

THE EFFECT OF MOISTURE ON THE ADSORPTION OF XENON BY ACTIVATED CARBON

Claudiu Lungu* and Dwight Underhill†

Abstract—The following procedure was used to determine the effect of moisture on the adsorption of xenon from air onto activated carbon: A known amount of water is added to a sample of dried activated carbon and allowed to equilibrate. This activated carbon is then split between two cylindrical beds placed in a temperature controlled water bath, and air is passed through the beds sequentially. Because the beds contain pre-moistened activated carbon from the same sample, the first bed acts as a buffer, maintaining a constant humidity in the second. The mean holdup time of a pulse of ^{133}Xe injected into the second bed is used to determine the adsorption coefficient for xenon under these conditions. Measurements were made for three carbons activated to 35, 40, and 59%, respectively, at temperatures of 25°C and 55°C. The effect of moisture on the same activated carbon at these two temperatures shows an affine relationship that could be helpful in extending these results to other temperatures. At low moisture uptakes, a plot of the log(adsorption coefficient) vs. moisture uptake gives a straight line.

Health Phys. 77(3):298–302; 1999

Key words: carbon, activated; water; adsorption; humidity, relative

INTRODUCTION

THE ADSORPTION of radioactive noble gases by activated carbon has many uses, including 1) the removal of fission product xenon and krypton from reactor off-gases; 2) the diffusive sampling of radon (Blue and Holcomb 1989); 3) the trapping of waste xenon from inhalation tests in hospitals and clinics; and 4) the removal of ^{41}Ar from air exposed to neutron fluxes. One recurring question in these applications is the effect of moisture on the adsorption process. Water vapor is strongly adsorbed by activated carbon and, in almost every case examined, will be at a far higher concentration than the noble gases of concern. The objective of this research was to obtain some understanding of the effect of coadsorption of

water vapor so that it may be put into perspective in the applications cited above.

Here the effect of coadsorbed water on the adsorption of ^{133}Xe from air was determined at two temperatures, using three adsorbent carbons having different activities. Xenon was chosen as the noble gas adsorbate because

1. ^{133}Xe , because of its clinical usage, is readily available;
2. ^{133}Xe , unlike radon, forms no decay products that may confound the detection equipment used to measure its concentration on passage through a test bed; and
3. The prior data are not definitive. For example, Collard et al. (1977) found a threefold reduction in the adsorption coefficient of xenon on a European activated carbon (RBL-3) as the relative humidity increased from 0% to about 62%. No information was given about the moisture content of the activated carbon. Konyashov et al. (1988) found that the adsorption coefficient of SKT-2 activated carbon for xenon decreased by a factor of 1.2 for each added percent (by weight) of toluene or xylene. They did not look at the effect of coadsorbed moisture. Scarpitta and Harley (1990) measured the rates of adsorption and desorption of ^{133}Xe from activated carbons at various moisture contents. Rate constants can be used to determine equilibrium coefficients, but such determinations are difficult.

It is hoped that accurate measurements of the adsorption of xenon in the presence of coadsorbed water will benefit those interested in related areas. As examples, the available data for the adsorption of krypton in the presence of moisture are highly scattered (Föster 1971), and theoretical analyses of the adsorption of radon have led to contradictory conclusions (Blue et al. 1995; Scarpitta 1995; Underhill 1996). Furthermore, carefully taken data may prove useful in understanding the basic physical chemistry of the adsorption process. From the viewpoint of coadsorption, this system (activated carbon, air, water vapor, plus the xenon coadsorbate) is very simple: the xenon coadsorbed with the water is present at trace concentrations, and forms (under the conditions of this experiment) no chemical bonds.

* School of Public Health, University of Minnesota, Minneapolis, MN 55455; † School of Public Health, University of South Carolina, Columbia, SC 29208.

For correspondence or reprints contact D. Underhill, School of Public Health, University of South Carolina, Columbia, SC 29208.

(Manuscript received 20 January 1998; revised manuscript received 15 December 1998, accepted 16 March 1999)

0017-9078/99/0

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MATERIALS AND METHODS

The adsorption coefficient of xenon on dry and on moistened activated carbon was determined from the delay in the transmission of a pulse of ^{133}Xe injected into a constant flow of air passing through a bed containing the activated carbon sample (Fig. 1). The carrier gas was either compressed "Zero Grade"[†] air for activated carbons having water contents $\leq 2\%$ by weight or air from the laboratory outlet for activated carbons having higher water content. In the latter case the air was passed sequentially through beds of activated carbon and anhydrous calcium sulfate to remove trace impurities and water vapor. To maintain the desired air flow ($1 \text{ dm}^3 \text{ min}^{-1}$ for the majority of trials), a regulator and a digital air flow controller[‡] were placed upstream of the bed.

The three activated carbons used here, AB/Adsorbit, AC, and 203C, are produced from the same coconut shell base material and differ only in their degree of activation and, in one case, mesh size.^{||} The 203C carbon has a slightly finer mesh size than the AB/Adsorbit and AC activated carbons, but this should not effect the adsorption coefficient. For each activated carbon, two carbon tetrachloride (CCl_4) activities are given (Table 1). The first are the manufacturer's stated minimum values for the activity. As these may underestimate the activity, additional measurements were made in our laboratory using the American Society for Testing and Materials (ASTM) CCl_4 activity test (ASTM 1993). These latter values are used in the analyses that follow.

Next, the activated carbons were oven-dried at 155°C in a dry air flow, usually about 48 h, until no mass change was observed on reweighing. This drying temperature was suggested by a standard procedure to determine the moisture content of activated carbon (ASTM 1970). Then the dried activated carbon was transferred to a glass jar and a known volume of deionized water was added. The jar was then sealed and shaken intermittently for a minimum of 48 h.

The activated carbon sample was split between two copper beds, 21 cm high and 5 cm in diameter, placed in a temperature controlled water bath. Air passed through the beds sequentially; but just before entering the bottom of each bed, it passed through a copper tubing coil to ensure thermal equilibrium with the water bath. Temperatures in the second bed were measured by a thermistor and stored on a Data Logger.[¶] A flexible rubber tube connecting the beds allowed the injection of the radioactive xenon at that point by a 1-cm^3 syringe.

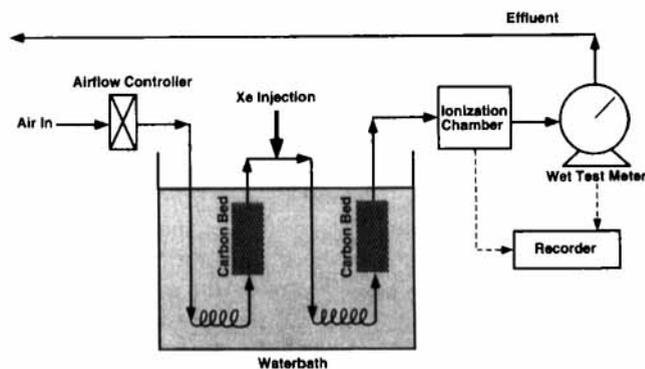


Fig. 1. The test system: 1. Air pressure regulator; 2. Air flow controller; 3. Columns containing adsorbent; 4. 1-cm^3 syringe; 5. Water bath; 6. Radiation monitor; 7. Wet test meter; 8. Strip chart recorder.

Table 1. Measured properties of the activated carbons.

Activated carbon designation	AB/Adsorbit	AC	203C
Nominal ASTM CCl_4 activity	35%	55%	20%
Measured ASTM CCl_4 activity	40%	59%	35%
Particle size, U.S. mesh	6×12	6×12	8×16
Bulk density, kg m^{-3}	0.52	0.48	0.56
Surface area, $\text{km}^2 \text{ kg}^{-1}$	0.850	1.150	0.700

Here the key concept is that the humidity of the air leaving the first bed remained constant (and equal to that leaving the second bed) throughout a test. This gave a simple and reproducible system in which measurements could be made in the second bed at a constant humidity.

This concept was verified experimentally. In a set of parallel tests, the air stream from the first bed was directed through a glass tube filled with a drying agent (anhydrous calcium sulfate[#]). The drying agent prior to its introduction into the system was weighed, with an additional weighing after each 10 dm^3 of additional air. The relative humidity (RH) was calculated from the weight gain of the drying agent (ΔW) as

$$RH = 100 \frac{\Delta W}{\Delta W_s}, \quad (1)$$

where ΔW_s is the weight gain were an equal volume of air saturated with water vapor passed through the drying tube. Note that if the effluent air from the first bed contained no water vapor, then $\Delta W = 0$; were the effluent from the first bed saturated with water vapor, then $\Delta W = \Delta W_s$. The relative humidity of the air passing through the first bed remained constant for at least the duration of the maximum test period, assuring no net loss or gain of water from the second bed during a test. Had a constant relative humidity not been observed, then increasing the amount of carbon in the first bed would lengthen the time for which the effluent from the first bed

[†] National Welders Supply Company, Inc., Charlotte, NC. The specifications for "Zero Grade" compressed air are: total hydrocarbons $<1 \text{ ppm}$ and water vapor $<3 \text{ ppm}$.

[‡] Model FM4575 Multichannel Mass Flowmeter and Flow Controller, Linde Division, Union Carbide Corp., Somerset, NJ.

[¶] Barnebey & Sutcliffe Corp., Columbus, OH.

^{||} Rustrak ranger, Gulton Instruments Co., East Greenwich, RI.

[#] "Indicating Drierite" (97% CaSO_4 , 3% CoCl_2); W. A. Hammond Drierite Co., Ltd., Xenia, OH.

maintained a constant relative humidity, but this was not necessary.

The effluent from the second adsorption bed passed through a flow-through ionization chamber** and a wet test meter connected in series to monitor the ^{133}Xe activity and the volume of effluent, respectively. A strip chart recorder connected to the ionization chamber registered the xenon activity in the effluent. A set of magnetic reed switches on the face of the wet test meter interrupted the strip chart recorder's circuit at every 0.5 dm^3 of flow, marking that point on the recorded breakthrough curve. From this curve the overall holdup volume, V_a (in dm^3), was determined through integration using Simpson's 1/3 rule:

$$V_a = \frac{\sum_i V_i A_i f_i \Delta V_i}{\sum_i A_i f_i \Delta V_i} \quad (2)$$

where

- V_i = the volume of air having passed through the activated carbon bed following the injection of the ^{133}Xe , dm^3 ;
- ΔV_i = the incremental volume throughput, 0.5 dm^3 ;
- A_i = the corresponding xenon activity in arbitrary units at V_i ; and
- f_i = the Simpson weighing factors, dimensionless.

The dead space volume, V_b , in the test system was found by injecting a xenon pulse in the absence of the activated carbon bed and analyzing the results with eqn (2). The adsorption coefficient of the activated carbon was calculated as

$$k = \frac{V_a - V_b}{m}, \quad (3)$$

where k = adsorption coefficient, $\text{dm}^3 \text{ kg}^{-1}$, and m = mass of the activated carbon, kg.

The measured adsorption coefficient included both the xenon adsorbed on the activated carbon and the xenon residing in the interparticle space. As the latter is about $1 \text{ dm}^3 \text{ kg}^{-1}$, it is unimportant in regard to the former and can be neglected. This entire procedure is described in Underhill (1969).

If the adsorption coefficient for xenon is linear, and the dynamic adsorption coefficient (which was measured here) and the static adsorption coefficient are—within experimental error—identical. Additionally, the adsorption coefficient will be independent of the quantity of tracer ^{133}Xe injected, the flow velocity of the air, and the mass of the activated carbon (Sun and Underhill 1982). This should be the case here for Nakhutin et al. (1975) found the adsorption isotherm for xenon at room temperature to be linear at vapor pressures up to about 1.3 mBar. In our tests the xenon loadings were far below this level.

RESULTS AND ANALYSIS OF DATA

Fig. 2 shows the effect of water content on the adsorption of xenon on each activated carbon at 25°C and 55°C . All adsorption coefficients are given in dm^3 (normalized to 25°C) per kg dry adsorbent. As expected, the higher the water content, the lower the adsorption coefficient for xenon. Fig. 3 shows the relative humidities corresponding to these measurements.

The first hypothesis examined here is that at any temperature the fractional reduction in the adsorption capacity is approximately the same at the same water uptake. Then, as is shown in Fig. 4, superposition of the results from measurements at the two temperatures is possible. To obtain this superposition, the results obtained at 55°C (the empty symbols) were shifted upward by a constant factor on the log scale until the root mean square of the differences between the two sets of data reached a minimum. The pairs of data track each other closely, with geometric standard deviations of 1.064, 1.198, and 1.202 for the AB/Adsorbit, AC, and 203C adsorbents, respectively. This agreement in tracking is useful in estimating the combined effects of temperature and water uptake on xenon adsorption over a wide range of conditions from sparse data. An example of sparse data would be if only two sets of measurements were available, one giving the effect of added water on the adsorption coefficient of xenon at a fixed temperature, and the other giving the adsorption coefficient of xenon on dry adsorbent at various temperatures.

The second hypothesis examined here is that the initial decrease in the xenon adsorption coefficient can be expressed as

$$k = k_0 \exp(-br), \quad (4)$$

where

k = adsorption coefficient of the activated carbon for xenon, $\text{dm}^3 \text{ kg}^{-1}$;

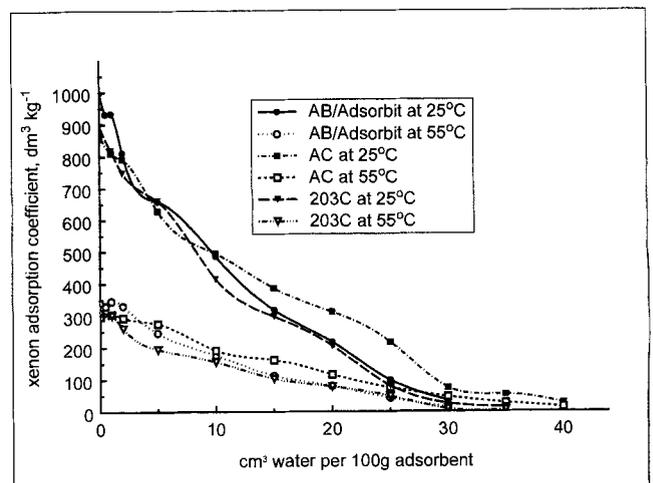


Fig. 2. The adsorption coefficient of xenon vs. water content of the activated carbon.

** Model TR-5 Flow-through Ion Chamber, Wm. B. Johnson & Assoc., Inc., Montville, NJ.

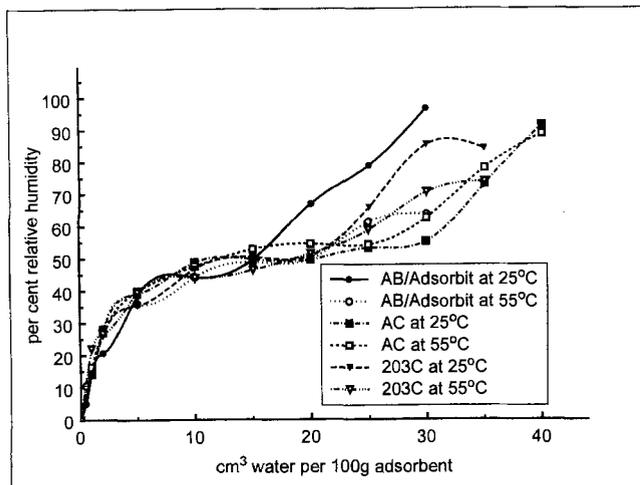


Fig. 3. Relative humidity vs. water content.

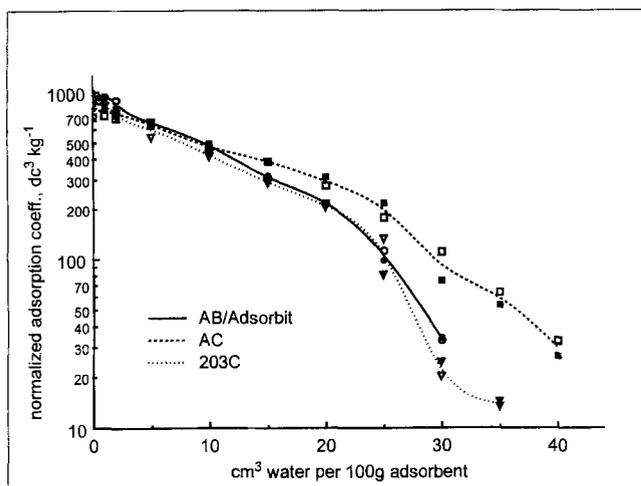


Fig. 4. Superimposition of adsorption data.

k_o = adsorption coefficient of the dry activated carbon for xenon, $\text{dm}^3 \text{kg}^{-1}$;
 b = a constant, dimensionless; and
 r = the ratio of volume of water added to the total micropore volume in the adsorbent, dimensionless.

Here the ratio r is calculated as

$$r = \frac{(\text{cm}^3 \text{ water per } 100 \text{ g activated carbon}) \times (\text{density of liquid } \text{CCl}_4)}{\text{CCl}_4 \text{ activity of the carbon}} \quad (5)$$

Eqn (5) is derived as follows:

1. The ASTM CCl_4 activity test is designed to give the increase in weight after the micropores of an activated carbon are filled with CCl_4 . This result is given in grams of CCl_4 per 100 g of activated carbon.

2. The micropore volume, in cm^3 per 100 g, is equivalent to the CCl_4 activity divided by the density of liquid CCl_4 at room temperature (1.594 g cm^{-3});
3. Then r is the volume of water added per 100 g of activated carbon, divided by the micropore volume in the same 100 g of activated carbon.

It is possible to have values for r greater than unity, for after the micropores are filled with water, the mesopores and macropores can take up additional water.

The dimensionless coefficient, b , was determined from the test data by finding the values of b and k_j that minimize the function

$$\sum_j \sum_i \left[\ln \left(\frac{k_{ij}}{k_j} \right) - br_{ij} \right]^2 \quad (6)$$

where

- k_{ij} = adsorption coefficient for the i^{th} measurement in the j^{th} set of tests. As there were two test temperatures and three activated carbons, there are six values for j ;
- k_j = a constant for the j^{th} data set. This constant is very close to the adsorption coefficient for xenon on dry adsorbent at the test temperature; and
- r_{ij} = value of r for the i^{th} measurement in the j^{th} set of tests.

Applying the above function to the test data for which the moisture uptake was less than 20% by weight gives a value of 1.74 for the dimensionless constant b .

Fig. 5 shows the theoretical curve given by eqn (4) along with the measured adsorption coefficients (the symbols); the root mean square difference between them is 5.7%. This finding of an exponential loss of xenon adsorption capacity with respect to added coadsorbate agrees with the results of Konyashov et al. (1988), but here the coadsorbate is water rather than toluene or xylene.

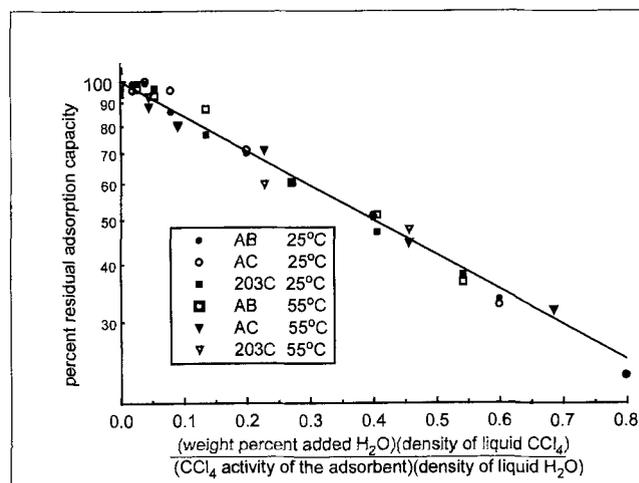


Fig. 5. Correlation of adsorption data at low water loadings.

For values of r over about 1, the adsorption coefficient is no longer predicted by the exponential curve. This corresponds to the point where sufficient water has been added to fill the micropore volume of the adsorbent, and may correspond to the "break point" reported by Scarpitta and Harley (1990) in their kinetic measurements of the adsorption of xenon.

DISCUSSION AND CONCLUSION

It was known earlier that adsorbed moisture reduced the ability of activated carbon to adsorb xenon, but the manner in which this reduction occurred was not certain. How this knowledge can be used is shown in the following example in which an activated carbon bed has adsorbed exhaled xenon used in clinical tests. Assume the exhaled moisture was initially confined to the first 10% of the bed, where the moisture loading was 18.8% on an activated carbon having a 30% CCl_4 activity. From eqn (5) the r value is 1.0, and then from eqn (4), using the value for b of 1.74, the reduction of the adsorption coefficient will be 82% in that volume of the bed where water has been adsorbed. The overall loss in the adsorption capacity (considering that the rest of the adsorption bed was unaffected) is 8.2%. Were this bed to be sealed and reused at some later time after the adsorbed moisture has redistributed evenly throughout the bed, then the reduction in the overall adsorption coefficient will be considerably greater—namely 16%. Next consider the same case with the single difference that the same amount of moisture is adsorbed on an activated carbon having a 60% CCl_4 activity. Then the initial reduction in activity will be 6.2%, and, after equilibration, 9.4%. One conclusion from these sample calculations is the need to consider not only the amount of water that is adsorbed, but its distribution and the activity of the adsorbent.

The exponential reduction in the adsorption coefficient observed here is certainly not just confined to the effect of coadsorbed moisture on the adsorption of xenon. As mentioned earlier, Konyashov et al. (1988) found an exponential decay in the adsorption coefficient of xenon as an activated carbon was loaded with toluene

or xylene. But the generality of this result—for example, does it apply to the adsorption of radon in the presence of coadsorbed vapors—is currently an open question.

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