

# 8

## **Removal of Gaseous Pollutants from Effluent Streams**

There are a variety of approaches to removing gaseous pollutants from effluent streams: absorption, adsorption, condensation, chemical reaction, incineration, and selective diffusion through a membrane.

Absorption is an operation involving 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 driving force for absorption is the difference between the partial pressure of the soluble gas in the gas mixture and its vapor pressure just above the surface of the liquid. It is necessary to employ a liquid solvent within which the gas to be removed is soluble. Water is, by itself, quite efficient for removing soluble acidic gases such as HCl and HF and the soluble basic gas  $\text{NH}_3$ . Gases of more limited solubility, such as  $\text{SO}_2$ ,  $\text{Cl}_2$ , and  $\text{H}_2\text{S}$ , can be absorbed readily in an alkaline solution such as dilute NaOH. Thus, when water is used as the solvent, it may contain added species, such as acids, alkalines, oxidants, or reducing agents to react with the gas being absorbed and enhance its solubility. Nonaqueous, organic liquids of low volatility can be used for absorption of gases with low water solubility, such as hydrocarbons. Examples of such solvents are dimethylaniline and amines. Organic solvents are often limited to treating particle-free gases to avoid sludge formation. To provide a large liquid surface area for mass transfer, a means of breaking the liquid stream into small droplets or thin films is provided in the gas absorber. The most commonly used devices are columns containing packing or regularly spaced plates, open spray chambers and towers, and combinations of sprayed and packed chambers. Countercurrent contact of liquid and gas is employed to maximize the driving forces.

Adsorption is employed to remove low concentration gases from exhaust streams by causing the gaseous solutes to intimately contact a porous solid to which the solute

will adhere. Gas adsorption is used industrially for odor control and for the removal of volatile solvents such as benzene, ethanol, trichloroethylene, and so on, from effluent streams.

Condensation can be used to remove species with relatively low vapor pressure and is carried out in a device that appropriately cools the gas stream and provides a means to remove the layer of condensed liquid. We will not consider condensation in this book.

The fourth and fifth methods of removing gaseous species from an effluent stream listed at the outset were chemical reaction and incineration. Although many of the separation processes involve chemical reaction, such as absorption of an acidic gas in an alkaline solvent, the chemical reaction category refers to those where the key element of the separation is the reaction itself. For example, even though SO<sub>2</sub> scrubbing by an aqueous solution containing lime involves a chemical reaction, the absorption is the key removal step. Incineration involves the combustion of the species and is an important process for the treatment of toxic species, where virtually complete removal is necessary. The waste gas is fed to a combustor where the unwanted species are burned at sufficiently high temperature to convert them to harmless products such as CO<sub>2</sub> and H<sub>2</sub>O. Selection of the combustion temperature is determined by the combustion chemistry of the particular substances to be removed.

The final separation method listed was selective diffusion through a membrane. Membrane processes have found application in removing gases such as CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub> from natural gas streams (Cooley and Dethloff, 1985). Due to its specialized nature and applications, we do not consider membrane diffusion here.

## 8.1 INTERFACIAL MASS TRANSFER

In the process of gas absorption the gaseous effluent stream containing the pollutant to be removed is brought into contact with a liquid in which it will dissolve. 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 the 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. To predict the extent to which a compound can be removed by gas absorption, we must be able to compute the rates of these three mass transfer processes.

The key process of mass transfer of a dissolving species through a gas to a liquid surface is that of diffusion of component *A* through a nondissolving background gas *B*. Fick's law in this case, referred to as diffusion of *A* through stagnant *B*,  $N_{B_z} = 0$ , becomes

$$N_{A_z} = -cD_{AB} \frac{dx}{dz} + N_{A_z}x \quad (8.1)$$

where *x* is the mole fraction of *A*. Integrating (8.1), in accordance with the situation in Figure 8.1(a), with  $N_{A_z} = \text{constant}$ , we obtain the flux of *A* as

$$N_{Az} = \frac{-cD_{AB}}{l} \ln \frac{1 - x_0}{1 - x_1} \tag{8.2}$$

We can rewrite (8.2) as

$$N_{Az} = \frac{-cD_{AB}}{l(x_B)_{lm}} (x_1 - x_0) \tag{8.3}$$

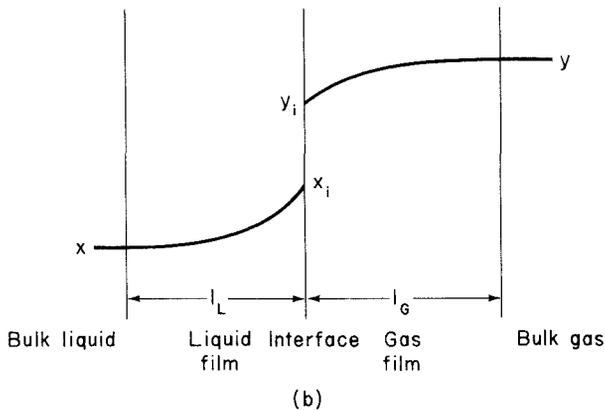
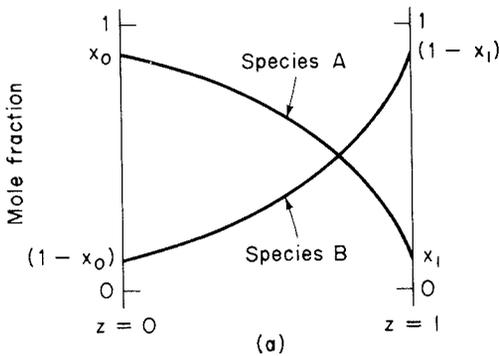
where  $(x_B)_{lm}$ , the log mean mole fraction of component B, is defined as

$$(x_B)_{lm} = \frac{(1 - x)_1 - (1 - x)_0}{\ln [(1 - x)_1 / (1 - x)_0]} \tag{8.4}$$

Partial pressures may be used instead of mole fractions, in which case (8.3) becomes

$$N_{Az} = \frac{-pD_{AB}}{RTl(p_B)_{lm}} (p_{A1} - p_{A0}) \tag{8.5}$$

where  $p$  is the total pressure.



**Figure 8.1** Binary mass transfer: (a) diffusion of A through stagnant B; (b) the two-film model of interfacial mass transfer.

In gas absorption, the gas is in turbulent flow and the transport of species occurs across a gas-liquid interface. Most situations of mass transfer in turbulent flow near an interface are too complicated to allow an exact evaluation of profiles and fluxes. Thus certain idealized models are postulated for the mass transfer in such a situation, models that enable the solution for the flux of a species in terms of readily measurable empirical coefficients.

Turbulent motion maintains a fairly uniform composition in the bulk gas. Close to the surface of the liquid, a laminar boundary layer exists in the gas across which species in the bulk gas must diffuse to reach the liquid surface. Similarly, on the liquid side, the bulk liquid is at a uniform composition with a thin layer near the surface of the liquid through which species diffuse from the interface into the bulk liquid. At steady state it can be assumed that the flux of species  $A$  from the bulk gas to the interface equals the flux of  $A$  from the interface to the bulk liquid. The simplest model one can envision for this situation is two stagnant layers on either side of the interface, as shown in Figure 8.1(b). Based on the form of (8.5) we assume that the flux of  $A$  is given by

$$N_{A_z} = k_G(p_A - p_{A_i}) = k_L(c_{A_i} - c_A) \quad (8.6)$$

where  $p_A$  and  $p_{A_i}$  are the partial pressures of  $A$  in the bulk gas and at the interface, respectively;  $c_A$  and  $c_{A_i}$  are the concentrations of  $A$  in the bulk liquid and at the interface, respectively; and  $k_G$  and  $k_L$  are mass transfer coefficients for the gas and liquid films, respectively. For the case considered earlier, we see that  $k_G$  and  $k_L$  are given by

$$k_G = \frac{pD_{AB}}{RTl_G(p_B)_{lm}} \quad (8.7)$$

and

$$k_L = \frac{D_{AB}}{l_L(x_B)_{lm}} \quad (8.8)$$

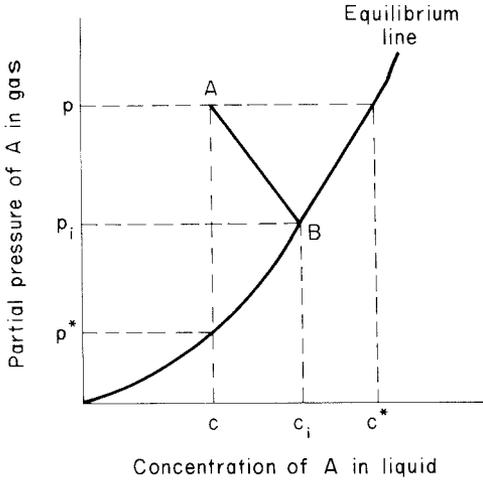
For dilute mixtures of  $A$  in  $B$ ,  $(x_B)_{lm} \approx 1.0$ .

Thus the mass transfer coefficients should depend on the molecular diffusivity of  $A$  in  $B$  and on the thickness of the film over which the diffusion takes place. Unfortunately, in mass transfer between turbulent gas and liquid streams, it is virtually impossible to specify  $l_G$  and  $l_L$  and, in fact, even to specify the precise location of the interface or the values of  $p_{A_i}$  and  $c_{A_i}$  at any time. Thus we usually write (8.6) as

$$N_{A_z} = K_G(p_A - p_A^*) = K_L(c_A^* - c_A) \quad (8.9)$$

where  $p_A^*$  is the equilibrium partial pressure of  $A$  over a solution of  $A$  having the bulk concentration  $c_A$ , and  $c_A^*$  is the concentration of a solution that would be in equilibrium with the partial pressure  $p_A$  of the bulk gas stream. We illustrate these points on the equilibrium diagram in Figure 8.2. The new coefficients  $K_G$  and  $K_L$  are called overall mass transfer coefficients. These must be determined experimentally.

Originally, in (8.6), the driving forces for diffusion were based on the actual interfacial compositions,  $p_{A_i}$  and  $c_{A_i}$ . Since we do not know these in general, we replaced



**Figure 8.2** Driving forces in the two-film model of interfacial mass transfer.

(8.6) with (8.9), in which the new overall mass transfer coefficients  $K_G$  and  $K_L$  were defined. The new driving forces for diffusion,  $p_A - p_A^*$  and  $c_A^* - c_A$  are shown in Figure 8.2. The point  $B$  on the equilibrium curve represents the interfacial composition, which we assume to be  $(p_{A_i}, c_{A_i})$ . The line  $AB$  has a slope  $-k_L/k_G$  and is given by

$$\frac{p_A - p_{A_i}}{c_{A_i} - c_A} = \frac{k_L}{k_G} \tag{8.10}$$

When the equilibrium line is given by Henry's law,

$$p_A^* = H_A c_A \tag{8.11}$$

we can explicitly relate  $k_G$  and  $k_L$  and  $K_G$  and  $K_L$  through (8.6) and (8.9) by

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H_A}{k_L} \tag{8.12}$$

and

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_A k_G} \tag{8.13}$$

If  $H_A \ll 1$ , species  $A$  is very soluble,  $K_G \approx k_G$ , and the overall process is controlled by diffusion through the gas film. On the other hand, if  $H_A \gg 1$ , species  $A$  is sparingly soluble and overall rate of mass transfer is liquid-film controlled. Note that we have drawn the equilibrium line in Figure 8.2 as curved, since  $H_A$  is not usually constant [and thus (8.12) and (8.13) are not generally valid].

It is also possible to express (8.6) in terms of mole fractions, in which case

$$N_{A_z} = k_y (y - y_i) = k_x (x_i - x) \tag{8.14}$$

where  $y$  and  $x$  refer to the gas and liquid phases, respectively.

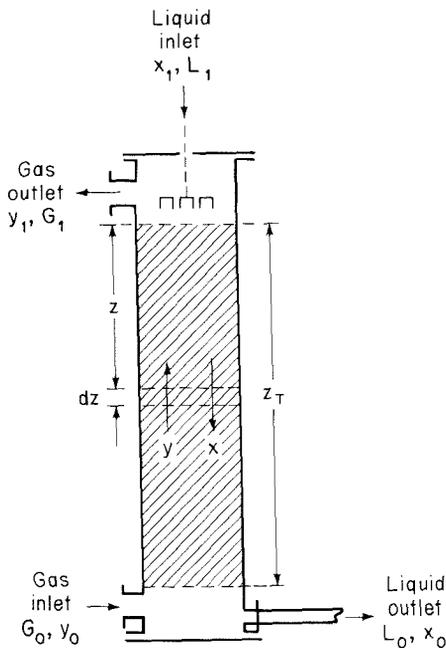
## 8.2 ABSORPTION OF GASES BY LIQUIDS

Gas absorption is usually carried out in a column or tower, in which the gas to be cleaned (the rich gas) enters at the bottom and flows countercurrent to the fresh liquid (the lean liquid), which is introduced at the top. The column is often packed with inert solids (e.g., ceramic beads) to promote better contact between the two streams. Such a tower is shown diagrammatically in Figure 8.3. Separation is achieved because of the solubility of the species in question in the liquid. In many pollution control applications the absorbing liquid is water, and the process is referred to as scrubbing.

### 8.2.1 Gas Absorption without Chemical Reaction

The conventional approach to the analysis and design of gas absorption towers is to assume that the partial pressure of the dissolving gas just above the liquid surface is that calculated from Henry's law neglecting the effect on the solubility of the gas of any further chemical reactions in the liquid. Such an approach can be termed "gas absorption without chemical reaction." The basic gas absorption design problem is the following. Given:

1. A rich gas stream entering at a rate  $G$  ( $\text{mol h}^{-1} \text{ m}^{-2}$  of empty tower) containing a known mole fraction of component,  $A$ ,  $y_0$
2. A desired exit gas mole fraction  $y_1$



**Figure 8.3** Countercurrent gas absorption tower.

3. A specified mole fraction of  $A$  in the inlet liquid,  $x_1$
4. The equilibrium curve of  $y$  versus  $x$  for the system

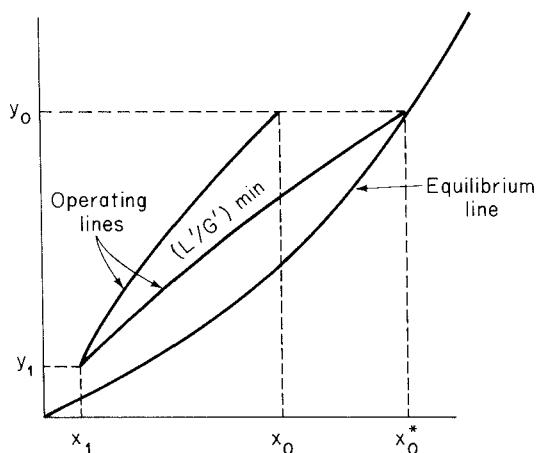
we wish to compute the height of the tower required to carry out the separation.\*

We assume that the gas and liquid phases are immiscible. For example,  $\text{SO}_2$  is removed from air by absorption in a liquid amine of low vapor pressure. The low vapor pressure of the amine ensures that virtually no amine evaporates into the gas phase, and operation at atmospheric pressure ensures that no air dissolves in the amine. Thus, even though  $\text{SO}_2$  is transferred between phases, the assumption of immiscibility refers to the fact that the two carrier streams, in this case air and amine, do not dissolve in each other to an appreciable extent.

We note that although the molal gas flow rate  $G$  is usually specified, that for the liquid phase is not. A little reflection will show that there is no maximum to the value of the liquid flow rate  $L$ , but, indeed, there is a minimum value of  $L$  below which the required  $A$  cannot be separated from the gas. Actually, the total gas and liquid flows are not constant through the tower. The gas flow  $G$  consists of  $A$  + inert gas, and  $L$  consists of  $A$  + inert liquid. By our assumption of immiscibility, the flow rates of inert gas and inert liquid always remain constant down the tower. We denote these flow rates by  $G'$  and  $L'$ , respectively. Thus, when we want to select the liquid flow rate, we really want to determine first the minimum  $L'$  and then add a comfortable operating margin to that minimum.

In Figure 8.4, point  $(x_1, y_1)$  denotes the top of the tower and point  $(x_0, y_0)$  the bottom. The driving force for mass transfer is proportional to the line  $AB$ , as shown in Figure 8.2. Point  $A$  must always lie above the equilibrium line; however, as  $A$  approaches  $B$ , the driving force for mass transfer approaches zero. When  $A$  actually coincides with  $B$  at any point in the tower, mass transfer ceases, because, of course, the

\*One would normally also determine the column diameter based on the liquid flow rate and desired pressure drop characteristics. We do not consider this aspect of the design here; rather, we simply assume that the column diameter is constant and known.



**Figure 8.4** Equilibrium and operating lines for a gas absorption tower.

two phases are in equilibrium at that point. Clearly, if a point is reached in an actual column where  $A$  and  $B$  coincide, no more mass transfer can take place past that point regardless of the height of the column.

To determine the minimum value of  $L'$ , we must perform a material balance on species  $A$  for the absorption tower. A balance on species  $A$  over the whole tower gives

$$L_1 x_1 + G_0 y_0 = L_0 x_0 + G_1 y_1 \quad (8.15)$$

where  $(G_0, L_0)$  and  $(G_1, L_1)$  represent the flows at the bottom and top of the column, respectively. At any point in the tower, where the flow rates are  $G$  and  $L$ , a balance around the top of the column gives

$$L_1 x_1 + Gy = Lx + G_1 y_1 \quad (8.16)$$

Rearranging (8.16), we have

$$y = \frac{L}{G}x + \frac{1}{G}(G_1 y_1 - L_1 x_1) \quad (8.17)$$

On a plot of  $y$  versus  $x$ , (8.17) represents a line, not necessarily straight (unless  $L$  and  $G$  are constant through the whole column), that relates the compositions of passing streams at any point. Such a line is called an *operating line*. The two ends of the column are represented by points  $(x_0, y_0)$  and  $(x_1, y_1)$ .

In order to draw the operating line, we need to know  $L$  and  $G$  at each point in the column. In the case of gas absorption, in which only component  $A$  is transferred between phases, we know that

$$G = \frac{G'}{1-y} \quad L = \frac{L'}{1-x} \quad (8.18)$$

where  $G'$  and  $L'$  are constant. Thus (8.16) becomes

$$L' \left( \frac{x_1}{1-x_1} - \frac{x}{1-x} \right) = G' \left( \frac{y_1}{1-y_1} - \frac{y}{1-y} \right) \quad (8.19)$$

If the mole fraction of  $A$  in each phase is small, then, for all practical purposes,  $G \approx G'$ ,  $L \approx L'$ , and the operating line is straight, with a slope of  $L'/G'$ .

We now consider the two operating lines shown in Figure 8.4, drawn for the case in which  $L/G$  varies over the tower. The average slope of the operating line is  $L/G$ , so that as  $L$  is decreased, the slope decreases. Point  $(x_1, y_1)$  is fixed, so as  $L$  is decreased, the upper end of the operating line, that is,  $x_0$ , moves closer to the equilibrium line. The maximum possible value of  $x_0$  and the minimum possible value of  $L'$  are reached when the operating line just touches the equilibrium line, as shown in Figure 8.4. At this point, an infinitely long column would be required to achieve the desired separation. We can find the minimum value of  $L'/G'$  by setting  $y = y_0$  and  $x = x_0^*$  in (8.19), where  $x_0^*$  is the abscissa of the point on the equilibrium line corresponding to  $y_0$ . Customarily, a value of  $L'/G'$  about 1.5 times the minimum is employed. This choice is an economic one. If  $L'/G'$  is large, the distance between the operating and equilibrium lines is large, the driving force is large, and a short column is needed. On the other hand, a high liquid

flow rate may be costly. Thus the optimum  $L'/G'$  results from a balance between capital equipment costs and operating costs.

Assuming that  $L'$  has been specified, we wish to determine the required column height. Let us consider a differential height of the column  $dz$ . If the interfacial area per unit volume is  $a$ , a balance on component  $A$  in the gas phase over the height  $dz$ , using (8.14), yields

$$Gy \Big|_{z+dz} - Gy \Big|_z = k_y a (y - y_i) dz \quad (8.20)$$

which, upon division by  $dz$ , and letting  $dz \rightarrow 0$ , gives

$$\frac{d(Gy)}{dz} = k_y a (y - y_i) \quad (8.21)$$

where  $y_i$  is a point on the equilibrium curve. Using (8.18), we see that

$$d(Gy) = G'd \left( \frac{y}{1-y} \right) = G' \frac{dy}{(1-y)^2} = G \left( \frac{dy}{1-y} \right) \quad (8.22)$$

Integrating (8.21) with the aid of (8.22) produces

$$\int_0^{z_T} dz = \int_{y_1}^{y_0} \frac{G}{k_y a (1-y)(y-y_i)} dy \quad (8.23)$$

To determine the total height  $z_T$ , we must evaluate the integral in (8.23). The method of integration depends on the shape of the equilibrium line, the variation in  $G$ , and the relative importance of the two mass transfer coefficients  $k_x a$  and  $k_y a$ .

From (8.14) we note that

$$\frac{y - y_i}{x_i - x} = \frac{k_x a}{k_y a} \quad (8.24)$$

Thus, at any point, (8.24) describes a straight line with slope  $-k_x a/k_y a$ , passing through  $(x, y)$  and  $(x_i, y_i)$ . From a knowledge of  $k_x a/k_y a$  we can determine  $x_i$  and  $y_i$  corresponding to any  $(x, y)$  on the operating line. Then (8.23) can be integrated. It is common to express (8.23) as

$$z_T = \left( \overline{\frac{G}{k_y a}} \right) \int_{y_1}^{y_0} \frac{dy}{(1-y)(y-y_i)} \quad (8.25)$$

where  $\overline{(G/k_y a)}$  is the average value of this group over the column. (Since  $G$  decreases from bottom to top, and  $k_y a$  also decreases from bottom to top, these changes somewhat compensate each other.) The functional dependence of  $k_x a$  and  $k_y a$  on the molal flow rates must be determined experimentally.

In deriving an expression for  $z_T$  we could have considered a liquid-side balance, in which case the equation corresponding to (8.25) is

$$z_T = \left( \overline{\frac{L}{k_x a}} \right) \int_{x_1}^{x_0} \frac{dx}{(1-x)(x_i-x)} \quad (8.26)$$

Either (8.25) or (8.26) is suitable for carrying out calculations.

The design method embodied in (8.25) and (8.26) is applicable to an equilibrium line of arbitrary shape. A strongly curved equilibrium line is often due to a significant temperature variation over the height of the tower. Appreciable temperature differences result from the heat of solution of a highly concentrated solute in the rich gas. If the rich gas contains a rather dilute concentration of solute, the temperature gradient in the column is small, and the equilibrium line is approximately straight. When the equilibrium line is straight, overall mass transfer coefficients, which are easier to determine experimentally than  $k_x a$  and  $k_y a$  can be used. The overall coefficients  $K_x a$  and  $K_y a$  are defined on the basis of the fictitious driving forces  $(x^* - x)$  and  $(y - y^*)$ .

The design equations analogous to (8.25) and (8.26) are, in this case,

$$z_T = \left( \frac{\overline{G}}{k_y a} \right) \int_{y_1}^{y_0} \frac{dy}{(1-y)(y-y^*)} \quad (8.27)$$

and

$$z_T = \left( \frac{\overline{L}}{K_x a} \right) \int_{x_1}^{x_0} \frac{dx}{(1-x)(x^*-x)} \quad (8.28)$$

which can be evaluated given the  $y^*$  versus  $x^*$  equilibrium line.

It has been customary in gas absorption design to express the equations for  $z_T$ , that is, (8.25)–(8.28), as the product of a number of *transfer units* and the depth of packing required by a single of these units (the height of a transfer unit). Then  $z_T$  is written

$$z_T = NH \quad (8.29)$$

where  $N$  is the number of transfer units and  $H$  is the height of a transfer unit (HTU). For example, using (8.25) and (8.27), we define

$$N_y = \int_{y_1}^{y_0} \frac{dy}{(1-y)(y-y_i)} \quad (8.30)$$

and

$$N_{0y} = \int_{y_1}^{y_0} \frac{dy}{(1-y)(y-y^*)} \quad (8.31)$$

where  $N_y$  and  $N_{0y}$  are based on the individual and overall driving forces, respectively. Of course,  $N_y$  and  $N_{0y}$  are different, and, in order to produce the same  $z_T$  in (8.29), they are compensated for by the corresponding  $H$ s. Thus

$$H_y = \frac{\overline{G}}{k_y a} \quad (8.32)$$

and

$$H_{0y} = \frac{\overline{G}}{K_y a} \quad (8.33)$$

Similar relations hold for the liquid-side equations. When the equilibrium line is straight, and  $G$  and  $L$  are constant throughout the tower,  $H_{0y}$  (and  $H_{0x}$ ) are constant.

Clearly, the concept of an HTU merely represents a different manner of viewing  $z_T$ . Its advantage is that the HTU is usually fairly constant for a particular type of tower (usually, with a value in the range 0.1 to 1.5 m), and data are often reported in terms of the HTU. Correlations for HTUs for packed absorption towers are presented by McCabe and Smith (1976).

**Example 8.1 Absorption of SO<sub>2</sub> from Air by Water**

A packed tower is to be designed for absorption of SO<sub>2</sub> from air by contact with fresh water. The entering gas has a mole fraction of SO<sub>2</sub> of 0.10, and the exit gas must contain a mole fraction of SO<sub>2</sub> no greater than 0.005. The water flow rate used is to be 1.5 times the minimum, and the inlet airflow rate (on an SO<sub>2</sub>-free basis) is 500 kg m<sup>-2</sup> h<sup>-1</sup>. The column is to be operated at 1 atm and 303 K. We wish to determine the required depth of the packed section for such a tower.

The following correlations are available for absorption of SO<sub>2</sub> at 303 K in towers packed with 1-in. rings (McCabe and Smith, 1976):

$$k_x a = 0.6634 \bar{L}^{0.82} \quad k_y a = 0.09944 \bar{L}^{0.25} \bar{G}^{0.7}$$

where  $\bar{L}$  and  $\bar{G}$  are the mass flow rates of liquid and gas, respectively, in kg m<sup>-2</sup> h<sup>-1</sup>, and  $k_x a$  and  $k_y a$  are in kg-mol m<sup>-3</sup> h<sup>-1</sup> mole fraction<sup>-1</sup>.

Equilibrium data for SO<sub>2</sub> in air and water at this temperature are available:

$p_{\text{SO}_2}$ (mmHg)	$c$ (gSO <sub>2</sub> /100 g H <sub>2</sub> O)
0.6	0.02
1.7	0.05
4.7	0.10
8.1	0.15
11.8	0.20
19.7	0.30
36.0	0.50
52.0	0.70
79.0	1.00

From these data we can calculate the equilibrium curve:

$$y = \frac{p_{\text{SO}_2}}{760} \quad x = \frac{c/64}{c/64 + 100/18}$$

The equilibrium curve is shown in Figure 8.5.

The first step in the solution is calculation of the minimum water flow rate. Using (8.19) with  $y_0 = 0.10$ ,  $x_1 = 0$ ,  $y_1 = 0.005$ , and  $x_0^* = 0.0027$ , we obtain  $L_{\text{min}} = 667$  kg-mol m<sup>-2</sup> h<sup>-1</sup>. Thus the actual water rate to be used is  $667 \times 1.5 = 1000$  kg-mol m<sup>-2</sup> h<sup>-1</sup>.

The equation for the operating line is

$$\frac{x}{1-x} = 0.0172 \frac{y}{1-y} - 0.000086$$

This line is shown in Figure 8.5.

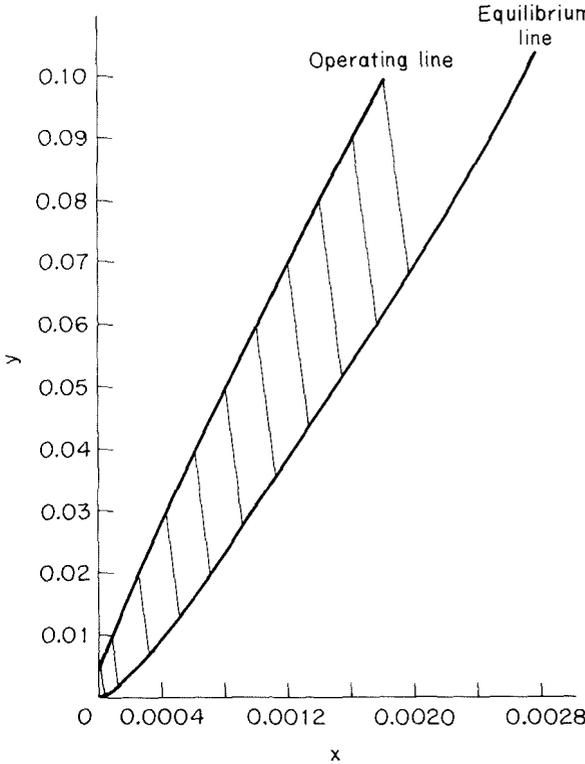


Figure 8.5 Equilibrium and operating lines for SO<sub>2</sub> absorption in water.

The SO<sub>2</sub> enters at a rate of 122 kg m<sup>-2</sup> h<sup>-1</sup> and leaves at a rate of 5.5 kg m<sup>-2</sup> h<sup>-1</sup>. The total exit gas rate is 505.5 kg m<sup>-2</sup> h<sup>-1</sup>. The freshwater feed at the top is 18,000 kg m<sup>-2</sup> h<sup>-1</sup>, and the rich liquor leaving at the bottom is 18,116.5 kg m<sup>-2</sup> h<sup>-1</sup>.

The liquid-side mass transfer coefficient will not change appreciably from the top to the bottom since *L* is nearly constant. We can calculate *k<sub>x</sub>a* from the average mass velocity of 18,058 kg m<sup>-2</sup> h<sup>-1</sup>:

$$k_x a = 2052.6$$

Because of the change of the total gas velocity from the top to the bottom, *k<sub>y</sub>a* will change somewhat over the tower. The values at the top and bottom are

$$(k_y a)_0 = 104.17$$

$$(k_y a)_1 = 89.48$$

We shall use the average value of 96.82.

Therefore, from any point (*x*, *y*) on the operating line, we can determine *x<sub>i</sub>*, *y<sub>i</sub>* by drawing a straight line with slope  $-2052.6/96.82 = -21.2$ . The integral in (8.25) can be evaluated graphically. Table 8.1 shows the calculation of the quantity  $1/(1 - y)(y - y_i)$  and the graphical integration (8.25). The value of the integral in (8.25) is found to be 5.72.

TABLE 8.1 EVALUATION OF INTEGRAND IN (8.25)

$y$	$1 - y$	$y_i$	$y - y_i$	$(1 - y)(y - y_i)$	$\frac{1}{(1 - y)(y - y_i)}$	$\Delta I$	$\Delta I \Delta Y$
0.005	0.995	0.0005	0.0045	0.0048	223		
0.01	0.99	0.002	0.0080	0.00792	126.5	164	0.82
0.02	0.98	0.0075	0.0125	0.01225	81.7	102	1.02
0.03	0.97	0.014	0.0160	0.01552	64.5	72	0.72
0.04	0.96	0.0215	0.0185	0.01775	56.4	60	0.60
0.05	0.95	0.0285	0.0215	0.0204	49	52.5	0.525
0.06	0.94	0.036	0.0240	0.0226	44.2	46.5	0.465
0.07	0.93	0.044	0.0260	0.0242	41.4	42.8	0.428
0.08	0.92	0.0520	0.0280	0.0258	38.8	40	0.400
0.09	0.91	0.0605	0.0295	0.0268	37.3	38	0.380
0.10	0.90	0.0685	0.0315	0.0283	35.3	36	0.360
							<u>5.718</u>

Finally, we evaluate the quantity  $k_y a/G$  at the two ends of the tower,

$$\left(\frac{k_y a}{G}\right)_0 = 5.448$$

$$\left(\frac{k_y a}{G}\right)_1 = 5.202$$

and use the average value of 5.325 to calculate  $z_T$  as 1.08 m.

### 8.2.2 Gas Absorption with Chemical Reaction

The equilibrium vapor pressure of  $\text{SO}_2$  over the liquid depends on the concentration of dissolved  $\text{SO}_2$ . In the previous analysis the concentration of dissolved  $\text{SO}_2$  is just equal to that which has been absorbed into the liquid at that point in the column. However, the equilibrium vapor pressure of the dissolved solute can be decreased almost to zero by adding a reagent to the absorbing liquid that reacts with the dissolved solute, effectively “pulling” more of the solute gas into solution. Some examples of the use of chemically enhanced absorption are the removal of acid gases (such as  $\text{SO}_2$ ) by alkaline solutions (see Section 8.4), the removal of odorous gases in oxidizing solutions, and the absorption of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in amine solutions.

We wish to consider the same situation as in the preceding section, except that to enhance the solubility of  $\text{SO}_2$  in the water an alkaline reagent will be assumed to have been added to the fresh liquid feed at the top of the column. It will be necessary to account for the chemical state of the dissolved  $\text{SO}_2$  in order to compute its equilibrium vapor pressure and, therefore, the gas-phase driving force for absorption. Let

$$G_0 = \text{total molar flow rate of entering gas, kg-mol m}^{-2} \text{ h}^{-1} \text{ of empty tower}$$

$y_0$  = mole fraction of  $\text{SO}_2$  in the entering gas

$y_1$  = desired mole fraction of  $\text{SO}_2$  in the exiting gas

$\text{pH}_0$  = initial pH of water feed

$W$  = volumetric flow rate of liquid fed to the top of the column per unit cross-sectional area of the tower,  $\text{m}^3$  of liquid  $\text{m}^{-2}$  of column  $\text{h}^{-1}$

In the design we need to derive equations for the compositions of the gas and liquid phases as a function of position in the unit. We let the position in the chamber be denoted by  $z$ , where  $z$  is the distance measured from the top of the unit, and  $z_T$  is the total height of the chamber (to be determined). We derive these equations by considering balances on  $\text{SO}_2$  both over a slice of differential depth and over the unit as a whole.

The total molar flow rate of gas introduced at the bottom of the unit is  $G_0$  ( $\text{kg}\cdot\text{mol m}^{-2} \text{h}^{-1}$ ), which consists of mole fractions  $y_0$  of  $\text{SO}_2$  and  $(1 - y_0)$  of air. Thus, the molar flow rate of air in the unit is  $(1 - y_0) G_0$ . If the mole fraction of  $\text{SO}_2$  at any depth in the chamber is  $y$ , the total molar flow rate of gas per unit cross-sectional area at that point is  $G = (1 - y_0) G_0 / (1 - y)$ .

We now perform a balance on gas-phase  $\text{SO}_2$  over a section of depth  $dz$ . At steady state:

flow in with gas at  $z + dz$  = flow out with gas at  $z$  + amount transferred to water

$$(8.34)$$

The first two terms of the balance are:

$$\text{flow in with gas at } z + dz = (1 - y_0) G_0 \left. \frac{y}{1 - y} \right|_{z+dz}$$

$$\text{flow out with gas at } z = (1 - y_0) G_0 \left. \frac{y}{1 - y} \right|_z$$

where we see that these two terms are each just  $yG$ , the molar flow rate of  $\text{SO}_2$  in the gas.

Thus, the balance on gas-phase  $\text{SO}_2$  becomes

$$(1 - y_0) G_0 \left. \frac{y}{1 - y} \right|_{z+dz} - (1 - y_0) G_0 \left. \frac{y}{1 - y} \right|_z = k_y a (y - y_i) dz \quad (8.35)$$

Dividing by  $dz$  and taking the limit as  $dz \rightarrow 0$  gives us

$$\frac{d}{dz} \left( \frac{y}{1 - y} \right) = \frac{k_y a (y - y_i)}{G_0 (1 - y_0)} \quad (8.36)$$

which is to be solved subject to

$$y(z_T) = y_0 \quad (8.37)$$

All the quantities in (8.36) are known except  $y_i$ , the  $\text{SO}_2$  mole fraction just above the liquid surface. To determine  $y_i$  we must consider the behavior of the liquid phase as a function of position in the chamber. Note that  $y_i = p_{\text{SO}_2}^s/p$ , where  $p_{\text{SO}_2}^s$  is the partial pressure of  $\text{SO}_2$  just above the liquid surface.

The absorption of  $\text{SO}_2$  by water leads to the equilibria given in Table 8.2. The concentrations of the dissolved sulfur species in the liquid, in units of  $\text{kg}\cdot\text{mol m}^{-3}$ , given  $p_{\text{SO}_2}^s$ , are found from the equilibrium constant expressions in Table 8.2 to be

$$[\text{SO}_2 \cdot \text{H}_2\text{O}] = K_{hs} p_{\text{SO}_2}^s \quad (8.38)$$

$$[\text{HSO}_3^-] = \frac{K_{hs} K_{s1} p_{\text{SO}_2}^s}{[\text{H}^+]} \quad (8.39)$$

$$[\text{SO}_3^{2-}] = \frac{K_{hs} K_{s1} K_{s2} p_{\text{SO}_2}^s}{[\text{H}^+]^2} \quad (8.40)$$

As we noted, to enhance the solubility of  $\text{SO}_2$  in the water it is customary to raise the pH of the feed drops over that for pure water through the addition of an alkaline substance. Thus let us presume that an amount of nonvolatile salt MOH that dissociates in solution into  $\text{M}^+$  and  $\text{OH}^-$  has been added to the feed water such that the initial pH is  $\text{pH}_0$ . Electroneutrality must always be maintained locally in the liquid, so the concentration of the ion  $\text{M}^+$  is found from the specified initial pH,

$$[\text{H}^+]_0 + [\text{M}^+]_0 = [\text{OH}^-]_0 \quad (8.41)$$

and since MOH is assumed to be nonvolatile,

$$[\text{M}^+] = [\text{M}^+]_0 = \frac{K_w}{[\text{H}^+]_0} - [\text{H}^+]_0 \quad (8.42)$$

TABLE 8.2 EQUILIBRIUM CONSTANTS FOR AQUEOUS ABSORPTION OF  $\text{SO}_2$

Reaction	Equilibrium constant expression	Equilibrium constant <sup>a,b</sup>
$\text{SO}_{2(g)} + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$	$K_{hs} = \frac{[\text{SO}_2 \cdot \text{H}_2\text{O}]}{p_{\text{SO}_2}} \text{ M atm}^{-1}$	$\log K_{hs} = \frac{1376.1}{T} - 4.521$
$\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$K_{s1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2 \cdot \text{H}_2\text{O}]} \text{ M}$	$\log K_{s1} = \frac{853}{T} - 4.74$
$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$K_{s2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} \text{ M}$	$\log K_{s2} = \frac{621.9}{T} - 9.278$
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_w = [\text{H}^+][\text{OH}^-] \text{ M}^2$	$\log K_w = \frac{4470.99}{T} + 6.0875 - 0.01706 T$

<sup>a</sup> Values of  $K_{hs}$ ,  $K_{s1}$ , and  $K_{s2}$  from Maahs (1982).

<sup>b</sup> Value of  $K_w$  from Harned and Owen (1958, pp. 643-646).

Electroneutrality at any time is expressed as

$$[\text{H}^+] + [\text{M}^+] = [\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] \quad (8.43)$$

which can be written in terms of  $[\text{H}^+]$  as

$$[\text{H}^+] + [\text{M}^+] = \frac{K_w}{[\text{H}^+]} + \frac{K_{hs}K_{s1}p_{\text{SO}_2}^s}{[\text{H}^+]} + \frac{2K_{hs}K_{s1}K_{s2}p_{\text{SO}_2}^s}{[\text{H}^+]^2} \quad (8.44)$$

or

$$[\text{H}^+]^3 + [\text{M}^+][\text{H}^+]^2 - (K_w + K_{hs}K_{s1}p_{\text{SO}_2}^s)[\text{H}^+] - 2K_{hs}K_{s1}K_{s2}p_{\text{SO}_2}^s = 0 \quad (8.45)$$

The local hydrogen ion concentration in the liquid is related to the  $\text{SO}_2$  partial pressure just above the drop surface by (8.42) and (8.45). Since there are two unknowns,  $[\text{H}^+]$  and  $p_{\text{SO}_2}^s$ , we need to obtain another equation relating these two quantities. At the top of the tower  $[\text{H}^+] = [\text{H}^+]_0$ ; however, as soon as the falling liquid encounters  $\text{SO}_2$ , absorption takes place and the hydrogen ion concentration begins to change. To calculate how  $[\text{H}^+]$  changes with  $z$ , we perform an overall material balance on  $\text{SO}_2$  between the bottom of the tower ( $z = z_T$ ) and any level  $z$ . That overall balance takes the form:

$$\begin{aligned} & \text{flow in with gas at } z_T + \text{flow in with water at } z \\ & = \text{flow out with water at } z_T + \text{flow out with gas at } z \end{aligned}$$

Two of the terms in this balance are:

$$\begin{aligned} \text{flow in with gas at } z_T &= G_0 y_0 \\ \text{flow out with gas at } z &= \frac{(1 - y_0) G_0 y}{1 - y} \end{aligned}$$

The quantity of  $\text{SO}_2$  flowing out with the water at  $z = z_T$  is just the difference between that fed to the unit in the gas and that allowed to leave with the cleaned gas:

$$\text{flow out with water at } z_T = G_0 y_0 - \frac{(1 - y_0) G_0 y_1}{1 - y_1}$$

The final term in the material balance is the quantity of  $\text{SO}_2$  flowing with the liquid across the plane at  $z$ . This flow is given by

$$W([\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}])$$

We can use the equilibrium relations to express this quantity as

$$WK_{hs}p_{\text{SO}_2}^s \left( 1 + \frac{K_{s1}}{[\text{H}^+]} + \frac{K_{s1}K_{s2}}{[\text{H}^+]^2} \right)$$

Collecting terms in the entire balance, we have

$$G_0 y_0 + WK_{hs}p_{\text{SO}_2}^s \left( 1 + \frac{K_{s1}}{[\text{H}^+]} + \frac{K_{s1}K_{s2}}{[\text{H}^+]^2} \right) = G_0 y_0 - \frac{(1 - y_0) G_0 y_1}{1 - y_1} + \frac{(1 - y_0) G_0 y}{1 - y} \quad (8.46)$$

or

$$\begin{aligned}
 WK_{hs}p_{\text{SO}_2}^s \left( 1 + \frac{K_{s1}}{[\text{H}^+]} + \frac{K_{s1}K_{s2}}{[\text{H}^+]^2} \right) \\
 = (1 - y_0) G_0 \left( \frac{y}{1 - y} - \frac{y_1}{1 - y_1} \right) \quad (8.47)
 \end{aligned}$$

Now, to place this equation in a more compact form, let

$$\begin{aligned}
 \eta = [\text{H}^+] \quad A = \frac{K_w}{[\text{H}^+]_0} - [\text{H}^+]_0 \quad B = K_{hs}K_{s1} \quad C = K_{hs}K_{s1}K_{s2} \\
 D = \frac{(1 - y_0) G_0}{W} \quad E = \frac{y_1}{1 - y_1}
 \end{aligned}$$

and (8.47) can be written as

$$p_{\text{SO}_2}^s = \frac{D\eta^2}{K_{hs}\eta^2 + B\eta + C} \left( \frac{y}{1 - y} - E \right) \quad (8.48)$$

Also, (8.45) becomes

$$p_{\text{SO}_2}^s = \frac{\eta^3 + A\eta^2 - K_w\eta}{B\eta + 2C} \quad (8.49)$$

Equating (8.48) and (8.49) yields a single nonlinear algebraic equation relating  $[\text{H}^+]$  (i.e.,  $\eta$ ) and  $y$ ,

$$y = \frac{f(\eta)}{1 + f(\eta)} \quad (8.50)$$

where

$$f(\eta) = \frac{(\eta^3 + A\eta^2 - K_w\eta)(K_{hs}\eta^2 + B\eta + C)}{D\eta^2(B\eta + 2C)} + E \quad (8.51)$$

Now return to (8.36). Using (8.49) and (8.50), (8.36) becomes

$$m_2(\eta) \frac{d\eta}{dz} = m_1(\eta) \quad (8.52)$$

where

$$\begin{aligned}
 m_1(\eta) &= \frac{k_y a}{G_0(1 - y_0)} \left[ \frac{f(\eta)}{1 + f(\eta)} - \frac{\eta^3 + A\eta^2 - K_w\eta}{p(B\eta + 2C)} \right] \\
 m_2(\eta) &= \frac{df(\eta)}{d\eta}
 \end{aligned}$$

Integrating (8.52) over the tower gives

$$\int_{\eta_0}^{\eta_T} \frac{m_2(\eta)}{m_1(\eta)} d\eta = \int_0^{z_T} dz = z_T \quad (8.53)$$

The upper limit of the integral in (8.53),  $\eta_T$ , is the solution of (8.50) at  $y(z_T) = y_0$ , that is,

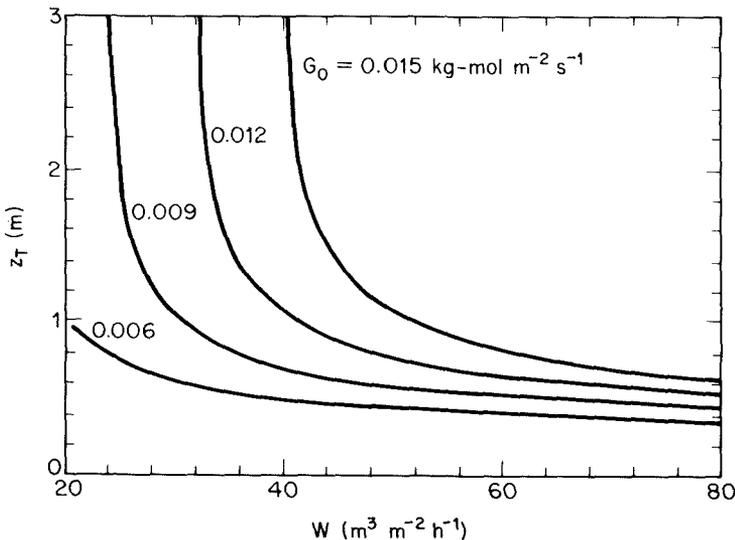
$$y_0 = \frac{f(\eta_T)}{1 + f(\eta_T)} \quad (8.54)$$

To determine the tower height  $z_T$  for a given set of operating conditions, we must first solve (8.54) for  $\eta_T$ , then evaluate the integral in (8.53) to find  $z_T$ .

### Example 8.2 Absorption of $\text{SO}_2$ with Chemical Reaction

Let us calculate the tower height  $z_T$  as a function of the water feed rate for gas molar flow rates ranging from 0.006 to 0.015  $\text{kg}\cdot\text{mol m}^{-2} \text{s}^{-1}$ . Let  $y_0 = 0.2$ ,  $y_1 = 0.01$ , and  $\text{pH}_0 = 11$ . Consider water volumetric flow rates from 20 to 30  $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$ . We use the correlation for  $k_y a$  from Example 8.1.

Figure 8.6 shows  $z_T$  as a function of  $W$  for  $G_0$  values ranging from 0.006 to 0.015  $\text{kg}\cdot\text{mol m}^{-2} \text{s}^{-1}$ . We see that at each gas flow rate, there is a liquid flow rate below which the specified separation cannot be achieved. As  $G_0$  increases, the value of this liquid flow rate also increases. Figure 8.7 shows  $z_T$  as a function of  $\text{pH}_0$  and  $G_0$ . For all gas flow rates, there is a  $\text{pH}_0$  value below which the required length does not change (e.g.,  $\text{pH}_0 = 11$  at  $G_0 = 0.009 \text{ kg}\cdot\text{mol m}^{-2} \text{s}^{-1}$ , since the capacity of the water is saturated). Very high values of  $\text{pH}_0$  promote more absorption and decrease the required scrubber length.



**Figure 8.6** Scrubber height as a function of water flow rate at several gas flow rates. Conditions are:  $T = 303 \text{ K}$ ,  $p = 1 \text{ atm}$ ,  $\text{pH}_0 = 11$ ,  $y_0 = 0.2$ ,  $y_1 = 0.01$ ,  $k_y a = 0.09944 \bar{L}^{0.25} \bar{G}^{0.7}$ .

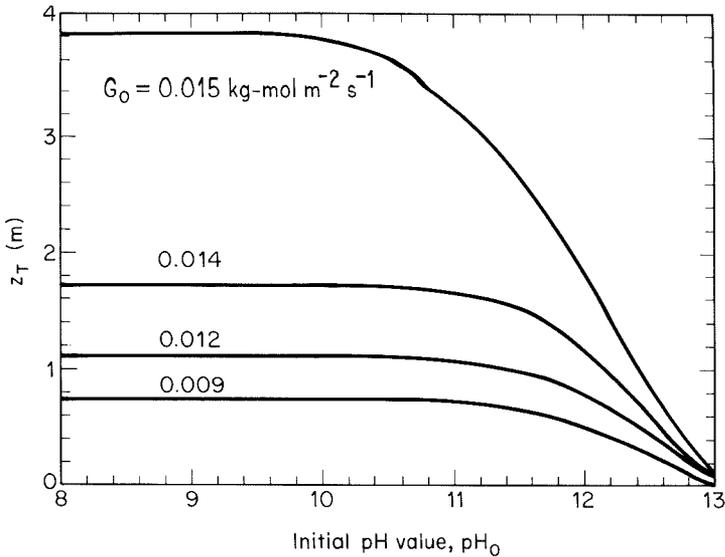


Figure 8.7 Scrubber height as a function of  $\text{pH}_0$  at several gas flow rates.  $W = 40 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ .

### 8.3 ADSORPTION OF GASES ON SOLIDS

Adsorption involves the use of a solid substrate to remove the contaminant. The intermolecular attractive forces in the bulk of a solid are, at its surface, available for holding other materials, such as gases and liquid. In adsorption, the thermal motion of a gas molecule is converted to heat as the molecule becomes bound to the surface. Adsorption is, therefore, an exothermic process. Conversely, regeneration of the adsorbent (or sorbent) by desorption of the adsorbed gas (the adsorbate or sorbate) is endothermic and energy must be supplied. Some adsorption processes occur so strongly that the adsorbed material can only be desorbed by removal of some of the solid substrate. In such a case, chemical bonds form between the adsorbent and the adsorbed species, and the adsorption process is referred to as chemisorption. For example, oxygen chemisorbed on activated carbon can only be removed as CO or CO<sub>2</sub>. Adsorption is particularly well suited to treating large volumes of gases with very dilute pollutant levels and to removing contaminants down to trace levels. The solids best suited for use as adsorbents are those with large surface/volume ratios, that is, very porous. Polar adsorbents such as activated aluminas, silica gels, and molecular sieves have high selectivity for polar gases. Such adsorbents also effectively remove water, a polar molecule, and thus in the presence of moisture can become ineffective due to the relatively large amount of water that is adsorbed. Activated carbon is a second class of adsorbent that is commonly used. Since activated carbon is composed largely of neutral atoms of a single species, there are no significant potential gradients to attract and orient polar molecules in preference to non-polar molecules. Activated carbon tends to adsorb all gases roughly in proportion to

their concentrations. Adsorption is usually carried out in a bed packed with a granular adsorbent sized to produce as little resistance to a flow as possible.

Potential adsorbents can be classified into three groups:

1. Nonpolar solids, where the adsorption is mainly physical
2. Polar solids, where the adsorption is chemical and no change in the chemical structure of the molecules or the surface occurs
3. Chemical adsorbing surfaces, which adsorb the molecules and then release them after reaction, which may be either catalytic, leaving the surface unchanged, or noncatalytic, requiring replacement of the surface atoms

The most important nonpolar adsorbing solid is carbon, which is very effective in binding nonpolar molecules, such as hydrocarbons. Activated carbon (charcoal, if the source is wood) is made by the decomposition of coals and woods. Activated carbon is used for the removal of hydrocarbons, odors, and trace impurities from gas streams.

The polar adsorbents generally used are oxides, either of silicon or other metals (e.g., aluminum). These materials adsorb both polar and nonpolar molecules, but they exhibit preference for polar molecules. Thus silicon and aluminum oxides are used to adsorb polar molecules such as water, ammonia, hydrogen sulfide, and sulfur dioxide.

The equilibrium characteristics of a solid-gas system are described by a curve of the concentration of adsorbed gas on the solid as a function of the equilibrium partial pressure of the gas at constant temperature. Such a curve is called an *adsorption isotherm*. In the case in which only one component of a binary gas mixture is adsorbed, the adsorption of that species is relatively uninfluenced by the presence of the other gas, and the adsorption isotherm for the pure vapor is applicable as long as the equilibrium pressure is taken as the partial pressure of the adsorbing gas.

Separation of one component from a gaseous mixture by adsorption on a solid may be carried out in a batchwise or continuous manner of operation. Continuous operation can, in turn, be employed in a series of distinct stages or in continuous contact, such as in gas absorption. When one component is being adsorbed, the design of the operation is, from the point of view of the calculational procedure, analogous to gas absorption, in that only one component is transferred between two essentially immiscible phases. A rather thorough treatment of gas adsorption operations is given by Treybal (1968). We consider here only the process of adsorption of a species as the gas is passed through a stationary (fixed) bed of adsorbent.

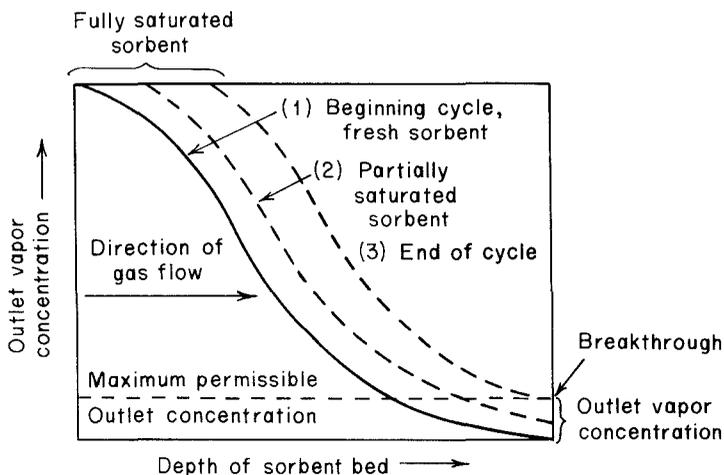
The key difference between gas absorption with two continuous countercurrent streams and gas adsorption in a fixed bed is that the former is a steady-state process, whereas the latter, due to the accumulation of adsorbed gas on the solid, is an unsteady-state process.

We will consider a mixture of two gases, one strongly adsorbed, which is to be passed through a bed initially free of adsorbent. When the mixture first enters the fresh bed, the solid at the entrance to the bed at first adsorbs the gas almost completely. Thus, initially the gas leaving the bed is almost completely free of the solute gas. As the layers of solid near the entrance to the bed become saturated with adsorbed gas, the zone of

solid in which the major portion of the adsorption takes place moves slowly through the bed, at a rate generally much slower than the actual gas velocity through the bed. Finally, the so-called adsorption zone reaches the end of the bed. At this point, the exit concentration of solute gas rises sharply and approaches its inlet concentration, since, for all practical purposes, the bed is saturated and at equilibrium with the inlet gas. The curve of effluent concentration as a function of time thus has an S-shaped appearance that may be steep or relatively flat, depending on the rate of adsorption, the nature of the adsorption equilibrium, the fluid velocity, the inlet concentration, and the length of the bed. The time at which the breakthrough curve first begins to rise appreciably is called the breakpoint. The passage of an adsorption wave through a stationary bed during an adsorption cycle is depicted in Figure 8.8.

When a bed reaches saturation, the adsorbed material must be removed from the solid. Desorption of an adsorbed solute by passing a solvent through the bed is called *elution*. The process of gas chromatography is based on the elution of a bed that contains small quantities of several adsorbed gases. As a suitable eluent is passed through such a bed, the adsorbed solutes are desorbed at different rates and pass out of the bed at different times, enabling their identification by comparison with eluent curves previously established for known species.

The design of a fixed-bed adsorption column would normally require that one predict the breakthrough curve, and thus the length of the adsorption cycle between elutions of the bed, given a bed of certain length and equilibrium data. Alternatively, one could seek the bed depth required for operation over a specified period of time to achieve a desired degree of separation. Because of the different types of equilibrium relationships that can be encountered and the unsteady nature of the process, prediction of the solute breakthrough curve is, in general, quite difficult. We present here a design method applicable only when the solute concentration in the feed is small, the adsorption isotherm



**Figure 8.8** Passage of an adsorption wave through a stationary bed during an adsorption cycle.

is concave to the gas-phase concentration axis, the adsorption zone is constant in height as it travels through the column, and the length of the column is large compared with the height of the adsorption zone (Treybal, 1968).

Let us consider the idealized breakthrough curve shown in Figure 8.9 resulting from flow of an inert gas through a bed with a rate  $\tilde{G}'$  kg m<sup>-2</sup> h<sup>-1</sup> containing an inlet solute concentration of  $Y_0$  kg solute/kg inert gas. The total amount of solute-free gas that has passed through the bed up to any time is  $w$  kg m<sup>-2</sup> of bed cross section. Values  $Y_B$  and  $Y_E$ , shown in Figure 8.9, mark the breakpoint and equilibrium concentrations, respectively;  $w_B$  and  $w_E$  denote the values of  $w$  at  $Y_B$  and  $Y_E$ , respectively. The adsorption zone, taken to be of constant height  $z_a$ , is that part of the bed in which the concentration profile from  $Y_B$  to  $Y_E$  exists at any time.

If  $\theta_a$  and  $\theta_E$  are the times required for the adsorption zone to move its own length and down the entire bed, respectively, then

$$\theta_a = \frac{w_a}{\tilde{G}'} \quad (8.55)$$

and

$$\theta_E = \frac{w_E}{\tilde{G}'} \quad (8.56)$$

If  $\theta_F$  is the time required for the adsorption zone to form, and if  $z$  is the length of the bed,

$$z_a = z \frac{\theta_a}{\theta_E - \theta_F} \quad (8.57)$$

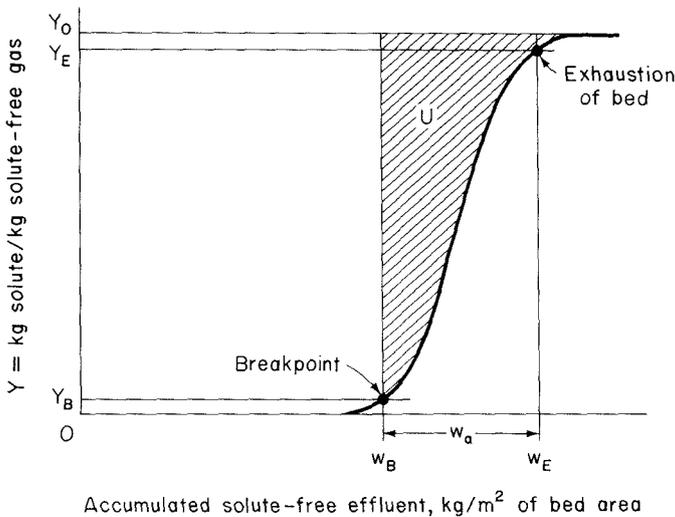


Figure 8.9 Typical breakthrough curve for adsorption of a gas on a solid.

The solute removed from the gas in the adsorption zone is  $U$  kg  $m^{-2}$  of bed cross section;  $U$  is shown in Figure 8.9 by the shaded area, which is

$$U = \int_{w_B}^{w_E} (Y_0 - Y) dw \tag{8.58}$$

If all the adsorbent in the zone were saturated, the solid would contain  $Y_0 w_a$  kg solute  $m^{-2}$ . Thus the fractional capacity of the adsorbent in the zone to continue adsorbing solute is  $f = U/Y_0 w_a$ . The shape of the breakthrough curve is thus characterized by  $f$ . If  $f = 0$ , the time of formation  $\theta_F$  of the zone should be the same as the time required for the zone to travel its own thickness,  $\theta_a$ , since the breakthrough curve will be a vertical line. If  $f = 1$ , the time to establish the zone should be zero. To satisfy these two limiting cases, one sets  $\theta_F = (1 - f)\theta_a$ . Thus (8.57) becomes

$$z_a = z \frac{\theta_a}{\theta_E - (1 - f)\theta_a} = z \frac{w_a}{w_E - (1 - f)w_a} \tag{8.59}$$

If the column contains  $z A_c \rho_s$  kg of adsorbent, where  $A_c$  is the cross-sectional area of the bed and  $\rho_s$  is the solid density in the bed, at complete saturation the bed would contain  $z A_c \rho_s X_T$  kg of solute, where  $X_T$  is the solute concentration on the solid in equilibrium with the feed. At the breakpoint,  $z - z_a$  of the bed is saturated, and  $z_a$  of the bed is saturated to the extent of  $1 - f$ . The degree of overall bed saturation at the breakpoint is thus

$$\alpha = \frac{(z - z_a)\rho_s X_T A_c + z_a \rho_s (1 - f) X_T A_c}{z \rho_s X_T A_c} = \frac{z - fz_a}{z} \tag{8.60}$$

The determination of the breakthrough curve can be carried out in the following way. Let us consider the adsorption column in Figure 8.10, where the adsorption zone  $z_a$  is in the column, and the solute composition in the gas is  $Y_0$  and 0 at the entrance and

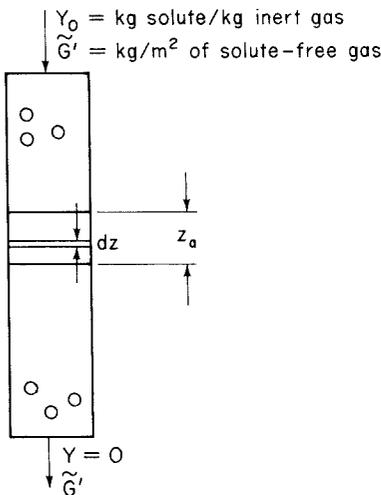


Figure 8.10 Fixed-bed adsorber with adsorption zone of depth  $z_a$ .

exit, respectively. Corresponding to these gas-phase compositions, we assume that those on the solid are  $X_T$  (saturation at the entrance to the column) and 0 (no adsorbed solute at the exit). If the column is considered to be infinitely long, the situation depicted in Figure 8.10 is applicable. This point will not really concern us since our only real interest is in the adsorption zone  $z_a$ . The operating line, which relates  $Y$  and  $X$  at any point in the column, is then a straight line connecting the origin with the point  $(Y_0, X_T)$  on the equilibrium curve.

Over a differential depth  $dz$  in  $z_a$  the rate of adsorption is

$$\tilde{G}' dY = K_Y a (Y - Y^*) dz \quad (8.61)$$

where  $K_Y a$  is the overall mass transfer coefficient for transfer from gas to solid phase. Thus, over the adsorption zone,

$$z_a = \frac{\tilde{G}'}{K_Y a} \int_{Y_B}^{Y_E} \frac{dY}{Y - Y^*} \quad (8.62)$$

and for any value of  $z$  less than  $z_a$ , but within the zone,

$$\frac{z}{z_a} = \frac{w - w_B}{w_a} = \frac{\int_{Y_B}^Y dY / (Y - Y^*)}{\int_{Y_B}^{Y_E} dY / (Y - Y^*)} \quad (8.63)$$

The breakthrough curve can be plotted directly from (8.63).

Table 8.3 lists the various types of adsorption equipment, together with brief comments on their operation and use.

### Example 8.3 Adsorption of Benzene from Air

Benzene vapor present to the extent of 0.025 kg benzene/kg air (benzene-free basis) is to be removed by passing the gas mixture downward through a bed of silica gel at 298 K and 2 atm pressure at a linear velocity of  $1 \text{ m s}^{-1}$  (based on the total cross-sectional area). It is desired to operate for 90 min. The breakpoint will be considered as that time when the effluent air has a benzene content of 0.0025 kg benzene/kg air, and the bed will be considered exhausted when the effluent air contains 0.020 kg benzene/kg air. Determine the depth of bed required.

Silica gel has a bulk density of  $625 \text{ kg m}^{-3}$  and an average particle diameter  $D_p$  of 0.60 cm. For this temperature, pressure, and concentration range, the adsorption isotherm is

$$Y^* = 0.167X^{1.5}$$

where  $Y^* = \text{kg benzene/kg air (benzene-free basis)}$  and  $X = \text{kg benzene/kg gel}$ . We assume that the height of a gas-phase transfer unit is given by

$$H_{0Y} = 0.00237 \left( \frac{D_p \tilde{G}'}{\mu_{\text{air}}} \right)^{0.51}$$

The cross-sectional area of the bed is  $1 \text{ m}^2$ .

TABLE 8.3 TYPES OF ADSORPTION EQUIPMENT

Type	Operation and use
Disposable and rechargeable canisters	Small flow; effluent with low sorbate concentration.
Fixed regenerable beds	When volume of flow or sorbate concentration is high enough to make recovery attractive, or when cost of fresh sorbent is expensive.
Shallow beds	Large gas volumes of low pollutant concentration.
Deep beds	When pollutant concentrations exceed 100 ppm or flow exceeds $4.7 \text{ m}^3 \text{ s}^{-1}$ ; typically, 0.3-1 m thick.
Traveling bed	Freshly regenerated adsorbent is added continuously to the top of the bed at a rate to maintain a constant solid depth. Saturated sorbent is continuously removed from the bottom of the bed and regenerated before return to the top. Gas to be treated enters the bottom and passes countercurrent to the slowly moving sorbent. Used for high concentrations of sorbates requiring high sorbent to gas ratio.
Fluid bed	Particles continuously removed and regenerated to maintain bed particles relatively unsaturated. Use for adsorption of organics from a moist stream where continuous carbon regeneration is needed.
Chromatographic baghouse	Granular adsorbent introduced continuously into the gas stream which conveys the particles through a line of sufficient length to provide appreciable contact. Sorbent removed in a baghouse.

First, we can compute  $H_{0Y}$ . The density of air at 298 K and 2 atm is  $2.38 \text{ kg m}^{-3}$ , and so  $\bar{G}' = 2.38 \text{ kg m}^{-2} \text{ s}^{-1}$ . The viscosity of air at 298 K is  $1.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ . Thus  $H_{0Y} = 0.071 \text{ m}$ .

The adsorption isotherm is shown in Figure 8.11. The operating line has been drawn to intersect the equilibrium curve at  $Y_0 = 0.025$ . From the problem specifications,  $Y_B = 0.0025$  and  $Y_E = 0.020$ . From Figure 8.11 we see that  $X_T = 0.284$ .

The integral in (8.62) can be evaluated numerically (see Table 8.4) as 5.925. Thus

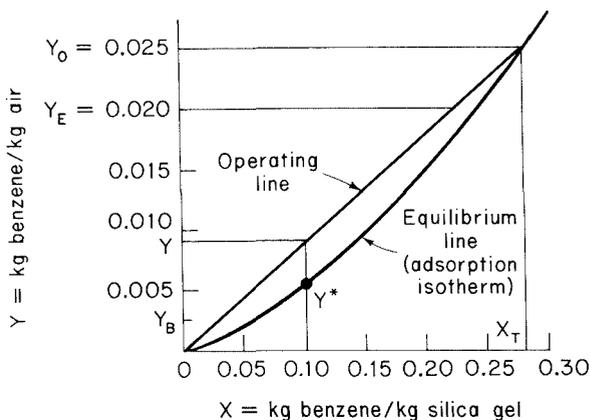


Figure 8.11 Equilibrium and operating lines for adsorption of benzene on silica gel.

TABLE 8.4 NUMERICAL EVALUATION OF INTEGRAL IN (8.62)

$Y$	$Y^*$	$Y - Y^*$	$\frac{1}{Y - Y^*}$	$\int_{Y_B}^{Y_E} \frac{dY}{Y - Y^*}$	$\frac{w - w_B}{w_a}$	$\frac{Y}{Y_0}$
0.0025	0.0009	0.0016	625		0	0.01
0.0050	0.0022	0.0028	358	1.1375	0.192	0.2
0.0075	0.0042	0.0033	304	1.9000	0.321	0.3
0.0100	0.0063	0.0037	270	2.6125	0.441	0.4
0.0125	0.0089	0.0036	278	3.3000	0.556	0.5
0.0150	0.0116	0.0034	294	4.0125	0.676	0.6
0.0175	0.0148	0.0027	370	4.8375	0.815	0.7
0.0200	0.0180	0.0020	500	5.9250	1.00	0.8

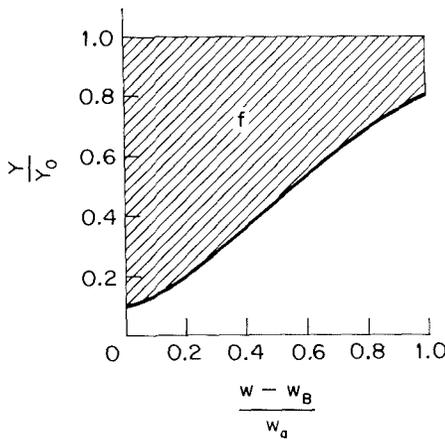


Figure 8.12 Breakthrough curve for adsorption of benzene on silica gel.

the height of the adsorption zone  $z_a$  is  $0.071 \times 5.925 = 0.42$  m. The extent of saturation,

$$f = \frac{\int_{w_B}^{w_E} (Y_0 - Y) dw}{Y_0 w_a} = \int_0^1 \left(1 - \frac{Y}{Y_0}\right) d \frac{w - w_B}{w_a}$$

is found to be 0.55. This quantity is shown in Figure 8.12.

Let us suppose the height of the bed is  $z$  meters. The degree of saturation of the bed at the breakpoint is  $\alpha = (z - 0.231)/z$ . The bed area is  $1 \text{ m}^2$ ; the apparent density of the packing is  $625 \text{ kg m}^{-3}$ ; thus the mass of the bed is  $625z$  kg. The mass of benzene adsorbed on the gel is then

$$625z \frac{z - 0.231}{z} 0.284 = 177(z - 0.231)$$

The mass of benzene that must be removed from the air over a 90-min period is 322 kg. Equating this mass removed with that on the packing at the breakpoint,

$$177(z - 0.231) = 322$$

we obtain the required bed depth of 2.04 m.

## 8.4 REMOVAL OF SO<sub>2</sub> FROM EFFLUENT STREAMS

As noted in Chapter 1, SO<sub>2</sub> is emitted from coal-fired power plants (about two-thirds of U.S. emissions), from industrial fuel combustion, sulfuric acid manufacturing, and smelting of nonferrous metals. The two basic approaches to SO<sub>2</sub> emission control are (1) to remove the sulfur from the fuel before it is burned, or (2) to remove SO<sub>2</sub> from the exhaust gases. There has been a significant amount of effort expended in the United States and worldwide on the development of processes in both categories. We will concentrate here on methods for the removal of SO<sub>2</sub> from exhaust gases.

The technical and economic feasibility of an SO<sub>2</sub> removal process depends on the type and quantity of effluent gases that must be cleaned. With regard to SO<sub>2</sub> removal, there are essentially two types of effluent gas treatment problems. The first is the problem of removing SO<sub>2</sub> from power plant flue gases. Power plant flue gases generally contain low concentrations of SO<sub>2</sub> (<0.5% by volume), but emitted at tremendous volumetric flow rates. For example, a coal-fired power plant burning 2% sulfur coal (by weight) will produce 40,000 kg of SO<sub>2</sub> for every 10<sup>6</sup> kg of coal burned. The second class of SO<sub>2</sub> effluent gas treatment problems comprises those resulting from the need to remove SO<sub>2</sub> from streams containing relatively high concentrations of SO<sub>2</sub> at low flow rates. Streams of this type are typical of those emitted from smelter operations. A smelter emission gas typically contains SO<sub>2</sub> at a concentration of about 10% by volume (100,000 ppm).

In this section we concentrate largely on the problem of SO<sub>2</sub> removal from power plant flue gases, so-called flue gas desulfurization (FGD), since it represents a more prevalent and, in many respects, the more difficult problem than that of SO<sub>2</sub> removal from smelting and other industrial operations. Elliot et al. (1982) have reviewed a number of processes for the cleaning of smelter gases, and we refer the reader to this source for those applications.

There are two ways of classifying flue gas desulfurization systems. The first is based on what is done with the SO<sub>2</sub>-absorbing or SO<sub>2</sub>-reacting medium, and by this means processes are categorized as *throwaway* or *regenerative*. In a throwaway process, the sulfur removed, together with the absorbing or reacting medium, is discarded. A process is regenerative if the sulfur is recovered in a usable form and the medium is reused. The second way of classifying FGD processes is by the phase in which the main removal reactions occur. By this means processes are categorized as *wet* or *dry*. Both wet and dry processes can be throwaway or regenerative, so there are, in effect, four categories of FGD processes.

In the majority of the throwaway processes an alkaline agent reacts with the SO<sub>2</sub>, leading to a product that is discarded. Commonly used agents in this type of process are limestone (CaCO<sub>3</sub>) and lime (CaO). In another type of throwaway process the agent is injected directly into the furnace, and the sulfated product is subsequently scrubbed out of the flue gas with water. Part of the SO<sub>2</sub> is captured chemically within the furnace, the rest in the scrubbing step.

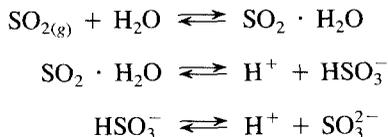
In the regenerative alkaline processes, an alkaline agent strips SO<sub>2</sub> from the flue gas stream, combining chemically with the SO<sub>2</sub>. In a separate regeneration step, the agent is reconstituted and sulfur is recovered, usually as liquid SO<sub>2</sub> or sulfuric acid.

Some of the agents used include  $\text{MgO}$ ,  $\text{Na}_2\text{SO}_3$ , and metal carbonates. Regenerative solid adsorption comprises several activated char processes, in which  $\text{SO}_2$  is adsorbed on char and desorbed to lead to the production of sulfuric acid.

### 8.4.1 Throwaway Processes: Lime and Limestone Scrubbing

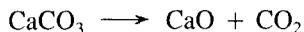
The most prevalent throwaway processes involve lime and limestone. Approximately 75% of all installed flue gas desulfurization systems use a lime or limestone slurry as the scrubbing liquor (Joseph and Beachler, 1981; Beachler and Joseph, 1984). In this process  $\text{SO}_2$  reacts with the lime or limestone slurry to form a  $\text{CaSO}_3/\text{CaSO}_4$  sludge that must be disposed of in a pond or landfill. Most wet scrubbing flue gas desulfurization systems are capable of reducing  $\text{SO}_2$  emissions by 90%. In dry scrubbing an alkaline slurry is injected in a spray dryer with dry particle collection. Spray dryers are units where hot flue gases are contacted with a fine, wet, alkaline spray, which absorbs the  $\text{SO}_2$ . The high temperature of the flue gas (393 to 573 K) evaporates the water from the alkaline spray, leaving a dry product that can be collected in a baghouse or electrostatic precipitator. Dry scrubbing can remove 75 to 90% of  $\text{SO}_2$  emissions.

In conventional limestone or lime scrubbing, a limestone/water or lime/water slurry is contacted with the flue gas in a spray tower. The essence of the process lies in the absorption equilibrium of  $\text{SO}_2$  in water as given in Table 8.2:



Limestone consists of a mixture of  $\text{CaCO}_3$  and inert siliceous compounds. Although limestone is very plentiful, it has been estimated that only about 2% of the deposits are of "chemical grade," that is, containing 95% or more  $\text{CaCO}_3$ . Calcium carbonate is relatively insoluble in water (0.00153 g per 100 g of  $\text{H}_2\text{O}$  at 273 K), and its solubility increases only slightly with increasing temperature. Although its low solubility is one of its main drawbacks for use in wet scrubbing, it can be finely pulverized to produce a limestone/water slurry.

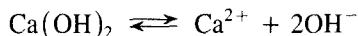
Lime ( $\text{CaO}$ , calcium oxide) can be obtained by heating (calcining)  $\text{CaCO}_3$  at about 1100 K:



When added to water, lime produces calcium hydroxide (slaked lime):

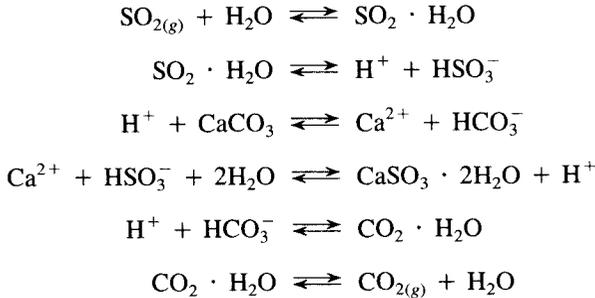


which dissociates according to

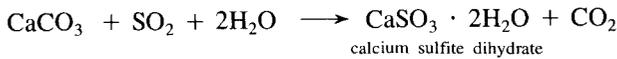


While still relatively insoluble (0.185 g per 100 g of H<sub>2</sub>O at 273 K), Ca(OH)<sub>2</sub> is considerably more soluble than CaCO<sub>3</sub>. The solubility of Ca(OH)<sub>2</sub> decreases as the temperature increases (0.078 g per 100 g of H<sub>2</sub>O at 373 K).

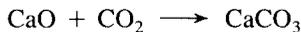
A chemical mechanism that is consistent with the overall stoichiometry of limestone scrubbing is



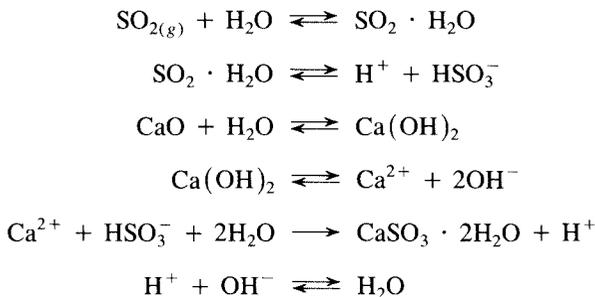
The overall reaction corresponding to this mechanism is



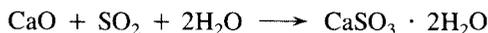
Two routes have been proposed for the mechanism of lime scrubbing. The first simply involves the conversion of the CaO to CaCO<sub>3</sub> by reacting with CO<sub>2</sub> in the flue gas,



in which case the mechanism for limestone above would also apply for lime. The second route involves the chemistry of lime itself:



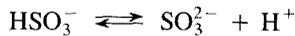
The overall reaction corresponding to this mechanism is



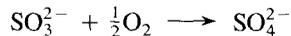
Lime is more reactive toward SO<sub>2</sub> than is limestone, although both are highly favorable reactants. In spite of the fact that lime scrubbing can achieve higher SO<sub>2</sub> removal efficiencies than limestone scrubbing, lime is more expensive and hence is not as widely in use as limestone. The critical step in both mechanisms is the formation of the

calcium ion, which reacts with the bisulfite ion to remove  $\text{SO}_2$  from the solution. We note that in the limestone system the formation of  $\text{Ca}^{2+}$  depends on the  $\text{H}^+$  concentration, whereas in the lime system the  $\text{Ca}^{2+}$  formation step is independent of pH. Thus, in order to drive the  $\text{H}^+ - \text{CaCO}_3$  reaction to the right, the limestone system must operate at a fairly high  $\text{H}^+$  concentration (low pH). The optimal operating pH for limestone scrubbing is between 5.8 and 6.2, whereas that for lime scrubbing is about 8.0.

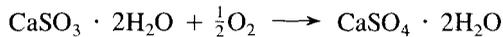
There is an additional problem related to the setting of the pH in lime and limestone scrubbing—the formation of calcium sulfate. Although the reaction was not used in either of the chemical mechanisms above, we know that the bisulfite ion is in equilibrium with the sulfite ion:



(Although it was not necessary to consider this reaction to explain the mechanism of  $\text{SO}_2$  removal, for lime scrubbing this reaction should be added due to the high pH employed.) Excess oxygen in the flue gas can lead to some dissolved oxygen in the slurry. The sulfite ion can be oxidized by dissolved  $\text{O}_2$  to the sulfate ion:



When this reaction occurs, the net result is conversion of  $\text{CaSO}_3$  to  $\text{CaSO}_4$ :



Calcium sulfate (gypsum) forms a hard, stubborn scale on the surface of the scrubber, and its formation must be avoided.

The solubility of  $\text{CaSO}_3$  increases markedly as the pH decreases (100 ppm at pH 5.8 and 1000 ppm at pH 4.4). Thus the rate of oxidation of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  increases as pH decreases. The  $\text{CaSO}_4$  formed by the oxidation has a solubility that decreases slightly as pH decreases. Because of both of these factors, but primarily the increased solubility of  $\text{CaSO}_3$  at low pH,  $\text{CaSO}_4$  precipitation occurs at low pH. Thus the pH must be kept sufficiently high to prevent  $\text{CaSO}_4$  scale formation. Limestone scrubbing systems operating at a pH around 6.0 can successfully avoid  $\text{CaSO}_4$  scale formation.

We noted that the optimal pH from the point of view of  $\text{Ca}^{2+}$  formation in lime scrubbing is about 8.0. At high pHs, however, the low solubility of  $\text{CaSO}_3$  leads to a phenomenon known as soft pluggage, the formation of large leafy masses of  $\text{CaSO}_3$  inside the scrubber. The soft pluggage can be dissolved by lowering the pH to promote  $\text{CaSO}_3$  solubility. As long as a pH of 8.0 is not exceeded, lime scrubbing can avoid soft pluggage.

Because neither lime nor limestone is particularly soluble, the liquid/gas ratio must be relatively high. For limestone scrubbing this ratio must exceed 65 gal per 1000  $\text{ft}^3$  of gas (0.0088  $\text{m}^3$  water per  $\text{m}^3$  of gas). For lime systems a liquid/gas ratio of 35 gal per 1000  $\text{ft}^3$  is adequate (0.0047  $\text{m}^3$  water per  $\text{m}^3$  of gas) due to the higher solubility of lime.

The scrubbing solution is sent from the tower to a retention tank where the precipitation of  $\text{CaSO}_3$ ,  $\text{CaSO}_4$ , and unreacted  $\text{CaCO}_3$  occurs. The residence time needed in the retention tank is about 5 min for a lime system and 10 min for limestone. The crystallized products from the retention tank constitute the waste sludge. Typical waste sludge compositions are given in Table 8.5.

**TABLE 8.5** TYPICAL COMPOSITIONS OF LIME AND LIMESTONE SCRUBBING WASTE SLUDGES

Compound	Percent dry weight
Limestone systems	
CaCO <sub>3</sub>	33
CaSO <sub>3</sub> · 2H <sub>2</sub> O	58
CaSO <sub>4</sub> · 2H <sub>2</sub> O	9
	100
Lime systems	
CaCO <sub>3</sub>	5
CaSO <sub>3</sub> · 2H <sub>2</sub> O	73
CaSO <sub>4</sub> · 2H <sub>2</sub> O	11
Ca(OH) <sub>2</sub>	11
	100

Source: Fellman and Cheremisinoff (1977).

The main problems with lime and limestone scrubbing are scaling and plugging inside the scrubber unit. The *dual alkali* system eliminates these problems. A solution of sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>)/sodium hydroxide (NaOH) is sprayed in the tower. Sulfur dioxide is absorbed and neutralized in the solution, and since both Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> are soluble in water, no precipitation occurs in the scrubber. The Na<sub>2</sub>SO<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> solution from the scrubber cannot simply be discarded because of water pollution problems and because NaOH is relatively expensive. Thus, in a separate tank, lime or limestone and some additional NaOH are added to the scrubbing effluent. The lime or limestone precipitates the sulfite and sulfate and regenerates the NaOH.

There are several dry throwaway processes. As mentioned earlier, a wet lime slurry can be injected into the tower, and SO<sub>2</sub> is absorbed by the droplets forming CaSO<sub>3</sub> and CaSO<sub>4</sub>. If the liquid/gas ratio is low enough, the water will evaporate before the droplets reach the bottom of the tower. The dry particles are subsequently collected, usually in a baghouse.

Direct injection of pulverized lime or limestone into the boiler has been demonstrated as an effective means of SO<sub>2</sub> removal. The SO<sub>2</sub> is adsorbed on the dry particles, and the dry SO<sub>2</sub>-laden particles are collected in a baghouse. The smaller the particle size, the more efficient the removal process.

**Example 8.4 pH Control in Lime Scrubbing (Shinsky, 1977)**

We noted above that the optimal pH for lime scrubbing of SO<sub>2</sub> is about 8.0. Let us see how this value can be determined. The idea is to determine the pH at which all of the SO<sub>2</sub> is converted to product.

The ions present in the lime scrubbing system must obey charge neutrality,

$$[H^+] + 2[Ca^{2+}] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}]$$

where we have included the sulfite ion, SO<sub>3</sub><sup>2-</sup>, for completeness. The equilibria involving sulfur compounds and water were given in Table 8.2. The additional one needed is the solubility product of CaSO<sub>3</sub>,

$$[Ca^{2+}][SO_3^{2-}] = K_s$$

Substituting the equilibrium expressions into the electroneutrality relation yields

$$\left(1 + \frac{2K_{s2}}{[H^+]}\right)[HSO_3^-]^2 + \left(\frac{K_w}{[H^+]} - [H^+]\right)[HSO_3^-] - \frac{2K_s[H^+]}{K_{s2}} = 0$$

This quadratic equation can be solved for  $[HSO_3^-]$  given a value of  $[H^+]$ , or pH, since  $[H^+] = 10^{-pH}$ .

Shinsky (1977) has carried out this solution and obtained

pH	$[HSO_3^-]$ (M)
3	0.159
4	0.050
5	0.0156
6	$4.4 \times 10^{-3}$
7	$7.7 \times 10^{-4}$
8	$8.8 \times 10^{-5}$
9	$9.0 \times 10^{-6}$
10	$9.0 \times 10^{-7}$

We now have the bisulfite ion concentration as a function of pH, and we need to connect the pH to the material balance. The total sulfur concentration in solution at any time is

$$[S] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}] + [CaSO_3]$$

Similarly, the total calcium concentration is

$$[Ca] = [Ca^{2+}] + [CaSO_3]$$

We can combine these two and eliminate  $[CaSO_3]$ ,

$$[Ca] - [S] = [Ca^{2+}] - [SO_2 \cdot H_2O] - [HSO_3^-] - [SO_3^{2-}]$$

The  $[Ca^{2+}]$  and  $[SO_3^{2-}]$  terms may be removed by using the electroneutrality relation, to give

$$[Ca] - [S] = \frac{1}{2}([OH^-] - [H^+] - [HSO_3^-]) - [SO_2 \cdot H_2O]$$

The right-hand side may be brought completely in terms of only  $[HSO_3^-]$  and  $[H^+]$  using the equilibrium constant expressions.

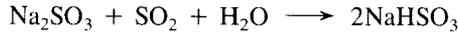
The difference  $[Ca] - [S]$  represents the difference between the reagent added and the absorbed  $SO_2$ . The difference has been computed by Shinsky (1977) as a function of pH:

pH	$[Ca] - [S]$ (M)
3	-0.09
4	-0.025
5	$-7.8 \times 10^{-3}$
6	$-2.2 \times 10^{-3}$
7	$-3.9 \times 10^{-4}$
8	$-4.3 \times 10^{-5}$
9	$5.0 \times 10^{-7}$
10	$5.0 \times 10^{-5}$

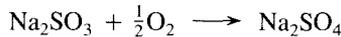
At a pH between 8.0 and 9.0 all the sulfur is predicted to be consumed, and this represents, therefore, the optimal pH for full utilization of the calcium.

### 8.4.2 Regenerative Processes

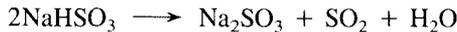
In regenerative processes the sulfur is recovered in a usable form. One of the oldest regenerative FGD processes is the *Wellman-Lord process*. In this process the flue gas is contacted with aqueous sodium sulfite, and the dissolved SO<sub>2</sub> reacts to form sodium bisulfite:



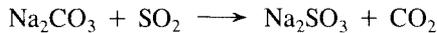
If excess oxygen is present in the flue gas, some of the Na<sub>2</sub>SO<sub>3</sub> is oxidized to sodium sulfate:



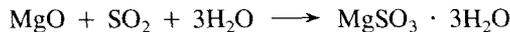
Part of the liquid stream leaving the bottom of the absorber is sent to a crystallizer where Na<sub>2</sub>SO<sub>4</sub>, which is less soluble than Na<sub>2</sub>SO<sub>3</sub>, crystallizes. The Na<sub>2</sub>SO<sub>4</sub> solids are removed and discarded. The remaining liquid is recycled to the process. The remainder of the liquid stream from the absorber is sent to a unit where it is heated:



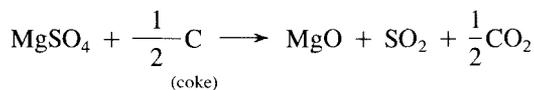
The SO<sub>2</sub> gas produced is quite concentrated (approximately 85% SO<sub>2</sub> and 15% H<sub>2</sub>O) and in that form can be reduced to elemental sulfur or oxidized to sulfuric acid. Finally, because some of the feed sodium is discarded with the Na<sub>2</sub>SO<sub>4</sub>, soda ash (Na<sub>2</sub>CO<sub>3</sub>) is added to the absorption tower to produce more sodium sulfite:



The magnesium oxide (MgO) process involves scrubbing the flue gas with a slurry of MgO and recycled MgSO<sub>3</sub> and MgSO<sub>4</sub>. Absorption takes place by the reactions



The absorbate enters a centrifuge system where the hydrated crystals of MgSO<sub>3</sub> and MgSO<sub>4</sub> are separated from the mother liquor. The liquor is returned to the absorber and the centrifuged wet cake is sent to a dryer. Regeneration takes place upon heating:



The flue gas from the heating step contains about 15 to 16% SO<sub>2</sub>, which can then be used for sulfuric acid production.

The catalytic process converts  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  by passing the flue gases over a vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) catalyst, which oxidizes  $\text{SO}_2$  to  $\text{SO}_3$ , followed by contacting the  $\text{SO}_3$  with water to form  $\text{H}_2\text{SO}_4$ . In the process, gas enters the catalyst bed, after particulate removal, at temperatures of 698 to 728 K. After the catalyst bed, the  $\text{SO}_3$  is contacted with water, and  $\text{H}_2\text{SO}_4$  is condensed. The advantages of the process are that the system is basically simple and catalyst recycle is not necessary. Disadvantages are that expensive, corrosion-resistant materials are needed, the catalyst is easily deactivated by certain particles, and the sulfuric acid produced is usually too dilute to be salable.

## 8.5 REMOVAL OF $\text{NO}_x$ FROM EFFLUENT STREAMS

Stationary source  $\text{NO}_x$  control is based on both modifications in combustion conditions (Chapter 3) and removal of  $\text{NO}_x$  from exhaust gases. Combustion and design modification techniques appear to be the most economical means of achieving substantial  $\text{NO}_x$  emission reductions. It is uncertain, however, whether the  $\text{NO}_x$  emission reductions attainable by use of combustion modification techniques alone can provide the overall level of  $\text{NO}_x$  control necessary to meet ambient air quality standards.

Typical uncontrolled and controlled  $\text{NO}_x$  concentrations in utility boiler flue gases are given in Table 8.6. Flue gas treatment (FGT) methods for  $\text{NO}_x$  removal are generally used together with combustion modifications. In Table 8.6 the flue gas treatment method indicated is selective catalytic reduction, a method that we will discuss shortly. To achieve an excess of 90%  $\text{NO}_x$  reduction, the combination of combustion modifications (to reduce 35 to 50% of the  $\text{NO}_x$  emissions) and FGT, such as by selective catalytic reduction (to remove 80 to 85% of the remaining  $\text{NO}_x$ ) is generally more economical than FGT alone.

For a number of reasons,  $\text{NO}_x$  removal from flue gases is more difficult than  $\text{SO}_2$  removal, and, as a result, technology for  $\text{NO}_x$  cleaning of flue gases is not as advanced as that for  $\text{SO}_2$ . The key problem is that  $\text{NO}$ , the principal  $\text{NO}_x$  species in flue gas, is relatively insoluble and unreactive. In addition, flue gases containing  $\text{NO}$  often also contain  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$  in greater concentrations than  $\text{NO}$ . These species are more reactive than  $\text{NO}$  and interfere with its removal.

**TABLE 8.6** UNCONTROLLED AND CONTROLLED  $\text{NO}_x$  CONCENTRATIONS (ppm) IN UTILITY BOILER FLUE GAS

Fuel	Without control	With combustion modifications	With combustion modifications and selective catalytic reduction
Gas	200	50	10
Oil	300	100	20
Coal	600	250	50

Source: Ando (1983).

### 8.5.1 Shell Flue Gas Treating System

There is at this time at least one commercially demonstrated dry simultaneous NO<sub>x</sub>/SO<sub>x</sub> removal process, the Shell Flue Gas Treating System. This process was originally designed for SO<sub>2</sub> control but was found also to be adaptable for NO<sub>x</sub> control (Mobley, 1979). Flue gas is introduced at 673 K into two or more parallel passage reactors containing copper oxide (CuO) supported on alumina (Al<sub>2</sub>O<sub>3</sub>), where the SO<sub>2</sub> reacts with the copper oxide to form copper sulfate (CuSO<sub>4</sub>):



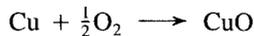
The CuSO<sub>4</sub> and, to a lesser extent, the CuO act as catalysts in the reduction of NO with added ammonia,



When the reactor is saturated with copper sulfate, the flue gas is switched to a fresh reactor, and the spent reactor is regenerated. In the regeneration cycle, hydrogen is used to reduce the copper sulfate to copper,



producing an SO<sub>2</sub> stream of sufficient concentration for conversion to sulfur or sulfuric acid. The copper is then oxidized back to copper oxide,



The process can be operated in the NO<sub>x</sub>-only mode by eliminating the regeneration cycle or in the SO<sub>x</sub>-only mode by eliminating the ammonia injection.

### 8.5.2 Wet Simultaneous NO<sub>x</sub>/SO<sub>x</sub> Processes

Although wet NO<sub>x</sub> removal processes do not as yet compete economically with dry NO<sub>x</sub> processes, wet simultaneous NO<sub>x</sub>/SO<sub>x</sub> processes may be competitive with the sequential installation of dry NO<sub>x</sub> control followed by SO<sub>2</sub> control by flue gas desulfurization (FGD). The first wet simultaneous NO<sub>x</sub>/SO<sub>x</sub> systems, called oxidation/absorption/reduction processes, evolved from FGD systems (Mobley, 1979). Since the NO is relatively insoluble in aqueous solutions, a gas-phase oxidant, such as ozone (O<sub>3</sub>) or chlorine dioxide (ClO<sub>2</sub>), is injected before the scrubber to convert NO to the more soluble NO<sub>2</sub>. The absorbent then forms, with SO<sub>2</sub>, a sulfite ion that reduces a portion of the absorbed NO<sub>x</sub> to N<sub>2</sub>. The remaining NO<sub>x</sub> is removed from the wastewater as nitrate salts, while the remaining sulfite ions are oxidized to sulfate by air and removed as gypsum. Oxidation/absorption/reduction processes have the potential to remove 90% of both SO<sub>x</sub> and NO<sub>x</sub> from combustion flue gas. However, the use of a gas-phase oxidant is expensive. Chlorine dioxide, although cheaper than ozone, adds to the wastewater problems created by the nitrate salts.

Absorption/reduction processes circumvent the need for use of a gas-phase oxidant

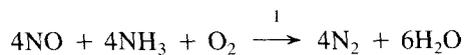
TABLE 8.7 COMPARISON OF DRY NO<sub>x</sub> AND WET SIMULTANEOUS NO<sub>x</sub>/SO<sub>2</sub> SYSTEMS

	Advantages	Disadvantages
Dry NO <sub>x</sub>	Low capital investment Simple process High NO <sub>x</sub> removal efficiency (>90%) Extensive tests in large units No waste stream generated	Sensitive to inlet particulate levels Requires ammonia Possible emission of NH <sub>3</sub> and (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Relative high temperatures (573 to 673 K)
Wet NO <sub>x</sub> /SO <sub>2</sub>	Simultaneous NO <sub>x</sub> /SO <sub>2</sub> removal Insensitive to particulate levels High SO <sub>2</sub> removal (>95%)	Expensive to process due to complexity and NO insolubility Formation of nitrates (NO <sub>3</sub> <sup>-</sup> ) and other potential water pollutants Extensive equipment requirements Formation of low-demand byproducts Flue gas reheat required Only moderate NO <sub>x</sub> removal High SO <sub>2</sub> to NO <sub>x</sub> ratios in feed required

through the addition of a chelating compound, such as ferrous-EDTA (ethylenediamine tetracetic acid), which has an affinity for the relatively insoluble NO. The NO is absorbed into a complex with the ferrous ion, and the SO<sub>2</sub> is absorbed as the sulfite ion. Then the NO complex is reduced to N<sub>2</sub> by reaction with the sulfite ion. A series of regeneration steps recovers the ferrous chelating compound and oxidizes the sulfite to sulfate, which is removed as gypsum. Although absorption/reduction processes also have the potential to remove 90% of both SO<sub>x</sub> and NO<sub>x</sub> from combustion flue gas, a large absorber is required, and the process is sensitive to the flue gas composition of SO<sub>2</sub>, NO<sub>x</sub>, and O<sub>2</sub>. The molar ratio of SO<sub>2</sub> to NO<sub>x</sub> must remain above approximately 2.5, and the oxygen concentration must remain low. Table 8.7 presents a comparison of the advantages and disadvantages of dry NO<sub>x</sub> and wet simultaneous NO<sub>x</sub>/SO<sub>x</sub> systems.

### 8.5.3 Selective Noncatalytic Reduction

There are two promising routes for NO<sub>x</sub> control involving the use of ammonia, one noncatalytic homogeneous reduction and the other selective catalytic (heterogeneous) reduction. Noncatalytic ammonia injection removes NO<sub>x</sub> from effluent gases by reducing NO to N<sub>2</sub> and H<sub>2</sub>O in the presence of oxygen. This process has been discussed in detail in Chapter 3. The overall reactions are:



The first reaction dominates at temperatures ranging from 1070 to 1270 K; above 1370 K the second reaction becomes significant, leading to the undesirable formation of NO.

The ammonia injection process is thus highly temperature sensitive, with maximum NO reduction occurring in the range 1200 to 1300 K. The ammonia injection NO<sub>x</sub> control system is commercially available and has been demonstrated on a number of boilers and furnaces.

#### 8.5.4 Selective Catalytic Reduction

*Selective catalytic reduction* (SCR) refers to the process wherein NO<sub>x</sub> is reduced by NH<sub>3</sub> over a heterogeneous catalyst in the presence of O<sub>2</sub>. The process is termed selective because the NH<sub>3</sub> preferentially reacts with NO<sub>x</sub> rather than with O<sub>2</sub>. The oxygen, however, enhances the reaction and is a necessary component of the process. Because of the need for oxygen to be present, SCR is most applicable to flue gases from flue-lean firing combustion systems. The predominant reaction is 1 above. Note that, in theory, a stoichiometric amount of NH<sub>3</sub> sufficient to reduce all the NO according to reaction 1 is in a 1 : 1 ratio to the NO. In practice, molar NH<sub>3</sub> : NO ratios in noncatalytic NH<sub>3</sub> injection range from 1.5 for NO levels below 200 ppm to approaching 1.0 as the NO level increases. In selective catalytic reduction a ratio of 1.0 has typically reduced NO<sub>x</sub> emissions by 80 to 90%.

The SCR processes are relatively simple, requiring only a reactor, a catalyst, and an ammonia storage and injection system. The optimum temperature for the noncatalyzed reaction is about 1300 K. The catalyst effectively reduces the reaction temperature to the range 570 to 720 K. To avoid the need to reheat the flue gas, the reactor is usually located just after the boiler, either before or after the particulate control device.

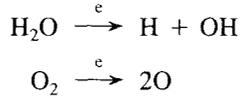
Many different types of catalyst compositions and configurations have been developed for SCR. Initially, catalysts were developed for flue gases without particles, such as those from natural gas firing. For these applications a catalyst of platinum (Pt) on an alumina (Al<sub>2</sub>O<sub>3</sub>) support was used. Alumina is poisoned by SO<sub>x</sub>, particularly SO<sub>3</sub>, so titanium dioxide (TiO<sub>2</sub>), which is resistant to SO<sub>x</sub> poisoning, was found to be an acceptable catalyst support. Vanadium compounds are resistant to SO<sub>x</sub> attack and also promote the reduction of NO<sub>x</sub> with ammonia. A common catalyst support is thus TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>.

A problem with SCR processes is the formation of solid ammonium sulfate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and liquid ammonium bisulfate, NH<sub>4</sub>HSO<sub>4</sub>, both of which are highly corrosive and interfere with heat transfer. The problem is most severe with high sulfur oil firing. With low sulfur oils, the SO<sub>3</sub> is not present in sufficient quantity. Tests with coal indicate that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> may deposit on the fly ash or be removed from the heat exchanger surface by the erosive action of the fly ash. The formation of these two substances is minimized by reducing the SO<sub>3</sub> and NH<sub>3</sub> in the effluent and by increasing the exhaust temperature of the flue gas.

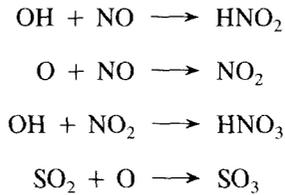
Selective catalytic reduction has achieved widespread use in Japan. By the beginning of 1985 about 160 SCR plants were in operation in Japan. About 60% of these SCR plants are being used with oil-fired utility boilers, 21% with coal-fired boilers, and 19% with gas-fired boilers (Ando, 1983, 1985).

### 8.5.5 NO<sub>x</sub> and SO<sub>x</sub> Removal by Electron Beam

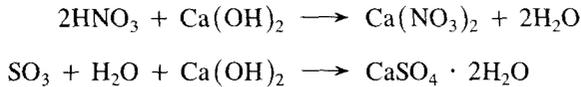
In the electron beam process, an electron beam is caused to penetrate into the effluent gas stream where collisions between the electrons and gas molecules produce ions that, in turn, interact with the gas to create free atoms and radicals that will react with pollutants in the gas stream (Bush, 1980). Primary reactions induced by the electron beam are the decomposition of water and oxygen by the electrons:



followed by reactions of the free atoms and radicals with pollutant species:



The essence of the process is thus that the hydroxyl radicals and oxygen atoms formed by the irradiation oxidize NO<sub>x</sub> and SO<sub>2</sub> to form the corresponding acids, which are then removed by appropriate neutralization of the acids with added basic substances, such as Ca(OH)<sub>2</sub>:

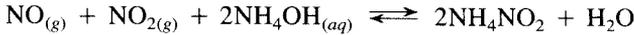


An electron beam is generated by accelerating electrons through a potential field (Gleason and Helfritch, 1985). The depth of penetration of the electron beam into a gas stream is proportional to the electron energy and inversely proportional to the gas density. The yield of a particular radical, such as OH, is proportional to the absorbed beam energy.

Electron beam treatment can be combined with conventional spray dryer alkali absorption and particulate collection (fabric filter or electrostatic precipitator). Flue gas exiting a boiler is first reacted in the spray dryer with lime and recycled fly ash. A typical operation would capture 50 to 60% of the SO<sub>2</sub> across the spray dryer, with the moisture content of the gas stream increasing from about 9 to approximately 13% by volume. The electron beam reactor then converts the NO and NO<sub>2</sub> to nitric acid (HNO<sub>3</sub>). The acid formed in the electron beam reactor is neutralized by the dispersed alkali particles in the gas stream and further neutralized in the downstream filter. The dry scrubbing step can be focused on SO<sub>2</sub> removal with only incidental NO<sub>x</sub> reduction, due possibly to NO—NO<sub>2</sub>—SO<sub>2</sub> reactions, since the electron beam step removes the NO<sub>x</sub>.

If the electron beam reactor is operated at reduced levels of irradiation, HNO<sub>3</sub> production can be minimized, and it is theoretically possible to produce a 50/50 mixture of NO<sub>2</sub> and NO from the effluent NO. Gleason and Helfritch (1985) have proposed that

reduced irradiation can be combined with subsequent contacting of the gas with an aqueous  $\text{NH}_4\text{OH}$  solution:



In this process, the reduction in power consumption associated with a lower-energy beam is offset by the need to introduce ammonia.

Although the electron beam reactor is a relatively new concept, simultaneous  $\text{NO}_x$  and  $\text{SO}_x$  removal at efficiencies exceeding 90% have been demonstrated for high-sulfur fuels.

### PROBLEMS

- 8.1.** A flue gas containing 3%  $\text{SO}_2$  by volume is to be scrubbed by a fresh absorbent to remove 90% of the  $\text{SO}_2$ . At equilibrium, the dissolved  $\text{SO}_2$  mole fraction in the absorbent is 0.0027 when the mole fraction in the gas phase is 0.03. What is the minimum  $L/G$  for the absorber? Assume that in this region the equilibrium line is straight.
- 8.2.** Ninety-five percent of the  $\text{SO}_2$  in a process effluent stream of  $\text{SO}_2$  and air is to be removed by gas absorption with water. The entering gas contains a mole fraction of  $\text{SO}_2$  of 0.08; the entering water contains no  $\text{SO}_2$ . The water flow rate is to be twice the minimum. The entering gas flow rate is  $100 \text{ mol min}^{-1}$ .
- (a) Assume for the purposes of the calculation that the equilibrium line for  $\text{SO}_2$  is straight with a slope of 35. Determine the depth of the packing needed. Use the relation for  $H_{Oy}$  given in Problem 8.3.
- (b) In the case in which both the operating and equilibrium lines are straight, that is, when the concentration of solute is lean ( $y \ll 1, x \ll 1$ ), the integral in (8.27) can be approximated by

$$\int_{y_1}^{y_0} \frac{dy}{y - y^*}$$

which can be integrated analytically. Show that in this case

$$z_T = \frac{G}{K_y a} \frac{y_0 - y_1}{(y - y^*)_{lm}}$$

where

$$(y - y^*)_{lm} = \frac{(y_0 - y_0^*) - (y_1 - y_1^*)}{\ln [(y_0 - y_0^*) / (y_1 - y_1^*)]}$$

Repeat case (a), assuming that the operating and equilibrium lines are both straight.

- 8.3.** An absorber is to be used to remove acetone from an airstream by contact with water. The entering air contains an acetone mole fraction of 0.11, and the entering water is acetone-free. The inlet gas flow rate is  $10 \text{ m}^3 \text{ min}^{-1}$ . The mole fraction of acetone in the air leaving the column is to be 0.02. The equilibrium curve for acetone-water at 1 atm and 299.6 K,

the conditions of operation of the tower, is given by (McCabe and Smith, 1976)

$$y = 0.33x e^{1.95(1-x)^2}$$

- (a) What is the water flow rate if it is to be 1.75 times the minimum?  
 (b) What is the required height of the tower if the gas-phase HTU is given by

$$H_{0y} = 3.3 \bar{G}^{0.33} \bar{L}^{-0.33} \text{ meters}$$

where  $\bar{G}$  and  $\bar{L}$  are the mass velocities, in  $\text{kg m}^{-2} \text{h}^{-1}$ ?

- 8.4.** Benzene vapor present at a concentration of 0.030 kg benzene/kg air is to be removed by passing the gas mixture downward through a bed of silica gel at 323 K and 2 atm pressure at a linear velocity of  $0.5 \text{ m s}^{-1}$  (based on the total cross-sectional area of  $1 \text{ m}^2$ ). The bed has a packing depth of 3 m. The breakpoint will be considered that time when the effluent air has a benzene content of 0.0030 kg benzene/kg air, and the bed will be considered exhausted when the effluent air contains 0.024 kg benzene/kg air. Determine the time required to reach the breakpoint. Pertinent data are given in Example 8.3.

Under these conditions the adsorption isotherm is

$$Y^* = 0.1167X^{1.3}$$

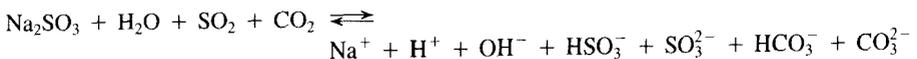
- 8.5.** A coal containing 3% sulfur by weight is burned at a rate of  $50 \text{ kg s}^{-1}$  in a 500-MW power plant. Ninety percent of the  $\text{SO}_2$  in the flue gas is to be removed by limestone scrubbing. Assume the limestone to be pure  $\text{CaCO}_3$ . Calculate the limestone feed rate needed to achieve the 90% removal assuming perfect stoichiometric reaction.

The stoichiometric ratio can be defined as the weight of reagent actually needed divided by the theoretical stoichiometric weight to remove the same quantity of  $\text{SO}_2$ . Stoichiometric ratios for 90%  $\text{SO}_2$  removal for lime systems range from 1.05 to 1.15, while those for limestone range from 1.25 to 1.6. Using actual ratios of 1.10 and 1.40, calculate the ratio of the weight of limestone to that of lime for this flue gas.

- 8.6.** A power plant flue gas contains 1000 ppm of NO and is emitted at a rate of  $1000 \text{ m}^3 \text{ s}^{-1}$  at 573 K and 1 atm. A selective catalytic reduction system is to be used to achieve 75% removal of the NO. Calculate the quantity of ammonia needed in  $\text{kg h}^{-1}$ .
- 8.7.** Section 8.2.2 considered the design of a packed  $\text{SO}_2$  absorber when the aqueous-phase  $\text{SO}_2$  equilibria are explicitly accounted for. For the conditions of Example 8.2, compute and plot the tower height as a function of the percentage of  $\text{SO}_2$  removed over the range of 90% to 97.5% removal. Assume  $G_0 = 30 \text{ kg-mol m}^{-2} \text{ h}^{-1}$ ,  $W = 50 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ ,  $\text{pH}_0 = 10$ , and  $y_0 = 0.2$ .

Note that to carry out this calculation it will be necessary to solve the nonlinear algebraic equation (8.54) to determine  $\eta_T$  and the numerically evaluate the integral in (8.53) to find  $z_T$ . The nonlinear algebraic equation can be solved by Newton's method, for example with the IBM Scientific Subroutine Package (SSP) RTNI, and the integral can be evaluated numerically by the IBM SSP Gaussian quadrature subroutine DQG32.

- 8.8.** In the dual alkali processes  $\text{SO}_2$  is absorbed from the flue gas by an  $\text{Na}_2\text{SO}_3$  solution. The spent solution is then sent to a regenerating system where lime is added to precipitate  $\text{CaSO}_3$  and regenerate  $\text{Na}_2\text{SO}_3$ . In this problem we want to determine the optimum pH at which to carry out the scrubbing step. The overall reaction in the system is



Equilibrium constants for the carbonate systems at 333 K are:

$$\frac{[\text{CO}_2 \cdot \text{H}_2\text{O}]}{p_{\text{CO}_2}} = K_{hc} = 0.0163 \text{ M atm}^{-1}$$

$$\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2 \cdot \text{H}_2\text{O}]} = K_{c1} = 10^{-6.35} \text{ M}$$

$$\frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = K_{c2} = 10^{-10.25} \text{ M}$$

The sodium mass in the system is just

$$[\text{Na}] = [\text{Na}^+]$$

whereas that for sulfur is

$$[\text{S}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$$

Derive an equation for  $[\text{Na}]$  as a function of pH,  $p_{\text{CO}_2}$ , and  $[\text{S}]$ . Calculate and plot  $[\text{Na}] - [\text{S}]$ , in M, as a function of pH over the range pH = 2 to 7 for  $[\text{S}] = 0.01 \text{ M}$  at  $p_{\text{CO}_2} = 0.16 \text{ atm}$ . For these conditions, what is the pH of complete sodium utilization?

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