Using Rosemount™ 3900 pH Sensor with low flow panel to measure high purity water

1.0 Introduction

Why is accurate pH measurement in high purity water critical?

Manufacturing industries protect valuable steam system equipment from corrosion by treating process water with chemicals. Achieving the right pH balance is a critical element of this water purification process: a pH level that is too high or too low can lead to boiler or steam turbine scaling and corrosion, and ultimately to system failure, plant downtime, and costly equipment replacement.

In high pressure steam systems, boilers may have conductivity as low as 5-10 µS/cm. This environment can create challenges for general purpose pH sensors, designed to operate best in applications with conductivity greater than 50 µS/cm. This paper will study how the Rosemount 3900 General Purpose pH Sensor with low flow panel solves these challenges and helps ensure reliable pH measurement of high purity water.

2.0 Why is measuring high purity water difficult?

Modern pH sensors contain two electrodes, a pH glass electrode and a reference electrode. Measuring pH requires an electrical bridge between the reference electrode and the glass electrode. A complication of high purity water is having very few ions to carry this electrical current. The reference junction completes the circuit by allowing fill solution to leak into the process. Electrical contact is maintained with the process solution through diffusion of the potassium and chloride ions into the process solution. This diffusion of ions generates a voltage, called the liquid junction potential. Diffusion is caused by concentration differences and eventually the system reaches an equilibrium. The amount of charge separation at equilibrium determines the liquid junction potential. A pH sensor contains potassium chloride (KCl) electrolyte and high purity water accelerates the diffusion, leading to premature failures. Junction potential from high conductivity water creates long come-down time to real process value. Read more in our white paper about the high purity challenge.

3.0 Traditional solution

Traditionally, the solution is to use a specialized sensor, however, there are a number of complications with that approach. These specialized sensors only work in one application, additional stockroom material needs to be set up in the customer's system, specialized training is needed and there is a higher cost of ownership.

4.0 Simplified solution

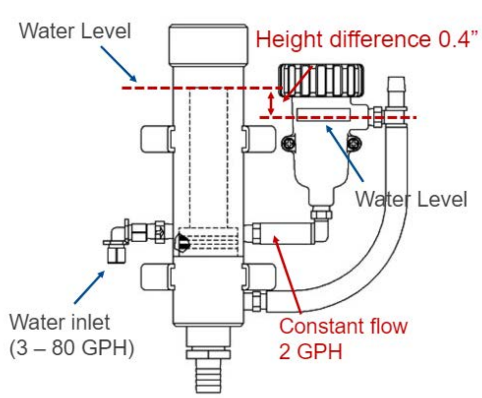
The Emerson solution is to use the Rosemount 3900 General Purpose pH Sensor with a low flow panel designed for this application, PN 00390-7101-0001. This panel regulates the sample flow, eliminating flow sensitivity and concerns over the ionic bridge between reference and glass electrodes. The panel minimizes water usage, and flow regulation minimizes leaching of the KCl electrolyte, which prolongs sensor life.

5.0 Advantages

The Rosemount 3900 can also be used in other plant applications so there is no need to set up special sensors in the stockroom, easing complexity for multiple functional groups in the plant. The sensor requires no specialized training and repair is by repair is by replacement of the sensor, minimizing operator interaction with the measurement. The panel has a long, useful life and does not need replacement. It is set up like a normal pH sensor so the operators can install it with confidence it is going to perform correctly and will not need frequent maintenance as many traditional solutions do. This simple installation is helpful because the operator can trust it is going to perform correctly and will not need frequent maintenance. This system also reduces water usage because it maintains a low flow rate through the panel with the constant head flow controller.

6.0 How the panel functions

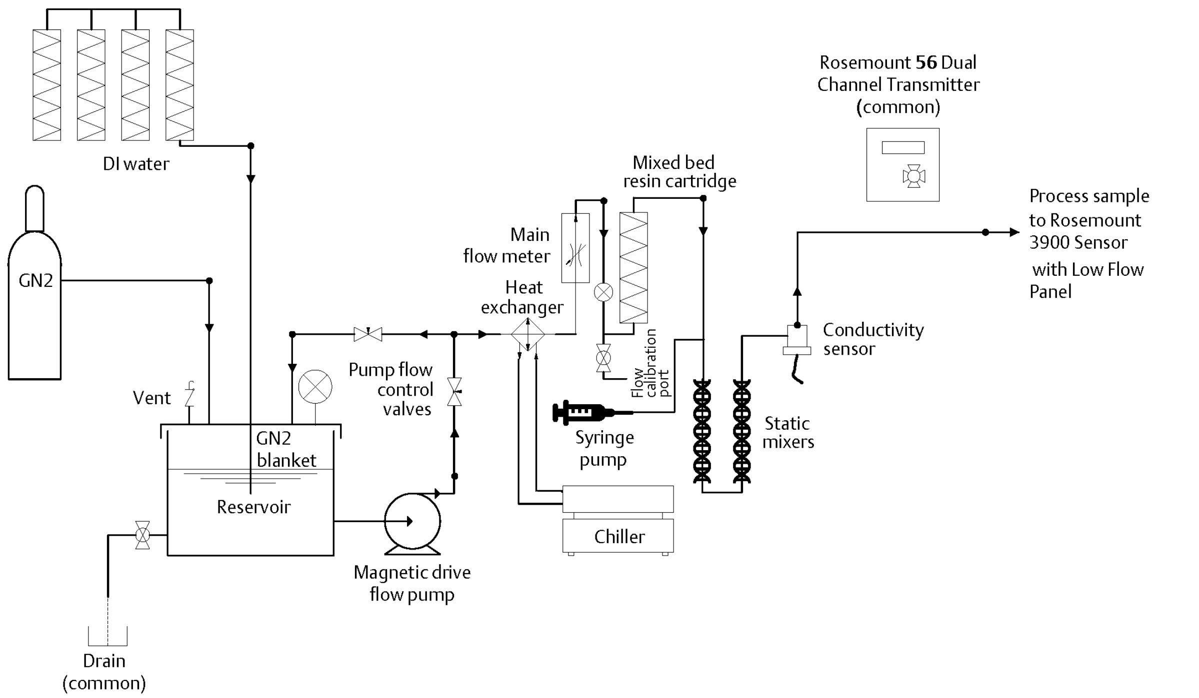
When our low flow controller is added to the Rosemount 3900, it creates a solution that reduces cost and saves time. By using the low flow controller, maintenance is reduced and the setup reduces electrolyte depletion; this increases sensor life and reduces water usage by more than two-thirds versus other side stream solutions. The water level is maintained by an inner drain that keeps the water column and, in turn, the head pressure and flow rate constant (2 GPH). The pressure the pH sensor experiences is constant by maintaining a height difference of 0.4" between the two chambers.



To validate the effectiveness of the Rosemount 3900 low flow panel solution, we conducted several accuracy and sensitivity tests. Details of each test setup and results are provided in 7.0: Testing setup and results.

7.0 Testing setup and results

Figure 1-1. Test setup schematic



7.1 Test setup

Deionized (DI) water with 18.2 MΩ·cm resistivity was transferred into a system reservoir with nitrogen blanket. The DI water was then pumped to a heat exchanger connected to a chiller to keep a constant temperature of 25 °C. A mixed bed resin cartridge was used for a final polish of the DI water, before it entered static mixers to mix with various concentrations of ammonium hydroxide solutions injected through a syringe pump. A conductivity sensor was used to monitor the conductivity of the resulting water before it traveled downstream to the low flow panels or regular flow cells with Rosemount 3900 pH Sensors installed.

First, we conducted an accuracy test with two-point buffer calibration. This shows how close the actual test values were to the predicted pH value after calibrating the sensor with two buffers, allowing the sensor slope to be calculated.

For any pH sensor, accuracy depends on its calibration method. This accuracy test, with two-point buffer calibration, represents the worst case scenario. A total of 14 units were tested.

- 4x Rosemount 3900 with low fow panel (3900LFC#1 – 3900LFC#4); sensor never used
- 8x Rosemount 3900 with regular flow cell (3900#1 – 3900#8); already exposed in 0.05 µS/cm water for 175 days
- 2x Rosemount 3200HP (already exposed in 0.05 µS/cm water for 175 days)

All sensors were calibrated in pH 4 and pH 10. After calibration, all sensors were exposed to 0.05 µS/cm water for six days.

- 3900LFC#1 – 3900LFC#4 were at a 3.75 GPH flowrate
- 3900#1 – 3900#8 were at a 2 GPH flowrate
- 2x Rosemount 3200HP were at a 2 GPH flowrate

Process pH and conductivity were changed by injecting ammonium hydroxide solution into the process at various rates, and the resulting theoretical process pH values were obtained referencing ASTM D5128. For accuracy test, five different pH values were tested, with their theoretical pH and conductivity shown in Table 1-1.

Table 1-1. Theoretical process pH and conductivity based on ASTM D5128

Theoretical pH	Conductivity (µS/cm)
8.65	1.24
8.89	2.15
9.02	2.91
9.18	4.17
9.38	6.58

7.2 Test results: two-point buffer calibration

Table 1-2 contains the accuracy results of sensors with low flow panels, in which the average pH readings of the four sensors are compared to the theoretical pH of the process. Overall, sensors exhibited good accuracy with average readings less than 0.1 pH different from theoretical process pH.

Table 1-2. Acccuracy test results of 3900LFC#1 – 3900 LFC#4 without one-point standardization

Test	Expected pH	Test average
1	8.65	8.57
2	8.89	8.83
3	9.02	8.99
4	9.18	9.17
5	9.38	9.37

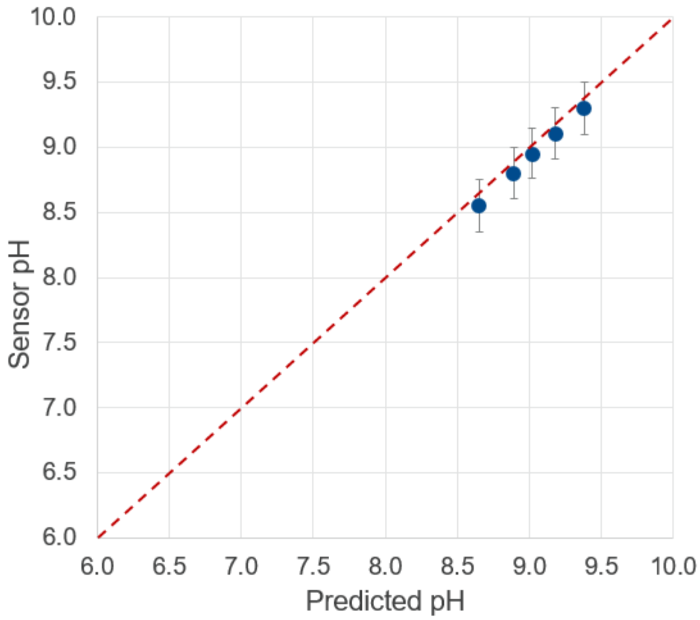
Accuracy results of the eight sensors tested with regular flow cells are shown in Table 1-3. The average sensor readings are also in good agreement with theoretical process pH, with a difference less than 0.15 pH unit.

Table 1-3. Accuracy test results of 3900#1 – 3900 #8 without one-point standardization

Test	Expected pH	Test average
1	8.65	8.54
2	8.89	8.79
3	9.02	8.92
4	9.18	9.07
5	9.38	9.26

Figure 1-2 shows the average sensor readings versus theoretical process pH values for all 12 sensors tested. The scale bars represent the standard deviations of individual sensor readings, showing a small variation between different sensors.

Figure 1-2. Sensor pH reading vs. predicted process pH for sensors without one-point standardization



Note
Averages and standard deviations are based on 12 sensors.

Accuracy results of Rosemount 3200HP Sensors are shown in Table 1-4, where they exhibited a measurement error of about 1.5 – 2 pH units. These results showed a wider deviation when compared to the results obtained with the Rosemount 3900 pH Sensors.

Table 1-4. Acccuracy test results of Rosemount 3200HP Sensor without one-point standardization

Test	Expected pH	Test average
1	8.65	6.55
2	8.89	6.96
3	9.02	7.25
4	9.18	7.59
5	9.38	7.91

7.3 Test results: one-point in-process standardization

A pH sensor can be standardized after a two-point calibration has been done to help compensate for effects of a pH sensor aging without changing the slope. Additional one-point standardization helps to improve the overall accuracy of the sensor.

Again, a total of 14 units were tested.

- 4x Rosemount 3900 with low flow panel (3900LFC#1 – 3900LFC#4)
- 8x Rosemount 3900 with regular flow cell (3900#1 – 3900#8)
- 2x Rosemount 3200HP Sensors

All sensors were pH 4 and pH 10 calibrated to determine sensor slope. All sensors were one-point standardized to pH 8.65 in process to adjust sensor offset.

Table 1-5. Acccuracy test results of 3900LFC#1 – 3900 LFC#4 with low flow panel and additional one-point standardization at pH 8.65

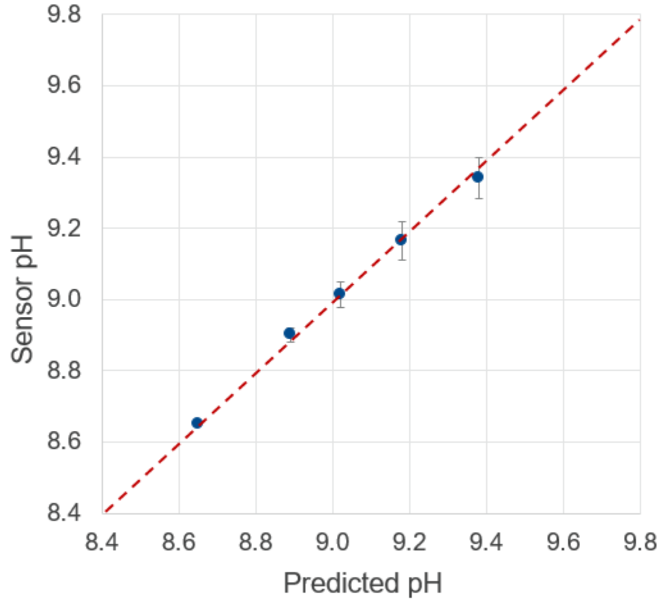
Test	Expected pH	Test average
1	8.89	8.89
2	9.02	9.03
3	9.18	9.18
4	9.38	9.36

Table 1-6. Acccuracy test results of 3900#1 – 3900 #8 with regular flow cell and additional one-point standardization at pH 8.65

Test	Expected pH	Test average
1	8.89	8.91
2	9.02	9.01
3	9.18	9.16
4	9.38	9.34

The results shown in Table 1-5 and Table 1-6 are considered good results with sensor average reading less than 0.05 pH from theoretical process pH. The combined results are shown in Figure 1-3.

Figure 1-3. Sensor pH reading vs. predicted process pH for sensors with additional one-point standardization at pH 8.65



Note
Averages and standard deviations are based on 12 sensors.

Table 1-7. Acccuracy test results of Rosemount 3200HP Sensors with additional one-point standardization at pH 8.65

Test	Expected pH	Test average
1	8.89	8.91
2	9.02	9.09
3	9.18	9.33
4	9.38	9.61

The results shown in Table 1-7 are considered good results if the test pH point is close to one-point standardization point (i.e. 8.65). As process pH moves away from one-point standardization pH point, measurement error increases.

Overall, the additional one-point standardization resulted in better accuracy results for both Rosemount 3900 and 3200HP Sensors. The Rosemount 3900 pH showed better accuracy as the process pH moved away from one-point standardization point.

7.4 Flow sensitivity testing

Next, a test was performed to determine the flow sensitivity. Flow sensitivity test results are shown below. Figure 1-4 shows the fluctuation if using the Rosemount 3900 Sensor in our regular flow cell (PN 24091-00). Figure 1-5 shows how stable the pH reading is when using the sensor with our low flow panel setup. The process pH was held constant during the test period.

Figure 1-4. Fluctuations of Rosemount 3900 Sensor in regular flow cell

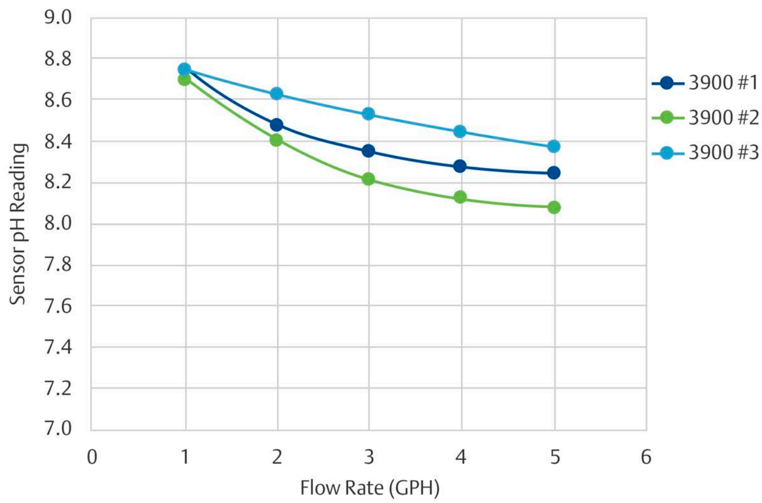
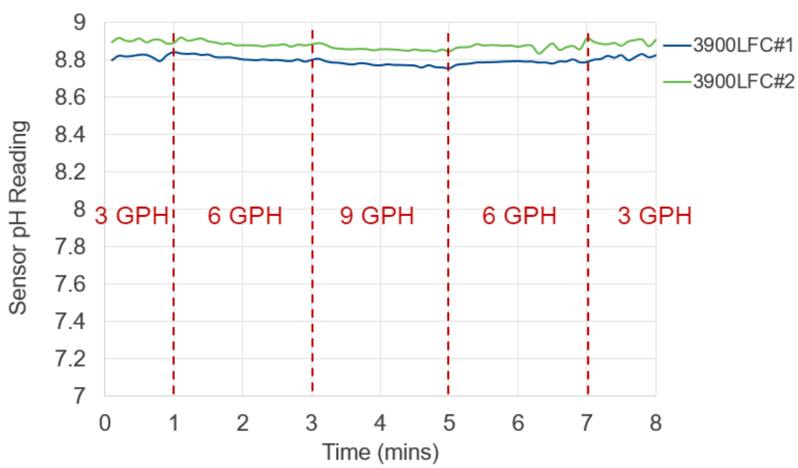


Figure 1-5. Stable pH reading using Rosemount 3900 Sensor with low flow panel setup



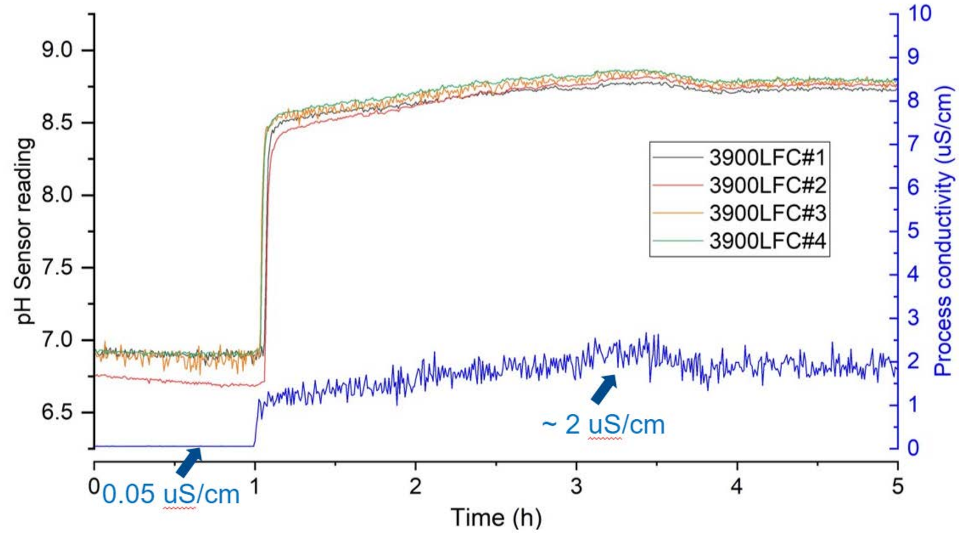
Without the low flow panel, the Rosemount 3900 is significantly affected by flow sensitivity, resulting in a reading shift of about 0.5 pH units as the flow rate increased from 1 GPH to 5 GPH. This is not desirable as the sensor reading may fluctuate upon process flow rate change. Using the low flow panel eliminates this flow sensitivity as shown in the lower graph. When process flow rate was changed among 3 GPH, 6 GPH and 9 GPH, the pH sensor reading was stable and did not show response to the flow rate.

7.5 pH response to conductivity and pH stability

Figure 1-6 shows the pH sensor reading as well as the process conductivity to illustrate how the pH trend follows the conductivity trend. The sensors were installed in the low flow panel and exposed to high purity water with 0.05 µS/cm conductivity. Sensors showed stable readings, demonstrating their functionality at low conductivity of 0.05 µS/cm.

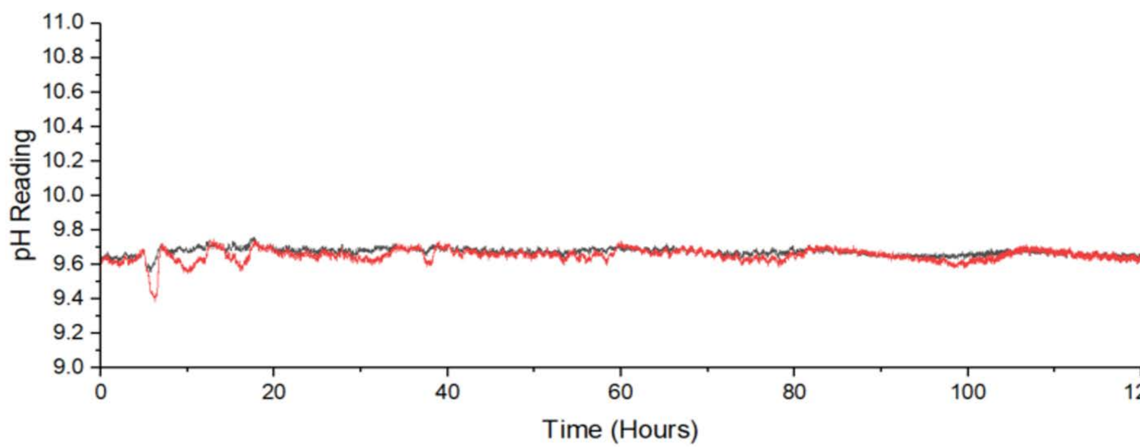
At one hour, ammonium hydroxide was injected into the process, leading to a process conductivity of approximately 2 µS/cm and an increase in process pH. All four pH sensors showed quick response to process pH change, and the sensor pH readings followed process conductivity closely. In addition, the readings from all four pH sensors agree with each other with a very small variation.

Figure 1-6. Rosemount 3900 pH reading shift following process conductivity shift



A stability test shown in Figure 1-7 was conducted with two Rosemount 3900 pH Sensors with low flow panel. Process pH of about 9.6 was kept constant by injecting ammonium hydroxide solution into the process at a constant rate, and the test was performed continuously for five days. As the graph shows, both sensors exhibited good stability, with the maximum fluctuation less than 0.2 pH.

Figure 1-7. Stability test ~3.25 µS/cm



8.0 Conclusion

Measuring pH correctly for high purity water applications is essential. The tests we conducted prove the reliability and effectiveness of the Rosemount 3900 General Purpose pH Sensor with the low flow panel. This solution is a cost-effective and reliable way to measure the pH in these difficult high purity applications. As shown in the results, it is more accurate and cost effective, while providing an easy solution for any operator at the site.

The best way to take the pH measurement is to do a normal two-point calibration followed by a one-point standardization to provide a stable and accurate measurement. Reference the ASTM D5128-14 standard, entitled, "Standard Test Method for On-Line ph Measurement of Water of Low Conductivity," which recommends this calibration procedure consisting of an initial two-point calibration followed by a one-point standardization. The one-point standardization is done to help compensate for the sensor aging at intervals determined by each customer.

To read more about high purity water pH measurement, reference the “High-Pressure Boiler Water Challenges” white paper. For Rosemount 3900 with low flow panel ordering information, reference the product data sheet.