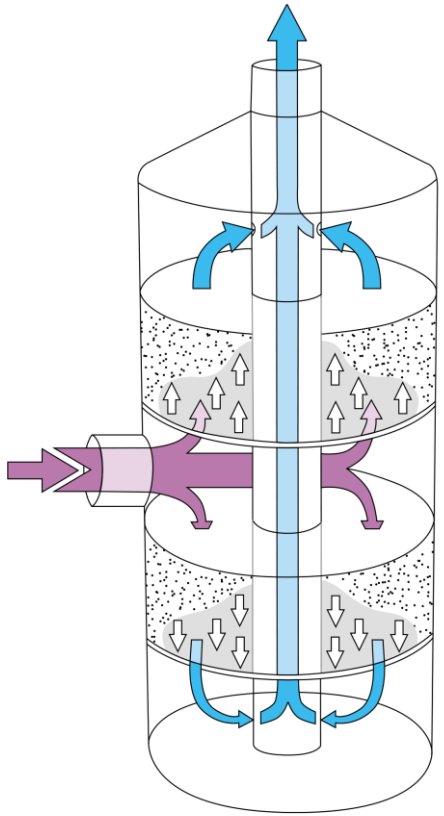
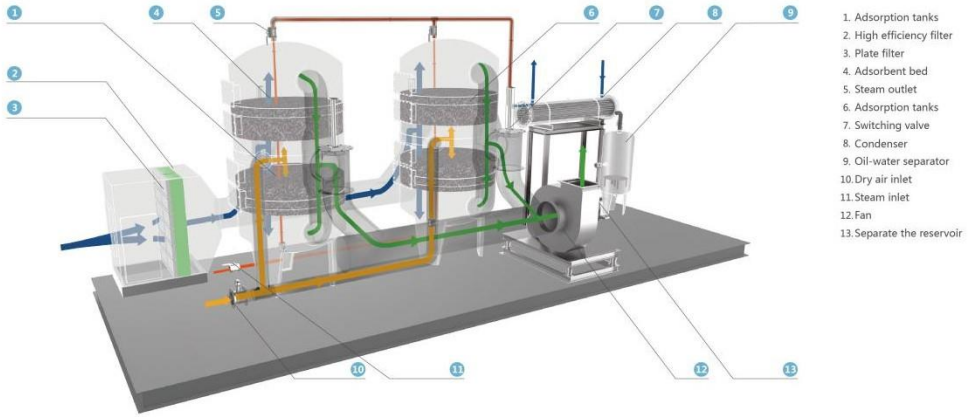
12 Gas Adsorption

12.1 Introduction

The removal of low-concentration gases and vapors from an exhaust stream by the adherence of these materials to the surface of porous solids is an example of a practical application of adsorption. With the proper selection of the adsorbing solid (adsorbent) and the contact time between the solid and the vapor-laden exhaust stream, very high removal efficiencies are possible. In addition, the process can be designed to provide economical recovery of the adsorbed vapor (adsorbate). Gas adsorption is used for industrial applications such as odor control; the recovery of volatile solvents such as benzene, ethanol, trichloroethylene, freon, and so forth; and the drying of process gas streams. However, in this chapter, we will concentrate on the control of volatile organic compounds (VOCs) in fixed- and fluidized-bed systems.





12.2 Adsorption Theory

Physical and Chemical Adsorption

The two distinct adsorption mechanisms that are recognized are physical adsorption and chemisorption.

Physical adsorption, also referred to as van der Waals adsorption, involves a weak bonding of gas molecules to the solid. The bond energy is similar to the attraction forces between molecules in a liquid. The adsorption process is exothermic, and the heat of adsorption is usually slightly higher than the heat of vaporization of the adsorbed material. The forces holding the gas molecules to the solid are easily overcome by either the application of heat or the reduction of pressure; either of these methods can be used to regenerate (clean) the adsorbent.

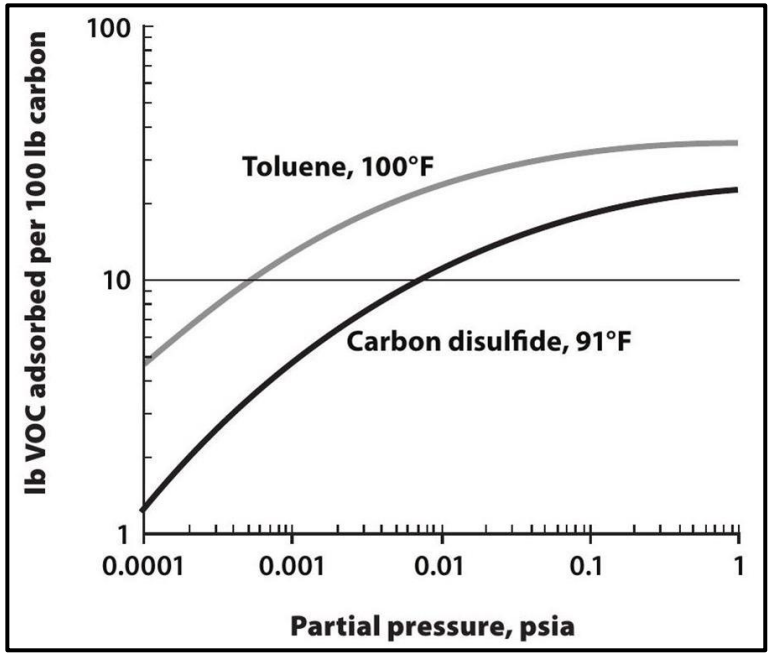
Chemisorption involves an actual chemical bonding by reaction of the adsorbate with the adsorbing solid. Heats of chemisorption are of roughly the same magnitude as heats of reaction, and chemisorption is not easily reversible. The oxidation of SO_2 to SO_3 on activated carbon is an example of chemisorption. Activated carbon and alumina can act as reaction catalysts with a number of gaseous mixtures; this fact must be considered when designing control and recovery systems. Except in some very specialized applications, if an adsorbate is chemically adsorbed to a significant extent, recovery of this material by an adsorption process is not feasible.

Adsorption Isotherms

Generally, the capacity of an adsorbent to adsorb a particular adsorbate is directly proportional to the molecular weight and inversely proportional to the vapor pressure of the adsorbate. The capacity of an adsorbent for a specific gas or vapor can be presented as an isotherm, as shown in Figure 12.2. A point on an isotherm represents the mass of adsorbate per unit mass of adsorbent under equilibrium conditions at the indicated temperature and gas-phase concentration. The isotherms shown in Figure 12.2 are typical for many organic solvents on activated carbon. However, isotherms for other gas-solid systems can assume other shapes, including S-curves and curves with distinct flat sections.

One of the best mathematical models for describing adsorption equilibrium is the Langmuir isotherm.

$$A + \sigma \underset{C_d}{\overset{C_a}{\rightleftharpoons}} A\sigma$$



It can be shown that the rate of contact of gas molecules with the adsorbent is proportional to the partial pressure $\bar{P}$ of the adsorbate. However, actual contact with the surface is limited to an area $(1 - f)$ not already occupied by adsorbate molecules, where f is the occupied fraction of the total solid surface. The rate of adsorption can then be found by

$$r_a = C_a \bar{P}(1 - f) \qquad (12.1)$$

where $r_a =$ rate of adsorption; $C_a =$ Adsorption rate constant.

Conversely, the rate of loss of molecules from the surface is proportional to the fraction of the surface occupied. Thus,

$$r_d = C_d f \qquad (12.2)$$

where $r_d =$ rate of loss by desorption; C_d = desorption rate constant.

At equilibrium, the rate of adsorption r_a is equal to the rate of desorption r_d, and the fraction of surface covered f is

$$f = \frac{C_a \bar{P}}{C_a \bar{P} + C_d} \qquad (12.3)$$

Since we assume a unimolecular coverage, the mass of adsorbate per unit mass of adsorbent a is also proportional to the fraction of surface covered. Thus,

$$a = C'_a f \qquad (12.4)$$

where C'_a = Adsorption rate constant.

Combining Eqs. (12.3) and (12.4), we obtain

$$a = \frac{(C_a C'_a / C_d)\bar{P}}{(C_a/C_d)\bar{P}+1} \qquad (12.5)$$

Since C_a, C_d, and C'_a are constants, Eq. (12.5) can also be written as

$$a = \frac{k_1 \bar{P}}{k_2 \bar{P}+1} \qquad (12.6)$$

where $k_1, k_2 =$ constants.
Equation (12.6) is called the Langmuir equation.
At very low adsorbate partial pressure, $k_2\bar{P}$ is approximately equal to zero, and Eq. (12.7) becomes

$$a = k_1 \bar{P} \qquad (12.7)$$

At high partial pressure,

$$a = \frac{k_1 \bar{P}}{k_2 \bar{P}} = \frac{k_1}{k_2} \qquad (12.8)$$

Hence, over a narrow intermediate range of $\bar{P}$,

$$a = k(\bar{P})^n \qquad (12.9)$$

where $k =$ constant;$n =$ constant (with a value between 0 and 1)
Equation (12.9) is commonly called the Freundlich equation.

Adsorption Potential

Goldman and Polanyi (1928) used the concept of adsorption potential to develop a single plot for the effect of temperature on adsorbent capacity. **Adsorption potential** is defined as the change in free energy accompanying the compression of one mole of vapor from the equilibrium partial pressure $\bar{P}$ to the saturated vapor pressure P_v at the temperature of adsorption T.

$$\Delta G_{\text{ads}} = RT \ln\left(\frac{P_v}{\bar{P}}\right) \qquad (12.10)$$

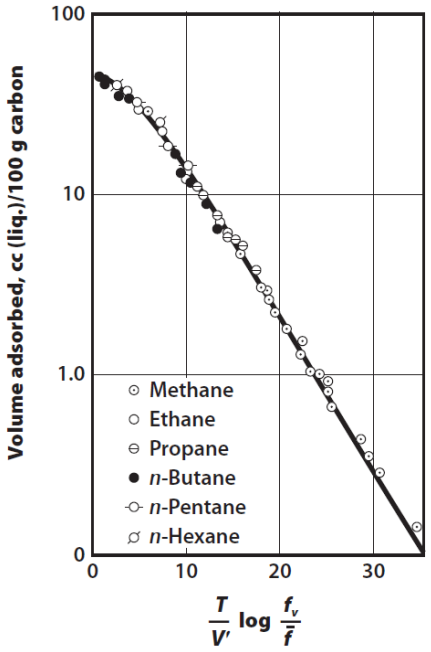
where $\Delta G_{\text{ads}} =$ change in free energy of adsorption, cal/gmol; $T =$ adsorption temperature, K; $P_v =$ vapor pressure at temperature T (in the same units as $\bar{P}$).

Dubinin (1947) found that when similar gases were adsorbed on the same adsorbent, the adsorption potentials were very nearly equal when the amount adsorbed was determined based on the product of the number of moles adsorbed multiplied by the molal volume. Thus,

$$\left[\frac{RT}{V'}2.303\log\left(\frac{P_v}{\bar{P}}\right)\right]_i = \left[\frac{RT}{V'}2.303\log\left(\frac{P_v}{\bar{P}}\right)\right]_j \qquad (12.11)$$

where V' = specific molal volume, $\mathrm{cm}^3/\mathrm{gmol}$; i, j = subscripts denoting different gases.

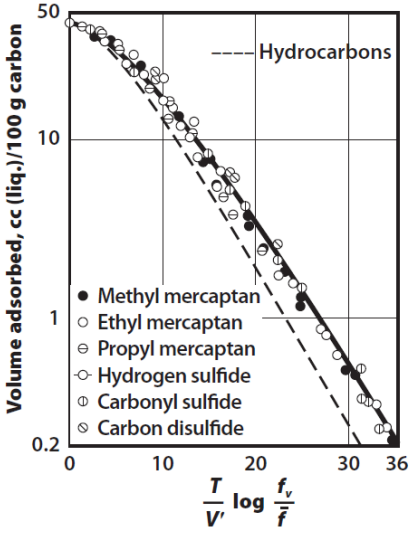
Grant and Manes (1966) used the work of Dubinin as modified by Lewis et al. (1950) to prepare plots of adsorption potential for hydrocarbons and reduced-sulfur gases. These plots are shown in Figure 12.3. Note that fugacities (thermodynamic potentials) were used in place of pressures to calculate the adsorption potentials. At the low partial pressures encountered in air pollution control, it is satisfactory to substitute $\bar{P}$ for $\bar{f}$ and P_v for f_v to facilitate the use of the Grant plot.



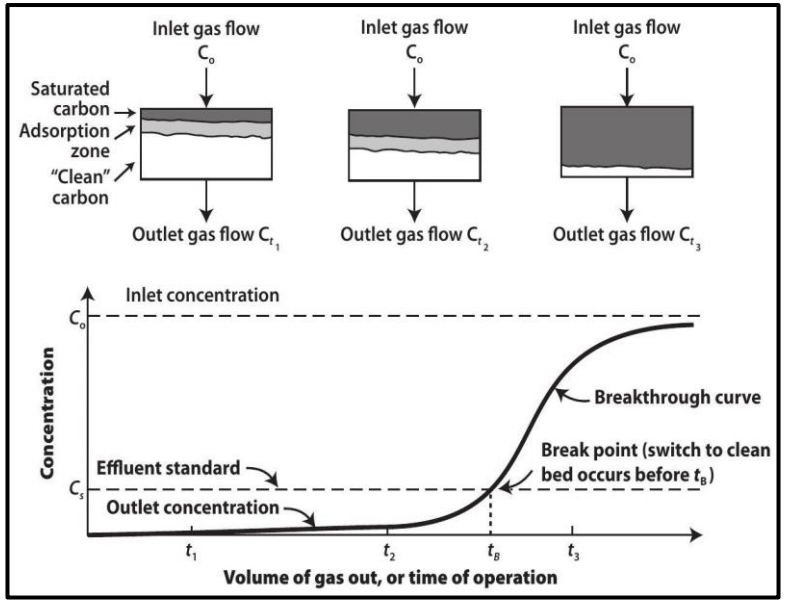
12.3 Fixed-Bed Adsorption Systems

Breakthrough Curves and Their Relationship to System Design

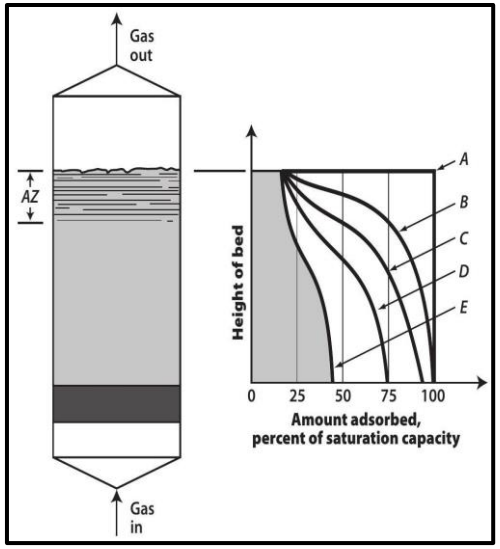
The dynamics of fixed-bed adsorption are shown graphically in Figure 12.4. In the upper part of the figure, a fixed bed is shown at three different times representing the interval from the initial admission of adsorbate to the time at which a significant concentration of adsorbate breaks through the bed. The plot in the lower half of the figure depicts the effluent concentration from the bed as a function of the volume of effluent, or time of operation. This type of plot is called a breakthrough curve, and provides valuable information on the adsorption rate in the bed. During depletion of the bed, an active adsorption zone (AZ) moves through the bed. Behind the AZ, the adsorbent is saturated, whereas in front of the AZ, the bed is virtually free of adsorbate. The length (or height) of the zone is a function of the rate of transfer of adsorbate from the gas to the adsorbent.



A shallow AZ indicates good adsorbent utilization and is represented by a steep breakthrough curve. Conversely, a wide or deep AZ denotes poor bed utilization and is indicated by a gradual slope on the breakthrough curve. The length of the AZ determines the minimum depth of the adsorbent bed.



Under actual plant operating conditions, bed capacity will seldom exceed 30 to 40% of that indicated by an equilibrium isotherm. Factors that contribute to bed capacity loss are shown graphically in Figure 12.5. Curve *A* represents the bed adsorbate concentration indicated by an isotherm for the bed operating temperature. A significant loss occurs because the bed must be taken out of service at or before the time that the leading edge of the AZ exits the bed. Since the adsorbent in the AZ is not saturated, the bed capacity is reduced by the area bounded by curve *B*. The heat of adsorption liberated as the AZ passes through the bed lowers the capacity as shown by curve *C*. Moisture reduces the bed capacity by two mechanisms: moisture in the influent gas displaces adsorbate (shown by curve *D*), and residual moisture remaining in the bed after regeneration further occupies some additional adsorption sites (shown by curve *E*). All of these losses are difficult to predict accurately. Pilot-scale breakthrough curves must be determined under conditions closely approximating plant operating conditions. Several mathematical procedures for calculating breakthrough curves have been reported (Treybal 1968; Wark, Warner, and Davis 1998). However, each of these procedures requires isotherm and mass transfer rate data, which will not normally be available for a specific control application. Hence, system design is based primarily on previous plant experience and pilot-scale studies.



Pressure Drop Across Fixed Beds

Figure 12.6 is a plot of pressure drop versus superficial bed velocity for several particle sizes. The fan energy usage resulting from pressure drop is a significant part of the overall operating cost of a fixedbed system. Both bed velocity and bed depth affect the pressure drop; the normal operating range of velocity is $50 - 100$ft/min, and bed depths range from 12 to 30 inches.

In the absence of measured pressure loss data, the pressure drop across the bed can be estimated with the Ergun equation (Ergun 1952):

$$\frac{\Delta P}{L} = \frac{(1-\varepsilon)G}{d_p \varepsilon^3 \rho_g g_c}\left[\frac{150\mu(1-\varepsilon)}{d_p} + 1.75G\right] \qquad (12.12)$$

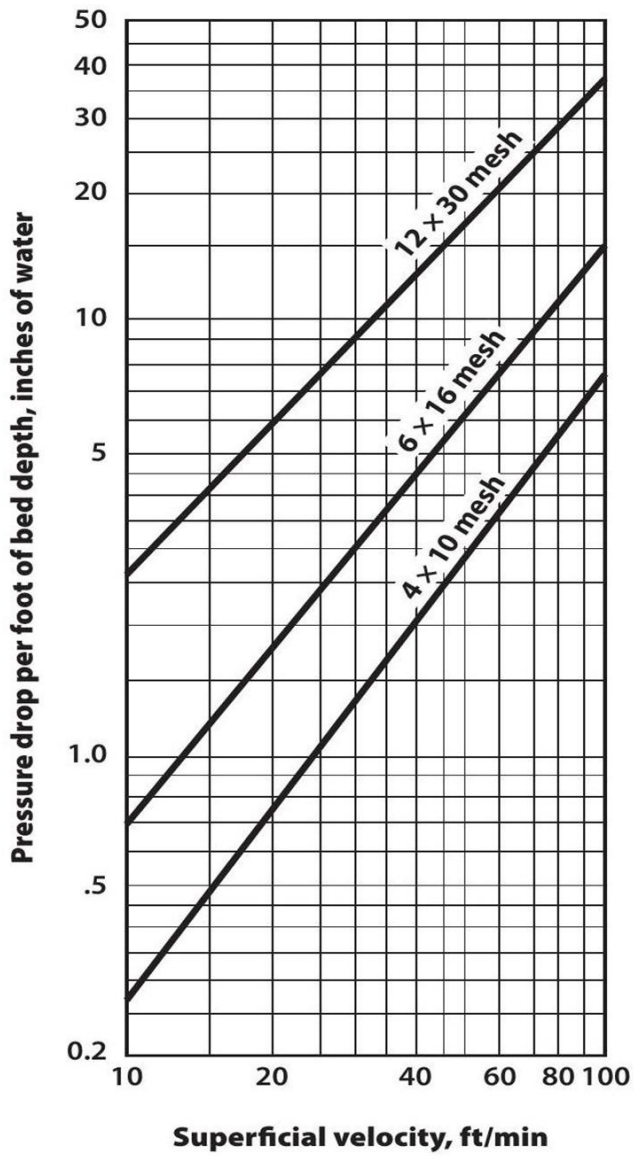
where $\Delta P =$ pressure drop, $\mathrm{lb_f/ft^2}$; $g_c =$ gravitational constant, $4.17 \times 10^8 \mathrm{lb_m} - \mathrm{ft/lb_f} - \mathrm{hr}^2$; $\varepsilon =$ void fraction, ft^3 voids $/\mathrm{ft}^3$ packed bed ; $d_p =$ particle diameter, ft; $\rho_g =$ gas density, $\mathrm{lb_m/ft^3}$; $L =$ bed depth, ft; $G =$ gas superficial mass flux $(= \rho_g 60\ \mathrm{V})$, $\mathrm{lb_m/hr - ft^2}$; $\mu =$ gas viscosity, $\mathrm{lb_m/hr - ft}$; $V =$ superficial gas velocity, ft/min.

A simpler, empirical equation published by the Union Carbide Corporation is as follows:

$$\Delta P = 0.37L\left(\frac{V}{100}\right)^{1.56} \qquad (12.13)$$

where $\Delta P =$ bed pressure drop, in. $\mathrm{H_2O}$; $L =$ bed depth, in.; $V =$ superficial gas velocity, ft/min.

Equation (12.13) is valid for velocities of $60 - 140$ft/min and bed depths of $5 - 50$ inches, and for 4×6 mesh sized carbon.



Adsorbent Regeneration

Material reversibly adsorbed on carbon or other adsorbents can be removed by

1. Contact with a hot inert gas (air can be used if the adsorbate is noncombustible)
2. Contact with low-pressure steam
3. Pressure reduction over the bed [also referred to as pressure swing adsorption (PSA)]

   Methods 1 and 2 are essentially the same. However, for most solvents, steam regeneration is much more effective than inert gas regeneration, which is used only in those cases where water would contaminate the recovered solvent either by chemical reaction or by formation of a mixture that is difficult to separate. Regeneration by pressure reduction is not often economical in recovery or pollution control adsorption systems, but has been used in the recovery of gasoline vapors from tank-truck loading operations (see Figure 12.7).

Most fixed-bed carbon systems are designed for steam regeneration. The quantity of steam required for regeneration is a function of carbon loading, ease of adsorbate removal, and bed geometry. The steam flow rate during regeneration can be specified as pounds of steam per pound of recovered solvent or as pounds of steam per pound of carbon. A properly designed system should require no more than $1 - 4$ pounds of steam per pound of recovered solvent or $0.2 - 0.4$ pounds of steam per pound of carbon. If the latter quantity is the largest (which is usually the case for low carbon loading), then that quantity should be specified.

Low-pressure saturated steam provides rapid heating of the adsorber vessel and carbon bed. Less than 10% of the total heat input is used in the desorption process. Approximately 70% of the heat exits as steam and approximately 20% heats the vessel and carbon. Efficient use of regenerating steam has the added benefit of minimizing the overhead condenser size.

The method used to contact the carbon bed with steam is an important design consideration. Rapid bed heat-up is desired, but care must be taken not to "cook" the contaminants in the bed (cooking permanently lowers the adsorbent capacity). One of the effects of cooking is the formation of polymers with low volatility. Steam flow into the bed is usually in the direction opposite the inlet gas flow so that contaminants are not driven farther into the bed.

12.4 Design of Fixed-Bed Carbon Adsorption Systems

The design and operation of a carbon adsorption (CA) system involves heat and mass transfer, fluid dynamics, process control, and chemical analysis. Each of these fundamental areas of engineering must be carefully considered and integrated into a working, economical system. Although engineers most often design from basic fundamentals, in CA design, the mass transfer aspects are usually based on pilot-plant and empirical data.

It has been shown that the shape of the breakthrough curve and hence the length of the adsorption zone are functions of the volatility of the adsorbate and the operating conditions of the adsorbent bed. Nevertheless, it is possible to make some generalizations which can be used in a preliminary design. In typical solvent recovery operations where adsorbate volatilities may be moderate (for VOCs with 8-12 carbons) to high (for $C_4 - C_7$ molecules), the AZ length will vary from 0.5 to 1.5 feet.

The carbon bed is contained in a steel vessel shaped like a large cylindrical drum positioned on its side, with a semispherical head on each end. The bed itself is shaped as a rectangular prism one to two feet tall, with a width slightly less than the diameter of the vessel, and with a length equal to that of the vessel minus the heads. The carbon is supported on a screen positioned inside the vessel such that the gas must flow upward or downward through the large rectangular face, and cannot flow around it. The actual dimensions of the bed typically are such that the length of the bed (L) is equal to twice the width (W). The following three requirements must be met.

1. The bed must contain a sufficient mass of adsorbent to provide a reasonable bed cycle time.
2. The superficial bed velocity must be high enough to provide satisfactory mass transfer rates, but low enough to allow a reasonable pressure drop.
3. The minimum bed depth must be greater than the length of one adsorption zone.

An important consideration that arises in the selection of pollution control equipment is whether to design the unit or to purchase a package unit from a supplier. Some generalizations can be made regarding this decision. If the CA system capacity is less than 20,000cfm, purchase of a package unit from a reputable company will usually save money. Systems larger than 20,000cfm are usually less expensive if designed in-house. Each case must be carefully considered.

Example 12.1

Prepare a preliminary design for a carbon adsorption (CA) system (including a fan) to control a stream of solvent-laden air from a plastics extruder local exhaust system. The exhaust stream temperature is 95°F, and it contains 1880 ppm of n-pentane ($n-\mathrm{C}_5$). The plant engineer has provided the following information:

1. Other gaseous contaminants: none
2. Particulate matter contaminants: plant fugitive dust only
3. Flow rate: 5500 acfm (continuous)
4. Extruder exhaust pressure (intake for the new fan): -4.5 in. $\mathrm{H_2O}$
5. The physical properties of the carbon are as follows: bulk density = $30\mathrm{lb_m}$ / ft^3, void fraction = 0.35, and particle size = 4×10 mesh (0.011ft)

Solution

（1）首先计算在操作周期内需要吸附的戊烷量

$$\mathrm{M} = \frac{1atm \times 0.00188 \times 5500}{0.73 \times 555} \times 72 \times 60 = 110\,\mathrm{lb/hr}$$

（2）查算活性炭的吸附能力

Using Fig.12.3,We must calculate the value of $[(T/V')\log(P_v/\bar{P})]$.

The specific molal volume can be calculated from the density of liquid n-pentane and molecular weight as follows:

$$V' = \frac{72\ \mathrm{g/gmol}}{0.64\ \mathrm{g/cm^3}} = \frac{112\ \mathrm{cm^3}}{\mathrm{gmol}}$$

Since n-pentane (in this case) is a pure component and the pressure is near atmospheric, we can calculate $\bar{P}$ from

$$P = y_{\mathrm{pentane}} \times 14.7\mathrm{psia} = \frac{1880\mathrm{ppm}}{1{,}000{,}000} \times 14.7 = 0.0276\mathrm{psia}$$

We can now solve for the abscissa of Figure 12.3 using pressures in place of fugacities.

$$\frac{T}{V'}\log\frac{P_v}{\bar{P}} = \frac{308\text{ K}}{112\text{cc/gmol}}\log\frac{16}{0.0276} = 7.6$$

From Figure 12.3, the volume adsorbed is about 18 cc liquid /100 g carbon. Therefore, the theoretical equilibrium adsorption capacity is given by

$$\frac{18\text{cc}}{100\text{ gC}} \times \frac{1\text{gmol}}{112\text{cc}} \times \frac{72\text{ g}}{\text{gmol}} = \frac{11.6\text{ g}n - \text{C}_5}{100\text{ gC}}$$

Since the operating or dynamic capacity is $25 - 50\%$ of the isotherm value, and since $n - \text{C}_5$ is fairly volatile, we choose a capacity factor of 30%. (For a final design, the capacity factor would be determined from experimental data.) Therefore,

$$\text{carbon capacity for design } = 0.3(11.6) = 3.5\frac{\text{lb}_\text{m}n - \text{C}_5}{100\text{lb}_\text{m}\text{C}}$$

(4)计算需要的活性碳量

We allow about one hour for regeneration and cooling. Thus, assuming 100% efficiency, a two-bed system will require a sufficient amount of carbon in each bed to adsorb $110\text{lb}_\text{m}n$ - C_5. This gives a minimum of:

$$\frac{\text{lb}_\text{m}\text{C}}{\text{bed}} = \frac{110\text{lb}_\text{m}n - \text{C}_5}{\text{hr}} \times 1\text{hr} \times \frac{100\text{lb}_\text{m}\text{C}}{3.5\text{lb}_\text{m}n - \text{C}_5} = 3143\frac{\text{lb}_\text{m}\text{C}}{\text{bed}}$$

Rounding this value to 3200lb_m and using a bulk carbon density of 30 $\text{lb}_\text{m}\text{C/ft}^3$,

$$\text{bed volume } = \frac{3200\text{lb}_\text{m}\text{C}}{30\text{lb}_\text{m}\text{C/ft}^3} = 106.7\text{ft}^3$$

（4）吸附床尺寸

Since n - C_5 is volatile, we use a minimum bed depth of 2 ft in our design. Assuming a rectangular bed with $L = 2W$,

$$\text{area of bed } = \frac{106.7}{2.0} = 53.4\text{ft}^2 \Longrightarrow W^2 = \frac{53.4\text{ft}^2}{2}$$

Therefore, $W = 5.2\text{ft}$ and $L = 10.4\text{ft}$. Rounding these values, we will use bed dimensions of $5.25\text{ft} \times 10.5\text{ft}$.

（5）核算空塔气速

Next, we check the superficial gas velocity.

$$V = \frac{5500\text{acfm}}{(5.25)(10.5)} = 100\,\frac{\text{ft}}{\text{min}}$$

This velocity is on the high end of the acceptable range. We will use this value in our preliminary design, but consideration should be given to buying some extra carbon and specifying a slightly longer and wider bed. (If a lower velocity is desired, and the bed depth must be kept at 2 feet, then the amount of carbon must be increased.) However, using our original dimensions:

mass of carbon /bed $= 10.5\text{ft} \times 5.25\text{ft} \times 2.0\text{ft} \times 30\text{lb/ft}^3 = 3308\text{lb carbon}$

total carbon to be purchased (two beds) $= 6616\text{lb carbon}$

(Note that if we made the bed 12 feet long by 6 feet wide, then the carbon needed for two beds would be 8640 lb , and the bed velocity would be 76ft/min.)

The anticipated run time before needing regeneration for a bed with 3308 lb of carbon is:

$$\frac{3.5\text{lb}n-\text{C}_5}{100\text{lbC}} \times \frac{1\text{hour}}{110\text{lb}n-\text{C}_5} \times 3308\text{lbC} = 1.05\text{hr}(63.2\text{ min})$$

(Note that if we had used a 12 -ft by 6 -ft bed with 4320 lb of carbon in it, we could have extended the run time to 82.5 minutes.)

（6） 再生需要的蒸汽量

Based on n - C_5 recovery, the steam requirement is

$$\underset{\text{required}}{\text{steam}} = \frac{3\text{lb}_\text{m}\text{stm}}{\text{lb}_\text{m}n-\text{C}_5} \times \frac{110\text{lb}_\text{m}n-\text{C}_5}{\text{hr}} \times 1.05\text{hr} = 330\,\frac{\text{lb}_\text{m}\text{stm}}{\text{regen}}$$

Based on the weight of carbon, the steam requirement is

$$\text{steam required } = 0.3\frac{\text{lb}_\text{m}\text{stm}}{\text{lb}_\text{m}\text{C}} \times 3308 = 992\frac{\text{lb}_\text{m}\text{stm}}{\text{regen}}$$

Assume that the regeneration takes 45 minutes, and the rest of the time is for bed cooling; thus the required steam flow rate is 992lb/0.75hr, or 1323lb/hr. Since the $n - \text{C}_5$ mass flow rate (carbon loading) is low, we will specify the higher of the two calculated steam rates, or 1323lb_mstm/hr. If plant steam is not available, a package boiler must be specified.

（7）床层压力降

For this application, assume that we will use either a 4×10 or 6×16 mesh carbon. From Figure 12.6 we obtain

$$\Delta P_{4\times10} = 7.5 \text{ in. H}_2\text{O/ft} \times 2\text{ft} = 15.0 \text{ in. H}_2\text{O}$$

$$\Delta P_{6\times16} = 15.0 \text{ in. H}_2\text{O/ft} \times 2\text{ft} = 30.0 \text{ in. H}_2\text{O}$$

Because of the high ΔP, we should definitely consider adding excess carbon and making the bed area larger, to reduce the superficial velocity and thus the ΔP. For now, assume the 4×10 mesh carbon.