

# A “How To” Guide for Adsorber Design

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## 1. Introduction

Adsorption is considered complicated, compared with distillation, absorption, and extraction. Just because the subject is perplexing, however, is no reason to avoid it. Hence, this article is an overview of taking a separation application from basic data and conditions to a preliminary design. The aim is to give simple, step-by-step procedures for designing ordinary adsorbers, as well as basic pressure swing adsorbers and temperature swing adsorbers. As background information, an introduction to adsorbents, their characteristics, and adsorption technology, in general, appeared in the other article, "Adsorbent Selection."

Some of the methods mentioned here are semiempirical, while others rely solely on first principles (solutions of differential mass balance equations) with no adjustable parameters. All the models featured here require only a calculator to solve. The biggest constraint, however, is that the basic properties required for simulation or design are not widely available, e.g., in handbooks or in property databases. Unfortunately, the more features a model takes into account, the more adjustable parameters are required, and the more experimental data are necessary to evaluate them, as explained below. The good news is that, with a relatively simple model and minimal data (described in the next section), one can get to an approximate design in the span of a few minutes.

To account for complex phenomena that may be encountered in adsorbers, requires more rigorous mathematical models than those discussed here. Those models employ more esoteric parameters and require substantial data to validate the model and evaluate the parameters. Generally, to cope with those it would be desirable to have a documented and user-friendly software package, a comprehensive database, and a fast PC or workstation. Even with such tools, inordinate effort may be required because to "predict" mass transfer rates, deviations from plug flow, heat effects, and other aspects, may require days, weeks, or even months of experimental effort. Even when the situation requires such a staunch effort, it may be prudent to start with a simple model using bounding assumptions and associated data in order to bracket the solution. The key is to recognize the characteristics of a situation and to apply a model that is neither unnecessarily complicated nor one that is oversimplified. That boils down to applying only assumptions which are known to be valid so that the results will be reasonably accurate.

Many assumptions can be forced to be valid by proper design, but others require caution. Order-of-magnitude analysis can often help sort out the effects in order to make that decision. For example, most simple models assume isothermal conditions. On the other hand, if an application involves significant heat of adsorption, or if the operating temperature is significantly different from ambient but the vessel is not adequately insulated, then it is prudent to account for heat effects. To illustrate, temperature shifts of about 20°C are common in pressure swing adsorption (PSA) air-drying and oxygen-separation (from air) systems. A shift of that magnitude does affect air drying, but does not affect oxygen separation for small units, though the effect on large units is significant. So, it is not enough to assess the effect; one should also assess the impact on performance while accounting for synergistic effects. In some instances, those effects may not be so obvious. Perhaps the most notorious case is the tendency of ketones to polymerize upon adsorption in certain activated carbons. The heat released has caused bed fires. To minimize risks, deluge systems are installed with carbon monoxide detectors that indicate smoldering combustion, so that today such accidents are rare.

## 2. Necessary Data

Certain general properties of adsorbents are involved in all adsorber design calculations. They can virtually never be predicted, but must be measured. In fact, vendor-supplied charts and tables are sometimes available, but are seldom guaranteed to be valid for design purposes. In those cases, measurements may be justified, too. The necessary properties are: *densities* and *void fractions*, *isotherms* (or other equilibrium data), *kinetics*, and *fixed bed dynamics*. These factors are intimately involved in adsorber models, which are covered in the next sections. In addition, though not strictly a property, *cost* is involved in every design decision.

Frequently, rough values of density or a range of nominal values are available from the vendor. Likewise, cost data are available as a function of quantity and required pretreatment, if any. Most vendors provide additional generic properties. If the potential sale is significant, they may even produce data. Otherwise, data for density, isotherms, and kinetics, might be found in books or monographs (e.g., Valenzuela and Myers, "Adsorption Equilibrium Data Handbook," Prentice Hall, 1989; Dobbs and Cohen, "Carbon Isotherms for Toxic Organics," EPA-600/8-80-023, 1980), journal articles (see, e.g., *Adsorption*, *AIChE Journal*, *Chemical Engng. Science*, *Industrial and Engng. Chem. Fundam.*, *Journal of Colloid and Interface Science*, *Langmuir*), graduate research theses from university libraries, or the world-wide web. Despite the spectrum of sources, it is rare to find the correct combination of adsorbent-adsorbate-temperature, range of data, lot number, pretreatment conditions, etc. As a result, those resources may be considered risky. Alternatively, you might arrange to conduct the measurements, either yourself or by someone else in your firm. Finally, since the tests are sometimes tedious and require special apparatus, you might arrange to have tests conducted by an independent firm. They frequently offer unbiased evaluations of adsorbents from various vendors, skill in conducting and analyzing the tests, and since they perform such measurements routinely, they are likely to be cost effective.

### *Densities and Void Fractions*

Three densities are relevant: bulk, particle, and solid, represented by  $\rho_B$ ,  $\rho_P$ ,  $\rho_S$ , respectively. Likewise, there are four pertinent void fractions,  $\epsilon_B$ ,  $\epsilon_P$ ,  $\epsilon_S$ , and  $\epsilon$ . The first three have the same associations as the densities having the same subscript. The last one,  $\epsilon$ , is the overall void fraction in the bed of adsorbent. They are related as:  $\rho_B = (1 - \epsilon_B) \rho_P = (1 - \epsilon_B)(1 - \epsilon_P) \rho_S = (1 - \epsilon) \rho_S$ .

The bed or bulk density is the mass of adsorbent in a specific volume. This can be measured simply using a graduated cylinder. Particle density is the mass of adsorbent per volume occupied by the particle. This is accurately and easily measured for true cylindrical pellets and beads, but is more difficult for distorted shapes and granular materials, though proprietary methods exist for obtaining accurate values even for those. Solid density is the mass of the adsorbent adsorbent per volume occupied by the particle, but with the pores deducted. It is measured by immersing a known amount of adsorbent in a liquid of known density and known total volume, then measuring the total mass. In this case, the characteristics of the liquid may dramatically affect the resulting value, because the liquid molecules may or may not be able to penetrate certain pores in a reasonable time due to steric reasons or surface tension. The greater the fraction of pores penetrated, the greater the apparent solid density.

Why be concerned with these for design purposes? There are several reasons. First, most

isotherm data are published as loading per unit mass, which is fine for determining total adsorbent cost, since prices are quoted per unit mass. Conversely, to determine the vessel dimensions from the necessary amount of adsorbent, or vice-versa, requires  $\rho_B$ . For pressure drop calculations, the relevant void fraction is  $\varepsilon_B$  since the fluid in the pores of the adsorbent is usually considered to be immobile. In contrast, for material balance equations, the fluid in the pores of the adsorbent cannot be ignored, so the relevant void fraction is  $\varepsilon$ .

### ***Isotherms***

Adsorption equilibrium data are commonly gathered at a fixed temperature and plotted or tabulated as *capacity* or *loading* versus the fluid-phase concentration (or partial pressure for gases and vapors). In that format the data comprise an *isotherm*. As mentioned earlier, adsorption capacity governs the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels. Information about the general nature of isotherms and about the multitude of equations that are used to fit data can be found in the previous article (*Chemical Engng.*, Nov. 1995). Some will be repeated here. For example, Figure 1 shows classifications suggested by Brunauer, Deming, Deming, and Teller, i.e., Types I-VI. Types I, II, and IV represent “favorable” equilibrium (concave downwards), while Types III and V represent “unfavorable” equilibrium (concave upwards). Type VI has two regions that are favorable and two that are unfavorable. Furthermore, Types IV and V exhibit hysteresis, which occurs when desorption occurs along a different path than adsorption, e.g., as a result of liquid-filled pores, and implies that uptake and release may be slow. For all that, only Type I adsorbents, over the range of relevant conditions, are generally suited to cyclic applications.

Standard measurement methods are available, e.g., *ASTM D 5919-96*, *MIL-D-3716B*, and *ANSI/AWWA B604-96*. The International Adsorption Society is developing a broad range of standard methods and has selected a group of standard adsorbent materials, which will be available through the *National Institute of Standards and Technology*.

Isosteres are an alternate form of equilibrium data, and are plotted on axes chosen so that they appear to be approximately linear to make interpolation and extrapolation easier. For example, partial pressure, dewpoint, or some other form of concentration is plotted versus temperature or inverse absolute temperature at specific extents of loading, usually as mass percent. A specific example is shown in Figure 2. The notations on that illustration are used later to explain aspects of temperature swing adsorption (TSA) gas drying.

A few common equations are prevalent for sizing conventional adsorbers and PSA units. They can accept any form of concentration,  $C$ , for the fluid phase, e.g., having units of mol/m<sup>3</sup>, lb/ft<sup>3</sup>, ppm, etc., or other convenient units, e.g., partial pressure of a vapor or gas. Likewise they can fit any adsorbent loading,  $n^*$ , e.g., having units of mol/m<sup>3</sup>, lb/ft<sup>3</sup>, lb/100 lb, etc. Generally, the parameters  $A$  and  $B$  are purely empirical. In addition, we will illustrate how adsorption isosteres (partial pressure versus temperature, for fixed loading) can be used to size TSA units.

The simplest equilibrium isotherm expresses loading as proportional to the fluid-phase concentration, and this results in *Henry's law*.

$$n^* = A C \quad (1)$$

In contrast, the *Langmuir isotherm* accounts for surface-coverage. That is, when the fluid concentration is very high, a monolayer forms on the adsorbent surface, having a loading of  $A/B$ . For some systems, the apparent level of saturation may represent multiple adsorbed layers.

$$n^* = \frac{A C}{1 + B C} \quad (2)$$

The parameter,  $A$ , is referred to as the Henry's law coefficient, since it is the slope of the isotherm at zero coverage. The *Freundlich isotherm* is the result of fitting isotherm data to a linear equation on log-log coordinates. It is probably the most commonly used isotherm equation, despite being "thermodynamically inconsistent," in that it does not have a finite Henry's law coefficient.

$$n^* = A C^B \quad (3)$$

One should be careful in choosing the form of an isotherm equation to fit a given set of data because there can be a substantial impact on calculations of fixed bed adsorption. When column performance is analyzed, some engineers feel it is acceptable to use *any* isotherm that fits the general trend of the data. Conversely, we have found that the precise shape of the isotherm, as well as heat effects, can affect the shape of a breakthrough curve. Frequently, such effects are unfairly attributed to "mass transfer" or "dispersion."

Selectivity describes, in the simplest possible form, the nature of multicomponent equilibria. Some common definitions are:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j} \quad (4)$$

$$\alpha'_{ij} = A_i / A_j \quad (5)$$

$$\beta_{ij} = \frac{1 + \frac{1 - \epsilon}{\epsilon} A_j}{1 + \frac{1 - \epsilon}{\epsilon} A_i} \quad (6)$$

The variables,  $x_i$  and  $y_i$ , are mole fractions in the fluid and adsorbed phases, respectively. The latter are impractical to measure but can be calculated. The advantage of eqs.(5) and (6), which apply to Henry's law and to the low concentration limit of the Langmuir isotherm, is that they are constant at a given temperature. Conventionally, component "i" is more strongly adsorbed than component "j." In that case,  $\alpha$  and  $\alpha'$  vary between unity and infinity, as does relative volatility, while  $\beta$  varies between zero and unity. When discussing selectivities, it is a good idea to specify the definition, or to speak of "good" or "bad" instead of "large" or "small."

### ***Kinetics***

Mass transfer *kinetics* is a catch-all term related to intraparticle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. Fast kinetics implies a sharp breakthrough curve, while slow kinetics leads to a distended breakthrough curve. The effect of a distended breakthrough curve can be overcome by adding adsorbent at the product end, or by increasing the cycle time (which reduces the throughput per unit of adsorbent). Both of these options

increase the amount of adsorbent required. To compensate for slow diffusion, it is also possible to use small particles, but there is a corresponding sacrifice due to increased pressure drop.

Intraparticle diffusion is characterized by an effective diffusivity,  $D_{eff} = D_{AB} \epsilon_p / \tau$  (where  $D_{AB}$  = adsorbate diffusivity in the fluid,  $\epsilon_p$  = particle void fraction, and  $\tau$  = tortuosity). It is used to assess the diffusional time constant:  $\ell^2 / D_{eff}$ , where:  $\ell$  = particle radius (for a sphere or cylinder shape) or half-thickness for a slab. That parameter is used with elapsed time,  $t$ , to define the dimensionless time:  $D_{eff} t / \ell^2$ . For example, the initial response ( $D_{eff} t / \ell^2 < 0.4$ ), and final response ( $D_{eff} t / \ell^2 > 0.4$ ) of a spherical particle to a sudden change of composition, respectively, are approximated by

$$F \equiv \frac{C_t - C_0}{C_f - C_0} \approx \left[ \frac{6}{\sqrt{\pi}} \left( \frac{D_{eff} t}{\ell^2} \right)^{1/2} - 3 \frac{D_{eff} t}{\ell^2} \right]_{initial} \approx \left[ 1 - \frac{6}{\pi^2} e^{-\pi^2 D_{eff} t / \ell^2} \right]_{final} \quad (7)$$

where the  $C_0$ ,  $C_f$ , and  $C_t$  represent the initial, final and instantaneous values of concentration averaged over the particle. From these approximations we can see that when  $D_{eff} t / \ell^2$  exceeds unity, what was going to happen is largely complete. Thus, when searching for an effective (fast) adsorbent, it is usually a safe bet to choose one having a large diffusivity, a small diameter, or both. Other concerns may overrule the selection of small particles, as mentioned later.

### Fixed Bed Dynamics

Interstitial mass transfer in fixed beds is important for designing many adsorbers. According to *Mass Transfer* by Sherwood, Pigford and Wilke (McGraw-Hill, 1974), virtually all data fits one equation, for both gases and liquids. The correlation employs the Colburn-Chilton  $j_D$ -Factor,  $j_D = (k / v_s) Sc^{0.667}$ , (where  $Sc = \mu / \rho D_{AB}$ ) and the Reynolds number,  $Re = \rho v_s d_p / \mu$ :

$$j_D = 1.17 Re^{-0.415} \quad 10 < Re < 2,500 \quad (8A)$$

Alternatively, the Yoshida et al. (*AIChE J.*, **8**, 5 (1962) correlation applies to even lower flow rates:

$$j_D = 0.91 \psi Re'^{-0.51} \quad Re < 50 \quad (8B)$$

where the modified Reynolds number is  $Re' = \rho v_s / \mu \psi a_i$ ,  $a_i$  = interfacial area/vol. =  $6(1-\epsilon) / d_p$ , and  $\psi$  = particle shape factor (=1.0 for beads, 0.91 for pellets, and 0.86 for flakes).

We are primarily interested in the fluid-to-particle mass transfer coefficient,  $k$ . It is mostly governed by the fluid properties (density,  $\rho$ , viscosity,  $\mu$ , and diffusivity,  $D_{AB}$ ) and superficial velocity,  $v_s$  (=  $Q / A_{cs}$ , where  $Q$  is the volumetric flow rate and  $A_{cs}$  is the cross-sectional area of the empty bed). Equation (8A) depends only on one adsorbent property, the particle diameter,  $d_p$ . As can be seen,  $k \propto d_p^{-0.415}$ , so for a given fluid and flow rate, a 10-fold reduction of the particle diameter would lead to only a 3-fold increase of the mass transfer coefficient. Conversely, a 10-fold velocity increase would lead to a 4-fold increase of the mass transfer coefficient. Equation (8B) depends on  $\psi$ ,  $\epsilon$ , and  $d_p$ , but the dependence on particle diameter is  $k \propto d_p^{-0.51}$ , which is practically the same as for eq. (8A).

Generally, a large value of  $k$  is good, but not at the expense of high velocity,  $v_s$ , not because of pumping or compression costs, but because the time of exposure in eq. (7) is inversely proportional to velocity. Thus, the faster the fluid is flowing, the less time the adsorbent has to respond.

The other major factor of bed dynamics is pressure drop. Most adsorbers are designed to operate with relatively low pressure drop, because large particles are used when ever possible, and because the velocity is typically low to allow equilibration of the fluid with the adsorbent. In addition, a small  $L/d_{bed}$  leads to low pressure drop.. Conversely, achieving good flow distribution and low dead volume implies a large  $L/d_{bed}$ . The most common equation that relates pressure drop in a fixed bed to the conditions and parameters is the Ergun equation:

$$\frac{\Delta P}{L} = \left( 150 \frac{1 - \epsilon_B}{Re} + 1.75 \right) \left( \frac{\rho v_s^2}{g_c d_p} \frac{1 - \epsilon_B}{\epsilon_B^3} \right) \quad (9)$$

where the Reynolds number is as above, and the bed void fraction is  $\epsilon_B$ . Generally, pipes, valves, and fittings pose as much of a flow restriction as the pressure drop in the bed of adsorbent.

### 3. Conventional Adsorber Modeling

The primary goal of conventional adsorber modeling is to predict or correlate breakthrough behavior. Oddly, the phenomena are widely different for uptake (i.e., exhaustion, loading, or simply adsorption) versus release (i.e., regeneration or desorption). Examples of both are shown in Figure 3. Typically, people are more concerned about the uptake step, so most models focus on that.

#### *Local Equilibrium Model*

Now that the basic concepts are sorted out, we can examine the effects of conditions and parameters on adsorber behavior. This section presents a brief overview of the simplest method for doing that, called a local equilibrium model. This type of model neglects all forms of diffusion, and produces results that are useful with extreme ease (compared with other more sophisticated methods). Furthermore it applies to any isotherm form, and can be used for uptake or regeneration.

Before delving into that, it might be helpful to look at the basic equation, because some of the terms that represent adsorbent properties appear in it. The material balance equation for solute ‘‘A’’ is:

$$\epsilon \frac{\partial C_A}{\partial t} + (1 - \epsilon) \rho_s \frac{\partial \bar{n}_A}{\partial t} + \epsilon v \frac{\partial C_A}{\partial z} = D_z \frac{\partial^2 C_A}{\partial z^2} \quad (10)$$

where:  $\epsilon$ =overall bed void fraction,  $\rho_s$ =solid density,  $C_A$ =solute concentration in fluid,  $\bar{n}_A$ =adsorbent loading (averaged),  $v$ =interstitial velocity ( $v_s$ =superficial velocity= $\epsilon v$ ), and  $D_z$ =axial dispersion coefficient. If the column is designed to eliminate flow maldistribution and dead-volume, the last term can be made negligible. Among these terms, the solid density and void fraction are inherent properties of the adsorbent, as is adsorbent loading but it also depends on other operating conditions.

The local equilibrium assumption basically says that there should be no concentration gradient within a particle or in the film surrounding a particle. Thus, the solid responds instantaneously:  $\bar{n}_A \sim n_A^*$  at a given position and time. As we have seen in eqs. (7) and (8), this implies that the particles are small or that the diffusivity is large. This leads to the simplest possible set of equations, and in virtually every case, the solution shows the best possible performance of an adsorber. The solution to eq. (10) yields the velocity of constant composition:

$$v_C = \left. \frac{dz}{dt} \right|_{C_A} = \frac{v_s}{\varepsilon + \rho_B \frac{\partial n_A^*}{\partial C_A}} \quad (11)$$

which can be used to evaluate breakthrough curves for regeneration.

A realistic breakthrough “curve” for uptake requires knowledge of mass transfer resistances. If the resistances are very small, the breakthrough front approaches a step change or a “shock wave” from the initial concentration to that of the feed. The speed at which it moves is most important, because that relates the amount of adsorbent to the amount of material processed. To estimate it involves the material balance in difference form, similar to eq. (10):

$$\varepsilon \left. \frac{\Delta C_A}{\Delta t} \right|_z + (1 - \varepsilon) \rho_B \left. \frac{\Delta n_A^*}{\Delta t} \right|_z + \varepsilon v \left. \frac{\Delta C_A}{\Delta z} \right|_t = 0 \quad (12)$$

Letting:  $v_{SH} = \Delta z / \Delta t$  (the velocity of the step-change),  $\Delta C_A = C_h - C_l$ ,  $\Delta n_A^* = n_h^* - n_l^*$  (where the subscripts *h* and *l* refer to “high” and “low,” respectively), and rearranging gives the *shock wave* velocity:

$$v_{SH} = \frac{v_s}{\varepsilon + \rho_B \frac{\Delta n_A^*}{\Delta C_A}} \quad (13)$$

To illustrate, for a feed concentration of  $C_h = C_{Feed}$  and the initial column contents at  $C_l = C_{Init} \sim 0$ , the Langmuir isotherm gives:

$$\frac{\Delta n^*}{\Delta C} = \frac{\frac{A C_h}{1 + B C_h} - \frac{A C_l}{1 + B C_l}}{C_h - C_l} = \frac{A}{(1 + B C_h)} \quad (14)$$

The ideal breakthrough time is  $t_{BT} = \Delta t_{SH}$ , and it may be evaluated as follows:

$$\Delta t_{SH} = \left[ \varepsilon + \rho_B \frac{\Delta n_A^*}{\Delta C_A} \right] \frac{L}{v_s} = \left[ \varepsilon + \rho_B \frac{\Delta n_A^*}{\Delta C_A} \right] \frac{V_{ads}}{Q} \quad (15)$$

where  $Q$  is the volumetric flow rate and  $V_{ads}$  is the volume of the adsorbent bed ( $= L A_{cs}$ ). This result applies to any favorable isotherm. It is restricted to isothermal plug flow with a constant fluid velocity. For uptake of a major gas component, allowance should be made for velocity variation.

Equations (7), (8), (9), (11), and (13) or (15) are elementary and each reveals an aspect of how properties and conditions affect performance.

### **Empirical Models**

Empirical models require much experimental data and/or experience, since their results rely on

fitted parameters. As a result, when conditions or materials change much, the predictions become prone to error. An example of that type of method is the *Length of Unused Bed* (LUB) approach that was suggested by Collins (*AIChE Symp. Ser.*, **63**, (74) 31(1967)). It involves observations about the *mass transfer zone* (MTZ), so experimental data are required. The concept assumes that the transition of concentration from that of the initial contents to that of the feed is due solely to mass transfer resistance. That method is unreliable for scale-up and when conditions vary widely. Therefore, no more will be said about it here.

The Wheeler - Robell equation (*J. Catal.*, **13**, 299 (1969)) is an empirically “corrected” local equilibrium model. Like other simple models it neglects axial dispersion. Unlike most other equation-based models, however, it applies to any isotherm form.

$$\frac{C_A}{C_{A_F}} = e^{-\frac{k_w}{Q} \left( \frac{C_{A_F} Q}{n_{A_{eff}}^* \rho_B} t - A_{CS} L \right)} \quad (16)$$

where  $k_w$  and  $n_{A_{eff}}^*$  are adjustable. Wheeler & Robell recommended judging  $n_{A_{eff}}^*$  from breakthrough data or from an isotherm. Discrepancies can arise due to ignoring fluid in the interstices. The equation can be modified by determining  $n_{A_{eff}}^*$  from breakthrough data or by predicting it via the local equilibrium model using isotherm data, such that  $t_{BT} \Rightarrow C_A / C_{A_F} = 0.5$ . The latter approach leads to the following relation for the effective capacity of the adsorbent:

$$n_{A_{eff}}^* = \frac{C_{A_F} Q t_{BT}}{\rho_B A_{CS} L - 0.693 \rho_B Q / k_w} \quad (17)$$

The result of inserting the local equilibrium model is:

$$\frac{C_A}{C_{A_F}} = e^{-\frac{k_w - 0.693 / \theta}{\varepsilon_B + \rho_B n_A^* / C_{A_F}} t - k_w \theta} \quad (18)$$

where the “empty bed contact time” is  $\theta = A_{CS} L / Q$ , in units consistent with  $k_w$ . The restrictions as written are: to uptake in a clean bed of adsorbent, and only to  $C_A / C_{A_F} = 0.5$ . It could be extended to an arbitrary (but uniform) initial condition.

### ***Analytic Models***

There are several analytic models, and they are generally quite restricted, e.g., to isothermal uptake with clean adsorbent obeying a simple (Henry or Langmuir) isotherm, but they can account for a wide variety of mass transfer resistances.

The Hougen - Marshall model (*CEP*, **43**, 197 (1947)) employs a Henry's law isotherm, assumes that film diffusion resistance predominates, and neglects axial dispersion. In the last case, the rate

equation needed for eq. (10) is:

$$(1 - \varepsilon) \rho_S \frac{\partial \bar{n}_A}{\partial t} = k_{eff} a_i (C_A - C_A^*) \quad (19)$$

where  $k_{eff}$  is the effective mass transfer coefficient and  $a_i$  is the interfacial area per unit volume of the adsorbent. The result is a relatively involved equation to predict the breakthrough curve:

$$\frac{C_A}{C_{A_F}} = \bar{J}(\tau, \zeta) = 1 - \int_0^{\zeta} e^{-(\tau + \zeta)} I_0(i(4\zeta\tau)^{1/2}) d\zeta \quad (20)$$

where the isotherm slope,  $A$ , and other parameters are combined as:

$$\tau = \frac{k_{eff} a}{(1 - \varepsilon) \rho_S A} (t - z/v) \quad (21)$$

$$\zeta = \frac{z k_{eff} a}{\varepsilon v} \quad (22)$$

$\tau$  is commonly called the “dimensionless time” and  $\zeta$  is commonly called the “number of transfer units.” The effective mass transfer coefficient,  $k_{eff}$ , can be estimated using the Chilton - Colburn  $j$ -factor to account for the dependence of flow rate, diffusivity, etc., as in eq. (8A) or (8B). The value can be further adjusted to reflect restricted diffusion in the pores, as and  $k_{eff} = k / \mathbb{T}$ , where  $\mathbb{T}$  is an apparent tortousity factor that lumps the fluid phase resistance (film diffusion) with the intraparticle mass transfer resistance.

The integration is involved, so  $\bar{J}(\tau, \zeta)$  is normally evaluated using approximations suggested by Thomas and Klinkenberg, first for  $\tau \zeta > 36$ :

$$\bar{J}(\zeta, \tau) \approx \frac{1}{2} [1 - erf(\sqrt{\zeta} - \sqrt{\tau})] + \frac{e^{-(\sqrt{\zeta} - \sqrt{\tau})^2}}{\sqrt{\pi} [(\zeta\tau)^{1/4} + \sqrt{\tau}]} \quad (23)$$

and for  $\tau \zeta > 3600$ :

$$\bar{J}(\zeta, \tau) \approx \frac{1}{2} [1 + erf(\sqrt{\tau} - \sqrt{\zeta})] \quad (24)$$

Note that  $erf(-x) = -erf(x)$ , and that  $erfc(x) = 1 - erf(x)$ . An approximation for  $erf(x)$  is:

$$erf(x) \approx 1 - (A_1 t + A_2 t^2 + A_3 t^3) e^{-x^2} \quad (25)$$

where  $t = (1 + A_4 x)^{-1}$ , and the parameters are:  $A_1 = 0.34802$ ,  $A_2 = -0.09588$ ,  $A_3 = 0.7478556$ , and  $A_4 = 0.47047$ . For example,  $erf(1) = 0.842701$ , while the equation above predicts 0.842718.

The Thomas model (*JACS*, **66**, 1664 (1944)) is similar to the Hougen - Marshall model, except that it incorporates the Langmuir isotherm. It is presented here in terms of film diffusion resistance,

but it can employ intraparticle diffusion or kinetic resistance. Its parameters are:

$$\Delta = \frac{k_{eff} a_i C_F}{(1 - \varepsilon) \rho_s n^*(C_F) \Omega} \quad (26)$$

where  $k_{eff}$  is the effective mass transfer coefficient, adjusted to account for restricted diffusion in the pores using an apparent tortousity,  $\mathbb{T}$ , and

$$\Omega = 1 + \frac{\bar{n}_A}{n^*(C_F)} (r^* - 1) \quad (27)$$

where  $\bar{n}_A / n^*(C_F) \approx 0.5$  if  $r^* < 1$ , or  $1/(r^*+1)$  if  $r^* > 1$ , according to Hiester and Vermeulen, and where  $r^* = (1 + B C_F)^{-1}$ .

$$\zeta = \Delta \frac{(1 - \varepsilon) \rho_s L}{\varepsilon} \frac{n^*(C_F)}{C_F} \quad (28)$$

$$\tau = \Delta \left( t - \frac{L}{v} \right) \quad (29)$$

The final result is:

$$\frac{C}{C_F} = \frac{\bar{J}(r^* \zeta, \tau)}{\bar{J}(r^* \zeta, \tau) + [1 - \bar{J}(\zeta, r^* \tau)] e^{(r^* - 1)(\tau - \zeta)}}$$

Under the asymptotic conditions cited previously, the Klinkenberg approximations are valid.

#### 4. Temperature Swing Adsorption Design

It is possible to design temperature swing adsorption (TSA) systems to handle either gas-phase or liquid-phase mixtures. Gas-phase TSA systems are relatively prevalent, mostly because of their popularity for drying. In contrast, liquid-phase TSA systems are relatively rare, though they can produce solvents of very high purity. An obscure but widespread example of a gas-phase TSA unit is built into some mufflers that protects against corrosion. They have a perforated cage that holds a small amount of zeolite, which adsorbs moisture as it cools when the car is shut-off, preventing acidic gases from condensing and corroding the metal. The moisture subsequently desorbs when the car is restarted and the zeolite is heated by the hot combustion gases. Determining the amount of zeolite necessary for that application requires the same steps as designing a gas dryer for a process application. In fact, gas-phase TSA applications besides drying can be analyzed by the same methods using a different measure of adsorbate content than dewpoint temperature.

Generally, TSA systems are designed as two identical, parallel beds that operate 180° out-of-phase. Generic design decisions involve the cycle time, steps, flow directions, regeneration gas, operating conditions (temperatures, flow rates, etc.), and of course vessel dimensions.

For TSA gas drying, graphical methods can be used to determine the regeneration gas temperature,  $T_R$ . Subsequently, the amount of desiccant required can be found from a material

balance, taking into consideration step times in the TSA cycle. To accomplish the first step, we will assume the following information is given: feed drybulb and dewpoint temperatures,  $T_F$  and  $T_{F,dp}$ , respectively, the product dewpoint temperature,  $T_{P,dp}$ , and the regenerant dewpoint temperature,  $T_{R,dp}$ . The last value depends on whether it is desired to use heated feed gas or a portion of the dried product gas to regenerate. We will consider both. Once that choice has been made, it is possible to layout a flowsheet, then to establish equipment specifications.

Isosteres, such as those shown in Figure 2 for silica gel, can be used most conveniently. The final loading achieved by regeneration is the lowest loading encountered during adsorption. Therefore, we must begin at the intersection of  $T_{P,dp}$  and  $T_F$  (labelled point ① in the figure), which determines the relevant limiting isostere (interpolated, if necessary). Choosing  $T_{R,dp}$  also sets the isothermal working capacity of the desiccant, i.e., the loading change between the exhausted and regenerated states at the specified dry bulb temperature, found by moving from point ① vertically to  $T_{R,dp}$  on the ordinate, which is labelled point ②. In fact, the entire bed of adsorbent cannot reach this condition unless breakthrough is complete, but allowing that would contaminate the product. Thus, true operation stops short of that point, which means a safety factor must be added to the bed size.

First, consider the case in which feed gas is heated and used to regenerate the bed. From point ②, we merely move horizontally to intersect the original isostere, labelled point ③, then move vertically to the abscissa to read the required regeneration temperature,  $T_R$ . An implicit assumption in this procedure is that sufficient feed gas is admitted to cool the bed back to  $T_F$  prior to approaching breakthrough at the product end. The path taken during the cooling step is along the relevant isostere.

Second, consider the case in which dried product gas will be heated and used to regenerate the bed. From point ②, we move diagonally to intersect the original product dewpoint temperature,  $T_{P,dp}$  labelled point ④, then move vertically to the abscissa to read the required regeneration temperature,  $T_R$ . An implicit assumption in this procedure is that sufficient feed gas is admitted to cool the bed back to  $T_F$  prior to approaching breakthrough at the product end. The path taken during the cooling step is viewed as being horizontal back to point ①, but the true path has a positive slope, implying that an even lower  $T_{P,dp}$  can be achieved.

The amount of adsorbent required can be estimated from a material balance, following eq. (15). It requires the feed step time,  $t_F$ , adsorbent properties, and the loading shift from initial to final,  $\Delta n_A^*$ , based on the difference between the feed and effluent concentrations,  $\Delta C_A$ :

$$V_{ads} = \frac{Q t_F}{\varepsilon + \rho_B \frac{\Delta n_A^*}{\Delta C_A}} \quad (31)$$

In this equation, the capacity in the interstitial voids, represented by  $\varepsilon$ , is frequently negligible.

For both process concepts, sufficient hot gas must be admitted to heat the bed to  $T_R$ , and that can be approximated by an energy balance. A rule-of-thumb is to add the enthalpies required to heat

the adsorbent plus the column wall (if not internally insulated) from  $T_F$  to  $T_R$ , plus the enthalpy of desorption, then multiply the sum by 2.5. Certain desiccants have a minimum  $T_R$  that is required to be effective, e.g., 200°C (400°F) for activated alumina. Another rule-of-thumb is to use 30 to 50°C (50 to 100°F) above the highest boiling point present.

There are two major advantages to regenerating with flow countercurrent to the feed. First, the hot regeneration gas initially contacts the desiccant layer at the outlet end of the bed, which determines the final dewpoint during adsorption. Thus, this layer is regenerated to the maximum possible extent. Second, the adsorbed water, which is most concentrated at the feed end, leaves the bed via the shortest distance. Thus, the total heat demand and required time are as low as possible. Conversely, co-current (to adsorption) regeneration requires bed inlet temperatures which are 20°C (or more) higher than for countercurrent regeneration to obtain the same product dewpoint, based on equal times, flow rates, and amounts of adsorbent.

It is advisable to use an inexpensive and thermally stable regeneration gas, e.g., air, flue gas, or nitrogen. For many gas processing applications, it is advisable to use a small slipstream of feed or dried product for regeneration rather than atmospheric gases, so as not to jeopardize product purity. For instance, natural gas drying units are regenerated with a small slipstream of natural gas, which is recycled upstream of the adsorption unit.

To regain the original adsorption capacity after heating the adsorbent bed, it must be cooled practically to the feed temperature. For dilute feeds, the feed itself may provide sufficient cooling capacity. If necessary, cool regeneration gas is used for cooling. If concentrated feed is used, cooling has to be carried out co-current to adsorption. Otherwise the adsorbent layer at the product end will be pre-loaded. Such pre-loading will significantly reduce the achievable product quality, as well as reduce the effective working capacity.

Cooling countercurrent to adsorption generally leads to product quality problems, unless recycled product is used. During cooling the temperature profile generally moves faster through the adsorbent bed than the mass transfer zone. If the bed temperature is much warmer than the operating temperature during adsorption, a spike may appear at the beginning of the adsorption cycle. The duration of that spike reflects the time until a length of cold bed is reached which allows a proper mass transfer zone to establish. Modest product quality requirements and/or low cost TSA units may use short cooling steps (or none), accepting the negative aspect of large spikes that occur, besides the fact that the initial product gas is warm.

## **5. Pressure Swing Adsorption Design**

Generally, PSA systems are designed as two or more identical, parallel beds that operate out-of-phase so that feed can be admitted to at least one of the beds continuously. Generic design decisions involve the cycle time, steps, flow directions, operating conditions (flow rates, pressures, etc.) and of course vessel dimensions.

Only an overview of PSA design can be given here. The topic is covered in more detail by Ruthven et al. (*Pressure Swing Adsorption*, VCH Wiley, 1994). We will use the results of the simplest local equilibrium model to predict PSA performance. The advantage of this simple model

is that few choices are necessary: the steps comprising the PSA cycle, operating conditions (feed composition, pressures, and step-times), and evaluate the selectivity. From that point, the model can predict overall performance in terms of: flow rates, product recovery, byproduct composition, and power requirements. For purposes of illustration, we will consider only the 4-step cycle shown in Figure 4, which employs pressurization by product. Several other cycles are discussed by Ruthven et al. Accordingly, the moles required for the feed, purified light product, and purge steps are:

$$\overline{Q}_{in} t|_F = \phi \varrho \quad (32)$$

$$\overline{Q}_{out} t|_F = \phi \varrho [1 + (\theta - 1) y_{A_F}] \quad (33)$$

$$\overline{Q}_{in} t|_{PU} = \phi \quad (\text{if } y_{A_{in}} = 0) \quad (34)$$

respectively, where:  $\varrho = P_H/P_L$  (the ratio of absolute pressures),  $\phi = \frac{\varepsilon A_{CS} Z P_L}{\beta_A R T}$ ,  $\beta = \beta_A / \beta_B$ ,

$\beta_i = 1 / \left( 1 + \frac{1 - \varepsilon}{\varepsilon} A_i \right)$ , and  $A_i$  is the Henry's law coefficient of component  $i$ .

The adsorbent selectivity,  $\beta$ , as defined in eq. (6) is a key element of the material balance equations. So, it can be related to velocities and measured in breakthrough experiments by simply monitoring the influent and effluent flow rates. For example, consider a fixed bed of adsorbent that is initially purged and pressurized with the light component. Feed is then admitted to the bed at the same pressure. The value of  $\beta$  may be found from:

$$\beta = 1 - \frac{1 - \overline{Q}_{out} / \overline{Q}_{in}}{y_{A_F}} \quad (35)$$

For bulk separations, the value determined this way is more reliable for design purposes than those determined via isotherm slopes, because operating conditions (feed composition, pressures, and cycle times) can be examined, as well as effects of minor variations in packing and/or adsorbent properties. Furthermore, when measured this way,  $\beta$  is known to depend on  $Re$  and there is usually a minimum value, close to that predicted from isotherm data, at which the combined effects of diffusion and dispersion are small. The typical optimum  $Re$  is in the range of 10 to 40.

All that is involved is to choose the operating conditions (feed composition, pressures, and step-times), and to evaluate the selectivity. From that point, the model can predict overall performance in terms of: flow rates, product recovery, byproduct composition, and power requirements. For example, the *recovery* of the light component for the PSA cycle is defined:

$$R_B = \frac{\overline{Q}_{out} t|_F - \overline{Q}_{in} t|_{PR} - \overline{Q}_{in} t|_{PU}}{\overline{Q}_{in} t|_F y_{B_F}} \quad (36)$$

As shown by Ruthven et al., the model gives:

$$R_B = (1 - \beta) \left[ 1 - \frac{1}{\varrho y_{B_F}} \right] \quad (37)$$

The bed is saturated with feed at high pressure at the end of the feed step. Thus, during blowdown the exhaust gas becomes enriched in component *A*. The composition shifts to  $y_{BD}$ :

$$y_{BD} = 1 - (1 - y_F) \left[ \frac{y_{BD}}{y_F} \rho^{\beta-1} \right]^{\frac{1}{\beta}} \quad (38)$$

The combined byproduct which is exhausted during blowdown and purge, contains the more strongly adsorbed component, which may also be valuable. The byproduct *enrichment* defined as,  $E_A = y_{Aw} / y_{Af}$ , can be used to find its overall concentration. The following relation applies for any cycle that splits a binary mixture in which the light component is obtained as a pure product, and the only other effluent stream is the byproduct:

$$E_A = \frac{1}{1 - y_{Bf} R_B} \quad (39)$$

In addition to the equations that define recovery and enrichment, an overall balance is required to determine the amount of adsorbent needed. Ordinarily, one would also choose the extent of purge, but that is assumed to be 100% here. Finally, to size the bed and to predict the necessary power requires stream flow rates, times, and pressures for individual steps. The flow rates indirectly affect the adsorbent selectivity via its dependence on Reynolds number, as mentioned previously. Hence, as feed velocity increases, both the step time and the bed size decrease, but the selectivity deteriorates. Thus, there is an economically optimum Reynolds number. So much for the design equations and conditions.

The first task in the design of a PSA system is to select the adsorbent. Important steps include: obtaining relevant isotherms and other properties, then estimating recovery of the desired product at various operating pressures (assuming that sufficient product purity could be attained), and finally estimating the costs of the adsorbent, power, vessels, valves, etc. to arrive at the total cost. Detailed design considerations would address the product purity question, and ancillary details that affect the optimum conditions, and therefore the cost. Such details, though, are beyond the scope of this article.

The purpose here is to illustrate a “back of the envelope” design of a PSA system. Given a production rate of 100 Nm<sup>3</sup> per hour of oxygen (at 4.0 bar) from air at ambient pressure and 45°C. For simplicity, the air is assumed to be nitrogen (78.0%), oxygen (21.0%) and argon (1.0%), dry and free of contaminants. The adsorbent is chosen to be zeolite 5A, for which isotherms of argon and oxygen are practically identical, so argon is lumped together with oxygen. The isotherms are essentially linear up to about 6 atm. In addition, the adsorbent - adsorbate interactions are characterized by  $\beta_A=0.100$ ,  $\epsilon=0.478$ ,  $\rho_B=810$  kg/m<sup>3</sup> and  $\beta=0.593$  (Kayser and Knaebel, *Chem. Eng. Sci.*, **41**, 2931-2938 (1986)).

The variables that affect the optimum pressure ratio are the recovery and the power requirement. We will consider adiabatic compression of an ideal gas,

$$\mathcal{P} = \frac{\gamma}{\gamma-1} \frac{QRT}{\eta} \left[ \rho_C^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (40)$$

where  $\gamma$  is the ratio of specific heats at constant pressure and constant volume,  $Q$  is the molar flow rate,  $\eta$  is the mechanical efficiency, and  $\rho_c$  is the compression ratio,  $P_{Ch}/P_{Cl}$ . For a 4-step cycle, it is common to operate above atmospheric pressure so that only a feed compressor is needed, so  $P_L = P_{Cl} \approx 1$  atm, and  $\rho_c \approx \rho$ . It is possible, however, to extend to sub-atmospheric pressure for blowdown and purge. This operating range is often referred to as *vacuum swing adsorption* (VSA). In that case,  $P_L < 1$  atm, and there are  $\rho_c$ 's for both a gas compressor and vacuum pump to be considered, along with equipment costs and power requirements, though  $\rho$  (and  $R_B$ ) for the PSA system would be unaffected by the absolute pressure.

## 6. Adsorber Design: Case Studies

A few illustrations are provided below. They are not meant to be comprehensive. To the contrary, a complete design would address the issues listed in Table 1. Some of those are relatively routine, but others could require substantial effort to resolve. All the major topics (basic adsorbent properties, application considerations, and equipment / flowsheet), play a significant role in economics.

In the same vein, there is no “expert system” that can pinpoint a successful adsorption process from the plethora of options. At the current state-of-the-art, the best that can be done is to offer some general, informal guidelines. Accordingly, two sets of recommendations are offered in Table 2, for gas-phase and liquid-phase applications, respectively. They were first suggested by Keller et al. (in *Hdbk. of Sep. Proc. Tech.*, R.Rousseau, Ed., Wiley, 1987). Some of the original suggestions have been changed to reflect the author’s views. As is the case for the methods and ideas cited so far, the guidelines are fallible, and must be checked with common sense, first, then verified with modeling and/or experiments.

### Example 1. Conventional Adsorber

- (A) Predict the uptake breakthrough pattern for CO<sub>2</sub>, at a feed mole fraction of  $y_{Af} = 0.1316$ , in air by activated carbon.
- (B) Predict the inert - purge regeneration of the column. That is, desorption of CO<sub>2</sub> using air under the reverse conditions.

---

#### DATA

|           |                           |            |         |          |                                |        |                  |
|-----------|---------------------------|------------|---------|----------|--------------------------------|--------|------------------|
| $\rho_B$  | = 0.360 g/cm <sup>3</sup> | $\epsilon$ | = 0.345 | $d_p$    | = 0.5 mm                       | $\psi$ | = 0.8345         |
| $d_{Bed}$ | = 0.718 cm                | $L$        | = 73 cm | $D_{AB}$ | = 0.134 cm <sup>2</sup> /s     | $\mu$  | = 0.00017 g/cm s |
| $P$       | = 1 atm                   | $T$        | = 0°C   | $Q$      | = 1.85 std. cm <sup>3</sup> /s |        |                  |

(A) Uptake Breakthrough

i) Uptake Time:  $\Delta t_{SH} = \left[ 1 + \frac{\rho_B}{\epsilon} \frac{\Delta n_A^*}{\Delta C_A} \right] \frac{L}{v}$

$$\frac{\Delta n_A^*}{\Delta C_A} = RT \frac{\Delta n_A^*}{\Delta p_A} = RT \frac{0.0112}{(1 + 7.258 \times 0.1316)} = 128.4 \frac{\text{cm}^3}{\text{g}}$$

$$v = \frac{Q}{A_{CS} \epsilon} = 13.24 \frac{\text{cm}}{\text{s}}$$

$$\therefore \Delta t_{SH} = 744. \text{ s} = 12.4 \text{ min}$$

ii) Use the modified Wheeler - Robell equation for a better estimate of breakthrough behavior for the uptake step:

$$\frac{C_A}{C_{AF}} = e^{\frac{k_w - 0.693 / \theta}{\epsilon + \rho_B n_A^* / C_{AF}} t - k_w \theta}$$

where:  $\theta = V_{Bed} / Q_F = 29.56 / 1.85 = 15.98 \text{ s}$ ,  $n_A^* / C_{AF} = 0.0007539 / 0.000005871 = 128.4 \text{ cm}^3/\text{g}$   
 $\epsilon + \rho_B \times n_A^* / C_{AF} = 0.345 + 0.36 \times 128.4 = 46.57$ . Choosing  $k_w = 3 \text{ s}^{-1}$  and  $t = 730 \text{ s}$ , yields  $C_A / C_{AF} = 0.2036$ .

Complete breakthrough curves, for values of  $k_w$  from 1 to 100  $\text{s}^{-1}$ , are shown in Figure 5. Generally, breakthrough data for the interstitial velocity, particle size, temperature, concentration, etc. would need to be obtained to determine the proper value of  $k_w$ .

iii) Use the Thomas model estimate the of breakthrough curve during the uptake step. First, evaluate properties and parameters:

$$n_A^* = \frac{A C_A}{1 + B C_A} = \frac{251.0 C_A}{1 + 1.627 \times 10^5 C_A}$$

$$r^* = (1 + B c_F)^{-1} = 0.5115$$

To evaluate the mass transfer coefficient, we can use eq. (8B):

$$j_D = 0.91 \psi Re'^{-0.51} \quad Re < 50 \quad (8B)$$

where  $j_D = (k / v_s) Sc^{0.667}$ ,  $\rho = PM / RT = 0.001294 \text{ g/cm}^3$ ,  $a_i = \text{interfacial area/vol.} = 6(1 - \epsilon_B) / d_p = 78.6 \text{ cm}^2/\text{cm}^3$ , and  $\psi = \text{shape factor} \approx 0.8345$ ,  $Sc = \mu / \rho D_{AB} = 0.980$ , the modified Reynolds number

is  $Re' = \rho v_s / \mu \psi a_i = 0.530$ , which yields:  $j_D = 1.277$ , and  $k = 4.86$  cm/s

Evaluating the other parameters:  $r^* = 0.5115$ , we assume that  $\bar{n} / n^*(C_F) \approx 0.5$ ,

$$\Omega = 1 + \frac{\bar{n}_A}{n^*(C_F)} (r^* - 1) = 0.7557$$

$$\Delta = \frac{ka C_F}{\rho_B n^*(C_F) \Omega \mathcal{F}} = 10.94 / \mathcal{F} \text{ s}^{-1}$$

$$\zeta = \Delta \frac{\rho_B}{\varepsilon} \frac{L}{v} \frac{n^*(C_F)}{C_F} = 8,079. / \mathcal{F}$$

$$\tau = \Delta \left( t - \frac{L}{v} \right) = 10.94 (t - 5.514) / \mathcal{F}$$

The product  $\tau \zeta \gg 10,000$ , so there is no question that the Klinkenberg approximations are valid. One quickly finds that, under these conditions,  $J(r^*\zeta, \tau) \approx 1$ , and that  $J(\zeta, r^*\tau) \approx 0$ . Thus, the solution reduces to:

$$\frac{C}{C_F} \approx \frac{1}{1 + [1 - 0] e^{(r^* - 1)(\tau - \zeta)}} = \frac{1}{1 + e^{(r^* - 1)(\tau - \zeta)}}$$

Breakthrough curves for values of  $\mathcal{F}$  (tortuosity) from 10 to 1000 are shown in Figure 6.

### (B) Regeneration Breakthrough

Use the local equilibrium assumption:

$$t_C |_{(z=L)} = \left[ 1 + \frac{\rho_B}{\varepsilon} \frac{\partial n_A^*}{\partial C_A} \right] \frac{L}{v}$$

From the isotherm (given previously):

$$\frac{dn_A^*}{dp_A} = \frac{A}{(1 + B p_A)^2}$$

$$\frac{dn_A^*}{dC_A} = RT \frac{dn_A^*}{dp_A}$$

To predict the effluent history: Find  $t$  for  $p_{CO_2} = 0.0, 0.1316$ , and, say,  $p_{CO_2} = 0.0439$  and  $0.0877$  atm.

|                                |        |         |         |         |
|--------------------------------|--------|---------|---------|---------|
| $p_{CO_2}$ (atm)               | 0      | 0.0439  | 0.0877  | 0.1316  |
| $dn^*/dp$ (mol/g atm)          | 0.0112 | 0.00644 | 0.00418 | 0.00293 |
| $dn^*/dC$ (cm <sup>3</sup> /g) | 251    | 144.4   | 93.7    | 65.67   |
| $t$ (s)                        | 1430   | 825     | 537     | 378     |
| $t$ (min)                      | 23.8   | 13.7    | 8.95    | 6.3     |

## Example 2. Adsorber for Dilute Aqueous Emissions

A common design situation exists when noxious or valuable contaminants are present in water. Examples are: the silver-laden waste from photographic developing, well-water containing sulfur or iron, or halogenated phenolics in wastewater. In the last case, the equilibration time for activated carbon is long, which means that the diffusivity is low, and that the breakthrough curve could be very distended.

Consider a feed concentration of 1 mg/l (or 1000 ppm) of 2-chlorophenol in 100 gpm water, using Filtrasorb-300 (Calgon Corp.) activated carbon ( $d_p=0.5$  mm,  $\rho_B=0.5$  g/cm<sup>3</sup>, and  $\epsilon=0.7$ ), with a minimum “on-line” time of 500 hr. The report by Dobbs and Cohen that was mentioned earlier indicates that Filtrasorb-300 adsorbs 57.1 mg/g at this concentration. They also noted that a fine powder (200x400 mesh, or 0.05 mm diameter) required about 2 hr to equilibrate. Equation (7) indicates how long a 0.5 mm diameter granule might take. Namely, the parameter  $D_{eff} t/l^2$  would be constant, as would the effective diffusivity. Thus,  $t_{0.5\text{ mm}} = t_{0.05\text{ mm}} (0.5\text{ mm}/0.05\text{ mm})^2$  or 200 hours! This material cannot be expected to exhibit a step change upon breakthrough. Therefore, a safety factor is essential. It is also a valid reason for using a slurry of carbon in the powdered form, even though a downstream filter is required to recover the waste.

Equation (15) can be used to estimate the equilibrium breakthrough time. From the data above, we find:  $\Delta q/\Delta C=57.1$  (mg/g)/0.001 (mg/cm<sup>3</sup>). Thus, the minimum volume of adsorbent is: 14. ft<sup>3</sup> or roughly 440 lb. A safety factor of 3 is recommended, but frankly given these kinetics, even that should be tested. Thus, the bed size would be about 50 ft<sup>3</sup>, containing about 1,600 lb of carbon. The remaining decision is the length-to-diameter ratio. To obtain a large mass transfer coefficient, that ratio should be large, but to minimize pressure drop, that ratio should be small.

## Example 3. PSA

Basis: costs of the major components are taken to be: \$5 per kg of 5A zeolite, \$0.05 per kW hr, and \$0.20 per Nm<sup>3</sup> of 95%-oxygen at 4 atm.

For the case of complete purge, recovery can be estimated. For  $P_L=0.25$  atm and  $P_H=4$ . atm,  $\rho=16$ , which implies a recovery, via eq (37), of 29.1%. The required net product, 100 Nm<sup>3</sup>/hr is equivalent to 1.24 mol/s. According to the definition of recovery, given by eq. (36), the molar feed rate,  $Q_{inf}$ , for the case of complete purge, is 19.36 mol/s. This is continuously fed, we will use two parallel columns to allow one to go through blowdown, purge and pressurization while the other column receives feed air.

From eq. (33) we find that for a given bed of adsorbent:  $\phi/t_F = 1.21$  mol/s, where  $\phi = \epsilon A_{CS} L P_L / \beta_A R T = 4.58 \times 10^{-5} V_{ads}$  and  $V_{ads}$  = the volume of the adsorbent (cm<sup>3</sup>). Accordingly,  $V_{ads}/t_F = 26,442.0$  cm<sup>3</sup>/s. The Reynolds number is defined as,  $Re = Q_{inf} M_F d_p / (A_{CS} \mu) = 148,000$ . /  $A_{CS}$ . Setting  $Re = 15$ , we find that  $A_{CS} = 9850$ . cm<sup>2</sup>; hence the column diameter is 112 cm. Returning to the ratio  $V_{ads}/t_F$ , we can determine  $L/t_F = 2.685$  cm/s. Now, we are free to choose the length of the bed, say,  $L=161$  cm. The result is that the feed-step duration,  $t_F=60$  s, and the

volume of adsorbent (for a two bed system) is  $V_{ads}=3.17 \text{ m}^3$ , which based on its bulk density of  $810 \text{ kg/m}^3$ , is equivalent to 2.57 metric tons of adsorbent.

Based on a mechanical efficiency of 80%, the required power can be estimated. First of all the power for compression of the feed from 1 atm to 4 atm is 109 kW, and that to compress the subatmospheric blowdown and purge effluent from 0.25 atm to atmospheric pressure is 28.8 kW. Note that the amount of gas evolved during blowdown at any intermediate pressure can be determined from eq. (38), assuming that the bed is saturated with feed prior to blowdown.

Hence the costs associated with the complete purge case would be: \$55,079 per year for power and \$12,851 for the adsorbent. Additional costs (for vessels, compressor, vacuum pump, valves, piping, instrumentation, site development, maintenance and fees) should be proportional to these. These are balanced against a projected value of \$160,000 per year for the product.

## **5. Conclusions**

In this article many concepts have been covered. The intention is to promote quick, reasonably reliable designs by taking into account the most important properties of adsorbents: capacity, kinetics, bed dynamics, adsorption dynamics, and to some extent cost. Because of the simplifications and idealizations, there are many factors that could not be addressed. In addition, it is likely that real-world cases will violate the assumptions in certain respects. Therefore, extreme caution is advised. The major points to keep in mind are that there are dozens if not hundreds of options to consider in designing an adsorber.

**Table 1. Adsorber Design Considerations**

I. Basic Adsorbent Properties

A. Isotherm Data

1. uptake / release measurements
2. hysteresis observed?
3. pretreatment conditions
4. aging upon multiple cycles
5. multicomponent effects

B. Mass Transfer Behavior

1. interface character
2. intraparticle diffusion
3. film diffusion
4. dispersion

C. Particle Characteristics

1. porosity
2. pore size distribution
3. specific surface area
4. density
5. particle size distribution
6. particle shape
7. abrasion resistance
8. crush strength
9. composition / stability
10. hydrophobicity

II. Application Considerations

A. Operating Conditions

1. flow rate
2. feed and product concentrations
3. pressure / temperature
4. desired recovery
5. cycle time
6. contaminants

B. Regeneration Technique

1. thermal: steam / hot fluid / kiln
2. chemical: acid / base / solvent
3. pressure shift
4. regenerant / adsorbate recovery or disposal

C. Energy Requirements

D. Adsorbent Life

1. attrition / swelling
2. aging / fouling

III. Equipment / Flowsheet

A. Contactor Type

1. fixed: axial / radial flow
2. pulsed / fluidized bed

B. Geometry

1. number of beds
2. bed dimensions
3. flow distribution
4. dead volumes

C. Column Internals

1. bed support / ballast
2. flow distribution
3. insulation

D. Miscellaneous

1. instrumentation
2. materials of construction
3. safety / maintenance
4. operation, start-up, shut-down



**Table 2. Cyclic Adsorption Process Options for Various Conditions**

(Adapted from Keller, et al., in *Hdbk. of Sep. Proc. Tech.*, R.Rousseau, Ed., Wiley, 1987)

Conditions

1. Feed is a liquid that can be vaporized at less than 200°C.
2. Feed is a liquid that cannot vaporize fully at less than 200°C.
3. Adsorbate concentration in the feed is less than 3%.
4. Adsorbate concentration in the feed is between 3 and 10%.
5. Adsorbate concentration in the feed is above 10%.
6. Adsorbate must be recovered at high purity: greater than 90% rejection of the carrier.
7. Adsorbate can only be desorbed by thermal regeneration.
8. Practical (cheap, noncorrosive, and nontoxic) displacement or purge agents cannot be easily separated from adsorbate.

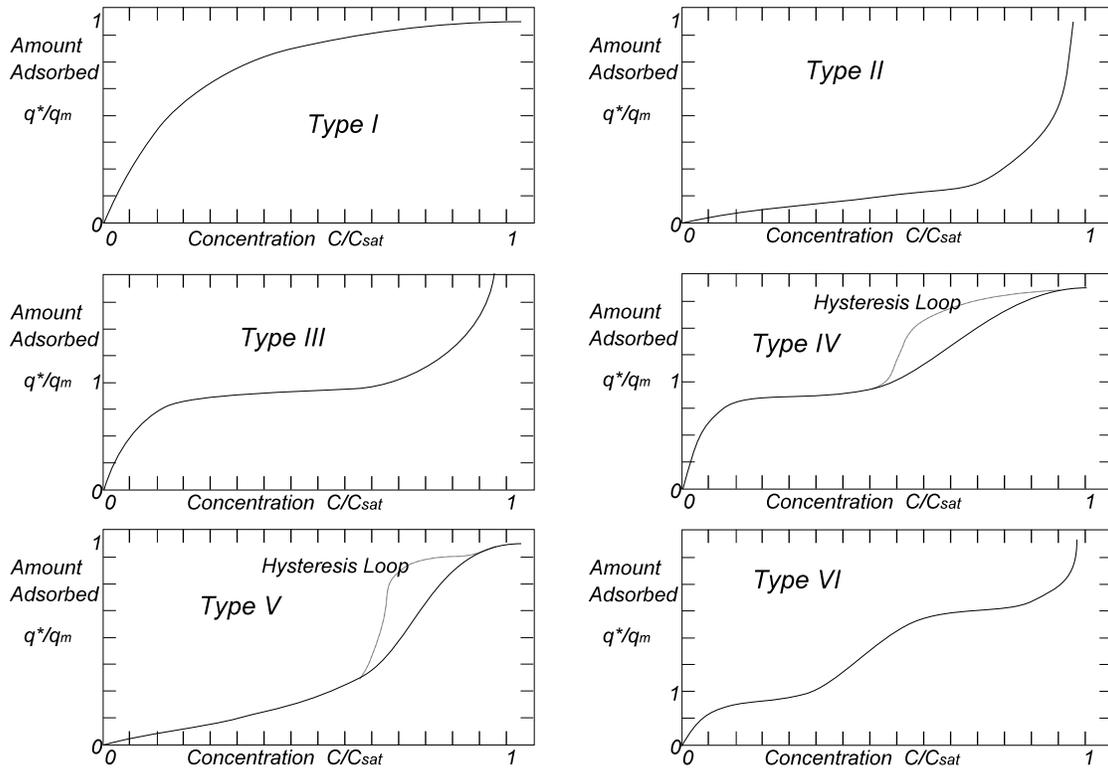
Process Options: Liquid Phase Applications

| <u>Statement No.</u> | <u>TSA</u> | <u>SMB</u> | <u>Chromatography</u> |
|----------------------|------------|------------|-----------------------|
| 1                    | Yes        | Yes        | Yes                   |
| 2                    | Yes        | Yes        | Yes                   |
| 3                    | Yes        | Maybe      | Yes                   |
| 4                    | Maybe      | Yes        | Maybe                 |
| 5                    | Not Likely | Yes        | Maybe                 |
| 6                    | Not Likely | Yes        | Maybe                 |
| 7                    | Yes        | Maybe      | No                    |
| 8                    | Maybe      | Not Likely | Not Likely            |

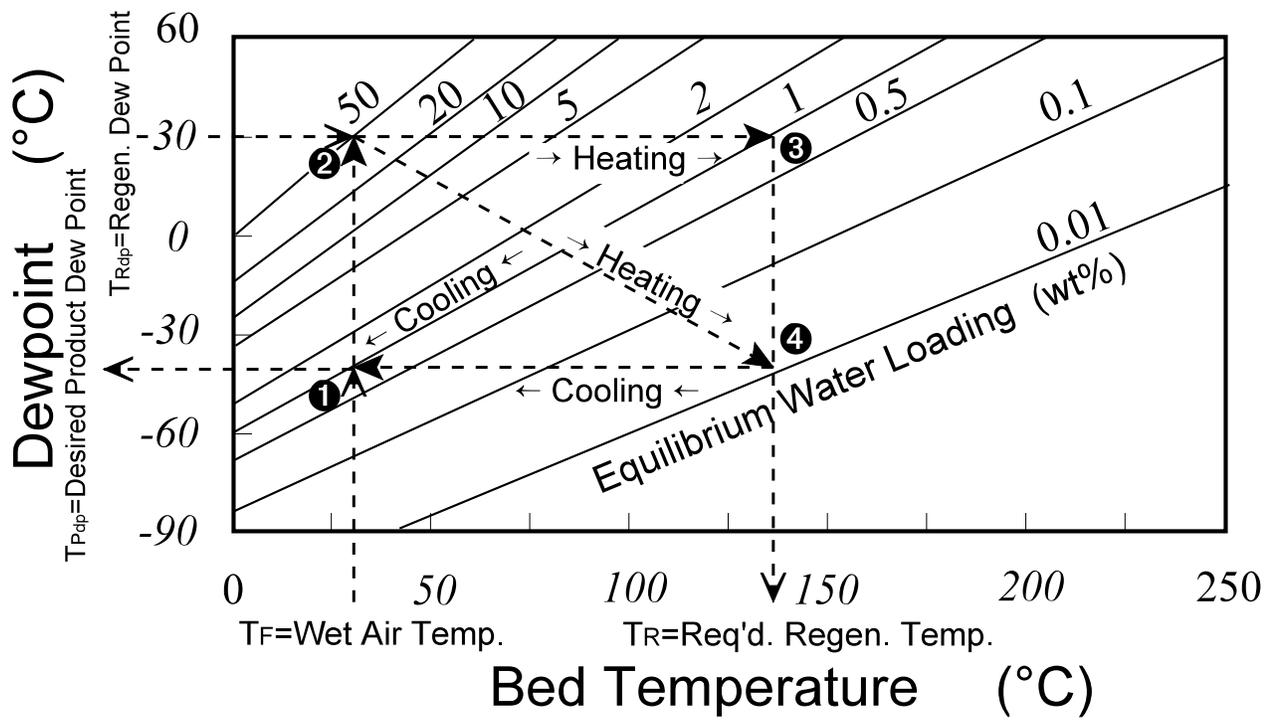
SMB= Simulated Moving Bed

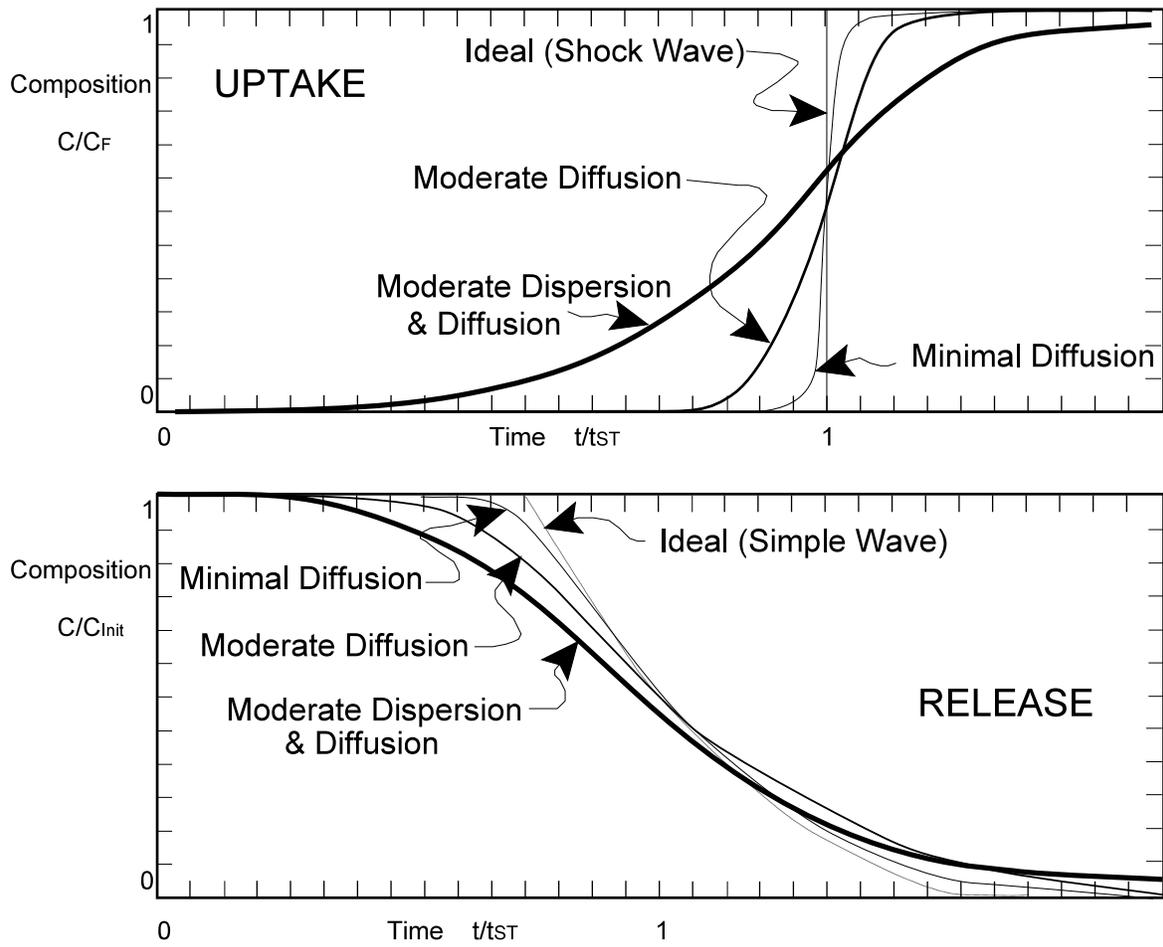
Process Options: Gas Phase Applications

| <u>Statement No.</u> | <u>Inert Purge</u> | <u>Displacement</u> | <u>TSA</u> | <u>PSA</u> | <u>Chromatography</u> |
|----------------------|--------------------|---------------------|------------|------------|-----------------------|
| 1                    | Not Likely         | Not Likely          | Maybe      | Maybe      | Not Likely            |
| 2                    | No                 | No                  | Not Likely | No         | No                    |
| 3                    | Yes                | Not Likely          | Yes        | Yes        | Yes                   |
| 4                    | Yes                | Yes                 | Yes        | Yes        | Yes                   |
| 5                    | No                 | Yes                 | Maybe      | Yes        | Not Likely            |
| 6                    | No                 | Yes                 | Yes        | Yes        | Yes                   |
| 7                    | No                 | No                  | Yes        | No         | No                    |
| 8                    | Not Likely         | Not Likely          | Maybe      | Maybe      | Not Likely            |

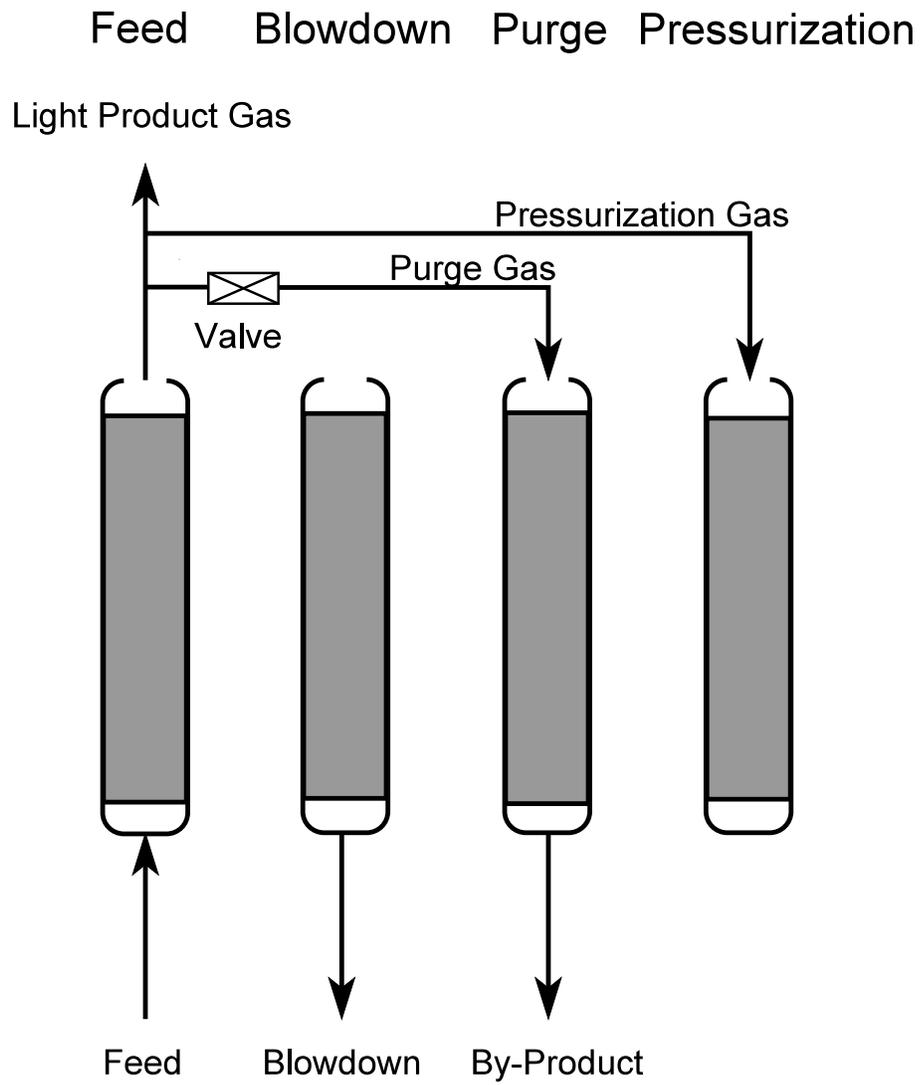


**Figure 1.** Isotherm classifications (Brunauer, Deming, Deming, & Teller (1940)).





**Figure 3.** Typical breakthrough curves for uptake and release.



**Figure 4.** Schematic diagram of a 4-step PSA cycle.