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David J. Wilson[a]; Tomás Cordero[a]; César Gómez-Lahoz[a]; Rafael G. Delgado[a]; José M. Rodríguez-Maroto[a]
[a] DEPARTAMENTO DE INGENIERÍA QUIÍMICA, FACULTAD DE CIENCIAS CAMPUS UNIVERSITARIO DE TEÁTIONS UNIVERSIDAD DE MÁLAGA, MÁLAGA, SPAIN

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Soil Cleanup by In-Situ Aeration. XX. Mass Transport of Volatile Organics in Wet Activated Carbon

DAVID J. WILSON,* TOMÁS CORDERO,
CÉSAR GÓMEZ-LAHOZ, RAFAEL GARCÍA DELGADO,
and JOSÉ M. RODRÍGUEZ-MAROTO
DEPARTAMENTO DE INGENIERÍA QUIÍMICA
FACULTAD DE CIENCIAS
CAMPUS UNIVERSITARIO DE TEÁTINOS
UNIVERSIDAD DE MÁLAGA
29071 MÁLAGA, SPAIN

ABSTRACT

A mathematical model for the adsorption of volatile organic compounds (VOCs) from wet gas streams by granular activated carbon columns is developed, and modeling results are discussed. Capillary condensation of water in the carbon pores is found to have a very damaging effect on the rate of VOC adsorption, since diffusion rates of VOCs into the pores are greatly reduced. Implications of the results for the operation of soil vapor extraction systems for the remediation of hazardous waste sites are discussed, and suggestions are made on how to deal with the problem.

INTRODUCTION

A major part of the cost of a soil vapor extraction (SVE) operation is the removal of the volatile organic compounds (VOCs) from the effluent gas pumped from the vacuum wells. A number of techniques exist for doing this, each with its advantages and drawbacks. These include combustion, catalytic oxidation, biofiltration, refrigeration, and activated carbon adsorption (1, 2). If a substantial portion of the VOCs being removed

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* Permanent address: Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, USA.

consists of chlorinated organics, combustion and catalytic oxidation are complicated by the need for supplementary fuel, by corrosion problems, and by the need for removal of HCl (and possibly chlorinated dioxins and furans) from the exhaust gas stream. Biofiltration has not yet been shown to be successful for such chlorinated VOCs as TCE. Refrigeration is currently not in use at even one SVE installation. Activated carbon suffers from the fact that the effluent gas streams are virtually always saturated with water vapor, resulting in very inefficient performance of the carbon. Typically, activated carbon costs constitute approximately half of the total cost of a SVE operation if activated carbon is used (3, 4). There is evidently a need for an improved technique for removing VOCs, particularly chlorinated solvents, from these gas streams.

There are two reasons for the poor performance of granular activated carbon in SVE. These are as follows.

First, one expects competition between water molecules and VOC molecules for the adsorption sites on the carbon. Even if the binding of the water to a site is weak, the water concentration in the gas stream is generally very much greater (except during a brief initial phase of the operation) than the concentration of the VOC, so the water may be effective in displacing VOC from adsorption sites, shifting the equilibrium to displace VOC back into the vapor phase. This phenomenon is also well known in soils (References 5, 6, and 7, for example), where it is called the "wet dog effect." We note, however, that the use of powdered activated carbon for the removal of organics from water is a well-established and effective technique, so this effect alone is evidently not sufficient to account for the very poor performance of granular activated carbon in SVE.

A second possible source of the problem is that at very high relative humidities one gets capillary condensation of water in the pores of materials which the water can wet. In order to be adsorbed, then, the VOC must diffuse down a pore filled with liquid water rather than a pore filled with gas. Diffusion constants in gases are typically 1000 to 10,000 times larger than they are in liquids (8). Also, the solubilities of the VOCs of interest in liquid water are typically low (<1000 mg/L). If the pores are filled with liquid water, one therefore expects the rate of adsorption of a VOC to be greatly decreased, since the rate of diffusion of VOC to the adsorption sites is drastically reduced.

An elegant general treatment of the kinetics of adsorption on activated carbon from the aqueous phase has been given by van Lier (9); his discussion provides the machinery for elaborations of the model to be described below should these be desired. A discussion of the effect of diffusion kinetics on adsorption rates for adsorbents exhibiting linear and

Freundlich isotherms has been given by Mattson and Mark (10). Information on the adsorption of water on activated carbon is summarized by Bansal, Donnet, and Stoeckli (11), who present a number of water adsorption isotherms on activated carbon showing the phenomenon of capillary condensation, which is discussed in some detail.

We present here an analysis of the adsorption of a VOC onto activated carbon from a stream of air having high relative humidity. This is then used to develop a mathematical model for the operation of an activated carbon column being used to treat a wet gas stream such as the off-gas obtained from a typical SVE well. The model yields results indicating that capillary condensation of liquid water in the pores of the carbon reduces the rate of diffusional mass transport sufficiently to account for the poor performance of carbon in SVE off-gas treatment. We close with a brief discussion of possible ways of mitigating this difficulty.

ANALYSIS

The assumptions on which our analysis is based are as follows.

1. The carbon is previously equilibrated with water vapor at the desired relative humidity H_R, the water adsorption follows a BET isotherm (11), and the water wets the carbon so that capillary condensation occurs at high relative humidities. This assumption is necessitated by computational requirements; extension of the model to include dynamic treatment of the water vapor as well as the VOC is easy conceptually, but adds very substantially to the length of the computer runs.

2. The VOC is adsorbed on the pore surfaces of the carbon according to a Langmuir adsorption isotherm (12). This requirement is easily relaxed; a Freundlich isotherm, for instance, could readily be used. The rate of the adsorption process is controlled by the rate of diffusion of VOC into the pores of the carbon.

3. The effective diffusion constant of the VOC in the pores is determined by the fraction θ_w of the pore volume that is filled with water.

4. Local equilibrium within a small segment of pore is assumed between the VOC in the vapor, aqueous, and adsorbed phases, which implies that radial VOC thermodynamic activity gradients do not exist in the pore. The vapor–aqueous partitioning of the VOC is governed by Henry's law.

We note that the objective here is not a detailed, extremely precise modeling of the adsorption of VOCs from wet gas streams, but a first assessment of the extent to which capillary condensation in the pores and the associated reduction in VOC diffusivity in the carbon may account for the poor performance of activated carbon in SVE.

Diffusion of VOC in Wet Pores

Consider a single cylindrical pore of length l_p and radius r_p. We wish to determine an effective diffusion constant for VOC in the pore. Let the cross-sectional area of the pore be A_p. To assign an effective diffusion constant D_{eff} to the pore, we consider the physical picture shown in Fig. 1. A fraction θ_w of the pore's cross-sectional area is occupied by water; the remainder by air. We examine diffusion transport from the left end of the pore to the right while maintaining a constant concentration C_0 of VOC in the gas phase at the left end and a concentration of 0 at the right end.

From Henry's law and our assumption of local equilibrium between phases at any point along the length of the pore, we have

$$C^g(x) = K_H C^a(x) \tag{1}$$

where $C^g(x)$ = gas-phase VOC concentration a distance x from the left end of the pore, g/cm^3

$C^a(x)$ = aqueous VOC concentration at the point x, g/cm^3

K_H = Henry's constant of the VOC, dimensionless

At steady-state with the boundary conditions indicated in the figure we have

$$C^g(x) = C_0(l_p - x)/l_p \tag{2}$$

and

$$C^a(x) = \frac{C_0}{K_H}(l_p - x)/l_p \tag{3}$$

The cross-sectional area of the pore occupied by water is $A_p\theta_w$; that occupied by air, $A_p(1 - \theta_w)$. Then the total diffusive flux of VOC in the pore is given by

$$F = (1 - \theta_w)A_pD_g\frac{C_0}{l_p} + \theta_wA_pD_w\frac{C_0}{l_pK_H} = D_{\text{eff}}A_p\frac{C_0}{l_p} \tag{4}$$

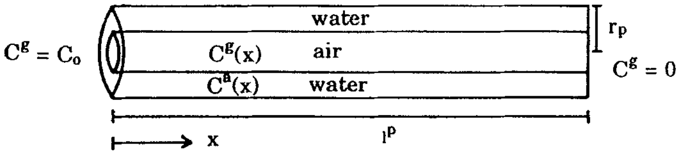

FIG. 1 Model used for calculating the effective diffusion constant D_{eff} of a VOC in a partly water-filled pore. θ_w = fraction of pore volume which is filled with water.

where D_g = diffusion constant of VOC in air in the pore, cm^2/s
D_w = diffusion constant of VOC in water, cm^2/s

This defines the effective diffusivity as

$$D_{\text{eff}} = (1 - \theta_w)D_g + \frac{\theta_w D_w}{K_H} \tag{5}$$

where we are using vapor concentrations in the pore in the expression for diffusion transport.

The BET Isotherm and the Kelvin Equation: Adsorption of Water

We shall use a BET-type isotherm for the adsorption of water; this is modified to take account of the fact that the adsorption is taking place in pores of finite diameter rather than on an isolated plane surface; see Adamson (12). Let

$\bar{v}$ = molecular volume of a water molecule, cm^3, = $\bar{V}/N_0$
$\bar{V}$ = molar volume of water, cm^3/mol
N_0 = Avogadro's number, 6.022×10^{23}
σ = area of adsorbing surface occupied by one water molecule, cm^2
a = effective radius of a water molecule, cm
$a = (3\bar{v}/4\pi)^{1/3}$
$\sigma = \pi a^2$

The volume of a single pore is given by $\pi r_p^2 l_p$, and the surface of the pore is assumed given by $2\pi r_p l_p$. The number of water molecules needed to produce a monolayer on the pore surface is given by $S = 2r_p l_p/a^2$, the number of surface adsorption sites, and the total number of water molecules required to fill the pore with condensed water is given by $3r_p^2 l_p/4a^3$. Therefore, the maximum number of molecules which can be associated with a single molecule in the monolayer is

$$n_m = \frac{3r_p^2 l_p}{4a^3} \bigg/ \frac{2r_p l_p}{a^2} = 3r_p/8a \tag{6}$$

Consider the following set of adsorption processes:

$$\begin{array}{ll} S_0 + H_2O \Leftrightarrow S_1 & K' = S_1/S_0C^w \\ S_{i-1} + H_2O \Leftrightarrow S_i & K = S_i/S_{i-1}C^w;\ i = 2, 3, \ldots, n_m \end{array} \tag{7}$$

where C^w = water vapor concentration in equilibrium with the surface
S_j = a surface site (or the concentration of surface sites) with j associated water molecules.

It is easily shown by recursion that

$$S_1 = K'S_0C^w \tag{9}$$

$$S_i = K'S_0K^{i-1}(C^w)^i \tag{10}$$

Then

$$S = S_0\{1 + K'C^w[1 + KC^w + (KC^w)^2 + (KC^w)^3 + \cdots + (KC^w)^{nm-1}]\} \tag{11}$$

which can be rewritten as

$$S = S_0\left\{1 + K'C^w\left[\frac{1 - (KC^w)^{nm}}{1 - KC^w}\right]\right\} \tag{12}$$

so

$$S_0 = \frac{S}{1 + K'C^w\left[\dfrac{1 - (KC^w)^{nm}}{1 - KC^w}\right]} \tag{13}$$

This yields

$$S_j = \frac{K'K^{j-1}(C^w)^jS}{1 + K'C^w\left[\dfrac{1 - (KC^w)^{nm}}{1 - KC^w}\right]} \tag{13}$$

Let $\bar{n}$ be the average number of H_2O molecules adsorbed per unit area, given by

$$\bar{n} = \sum_{p=1}^{nm} pS_p \tag{14}$$

Then

$$\bar{n} = \frac{K'C^w \sum_{p=1}^{nm} p(KC^w)^{p-1}}{1 + K'C^w\left[\dfrac{1 - (KC^w)^{nm}}{1 - KC^w}\right]} \tag{15}$$

Now

$$\sum_{p=1}^{n} px^{p-1} = \frac{d}{dx}\left[\sum_{p=1}^{n} x^p\right] = \frac{d}{dx}\left[\frac{1 - x^{n+1}}{1 - x}\right]$$

$$= \frac{1 - (n + 1)x^n + nx^{n+1}}{(1 - x)^2}$$

Use of this identity in Eq. (15) then gives

$$\bar{n} = K'C^w \frac{1 - (n_m + 1)(KC^w)^{nm} + n_m(KC^w)^{nm+1}}{(1 - KC^w)[1 + (K' - K)C^w - K'C^w(KC^w)^{nm}]} \tag{16}$$

Let

$$KC^w = x = C^w/C_{\text{sat}} \tag{17}$$

and

$$C_{\text{sat}}(r_p) = C_{\text{sat}} \exp\left[-\frac{\gamma\bar{V}}{r_pRT}\right] \tag{18}$$

which is a form of the Kelvin equation (11). Here

C_{sat} = water vapor concentration in equilibrium with a plane water surface at temperature T, g/cm³

$C_{\text{sat}}(r_p)$ = water vapor concentration at which the pores are filled by capillary condensation, g/cm³

γ = surface tension of water, dynes/cm

R = molar gas constant, ergs/mol·deg

T = temperature, degrees K

(Note that a factor of 2 is missing from the numerator of the argument of the exponential; this is because we are dealing with a cylindrical, rather than a spherical, water surface.) Now K'/K is just the BET parameter c, and θ_w, the fraction of the pore volume that is filled, is given by $\bar{n}(x)/\bar{n}(x_m)$, where $x_m = C_{\text{sat}}(r_p)/C_{\text{sat}}$—the value of x for which pore condensation occurs. This yields finally

$$\theta_w = \frac{x}{x_m} \frac{(1 - x_m)[1 - (n_m + 1)x^{nm} + n_m x^{nm+1}][1 + (c - 1)x_m - cx_m^{nm+1}]}{(1 - x)[1 + (c - 1)x - cx^{nm+1}][1 - (n_m + 1)x_m^{nm} + n_m x_m^{nm+1}]} \tag{19}$$

For comparison, use of the same approach with the simple BET isotherm yields

$$\theta_w = \frac{x(1 - x_m)[1 + (c - 1)x_m]}{x_m(1 - x)[1 + (c - 1)x]} \tag{20}$$

where c = K'/K, large if the binding of water in the monolayer is strong, dimensionless

C_w = water vapor concentration in contact with the carbon, g/cm³

Effect of H_R on VOC Diffusion in the Pores

Figure 2 shows the dependence of $C_{sat}(r_p)/C_{sat}$ on $2r_p = d$ for water in wetted pores having diameters d in the range 20 to 500 Å. Capillary condensation in the pores of activated carbon is possible in these mesopores at relative humidities well below 100%; it occurs in the micropores at even lower relative humidities.

Figures 3(a,b), 4(a,b), and 5(a,b) show plots of θ_w, D_{eff}, and a time constant τ, respectively, versus relative humidity H_R for pore diameters of 50, 100, 200, and 400 Å. Figures 3(a), 4(a), and 5(a), utilize Eq. (20) for the calculation of θ_w; Figs. 3(b), 4(b), and 5(b) use Eq. (19). The other parameters used in the calculations are given in Table 1.

In Figs. 3(a,b) we see that the adsorption isotherms predict that pore condensation occurs rather abruptly and at relative humidities substantially below 100%. Since SVE off-gases are typically almost saturated, we see that one can generally expect water-filled pores within a few days after a carbon canister is put in service.

The effective pore diffusivity D_{eff} (calculated from Eq. 5) is plotted against H_R in Figs. 4(a,b). D_{eff} shows a marked fall-off as H_R increases to the point at which pore condensation occurs; it then remains constant as H_R increases up to 100% since there is no further change in the water

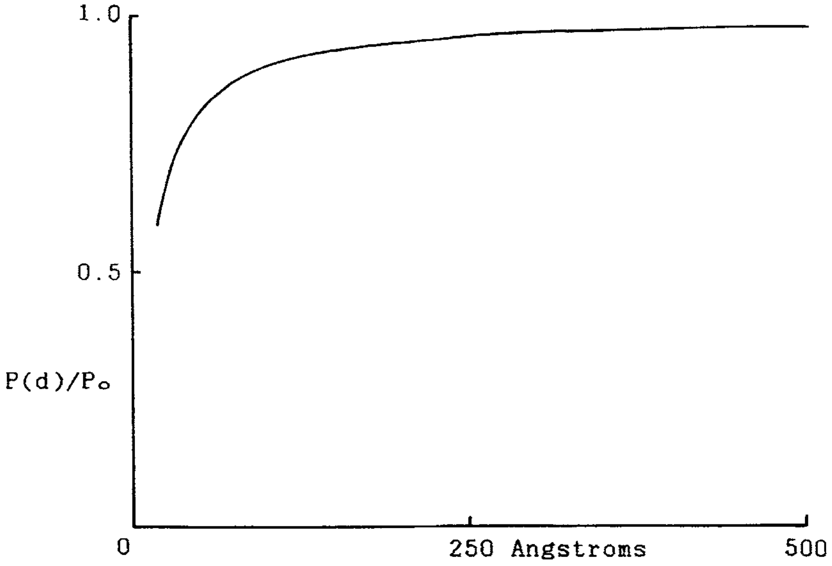

FIG. 2 Plot of $C_{sat}(d)/C_{sat}$ versus pore diameter $d = 2r_p$ for water at 20°C in a wetted cylindrical pore, according to the Kelvin equation.

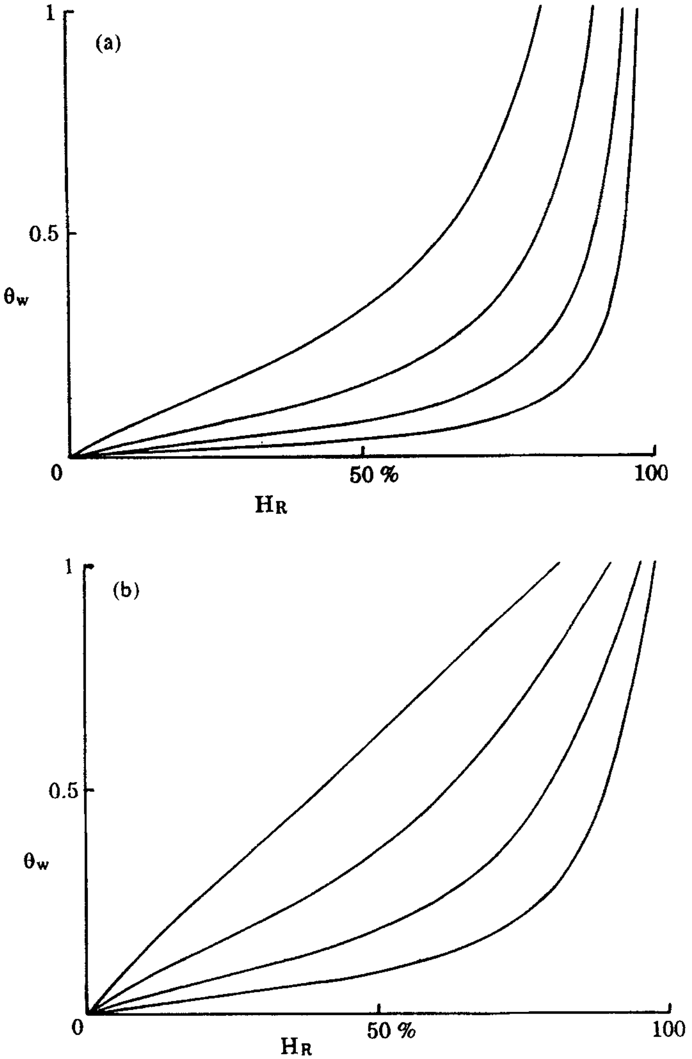

FIG. 3 Plots of θ_w, the water-filled fraction of the pore volume, versus the relative humidity H_R. Pore diameters are 50, 100, 200, and 400 Å. See Table 1 for the values of the other parameters. Equation (20), the BET isotherm, was used for Figs. 3(a), 4(a), and 5(a); Eq. (19), the BET isotherm modified for the effect of finite pore diameter, was used for Figs. 3(b), 4(b), and 5(b).

TABLE 1
Default Parameters Used in the Calculations Shown in Figs. 3–5

Pore length	0.1 cm
Pore diameter (as indicated in the figures)	5, 10, 20, 40 × 10^{-7} cm
Temperature	20°C
Surface tension of water	72 dynes/cm
C_{sat}	9.605 × 10^{-7} mol/mL
BET parameter c for water	4

content of the pores after they are saturated. This fall-off in D_{eff} is due to the very small size of aqueous-phase diffusion constants compared to gas-phase diffusion constants. In these calculations the gas-phase diffusion constant was taken to be only 100 times as large as the aqueous-phase diffusion constant to avoid excessively "stiff" differential equations (which cause computational problems). In fact, gas-phase diffusion constants are typically three or four orders of magnitude larger than aqueous-phase diffusion constants, although the gas-phase constants should be reduced somewhat in pores because of the reduction in mean free path of the molecules.

It is possible to estimate a time constant for pore diffusion from the lowest eigenvalue of the appropriate diffusion problem. We consider the time-dependent one-dimensional diffusion equation (Eq. 21) with its associated boundary conditions:

$$\frac{\partial C}{\partial t} = D_{eff}\frac{\partial^2 C}{\partial x^2} \tag{21}$$

$$C(0, t) = C_0 \tag{22}$$

$$\frac{\partial C(l_p, t)}{\partial x} = 0 \tag{23}$$

Separation of variables and the usual eigenvalue/eigenfunction analysis give for the eigenvalues

$$\lambda_n = \left[\frac{(2n - 1)\pi}{2l_p}\right]^2 D_{eff}, \qquad n = 1, 2, \ldots \tag{24}$$

The reciprocals of these eigenvalues are the time constants τ_n associated with the pore diffusion process. The largest time constant, τ_1, is given by

$$\tau_1 = \tau = \frac{4l_p^2}{\pi^2 D_{eff}} \tag{25}$$

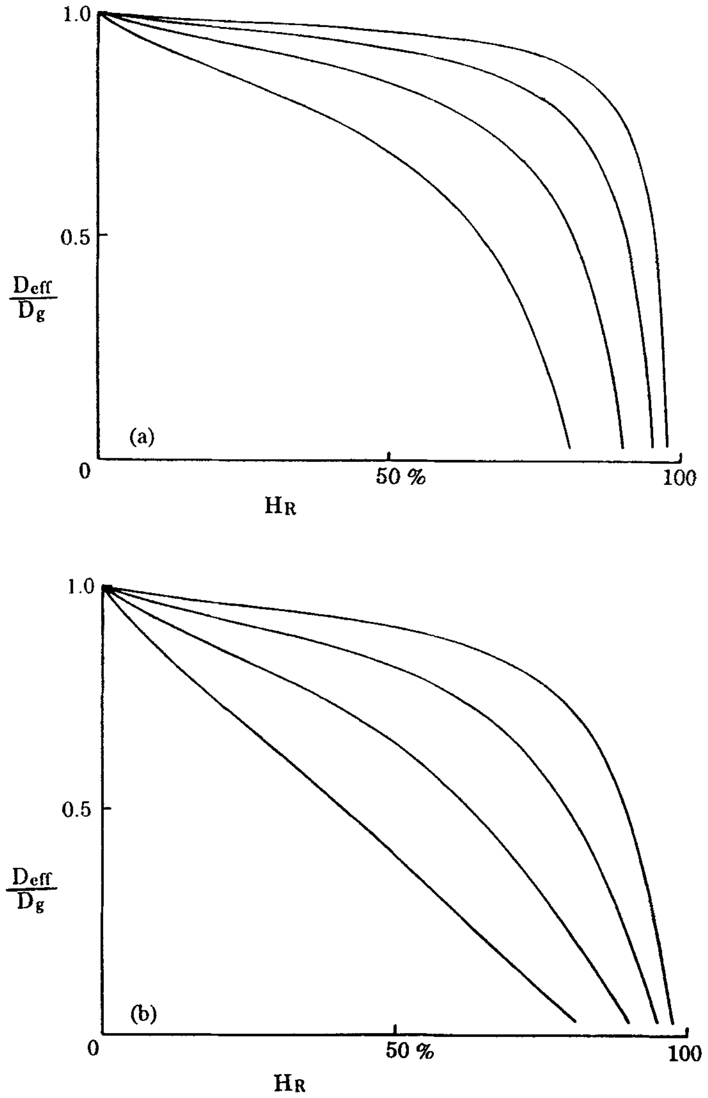

FIG. 4 Plots of the effective VOC diffusion constant in the pores, D_{eff}, versus H_R for pore diameters of 50, 100, 200, and 400 Å. Other parameters are given in Table 1.

This is a rough measure of the contact time needed to get effective removal of VOC from the gas stream. Plots of τ versus relative humidity are given in Figs. 5(a,b). We see spectacular increases in τ just as H_R increases up to the point where capillary condensation of water in the pores is complete. We shall see that this corresponds to equally spectacular deterioration in the effectiveness of activated carbon for VOC removal unless the gas flow rates are greatly decreased if the gas being treated has a high enough relative humidity that capillary condensation takes place in the pores.

Diffusion and Adsorption in a Wet Pore

We next examine the diffusion of VOC into a single pore, partially filled with water, and with Langmuir adsorption of this VOC on the pore surface. The geometry is indicated in Fig. 6. Notation is as follows.

Δv = volume of a volume element in the pore, $\pi r_p^2 \Delta u$, cm^3
C_{ij}^a = aqueous VOC concentration in the ijth volume element, g/cm^3
C_{ij}^g = vapor phase VOC concentration in the ijth volume element, g/cm^3
Γ_{ij} = surface phase VOC concentration in the ijth volume element, g/cm^2
C_i^{gm} = vapor phase VOC concentration in the mobile gas phase at the mouth of the pore, g/cm^3
m_{ij} = total mass of VOC in the ijth volume element, g

We drop the subscripts i, j for the moment. A mass balance on the ijth volume element gives

$$m = \theta_w \pi r_p^2 \Delta u C^a + (1 - \theta_w) \pi r_p^2 \Delta u C^g + 2\pi r_p \Delta u \Gamma \tag{26}$$

We assume Langmuir adsorption for the VOC, so have

$$\Gamma = \frac{\Gamma_{\max} C^g}{C^{g\prime} + C^g} \tag{27}$$

where $\Gamma_{\max}$ and $C^{g\prime}$ are Langmuir isotherm parameters pertaining to adsorption in which VOC displaces H_2O from the adsorption site. Also, we have

$$C^g = K_H C^a \tag{28}$$

Substitution of Eqs. (27) and (28) into Eq. (26) then yields

$$m = \pi r_p^2 \Delta u [\theta_w / K_H + 1 - \theta_w] C^g + \frac{2\pi r_p \Delta u \Gamma_{\max} C^g}{C^{g\prime} + C^g} \tag{29}$$

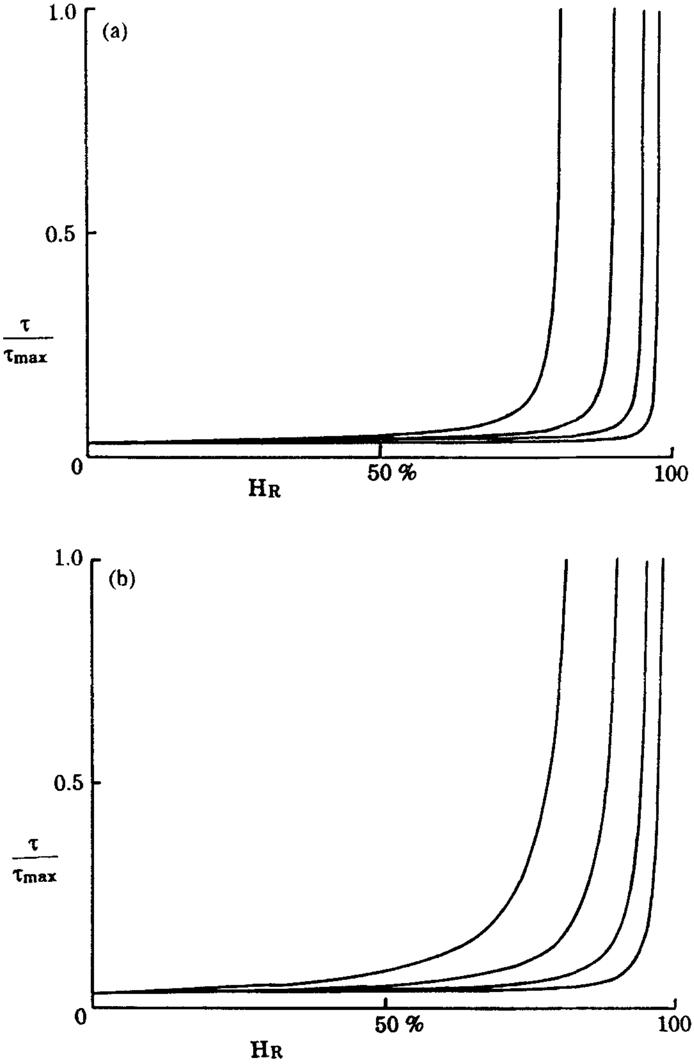

FIG. 5 Plots of diffusion time constant τ versus relative humidity H_R for pore diameters of 50, 100, 200, and 400 Å. $\tau = 4l_p^2/(\pi^2 D_{eff})$. See Table 1 for the other parameter values.

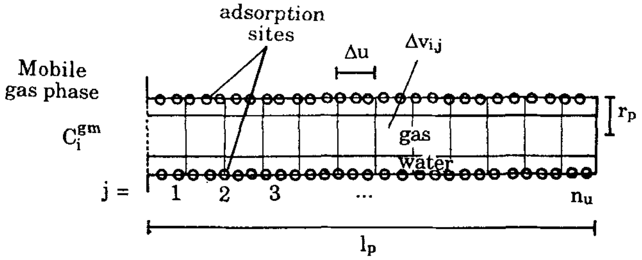

FIG. 6 Geometry and notation for diffusion and adsorption in a single partially water-filled pore.

This is more conveniently written as

$$m = \alpha C^g + \frac{\beta C^g}{1 + \delta C^g} \tag{30}$$

where

$$\alpha = \pi r_p^2 \Delta u(\theta_w/K_H + 1 - \theta_w)$$
$$\beta = 2\pi r_p \Delta u \Gamma_{max}/C^{g\prime}$$
$$\delta = 1/C^{g\prime}$$

Rearrangement then gives

$$\alpha\delta(C^g)^2 + (\alpha + \beta - \delta m)C^g - m = 0 \tag{31}$$

from which we obtain

$$C^g = \frac{(\delta m - \alpha - \beta) + [(\delta m - \alpha - \beta)^2 + 4\alpha\delta m]^{1/2}}{2\alpha\delta} \tag{32}$$

(It is easily shown that the positive sign must be used to avoid values of C^g which are physically impossible.)

We now examine the diffusion mass transport between the slabs into which the pore is partitioned for mathematical analysis. We reintroduce the subscripts. Generally,

$$\frac{dm_{ij}}{dt} = \frac{D_{\text{eff}}\pi r_p^2}{\Delta u}(C^g_{i,j+1} - 2C^g_{ij} + C^g_{i,j-1}), \qquad j = 2, 3, \ldots, n_u - 1 \tag{33}$$

For the slab at the back end of the pore we have

$$\frac{dm_{i,nu}}{dt} = \frac{D_{\text{eff}}\pi r_p^2}{\Delta u}(C^g_{i,nu-1} - C^g_{i,nu}) \tag{34}$$

and for the slab at the mouth of the pore,

$$\frac{dm_{i,1}}{dt} = \frac{D_{\text{eff}}\pi r_p^2}{\Delta u}\left[C_{i,2}^g - C_{i,1}^g + 2(C_i^{gm} - C_{i,1}^g)\right] \tag{35}$$

Construction of the Column Model for VOC Adsorption from Wet Gas on Activated Carbon

To proceed, we need an estimate of the number of pores per unit volume of carbon. This can be obtained in two ways, as follows.

First, we may use the value of the pore porosity of the carbon bed, ν_p (dimensionless). We define n as the number of pores per unit volume of carbon bed. Then

$$n\pi r_p^2 l_p = \nu_p$$

which yields

$$n = \frac{\nu_p}{\pi r_p^2 l_p} \tag{36}$$

Alternatively, we may use the surface area per unit mass of carbon, S. Let ρ_c be the bulk density of the carbon, so $S\rho_c$ gives the surface area per unit volume. Then

$$n'(2\pi r_p l_p + \pi r_p^2) = S\rho_c$$

We neglect the second term in the parentheses (since $r_p \ll l_p$) to obtain

$$n' = \frac{S\rho_c}{2\pi r_p l_p} \tag{37}$$

In the following work, Eq. (36) will be used.

Consider an activated carbon column having a bed of length L and radius R. We partition it for analysis as indicated in Fig. 7. Here

q = volumetric air flow rate, cm^3/s (approximated as incompressible,

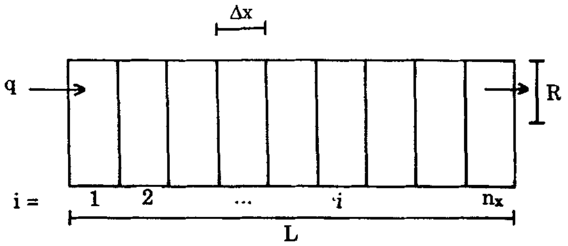

FIG. 7 Geometry and notation for the activated carbon column.

given the low pressure drops generally used across activated carbon canisters in SVE work)

$\Delta x = L/n_x$

$\Delta V = \pi R^2 \Delta x$

ν_m = mobile (interparticle) air porosity of the carbon bed

A mass balance on VOC in the mobile gas phase in the ith volume element gives

$$\nu_m \Delta V \frac{dC_i^{gm}}{dt} = q(C_{i-1}^{gm} - C_i^{gm}) - n\Delta V \frac{2D_{\text{eff}}\pi r_p^2}{\Delta u}(C_i^{gm} - C_{i,1}^g), \qquad i = 1, 2, \ldots, n_x \tag{38}$$

where C_0^{gm} = influent VOC concentration
n = number of pores per cm^3 of carbon bed

The total mass of VOC in the jth slab of all the pores in the ith volume element is given by

$$M_{ij} = n\Delta V m_{ij} \tag{39}$$

This permits us to write Eq. (30) as

$$M_{ij} = n\Delta V \alpha C_{ij}^g + \frac{n\Delta V \beta C_{ij}^g}{1 + \delta C_{ij}^g} \tag{40}$$

or

$$M_{ij} = \alpha' C_{ij}^g + \frac{\beta' C_{ij}^g}{1 + \delta C_{ij}^g} \tag{41}$$

As before, this yields

$$C_{ij}^g = \frac{(\delta M_{ij} - \alpha' - \beta') + [(\delta M_{ij} - \alpha' - \beta')^2 + 4\alpha'\delta M_{ij}]^{1/2}}{2\alpha'\delta} \tag{42}$$

Equations (33), (34), and (35) can be written in terms of M_{ij}; the results are

$$\frac{dM_{ij}}{dt} = \frac{n\Delta V D_{\text{eff}}\pi r_p^2}{\Delta u}(C_{i,j+1}^g - 2C_{ij}^g + C_{i,j-1}^g) \tag{43}$$

$$\frac{dM_{i,nu}}{dt} = \frac{n\Delta V D_{\text{eff}}\pi r_p^2}{\Delta u}(C_{i,nu-1}^g - C_{i,nu}^g) \tag{44}$$

$$\frac{dM_{i,1}}{dt} = \frac{n\Delta V D_{\text{eff}}\pi r_p^2}{\Delta u}[C_{i,2}^g - C_{i,1}^g + 2(C_i^{gm} - C_{i,1}^g) \tag{45}$$

Equation (38) is rewritten as

$$\frac{dC_i^{gm}}{dt} = \frac{q}{v_m \Delta V}(C_{i-1}^{gm} - C_i^{gm}) - \frac{2nD_{\text{eff}}\pi r_p^2}{\Delta u v_m}(C_i^{gm} - C_{i,1}^{g}) \tag{46}$$

The C_{ij}^{g} needed in Eqs. (43)–(46) are obtained from Eq. (42).

An outline of the modeling procedure is as follows.

1. A value of $C_{\text{sat}}(r_p)$, the water vapor concentration at which pore condensation is 100% ($\theta_w = 1$), is calculated from Eq. (18).
2. $C_{\text{sat}}(r_p)$ and C_w (the water vapor concentration in the gas stream) are then used to calculate a value of θ_w, the fraction of the pore space occupied by water, from Eq. (19) or Eq. (20).
3. This value of θ_w is used in Eq. (5) to calculate an effective pore diffusivity for the VOC in the carbon.
4. The number of pores per unit volume n is calculated from Eq. (36) or, if desired, from Eq. (37).
5. The modeling equations are the differential equations (43)–(46) and the algebraic equations (42). One integrates the differential equations forward in time, calculating the C_{ij}^{g} from the algebraic equations at each step in time.

The effluent VOC concentration is given by

$$C_{\text{effl}}^{g} = C_{nx}^{gm} \tag{47}$$

The total mass of VOC in the pores of the carbon (adsorbed, aqueous phase, and gas phase) is given by

$$M_{\text{tot}} = \sum_{i=1}^{n_x} \sum_{j=1}^{n_u} M_{ij} \tag{48}$$

RESULTS AND CONCLUSIONS

The program was implemented in TurboBASIC and run on a computer equipped with an 80486-DX microprocessor operating at 50 MHz. Runs required from 1 to 4 hours, depending on the parameters used. Default values of the model parameters are given in Table 2. A value of 2×10^{-4} cm^2/s was chosen for D_g, the diffusion constant of VOC in the gas phase, which is substantially smaller than the normal values of such diffusion constants. This is to take into account the fact that the diffusion here is taking place in pores, and the mean free path of the molecules is therefore substantially reduced below what it would be in the free gas phase. This also reduces the stiffness of the differential equations, so that larger time increments can be used in the numerical integration. Our most significant result, the drastic deterioration of the performance of the carbon when

TABLE 2
Default Parameters Used in the Model Calculations

Column length	25 cm
Column diameter	5 cm
Gas flow rate	1.0 mL/s
Mobile (interparticle) air porosity of carbon bed	0.3
Immobile (pore) porosity of carbon bed	0.4
Pore length	0.1 cm
Pore diameter	3.0×10^{-7} cm
Temperature	20°C
Surface tension of water	72 dynes/cm
C_{sat}	9.605×10^{-7} mol/mL
BET parameter c for water	6
Diffusion constant of VOC in air in pore	2.0×10^{-4} cm^2/s
Diffusion constant of VOC in water in pore	2.0×10^{-6} cm^2/s
Henry's constant of VOC in water (TCE)	0.2821
VOC $\Gamma_{\max}$ on carbon (Langmuir parameter)	0.1 mg/m^2
VOC C_g' on carbon (Langmuir parameter)	10 mg/m^3
Influent VOC concentration	10 mg/L
Surface area of carbon bed	533 m^2/cm^3
Total adsorption capacity of carbon column	26.18 g VOC
n_x	12
n_u	6
Δt	1.0, 2.5, 5 seconds

pore condensation occurs, is quite insensitive to the value of D_g so long as it is at least an order of magnitude or more larger than D_w.

The effect of relative humidity H_R on the VOC breakthrough curves is shown by the plots of effluent VOC concentration versus time displayed in Fig. 8, which shows plots of the column effluent VOC concentration versus time. The pore diameter is 30 Ångstroms, and the relative humidity values are 30, 50, 65, and 70%. Corresponding values of θ_w are 0.333, 0.554, 0.848, and 1.000. The effective diffusivities are 135.8, 93.0, 36.4, and 7.09×10^{-6} cm^2/s. The time constants τ are 29.8, 43.6, 111.3, and 571.7 seconds.

The results clearly show the devastating effect of pore condensation on the performance of the activated carbon at the flow rate used in these runs (1 mL/s). The volume of mobile gas contained within the column (interparticle voids volume) is 147.3 cm^3, so the contact time of the gas in the column is 147.3 seconds, only about one-fourth the value of τ at saturation. It is therefore not surprising that the performance of the column is extremely poor when the carbon pores are saturated with liquid water. The effect is due solely to the greatly reduced diffusivity of the VOC in the pores; the adsorption isotherm parameters for the VOC were held constant in all the runs.

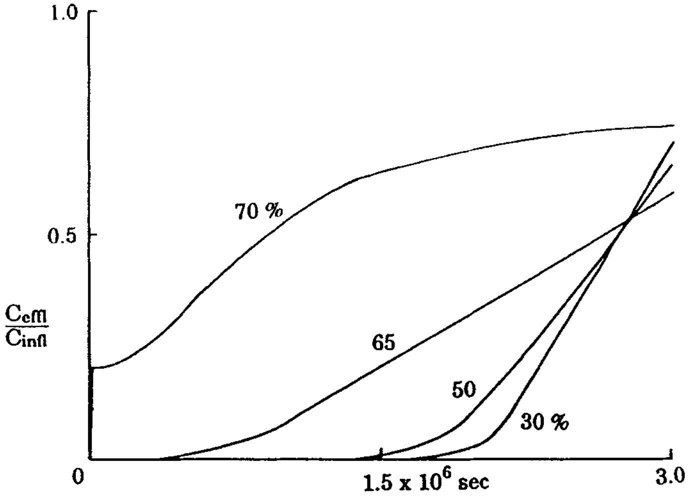

FIG. 8 Plots of normalized effluent VOC concentration $C_{\text{effl}}/C_{\text{infl}}$ versus time; effect of relative humidity H_R on the breakthrough curve. Pore diameter r_p = 30 Å; H_R = 30, 50, 65, and 70%, right to left at the bottom. Other parameters as in Table 2. τ = 29.84, 43.56, 111.27, and 571.65 seconds; contact time of gas in the column = 147.3 seconds. θ_w was calculated from H_R by means of Eq. (20) for the runs plotted in Figs. 8, 9, and 10.

Another set of runs was made which used parameters identical to those used in the runs plotted in Fig. 8 except that the pore diameter was increased to 45 Å and the pore porosity was increased to 0.6 (to maintain the surface area of the carbon constant). The results are shown in Fig. 9 as plots of column effluent VOC concentration versus time; relative humidities of 30, 50, 65, and 70% were used, as before. The corresponding values of θ_w are 0.229, 0.381, 0.583, and 0.692, so none of the runs deal with systems in which pore condensation (θ_w = 1) has occurred. The largest time constant is 61.0 seconds; the contact time of the gas in the column is more than twice this size. We therefore find that in all of these runs the carbon performs rather efficiently.

One expects that operating the column at a reduced air flow rate should result in improved performance if the system is diffusion-limited. As seen in Fig. 10, the plots of effluent VOC concentration versus volume of gas passed through the column show that this is indeed the case. A pore diameter of 30 Å was used in these runs. The value of the relative humidity was held constant at 65%, so the values of θ_w and D_{eff} are constant; the flow rates used were 1.0, 0.5, and 0.25 mL/s, corresponding to contact times of 147.3, 294.5, and 589 seconds. The value of τ was 111.3 seconds. Evidently the gas contact time in the canister should be somewhat more

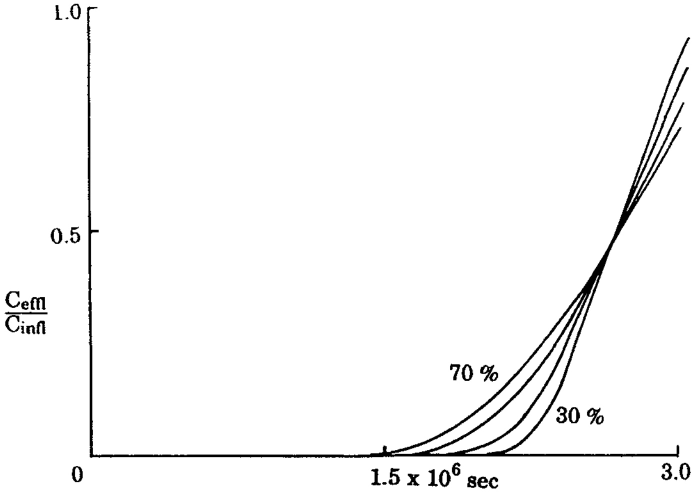

FIG. 9 Plots of normalized effluent VOC concentration versus time; effect of relative humidity. Pore diameter = 45 Å; v_p = 0.6; H_R = 30, 50, 65, and 70%; other parameters as in Table 2. τ = 26.00, 32.06, 46.34, and 60.98 seconds; contact time of gas in the column = 147.3 seconds.

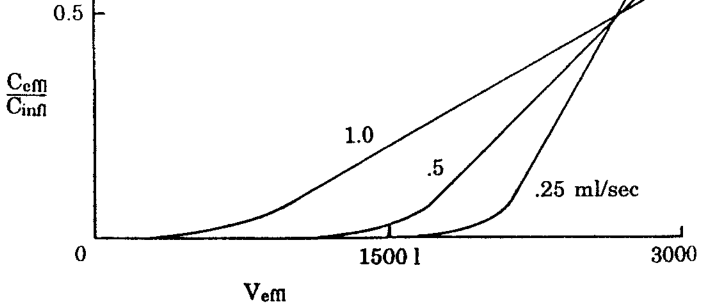

FIG. 10 Plots of normalized effluent VOC concentration versus effluent gas volume; effect of gas flow rate. Pore diameter r_p = 30 Å; H_R = 65%; gas flow rate = 1.0, 0.5, and 0.25 mL/s; other parameters as in Table 2. τ = 111.27 seconds; contact times = 147.3, 294.6, and 589.2 seconds, respectively.

than twice the value of τ in order for the carbon to perform reasonably efficiently.

The model assumes that the carbon is initially equilibrated with air at a given relative humidity, after which the VOC-containing gas stream is passed through the column. This was dictated by computational constraints and is not, of course, the way in which SVE activated carbon units are operated. It is, however, an adequate approximation to what is happening in the column except for a very short period at the beginning of the cleanup when high VOC concentrations are expected. Let us explore this point in more detail. We assume a carbon canister containing 800 kg of active carbon having a bulk density of 400 kg/m^3 and a bulk pore porosity of 0.40 (dimensionless). The total pore volume is then 0.80 m^3. Let the temperature be 20°C; then the concentration of saturated water vapor is given by

$$[H_2O]_{sat} = \frac{1.548 \times 10^6 \exp(-5282.6/T)}{0.08206T} = 9.52 \times 10^{-4} \text{ mol/L}$$

which gives $C_{sat} = 0.0171$ g/L. One liter of saturated air therefore contains 0.0171 mL of condensed water at 20°C, and 1 m^3 contains 17.1 mL of condensed water. The volume of air required to saturate the pore volume of the carbon in the canister is given by

$$\frac{8.0 \times 10^5 \text{ cm}^3 \text{ H}_2\text{O}}{17.1 \text{ cm}^3 \text{ H}_2\text{O/m}^3 \text{ air}} = 4.68 \times 10^4 \text{ m}^3 \text{ of air}$$

Let us assume an air flow rate through the canister of 100 ft^3/min, or 2.83 m^3/min. The canister will be saturated with water after

$$\frac{4.68 \times 10^4 \text{ m}^3}{2.83 \text{ m}^3\text{/min}} = 1.653 \times 10^4 \text{ min} = 11.48 \text{ days}$$

This calculation neglects the entrained droplets of liquid water which are not taken out by the demister, which would make the figure somewhat less. It also neglects the fact that not all of the water vapor is removed from the gas stream by the carbon, which would make the figure somewhat larger. However, the conclusion that the carbon in the canister will be saturated with water within a week or two of service remains valid.

In the initial stages of the cleanup, when off-gas VOC concentrations are high, carbon canisters have to be changed frequently in any case, so saturation with water is not a serious problem during this phase. During the bulk of the cleanup period, however, we expect good performance of the carbon for a few days while it is in the process of being saturated with water, followed by a lengthy period of poor performance after the pores are filled with water due to capillary condensation. One expects the effluent soil gas to be virtually saturated with water vapor at any flow rate, while the VOC concentrations may be very markedly reduced due to diffusion transport limitations in the soil being treated if gas flow rates are high (13).

The results of these model calculations should not be interpreted quantitatively, since the model used for the carbon is oversimplified. For example, the pores are assumed to be cylindrical and all of the same size, and the adsorption sites are assumed to be identical in their properties. Still, the results indicate very clearly that the effect of capillary condensation on the performance of activated carbon in SVE systems can be expected to be severe. We shall briefly mention three possible ways to circumvent this difficulty.

The first approach simply involves operating the SVE wells at lower air flow rates so as to increase the residence time of the off-gas in the carbon bed. Since VOC diffusion kinetics in the soil are usually the rate-limiting factor in SVE cleanups, operation of the wells at reduced flow rates should not greatly prolong cleanup times. Lower gas flow rates should result in an increased fraction of biodegradable VOCs which are destroyed by microorganisms, probably considerably higher concentrations of VOCs in the off-gas, and a reduced volume of off-gas to pump and to treat, as well as more efficient performance of the activated carbon. All these factors should result in substantial improvements in the economics of the SVE process when activated carbon is used for off-gas treatment.

The second approach is a good deal more speculative in nature. It involves the development of activated carbons or other reasonably economical adsorbents which are of sufficiently low polarity that the contact angle of water on the surface is 90° or greater, so that capillary condensation does not occur. Some nonpolar resins are available which must be specially hydrated before they can adsorb VOCs from liquid water; these would be quite satisfactory, but they are quite expensive. Another possibility is the treatment of the carbon with reagents (such as sodium *t*-butoxide or a strong reducing agent) to block or destroy the polar sites, principally phenolic OH groups.

The third approach is to use countercurrent flow refrigeration to remove a substantial portion of the water vapor from the stream of effluent soil gas by condensation. After condensation of water vapor, the gas is rewarmed to, say 20°C, resulting in a relative humidity of perhaps 40%, at which point capillary condensation would not occur. The use of condensation to remove water makes the gas treatment train somewhat more complex, but it should permit the use of regular granular activated carbon at high gas flow rates.

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