Flue gas desulfurization: a re-emerging technology for controlling \(SO_2\) emissions at power plants

By Brad Buecker and Paul Dyer, PE

Increasingly stringent sulfur dioxide (\(SO_2\)) emissions regulations have generated renewed interest in flue gas desulfurization (FGD). A number of projects at major utilities are either in design or being planned. This article examines FGD technology and how modern systems have advanced from the days when scrubbers were the nightmare of some power plant managers and operators.

**Wet-Limestone Scrubbing**

Wet-limestone scrubbing has been and will continue to be a popular method for many FGD applications. A generic flow diagram of the wet scrubbing process is outlined in Figure 1. Wet-limestone scrubbing is a classic example of an acid-base chemistry reaction applied on a large industrial scale, where alkaline limestone slurry reacts with acidic sulfur dioxide.

The fundamental chemistry is outlined below:

As flue gas passes through the scrubber and is contacted by the limestone slurry sprays, sulfur dioxide absorbs into the liquid. Theoretical chemists argue that sulfur dioxide forms only a hydrated compound, where individual \(SO_2\) molecules are surrounded by water. However, when \(SO_2\) is introduced to water, a pH depression
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occurs, in which the following reactions are representative:

**Equation 1**
$$\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_3 \leftrightarrow \text{H}^+ + \text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$$

Limestone, whose primary components are calcium carbonate (CaCO$_3$) with lesser amounts of magnesium carbonate (MgCO$_3$), when introduced to water will raise the pH according to the following mechanism:

**Equation 2**
$$\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$$

However, CaCO$_3$ is only very slightly soluble in water, so this reaction is minor in and of itself. In the presence of acid, calcium carbonate reacts much more vigorously, and it is the acid generated by absorption of SO$_2$ into the liquid that drives the limestone dissolution process.

**Equation 3**
$$\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2\uparrow$$

Equations 1, 2 and 3 when combined illustrate the primary scrubbing mechanism.

**Equation 4**
$$\text{CaCO}_3 + 2\text{H}^+ + \text{SO}_3^{2-} \rightarrow \text{Ca}^{2+} + \text{SO}_3^{2-} + \text{H}_2\text{O} + \text{CO}_2\uparrow$$

In the absence of any other factors, i.e., oxygen in flue gas, calcium and sulfite ions will precipitate as a hemihydrate, where water is actually included in the crystal lattice of the scrubber byproduct.

**Equation 5**
$$\text{Ca}^{2+} + \text{SO}_3^{2-} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}\downarrow$$

However, oxygen in the flue gas has a major impact on chemistry, and in particular on byproduct formation. Aqueous bisulfite and sulfite ions react with oxygen to produce sulfate ions (SO$_4^{2-}$).

**Equation 6**
$$2\text{SO}_3^{2-} + \text{O}_2 \rightarrow 2\text{SO}_4^{2-}$$

Approximately the first 15 mole percent of the sulfate ions co-precipitate with sulfite to form calcium sulfite-sulfate hemihydrate [(CaSO$_3$ $\cdot$ CaSO$_4$) $\cdot$ $\frac{1}{2}$H$_2$O]. Any sulfate above the 15 percent mole ratio precipitates with calcium as gypsum.

**Equation 7**
$$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}\downarrow$$

Calcium sulfite-sulfate hemihydrate is a soft material that tends to stick to surfaces, which can cause deposit build-ups. And, the compound has little practical value as a
One potential drawback of wet-limestone systems is that they can emit very fine particulates and aerosols.

chemical commodity. Many scrubbers are equipped with forced-air oxidation systems to introduce additional oxygen to the scrubber slurry to prevent deposit buildups. A properly designed oxidation system will convert all of the liquid sulfite and bisulfite ions to sulfate ions. Sulfate precipitates with calcium as gypsum, which forms a cake-like material when subjected to vacuum filtration. In many cases, 85 percent to 90 percent of the free moisture can be removed by this relatively simple mechanical process. Gypsum is the primary ingredient of wallboard, and a number of FGD systems throughout the world produce wallboard-grade byproduct.

Problems that plagued first- and second-generation wet-limestone scrubbers included poor SO₂ removal, scale formation in the scrubber vessels and poor utilization of the limestone reagent. Spray nozzle efficiency, scrubber vessel configuration, limestone reactivity and particle size are all factors that influence these processes.

Adequate mixing of the flue gas and slurry is very critical, and early scrubber towers usually were equipped with internal packing or trays to enhance gas-liquid contact. While the theoretical concept behind these mixing devices was valid, the material would often become plugged with scale, necessitating periodic cleaning, replacement or laborious control methods.¹ In some early designs, the packing consisted of plastic balls, which would “cement” together. One can only imagine the mess caused by this process. Spraying technology has greatly improved in the last few years, and open spray towers are now becoming popular.² A technique that is still common is to introduce the flue gas in a tangential pattern to the scrubber tower. This imparts a centripetal motion to the gas and forces it to swirl around the tower as it passes upward. The swirling action improves slurry-gas mixing and increases gas residence time in the vessel.

Limestone reactivity is another key factor. In general, limestones with 94 percent or greater calcium carbonate content provide suitable alkalinity for reaction. Impurities in the stone may cause significant operating difficulties. Magnesium, a common substitute for calcium, can be helpful or harmful depending upon its chemical makeup within the stone. If the magnesium exists as homogenous magnesium carbonate (MgCO₃), it can enhance SO₂ removal by providing extra alkalinity to the scrubbing solution. However, magnesium often co-exists with calcium in a crystal matrix known as dolomite (CaCO₃·MgCO₃). Dolomite is rather un-reactive, and stones containing a significant dolomite content may require excess feed to achieve the required SO₂ removal. Limestones typically also contain inert materials, including siliceous compounds such as quartz. These have different densities than the
scrubber byproducts and may negatively influence performance of slurry separation devices. Iron in limestone can form oxides that plug vacuum filter cloths. Iron can also influence gypsum scale formation on scrubber vessel internals, although this is often not a problem in forced-oxidation systems.

Limestone reactivity is greatly influenced by particle size. A typical method, past and present, of preparing limestone slurry is to grind the raw limestone with water in a ball mill. This produces a suspended solution of fine limestone particles (slurry), which is then pumped to the reaction vessel. Smaller particle size increases the total surface area of the limestone reactant. Grind size is determined by passing a slurry sample through progressively smaller sieves. A typical specification for grind size in first-generation scrubbers was 70 percent passage through a 200-mesh (200 grids-per-inch) screen. However, scrubber designers, operators and chemists came to realize that this size was too coarse to promote good utilization. Nowadays, 90 percent or greater passage through a 325-mesh screen is more desirable.

Even with a well-ground, high-purity limestone, utilization may fall short of expected levels. A modern approach is the use of supplemental additives to enhance performance. One of the most popular of these is adipic acid (HOOCCH₂CH₃CH₂CH₂COOH), which goes by the common name of dibasic acid (DBA). DBA functions by assisting limestone dissolution, which in turn increases sulfur dioxide removal kinetics.

Improvements also have been made in the choice of scrubber vessel construction materials. Chlorine in coal converts to hydrogen chloride (HCl) during combustion. HCl of course is an acid and it reacts with limestone to produce calcium and magnesium chloride (CaCl₂ and MgCl₂). Both are very soluble salts. Chloride concentrations may reach several thousand milligrams per liter (mg/L). Many first- and second-generation designs incorporated stainless steels in system components. These materials proved to be unstable when exposed to high chloride concentrations, as chlorides penetrated the protective oxide layer on stainless steels and initiated pitting. Various inorganic and organic linings were tested over the years, but these often, but not...
always, failed due to poor application or simply the stressful nature of the scrubber environment. More exotic materials are not always the answer. Even titanium will fail in the presence of porous slurry deposits that allow chloride to concentrate at the metal substrate. These conditions are prevalent at the wet-dry interface where flue gas first contacts the slurry sprays. A retrofit technique for some scrubber components, such as scrubber vessel outlet ducts, is overlay (commonly termed wallpapering) of the base metal with a corrosion-resistant material. The most common choices have been the nickel-based alloys C-276 and C-22.

An issue of continuing importance is byproduct disposal. At plants equipped with forced-air oxidation systems and vacuum filters to produce high-grade gypsum, sale of the byproduct is obviously the most desirable choice. Other options include gypsum production with landfill of the byproduct, or no forced oxidation with disposal of the byproduct slurry in retention ponds. Some utilities own enough land that the retention ponds can actually be sized to serve as evaporation ponds so that liquid discharges are not an issue. Disposal requirements will undoubtedly become more important in the future due to water conservation issues. Some plant personnel are facing regulations that require minimized or zero liquid discharges. No longer can a scrubber be planned without giving thought to liquid discharge issues.

One potential drawback of wet-limestone systems is that they can emit very fine particulates and aerosols. Health and regulatory officials are becoming increasingly concerned about the effects of fine particulates on human well being, and regulations are becoming stricter with regard to particulate discharge.

Other drawbacks of wet-limestone scrubbing are large upfront capital costs and large equipment size, and substantial predictive and corrective maintenance requirements. Substitution of hydrated lime as the reactant reduces equipment size and costs but increases reagent costs and material handling issues. Thus, limestone is more popular as a reagent for wet systems. As the next section outlines, at plants using low-sulfur coal semi-dry, wet-lime spray dry scrubbing is popular.

**Spray-Drying Technology**

In a spray dry scrubber, slaked lime \([\text{Ca(OH)}_2]\) is injected into the flue gas at a point downstream of the economizer and air heater. Figure 2 outlines a spray-drying scrubber arrangement. As the particles intermingle with the gas, \(\text{SO}_2\) reacts with the lime to produce calcium sulfate and sulfate byproducts. These are similar to the byproducts from wet-limestone scrubbers, but the big difference is that the warm temperature of the flue gas dries the particles so that they can be collected in a downstream baghouse. Some particles fall out in the reaction vessel, as well. It is common to recycle a portion of the reaction products to the scrubber inlet to improve reagent utilization.

The spray-drying process offers several
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Advantages over wet processes. First, the reaction products can be blended with fly ash and disposed with conventional ash-handling equipment. This eliminates the need for expensive and maintenance-intensive dewatering and sludge disposal equipment. Also, the drying process does not expose the scrubber materials to chlorides as in wet systems. This relaxes requirements for materials of construction, which in turn lowers capital and erection costs. Operation of spray dryers is simpler than wet systems, and the use of a baghouse minimizes particulate emissions.

Two primary drawbacks with spray-drying systems are reagent cost and waste disposal. Lime is much more expensive than limestone. With regard to reagent disposal, the product cannot be converted to wallboard-grade gypsum. Blending the product with fly ash reduces the value of the ash. Pure ash is often suitable as a supplement to construction materials, such as bed fill for road construction. Inclusion of scrubber byproducts can negate this advantage.

Multi-Pollutant Control Technologies
This article focused on flue gas desulfurization only. However, some companies have devoted much time and effort to developing multi-pollutant control technologies. The Powerspan Corporation has been testing a process (ECO®) that removes SO₂, NOₓ, mercury and fine particulates in a three-step process. Check www.powerspan.com for more details. The BOC Group has been testing a retrofit technology (LoTOx®) that enhances NOₓ and possibly mercury removal in existing wet-limestone scrubbers. The Web site for more information is www.boc.com.

Implications of Reliable Scrubbing Technology
A recent column in an energy magazine that discussed potential air pollution control issues also offered an interesting prognostication about future coal-fired power production. The comment was, "As the second, more stringent phase of air-emissions reductions is implemented, the coal-producing regions likely to experience the biggest boost are the currently depressed Midwest regions that produce high-sulfur coal." A critical factor regarding this issue involves flue gas scrubbing. In some measure, new coal-fired power construction will be dictated by an economic/regional issue, where plant owners and managers must decide between use of local coal, which would benefit the regional economy but at potentially higher mining and pollution control costs versus Powder River Basin (PRB) coal with cheaper mining costs but lower quality and higher transportation costs.

Another benefit that scrubbing may offer revolves around the extremely contentious issue of continued power production using coal versus the large carbon dioxide emissions produced by...
coal combustion. Coal-fired boilers can be defined by many different categories, but one of the most basic is sub-critical (steam pressures less than 3,208 pounds per square inch absolute (psia)) and supercritical (steam pressures greater than 3,208 psia). The top efficiency of a sub-critical unit (fuel input versus electrical output) is about 35 percent. The most modern supercritical designs are closing in on 45 percent efficiency. Not only does this economic advantage make supercritical technology attractive, but a long-term benefit of supercritical power production is lower carbon dioxide emissions than those from an equivalent sub-critical counterpart. Steam temperatures have been limited to 1,100 degrees Fahrenheit or so because of metalurgy issues, but researchers continue to investigate alloys for higher temperature duty. According to a recent report:

In the U.S., a new DOE [U.S. Department of Energy] program has been initiated for materials development, with a consortium of funding agencies and contractors including DOE, EPRI [Electric Power Research Institute], Ohio Coal Development Office, Energy Industries of Ohio and the U.S. boiler manufacturers (Alstom Power, Babcock Power, Babcock & Wilcox, Foster-Wheeler). This work could potentially take the steam operating temperatures to above 750 degrees Celsius [1,382 degrees Fahrenheit].

If this breakthrough occurs, it could mean supercritical efficiencies of 50 percent or greater. A supercritical boiler with a back-end FGD system could replace an old, sub-critical unit with substantially lower CO2 emissions. The majority of coal-fired power plants constructed in Europe, Russia and Japan over the last two decades have been supercritical units, and this trend appears to be gaining interest in the United States. In fact, some states, and most notably Illinois, are actively seeking and offering financial incentives for projects of this type.

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