Coal fired power plant emissions are a global concern. The burning of coal produces sulfur dioxide (SO₂). When released into the atmosphere SO₂ combines with water to form sulfuric acid (H₂SO₄). Coal fired power plants will use a flue gas desulfurization (FGD) scrubber to remove the SO₂ before release up the stack. The scrubbing process is pH dependent. In this paper we will explore some of the challenges in this type of pH measurement.

The FGD scrubber uses chemical reagents sprayed into the flue gas to react with the SO₂. Many different reagents have been used over the years. Examples include ammonia, caustic, lime, limestone, and sodium carbonate. Due to cost, the most common reagents are Lime (CaO) and Limestone (CaCO₃). Since both chemicals are very similar we will limit the scope of this paper to them. Both materials are solids thus they are mixed with water to form a slurry. The chemistry is as follows:

Lime: \[ \text{CaO} + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{CaSO}_3 + 2\text{H}_2\text{O} \]
Limestone: \[ \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{CaSO}_3 + 2\text{H}_2\text{O} + \text{CO}_2 \]

Downstream from the boiler the flue gas passes through an electrostatic precipitator (ESP). The ESP removes fly ash so it does not pass into the atmosphere. Quench water cools the flue gas at the entrance of the scrubber. Quenching reduces evaporation losses thus lowering chemical usage. Inside the scrubber spray nozzles mist the lime slurry down on the flue gas. This section is referred to as the absorber. The slurry and quench water collects in the bottom of the absorber. A paste-like calcium sulfite (CaSO₃) sludge forms in the liquid. CaCO₃ can be very difficult to remove if it settles out at the bottom of the absorber. More recent scrubber designs will blow outside air through liquid to convert the sulfite to sulfate in the following reaction.

\[ \text{CaSO}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} \]

The addition of air is referred to as forced oxidation. The resulting calcium sulfate (CaCO₃) crystallizes in the liquid and is easily removed through filtration. An added benefit from the process is that CaCO₄ (known as gypsum) can be sold as additive for wallboard and cement production.

As the flue gas continues through the scrubber it will pass through mist eliminators to further remove any entrained liquid. The final flue gas may still contain some trace sulfur compounds. It will be reheated to avoid corrosion prior to entering the stack for release into the environment.

**Measurement challenges**

FGD scrubbers have multiple variables that can effect their efficiency. These include:

- flue gas flow rate
- changing coal supplies
- coal sulfur content
- coal moisture
- chloride content
- fly ash content

The pH of the slurry in the absorber is one of the main control parameters of the scrubber. It is typically kept in a...
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range of 5.7 to 6.8pH. If the slurry drops below 5pH then the scrubber will not efficiently remove SO₂ from the flue gas. If the pH gets above 7.5pH then CaCO₃ / CaCO₄ scale can begin to plug nozzles, mist eliminators, and other hardware. In addition to build-up problems, maintaining high pH increases reagent chemical usage resulting in additional wear on pumps and valves plus increased chemical cost.

The slurry in the bottom of the scrubber is typically 5-15% solids. It is continuously recirculated to through the spray nozzles to use up the residual lime compounds. Solids concentration is controlled by bleeding off the bottom of the absorber to either waste or gypsum production.

pH Measurement Solutions
pH measurement can be difficult in these applications. Problems include:

- High sulfides that attack the sensor
- Heavy metals that attack the sensor
- Abrasion and coating due to particulates
- Elevated temperatures shorten sensor life

Barben Performance Series pH sensors with Axial Ion Path® reference technology help to overcome the issues listed above. The internal filtering junction prevents chemical ingress into the sensor while the Axial Ion Path® seals ensure that the measurement signal is maintained. Barben sensors are rated up to 130°C (266°F) so they can easily handle the slurry temperatures.

Barben Analytical recommends mounting the pH sensor directly on the recirculation piping using a retractable sensor such as the 547 or 567 "Hot Tap" sensor. Installation in the recirculation piping improves speed of response while the slurry flow rate helps keep build-up from forming on the electrode tip. Material of construction should be either Hastelloy or Kynar to best deal with the corrosive nature of the process. Barben sensors should be specified with "CR" Coat Resistant high temperature glass electrodes.

Barben pH sensors will easily connect to most modern pH analyzers in use today. Wiring diagrams for commonly available instruments can be found on www.BarbenAnalytical.com or via request from technical support.

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