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Estimating Service Lives of Organic Vapor Cartridges II: A Single Vapor at All Humidities

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A widely used equation model for estimating service lives of organic vapor air-purifying respirator cartridges has been updated with more recent research results. It has been expanded to account for effects of high relative humidities. Adsorption capacity competition between water vapor and organic vapor is largely explained by mutual exclusion of adsorption volume of the activated carbon. The Dubinin/Radushkevich equation is used to describe the adsorption isotherms of both water and organic vapors. Effects of relative humidity and adsorbed water on adsorption rates are described by an empirical correlation with breakthrough times. The dynamic natures of adsorption and competition are incorporated using an expanding zone model with displaced water rollup. The complete model has been tested and verified with published and unpublished data from many sources.

Keywords cartridge, humidity, organic vapor, respirator, service life

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INTRODUCTION

Air-purifying respirators and their organic vapor (OV) cartridges and larger canisters are sometimes used or proposed for use in high humidity environments. Such cartridges (from here on this term will include canisters) almost always contain granules of activated carbon. The effect of high humidity in reducing OV breakthrough times (service lives) of gas mask canisters and air-purifying respirator cartridges has long been recognized.(1,2) Such reductions are most often seen for physically adsorbed OVs; breakthrough times may actually increase at high humidities with certain chemicals (e.g., organic acids or bases) that are removed by reactions with impregnants placed on carbon granules. This article will consider only cases of physical adsorption on activated carbons.

Limited data on humidity effects have been correlated in tables or expressed as empirical equations; however, means are lacking for predicting reduced breakthrough times at high humidities for varieties of cartridges, chemicals, use conditions, and environmental conditions. Wood(3) published a single OV (dry conditions) cartridge service life prediction model that has been widely accepted and used. It applied the Dubinin-Radushkevich (DR) isotherm equation with correlations for DR input parameters and adsorption rates. Some of these correlations have since been updated.(4–6) The objective of the work reported in this article was to update and extend this model to high-humidity environments and to cases where water may be adsorbed on the cartridge carbon prior to use.

BACKGROUND

Breakthrough Times at High Humidities

Nelson et al.(7,8) extensively measured breakthrough curves and times of several chemical vapors for two brands of commercial respirator cartridges at wide-ranging humidities. In addition to varying the humidity (use, test, or Run relative humidity [RH], as it will be used in the article) of the air entering the cartridges, Nelson et al. also varied the amount of water initially present on the carbons. The latter was expressed as the humidity (preconditioned, pre-equilibrated, or Pre RH) at which the carbons in the cartridges were equilibrated before testing. Such preconditioning represents exposure of a cartridge carbon bed to high-humidity air for a long period before using it to remove OVs. Most high-humidity experiments were done at only one concentration—1000 ppm, one airflow rate—53.3 L/min, and one temperature—22°C.

Nelson et al. reduced their experimental results at these conditions to a table of breakthrough time correction factors (multipliers) at Pre RHs and Run RHs of 0, 20, 50, 65, 80, and 90%. Average correction factors, normalized to the 50% Pre RH/50% Run RH condition average, ranged from 0.48 at 90%/90% to 1.04 at 65%/20%. Below 50% (both Pre RH and Run RH), the humidity effects were observed to be relatively slight. Others have seen little or no effects below 50% RH.(1,2)

There has been a tendency to use these published factors to account for high humidities. This must be avoided for the following reasons. As Nelson et al.(7) pointed out, these average correction factors were determined from a small number of OVs and brands of cartridges, not all at each set of Pre/Run conditions. They also observed that humidity has a greater effect on cartridge performance at lower concentrations. These factors were reported for only one OV breakthrough fraction—10% of the test (challenge) concentration—and may not apply at others.

Werner$^{(9)}$ reported similar tables of 1 and 50% breakthrough time correction factors for 300–1300 ppm trichloroethylene in 0, 25, 50, 65, and 85% RH air passed through narrow (2.54 cm) and long (13.5 cm) packed beds of a dried (0% Pre RH) activated carbon. Unlike Nelson et al.,$^{(7)}$ Werner observed significant humidity effects below 50% Run RH, which can be attributed to starting with very well dried carbon. Reported 10% breakthrough correction factors at 50% RH relative to those at 5% RH varied from 0.58 for 300 ppm to 0.83 for 1300 ppm. At the highest humidity, 85% Run RH, they ranged from 0.09 to 0.27, lower factors at lower OV concentrations, just as Nelson et al.$^{(7)}$ observed. Werner also noted that breakthrough curves broadened above 5% Run RH, reflecting a decrease in adsorption rate.

Adsorption Capacities at High Humidities

Werner,$^{(9)}$ Wood,$^{(10)}$ and Underhill$^{(11)}$ have each analyzed Werner's capacity (50% breakthrough fraction) ratio results by different theories. Others have developed empirical functions to correlate other humidity effect capacity data.$^{(12,13)}$ Such empirical and correlation models for high-humidity OV capacities require much experimental data specific for each OV and system; therefore, they have limited applicability for a general predictive breakthrough time model.

More general predictive models for high-humidity OV capacities have been reviewed and compared by Wood$^{(14)}$ using an equilibrium data set from Okazaki et al.$^{(15)}$ Wood's conclusion was that the Okazaki and Doong-Yang$^{(16)}$ models were the best predictors of these data. The Doong-Yang model, which combines volume exclusion and adsorption potentials, is the simpler of these two to apply; it requires only the single vapor (OV and water) DR adsorption isotherm equations. The idea of volume exclusion is that the portion of fixed micropore volume of the activated carbon filled with water is not available to OV, and vice versa. Lodewyckx and Vansant$^{(17)}$ also successfully applied a volume exclusion model; however, it did not work as well with the Okazaki data set and DR isotherms.$^{(14)}$

Adsorption Rates at High Humidities

The work of Hall et al.$^{(18,19)}$ resulted in an empirical model for effects of humidity on adsorption rate coefficients. Rate coefficients calculated from partial breakthrough curves (0.5 to 4% breakthrough) and the Wheeler equation were plotted against RH. Test humidities were kept the same as preequilibration humidities. The conclusions were: (1) no effect of RH on k_v below 50% RH, (2) apparent linear decrease in k_v with RH above 50% RH, and (3) different rates of decrease for different compounds. These results can be expressed as an equation:

$$k_v(\text{min}^{-1}) = a - b(\%RH - 50) \text{ for } RH \geq 50\% \qquad \textbf{(1)}$$

TABLE I. Empirical Parameters$^{(19)}$ for RH Effects on Adsorption Rate Coefficients

Compound	Concentration (ppm)	Parameters a	b	Ratios b/a
Carbon tetrachloride	14,600	6530	64	0.0098
1,1,1-Trichloroethane	6300	7930	63	0.0079
Trichloroethylene	7800	8090	74	0.0091
Propanol	7600	3700	7	0.0019

Parameter values from Hall's dissertation$^{(19)}$ are listed in Table I. Propanol, the only water-soluble compound of the four, had a much lower rate of decrease (b/a) with increasing RH. Quantitative generality of these parameters cannot be assumed, since they are based on limited data at limited conditions.

Lodewyckx and Vansant$^{(20,21)}$ also examined the influence of humidity on the overall mass transfer (adsorption rate) coefficient. Organic vapor concentrations were kept at 5 g/m^3. The reaction kinetic form of the Wheeler-Jonas equation was applied to measured 0.1 and 1% breakthrough times to calculate capacities W_e and rate coefficients k_v. Unlike with capacities,$^{(17)}$ they found very little influence of the kind of OV on the decrease of k_v with increasing relative humidity. The ratio A_{tot}, the amount of water present in the carbon pore system to the total pore volume (TPV), was the important parameter in determining the corrected adsorption rate coefficient, k_v':

$$k_v' = k_v(1 - A_{tot}/TPV) \qquad \textbf{(2)}$$

The TPV is the sum of the micropore, mesopore, and smaller macropore volumes; it can be determined by the total volume of liquid nitrogen adsorption. The A_{tot} is the sum of preadsorbed water (determined from the isotherm) plus water adsorbed from (or minus that desorbed into) the flowing airstream (determined by an empirical equation). The effects of both carbon prehumidification and air humidity are taken into account by this model.

While this model did not predict measured rate coefficients exactly, it did account for observed trends.$^{(20)}$ Uncertainties in experimental breakthrough times are amplified in calculations of experimental rate coefficients. A difficulty of the Lodewyckx model is requiring an adsorption isotherm for water on the carbon of interest. This isotherm can, itself, be changing with time.$^{(17)}$

Wood and Lodewyckx$^{(22)}$ analyzed these data plus some more in a different way. They found a correlation between the wet/dry rate coefficient ratio and the wet/dry breakthrough time ratio, such that:

$$k_v(\text{wet}) = k_v(\text{dry})\{0.33 + 0.67[t_b(\text{wet})/t_b(\text{dry})]\} \qquad \textbf{(3)}$$

$\leq k_v(\text{dry})$, where "wet" refers to having significant adsorbed water A_{tot}. This relationship is apparently independent of OV, carbon, breakthrough fraction, and OV concentration.

HIGH-HUMIDITY MODEL DESCRIPTION

Drawing on this background and making some assumptions, we built a mathematical model for estimating service lives that incorporates high-humidity effects.

Reaction Kinetic Breakthrough Time Equation

An OV in air flowing through a packed granular activated carbon bed adsorbs at the inlet side of the bed and forms a vapor/adsorbate wavefront that moves through the bed as more OV is added (Figure 1). The spread and shape of the wavefront is determined by the adsorption rate(s): a higher rate produces a steeper wavefront; a constant rate along the wavefront produces a symmetrical, reverse S shape. Breakthrough time of the OV is defined as when the leading "front" of the vapor wavefront reaches a selected breakthrough concentration at the exit of the bed. A breakthrough curve describes the exit concentration (or ratio) as a function of time and is a reflection of the vapor wavefront in the bed. The speed of movement of the wavefront through the bed is determined by the amount (concentration) of vapor entered balanced against the amount adsorbed.

We first assume (Assumption 1) the breakthrough time equation that has been derived by different researchers(3) for the ideal, single adsorption rate, single vapor case. The reaction kinetic form of the Wheeler-Jonas breakthrough time equation(4) has a capacity term minus a kinetic term:

$$t_b = \frac{W_e W}{C_o Q} - \frac{W_e \rho_B}{k_v C_o} \ln\left(\frac{C_o - C}{C}\right) \qquad \textbf{(4)}$$

It includes (1) carbon bed parameters of bed weight W (g) and packed density ρ_B (g/cm^3); (2) use parameters of challenge vapor concentration C_o (g/cm^3), breakthrough concentration C (g/cm^3), and airflow rate Q (cm^3/min); (3) vapor/carbon interaction parameters of adsorption rate coefficient k_v (min^{-1}) and adsorption capacity W_e (g/g carbon) at C_o. With these units time is in minutes. When this relationship is plotted as C/C_o vs. t_b, an S-shaped breakthrough curve is obtained. Although Eq. 4 was developed for a single vapor, we assume it also to describe OV breakthrough times in humid air (Assumption 2), recognizing that adsorption capacities and rate coefficients will be changed by the presence of water vapor.

Single Organic Vapor Equilibrium Capacity

We chose (Assumption 3) the DR equation(23) to calculate equilibrium W_e (g/g carbon) of individual organic vapors:

$$W_e = W_o\, d_L \exp[-(RT/\beta E_o)^2\{\ln(p_{sat}/p)\}^2] \qquad \textbf{(5)}$$

This contains two activated carbon characteristics:

W_o = micropore volume (or adsorption space, cm^3/g)
E_o = adsorption energy of a reference adsorbate (units of RT, e.g., kJ/mol)

which can be obtained from experimental data (see Appendix) if not available from the cartridge or carbon manufacturer. The DR equation also contains three characteristics of the vapor:

(1) β = affinity (or similarity) coefficient, relative to the reference adsorbate, taken (Assumption 4) to be benzene for which $\beta = 1$. It is calculated (Assumption 5) for OVs from a correlation with molar polarizability P_e (cm^3/mol),(4)

$$\beta_{OV} = 0.0862 P_e^{0.75} \qquad \textbf{(6)}$$

where $P_e = [(n_D^2 - 1)/(n_D^2 + 2)](M_w/d_L)$ for molecular weight M_w(g/mol), liquid density d_L (g/cm^3), and refractive index n_D. The latter three parameters can usually be found in common references;(24,25) if not, there are alternate ways to obtain P_e.(4)

(2) d_L = liquid density (g/cm^3), taken (Assumption 6) as a value in the range 20–25°C, usually found in these references. At much different temperatures this value would need to be modified. This assumption limits the model (without further modification) to chemicals that exist as liquids at the application temperature.

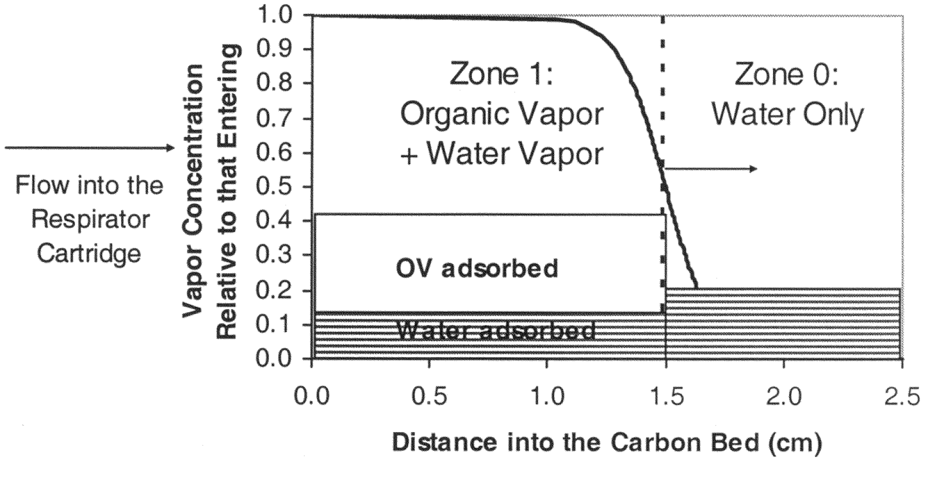

FIGURE 1. Two-zone humid air model

(3) p_{sat} = bulk liquid saturation vapor pressure (kPa) at temperature T (°K). We have preferred (Assumption 7) using the Antoine equation, p_{sat} (torr) = exp [A − B/(C+T)], whose parameter values are available from many sources.$^{(26-30)}$ Caution: The Antoine equation and parameters should not be used at temperatures beyond the range of vapor pressure data used to obtain those parameters. Large errors in calculated vapor pressures could result. Such ranges are usually specified with the published parameters. Vapor pressures can also be calculated from other vapor pressure correlation equations and corresponding parameter values$^{(31)}$ or from fitting vapor pressure and/or boiling point data$^{(24)}$ to the Antoine or another equation. Care must be taken to convert the parameters to the desired units. We have chosen to use vapor pressures in units of kPa = 7.50062 torr = 9.8692 × 10^{-3} atm.

In addition to temperature, the DR equation requires the challenge vapor concentration in air to be expressed in the same units as p_{sat}. Pressure p can be calculated from vapor concentration C_o (ppm) and atmospheric pressure P_{atm}(kPa) by p (kPa) = 10^{-6} C_o P_{atm}. The vapor concentration in gravimetric units can be calculated by the Ideal Gas Law (Assumption 8) as C'_o (g/cm^3) = 10^{-6} C_o M_w P_{atm}/RT, where R has the units corresponding to application atmospheric pressure P_{atm} (e.g., R = 82.0254 atm-cm^3/mol-deg for P_{atm} in atm).

Water Vapor Equilibrium Capacity

We have likewise chosen (Assumption 9) DR Eq. 5 to calculate equilibrium adsorption capacity W_{H_2O} (g/g carbon) of water vapor in the absence of OV. Furthermore, the micropore volume W_o and reference adsorption energy E_o were taken (Assumption 10) to be the same for water as for an OV on the same carbon. Water vapor pressure Antoine and other parameters are readily available.$^{(5)}$

These assumptions leave only one additional parameter needed for the DR Eq. 5, the affinity coefficient of water, β_{H_2O}. This is treated as an adjustable parameter (a property of the activated carbon) with a tentative value of $\beta_{H_2O} = 0.06^{(4)}$ (Assumption 11) for the adsorption branch of the water isotherm in the absence of OV. Thus, for a carbon prehumidified at Pre RH the volume of water adsorbed per gram of carbon at equilibrium is given by:

$$V_{adsH_2O}(\mathrm{cm^3/g}) = W_o \exp\left\{-\left(\frac{RT}{\beta_{H_2O}E_o}\right)^2 (\ln(\mathrm{Pre\ RH}))^2\right\} \tag{7}$$

Effects of Water on OV Capacity

Having the parameters and equations to calculate capacities of pure OV and pure water, we next needed to be able to calculate equilibrium capacities when both are adsorbed on activated carbon. We chose (Assumption 12) the volume exclusion theory applied by the modified DR equations of Doong and Yang.$^{(16)}$ For simplicity the hysteresis terms were eliminated (Assumption 13), leaving:

$$V_{adsOV}(\mathrm{cm^3/g}) = (W_o - V_{adsH_2O}) \exp\left\{-\left(\frac{RT}{\beta_{OV}E_o}\right)^2 \left(\ln\frac{p_{satOV}}{p_{OV}}\right)^2\right\} \tag{8}$$

$$V_{adsH_2O}(\mathrm{cm^3/g}) = (W_o - V_{adsOV}) \exp\left\{-\left(\frac{RT}{\beta_{H_2O}E_o}\right)^2 \left(\ln\frac{p_{satH_2O}}{p_{H_2O}}\right)^2\right\} \tag{9}$$

for equilibrium volumes of the two adsorbates competing for available micropore volume W_o. Note that p_{H_2O}/p_{satH_2O} is relative humidity RH. These two linear equations can be solved analytically for the adsorbed volumes V_{adsH_2O} and V_{adsOV}.

Since water adsorbs slowly on activated carbon (Assumption 14), its equilibrium will be approached only with increasing time of exposure to humid air. Lodewyckx and Vansant$^{(17)}$ developed an empirical equation from which we can calculate the extent (fraction) of equilibrium reached at time t as (Assumption 15):

$$\Delta V_{adsH_2O}/\Delta A_{tot} = \left(1 - \exp\left[-\frac{0.00005 T v_L t}{d_B\sqrt{|\Delta A_{tot}|}}\right]\right) \tag{10}$$

Here, temperature T is in °C, linear velocity v_L is in cm/s, bed depth d_B is in cm, time t is in min, and ΔA_{tot} (g/g carbon) is the difference (+ or −) between two equilibrium water capacities. The gravimetric (and equal volumetric) capacities at the exposure RH (Run RH) and at the RH (Pre RH) at which the carbon was previously equilibrated can be obtained from a water isotherm plot or, as in our case, applying the DR equation. For equilibrium or the same RH, Eq. 10 is 1.00.

First, Eq. 10 fraction (Fract_{H_2O}) is applied (Assumption 16) to the difference in equilibrium water volumetric capacities determined, as if no OV were present, so that

$$V_{adsH_2O} = V_{ads}(\mathrm{PreRH}) + \mathrm{Fract}_{H_2O}[V_{ads}(\mathrm{RunRH}) - V_{ads}(\mathrm{PreRH})] \tag{11}$$

Then the result is balanced with the OV capacity by solving Eqs. 8 and 9.

Water Solubility

One more contribution to V_{adsOV} needs to be included, that due to solubility, if any, of the OV in the adsorbed water phase, which is otherwise excluding the OV. The presence of condensed water enhances the capacity, improves retention, and extends breakthrough times of a water-soluble OV, at least compared to what these would be if the OV were not water soluble. The Wohleber-Manes$^{(32,33)}$ semiempirical application of the Polanyi adsorption potential model for soluble liquids (Assumption 17) has been adapted to account for adsorption of an OV dissolved in water. According to this theory the OV adsorption potential in the presence of air at RH is

$$\varepsilon_{RH} = \left(\frac{RTV_m}{\gamma_h - 0.28}\right)\left[\frac{1}{V_m}\ln\left(\frac{p_{sat}}{p}\right) - \frac{1}{18}\ln\left(\frac{1}{RH}\right)\right] \tag{12}$$

where $\gamma_h = 4.24\ (P_e/V_m)$ for OV molar volume V_m and molar polarizability P_e is the scale factor of an OV relative to heptane. For a completely water-miscible OV in a water volume of V_{adsH_2O} (calculated from Eqs. 8 and 9) we calculate the volume of OV adsorbed from the aqueous phase as:

$$V'_{adsOV} = V_{adsH_2O}\exp[-(\varepsilon_{RH}/\beta_{OV}E_o)^2] \tag{13}$$

For a lesser soluble OV we multiply this by a solubility factor S_f defined as the fraction in parts by liquid volume of OV that can be dissolved in one part of water volume (Assumption 18). The range of S_f is taken to be from zero for a totally immiscible OV to 1.0 for a totally miscible one (Assumption 19). Miscibilities and such volume/volume ratios can often be found in common references.(25,34,35) A conservative estimate for S_f is zero, but this should not be used for alcohols, amines, or other polar compounds, which are often to some extent water soluble. Solubility units in reference books may need to be changed to conform to this definition of S_f.

The total gravimetric capacity of the activated carbon for the OV in the presence of adsorbed water then becomes:

$$W_{e,OVtotal} = (V_{adsOV} + V'_{adsOV})d_L \tag{14}$$

OV Adsorption Rate (Dry)

Since we first introduced an estimation model for breakthrough time of a single vapor,(3) Wood and Lodewyckx(6) have published an empirical equation for adsorption rate coefficients of organic vapors on activated carbons. The result for $C/C_o = 0.1\%$ breakthrough fraction was:

$$k_{v0.1\%} = 800\beta_{OV}^{0.33}v_L^{0.75}d_p^{-1.5}(W_e/M_w)^{0.5}\text{min}^{-1} \tag{15}$$

where linear flow velocity v_L (cm/s) $= Q/60A_B$ for bed cross sectional area A_B (cm^2), d_p (cm) = average carbon granule diameter; and M_w (g/mol) = molecular weight of the OV. We adopted (Assumption 20) this single vapor (dry) rate coefficient equation with β_{OV} given by Eq. 6.

Wood(5) has quantified the asymmetry (skew) often observed for OV breakthrough curves. We take Wood's equations (Assumption 21) to calculate rate coefficients at other breakthrough fractions (up to $C/C_o = 0.5$) as

$$k_{v(C/Co)} = \left[\frac{1 + b\ln(C_o/C - 1)}{1 + b\ln(999)}\right]k_{v0.1\%} \tag{16}$$

where b is a quadratic root solution of a correlation for the skew parameter $S = k_{v1\%}/k_{v10\%}$:

$$S = \left[\frac{1 + b\ln(99)}{1 + b\ln(9)}\right] = 1.41 - 0.0000324\left[\frac{1 + b\ln(9)}{1 + b\ln(C_o/C - 1)}\right]k_{v(Co/C)} \tag{17}$$

which has a lower limit such that $S \geq 1$.

Effect of Water on OV Adsorption Rate

We also assumed (Assumption 22):

$$k^{Wet}_{v(C/Co)} = \left[0.3 + 0.7\left(\frac{W_e^{Wet}}{W_e^{Dry}}\right)\right]k^{Dry}_{v(C/Co)} \tag{18}$$

which we derived from the empirical correlation, Eq. 3, observed by Wood and Lodewyckx(22) for the indirect effect of adsorbed water on an OV adsorption rate coefficient. This has an upper limit of k_v(dry). A rate coefficient reduction has also been observed for organic covapors.(36)

Expanding Zone Model

With water vapor and one OV we defined (Assumption 23) two zones within the bed (Figure 1): Zone 0, nearer to the exit of the bed, at first contains only water vapor and Zone 1, nearer the inlet of the bed, contains both water vapor and the OV. For mathematical simplicity we initially assumed an infinitely fast OV adsorption rate (Assumption 24), producing a flat wavefront and zone boundary (dotted line). The depth of the OV boundary at time t depends on OV capacity in Zone 1 (in the presence of water and calculated by the above equations) and challenge vapor concentration. When that depth reaches the bed depth, equilibrium breakthrough time τ has been reached. After τ is calculated by the model, the finite kinetics of OV adsorption are added (as discussed below) to calculate breakthrough at any selected breakthrough fraction of challenge, C/C_o.

Assuming infinitely fast OV adsorption kinetics reduced the problem of predicting OV breakthrough time to determining the adsorbed phase concentrations of water and OV in Zone 1. In Zone 1 the vapor phase concentrations of OV and water are taken (Assumption 25) to be those entering the carbon bed. Because water adsorption on carbon is relatively slow, the (pseudo) equilibriums in Zone 1 are changing with time as more water and more OV enter it.

Water Vapor Rollup

Another phenomenon that must be taken into account (Assumption 26) is displacement of water vapor as the OV wavefront moves through a prehumidified carbon bed.(17) This causes the carbon in Zone 0 to be exposed to an RH higher than that entering the bed. This phenomenon has been called "rollup" or "rollover." The extent of this rollup depends on the airflow Q, the average speed of wavefront movement W/τ (g/min), and the relative adsorption capacities of water in Zones 0 and 1:

$$\text{Rollup RH} = \text{Run RH} + \frac{(V_{adsH_2O,Zone0} - V_{adsH_2O,Zone1})(Wd_{H_2O}RT)10^6}{M_{wH_2O}\,P_{satH_2O}Q\tau} \tag{19}$$

where d_{H_2O} is the density of water. Water supersaturation of air is not allowed (Assumption 27), so the upper limit of Rollup RH is 1.00. Because of the water rollup effect in Zone 0, V_{ads}

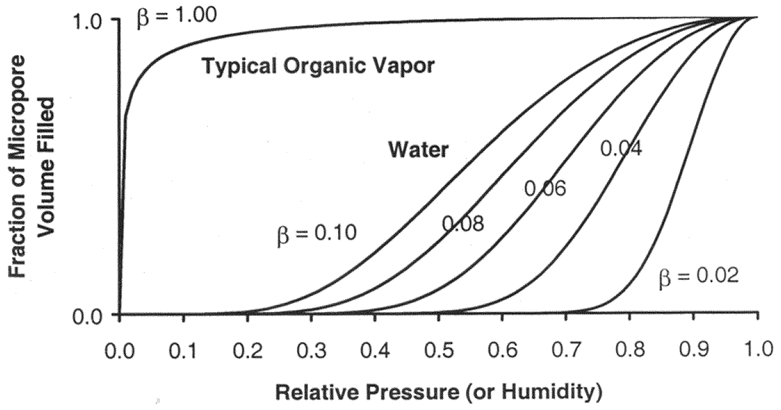

FIGURE 2. Dubinin/Radushkevich isotherm plots for various values of the affinity coefficient β

(Run RH) in Eqs. 8 and 9 is replaced by V_{ads}(Rollup RH) to calculate V_{adsH_2O} as a function of time in Zone 0.

Effects of OV on Water Affinity

Experience with this model has shown that it is necessary to assume (Assumption 28) that the affinity coefficient of water β_{H_2O} (base value) is halved in Zone 1, relative to its value in Zone 0 (e.g., 0.03 instead of 0.06). This may due to the preferential adsorption of OV and subsequent increasing of the hydrophobicity of the activated carbon. A lower β_{H_2O} would have the effect of shifting the water isotherm higher on the RH scale (Figure 2).

Also, it is necessary to assume (Assumption 29) a β_{H_2O} affinity coefficient 1.67 times larger than the base value (e.g., 0.10 instead of 0.06 in Zone 0; 0.05 instead of 0.03 in Zone 1) when the carbon bed has been preconditioned at a RH greater than 50%. We attribute this to a well-known hysteresis effect for water on carbon that shifts the isotherm desorption branch to lower RHs.(37) The cause of this hysteresis could also make displacement of high loadings of water by OV more difficult. Hysteresis is therefore approximated by increasing the one parameter, β_{H_2O} (Figure 2).

MODEL TESTING WITH DATA

The first set of data we examined to test the service life predictive model is that of Lavanchy and Stoeckli.(38) They measured breakthrough curves for mixtures of vapors, including 2-chloropropane (four concentrations) and water vapor (four relative humidities, 0–80%) on U03 active carbon (preconditioned at the test humidities). They reported and compared 10% breakthrough times with those predicted by their dynamic simulation. Micropore volume $W_o = 0.495$ cm^3/g and characteristic (adsorption) energy $E_o = 16.950$ kJ/mol

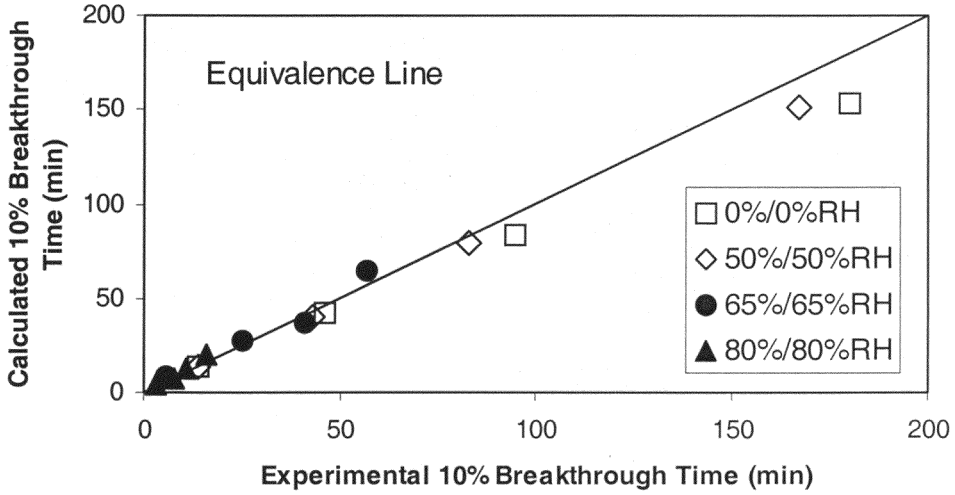

FIGURE 3. Comparisons of model-calculated breakthrough times of 2-chloropropane with experimental ones from the work of Lavanchy and Stoeckli.(38) Water affinity coefficient $\beta_{H_2O} = 0.06$.

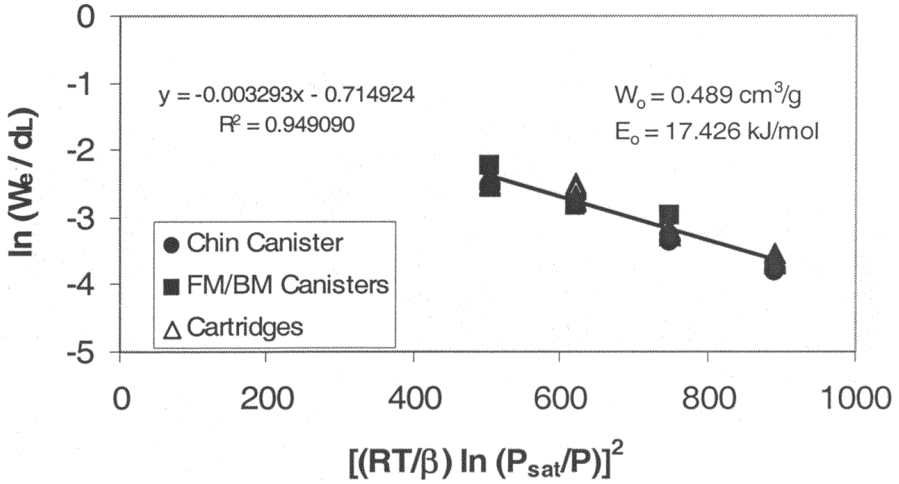

FIGURE 4. Dubinin/Radushkevich plot from 1% breakthrough times for all cartridges and canisters from manufacturer B in the work of Moyer and Peterson[(40)]

were taken from Lavanchy and Stoeckli's DR analysis of benzene isotherms.[(39)] We assumed a water affinity coefficient of $\beta_{H_2O} = 0.06$ (with model adjustments for organic vapor in Zone 1 and for preadsorbed water) and $\beta_{OV} = 0.85$ from the polarization correlation, Eq. 6. With these inputs we applied our model to predict these breakthrough times. Very good agreements with the experimental ones are shown in Figure 3.

The second example is from the work of Moyer and Peterson,[(40)] who measured breakthrough times of methylene chloride on a variety of sizes and lots of cartridges and canisters from two manufacturers. We used the model to calculate 1% breakthrough times to compare with theirs for challenge concentrations of 75 to 1000 ppm and relative humidities of 50 and 80% for as-received (AR) units. In this case W_o and E_o were not known for the carbons, so we first applied the model with dry 1% breakthrough time data to generate D/R plots (as described in the Appendix). Figure 4 shows one of these plots with three sizes from Manufacturer B. The data are consistent, confirming the use of the same (or equivalent) carbon in all sizes and allowing the calculation of $W_o = 0.489$ cm^3/g and $E_o = 17.426$ kJ/mol for it. Using these in the model and again assuming $\beta_{H_2O} = 0.060$ produced the very good agreements shown in Figure 5.

A similar D/R analysis of Moyer and Peterson's data (1% breakthrough times, 75–1000 ppm) for the four lots of

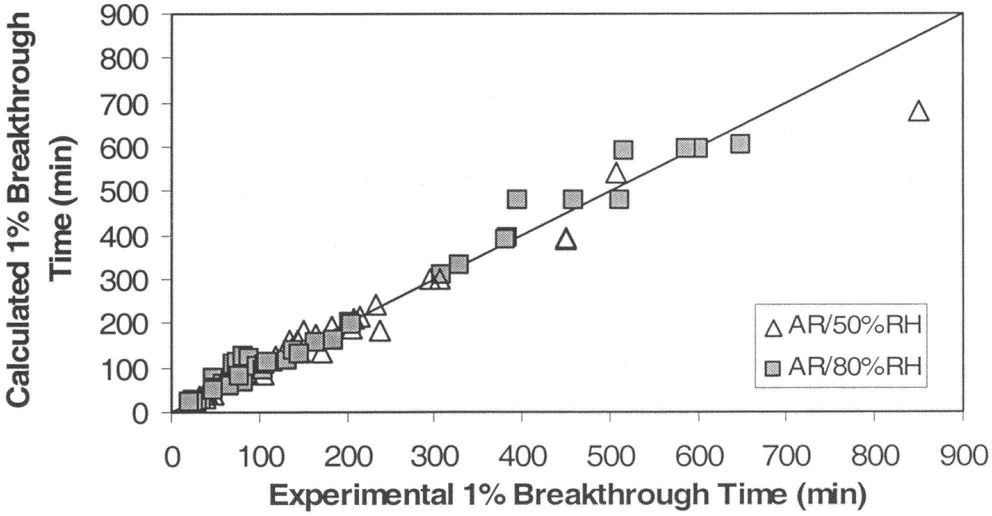

FIGURE 5. Comparisons of model-calculated breakthrough times with experimental ones for methylene chloride and all cartridges and canisters from manufacturer B in the work of Moyer and Peterson.[(40)] Water affinity coefficient $\beta_{H_2O} = 0.06$.

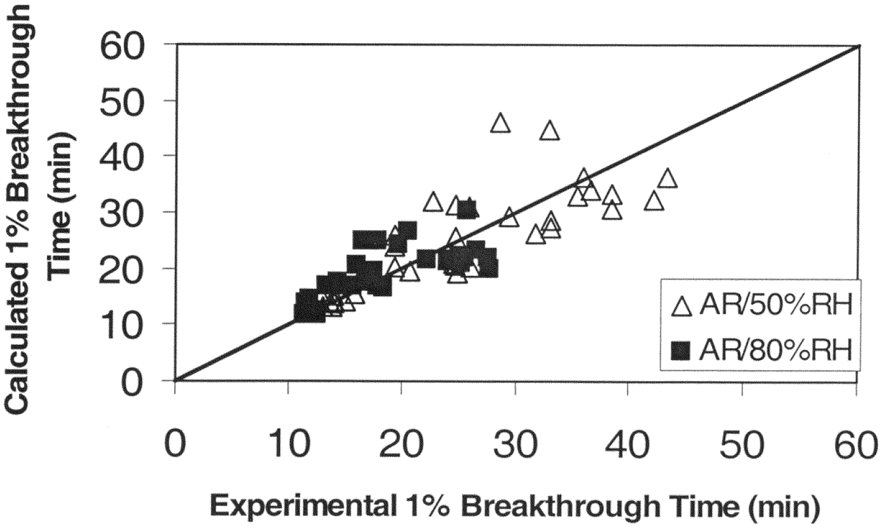

FIGURE 6. Comparisons of model-calculated breakthrough times with experimental ones for methylene chloride and all four lots of cartridges from manufacturer A in the work of Moyer and Peterson.(40) Water affinity coefficient $\beta_{H_2O} = 0.025$.

Manufacturer A cartridges showed that these lots were essentially identical. The plot yielded $W_o = 0.162$ cm^3/g and $E_o = 26.454$ kJ/mol. In this case, however, it was necessary to take $\beta_{H_2O} = 0.025$ in order to get the agreements with high-humidity data shown in Figure 6.

Ferry(41) reported 10 and 25 ppm breakthrough times for 500–10,000 ppm hexane, 30–80% RH, and cartridges containing two different carbons (preconditioned). Our DR plots and best high-humidity data fits yielded the parameters: $W_o = 0.677$ cm^3/g, $E_o = 11.824$ kJ/mol, and $\beta_{H_2O} = 0.060$ for the Chemviron FIAB 1222 carbon and $W_o = 0.525$ cm^3/g, $E_o = 14.302$ kJ/mol, and $\beta_{H_2O} = 0.045$ for the Norit R1 Extra carbon. The resulting model vs. experimental breakthrough time agreements are shown in Figures 7 and 8.

Petrova and Nickolaev(42) provided results from which 5% breakthrough times can be calculated for 10 g/m^3 of three chlorocarbons, 0 to 90% RH air, and initially dry AR-3 carbon beds. In related work at dry conditions they reported the equivalent of $W_o = 0.338$ cm^3/g and $E_o = 19.123$ kJ/mol. We had to make guesses for bed density (0.40 g/cm^3) and granule diameter (0.2 cm). Figure 9 shows good predictions by the model (except at the shortest breakthrough times) with $\beta_{H_2O} = 0.060$.

Lodewyckx and Vansant(21,22) measured 0.1% breakthrough times for 5 g/m^3 carbon tetrachloride on three activated carbons, varying Pre RH and Run RH from 0 to 90%. We predicted these times using the cartridge, carbon, and experimental parameters that they provided.(43) Airflow rate was

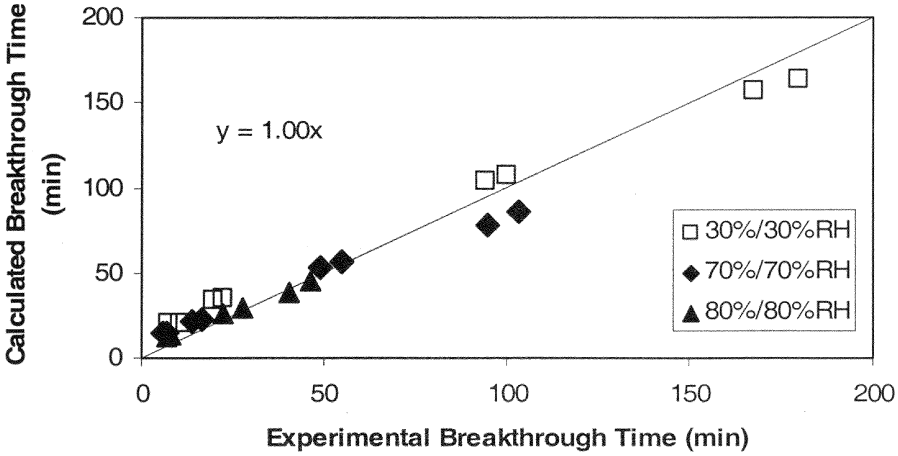

FIGURE 7. Comparisons of model-calculated breakthrough times with experimental ones for hexane on Chemviron FIAB 1222 carbon in the work of Ferry.(41) Water affinity coefficient $\beta_{H_2O} = 0.06$.

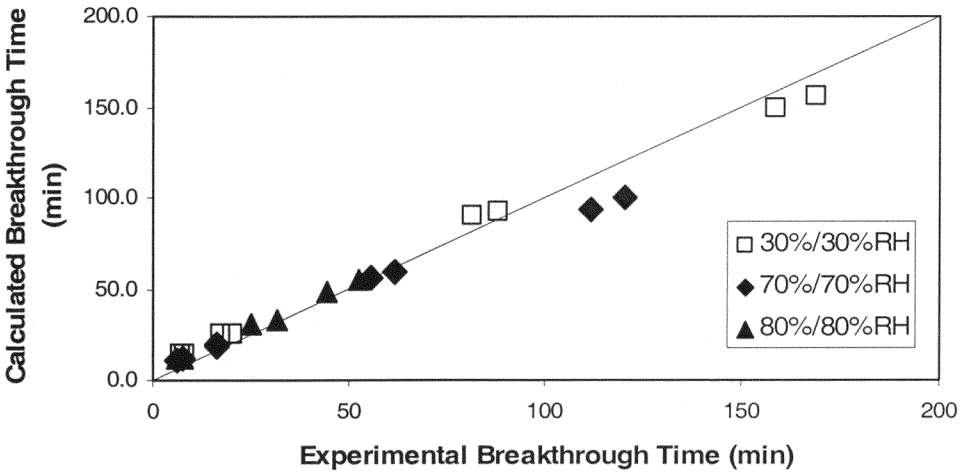

FIGURE 8. Comparisons of model-calculated breakthrough times with experimental ones for hexane on Norit R1 Extra carbon in the work of Ferry.(41) Water affinity coefficient $\beta_{H_2O} = 0.045$.

30,000 cm^3/min. The results fell into two groups, illustrated by Figures 10 and 11. The dry ($\leq$50% RH) carbon/dry air, dry/wet, and wet/wetter combinations gave fair agreement (Figure 10), but with more scatter than observed in other data sets. We attribute this greater experimental scatter to more sensitivity of the adsorption wavefront at such a low (0.1%) breakthrough fraction to water loading and granule heterogeneity. The model did very poorly when the carbon was initially wet ($>$50% RH equilibration) and used at the same high or lower humidity (Figure 11). We attribute this to significant cooling of the bed as water was rapidly evaporated and/or displaced. The current model does not account for such cooling, which presumably slowed down the water removal. In some such cases the model greatly overestimated breakthrough times. In other cases (e.g., 90%/0%) where there was sufficient time (e.g., $>$150 min) for the bed to recover from cooling before CCl_4 breakthrough, the model gave reasonable agreements with experimental breakthrough times.

Lodewyckx and Vansant(22) also measured humidity effects on the BPL carbon using six other organic vapors. Figure 12 shows the agreement of model calculations with experimental 0.1% breakthrough times for all seven compounds and BPL carbon for those cases in which cooling is not expected to have occurred. The average +7% bias could be corrected by choosing a correspondingly smaller value for BPL micropore volume.

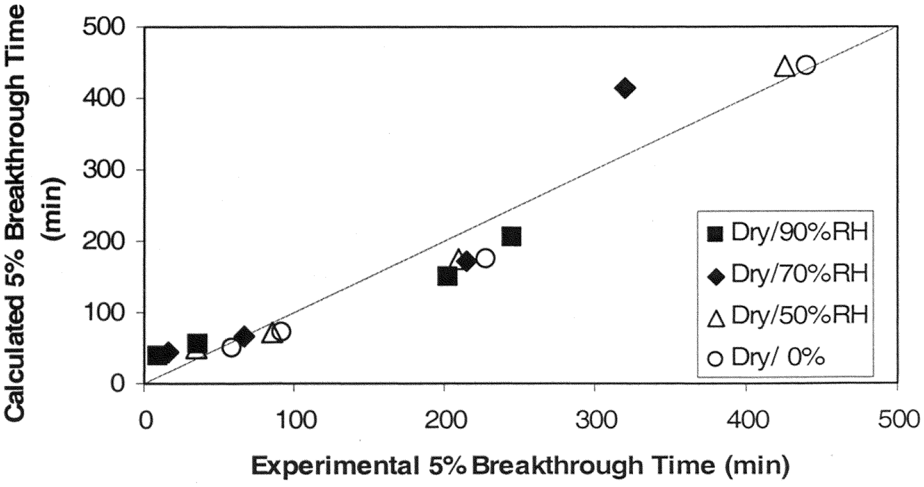

FIGURE 9. Comparisons of model-calculated breakthrough times with experimental ones for four chlorocarbons in the work of Petrova and Nickolaev.(42) Water affinity coefficient $\beta_{H_2O} = 0.06$.

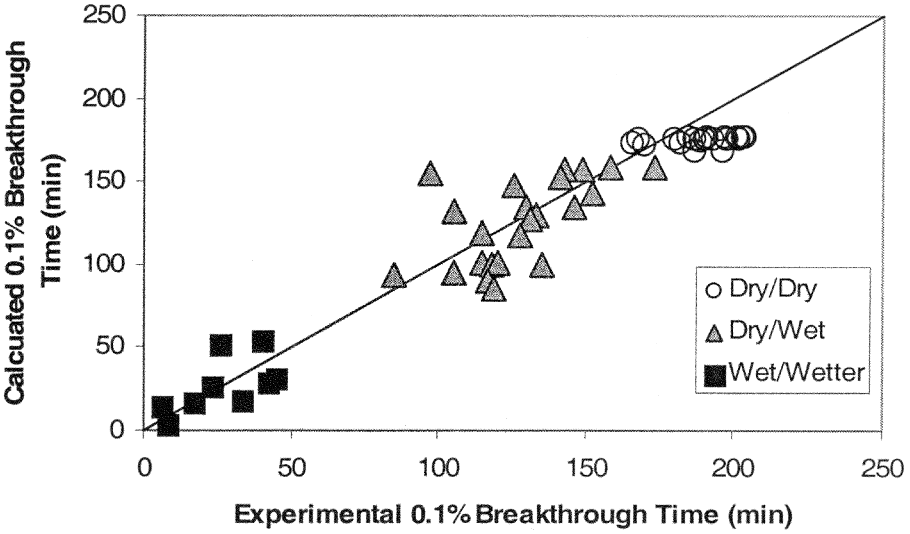

FIGURE 10. Comparisons of model-calculated breakthrough times with experimental ones for carbon tetrachloride on three carbons from the work of Lodewyckx and Vansant.(21,22) Water affinity coefficient $\beta_{H_2O} = 0.06$.

Maggs and Smith(44) measured 1% breakthrough times for vapors of four anesthetics removed by four activated carbons at three humidity combinations. The carbons were packed into a typical respirator cartridge configuration (8.6 cm diameter). Figure 13 shows the agreement of model estimates with experimental times. We obtained micropore volumes and reference adsorption energies using the dry/dry breakthrough times for the four chemicals (see Appendix). Unlike the Lodewyckx/Vansant results, almost as good agreement was obtained for 80% RH/80% RH as for the cases with initially dry carbon. This can be attributed to lower experimental airflow rates (usually 4000 cm^3/min), which would have produced less cooling by water displacement.

Nearly all the data considered above have been for water-insoluble compounds. For those compounds that have significant water solubility, additional retention on wet carbon must be taken into account (see discussion above). The 10% breakthrough times from Kawar and Underhill's(45) study with five water-miscible compounds (solubility factor = 1.0) at 0 and 100% RH provide an extreme test of the water correction in our model. We again used dry breakthrough times with a DR plot to obtain micropore volume (0.37 cm^3/g) and

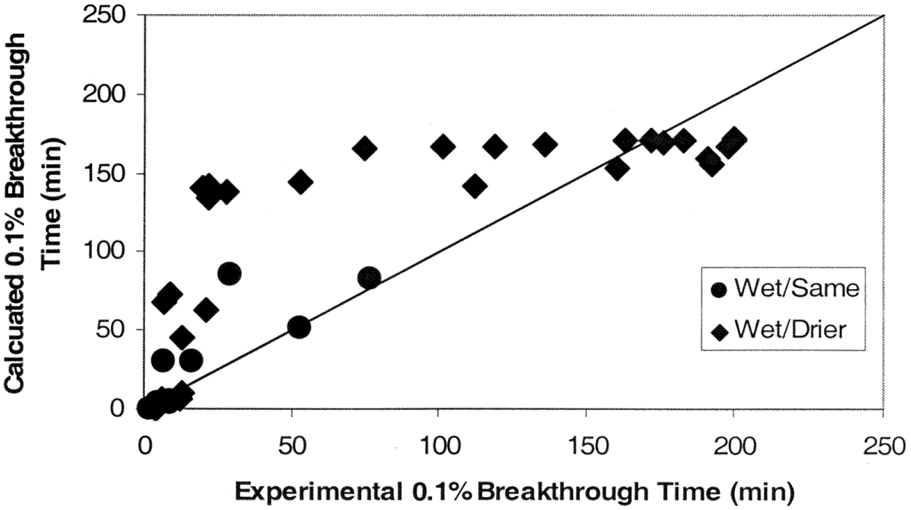

FIGURE 11. Comparisons of model-calculated breakthrough times with experimental ones for carbon tetrachloride on three initially wet carbons from the work of Lodewyckx and Vansant.(21,22) Water affinity coefficient $\beta_{H_2O} = 0.06$.

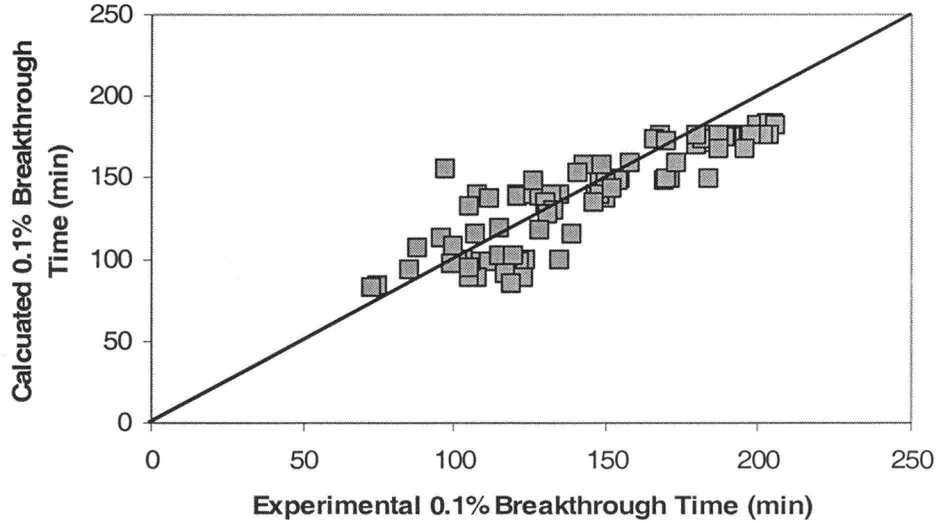

FIGURE 12. Comparisons of model-calculated breakthrough times with experimental ones for seven chemicals on initially dry BPL-HA carbon from the work of Lodewyckx and Vansant.(22) Water affinity coefficient $\beta_{H_2O} = 0.06$.

reference adsorption energy (26.70 kJ/mol). Figures 14 and 15 show the model predictions ($\beta_{H_2O} = 0.06$) without and with solubility corrections. The corrections move the 100% Run RH calculated values closer to the equivalence line. The large data scatter around this line, even on log-log scales, we attribute to the difficulty inherent in conducting experiments at 100% RH, where condensation due to apparatus cold spots and air supersaturation are common problems.

Acetic acid is a special case; as an organic acid it partially dissociates into ions in aqueous solution, increasing its retention on wet carbon. The model corrections for solubility do not take dissociation into account and, therefore, grossly underestimate the breakthrough times at high humidities. The discrepancy is greater at lower vapor (and corresponding aqueous phase) concentrations, where dissociation is greater.

The data of Nelson et al.(7,8) from the 1970s for initially dry ($\leq$50% RH) cartridges illustrate another effect not included in the model. Reported and best fit parameters for this set of data were $W_o = 0.729$ cm^3/g, $E_o = 15.19$ kJ/mol, and $\beta_{H_2O} = 0.04$. Figure 16 shows good agreement of model-estimated and experimental 1% breakthrough times for insoluble and water-soluble compounds, except for methyl acetate. The longer

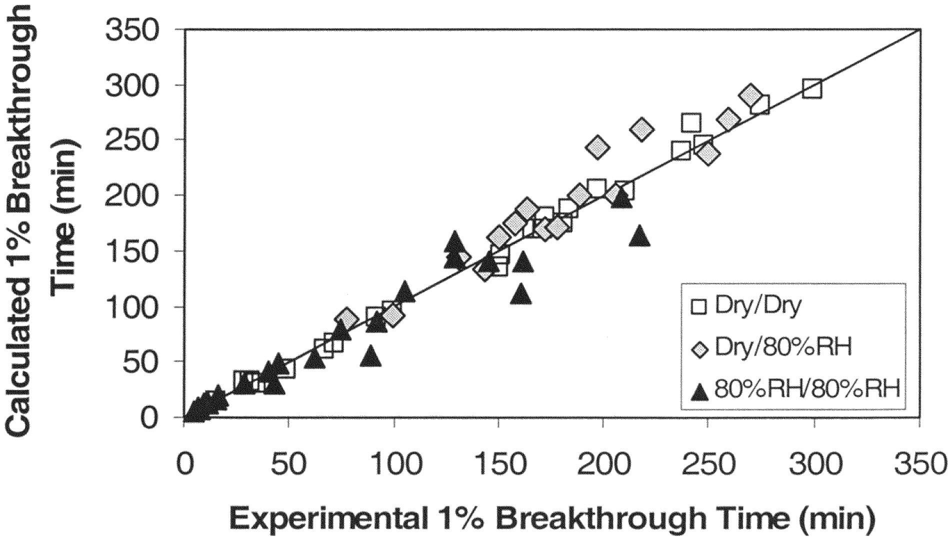

FIGURE 13. Comparisons of model-calculated breakthrough times with experimental ones for four chemicals on four carbons from the work of Maggs and Smith.(44) Water affinity coefficient $\beta_{H_2O} = 0.06$.

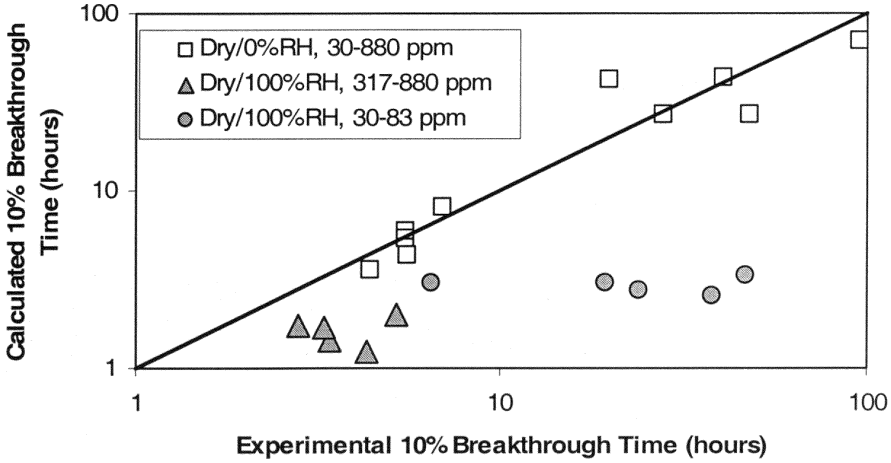

FIGURE 14. Comparisons of model-calculated breakthrough times with experimental ones for five water-miscible carbons at 100% RH from the work of Kawar and Underhill.[45] No water solubility included. Water affinity coefficient $\beta_{H_2O} = 0.06$.

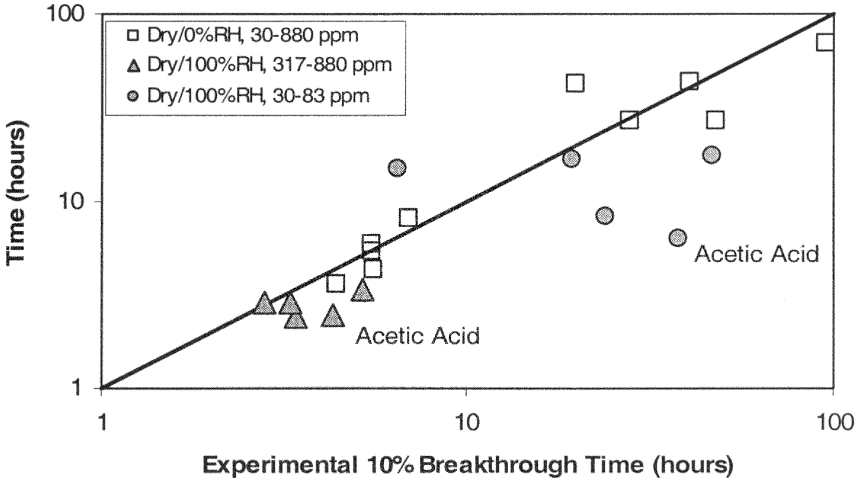

FIGURE 15. Comparisons of model-calculated breakthrough times with experimental ones for five water-miscible carbons at 100% RH from the work of Kawar and Underhill.[45] Water solubility is included with water affinity coefficient $\beta_{H_2O} = 0.06$.

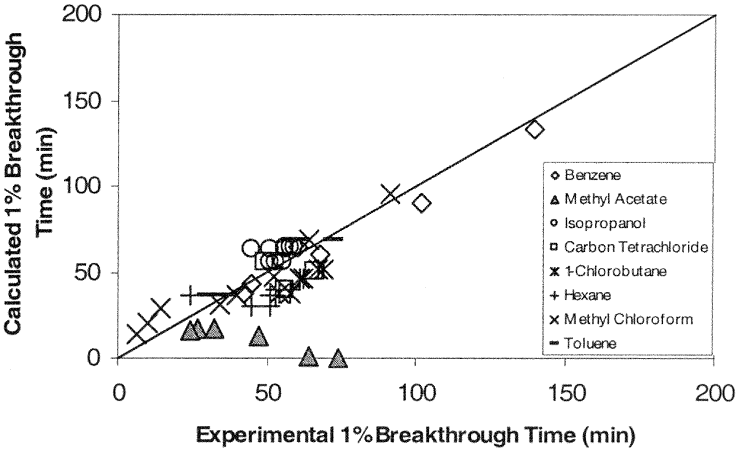

FIGURE 16. Comparisons of model-calculated breakthrough times with experimental ones for eight chemicals at high humidities on as-received MSA cartridges from the work of Nelson et al.[7,8] Water affinity coefficient $\beta_{H_2O} = 0.04$.

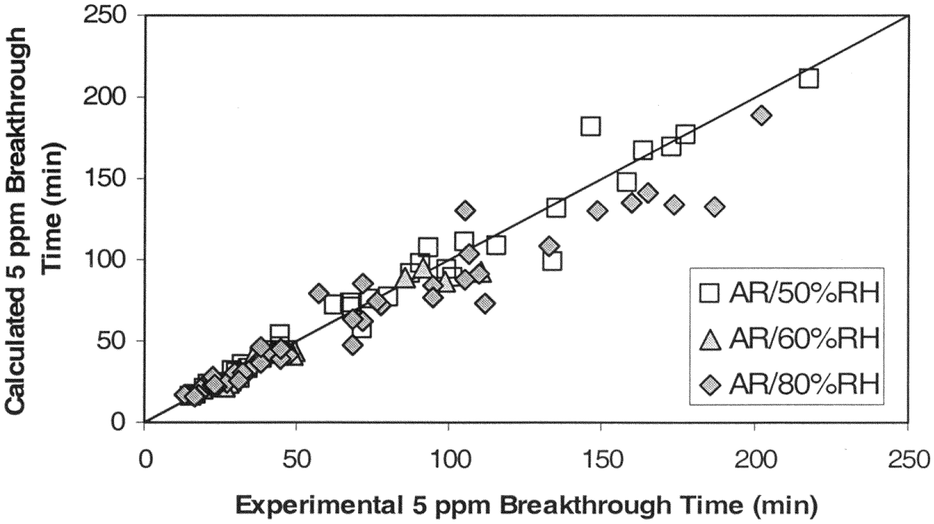

FIGURE 17. Comparisons of model-calculated breakthrough times with experimental ones for twelve chemicals on a coconut shell activated carbon from the work of Smith.(46) Water affinity coefficient $\beta_{H_2O} = 0.06$.

the breakthrough time of (water-soluble) methyl acetate, the longer it has to hydrolyze in adsorbed water to form acetic acid (water miscible and partially dissociated) and methanol (water miscible). At higher vapor concentrations of methyl acetate the model predicts shorter breakthrough times, but hydrolysis accelerates to create longer breakthrough times.

Figure 17 shows another comparison of model estimates with experimental breakthrough times. This work of Smith(46) included 12 chemical vapors (both soluble and insoluble) at a wide range of concentrations (750–10,000 ppm) on one organic vapor cartridge (as received, run at 22–80% RH). Dry conditions data were used to derive a micropore volume (0.505 cm^3/g) and reference adsorption energy (18.78 kJ/mol). We used a water affinity coefficient of 0.06.

Busmundrud(47) studied water-soluble (assumed $S_f = 1.0$) DMMP (dimethyl methyl phosphonate) and partially soluble ($S_f = 0.0025$) n-amyl acetate retention on a TEDA (triethylene diamine)-impregnated carbon. We calculated $W_o = 0.267$ cm^3/g (low value partially due to the weight of impregnants) and $E_o = 19.81$ kJ/mol from dry condition data

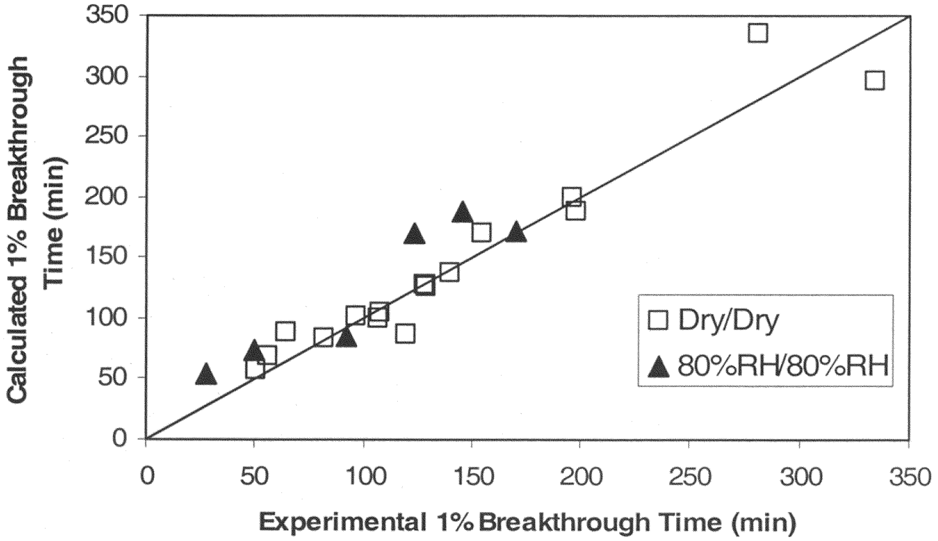

FIGURE 18. Comparisons of model-calculated breakthrough times with experimental ones for two chemicals on an ASC-TEDA impregnated Chemviron activated carbon from the work of Busmundrud.(47) Water affinity coefficient $\beta_{H_2O} = 0.06$.

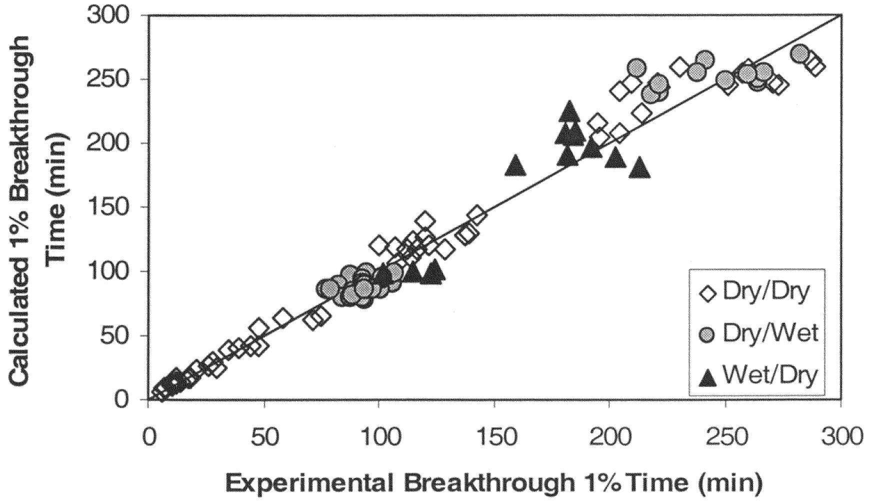

FIGURE 19. Comparisons of model-calculated breakthrough times with experimental ones for five chemicals on a Scott cartridge from the work of Nelson.(48) Water affinity coefficient $\beta_{H_2O} = 0.06$.

and assumed $\beta_{H_2O} = 0.06$. We calculated experimental 1% breakthrough times from reported values of capacity W_e and adsorption rate coefficient k_v. Figure 18 shows good agreement of 1% breakthrough times for both dry/dry and wet/wet test conditions.

Figure 19 shows comparisons of 10-ppm breakthrough times for data developed by Nelson(48) using a Scott half-mask respirator cartridge and four chemicals (carbon tetrachloride, ethyl acetate, heptane, and methyl ethyl ketone) of varying vapor concentrations (500–20,000 ppm) and water-solubilities. Flow rates were either 16 or 32 L/min per cartridge. All the dry/dry breakthrough times were used to obtain $W_o = 0.44$ cm^3/g and $E_o = 25.58$ kJ/mol by iteration of the model (see Appendix). Calculated breakthrough times with $\beta_{H_2O} = 0.060$ for dry/dry, dry/wet, and wet/dry conditions agreed well with experimental ones (Figure 19).

Mine Safety Appliances Company (MSA)(49) developed and published breakthrough time data for 1–3 breakthrough concentrations of 13 organic vapors at 3 relative humidities and 3 challenge concentrations each on as-received GMA Advantage 200 cartridges. Using the reported micropore volume of 0.75 cm^3/g and the highest (nearest equilibrium) breakthrough times for dry (AR/50% RH) tests, we obtained a corresponding $E_o = 17.29$ kJ/mol from a DR plot. Taking $\beta_{H_2O} = 0.060$ we then estimated the (lowest of the 1–3 reported) breakthrough times shown in Figure 20.

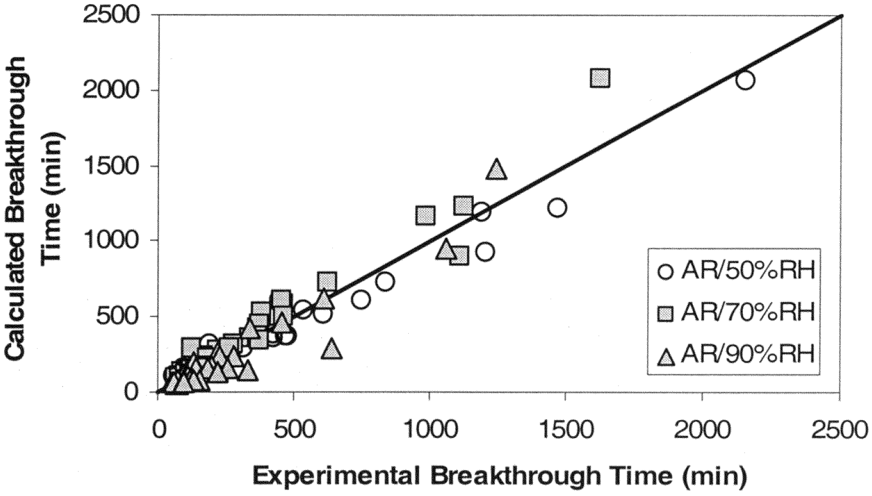

FIGURE 20. Comparisons of model-calculated breakthrough times with experimental ones for 13 organic vapors on an MSA cartridge.(49) Water affinity coefficient $\beta_{H_2O} = 0.06$.

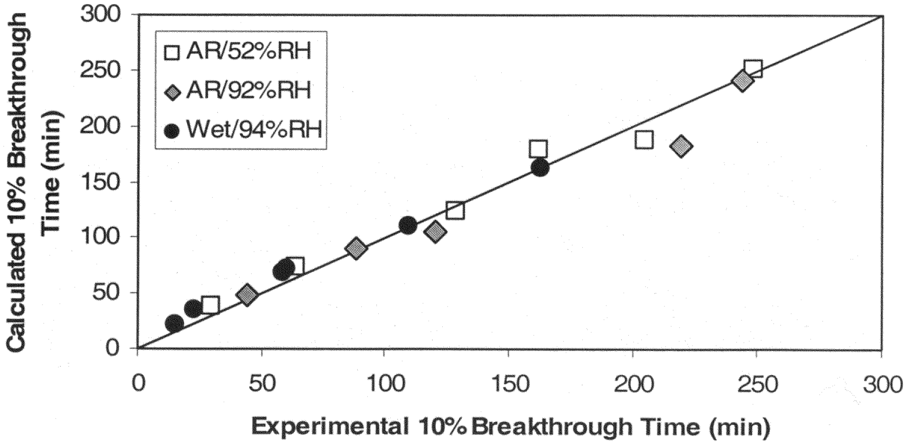

FIGURE 21. Comparisons of model-calculated breakthrough times with experimental ones for carbon tetrachloride on carbon from an MSA cartridge from the work of Cohen et al.(50) Water affinity coefficient $\beta_{H_2O} = 0.024$.

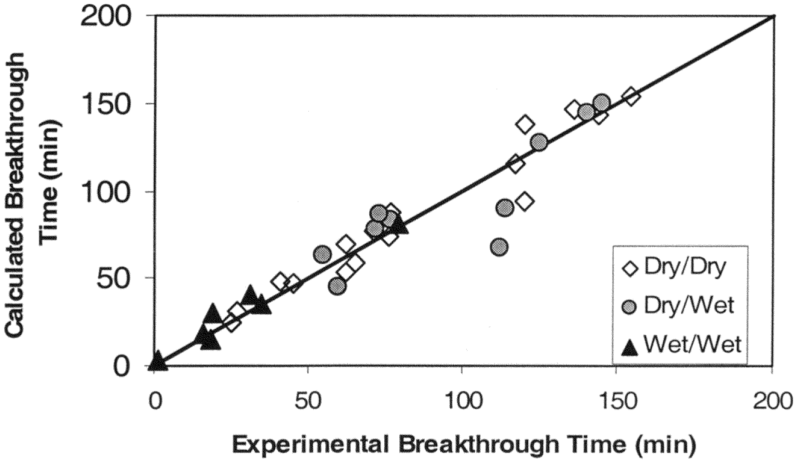

FIGURE 22. Comparisons of model-calculated breakthrough times with experimental ones for seven organic vapors on two carbons from the work of Swearengen and Weaver.(52, 53) Dry = AR, 20% RH, or 50% RH; wet = 85% RH. Water affinity coefficient $\beta_{H_2O} = 0.06$.

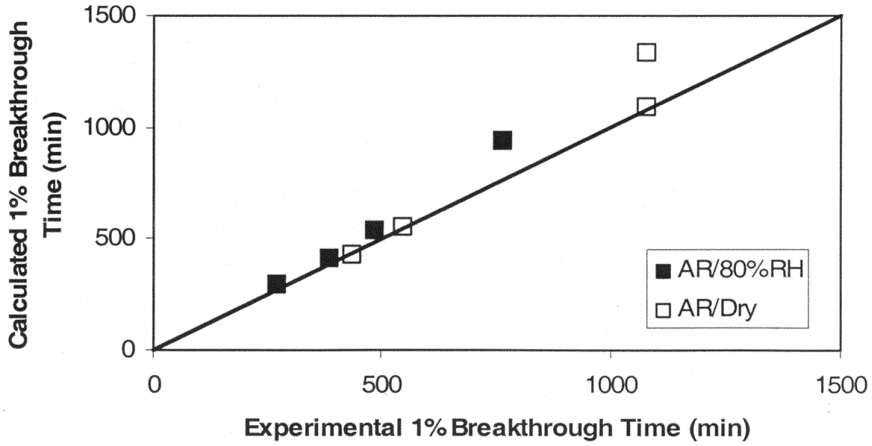

FIGURE 23. Comparisons of model-calculated breakthrough times with experimental ones for four organic vapors on an MSA GMA canister from the work of Stampfer.(54) Dry = <15% RH. Water affinity coefficient $\beta_{H_2O} = 0.06$.

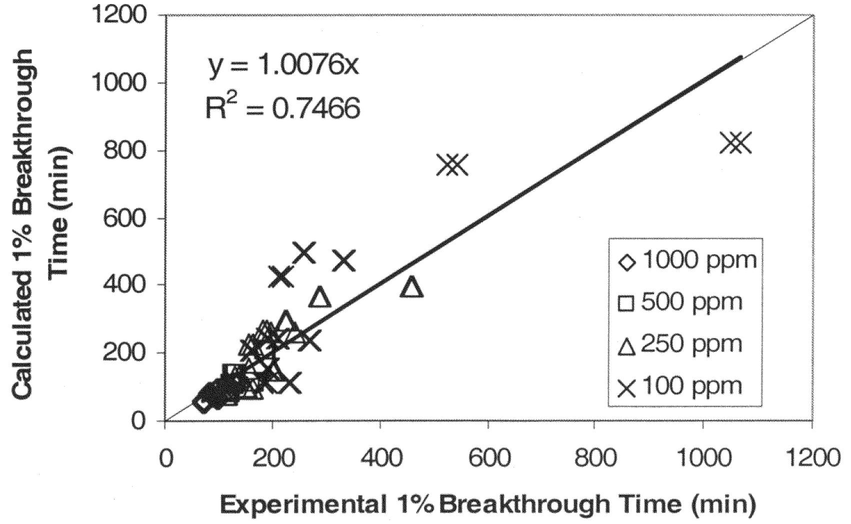

FIGURE 24. Comparisons of model-calculated breakthrough times with experimental ones for 100–1000 ppm of eight organic vapors at 65–90% RH with as-received 3M cartridges.(55) Water affinity coefficient $\beta_{H_2O} = 0.06$.

Cohen et al.(50) also used MSA cartridges and carbon from them for respirator cartridge tubes. We assumed $W_o = 0.75$ cm^3/g and used breakthrough time data for 1000 ppm of three chemicals at dry conditions from a subsequent paper(51) to get $E_o = 14.58$ kJ/mol from a linearized DR plot. The base value of β_{H_2O}, which best reproduced high-humidity breakthrough times, was 0.024. Figure 21 shows a comparison of model calculations with experimental carbon tetrachloride breakthrough time data. In their experiments "wet" corresponded to pre-equilibration at a fixed 0.25 g/g water loading, rather than equilibrium at a fixed RH. The model Pre RH was adjusted to 86.1% for $\beta_{H_2O} = 0.024$ to produce this initial water loading.

Swearengen and Weaver(52,53) measured breakthrough times for seven chemicals, singly and in binary mixtures, at various Pre RHs and Run RHs. They used two very different (35 g/cartridge vs. 42 g/cartridge) lots of MSA cartridges. Dry 1% breakthrough time data for single vapors with the former yielded $E_o = 18.70$ kJ/mol and $W_o = 0.606$ cm^3/g. We assumed a value of $W_o = 0.560$ cm^3/g for the denser carbon used at the AR/85% RH condition. Figure 22 shows a comparison of model-estimated ($\beta_{H_2O} = 0.06$) breakthrough

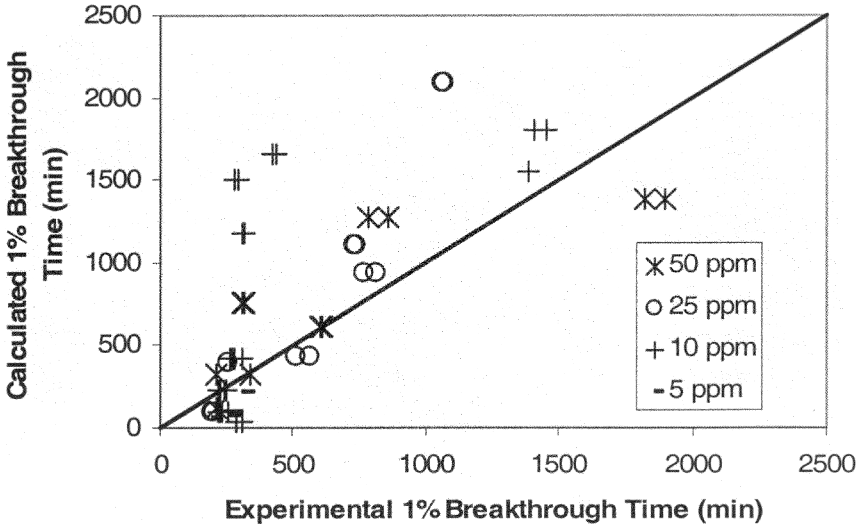

FIGURE 25. Comparisons of model-calculated breakthrough times with experimental ones for 5–50 ppm of eight organic vapors at 65–90% RH with as-received 3M cartridges.(55) Water affinity coefficient $\beta_{H_2O} = 0.06$.

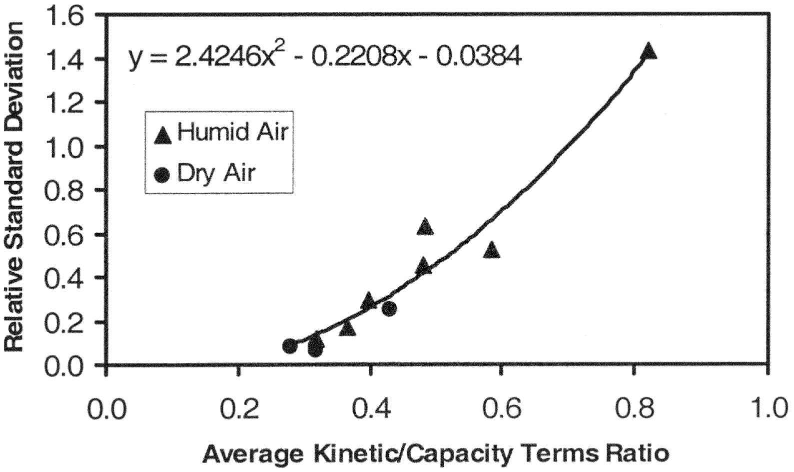

FIGURE 26. A plot of relative standard deviations of model estimates from experimental breakthrough times at each concentration vs. the average ratio of kinetic and capacity terms of Eq. 4. 3M data (at dry conditions plus those in Figures 24 and 25) were used.

times with experimental ones for three humidity combinations. Water solubility factors were included, when appropriate.

Stampfer(54) included some high-humidity conditions in his studies of OV breakthroughs of as-received MSA GMA cartridges. Our analysis of dry data for chloroform, benzene, and acrylonitrile yielded $E_o = 21.512$ kJ/mol and $W_o = 0.217$ cm^3/g. The model was then applied with $\beta_{H_2O} = 0.06$ to calculate the breakthrough times compared with experimental ones in Figure 23.

UNCERTAINTY ANALYSIS

A set of experimental data supplied to us by 3M Corporation(55) was valuable in identifying and quantifying uncertainties in model estimates of breakthrough times. This data set is unique by including vapor concentrations as low as 5 ppm with RHs up to 90%. Dry ($\leq$50% RH) data for the nine chemicals at 100–1000 ppm yielded $W_o = 0.597$ and $E_o = 17.96$. We used $\beta_{H_2O} = 0.060$. At higher humidities (65–90% RH with as-received cartridges) the agreements between the model estimates and measurements were mixed. Figure 24 shows good agreements of 1 and 10% breakthrough times at the higher concentrations (100–1000), but scatter around the equivalence line increases with decreasing concentration. At lower concentrations (5–50 ppm) this scatter gets worse (Figure 25). The errors are not consistently high or low; therefore, they are not likely due to a consistent bias.

Our explanation for this phenomenon is the increasing contribution of the less-well defined kinetic (second) term of Eq. 4. This term can be considered a "correction" to the first (capacity) term; it calculates the time from the stoichiometric center of the wavefront moving through the bed (Figure 1) to a point on its "leading tail" (the vapor that exits the cartridge bed first). The shape of and concentration on extremes of this "tail" are very sensitive to carbon granule activation and size. This is one reason the rate coefficient k_v cannot be reproduced precisely in experiments.

In one paper, Wood and Lodewyckx(6) reported a new correlation for k_v, now used in our model. The relative standard deviation (RSD) for k_v from a fit of Eq. 4 to a large database was ±29%. In another paper(22) on humidity corrections for k_v the RSD for the data correlation was ±16%. There are other sources of uncertainty, such as the correlation for breakthrough skew,(5) which had RSDs up to 11%. So, it should not be surprising that as the kinetic term becomes more significant in the calculation of the breakthrough time, the breakthrough time estimate becomes more uncertain. As a further complication, the value of the capacity term decreases at lower concentrations and higher humidities.

We have been able to quantify uncertainty in model estimates by using the dry and high-humidity data from 3 M. Grouping the data by vapor concentrations we calculated RSDs for the differences of estimates from measured breakthrough times. Figure 26 shows the increase in RSD with the increase in average ratio of the kinetic/capacity terms of Eq. 4 calculated by the model. This relation seems to be the same for both dry and high-humidity experiments. The best-fit quadratic equation shown can be used to calculate confidence limits for the model estimates.

DISCUSSION AND CONCLUSIONS

The service life estimation model described has been verified and some of its limits have been discovered. When appropriate values of the parameters W_o, E_o, and β_{H_2O} are used, the model reproduces experimental breakthrough times quite well in most cases. It takes into account and makes correction for water solubility of the OV. A water solubility factor is needed as input, but cannot account for hydrolysis (e.g., methyl acetate), dissociation (e.g., acetic acid), or reactive/catalytic removal by the activated carbon itself, its impregnants, or any other adsorbed compound. When these occur the model estimates are more conservative (low).

Uncertainties in the service life (breakthrough time) estimates given by the model depend on (1) the accuracies of the input parameters, and (2) the relative contribution of the kinetic term of Eq. 4. The latter has been quantified.

A common value for the base water affinity coefficient β_{H_2O} was 0.06. This is in good agreement with theoretical and experimental values.[(4)] However, in a few cases, including the most often referenced Nelson et al.[(7,8)] results, we needed to choose a smaller value to reproduce high-humidity breakthrough time data. Whether these actually reflect more hydrophobic activated carbons or are simply data artifacts remains to be determined.

The equation model described here has been implemented as both a spreadsheet and as an interactive computer program.[(56)] In doing so, we found that incrementation (from zero) of the adsorbed OV capacity was more often successful than iteration in converging to water rollup in Zone 0.

ACKNOWLEDGMENTS

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APPENDIX

Obtaining Input Parameters

Micropore volume, W_o, a characteristic of any batch of activated carbon granules, is an essential parameter for use of the DR Eq. 5. There are several ways to obtain this parameter value. The best way is from a plot of the linearized form of the DR adsorption isotherm equation:

$$\ln(W_e) = \ln(W_o d_L) - [(RT/\beta E_o)\ln(p_{sat}/p)]^2 \qquad \textbf{(20)}$$

This predicts that a plot of $\ln(W_e/d_L)$ vs. $[(RT/\beta)\ \ln(p_{sat}/p)]^2$ will produce a straight line with an intercept of $\ln W_o$ (cm^3/g) and a slope equal to $-1/E_o^2$. Figure 4 is an example of this.

Alternately, isotherm data, W_e vs. p (or C), can be fit to the original DR Eq. 5 to find the best values of W_o and E_o. A spreadsheet or interactive computer program can be used to do this. Usually the sum of the squares of deviations of calculated values from experimental ones are minimized to get best (least squares) fits.

What are required, then, are values of equilibrium adsorption capacities W_e (g/g) at corresponding values of the vapor pressures p (or concentrations C), relative to those (p_{sat} or C_{sat}) that would exist for the pure chemical at temperature T. Affinity coefficient(s) β of the vapor(s) and liquid densit(ies) d_L (g/cm^3) are also needed. Theoretically, results calculated from data for different vapors will fall on the same straight line, if the proper values of β and d_L are chosen. Usually, benzene is chosen as the reference ($\beta_{benzene} = 1.00$) and $\beta = \beta_{vapor}/\beta_{benzene}$. This does not mean that benzene, a very toxic chemical, must be used as one of the vapors. There are correlations[(4)] to calculate β; the same one should be used for both the DR plot and model predictions. We prefer to use the correlation in Eq. 6.

One way to obtain the equilibrium adsorption capacities is from equilibrium measurements. A measured weight of dry activated carbon is placed in contact with vapor of a selected chemical at a controlled temperature. The vapor pressure (concentration) is maintained at a selected value or allowed to drop to a measured value as the chemical is adsorbed. When no more vapor is adsorbed, usually determined by no more weight gain of the carbon with increasing time, the adsorption equilibrium has been reached. Alternately, the vapor concentration can be monitored to constancy to determine equilibrium. A closed container can be used or the vapor/air mixture can be flowed through a packed carbon bed or cartridge.

A second way is from breakthrough studies with dry air and carbon. Flowing a fixed vapor/air mixture of concentration C_o (g/cm^3) at flow rate Q (cm^3/min) through a packed activated carbon bed of weight W and measuring the concentration C eluting versus time will produce an S-shaped curve. By integrating the area above the complete breakthrough curve

$$\tau = \int_0^\infty (1 - C/C_o)dt \qquad \textbf{(21)}$$

the stoichiometric time, τ (min), corresponding to the geometric center of the breakthrough curve can be found. Alternately, τ can be obtained from fitting a breakthrough curve to an equation.(57) Equilibrium adsorption capacity is then the first (stoichiometric) term of Eq. 4:

$$W_e = \tau C_o Q/W \qquad \textbf{(22)}$$

For best accuracy, this approach requires that all (or most) of the breakthrough curve be measured, since the breakthrough curve may not be symmetrical.(5)

A third way of obtaining micropore volume and adsorption energy is from dry condition breakthrough times at breakthrough fractions (e.g., $C/C_o = 0.01$) below the stoichiometric time. The model described in this article, either as a computer program or spreadsheet, can be used to approximate the unknown kinetics. Initially, a value (e.g., 18.0) is assumed for the adsorption energy. All other parameters of the system, including breakthrough concentration or fraction, are entered into the model. Micropore volume is guessed and then adjusted to reproduce the experimental breakthrough time. Stoichiometric time τ from the model is used to calculate equilibrium adsorption capacity by the above Eq. 22. These capacities are then used as described above to obtain the micropore volume and a better value of the adsorption energy.

An example of this latter method is shown in Figure 27 for 10 ppm breakthrough time data reported by Nelson(48) for four chemicals at 50% RH conditions. Our initial guess for E_o was 18.00 kJ/mol. We adjusted W_o for each reported experiment until the model reproduced each breakthrough time exactly. Logarithms of volumetric capacities (W_e/d_L) obtained from the model were plotted against the corresponding squares of the potential functions divided by the appropriate affinity coefficient. The first-iteration slope yielded 25.565 kJ/mol, which was used for repeated calculations and plot. This second plot (Figure 27) and the next iteration both produced a slope corresponding to a reference adsorption potential of $E_o = (1/0.001528)^{1/2} = 25.582$ kJ/mol and an intercept corresponding to a micropore volume of $W_o = \exp(-0.821951) = 0.440$ cm^3/g. When these values were subsequently used in the model, the predicted breakthrough times plotted (vs. experimental ones) in Figure 19 were obtained for the four chemicals at all humidity conditions.

Another way to estimate micropore volume is from the carbon tetrachloride activity (CTA) number obtained by the procedures specified in ASTM D3467-94.(58) At the specified test conditions of 25°C and 250 mg/L CCl_4 (vs. 943 mg/L

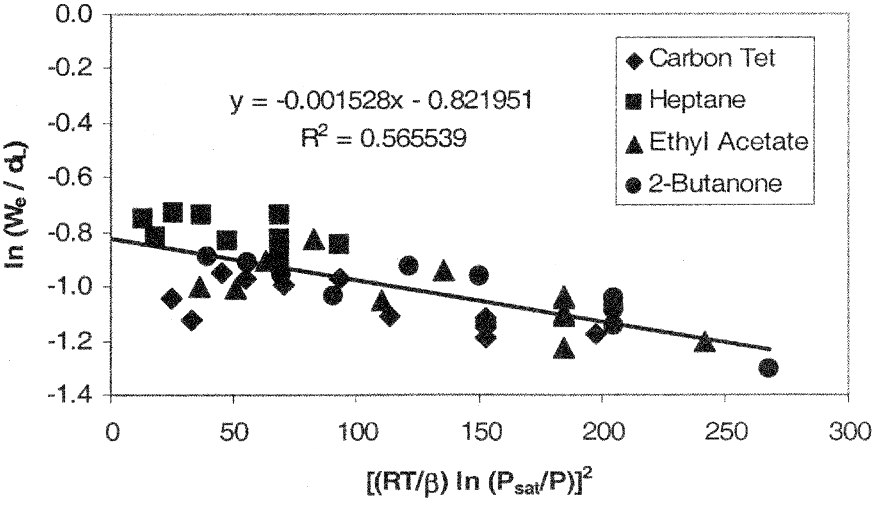

FIGURE 27. A linearized Dubinin/Radushkevich Equation plot of data from Nelson(48) from which micropore volume and adsorption energy were derived for calculating the results in Figure 19

saturation vapor pressure) and taking $\beta = 1.01$, the fraction of micropore volume filled at equilibrium ($W_e/W_o d_L$) varies from 95% at $E_o = 15$ kJ/mol to 98% at $E_o = 25$ kJ/mol. So, for example, a CTA of 75 g/100 g carbon divided by liquid density 1.589 g/cm^3 gives 0.47 cm^3/g, which should be within 5% of the micropore volume W_o. Since the use of carbon tetrachloride is not desirable,(59) ASTM has published methods using butane (D5742-95)(60) or 1,2-dichlorotetrafluoroethane (D5020-89),(61) which can be used to calculate equivalent CTA.

Wood(62) has published a correlation (±10%) between DR micropore volumes for organic vapors and nitrogen BET surface area: $W_o(\text{cm}^3/\text{g}) = 0.00041\ A_s(\text{m}^2/\text{g})$. The correlation (±15%) with DR micropore volume measured with liquid nitrogen at 77°K was: $W_o(\text{cm}^3/\text{g}) = 1.1\ W_{N2}(\text{cm}^3/\text{g})$. These can be used to estimate micropore volume, but with less reliability than the above methods. As a last resort, one can make a guess for W_o. An activated carbon of average quality has a micropore volume near 0.5 cm^3/g. Model-estimated breakthrough time is nearly proportional to micropore volume, so accuracy of the former is directly dependent on accuracy of the latter model input.

The adsorption energy parameter (benzene reference), E_o, is best determined by DR plots or fits as described above. If the data for this are not available, as little as a micropore volume value and one breakthrough time can be combined with the model to roughly estimate E_o. The micropore volume and other parameters are put into the model and the input E_o is varied until the experimental breakthrough time is reproduced. If no measured breakthrough time is available, but the cartridge has passed a certification test, the conditions and minimum acceptable breakthrough time of the certification test can be used with the model to estimate a minimum E_o in this way. As a last resort, one can use a default value of 18 kJ/mol for an average activated carbon. Again, the accuracy of the model-estimated breakthrough time is related to the accuracy of E_o model input.

A common value for the affinity coefficient of water β_{H_2O} is 0.06 (see model test results). However, it is better to derive β_{H_2O} from experimental data than to assume it. Data needed are breakthrough times at high relative humidities (preferably ≥80%), as well as data at dry conditions (≤50% RH). The procedure is to first obtain all model parameters for dry condition data, as described above and below. Then apply the model to the high-humidity data, using $\beta_{H_2O} = 0.06$. If the high-humidity experimental breakthrough times are not well estimated, the value of β_{H_2O} should be adjusted until they are.

Other parameters that are needed for the model calculations include those that describe the activated carbon bed geometry: (1) depth and cross-sectional area, or (2) depth and diameter for a round cross section. Also needed is the average weight of carbon (dry) or its packing density, each of which can be used to calculate the other. The preceding parameters may be available from the manufacturer; alternately, they can be measured after carefully opening up the cartridge(s). If more than one cartridge of the same type is used on a respirator, the cross-sectional area and carbon weight must be multiplied by that number. Average activated carbon granule size can be estimated from the mesh size fraction range, measured or obtained from the manufacturer.

Finally, the water content of the carbon before use must be known, measured (by drying), or calculated; this is expressed in the model as the RH (Pre RH) whose equilibrium with the carbon would produce this loading. In the absence of other data for a fresh cartridge or other carbon bed, Pre RH = 20% can be assumed. The caution is that some carbons impregnated with chemicals for acid gas and/or ammonia removal may also have some water added by the manufacturer. When the carbon has been rigorously dried before use or testing, RH = 1% can be assumed for the model calculations.