Adsorption With Activated Carbon

Economical removal of malodorous and toxic organics

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One of the most effective methods of controlling organic emissions, sometimes known as hazardous air pollutants (HAPs), from industrial and commercial sources is also one of the most economical—adsorption.

This process, which uses activated carbon as the adsorbing medium, is a method of filtration whereby malodorous or toxic organic vapors can be economically removed from an exhaust stream, even in low concentrations.

Adsorption occurrences

Physical adsorption occurs when organic molecules are held on the surface and in the pores of the adsorbent by the weak Van der Waals force of attraction and is generally characterized by low heat absorption, on the order of 10 kcal/g-mol or less, and by the fact that the adsorption equilibrium is reversible and rapidly established.

The adsorption capacity of activated carbon for a given HAP is often represented by an adsorption isotherm that relates the amount of HAP adsorbed (adsorbate) to the equilibrium pressure (concentration) at constant temperature (Fig. 1).

Typically, the adsorption capacity of activated carbon increases as the molecular weight of the HAP increases.

Table 1. Retentivity of organics is activated carbon.

Substance	Formula	Molecular wt.	Boiling point @ 14.7 psia, °F	Approximate retentivity @ 68°F and 14.7 psia
Butane	C_4H_{10}	58	33.8	8
Decane	$C_{10}H_{22}$	142	447.8	25
Toluene	C_7H_8	92	231.4	29
Methyl chloride	CH_3Cl	50.5	289.6	5
Methylene chloride	CH_2Cl_2	85	104.225	
Formaldehyde	HCHO	30	-5.8	3
Methyl alcohol	CH_3OH	32	148.5	10
Isopropyl alcohol	C_3H_7OH	60	181.4	26

Unsaturated compounds are more completely adsorbed than saturated compounds and cyclical compounds are more easily adsorbed than linearly structured materials.

Other effects

Adsorption capacity is enhanced by lower operating temperatures and higher HAP concentrations. Because activated carbon is non-polar, it is capable of adsorbing organic gases and vapors in preference to water vapor in a gas stream.

In fact, activated carbon that has adsorbed moisture will lose this moisture by displacement in preference for organic vapors. Halogenated compounds are strongly affected by increased relative humidity, whereas aromatic compounds are only weakly affected. However, because water vapor competes with the HAP in the emission stream for adsorption sites on the carbon surface, emission stream humidity levels exceeding 60% RH are not desirable.

For these reasons, activated carbon becomes the right adsorbent for high-capacity, non-selective adsorption of gases at ambient temperature, suitable for most HAPs with molecular weights between 40 and 150 and boiling points from 100°F to 500°F.

Retentive ability

The ability of activated carbon to retain the adsorbed HAP is an important characteristic that lends itself to industrial

and commercial applications for this process.

Once adsorbed, the HAP must remain within the bed and not be released as additional quantities of gas are passed through the bed. The retentive capacity of activated carbon is a useful measurement to demonstrate this physical property.

Retentivity, as determined in laboratory studies, represents the amount of adsorbate that carbon, initially saturated with the HAP, can retain when pure air is passed through the bed. Some selected retentivity values for different organic materials are given in Table 1.

As a general rule, the more condensible the organic vapor is at the condition imposed, the higher the adsorption capacity and retentivity of the carbon will be.

The application of activated carbon adsorption in air pollution control is a dynamic process. As the contaminated stream is passed through the carbon bed and adsorption occurs, the saturation zone within the bed moves forward until the breakthrough point is reached and the HAP's exit concentration begins to rise rapidly.

The zone of the bed where a concentration gradient is present is often called the mass transfer zone (MTZ). As the flow of gas continues, the MTZ progressively advances through the bed, contacting new layers of carbon unsaturated with contaminants. The adsorption wave will develop as indicated in Fig. 2 and will continue to propagate through the bed until breakthrough occurs.

Table 2 lists the calculated lengths of the MTZ for various concentrations of benzene.

For example, these data indicate that the adsorption wave for an air stream containing 286 ppb of benzene will be contained in a l-in thick carbon bed. The average degree of saturation in the MTZ

Fig. 1. Toluene isotherms.

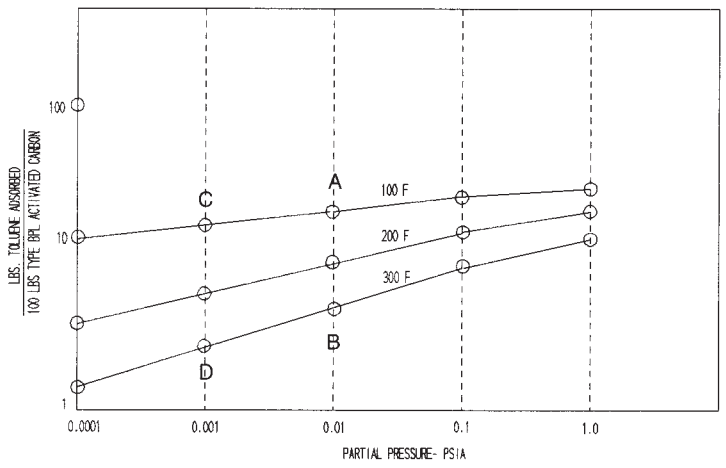
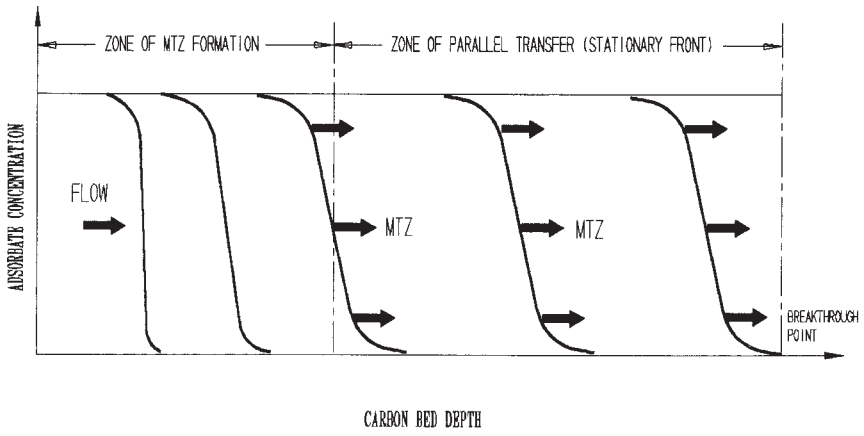


Fig. 2. MTZ and dynamic adsorption.



is normally 50% of the "capacity to saturation," which is obtained from an adsorption isotherm. The adsorber bed depth may be calculated in terms of the number of transfer units.

$$H = \frac{V_g}{S\beta}\int_{C_1}^{C_0}\frac{dc}{C - C_s} \qquad (1)$$

where:

V_g = gas flow amount;
S = adsorber cross section;
β = mass transfer coefficient;
C_0 = HAP inlet concentration;
C_1 = HAP outlet concentration;
C_S = equilibrium adsorbate concentration (adsorption isotherm).

The ratio $V_g/S\beta$ is the height of one mass transfer unit and the integral ($\int$) between C_1 and C_0 of $dc/C\text{-}C_S$ is the number of transfer units (NTU).

For the initial zone of the adsorption isotherm where the ratio between the HAP partial pressure and the saturation vapor pressure (P/Ps) is less than 0.17, the mass transfer coefficient is given from the empirical equation:

$$Nu = 1.6\,Re^{0.54} \qquad (2)$$

where:

Nu (Nusselt number) = $\beta d_c^2/D$;
Re (Reynolds number) = wd_c/υ.
Then:

$$\beta = 1.6\frac{Dw^{0.54}}{\upsilon^{0.54} d_c^{1.46}} \qquad (3)$$

Fig. 3. Effect of bed depth, HAP concentration and removal efficiency on cycle time.

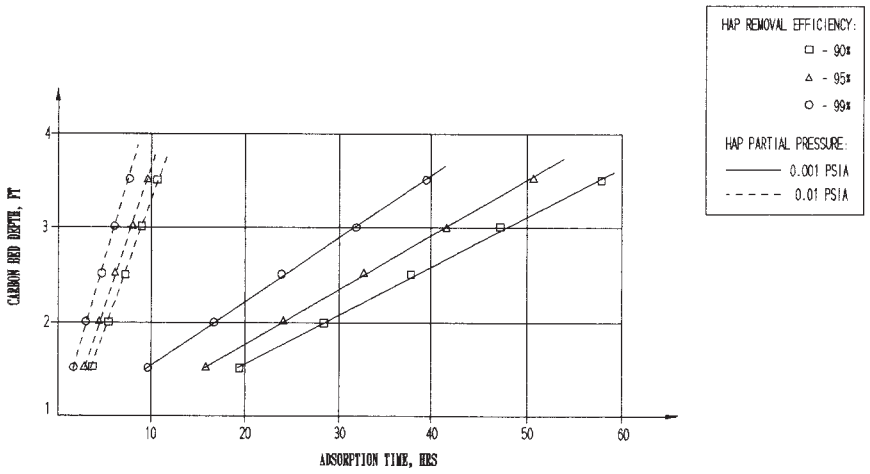
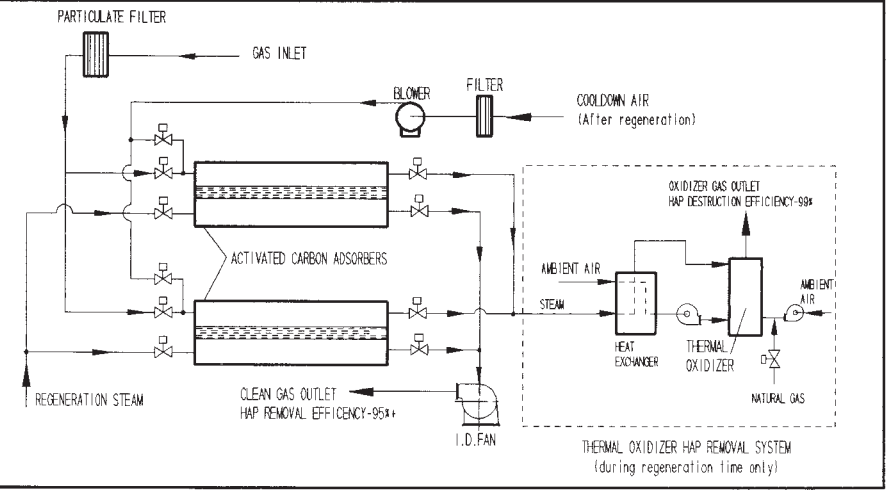


Fig. 4. Carbon adsorption/thermal oxidation system.



where:

w = gas velocity;

d_c = carbon particle diameter;

D = diffusion coefficient;

υ = kinematic viscosity.

Computer calculations have been developed and used to obtain the predicted breakthrough times for different carbon bed depths and HAP removal efficiencies.

A toluene adsorption isotherm is shown in Fig. 1, and Fig. 3 indicates the calculated breakthrough time for various removal efficiencies, concentrations and bed depths.

Working with mixtures

The adsorption process becomes complex if several compounds are present in the inlet gas to the carbon bed, as the various organics will be adsorbed in an inverse relationship to their relative volatility.

At the beginning of the cycle, all organic components will be adsorbed equally; but as the quantity of the highest boiling constituent retained in the bed increases, the lowest boiling component begins to revaporize. After this breakthrough point is reached, the exit vapor contains the most volatile material.

This will continue until the second breakthrough point is reached, after which the next most volatile component will start to desorb from the carbon surface. To obtain effective control in this case, the adsorption cycle must be stopped once the first breakthrough point is reached, as determined by the detection of any organic vapors in the discharge.

Tabel 2. Predicted MTZ length.

Benzene concentration, ppb	MTZ length, in
100	1.15
286	1.0
862	0.998
3,216	0.961

Two important factors that influence the adsorption capacity and operating economics of a carbon adsorber are the area of the bed and the mesh size of the carbon.

The cross-sectional area of a carbon bed vessel should be designed for a linear gas velocity through the carbon of 15 fpm to 60 fpm. This linear gas velocity, also known as "contact velocity," is important to allow sufficient time to establish the adsorption equilibrium. The particle size of the carbon affects the resistance to the flow of gases through the bed. The resistance should be minimized in order to reduce power consumption and prevent gas channeling through the bed. For a carbon bed 18-in deep and a maximum gas velocity of 60 fpm, the pressure drop through 4.6-mesh carbon is approximately 2-in W.C.

Continuous process

Most industrial activated carbon systems have at least two adsorption beds to allow for continuous flow at maximum condition. The adsorbers are cycled in and out of service, resulting in each adsorber operating in a batch mode. The modes are characterized by an adsorption cycle and desorption or regeneration cycle.

In the adsorption cycle, the HAP-laden gas stream is directed to the first adsorber containing freshly regenerated carbon. The organics are adsorbed onto

the carbon surface until the HAP concentration reaches a predetermined level and then the flow of contaminated gas is transferred to the second bed and the first bed is regenerated (Fig. 4).

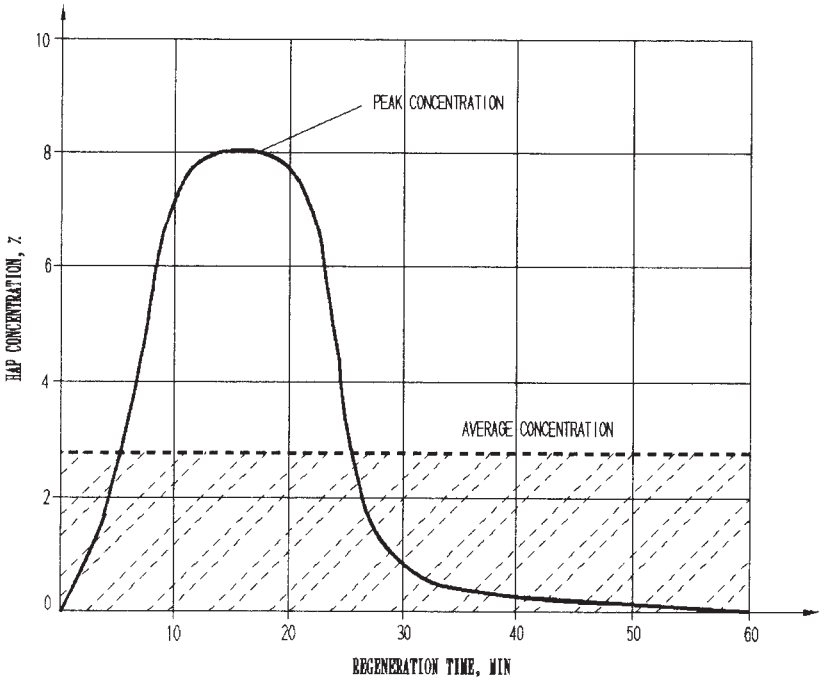
The automatic switchover from one bed to the other is handled by a microprocessor-based control system. The cycling permits uninterrupted filtration of the effluent gas from a continuous process.

While the second carbon bed is in service, the first bed is regenerated so that it will be ready for a new adsorption cycle when the second bed reaches its design limit of saturation. The thermal regeneration cycle desorbs most of the retained HAP and reconditions the carbon bed.

The most common heat source is low-pressure steam, which is introduced countercurrently to the HAP-laden waste gas flow. The steam requirements for desorption vary, depending on external heat losses as well as the nature of the HAP and regeneration time, but generally range from 3 lb to 10 lb of steam per pound of desorbed HAP. Because the boiling points of the organic compounds in the inlet gas may differ, the temperature of the desorbing steam should be greater than the highest boiling point in order to drive off all of the organics from the carbon surface in the regeneration cycle.

Based on experimental data from a typical installation, it was determined that more than 95% of the HAP was desorbed from the carbon bed during the first 30 min after the regeneration cycle starts.

Fig. 5. HAP concentration versus regeneration time.



During the first 10 min, the concentration of the HAP in the regeneration steam rapidly rises to a peak and remains at that level for approximately 10 min before rapidly declining over the next 10 min. The concentration then gradually decreases over the remainder of the 60-min regeneration cycle until all of the HAPs have been desorbed and the level of organics in the stream is below the detectable limit (Fig. 5).

Economical destruction

The high concentration of organics in the regeneration steam, combined with the short duration of the desorption cycle, permits economical destruction of the HAPs in a thermal oxidizer.

Although thermal oxidation is a costly disposal method for treating the low concentrations of organics contained in the process exhaust, the carbon adsorption process collects the HAP over a long period and acts as a storage container until the desorption process is scheduled.

A properly designed thermal oxidizer, which incorporates an effective heat exchanger and advanced refractory lining, is able to utilize the calorific value of the desorbed HAP to generate the temperatures required for destruction with minimal auxiliary fuel consumption. A destruction efficiency of more than 99% can be achieved for most organics at temperatures ranging from 1,400°F to 2,000°F with residence times of 0.5 sec to 2.0 sec.

To receive information on the control of HAPs: Croll-Reynolds Clean Air Technologies, Westfield, NJ.