

Before we leave this example, we should look back and see what we have wrought. Since the absorption tower neither creates nor destroys matter, the mass of NH_3 entering and leaving the column must be the same. If we assume isothermal, steady-state conditions (that is, gas and liquid rates in and out are equal), we can solve the mass-balance equation (Equation 6-32) for x_1 . After some calculations we find $x_1 = 0.08734$. This is 90,300 mg/L of NH_3 . This is a classic example of a multimedia problem. In solving an air pollution problem, we have created a serious water pollution problem. Catch-22!

Adsorption. This is a mass-transfer process in which the gas is bonded to a solid. It is a surface phenomenon. The gas (the *adsorbate*) penetrates into the pores of the solid (the *adsorbent*) but not into the lattice itself. The bond may be physical or chemical. Electrostatic forces hold the pollutant gas when physical bonding is significant. Chemical bonding is by reaction with the surface. Pressure vessels having a fixed bed are used to hold the adsorbent (Figure 6-26). Active carbon (activated charcoal), molecular sieves, silica gel, and activated alumina are the most common adsorbents. Active carbon is manufactured from nut shells (coconuts are great) or coal subjected to heat treatment in a reducing atmosphere. Molecular sieves are dehydrated zeolites (alkali-metal silicates). Sodium silicate is reacted with sulfuric acid to make silica gel. Activated alumina is a porous hydrated aluminum oxide. The common property of these adsorbents is a large "active" surface area per unit volume after treatment. They are very effective for hydrocarbon pollutants. In addition, they can capture H_2S

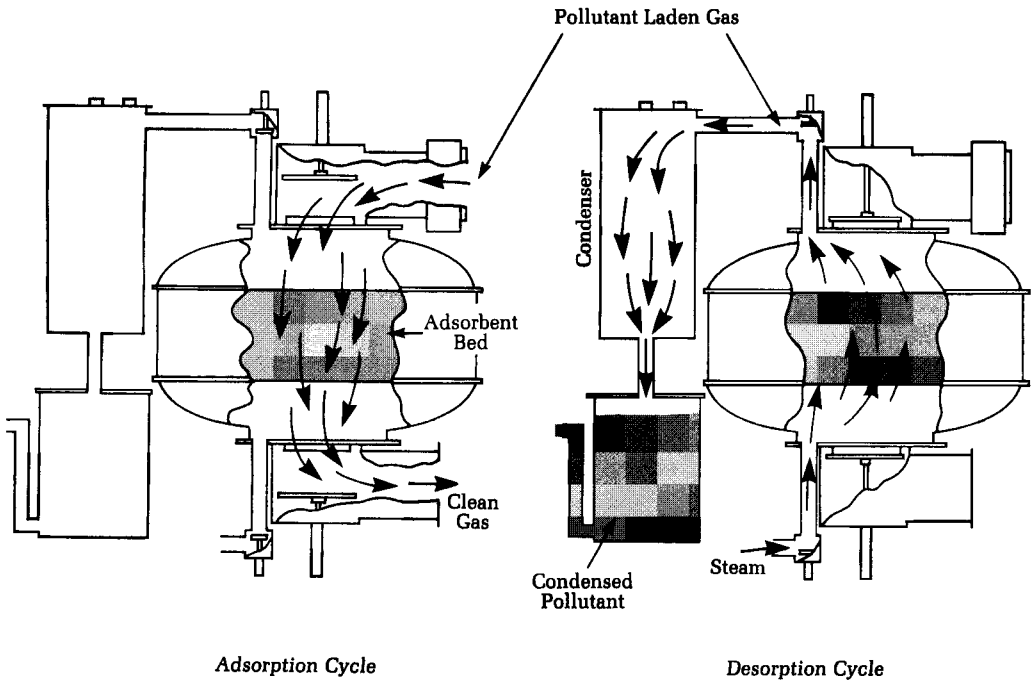


FIGURE 6-26
Adsorption system.

and SO₂. One special form of molecular sieve can also capture NO₂. With the exception of the active carbons, adsorbents have the drawback that they preferentially select water before any of the pollutants. Thus, water must be removed from the gas before it is treated. All of the adsorbents are subject to destruction at moderately high temperatures (150°C for active carbon, 600°C for molecular sieves, 400°C for silica gel, and 500°C for activated alumina). They are very inefficient at these high temperatures. In fact, their activity is regenerated at these temperatures!

The relation between the amount of pollutant adsorbed and the equilibrium pressure at constant temperature is called an *adsorption isotherm*. The equation that best describes this relation for gases is the one derived by Langmuir.⁵⁴

$$W = \frac{aC_g^*}{1 + bC_g^*} \quad (6-48)$$

where W = amount of gas per unit mass of adsorbent, kg/kg

a, b = constants determined by experiment

C_g^* = equilibrium concentration of gaseous pollutant, g/m³

In the analysis of experimental data, Equation 6-48 is rewritten as follows:

$$\frac{C_g^*}{W} = \frac{1}{a} + \frac{b}{a}C_g^* \quad (6-49)$$

In this arrangement, a plot of (C_g^*/W) versus C_g^* should yield a straight line with a slope of (b/a) and an intercept equal to ($1/a$).

In contrast to absorption towers where the collected pollutant is continuously removed by flowing liquid, the collected pollutant remains in the adsorption bed. Thus, while the bed has sufficient capacity, no pollutants are emitted. At some point in time, the bed will become saturated with pollutant. As saturation is approached, pollutant will begin to leak out of the bed. This is called *breakthrough*. When the bed capacity is exhausted, the influent and effluent concentration will be equal. A typical breakthrough curve is shown in Figure 6-27. In order to allow for continuous operation, two beds are provided (Figure 6-26). While one is collecting pollutant, the other is being regenerated. The concentrated gas released during regeneration is usually returned to the process as recovered product. The critical factor in the operation of the bed is the length of time it can operate before breakthrough occurs. The time to breakthrough may be calculated from the following:⁵⁵

$$t_B = \frac{Z_t - \delta}{v_f} \quad (6-50)$$

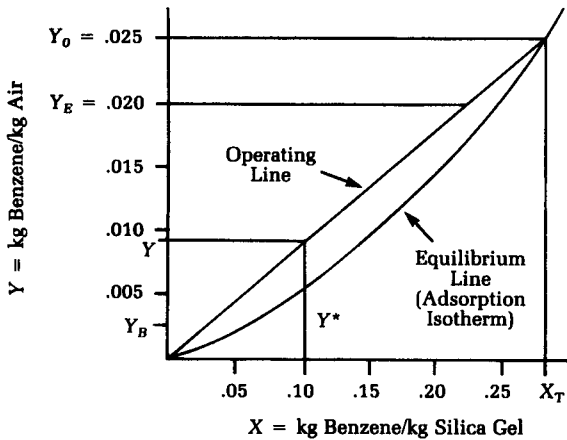
where Z_t = height of bed, m

δ = width of adsorption zone, m

v_f = velocity of adsorption zone as defined by Equation 6-52, m/s

⁵⁴A. J. Buonicore and L. Theodore, *Industrial Control Equipment for Gaseous Pollutants, Vol. I*, Cleveland: CRC Press, pp. 149–150, 1975.

⁵⁵M. Crawford, *Air Pollution Control Theory*, New York: McGraw-Hill, p. 516, 1976.


FIGURE 6-28

Equilibrium and operating lines for adsorption of benzene on silica gel. (Source: John H. Seinfeld, *Air Pollution*, New York: McGraw-Hill, 1975. Reprinted by permission.)

The velocity of the adsorption zone may be calculated from the properties of the system:

$$v_f = \frac{(Q_g)(1 + bC_g^*)}{a\rho_s\rho_g A_c} \quad (6-52)$$

where ρ_s, ρ_g = density of solid and gas, kg/m^3 (Note that ρ_s is the density of the adsorbent "as packed.")

A_c = cross-sectional area of bed, m^2

Example 6-8. Determine the breakthrough time for an adsorption bed that is 0.50 m thick and 10 m^2 in cross section. The operating parameters for the bed are as follows:

Gas flow rate = 1.3 kg/s of air

Gas temperature = 25°C

Gas pressure = 101.325 kPa

Bed density as packed = 420 kg/m^3

Inlet pollutant concentration = 0.0020 kg/m^3

Langmuir parameters: $a = 18$; $b = 124$

Width of adsorption zone = 0.03 m

Solution. Using Table A-3 in Appendix A and the gas temperature and pressure, we interpolate to find $\rho_g = 1.184 \text{ kg/m}^3$. Then the face velocity of the adsorption wave is

$$\begin{aligned} v_f &= \frac{(1.3 \text{ kg/s})[1 + 124(0.0020 \text{ kg/m}^3)]}{(18)(420 \text{ kg/m}^3)(1.184 \text{ kg/m}^3)(10 \text{ m}^2)} \\ &= 1.8 \times 10^{-5} \text{ m/s} \end{aligned}$$

The breakthrough time is calculated directly from Equation 6-50:

$$\begin{aligned} t_B &= \frac{0.50 \text{ m} - 0.03 \text{ m}}{1.8 \times 10^{-5} \text{ m/s}} \\ &= 2.6 \times 10^4 \text{ s or } 7.2 \text{ h} \end{aligned}$$

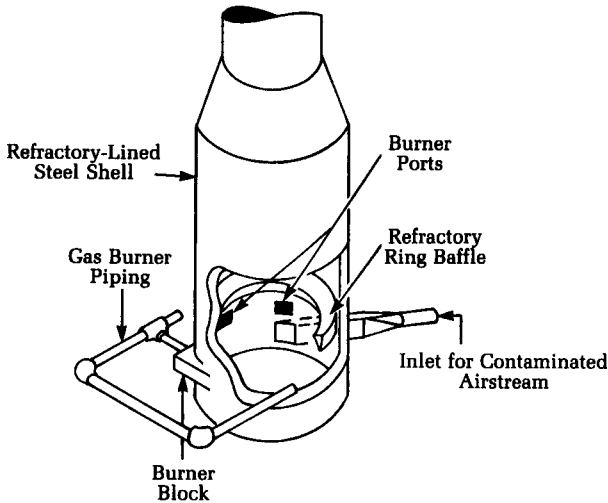


FIGURE 6-29
Direct flame incineration.

Combustion. When the contaminant in the gas stream is oxidizable to an inert gas, combustion is a possible alternative method of control. Typically, CO and hydrocarbons fall into this category. Both direct flame combustion by afterburners (Figure 6-29) and catalytic combustion have been used in commercial applications.

Direct flame incineration is the method of choice if two criteria are satisfied. First, the gas stream must have an energy concentration greater than 3.7 MJ/m^3 . At this energy concentration, the gas flame will be self-supporting after ignition. Below this point, supplementary fuel is required. The second requirement is that none of the by-products of combustion be toxic. In some cases the combustion by-product may be more toxic than the original pollutant gas. For example, the combustion of trichloroethylene produces phosgene, which was used as a poison gas in World War I. Direct flame incineration has been successfully applied to varnish-cooking, meat-smokehouse, and paint bake-oven emissions.

Some catalytic materials enable oxidation to be carried out in gases that have an energy content of less than 3.7 MJ/m^3 . Conventionally, the catalyst is placed in beds similar to adsorption beds. Frequently, the active catalyst is a platinum or palladium compound. The supporting lattice is usually a ceramic. Aside from expense, a major drawback of the catalysts is their susceptibility to poisoning by sulfur and lead compounds in trace amounts. Catalytic combustion has successfully been applied to printing-press, varnish-cooking, and asphalt-oxidation emissions.

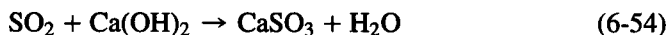
Flue Gas Desulfurization (FGD)

Flue gas desulfurization systems fall into two broad categories: nonregenerative and regenerative. Nonregenerative means that the reagent used to remove the sulfur oxides from the gas stream is used and discarded. Regenerative means that the reagent

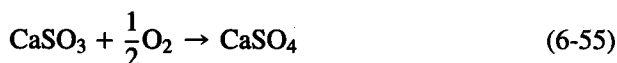
is recovered and reused. In terms of the number and size of systems installed, non-regenerative systems dominate.

Nonregenerative systems. There are nine commercial nonregenerative systems.⁵⁷ All have reaction chemistries based on lime (CaO), caustic soda (NaOH), soda ash (Na₂CO₃), or ammonia (NH₃).

The SO₂ removed in a lime/limestone-based FGD system is converted to sulfite. The overall reactions are generally represented by:⁵⁸



when using limestone and lime, respectively. Part of the sulfite is oxidized with the oxygen content in the flue gas to form sulfate:



Although the overall reactions are simple, the chemistry is quite complex and not well defined. The choice between lime and limestone, the type of limestone, and method of calcining and slaking can influence the gas-liquid-solid reactions taking place in the absorber.

The principal types of absorbers used in the wet scrubbing systems include venturi scrubber/absorbers, static packed scrubbers, moving-bed absorbers, tray towers, and spray towers.⁵⁹

Spray dryer-based FGD systems consist of one or more spray dryers and a particulate collector.⁶⁰ The reagent material is typically a slaked lime slurry or a slurry of lime and recycled material. Although lime is the most common reagent, soda ash has also been used. The reagent is injected in droplet form into the flue gas in the spray dryer. The reagent droplets absorb SO₂ while simultaneously being dried. Ideally, the slurry or solution droplets are completely dried before they impact the wall of the dryer vessel. The flue gas stream becomes more humidified in the process of evaporation of the reagent droplets, but it does not become saturated with water vapor. This is the single most significant difference between spray dryer FGD

⁵⁷S. B. Hance and J. L. Kelly, "Status of Flue Gas Desulfurization Systems," Paper No. 91-157.3, 84th Annual Meeting of the Air and Waste Management Association, 1991.

⁵⁸H. T. Karlsson and H. S. Rosenberg, "Technical Aspects of Lime/Limestone Scrubbers for Coal fired Power Plants, Part I: Process Chemistry and Scrubber Systems," *Journal of the Air Pollution Control Association*, vol. 30 (6), pp. 710-714, 1980.

⁵⁹Black & Veatch Consulting Engineers, *Lime FGD Systems Data Book - Second Edition*, EPRI Publication No. CS-2781, 1983.

⁶⁰Historically, from a mass transfer point of view, spray drying refers to the evaporation of a solvent from an atomized spray. Simultaneous diffusion of a gaseous species into the evaporating droplet is not true spray drying. Nonetheless, many authors have adopted the term "spray drying" as synonymous with dry scrubbing.

and wet scrubber FGD. The humidified gas stream and a significant portion of the particulate matter (fly ash, FGD reaction products, and unreacted reagent) are carried by the flue gas to the particulate collector located downstream of the spray dryer vessel.⁶¹

Control Technologies for Nitrogen Oxides

Almost all nitrogen oxide (NO_x) air pollution results from combustion processes. They are produced from the oxidation of nitrogen bound in the fuel, from the reaction of molecular oxygen and nitrogen in the combustion air at temperatures above 1,600 K (see Equation 6-12), and from the reaction of nitrogen in the combustion air with hydrocarbon radicals. Control technologies for NO_x are grouped into two categories: those that prevent the formation of NO_x during the combustion process and those that convert the NO_x formed during combustion into nitrogen and oxygen.⁶²

Prevention. The processes in this category employ the fact that reduction of the peak flame temperature in the combustion zone reduces NO_x formation. Nine alternatives have been developed to reduce flame temperature: (1) minimizing operating temperatures, (2) fuel switching, (3) low excess air, (4) flue gas recirculation, (5) lean combustion, (6) staged combustion, (7) low NO_x burners, (8) secondary combustion, and (9) water/steam injection.

Routine burner tune-ups and operation with combustion zone temperatures at minimum values reduce the fuel consumption and NO_x formation. Converting to a fuel with a lower nitrogen content or one that burns at a lower temperature will reduce NO_x formation. For example, petroleum coke has a lower nitrogen content and burns with a lower flame temperature than coal. On the other hand, natural gas has no nitrogen content but burns at a relatively high flame temperature and, thus, produces more NO_x than coal.

Low excess air and flue gas recirculation work on the principle that reduced oxygen concentrations lower the peak flame temperatures. In contrast, in lean combustion, additional air is introduced to cool the flame.

In staged combustion and low NO_x burners, initial combustion takes place in a fuel-rich zone that is followed by the injection of air downstream of the primary combustion zone. The downstream combustion is completed under fuel-lean conditions at a lower temperature.

Staged combustion consists of injecting part of the fuel and all of the combustion air into the primary combustion zone. Thermal NO_x production is limited by the low flame temperatures that result from high excess air levels.

⁶¹A. L. Cannell and M. L. Meadows, "Effects of Recent Operating Experience on the Design of Spray Dryer FGD Systems," *Journal of the Air Pollution Control Association*, vol. 35 (7), pp. 782-789, 1985.

⁶²A. Prasad, "Air Pollution Control Technologies for Nitrogen Oxides," *The National Environmental Journal*, May/June, pp. 46-50, 1995.