Flue Gas Desulfurization

Flue gas desulfurization is commonly known as FGD and is the technology used for removing sulfur dioxide (SO_2) from the exhaust flue gases in power plants that burn coal or oil to produce steam for the steam turbines that drive their electricity generators.

Sulfur dioxide is responsible for acid rain formation. Tall flue gas stacks disperse the emissions by diluting the pollutants in ambient air and transporting them to other regions. As a result of stringent environmental protection regulations regarding SO_2 emissions that have been enacted in a great many countries, SO_2 is now being removed from flue gases by a variety of methods:

- Wet scrubbing using slurry of sorbent, usually limestone or lime, to scrub the gases.
- Spray-dry scrubbing using similar sorbent slurries.
- Dry sorbent injection systems.

For a typical coal-fired power station, FGD will remove 95 percent or more of the SO_2 in the flue gases. Methods for removing sulfur dioxide from boiler and furnace exhaust gases have been studied for over 150 years.

Sulfuric acid mist formation

Fossil fuels such as coal and oil contain significant amounts of sulfur. When burned, about 95 percent or more of the sulfur is generally converted to sulfur dioxide (SO_2). This happens under normal conditions of temperature and of oxygen present in the flue gas. However, there are circumstances under which this may not be the case.

For example, when the flue gas has too much oxygen and the SO_2 is further oxidized to sulfur trioxide (SO_3). Actually, too much oxygen is only one of the ways that SO_3 is formed. Gas temperature is also an important factor. At about 800 °C, formation of SO_3 is favored. Another way that SO_3 can be formed is through catalysis by metals in the fuel. This is particularly true for heavy fuel oil, where significant amounts of vanadium are present. In whatever way that SO_3 is formed, it does not behave like SO_2 in that it forms a liquid aerosol known as sulfuric acid (H_2SO_4) 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.

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: $CaCO_3$ (solid) + SO_2 (gas) → $CaSO_3$ (solid) + CO_2 (gas)

When wet scrubbing with a $Ca(OH)_2$ (lime) slurry, the reaction also produces $CaSO_3$ (calcium sulfite) and can be expressed as: $Ca(OH)_2$ (solid) + SO_2 (gas) → $CaSO_3$ (solid) + H_2O (liquid)

When wet scrubbing with a $Mg(OH)_2$ (magnesium hydroxide) slurry, the reaction produces $MgSO_3$ (magnesium sulfite) and can be expressed as: $Mg(OH)_2$ (solid) + SO_2 (gas) → $MgSO_3$ (solid) + H_2O (liquid)

Some FGD systems go a step further and oxidize the $CaSO_3$ (calcium sulfite) to produce marketable $CaSO_4 \cdot 2H_2O$ (gypsum): $CaSO_3$ (solid) + ½O_2 (gas) + $2H_2O$ (liquid) → $CaSO_4 \cdot 2H_2O$ (solid)

Types of wet scrubbers used in FGD

To promote maximum gas-liquid surface area and contact time, a number of wet scrubber designs have been used. Common ones are:

Mobile-bed scrubbers - Venturi-rod scrubbers

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.

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 SO_2 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

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 slurry. The high speed of a venturi would cause erosion problems, while a packed tower would plug up if it tried to circulate slurry. Countercurrent 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 SO_2. 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 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 ($CaSO_3$) that must be disposed of. Fortunately, calcium sulfite can be oxidized to produce by-product gypsum ($CaSO_4 \cdot 2H_2O$) 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 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.

Chemistry

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. However, the accelerator design principles and manufacturing quality need further improvement for continuous operation in industrial conditions.

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 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.

Facts and statistics

The information in this section was obtained from a US EPA published fact sheet. 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 is 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 SO_2 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 bag houses.

The capital, operating and maintenance costs per short ton of SO_2 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. Hydrodesulphurization 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 SO_2 to form sulfates which become part of the ash.

Sources: Wikipedia.org