OPTIMIZING ON-LINE PH ANALYSIS FOR LONGER LIFE IN FLUE GAS DESULFURIZATION SYSTEMS

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ABSTRACT

Due to environmental regulations, industrial operations with coal-fired boilers that exhaust sulfur dioxide gas have been required to minimize their emissions. Flue gas desulfurization (FGD) systems have been installed over the last few years to assist in accomplishing this goal. One of the most common methods is using a wet scrubber with lime slurry. One way to automate scrubber control is using pH analysis of the slurry. In this abrasive, hot and highly sulfurous environment, there have been many challenges to maximizing pH sensor life, calibration, and response time. There are four critical ways to resolve these challenges with pH sensors: location, mounting, cleaning, and sensor type. Scrubber systems in Utah, Illinois, South Carolina, and Florida were studied for recommendations on best practices for successful pH control.

INTRODUCTION

Coal-fired utility power plants generate flue gases that contain nitrogen oxides (NO_x), sulfur oxides (SO_x) and other noxious chemicals that go out their stacks unless the plants have treatment systems for environmental remediation.[1]For the reduction of SO_x, wet or dry scrubbers can be used. In the case of wet scrubbers, there are several technologies that can be used, but many use lime or limestone slurries. With both systems, pH is a parameter that can be controlled to maximize SO_x removal while minimizing scale buildup. The chemistry for lime slurries involve dissolving lime (CaO) solids in water, and then spraying the solution on SO_x gases to produce Calcium Sulfite ($CaSO_3$) or Calcium Sulfate ($CaSO_4$) which are then removed as a sludge. For example with the lime slurry method:

$CaO + H_2O \rightarrow Ca(OH)_2$ Equation 1

$Ca(OH)_2 \rightarrow Ca^{++} + 2\ OH^-$ Equation 2

$Ca^{++} + 2\ OH^- + SO_3^- + 2H^+ \rightarrow CaSO_3 + 2H_2O$ Equation 3

With this lime in this solubilized condition, pH plays a part in how efficiently the SO_3 is removed and calcium sulfite is created. The pH can be manipulated by the quantity of water or lime is added to the slurry. The pH of 8-9 is usually maintained to maximize the gas removal but minimize scale buildup. Scaling clogs nozzles and pipe. [2]

Automated control of pH is used to optimum these processes, but the chemistry, abrasiveness and high temperatures combine to create a short life for the sensors and needs for frequent maintenance. There are several considerations to improve pH performance and life.

LOCATION AND MOUNTING

To select the optimum location for pH measurement in wet scrubber slurry, representative sampling, minimum abrasion, and good contact are necessary. The best location for all three would be in-line at a horizontal pipe location, away from an elbow. Because pH needs regular cleaning and calibrating, the location needs to be easily and safely accessible for those responsible for maintenance. If the sample point is above ground, a safe ladder or stairs and a stable flat surface should be available.

The sensor should then be set at slightly greater than 45+° angle from the top, as shown in Figure 1[3]. Placing the sensor straight down causes more of a chance for air pockets to give false readings. Placing the sensor straight up to the pipe puts the tip in line for more abrasion, scaling and buildup.

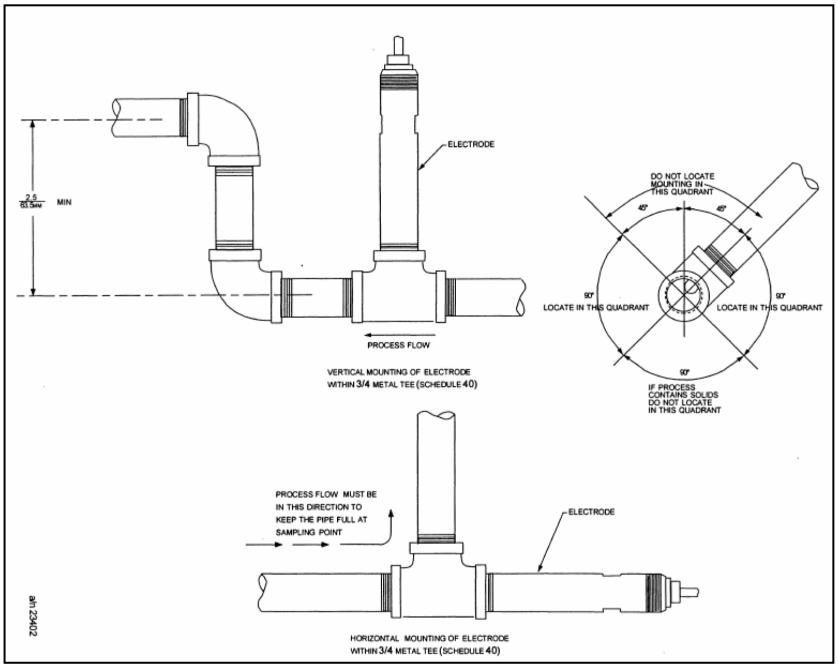

FIGURE 1: PROPER IN-LINE LOCATION OF PH SENSOR

It is also important to install the sensor in a location where it will not dry out. Diffusion of electrolyte from the pH reference is essential to make good electrical contact within the measuring electrode. If the electrolyte dries out, the pH probe will not measure. The sensor may be ruined and need replacement. Depending on the sensor type, if electrolyte dries out in the porous junction, the sensor might be revived by replacing the junction tip, if possible. Or the sensor may be revived by rewetting it in a beaker of water for a few hours. However, this does not work most of the time. If the scrubber line is going to be down for an extended period and the sensor may go dry, remove it and place it in water until the system is ready to start up again.

In locating the pH sensor in-line in a horizontal pipe, the method for insertion and removal should be easy to use with minimum tool use. The pipe needs to be able to be valved out to eliminate the chance for process fluid spillage. Then the easier the sensor is to remove to change out, clean or calibrate, the more successful will be its use. Some sensors have nut-type adapters and nut systems, as shown in Figure 2[4]. These allow the operator to unscrew the nut and then just remove the adaptor that is held on with friction from two o-rings.

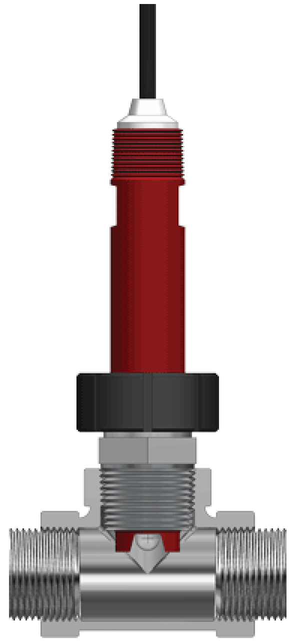

FIGURE 2: NUT ADAPTER SYSTEM

Using a typical ¾” NPT combination pH sensor selected for rough use, there is another method to mount the sensor is using a modified 1” X 1/2” Coupling with a plug drilled out and modified for ¾” NPT threads as shown in Figure 3.

FIGURE 3: COUPLER AND MODIFIED PLUG SYSTEM

There are many installations that use more typical stainless steel insertion/removal devices, but they take up more space, usually need tools, and take more time to use.

Because of the importance of the pH measurement, redundant pH sensors may be installed at the same process point. Three are usually recommended in this case.

The important point is to make the pH location and mounting easy to access for optimum performance and regular maintenance.

CLEANING AND CALIBRATION

PH sensors need regular cleaning and calibration for optimum performance and in a wet scrubber application it is even more important. The slurry causes scale to build up on the sensor tip. The cleaning and calibration frequency should be set on the speed of scale buildup. If scale builds up too thickly before cleaning, it becomes more difficult to clean and damage could be caused in the process.

With a new installation, the pH sensor should be calibrated after initial warm-up using a two-point buffer method. Then for the first two weeks or so, the sensor should be checked every day for slurry and scale buildup, which if significant requires cleaning. It should also be checked against the portable pH meter until the pH difference between the two moves beyond 0.5 or 1.0. If the pH goes significantly different, it should be cleaned and then calibrated with the portable pH meter. After a few weeks, a regular cleaning and calibration schedule can be set. If the pH sensor does not survive the first two weeks, a different type sensor may be needed.

For scaling and slurry buildup, the following are recommended procedures for cleaning:

1. Put the pH analyzer output on hold.

2. Knock off slurry buildup up with soft nylon brush. Wire brushes will remove the thin, hydrogen sensitive-membrane right off the tip or scar it enough that it will not read properly.

3. Soak the sensor in a 5% muriatic solution for the shortest time that will accomplish removal of scale. It could be 5-10 minutes if cleaning is done on an appropriate frequency. Overuse of acid cleaning could reduce the life of the sensor.

4. Scale is clear when wet. Dry the sensor first and check the tip in light to see if scale is fully removed.

5. Rinse the sensor well and then check the calibration. If significantly different, run a sample calibration.

6. Replace the sensor in the process.
7. Take the analyzer output off hold.

SENSOR SELECTION

Higher temperatures at higher pH ranges reduce pH life due to consumption of the hydrogen sensitive ions on the glass membranes. Electrolyte, typically potassium chloride in gel or liquid form, tends to diffuse faster with temperature and high flow. Abrasion from the lime slurry also removes the membrane surface over time. Selection of the best sensor type for this application will give longer life and more reliable control.

Many pH sensors for these applications are typically of the combination style, which mean they have a measuring electrode, either glass or ISFET (ion sensitive field effect transistor) and a reference electrode, usually silver/silver chloride based.

There are many combination pH sensor choices on the market that are called rugged or robust compared to general purpose sensors that have been shown to better withstand the abrasive and highly alkaline FGD slurry. There are various designs of reference protection that allow electrolyte diffusion, but reduce the infiltration of contaminants from the process fluid that could plug the junction or cause fouling of the reference.

The porous junctions at the tip areas may be composed of double or multiple sections that slow contamination that would cause significant poisoning of the silver reference material. Materials of porous junctions in rugged pH sensor configurations may be composed of solid polytetrafluoroethylene (PTFE), ceramic, or fibrous polyvinylidene fluoride (PVDF).

Past the porous junctions inside the sensors, several pH sensor designs use wood or acrylic material containing electrolyte that slow the movement of contaminants toward the silver, while maintaining the required electrical connection of the reference with the measuring electrodes.

An additional method to delay reference poisoning with solid reference designs is to locate the reference wire at the back of the sensor body, compared to hanging it from the back partway toward the front.

Regarding the ruggedized glass measuring electrodes, the tip may have a thicker glass and more hydrogen-sensitive material on the membrane. Some sensors have flat glass on the tip rather than hemispherical or round glass to avoid breakage due to hard materials, this is less important in FGD applications (although they are successfully used in the pulp and paper industry with heavy pulp slurry). In lime slurry, the flat tip actually does not have as large a measuring surface and has been shown to wear out faster than rounded-type tips.

Recently, ISFET measuring electrode technology was been introduced together with known rugged reference technologies to provide longer life.

In comparison to the rugged pH sensor designs, general purpose pH sensors may not last a whole day in the high sulfur, high temperature, and highly abrasive environment. Depending on which ruggedized pH technology is selected with which installation style and maintenance frequency, the sensors may last from a few weeks to many months in operation.

CASE STUDIES

These are a few of the wet scrubber plants that have evaluated ruggedized pH sensors for wet scrubber control.

FLORIDA

A medium-sized power plant in central Florida has had success controlling slurry pH with a process pH sensor system. Through trial and error plant personnel found that an easily accessible, horizontal installation at 45° angle worked well for their pH sensors. They designed the coupling and modified plug installation and it has worked well for them. Although plant continues to look for longer pH life of their ruggedized sensors, the sensors are lasting more than six months now with the current installation method and maintenance procedure.

UTAH

A small power plant in Utah evaluated various pH sensors with different technologies for life and performance on their lime slurry wet scrubber system. The rugged-design sensors lasted three weeks with good response before the plant went on extended outage. Plant personnel took the sensors out of the process and capped them to keep them wet, but the plant was down for almost a year, so by the time the plant were prepared to go back on line, the sensors had all dried out and could not be revived. This stresses the importance of keeping pH sensors wet.

At a nearby copper mine that uses lime slurry at 9-10 pH and 80°C, an evaluation was run to compare rugged technologies for operating life.

SOUTH CAROLINA

A small power plant in South Carolina initially set up their pH sensor on a vertical down-flowing pipe with the sensor pointed up at 45° from horizontal. They had been controlling lime addition from their pH reading, but the pH probe failed in a few days. When arriving there, slurry was flowing out of the scrubber tank, down the street. The sensor location was moved to a sink at the bottom of the tank beside the vertical pipe. This gave the pH sensor a less abrasive location, but there was a great deal of waste with this sampling method.

ILLINOIS

A small university power plant changed their pH sensor at their scrubber from general purpose to a ruggedized one. They found with the thicker glass membrane and better protection for the reference they went from changing the sensors every two days to several months. They found that the maintenance interval for cleaning and calibration was one week.

TABLE I. SENSOR TYPES AND EXPECTED LIFETIME

pH Sensor Type	Lifespan
General Purpose	4 weeks
ISFET measuring/ GP reference	4 weeks
GP with Reference Electrode at Rear	6 weeks
ISFET with Reference Electrode at Rear	8 weeks
Rugged glass with Wood Reference and Electrode at Rear	> 9 months
ISFET with Wood Reference and Electrode at Rear	>9 months

CONCLUSION

PH has been to shown to be an important parameter to measure for adequate flue gas desulfurization control with systems using wet scrubbers using lime slurry. With appropriate location, installation, maintenance and sensor choice, FGD can be automated to optimize SOx removal, lime use and process performance.

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