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Flue-gas desulfurization

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Flue gas desulfurization (FGD) is a technology used to remove sulfur dioxide (SO₂) from the exhaust flue gases of fossil fuel power plants. Fossil fuel power plants burn coal or oil to produce steam for steam turbines, which in turn drive electricity generators.

Sulfur dioxide is one of the elements forming acid rain. Tall flue gas stacks disperse emissions by diluting the pollutants in ambient air and transporting them to other regions.

As stringent environmental regulations regarding SO₂ emissions have been enacted in many countries, SO₂ is now being removed from flue gases by a variety of methods. The below is among the common methods used:

- Wet scrubbing using a slurry of alkaline sorbent, usually limestone or lime, or seawater to scrub gases;
- Spray-dry scrubbing using similar sorbent slurries;
- Wet sulfuric acid process recovering sulfur in the form of commercial quality sulfuric acid;
- SNOX Flue gas desulfurization removes sulfur dioxide, nitrogen oxides and particulates from flue gases;
- Dry sorbent injection systems.

For a typical coal-fired power station, FGD will remove 95 percent or more of the SO₂ in the flue gases.



Before flue gas desulfurization was installed, the emissions from this power plant in New Mexico contained a significant amount of sulfur dioxide.

Contents

- 1 History
- 2 Sulfuric acid mist formation
- 3 FGD chemistry
 - 3.1 Basic principles
 - 3.2 Scrubbing with a basic solid or solution
 - 3.2.1 Types of wet scrubbers used in FGD
 - 3.2.1.1 Mobile-bed scrubbers
 - 3.2.1.2 Venturi-rod scrubbers
 - 3.2.1.3 Plate towers
 - 3.2.1.4 Packed bed scrubbers
 - 3.2.1.5 Spray towers
 - 3.2.2 Scrubbing reagent
 - 3.3 Scrubbing with sodium sulfite solution
 - 3.4 Gas phase oxidation followed by reaction with ammonia

- 4 Facts and statistics
- 5 Alternative methods of reducing sulfur dioxide emissions
- 6 See also
- 7 References
- 8 External links

History

Methods of removing sulfur dioxide from boiler and furnace exhaust gases have been studied for over 150 years. Early ideas for flue gas desulfurization were established in England around 1850.

With the construction of large scale power plants in England in the 1920s, the problems associated with large volumes of SO₂ from a single site began to concern the public. The SO₂ emissions problem did not receive much attention until 1929, when the House of Lords upheld the claim of a landowner against the Barton Electricity Works of the Manchester Corporation for damages to his land resulting from SO₂ emissions. Shortly thereafter, a press campaign was launched against the erection of power plants within the confines of London. This outcry led to the imposition of SO₂ controls on all such power plants.^[1]

The first major FGD unit at a utility was installed in 1931 at Battersea Station, owned by London Power Company. In 1935, an FGD system similar to that installed at Battersea went into service at Swansea Power Station. The third major FGD system was installed in 1938 at Fulham Power Station. These three early large-scale FGD installations were abandoned during World War II. Large-scale FGD units did not reappear at utilities until the 1970s, where most of the installations occurred in the United States and Japan.^[1]

As of June 1973, there were 42 FGD units in operation, 36 in Japan and 6 in the United States, ranging in capacity from 5 MW to 250 MW.^[2] As of around 1999 and 2000, FGD units were being used in 27 countries, and there were 678 FGD units operating at a total power plant capacity of about 229 gigawatts. About 45% of the FGD capacity was in the U.S., 24% in Germany, 11% in Japan, and 20% in various other countries. Approximately 79% of the units, representing about 199 gigawatts of capacity, were using lime or limestone wet scrubbing. About 18% (or 25 gigawatts) utilized spray-dry scrubbers or sorbent injection systems.^{[3][4][5]}

Sulfuric acid mist formation

Fossil fuels such as coal and oil contain a significant amount of sulfur. When fossil fuels are burned, about 95 percent or more of the sulfur is generally converted to sulfur dioxide (SO₂). Such conversion happens under normal conditions of temperature and of oxygen present in the flue gas. However, there are circumstances under which such reaction may not occur.

For example, when the flue gas has too much oxygen and the SO₂ is further oxidized to sulfur trioxide (SO₃). Actually, too much oxygen is only one of the ways that SO₃ is formed. Gas temperature is also an important factor. At about 800 °C, formation of SO₃ is favored. Another way that SO₃ can be formed is through catalysis by metals in the fuel. Such reaction is particularly true for heavy fuel oil, where a significant amount of vanadium is present. In whatever way SO₃ is formed, it does not behave like SO₂ in that it forms a liquid aerosol known as sulfuric acid (H₂SO₄) mist that is very difficult to remove.

Generally, about 1% of the sulfur dioxide will be converted to SO_3 . Sulfuric acid mist is often the cause of the blue haze that often appears as the flue gas plume dissipates. Increasingly, this problem is being addressed by the use of wet electrostatic precipitators.

FGD chemistry

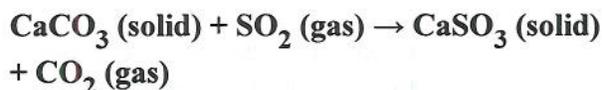
Basic principles

Most FGD systems employ two stages: one for fly ash removal and the other for SO_2 removal. Attempts have been made to remove both the fly ash and SO_2 in one scrubbing vessel. However, these systems experienced severe maintenance problems and low removal efficiency. In wet scrubbing systems, the flue gas normally passes first through a fly ash removal device, either an electrostatic precipitator or a wet scrubber, and then into the SO_2 absorber. However, in dry injection or spray drying operations, the SO_2 is first reacted with the sorbent and then the flue gas passes through a particulate control device.

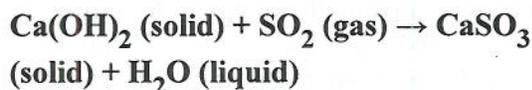
Another important design consideration associated with wet FGD systems is that the flue gas exiting the absorber is saturated with water and still contains some SO_2 . These gases are highly corrosive to any downstream equipment such as fans, ducts, and stacks. Two methods that can minimize corrosion are: (1) reheating the gases to above their dew point, or (2) choosing construction materials and design conditions that allow equipment to withstand the corrosive conditions. Both alternatives are expensive, and engineers designing the system determine which method to use on a site-by-site basis.

Scrubbing with a basic solid or solution

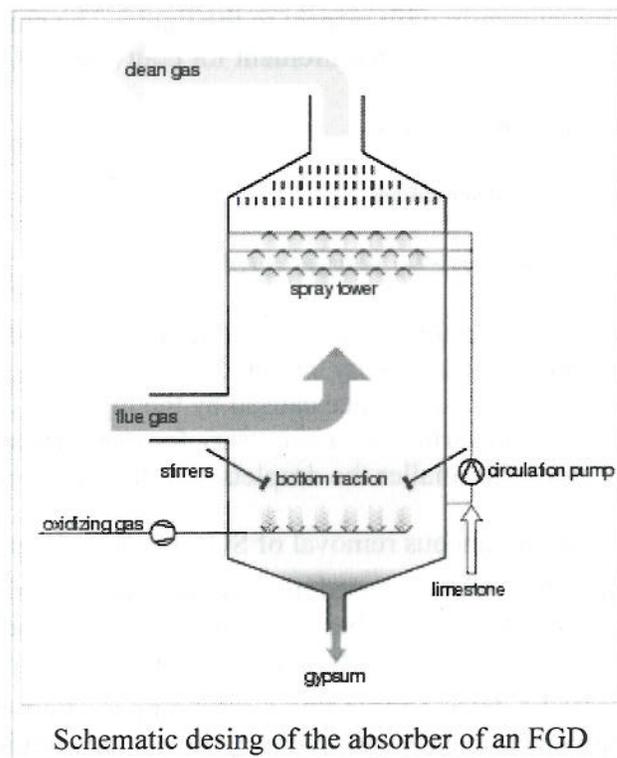
SO_2 is an acid gas and thus the typical sorbent slurries or other materials used to remove the SO_2 from the flue gases are alkaline. The reaction taking place in wet scrubbing using a CaCO_3 (limestone) slurry produces CaSO_3 (calcium sulfite) and can be expressed as:

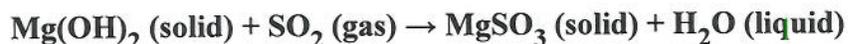


When wet scrubbing with a $\text{Ca}(\text{OH})_2$ (lime) slurry, the reaction also produces CaSO_3 (calcium sulfite) and can be expressed as:

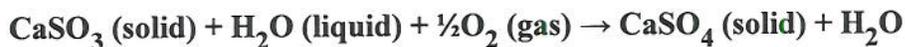


When wet scrubbing with a $\text{Mg}(\text{OH})_2$ (magnesium hydroxide) slurry, the reaction produces MgSO_3 (magnesium sulfite) and can be expressed as:

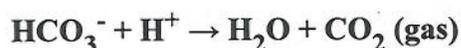
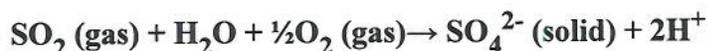




To partially offset the cost of the FGD installation, in some designs, the CaSO_3 (calcium sulfite) is further oxidized to produce marketable $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum). This technique is also known as **forced oxidation**:



A natural alkaline usable to absorb SO_2 is seawater. The SO_2 is absorbed in the water, and when oxygen is added reacts to form sulfate ions SO_4^{2-} and free H^+ . The surplus of H^+ is offset by the carbonates in seawater pushing the carbonate equilibrium to release CO_2 gas:



Types of wet scrubbers used in FGD

To promote maximum gas-liquid surface area and residence time, a number of wet scrubber designs have been used, including spray towers, venturis, plate towers, and mobile packed beds. Because of scale buildup, plugging, or erosion, which affect FGD dependability and absorber efficiency, the trend is to use simple scrubbers such as spray towers instead of more complicated ones. The configuration of the tower may be vertical or horizontal, and flue gas can flow cocurrently, countercurrently, or crosscurrently with respect to the liquid. The chief drawback of spray towers is that they require a higher liquid-to-gas ratio requirement for equivalent SO_2 removal than other absorber designs.

Mobile-bed scrubbers

Venturi-rod scrubbers

Main article: venturi scrubber

A venturi scrubber is a converging/diverging section of duct. The converging section accelerates the gas stream to high velocity. When the liquid stream is injected at the throat, which is the point of maximum velocity, the turbulence caused by the high gas velocity atomizes the liquid into small droplets, which creates the surface area necessary for mass transfer to take place. The higher the pressure drop in the venturi, the smaller the droplets and the higher the surface area. The penalty is in power consumption.

For simultaneous removal of SO_2 and fly ash, venturi scrubbers can be used. In fact, many of the industrial sodium-based throwaway systems are venturi scrubbers originally designed to remove particulate matter. These units were slightly modified to inject a sodium-based scrubbing liquor. Although removal of both particles and SO_2 in one vessel can be economic, the problems of high pressure drops and finding a scrubbing medium to remove heavy loadings of fly ash must be considered. However, in cases where the particle concentration is low, such as from oil-fired units, it can be more effective to remove particulate and SO_2 simultaneously.

Plate towers

Packed bed scrubbers

A packed scrubber consists of a tower with packing material inside. This packing material can be in the shape of saddles, rings, or some highly specialized shapes designed to maximize contact area between the dirty gas and liquid. Packed towers typically operate at much lower pressure drops than venturi scrubbers and are therefore cheaper to operate. They also typically offer higher SO₂ removal efficiency. The drawback is that they have a greater tendency to plug up if particles are present in excess in the exhaust air stream.

Spray towers

Main article: spray tower

A spray tower is the simplest type of scrubber. It consists of a tower with spray nozzles, which generate the droplets for surface contact. Spray towers are typically used when circulating a slurry (see below). The high speed of a venturi would cause erosion problems, while a packed tower would plug up if it tried to circulate a slurry.

Counter-current packed towers are infrequently used because they have a tendency to become plugged by collected particles or to scale when lime or limestone scrubbing slurries are used.

Scrubbing reagent

As explained above, alkaline sorbents are used for scrubbing flue gases to remove SO₂. Depending on the application, the two most important are lime and sodium hydroxide (also known as caustic soda). Lime is typically used on large coal or oil fired boilers as found in power plants, as it is very much less expensive than caustic soda. The problem is that it results in a slurry being circulated through the scrubber instead of a solution. This makes it harder on the equipment. A spray tower is typically used for this application. The use of lime results in a slurry of calcium sulfite (CaSO₃) that must be disposed of. Fortunately, calcium sulfite can be oxidized to produce by-product gypsum (CaSO₄ · 2H₂O) which is marketable for use in the building products industry.

Caustic soda is limited to smaller combustion units because it is more expensive than lime, but it has the advantage that it forms a solution rather than a slurry. This makes it easier to operate. It produces a solution of sodium sulfite/bisulfite (depending on the pH), or sodium sulfate that must be disposed of. This is not a problem in a kraft pulp mill for example, where this can be a source of makeup chemicals to the recovery cycle.

Scrubbing with sodium sulfite solution

It is possible to scrub sulfur dioxide by using a cold solution of sodium sulfite, this forms a sodium hydrogen sulfite solution. By heating this solution it is possible to reverse the reaction to form sulfur dioxide and the sodium sulfite solution.

In some ways this can be thought of as being similar to the reversible liquid-liquid extraction of an inert gas such as xenon or radon (or some other solute which does not undergo a chemical change during the extraction) from water to another phase. While a chemical change does occur during the extraction of the sulfur dioxide from the gas mixture, it is the case that the extraction equilibrium is shifted by

changing the temperature rather than by the use of a chemical reagent.

Gas phase oxidation followed by reaction with ammonia

A new, emerging flue gas desulfurization technology has been described by the IAEA.^[6] It is a radiation technology where an intense beam of electrons is fired into the flue gas at the same time as ammonia is added to the gas. The Chendu power plant in China started up such a flue gas desulfurization unit on a 100 MW scale in 1998. The Pomorzany power plant in Poland also started up a similar sized unit in 2003 and that plant removes both sulfur and nitrogen oxides. Both plants are reported to be operating successfully.^{[7][8]} However, the accelerator design principles and manufacturing quality need further improvement for continuous operation in industrial conditions.^[9]

No radioactivity is required or created in the process. The electron beam is generated by a device similar to the electron gun in a TV set. This device is called an accelerator. This is an example of a radiation chemistry process^[8] where the physical effects of radiation are used to process a substance.

The action of the electron beam is to promote the oxidation of sulfur dioxide to sulfur(VI) compounds. The ammonia reacts with the sulfur compounds thus formed to produce ammonium sulfate which can be used as a fertilizer according to the IAEA. In addition, it can be used to lower the nitrogen oxide content of the flue gas. This method has attained industrial plant scale.^{[7][10][11]}

Facts and statistics

The information in this section was obtained from a US EPA published fact sheet.^[12]

Flue gas desulfurization scrubbers have been applied to combustion units firing coal and oil that range in size from 5 MW to 1500 MW. Scottish Power are spending £400 million installing FGD at Longannet power station which has a capacity of over 2 GW. Dry scrubbers and spray scrubbers have generally been applied to units smaller than 300 MW.

Approximately 85% of the flue gas desulfurization units installed in the US are wet scrubbers, 12% are spray dry systems and 3% are dry injection systems.

The highest SO₂ removal efficiencies (greater than 90%) are achieved by wet scrubbers and the lowest (less than 80%) by dry scrubbers. However, the newer designs for dry scrubbers are capable of achieving efficiencies in the order of 90%.

In spray drying and dry injection systems, the flue gas must first be cooled to about 10-20 °C above adiabatic saturation to avoid wet solids deposition on downstream equipment and plugging of baghouses.

The capital, operating and maintenance costs per short ton of SO₂ removed (in 2001 US dollars) are:

- For wet scrubbers larger than 400 MW, the cost is \$200 to \$500 per ton
- For wet scrubbers smaller than 400 MW, the cost is \$500 to \$5,000 per ton
- For spray dry scrubbers larger than 200 MW, the cost is \$150 to \$300 per ton
- For spray dry scrubbers smaller than 200 MW, the cost is \$500 to \$4,000 per ton

Alternative methods of reducing sulfur dioxide emissions

An alternative to removing sulfur from the flue gases after burning is to remove the sulfur from the fuel before or during combustion. Hydrodesulfurization of fuel has been used for treating fuel oils before use. Fluidized bed combustion adds lime to the fuel during combustion. The lime reacts with the SO₂ to form sulfates which become part of the ash.

See also

- Incineration
- Scrubber
- Flue gas emissions
- Flue gas stacks

References

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- [^] Rubin, E.S., Yeh, S., Hounsell, D.A., and Taylor, M.R., *Experience curves for power plant emission control technologies*, Int. J. Energy Technology and Policy, Vol. 2, Nos. 1/2, 2004
- [^] Beychok, Milton R., *Comparative economics of advanced regenerable flue gas desulfurization processes*, EPRI CS-1381, Electric Power Research Institute, March 1980
- [^] IAEA Factsheet about pilot plant in Poland.
- [^] ^{*a b*} *Electron beam application in gas waste treatment in China* by Haifeng Wu, INET Tsinghua University, Beijing, China.
- [^] ^{*a b*} Section of IAEA 2003 Annual Report
- [^] *Application of ionizing radiation to environmental protection* by A.G. Chmielewski, Warsaw University of Technology, Poland.
- [^] Chubu Electric Power Company pilot plant in Japan.
- [^] *Industrial Plant for Flue Gas Treatment with High Power Electron Accelerator* by A.G. Chmielewski, Warsaw University of Technology, Poland.
- [^] Air Pollution Control Fact Sheet US EPA date coded 2003, accessed June 24, 2006

External links

- Schematic of desulfurization plant
- 5000 MW FGD Plant (includes a detailed process flow diagram)
- New innovative design using Gas Suspension Absorption
- Flue Gas Desulfurization Fact Sheet
- Description of Lentjes seawater process
- Alstom presentation to UN-ECE on air pollution control (includes process flow diagram for dry, wet and seawater FGD)
- Institute of Clean Air Companies - national trade association representing emissions control manufacturers

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