Liquid Analysis Measurements for Wet Gas Scrubbers

Introduction

Wet gas scrubbers are used in a wide range of industrial facilities to remove pollutants from gas streams. Scrubbers work by contacting the gas stream with an aqueous solution or slurry containing a chemical that absorbs or destroys the pollutant. The most common application for scrubbers is to clean gas emissions to ensure they meet regulatory requirements and are not hazardous to plant personnel, the local community, or the environment. The gases removed by scrubbing include sulfur dioxide (SO_2) from combustion processes and a variety of by-product or waste gases such as chlorine (Cl_2), hydrogen chloride (HCl), and hydrogen sulfide (H_2S).

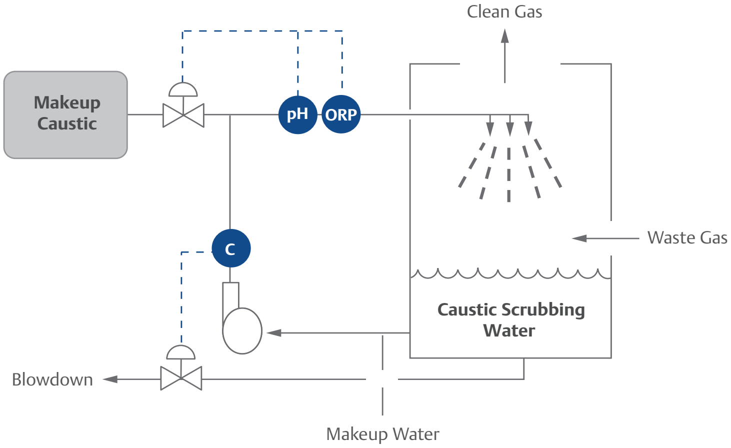
This application note provides a general overview of liquid analysis measurements in scrubbers, as well as more detailed descriptions of how pH is used in two common types of flue gas desulfurization scrubber systems.

Scrubber Process Overview

The design of a scrubber system depends on a variety of factors including the type of pollutant, the pollutant concentration range, and the gas flow rate. Scrubbing systems may have only a single scrubber or may include multiple scrubbers with different scrubbing solutions to remove different pollutants. The concentration of the scrubbing chemical is a key process parameter that determines the effectiveness of the scrubber.

In batch scrubbers, a high starting concentration of scrubbing chemical is used and then allowed to deplete to near exhaustion as it absorbs or reacts with the pollutant. When the concentration of scrubbing chemical falls below a threshold value, the scrubbing solution is blown down and replaced with fresh scrubbing solution. In continuous scrubbers a target concentration of scrubbing chemical is maintained by continual replenishment and blowdown. The concentration of the scrubbing chemical is usually monitored by pH or conductivity measurement.

Figure 1 - Typical Wet Gas Scrubber Process



Monitoring Scrubbing Chemical Concentration with Conductivity

Conductivity sensors require less frequent maintenance and replacement than pH sensors and therefore are the preferred method for monitoring scrubbing chemical effectiveness in some scrubber applications. However, conductivity is a non-specific measurement that is influenced by both the scrubbing chemical concentration and the by-products produced during the scrubbing process.

Conductivity works well in batch scrubber processes where there is a measurable change in conductivity (usually a decrease) as the scrubbing chemical is depleted, and where this change in conductivity is not masked by the formation of scrubbing by-products. A good example is a batch scrubbing process of chlorine gas (Cl_2) using strong caustic (10-15 % NaOH).

Difficulties can arise, however, when more than one gas is being scrubbed. In these cases, the by-products formed can depend on the relative proportions of the gases, causing variations in the conductivity background. When the conductivity background is unstable conductivity does not provide a good measure of scrubbing chemical concentration, but it may still be used as an alarm point to alert the operator to check a grab sample.

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Monitoring Scrubbing Chemical Concentration with pH

pH is usually the best way to monitor scrubbing chemical concentration in continuous scrubbing and batch processes that are subject to significant background conductivity variations.

Continuous scrubbing processes for acidic pollutants are controlled by maintaining an excess concentration of a basic scrubbing chemical, such as caustic (NaOH) or lime (CaO). pH provides a good measure of the concentration of the basic scrubbing chemical because the measurement is specific to hydrogen ions (H+). Therefore, it can be used with minimal effects from the buildup of by-products in the scrubber solution.

A common misapplication is to use a pH measurement in a batch scrubber using a strong caustic (10–15 % NaOH) scrubbing solution. The initial caustic concentration is off-scale (greater than 14 pH) and can destroy the glass electrode. The pH response follows a strong-acid/strong-base titration curve, which results in a reading that only drops back on scale near the point of complete exhaustion of the caustic, followed by a sudden drop at the exhaustion point.

Monitoring Scrubbing Chemical Concentration with ORP

ORP (Oxidation-reduction potential) measurement may also be used along with a pH measurement if the scrubbing reaction involves an oxidation and reduction reaction. In general, the ORP measurement is limited to indicating the complete exhaustion of a particular chemical and is not a good indication of concentration.

Additional Applications of pH and Conductivity

The scrubbing chemical in a spent scrubber solution is sometimes regenerated on site for reuse in the scrubber. An example is the regeneration of caustic (NaOH) in spent sulfur dioxide (SO_2) scrubbing solution from sodium sulfate (Na_2SO_4) using lime (CaO). In this process, conductivity can be used to measure the concentration of the caustic produced.

In addition, by-products from the scrubbing reaction can sometimes be recycled for use in the plant or sold. These include sodium hypochlorite (NaOCl) from chlorine scrubbing with caustic, gypsum ($CaSO_4$) from sulfur dioxide scrubbing with lime, and ammonium sulfate (NH_4HSO_4) as a raw material for fertilizers from sulfur dioxide scrubbing with ammonium hydroxide (NH_4OH). pH and conductivity can be used in the processing of these by-products.

Finally, conductivity can be used to monitor the buildup of dissolved solids in the scrubbing solution. When the conductivity of the solution gets too high, a blowdown can be initiated to control the buildup of scale throughout the process.

Lime Scrubbing Systems for Flue Gas Desulfurization

One of the most common scrubber applications is flue gas desulfurization. Two common flue gas scrubbing systems used in industry are lime and magnesium oxide desulfurization systems.

In lime or limestone scrubber systems the flue gas is bubbled through the scrubber and the slurry is added from above. The lime or limestone reacts with the SO_2 in the flue gas to create insoluble calcium sulfite ($CaSO_3$) as shown in the equations below.

Limestone: $CaCO_3^{(s)} + SO_2^{(g)} \rightarrow CaSO_3^{(s)} + CO_2^{(g)}$

Lime: $Ca[OH]_2^{(s)} + SO_2^{(g)} \rightarrow CaSO_3^{(s)} + H_2O^{(l)}$

The resulting calcium sulfite may be further reacted with oxygen to produce gypsum ($CaSO_4 \cdot 2[H_2O]$) by the following reaction.

$CaSO_3^{(s)} + ½O_2^{(g)} + 2H_2O^{(l)} \rightarrow CaSO_4 \cdot 2(H_2O)^{(s)}$

The scrubbed gas is typically heated to prevent condensation and then discharged in a stack. The spent scrubbing solution is sent to a clarifier where the solids settle out and are removed. After the solids are removed and make-up water is added, the scrubbing solution is recycled to the scrubber.

A pH sensor in a recirculating tank is used to control the feed of solid lime or limestone. The lime or limestone feed is in the form of a slurry because neither substance dissolves well in water. Lime slurry is more alkaline, having a pH of 12.5, while limestone slurry is roughly neutral. A lime-based system will therefore add more lime when pH drops below 12 and a limestone-based system will be controlled to around 6 pH. If lime or limestone slurry is not continually added, the SO_2 gas will quickly drive the pH acidic.

The calcium compounds produced in scrubbers tend to accumulate in recirculation loops and can cause a buildup of scale. Scale on the spray nozzles affects the atomization of the water droplets and reduces the scrubbing efficiency. Scale on the return piping reduces flow rate and changes the thermal balance of the system. The tendency to scale is limited by additives such as chelating agents and phosphates, but these additives are generally only effective at higher pH levels. pH control is necessary to prevent scaling, as it is much easier to prevent scaling than to remove it.

Temperature is also monitored because the solubilities of lime, limestone, and gypsum are unusual in that they decrease with increasing temperature. Since neutralizing reactions produce heat, scaling problems are doubly influenced when the scrubber has a heavy load.

Magnesium Oxide Scrubbing Systems for Flue Gas Desulfurization

In magnesium oxide (MgO) scrubbers the flue gas enters the scrubber and contacts the MgO slurry. The SO_2 is absorbed in the scrubber slurry and forms insoluble magnesium sulfite ($MgSO_3$) as in the equation below.

$$MgO^{(s)} + SO_2^{(g)} \rightarrow MgSO_3^{(s)}$$

Oxygen injected at the base of the scrubber further oxidizes the $MgSO_3$ to magnesium sulfate ($MgSO_4$). A bleed line from the scrubber recirculation line carries the slurry to a centrifuge where $MgSO_3$ crystals are separated from the scrubber slurry. The $MgSO_3$ and $MgSO_4$ is used in the acid plant to produce SO_2 for sulfuric acid production. The MgO reagent is regenerated and returned to the scrubber system.

The pH of the slurry must be carefully maintained between 4.5 and 5.0 because the $MgSO_3$ has a very limited solubility above pH 5.0. Proportional control, using the 4–20 mA current output, is desirable when hold-up time in the recirculating tank is five minutes or less. When hold-up time is fifteen minutes or more, a less expensive on/off control by the pH analyzer is adequate.

If the pH of the scrubber slurry is too low, SO_2 will not be absorbed, corrosion will result, and SO_2 regulatory emissions standards will be violated. If the pH is too high, SO_2 will be absorbed but reagent usage will be excessive, and scale will form inside the scrubber leading to plugging due to formation of calcium carbonate ($CaCO_3$).

Table 1 - Typical Scrubber Applications

Gas	Scrubber Solution	Measurement
Chlorine	Caustic (10–15 %)	Conductivity
	White Liquor (pulp and paper)	pH, ORP
Sulfur Dioxide	Lime	pH
	Magnesium Oxide	pH
	Caustic (weak)	pH
	Caustic (strong)	Conductivity
Hydrogen Chloride	Caustic (10–15 %)	Conductivity
Hydrogen Sulfide	Caustic (10–15 %)	Conductivity
	Sodium Hypochlorite	Conductivity, ORP

The Emerson Solution

For conductivity measurement in scrubbers, toroidal sensors are the right choice due to their resistance to fouling and corrosion. The sensor should be located where it will be exposed to a representative sample. The Rosemount™ 228 Toroidal Conductivity Sensor is a good choice for most scrubbers, but in cases where there is a large loading of particulates, the large bore Rosemount 226 Toroidal Conductivity Sensor or the Rosemount 242 Flow Through Toroidal Conductivity Sensor (for extreme cases), may be preferred.

In batch scrubbers, where concentration measurement is desired (typically caustic scrubbers), the Rosemount 56 Dual Channel Transmitter is an excellent choice to pair with a Rosemount conductivity sensor due its built-in conductivity/concentration curve functionality. The best way to monitor the process using the Rosemount 56 is to measure the conductivity of the scrubber solution over at least three cycles and use the conductivity data gathered, along with concentration data from titrations to develop the conductivity/concentration curve.

The biggest problem encountered in scrubber pH applications is sensor coating, especially in applications using lime as the scrubbing chemical. The Rosemount 396P pH/ORP Sensor is ideally suited for this application because it has a large area reference junction that resists coating and plugging. This sensor is available in threaded or retractable mounting configurations and is compatible with the full line of Rosemount liquid analysis transmitters. To minimize coating effects, the sensor should be mounted so that it is exposed to a high sample flow rate. In more extreme cases, a flow-powered cleaner or jet spray cleaning can reduce the need for manual cleaning, depending upon the nature of particulates present.

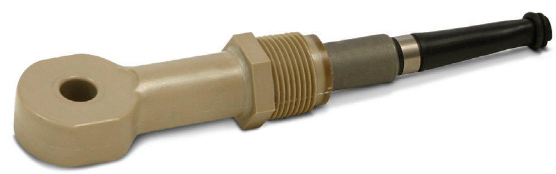
pH is not applicable to batch scrubbers using strong caustic (10–15 % NaOH). Strong caustic dehydrates the pH glass and greatly reduces sensor life. The effects of the byproducts of the scrubbing reaction on the health of the pH sensor should also be considered. In some scrubbers the byproducts can result in a strongly oxidizing solution which can poison the pH sensor reference electrode.

Important Questions for Scrubber Applications

1. Which gas or gases are being scrubbed?
2. What is being used as the scrubbing chemical, and what is its concentration range?
3. How is the scrubber operated? Is a target concentration of scrubbing chemical being maintained with continual blowdown and replenishment, or is the scrubbing chemical allowed to deplete down to a certain concentration? What is that concentration?

Rosemount 396P pH/ORP Sensor

Rosemount 396R/396RVP pH/ORP Sensor



Rosemount 228 Toroidal Conductivity Sensor

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