TECHNOLOGIES OF GASEOUS POLLUTANT EMISSION CONTROL

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Summary

Any gas that is present in the air in a concentration that causes some deleterious effect is considered a gaseous pollutant. However, there are several substances that, by virtue of their massive rates of emission and harmful effects, are considered the most significant pollutants. Four major primary gaseous air pollutants (so called because they are exited from the exhaust pipe into the atmosphere) include sulfur oxides (SOx), nitrogen oxides (NOx), volatile organic compounds (VOCs), and carbon monoxide (CO). Basically these four pollutants are emitted during fossil fuel combustion both from stationary and mobile sources, but each can be emitted from non-combustion processes as well such as SOx from smelting furnaces, escape of organic vapors from oil tanks, and NOx from agricultural operations.

Due to the emissions of the primary pollutant, the secondary pollutants are possibly formed by chemical reaction in the atmosphere. Of major concerns are ozone (or more generally photochemical oxidants) and acidic deposition (as usually called acid rain). The former are formed in the low atmosphere by chemical reactions involving sunlight, hydrocarbons and nitrogen oxides, while the latter are originated from the reactions of acid precursors such as SOx and NOx with water and catalytic metals in airborne particulate. By and large our focus in this chapter is on the major primary pollutants, given the fact that the control of the primary pollutants is also the main cause to reduce the pollution level of the secondary pollutants.

There are a variety of approaches to remove gaseous pollutants from effluent streams: absorption, adsorption, condensation, catalytic conversion, incineration and a few new technologies. For each technology mentioned, the general principle was introduced first, and then the popular design of equipment was summarized. The importance was also attached to the advantages and disadvantages of main technologies, and their capability in specific applications. Special attention was paid to the introduction of the applications and on-going researches in the gaseous purification, such as the wet FGD, SCR and so on.

1. Absorption

1.1. General Principle

Absorption is an operation involving selective mass transfer of a soluble vapor component to a solvent liquid in a device that promotes intimate contact between the gas and the liquid. The separation principle involved is the preferential solubility of a gaseous component in the liquid. So-called physical absorption takes use of the remarkable solubility of a gaseous pollutant in the solvent, and involves only the dissolution process. For example, water is, by itself, quite efficient for removing soluble acidic gaseous such as HCl, HF and the soluble basic gas NH_3.

Gases of very little solubility such as SOx, H_2S and NOx, can be absorbed readily in an alkaline solution such as NaOH. Thus, when water is used as the solvent, it may contain added species, such as acids, alkaline, oxidants, or reducing agents to react with the gas being absorbed and enhance its solubility.

The equilibrium vapor pressure can be decreased almost zero by adding a chemical reactant to the absorbing liquid. This in effect ties up or chemically changes the solute gas, since the driving force for absorption is the difference between the partial pressure of the soluble gas in the gas mixture and its equilibrium vapor pressure just above the surface of the liquid. Due to chemical reactions involved, such an operation is called chemical absorption.

Both in the physical and chemical absorption, the mechanism by which the species is removed from the gas consists of three steps that occur in series: (1) diffusion of the pollutant molecules through the gas to the surface of absorbing liquid, (2) dissolution into the liquid at the interface, and (3) diffusion of the dissolved species from the interface into the bulk of the liquid.

In the chemical absorption, the dissolved species reacts with the liquid species during its diffusion and/or residence in the bulk. Figure 1 gives the scheme of the absorption process.

P_A: Partial pressure of pollutant A in the gas

P_{Ai}: Partial pressure of A at the interface

C_A: Concentration of dissolved A at the interface
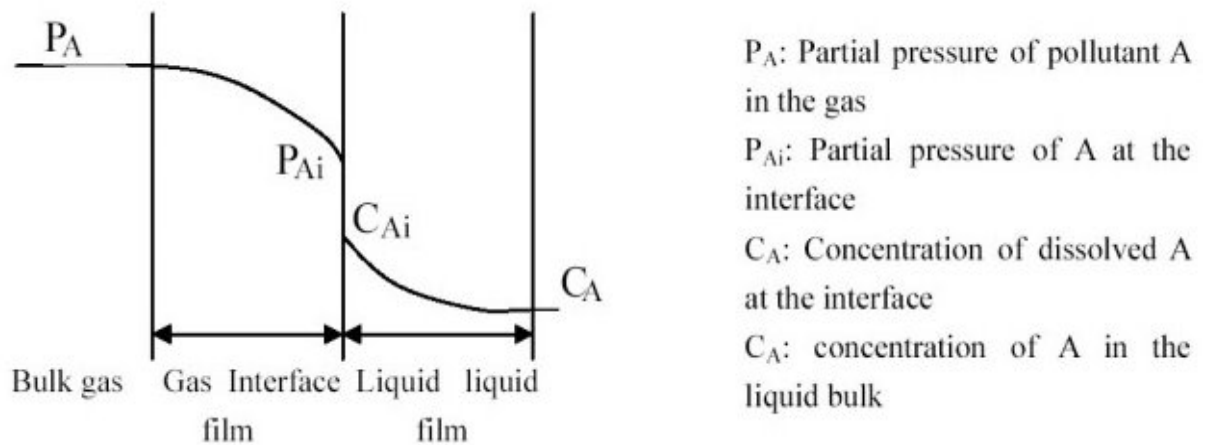
C_A: concentration of A in the liquid bulk

Figure 1: The scheme of absorption process: two film model

The frequently encountered examples of the application of gas absorption in air pollution control include:

- Control of sulfur dioxide and nitrogen oxides from combustion sources
- Removal and recovery of ammonia in fertilizer manufacture
- Removal of hydrogen fluoride from glass furnace exhaust
- Control of odorous gases from rendering plants
- Recovery of water-soluble solvents such as acetone and methyl alcohol.

1.2. Gas Absorption Equipment

To achieve the high performance of absorption and low cost of both capital and operation, the effective absorption equipment tends to meet the following criteria.

- large contact surface between gas and liquid;
- enough contact time between two phases;
- highly turbulent mixing of gas and liquid;
- steady operation and appropriate flexibility;
- low pressure drop;
- simple device easy for maintenance;
- Anti-corrosion and anti-congestion while necessary.

There are two common types of towers, plate and packed, make effective pollution control devices. They utilize simple mechanical methods of achieving good contacting between the gas and liquid phases to provide favorable overall mass transfer. The three general types of towers are packed, bubble cap and perforated-plate towers.

1.2.1. Packed Towers

The typical schematics of packed towers are displayed in Figure 2. Within the tower, a pack material is filled, supported on the plate. The liquid enters at the top of the tower and distributed by the distributor such as a spray system, overflow weirs, or a perforated distribution plate. The liquid is scattered to form the film on the surface of packing and flow downward through the voids between the packings.

The gas flows upward through the packing. The wetting surfaces of packing thus compose of the contact sites of the gas and liquid. There are many types of packings, some of which the commercially used are Raschig rings, Berl saddles, Pall rings, Intalox saddles, and cannon packings. In general, it's required for the packings to have large surface per unit volume, and low pressure drop of gas through it.

The packing in the tower can be installed as an entire column. However, when the liquid flows through the packing, it tends to flux onto the tower wall, and makes the packing in the center not fully wetted. To overcome such a wall effect, sometimes it's necessary to add intermediate packing support plates to divide the packing into several layers, as displayed in Figure 2.

Usually, the ratio of tower diameter to the packing size is required to be larger than 8 to avoid the wall effect. When the multi layers of packing are installed, each layer should keep below 3-5 meters high. Or based on the recommended factors for specific packing types, for example, the packing height is suggested to be 3 times as much as the tower diameter for Raschig ring, and 5-10 times of the tower diameter for Pall rings and saddles.
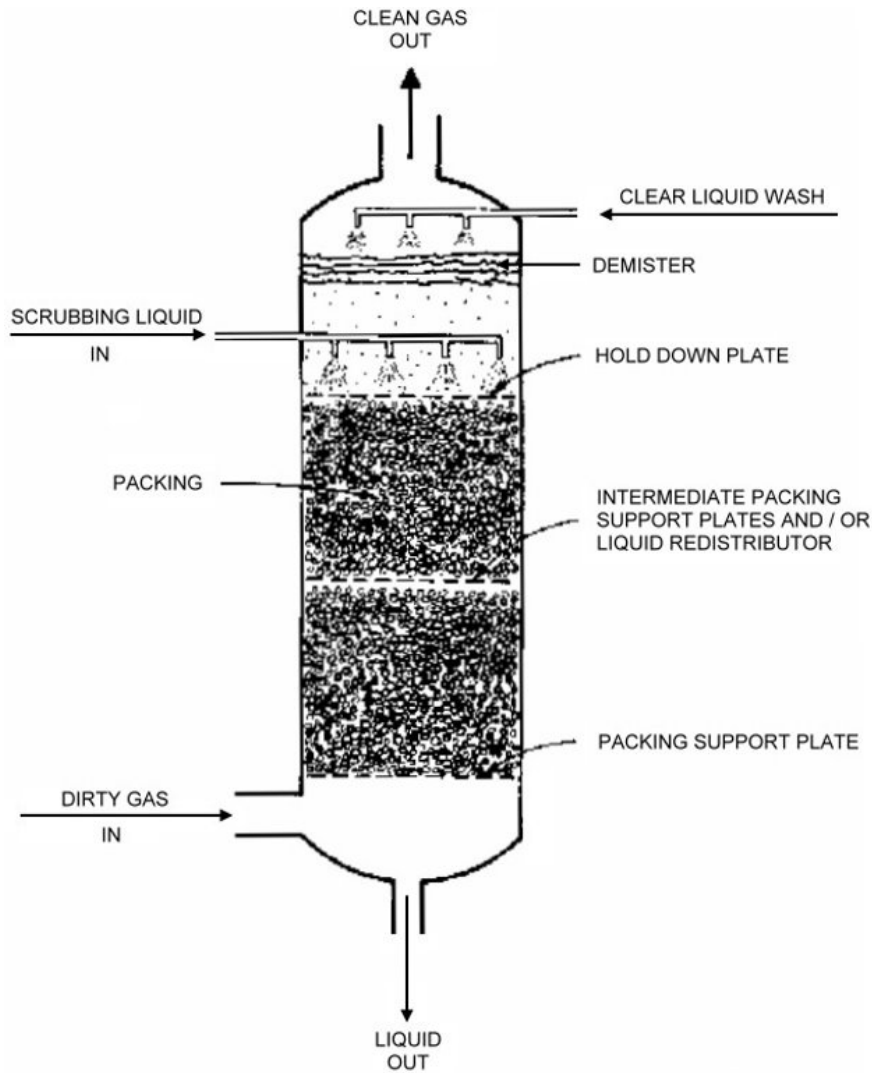
Figure 2: Countercurrent packed tower absorber

In the commercial operation, usually the gas superficial velocity ranges between 0.3-1.5 m/s, and the liquid/gas flow ratio between 0.5-2.0 kg/kg except for the gas with low solubility. The structured and random packings are adopted to have a pressure loss from 0.15-0.60 kPa.

The advantages of packed tower lie in its simple structure, ease in manufacture by the corrosion resistant materials, low pressure drop, and fair performance to guarantee the gas-liquid contact. There are several disadvantages at the same time, such as the tendency of packings to clog while the gas for treatment contains the particulates, and the considerable loss of packings during the maintenance.

1.2.2. Plate Towers

Plate towers are essentially vertical cylinders in which the liquid and gas are contacted in stepwise fashion (stage operation) on plates or trays. The liquid enters at the top and flows downward via gravity. On the way, it flows across each plate and through a

downspout to the plate below. The gas passes upward through openings of one sort or another, the bubbles through the liquid to form a froth, disengages from the froth, and passes on to the next plate above.

In bubble cap towers, the gas enters each plate through the gas risers, and is forced into the bubble cap, out through the slots as bubbles, and into the surrounding liquid on the plate. Figure 3(a) shows the scheme of the column. The height of liquid on each plate depends on the height and design of the liquid overflows as well as on the liquid and gas flow rates. The gas pressure drop across each plate increases with liquid height on the plate and gas flow rates. The bubble cap plate design is the most flexible of plate designs for high and low gas and liquid rate. On the average, plates are usually spaced approximately 0.6 m apart.

The sieve plate towers are designed similar to bubble cap towers except instead of the risers and caps, the plates simply have holes (3mm-20 mm in diameter) in them. The sieve plate is made with or without the downcomer. With the downcomer, the liquid flows across the plate floor and over a weir if used, and then through the downcomer to the plate below. Figure 3(b) demonstrates the operation dynamically. These plates are not generally suitable for columns operating under variable load. Plate spacing in this case usually averages about 0.3 m. In sieves without the downcomer, at the same time the gas rises through the holes, the liquid head forces liquid countercurrent through these holes and onto the plate below. In general, sieve plates are used in systems where high capacity near-design rates are to be maintained.

1.3. Flue Gas Desulfurization by Absorption Cleaning

1.3.1. Wet Lime/Limestone FGD

The wet lime/limestone FGD is the most widely used to deal with flue gas SO_2 removal in the world, due to the cheap and well available sources of limestone. It shares over 80% of total FGD installations around the world.

In a conventional lime/limestone FGD process, the flue gas passes countercurrent to a scrubbing slurry stream containing water and limestone/lime particles. In the tower, the SO_2 dissolves in the slurry and reacts with limestone/lime, and produces solid $CaSO_3$. The overall reaction equations are:

$$CaCO_3 + SO_2 + 2H_2O \rightarrow CaSO_3 \times 2H_2O + CO_2 \uparrow$$

$$CaO + SO_2 + 2H_2O \rightarrow CaSO_3 \times 2H_2O$$
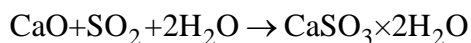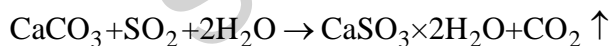
The product is almost oxidized to $CaSO_4$, partly by the excess oxygen in the flue gases in the tower, partly in the effluent hold tank usually sparged with air. The slurry is recirculated from the hold tank. A side stream is taken to a thickener and filter to remove solids. Figure 4 shows the scrubber vessel as a spray tower with multiple sprays and a mist eliminator.
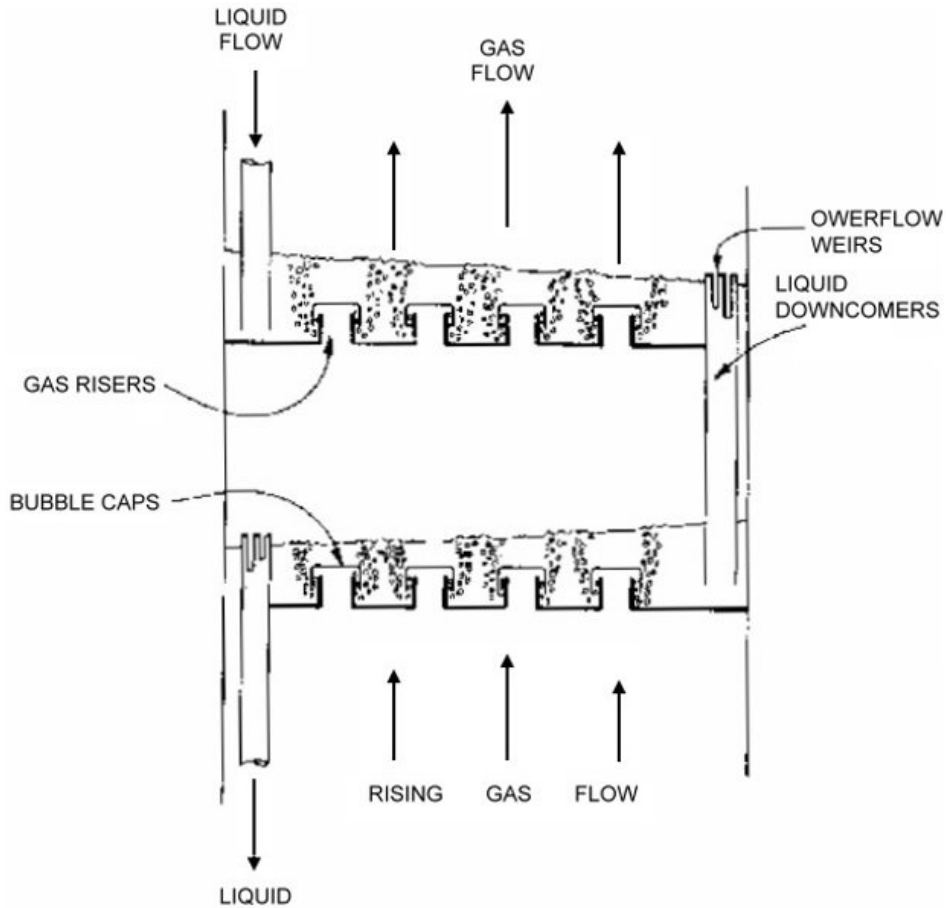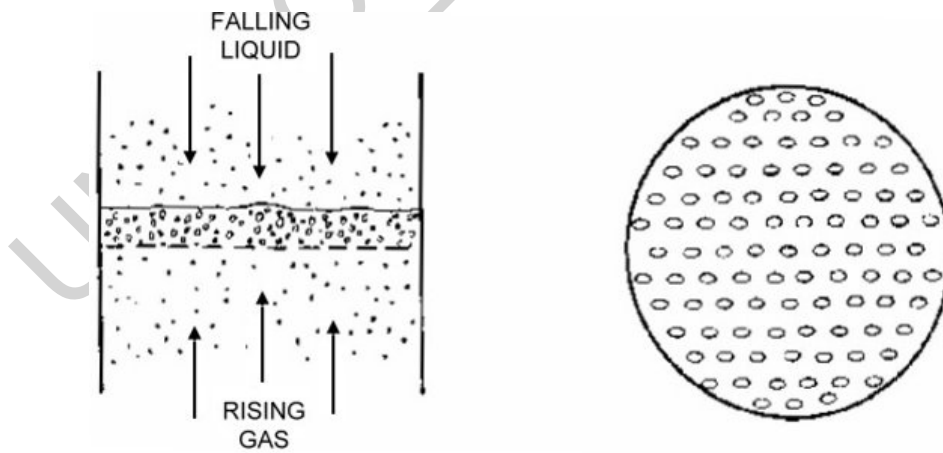
Figure 3a: Cross section of bubble cap tower

Figure 3b: Typical sectional views of a sieve-plate tower

The factors that affect the absorption efficiency of SO_2 are liquid/gas ratio, Ca/S ratio, velocity of the flue gas, pH of the slurry, and the concentration of SO_2 in the flue gas and so on. The principal problems encountered during the lime/limestone technology development include the corrosion, solids deposition, scaling and plugging, mist eliminator plugging, poor reagent utilization and poor solid-liquid separation. By now these problems have largely been solved, and these devices reasonably reliable and
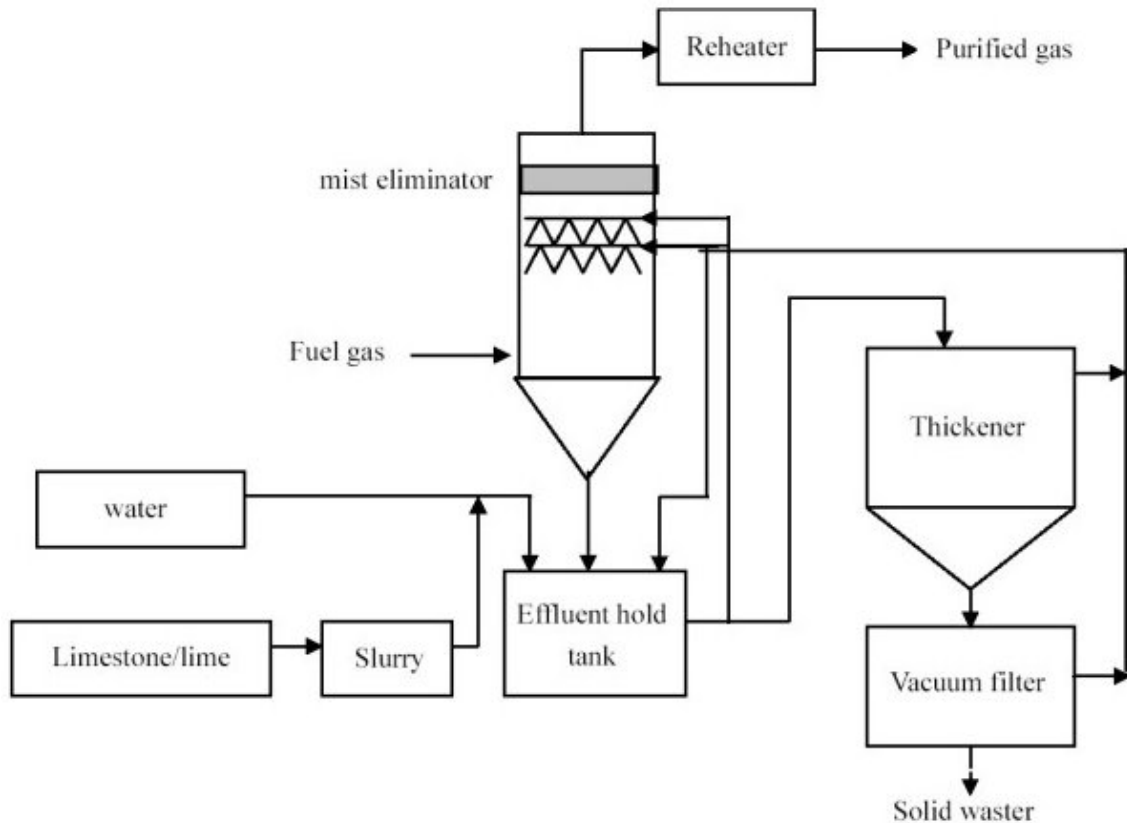
useful if designed and operated properly.

Figure 4: A flow chart of Lime/limestone FGD

1.3.2. Spray Drying Absorption

In the spray drying process, the reagent, typically $Ca(OH)_2$, is mixed with water into a slurry. The wet slurry is atomized as liquid droplets and injected into the tower. The freshly formed drops behave very much like the drops in a wet limestone/lime scrubber. The SO_2 dissolves in the water and reacts there with the dissolved $Ca(OH)_2$ to form $CaSO_3$ and $CaSO_4$.

While the liquid/gas ratio is low enough, the water in slurry evaporates from the drops before the drops reach the exit of the tower. The individual fine particles in them coalesce to form a single porous particle from each drop, and subsequently removed in a fabric filter or ESP downstream.

This is also called a wet-dry system because part of it is like a wet lime scrubber and part is like dry sorbent injection. At present, about 10% of FGD installations in power plants are the users of this technology.

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