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 not only saves both time and expense but 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**

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

**Absorption process**

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

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, and temperature of liquid and the liquid/gas ratio. When the pH of the absorbing solution is below 5, calcium hydrogen sulfite (Ca(HSO\(_3\))\(_2\)) is generated. Ca(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 to between 5 and 6.

**Oxidation process**

- Reaction formula: \( \text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + \text{Aq} \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{Aq} \)

In this process, calcium sulfite (CaSO\(_3\)·\(\frac{1}{2}\)H\(_2\)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 by adding acid from the cooling tower.
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.

<table>
<thead>
<tr>
<th>pH System with Chemical Cleaning</th>
<th>General pH Analyzer</th>
</tr>
</thead>
</table>
| Cleaning                        | “Automatic acid cleaning: 2 or 3 times/day, user programmable”  
Manual acid cleaning: approx. monthly” | “Manual acid cleaning: once/day” |
| Other maintenance               | Replenishment of chemical tank: approx. every 2 months | – |

Acid cleaning is done with a 4% hydrochloric acid solution

Measurement System

EXA AUTO CLEAN chemical cleaning system
1: PH8HS3 holder
2: PH8SM3 operating unit
EXA PH 4-wire pH measurement system
3: PH400G 4-wire pH converter
4: PH8EFP KCl refillable pH detector

Operation Outline

Measurement Status

Sequence Operation
[Measurement]
Measurement takes place when cleaning command is not issued or when measurement command is issued.

Cleaning Status

[Cleaning]
The pH detector is pulled out of the solution and housed in the cleaning chamber where chemical cleaning takes place. After cleaning, the system moves to measurement mode in accordance with the programmed sequence.

Utilities

Power supply: 100 V AC, 50/60 Hz
Power consumption: approx. 60 VA
Air source: pressure: 300 to 950 kPa
Maximum consumption: approx. 20 L/min
Chemical cleaning solution consumption: approx. 100 mL
Tank effective capacity: approx. 17 L

Notes

• An organic solvent cannot be used for cleaning.
• Deterioration of materials in chemical solution piping and air piping

When the system is installed in a location where it is exposed to direct sunlight, the polyethylene resin piping will last approximately one year. (It is recommended that fluoro resin piping be used.)