

pH Measurement and Installation Guidelines for SO₂ Scrubbers

Technical Paper

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Abstract

All industries are now facing new environmental laws and regulations. One new law, the Clean Air Act (CAA), will force many utilities to clean their flue gas emissions before release into the environment. By far the most common way to meet these new regulations will be by scrubbing the flue gas emissions using a wet lime or limestone scrubber. These flue gas scrubbers are extremely pH sensitive and more often than not making pH measurements in a SO₂ scrubber can be very challenging.

The objective of this paper is to give pH sensor application and installation guidelines for these Flue Gas Desulfurization (FGD) systems. Exact pH sensor installation guidelines are discussed as well as some of the advancements made in pH sensor technology.

After years of debate the Clean Air Act (CAA) has been signed into law. This new act is forcing utilities into rethinking environmental law compliance and power demand strategies while still fulfilling their need to provide low-cost reliable electric power. The CAA calls for a two-step program that will reduce SO₂ emissions to 1980 levels of 10 million total tons, by the year 2000. After that there is a nationwide SO₂ emission cap of 8.9 million tons/year. All generators that burn fossil fuels after the year 2000 will be forced to possess an emissions allowance for each ton of SO₂ they emit. The reductions will be achieved in the following way: By January 1, 1995 (Phase 1) half of the total SO₂ reductions must occur, requiring 110 of the largest SO₂ emitting control stations (located in 21 states) to cut SO₂ emissions to 2.5 lb/million Btu. These plants have already been identified in the CAA. By the year 2000 (Phase 2), virtually all power plants above 75 MW and discharging SO₂ at a rate of more than 1.2 lb/million Btu must reduce emissions to that level. Other limits will be established for smaller units.

While the Clean Air Act (CAA) initially targets electric utilities for the largest SO₂ emissions reductions, Chemical, Pulp & Paper and other industries can also expect to see increased scrutiny in this area. Numerous sources such as boilers and incinerators that are within a typical plant can emit these compounds. The term Flue Gas Desulfurization, (FGD) has now also become important to the CPI and Chemical Pulping Engineer.

To control emissions there are several options to choose from:

1. Change fuels.
2. Circulating or bubbling fluidized bed combustion, and furnace and in-duct injection systems of calcium and sodium based sorbents for SO₂ and NO_x removal.
3. Advanced systems that include selective catalytic reduction (SCR); downstream processes and slagging combustors that simultaneously remove NO_x, SO₂, and/or flyash; and repowering schemes such as pressurized fluidized-bed combustion (PFBC), and coal-gasification.
4. Wet lime/limestone and other wet FGD systems.

Much effort has been put into providing alternatives to the scrubber but, two facts suggest that scrubbers will have a lead role:

1. No other commercial process has proven as efficient for removing SO₂.
2. Scrubbers are a known quantity and have established a presence and good track record at utility power plants. The fear of the technology has been replaced by measured understanding and increasing acceptance.

We are already seeing the first effects of the Clean Air Act (CAA) with several major power facilities signing contracts for Flue Gas Desulfurization (FGD) systems. It is believed this option was chosen due to prior field testing and the desire to use locally available coal.

Scrubber Technologies and How They Operate

There are several types of wet flue gas desulfurization processes. Three of the most common types employ lime or limestone, sodium alkali, or dual-alkali. Dual-alkali employs two alkali feed streams, typically pebble lime and soda ash. Currently, these make up about 90% of all FGD systems operating in the US. In general, sodium based and dual alkali systems are chosen for smaller boilers and lime/limestone systems are used in large boiler applications.

The focus of this section will be on the wet lime/limestone scrubber with and without forced oxidation because these are by far the most viable technologies for meeting the CAA regulations.

a) Wet Lime/Limestone Scrubber Systems

In a lime/limestone scrubber a slurry containing calcium hydroxide or calcium carbonate removes SO₂ from flue gas. This is done in an absorber. (See Figures 1 and 2) SO₂ chemically reacts with lime or limestone to form calcium sulfite and calcium sulfate. These sulfite and sulfate crystals are only slightly soluble in water and precipitate from the solution. A major problem with crystallization of these compounds is the potential for scale formation on scrubber internals. Uncontrolled scale can plug the spray nozzles, mist eliminators, piping and other equipment. Plugged systems must be shut down and cleaned.

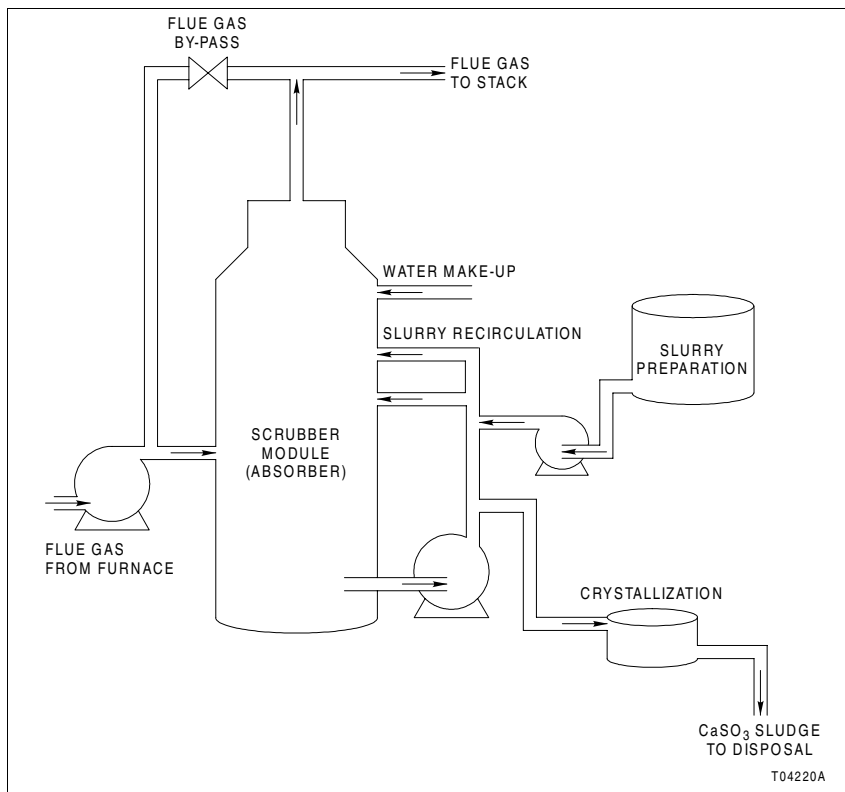


Figure 1. Limestone Scrubber

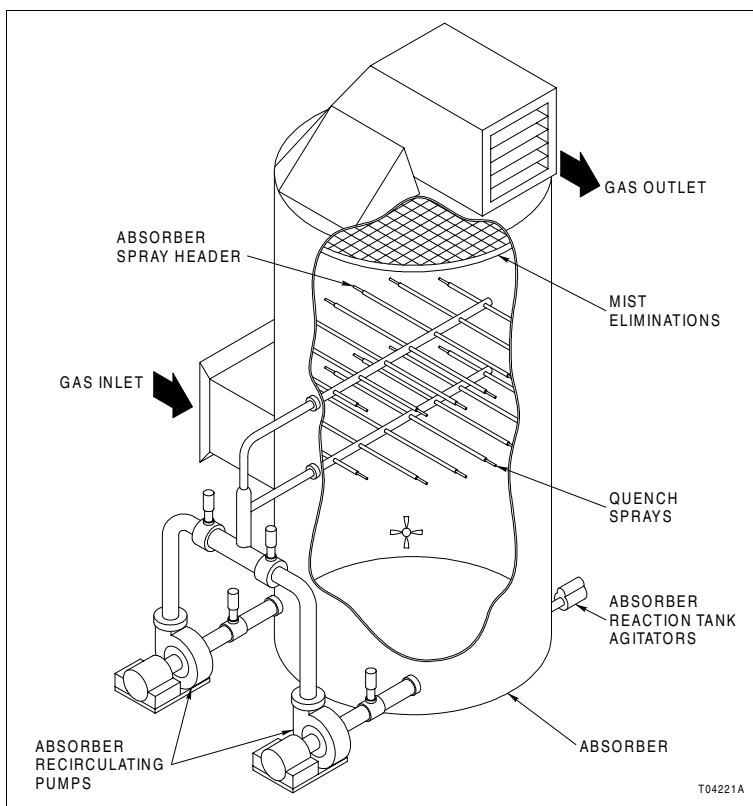
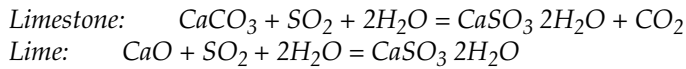


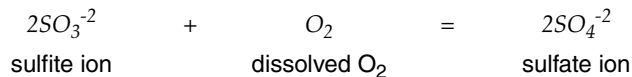
Figure 2. Absorber

Shown below are the overall reactions for wet scrubbing of SO₂ with limestone and lime. Scrubbing with either limestone or lime results in the formation of calcium sulfite dihydrate.



Thermodynamic calculations indicate that the reaction of lime with SO₂ should be more favorable by several orders of magnitude than the reaction of limestone with SO₂ but both reactions are highly favorable.

As the scrubbing of SO₂ takes place, the sulfite ion undergoes oxidation by dissolved oxygen in the absorbent solution to form sulfate ions (SO₄²⁻).



Calcium sulfate upon precipitation from solution, forms a hard stubborn scale on all component surfaces.

CaSO₄ concentration decreases slightly as pH decreases. Furthermore, because the concentration of oxygen dissolved in the slurry is constant, the formation of sulfate depends only on the concentration of SO₃. The precipitation of CaSO₄ increases as pH decreases, thus CaSO₄ is apt to form scale at a lower pH. Hard scale formation can be controlled by keeping the pH high.

The solubility of CaSO₃ increases greatly as pH decreases or conversely CaSO₃ forms a precipitate as pH increases. If pH is too high, "soft pluggage" occurs. Soft pluggage is due to formation of calcium sulfite precipitates which appear as large leaf like masses. Obviously maintenance of equipment that has soft pluggage is easier than with equipment that has hard scale. In many cases where soft pluggage has occurred, it can be melted off simply by lowering the pH (increasing solubility).

It is obvious that a potential dilemma exists, operation at too low pH promotes the formation of hard scale and operation at too high of a pH promotes the formation of soft pluggage. Only through experience can the proper pH range be determined. Typically limestone is added to achieve the desired level of SO₂ removal based on the sulfur content of the coal, the boiler load and the monitored SO₂ concentration of the flue gas, while maintaining the pH in the reaction tank at 5.5 to 6.0 pH.

The calcium sulfite or calcium sulfate slurry with 2-15% solids passes through the scrubber into a holding tank, which is designed to allow enough time for solid precipitation to occur. Fresh lime or limestone is also added to the tank. A large portion of the slurry is recirculated to the scrubber; the remainder is continuously withdrawn from the holding tank. Solids are removed from the withdrawn slurry by settling ponds or by clarification and vacuum filtration. In the former, the settling pond serves as a liquid clarifier as well as a final disposal site for solids. Solids removed by filtration are usually disposed of in a landfill. In both types of treatment the clarified liquid is recycled to the scrubber. (See Figure 1).

b) Forced Oxidation Scrubber System

The current trend for new FGD systems selected for Phase 1 compliance shows that almost all limestone units will operate in a forced oxidation mode to produce gypsum.

The units are almost exactly the same as conventional lime/limestone scrubbers except that by forcing air into the absorber or an external oxidizer with a blower, the calcium sulfite will be changed to calcium sulfate to produce a saleable wallboard grade gypsum. If this gypsum cannot be sold to a wallboard manufacturer many times it can be given away which drastically reduces disposal costs.

There are two basic approaches to aeration of the limestone slurry to produce gypsum. It can either be done in the scrubber itself or it can take place in an external oxidizer. Forced oxidation is very common and has been done for years in places like Europe and Japan. U.S. FGD systems handle coals with much higher sulfur content which helps to explain why we are somewhat behind. It is expected that with new installations as well as for retrofits forced oxidation will be the process of choice. This will apply to the U.S. as well as most other countries in the world. (Figure 3)

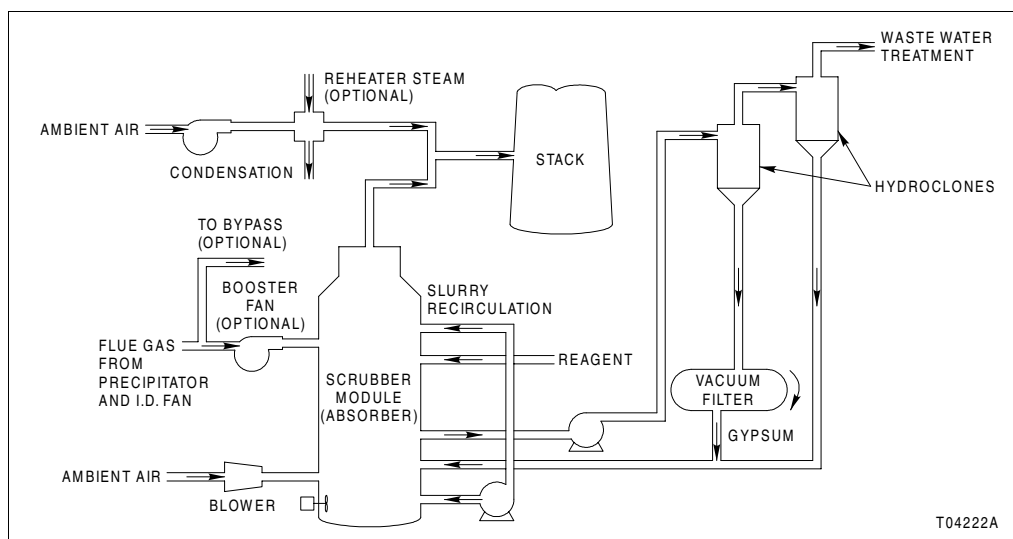


Figure 3. Forced Oxidation Scrubber (Produces Wallboard Quality Gypsum)

c) Advanced Scrubber System

A somewhat typical, yet advanced overseas system is described below. The flue gas is treated by two trains of hot side electrostatic precipitators (ESP's) and selective catalytic reduction (SCR) reactors and then passes through two regenerative reheaters arranged in parallel. A fan is located between the reheater and scrubber and a scavenging fan is added to prevent leakage of the untreated gas into the cleaned gas. Flue gas is introduced into the first scrubber with a six-stage spray. Cleaned gas flows to a mist eliminator and finally through the reheater on out to the stack.

Limestone slurry is fed into the main scrubber and a portion of the circulating slurry in the main scrubber is fed into the first scrubber. Calcium sulfite slurry leaving the first scrubber is acidified with a small amount of sulfuric acid, then oxidized with air bubbles in the oxidizer. Gypsum is separated in a thickener, then further dewatered in a centrifuge. (Figure 4)

pH Measurement of Scrubbers

As we have learned, pH is a critical factor for proper operation of a scrubber. It is also difficult to measure due to 2-15% solids and tendencies towards scaling and plugging. Also the slurry is very abrasive and corrosive. This has led some utilities to resort to taking

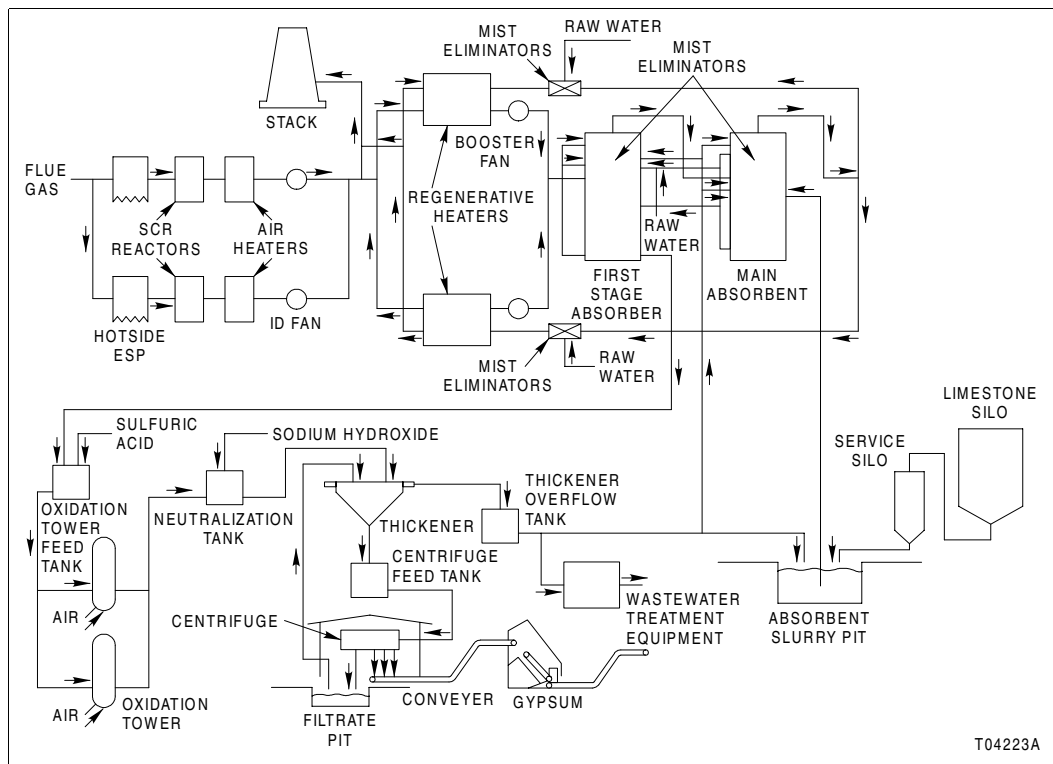


Figure 4. Flue Gas Desulfurization System

grab samples for laboratory analysis and pH control because of the high maintenance involved with on-line pH measurements. With the proper pH sensor technology and simple but well planned installation guidelines, the problems of clogged sample lines, high sensor maintenance and pH sensors that simply do not work can be greatly reduced.

There have been several significant advancements in sensor technology and application expertise that have drastically reduced pH measurement problems. With these advancements, a stable, accurate and low maintenance pH measurement can be achieved. These significant advancements are:

1. A patented Solid State reference element that has solved the pumping, poisoning and plugging problems associated with most pH electrodes.
2. The advent of reliable in-line ball valve insertion sensors coupled with years of application experience give new installation guidelines and sensor recommendations.
3. New glass electrode styles such as flat glass.

With these new advancements, pH sensor maintenance has been reduced while sensor life has significantly increased.

Solid State Reference

A pH sensor is a two-element device; a glass electrode is the active element that produces a voltage, which is proportional to pH changes. The second element is the reference element, which is designed to maintain a stable voltage, so that both elements combined

together in a pH sensor will produce voltage changes that are only proportional to pH changes.

pH sensor design is dependent upon maintaining a constant reference potential that at the same time does not break the electrical connection between the two half-cells. This electrical connection is formed through the reference element, the electrolyte solution surrounding it, directly through the process solution and through the glass electrode. The area where the reference element comes in contact with the process is called the liquid junction.

There are many different reference designs which all attempt to improve the life of a pH sensor. Most revolve around the material, size and number of liquid junctions as well as the use of liquid, gel or slurry electrolyte solution. The size and number of junctions and electrolyte variations are changed by different manufacturers in an attempt to reduce the typical problems associated with this part of the pH sensor. The typical problems can be listed as the three P's (Plugging, Pumping and Poisoning of the reference element).

Plugging of the reference element happens when the liquid junction becomes coated with the process solution and the electrical connection between the glass electrode and the reference is cut off. This problem is usually created because the liquid junction is very small. In most cases a small liquid junction is an attempt to keep the electrolyte in the reference and keep the process solution out of the reference. In scrubber pH control coating of the liquid junction is a common problem.

The second problem results from the type of electrolyte within the reference element. The easier the process can pump this electrolyte solution out of the sensor the easier it will be replaced with process solution within the sensor. Gel and slurry type electrolyte solutions within the reference element are attempts to stop the pumping and eventual poisoning of the reference element. Pumping of the electrolyte solution is especially prevalent in applications that have elevated temperatures and pressure fluctuations. The process solution, which is now in the reference as pumping takes place, will give very unstable pH readings and eventually kill the sensor. These unstable readings are due to changing the previously stable reference potential.

With advancements in reference technology such as the Solid State reference, problems associated with flowing, non-flowing, liquid or gel filled reference elements that have single, double or even triple junctions are greatly reduced. With the ABB solid state reference, the liquid junction has been designed to be very large (compared to any other pH sensor on the market) and, as the name states, does not have a liquid, gel or slurry filled reference. The reference half-cell is made of a solid matrix of independent isolated wooden dowels that are saturated with KCl solution. This solid matrix gives a reference element that cannot be pumped by the process, which would leave gaps easily filled with process solution. The use of wood allows for using a reference design with a large annular liquid junction that is continuous throughout the reference and will resist fouling ensuring a low resistance interface to the process free of junction potentials that cause erratic measurement. This pH sensor reference design is patented and has well over ten years of proven industrial field experience. (See Bailey Technical Paper TP88-6 pH Reference Evolution ... A Revolution!)

Installation Guidelines

Density and pH are the primary control elements for monitoring the efficiency of a SO₂ scrubbing system. (With pH being the primary control element) Even though scrubber slurries are very abrasive one of the keys to an accurate, low maintenance pH

measurement is to have the sensor exposed directly to the process flow. The flow past the pH sensor will create a cleaning by velocity. With velocity cleaning, maintenance is reduced because pH sensor coating is reduced. This velocity cleaning is accomplished by mounting the pH sensor into the main recirculation line to the spray tower or by taking a sample line off of this main line. Today's more advanced pH sensors with rugged designs are able to withstand this abrasive slurry at velocities of 6–9 ft/sec. and produce accurate, stable and repeatable pH measurements.

In years past a common pH sensor installation for SO₂ scrubbers was by submersion into the bottom of the absorber. The submersible application was used because the sensor would be easy to access for maintenance. While access is a noble design criteria, installing the sensor into an area that is not well mixed is an invitation for sensor coating and poor control.

There have been several other methods used to install pH sensors in absorbers. Some methods have had better success than others. One is to install the sensor through the absorber wall and attach a small bucket or cup at the end of the sensor to catch process fluid. This cup is installed inside the absorber and will constantly be refilled with solution caught from the spray and mist. This collection system allows a pH measurement and at the same time keeps the pH sensor wet (which is required). Another variation on this is to install the sensor near one of the trays so that it can catch the process solution as it filters through the absorber. These methods have seen limited application and success. Currently these types of installation are in the experimentation stage and are not to be considered a viable pH measurement location at this time. However this type of installation does eliminate lag time in the control loop by measuring the pH directly where the reaction is taking place.

The two most viable pH sensor installations, we have found, use a TB557 ball valve insertion pH probe. The first is to install a sample line off of the main recirculation line or to ball valve insert the sensor directly into the main line. Both installations ensure a strong fluid velocity for self-cleaning of the sensor and a representative sample of the process fluid. (Figure 5)

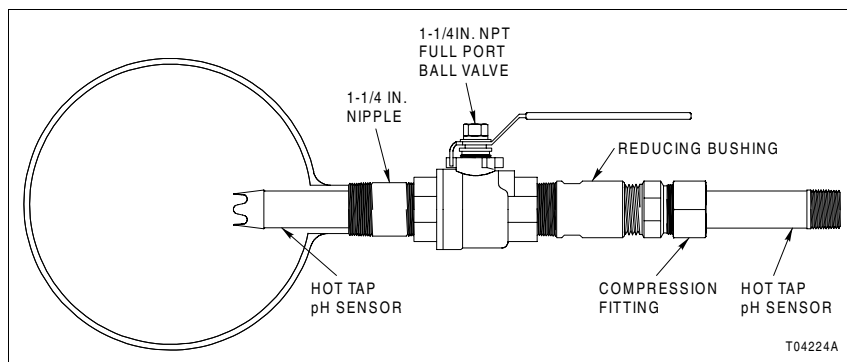


Figure 5. Hot Tap pH Sensor Installation in Main Absorber Recirculation Line to Spray Tower

The first installation uses sample lines that branch off from the main recirculation lines of the scrubber. This line should be at least two inches in size. When using this method of installation do not install any sample pots or flow cells in the line. They usually increase fouling rather than reduce it because process flow and velocity is reduced enough to coat the sensor and in some cases plug the line. A good flow velocity to shoot for is between 6–9 ft/s to ensure good cleaning and clear lines. (Figure 6)

When designing a sample line system it is critical to install a couple of additional valves. A valve should be placed where the sample line comes off the main line to isolate the sys-

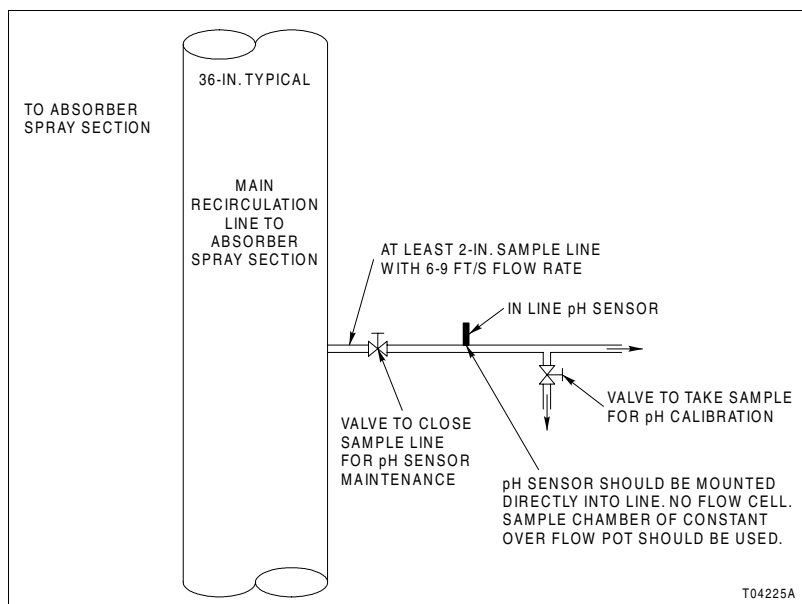


Figure 6. pH Sensor Sample Line Installation Guidelines

tem without shutting down the entire scrubber. A sample valve should be installed close to the sensor off the sample line. This valve can also be used to flush the sample line to prevent plugging. This way it is very easy to calibrate the sensor using a grab sample of the process. In a grab sample calibration the process pH reading is compared to a lab pH reading. This method, when done properly, is the most accurate and preferred way to calibrate an industrial pH system. (See Bailey Technical Paper TP90-2 Calibration and Troubleshooting of pH Loops).

When retrofitting an existing sample line system, follow the recommendation above and be sure to eliminate any sample pots or flow cells. In most cases increasing the size of the sample lines reduce plugging problems.

The second recommended ball valve style installation is to use a ball valve insertion probe mounted directly into the main slurry recirculation lines. In many cases these pipes will be lined which makes retrofitting to this type of installation very difficult for existing scrubbers. Fortunately, several scrubber manufacturers now design and install their pH control systems around this exact method.

When in the main lines, ball valve insertion sensors are typically mounted on the suction side of the recycle pumps in a horizontal pipe out of the absorber/reaction vessel. Certain absorber configurations share a common header. For these types of scrubbers one pH sensor for each spray head is recommended. Multiple sensor locations, one sensor in each recirculation line, have unique advantages. In scrubbers where the absorber is divided into two parts, a pre-scrubber (quencher) followed by the main scrubber. The quencher cools the flue gas and removes impurities such as particulate typically in the form of chloride salts. With separate monitoring the absorption loop can be operated at a high pH to enhance SO₂ absorption and improve reagent usage. The quencher loop can be operated at a lower pH so that liquor concentration effects can be isolated. A pH of about 4.5 is generally accepted as the best control point for quencher control (Figure 7)

Advantages of this installation include no special piping modifications, reduced pH sensor maintenance and longer sensor life. The key to this installation is a durable pH probe worthy of such harsh conditions.

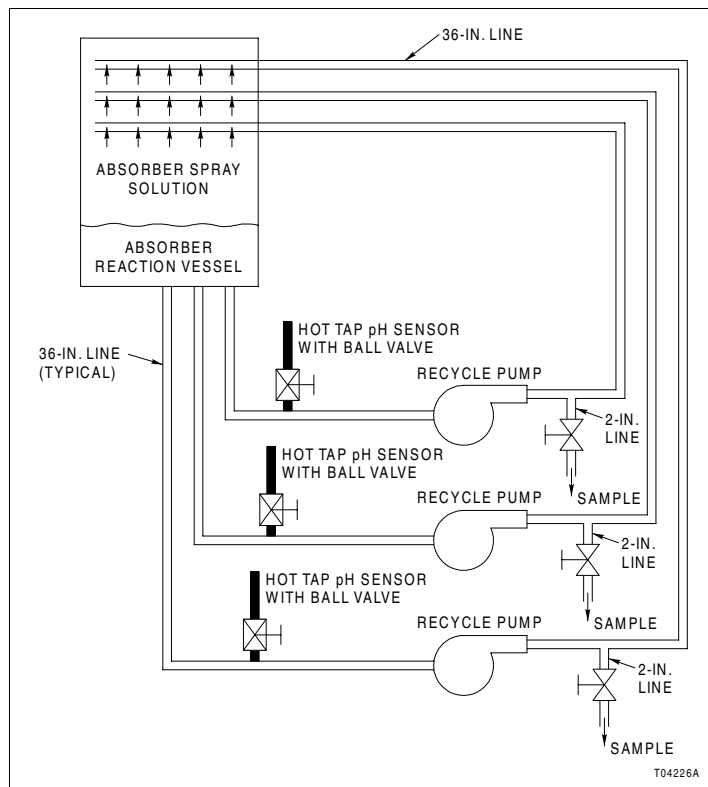


Figure 7. Hot Tap pH Sensor Location for Main Recirculation Lines

Many times when retrofitting an existing pH control system access to the main recirculation lines is not available. Here the biggest problem is that most recirculation lines in a scrubber are rubber lined. In this case mount the sensor through the absorber wall near the inlet of the recirculation pumps. This type of installation ensures the sensor is always wet and representative, well mixed process solution is seen by the sensor. This installation also benefits from a process fluid velocity cleaning of the sensor. A ball valve insertion style sensor would be the best sensor of choice for this installation since the sensor assembly can be easily removed from the absorber without interrupting operation.

Flat Glass

The Solid State pH sensor has been taken one step further by providing a flat glass pH measuring electrode. With a flat glass electrode, sensor life can be doubled or even tripled in high measurements.

Reduced breakage due to sensor handling is one key advantage to a flat glass electrode. The glass electrode does not protrude and therefore it is very difficult to drop it in a way that could damage the glass electrode. Also, in many cases the solids in scrubber slurries will be at least 100 mesh in size and can be physically damaging. With a flat glass sensor style, the glass electrode is more protected from this slurry than a standard electrode. Installation of this special sensor is accomplished exactly the same way as our standard pH sensors.

Conclusion

Compliance to the CAA will most likely involve the purchase and operation of a FGD system for coal based electric utilities. The cost of this equipment, in both capital and maintenance, is high. Proper pH control is a critical factor in attaining scrubbing efficiency and controlling maintenance costs. Time, dollars and limited resources cannot be wasted in maintaining inferior or poorly installed pH equipment. In this day utilities are expected to produce more with less. .less resources, less expense and less pollution. Proper attention to your pH will help you obtain these elusive goals.

The key to a long lived and accurate pH measurement is based on two critical factors. The first is the type of pH sensor chosen. The second is how the pH sensor is installed. Without the proper sensor technology, pH measurements cannot be made in even the best locations. These locations are where the process fluid helps keep the sensor clean. These are the locations that are also the toughest on the pH sensor. With a combination of great sensor technology as well as proper sensor mounting, large amounts of money can be saved in chemical and labor costs. In many cases, reduced chemical and labor costs have resulted in savings of literally thousands of dollars per year!

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