

Accurate pH Measurement in Limestone-Gypsum Flue Gas

Industry: Chemical, Refining, Power, Oil and Gas
Product: PH450

Introduction

In limestone-gypsum flue gas desulfurization systems, the consumption of a desulfurization agent (lime) is controlled using online pH analyzers. Of great concern in the pH measurement is heavy lime scaling on the pH electrode. To ensure accurate measurements, frequent cleaning of the electrodes with acid is required, adding to both maintenance workload and cost.

The EXA AUTO CLEAN chemical cleaning system automates the acid cleaning process, which saves both time and expense, and also ensures precise pH measurement over long periods.

Expected Benefits

- Improves the efficiency of a limestone-gypsum flue gas desulfurization system
- Ensures stable, continuous pH measurement
- Reduces operating costs
- Eliminates manual cleaning

Process Overview

Limestone-gypsum flue gas desulfurization consists of two processes: absorption and oxidation.

Absorption process

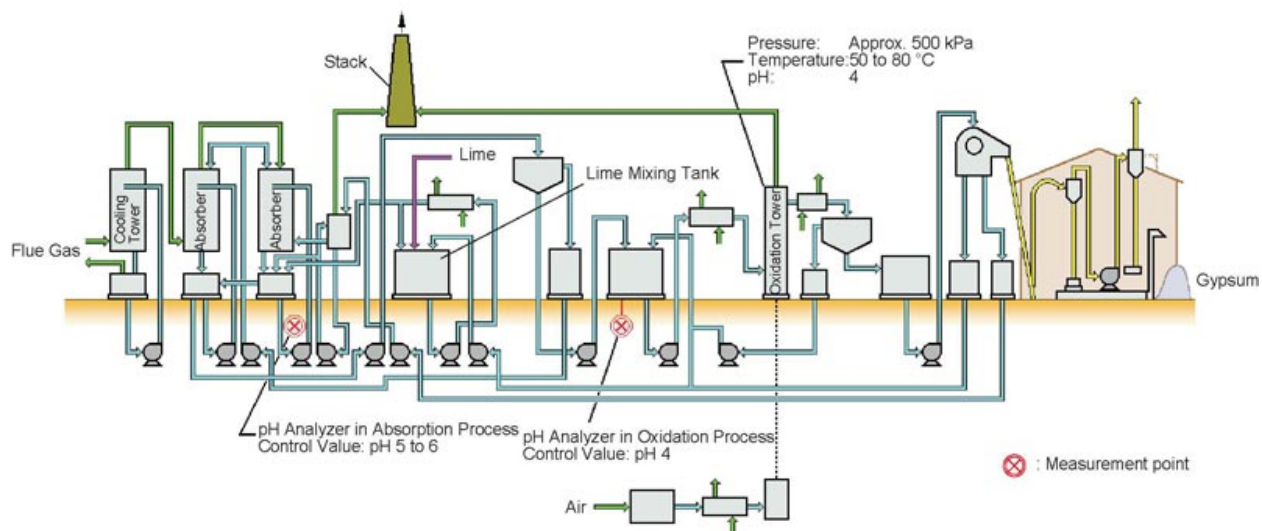
Reaction formula: $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$, $2\text{CaCO}_3 + 2\text{SO}_2 + 1/2\text{H}_2\text{O} \rightarrow 2\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O} + \text{CO}_2$

In this process, it is important to promote the reaction of calcium (Ca) and to achieve a target desulfurization rate. The absorption rate is affected by the pH, concentration, temperature of liquid, and the liquid/gas ratio. When the pH of the absorbing solution is below 5, calcium hydrogen sulfite ($\text{Ca}(\text{HSO}_3)_2$) is generated. $\text{Ca}(\text{HSO}_3)_2$ is converted into sulfur dioxide (SO_2) in a reversible reaction, thereby reducing the desulfurization rate. When the pH of the absorbing solution is 7 or higher, carbon dioxide (CO_2) in the flue gas reacts with calcium (Ca) to produce calcium carbonate (CaCO_3). This increases lime consumption. Since the pH has an influence on the subsequent oxidation process, the pH of the absorbing solution should be kept between 5 and 6.

Oxidation process

Reaction formula: $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O} + 1/2\text{O}_2 + \text{Aq} \rightarrow \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{Aq}$

In this process, calcium sulfite ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$) generated in the absorption process is oxidized with air to calcium sulfate (CaSO_4) under a pressure of approximately 500 kPa and a temperature of 50 to 80 °C. The pH of the absorbing solution in the absorber is approximately 6. It should be kept at around 4.



Solution Details

Field Data

Deposits of crystalline substances (e.g., CaCO_3) on electrodes in limestone-gypsum flue gas desulfurization systems decrease the accuracy of pH measurements. The cleaning of the electrodes and the reduction of maintenance time and cost are key points to consider when selecting a pH analyzer for the system.

	pH System with Chemical Cleaning	General pH Analyzer
Cleaning	Automatic acid cleaning: 2 or 3 times/day, user programmable Manual acid cleaning: approx. monthly	Manual acid cleaning: once/day
Calibration	Manual calibration: weekly	Manual 2-point calibration: weekly
Other maintenance	Replenishment of chemical tank: approx. every 2 months	

Acid cleaning is done with a 4% hydrochloric acid solution

Measurement System

Chemical Cleaning System

1: K1547PJ Hastelloy Spray Cleaning System

EXA PH 4-wire pH measurement system

1: PH450G 4-wire pH converter

pH Electrode

1. FU20 all-in-one sensor

Operation Outline

Measurement takes place prior to cleaning. The instrument holds the last measured value while the cleaning nozzle spray the electrode for a set period of time, once the wash is complete the unit allows for recovery time before returning to measurement mode.

Notes

- An organic solvent cannot be used for cleaning, however 5-10% HCl is recommended.