at the University of Texas Pickle Research Campus. Teresa Wang is a chemical engineering graduate of the University of Texas. The authors would like to acknowledge: Scott Broadley at Broadley-James Corporation, Jim Gray at Rosemount Analytical Inc., Mark Nixon at Emerson Process Management, and Frank Seibert at the University of Texas Pickle Research Campus for their technical and financial support for studies on the use of wireless measurements.

RESOURCES

- Advanced pH Measurement and Control, 3rd Ed., ISA, 2005
www.isa.org/link/AdvancedpH
- “What have I Learned - Unexpected Wireless Benefits”
www.modelingandcontrol.com/
- All in one network
www.isa.org/intech/20091201
- Essentials of Modern Measurements and Final Elements - A Guide to Design, Configuration, Installation, and Maintenance, ISA, 2010
www.isa.org/link/EssentialsMM_bk

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Rosemount Analytical
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949-757-8500
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