HORIBA
Process & Environmental

Application Note

pH meter for fluoride treatment in semiconductor factory

1 Fluoride treatment

The hydrofluoric acid waste must be neutralized before it can re-enter the environment. Figure 1 shows an example of the neutralization process. pH meters are used to measure and control the neutralization process.

Lime, ($Ca(OH)_2$), is injected into the neutralization tank to capture the fluorine atoms. The chemical reaction is described

$$2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O$$

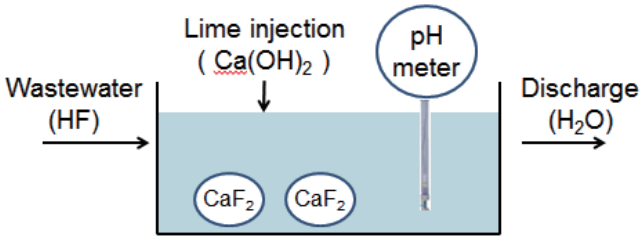
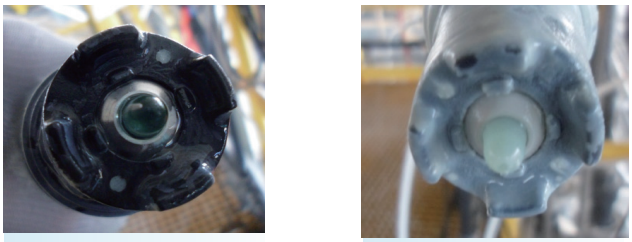


Fig 1 Example of fluoride neutralization

2 Issues on pH measurement

The CaF2 suspended solid generated in the neutralization process sticks to all of the components of the system including the pH electrode. Figure 2 shows the scale covering the pH electrode.



Before use | 8 days measurement

Fig 2 Scales covering on the electrode

As the scale accumulates on the pH electrode, the reading is no longer accurate. The electrode surface must be cleaned or replaced frequently.This cleaning or replacement is a significant cost in the neutralization process. Additionally, the person cleaning the electrode must use a strong acid which could endanger their safety.

3 HORIBA pH meter

1 pH meter with auto cleaning and calibration

The AH-151 from HORIBA automates this pH monitoring process steps of monitoring, cleaning and calibrating. The Lifting Unit shown in Figure 3 removes the electrode from the process tank so the Operations Unit can control the cleaning and calibration processes.

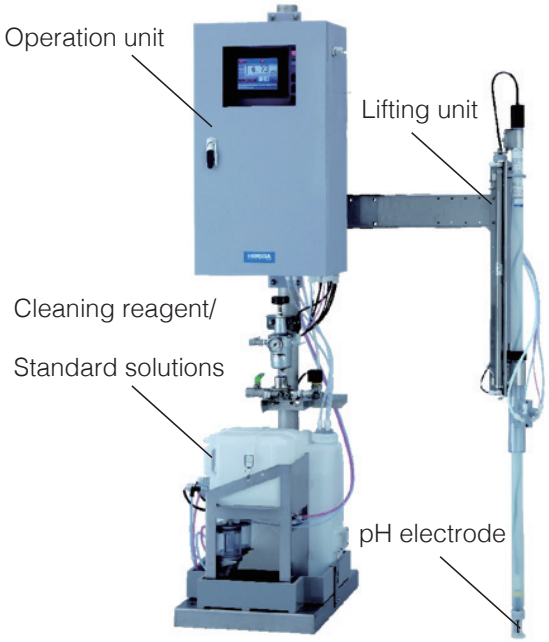


Fig 3 HORIBA pH meter AH-151

The Operations Unit delivers the strong acid to remove the scale from the probe tip. Then the calibration process is run ensuring an accurate reading.
Figure 4 illustrates how the cleaning and calibration chemistries are delivered to the probe tip. The cleaning acid is released to dissolve the scale followed by a rinse. Once the cleaning process is complete, the pH standards are sprayed to adjust the reading as necessary.These processes are run automatically as they were programmed by the user.The user can determine the intervals between cleanings and the amount of acid used as well as the calibration process.

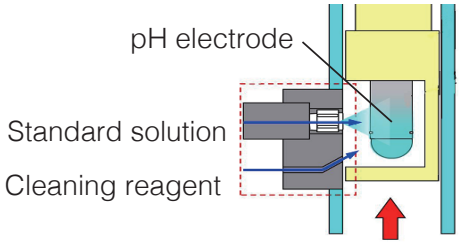


Fig 4 Image of cleaning and calibration

2 Durable pH electrode

HORIBA's 6108 pH electrode has been designed for tough conditions and is shown in Figure 5. This electrode has proprietary trace elements and a thicker wall to withstand the harsh application.Its lower surface area reduces the buildup of the scale.

Fig 5 HORIBA pH electrode 6108

4 Result of the field test

HORIBA conducted a field test with a semiconductor manufacturer in Texas, USA. The customer's standard type of pH meter was facing the problem described in section 2. HORIBA's AH-151 was installed for the evaluation alongside the existing meter. Fig 6 shows the appearance of the HORIBA 6108 electrode after 1 month's service. The electrode does not show any signs of scale.

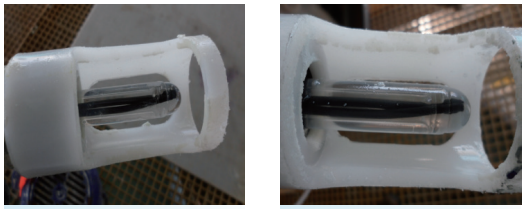


Fig 6 Electrode before and after measurement

Figure 7 compares the measurement results during the field test. During the fluoride neutralization process, the pH value periodically goes up and down.The test results show that the existing meter did not track and trend the pH value after a few hours. In comparison, the Horiba AH-151 performed stable measurement without human intervention.

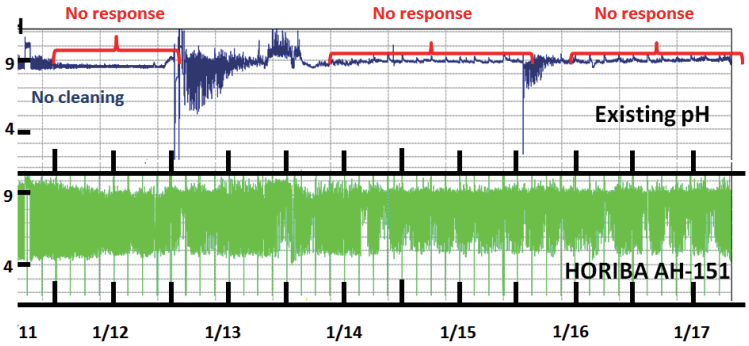


Fig 7 Measurement result

Table 1 shows the comparison regarding the maintenance. Replacement of the electrode and labor are significantly reduced. User expects 91% cost reduction by using AH-151 annually.

	Existing pH monitor (2unis)	HORIBA AH-151 (2 units)
Calibration	2 time/Month	2 times/3 days (Auto)
Cleaning	4 time/week	2 times/3 hours (Auto)
Replacement of electrode	48 pc/year	2 pc/year
Maintenance contract	Yes	No need
Annual Labor	98 hour/year	6 hour/year
Annual Buffer solution	16 L / year	24 L / year
Annual Cleaning solution	48 L /year	292 L /year

Table 1 Comparison regarding the maintenance

5 Conclusion

HORIBA's AH-151 pH monitoring system utilizing the 6108 electrode was able to perform the pH monitoring, cleaning and calibration necessary to maintain the hydrofluoric acid neutralization process. The AH-151 provided positive results in the areas of accuracy, safety and cost.

HORIBA Instruments Incorporated

Irvine Office
9755 Research Drive,
Irvine, CA 92618, U.S.A.
Phone: 1 (949) 250-4811
Fax: 1 (949) 250-0924

Alvin, TX Office
5318 W.FM517 Rd, Alvin,
TX 77511, U.S.A
Phone: 1 (281) 482- 4334
Fax: 1 (281) 614-0303