CHAPTER **14**

Sorption of Radon on Porous Materials and the Importance of Controlling Radon in the Indoor Environment

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ABSTRACT

Sorption coefficients have been measured for a range of porous materials common in the indoor environment. Coefficients can vary widely, by factors of a hundred or more, but generally are small compared with well-known adsorbents such as activated charcoal. Almost all coefficients decrease with increasing temperature and moisture. An important consequence of the presence of sorption appears to be its role in retarding the transport of radon through porous materials. Since sorption can also cause a strong temperature and moisture dependence in the effective diffusion coefficient, it should be more often explicitly incorporated in radon transport models than is presently the case. Other identified, but less likely, consequences of sorption include its ability to cause pulsed releases of radon to indoor air, and to act as a reservoir for radon reducing the concentration of radon in the indoor air.

INTRODUCTION

The subject of sorption of gases on porous materials is proving important in a number of environmental and pollution contexts. Sorption can be important for retarding transport of pollutant vapors through soil[1,2] as well as release or retention of pollutants in indoor air (see other chapters of this volume). Despite a long history of radon gas as a pollutant, first in mine atmospheres and more recently in indoor air, surprisingly little study has taken place on the sorption properties of radon on porous materials common in the indoor and outdoor environments. In

1980 Tanner[3] reviewed the limited data available on radon sorption and recommended that this was an important subject requiring greater priority in radon research. Several more recent papers have presented evidence for desorption as an important mechanism enhancing release of radon from certain materials (concrete, soil, tailings) with increasing temperature and moisture.[4,5] Unfortunately, the experimental procedures used in those papers did not directly measure sorption so it was difficult to evaluate and quantify the specific role of sorption in the reported observations. Responding to this need for sorption specific measurements, Schery and Whittlestone[6] developed a procedure for directly measuring sorption of radon on porous materials and reported results for soils and rocks common in the outdoor environment.[7] Certain situations were identified where sorption might play an important role in release of radon to the atmosphere. These situations included unvegetated soils in arid and semi-arid climates and dry, loose materials (rocks, etc.) at the extreme surface of the earth. However, it was pointed out that the moisture content of most soils is significant, particularly below the surface skin. Based on the measured moisture dependence of sorption coefficients, this moisture content of soils would reduce the importance of sorption over much of the surface of the earth.

Since the indoor environment would normally be expected to be drier than the outdoor environment, the indoor environment seems a particularly suitable place to look for a larger role of sorption in the transport of radon through porous materials. Furthermore, the indoor environment is of particular interest in light of the recent awareness of radon as an important indoor pollutant. The goal of the research reported in this paper is to extend the measurements of Schery and Whittlestone[7] to a representative cross section of porous materials important for radon transport in the indoor environment, and see if there are any circumstances under which sorption is important for control of radon in indoor air.

EXPERIMENTAL PROCEDURE

The experimental technique is that developed by Schery and Whittlestone.[6,7] Air containing trace amounts of radon is passed over milliliter-size samples of porous media until equilibration is reached between radon in the air of the pore space and radon sorbed on the grains of the porous media. Samples are counted in a gamma detector, and from the count rate from radon and its progeny, and from the concentration of radon in the pore air, the sorption coefficients can be deduced. Calculation of the sorption coefficients requires a correction for the radon residing in the pore space of the samples based on separate measurements of porosity or solid grain volume.

For the present measurements, radon-enriched air was produced by passage of dried air through a commercial 290-kBq ^{226}Ra source (Pylon Ltd., Canada). The air was filtered, then passed through a series of 7-ml vials that were in a temperature-

controlled chamber. The vials were made of glass with a brass top sealed by a small O-ring in order to minimize sorption in the containers themselves. A constant-flow pump at the entrance to the system provided flow rates in the range of 1 to 10 ml min^{-1} while maintaining an overpressure in the system to minimize inward leaks. At these low flow rates the radon activity was high enough that no correction was necessary for the natural radioactivity content of samples. Moisture content of the samples was controlled by direct addition of water or by bubbling of the radon-rich air through a vial of water placed before a sample. Samples were removed one at a time from the temperature controlled chamber, were counted for 5 to 10 min in a 5-cm diameter by 8-cm depth NaI well detector with a gate set to count all gamma rays above 85 keV, were weighed for moisture content, and then were returned to the chamber.

The sorption coefficient k (ml g^{-1}, the volume of air in contact with the sample that would contain the same activity as sorbed in a unit mass of the sample) was deduced by comparison of the counts for an unknown sample to counts from two reference samples in the same sample set. Usually the reference vials consisted of an empty vial, and a vial of smooth glass beads of known porosity and negligible sorption. For a given temperature and moisture, measurements were repeated until steady-state results were obtained. Typically, 12 to 24 h were required to reach the steady-state, presumably reflecting the time necessary for diffusion of radon through the samples, sorption of radon by the grains, and ingrowth of radon progeny which provide most of the gamma rays which were detected.

The porosity or solid grain volume of samples was determined separately using the gas expansion method.[8] Air was used as the gas with small displacements from atmospheric pressure and with equilibration times less than a minute. Moisture content was determined by comparing wet weight to dry weight obtained by drying to constant weight in an oven at 80°C. Measurements were carried out at atmospheric pressure averaging about 85 kPa at the Socorro, New Mexico laboratory. The accuracy of the technique was checked by measuring the sorption coefficient of water as a function of temperature (for this case the sorption mechanism is solution and the bulk volume constitutes the "grain" volume). The results compared with the accepted values of k for water[9] are shown in Figure 1. Within error bars, reflecting repeatability of measurements at a given temperature, good agreement is obtained. For the routine measurements reported in this paper, the absolute error is estimated to be about ±25%. Greater accuracy was possible but not felt warranted given the difficulty of characterizing the chemical composition, pore structure, etc., of complex porous environmental materials with equivalent accuracy.

Auxiliary measurements were made on some samples to provide more information on their physical and chemical structure. Internal surface area was measured at liquid nitrogen temperature with a commercial instrument (Monosorb Surface Area Analyzer, Quantachrome, Model MS-13) using 30-mol percent nitrogen in helium carrier gas.
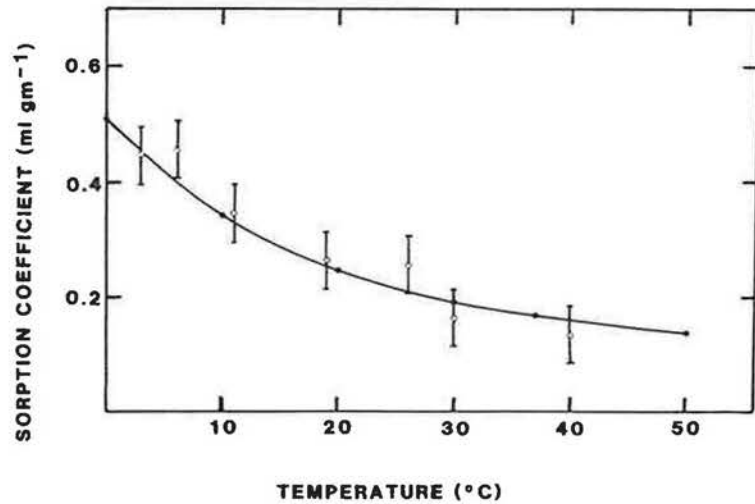
Figure 1.   Measurements of the sorption coefficient for water (open circles) compared with the accepted values (filled circles) as a function of temperature. The solid curve is an approximate visual fit to the accepted values.

RESULTS

Representative results for sorption coefficients of dry samples as a function of temperature are shown in Figure 2. In most cases, the sorption coefficient decreased with increasing temperature. There are a few exceptions, such as the cases for certain wood products such as dried pine (lumber) and paper (newsprint). This anomalous behavior might be the artifact of some unknown indirect effect of temperature in our procedure (for example, the time needed to achieve the steady-state at different temperatures was checked) but was persistent over many replications.

Representative results for sorption coefficients as a function of moisture at a fixed temperature of 26°C are shown in Figure 3. A trend of decreasing sorption with increasing moisture is evident. This trend was seen with all samples over the range of moistures studied (generally up to a maximum moisture content less than 25%).

Further information is tabulated in Table 1 for those samples for which sufficient data were obtained to establish a temperature and moisture dependence. The sorption coefficient (k) data for each sample were fit with the two-dimensional, three-parameter, linear function

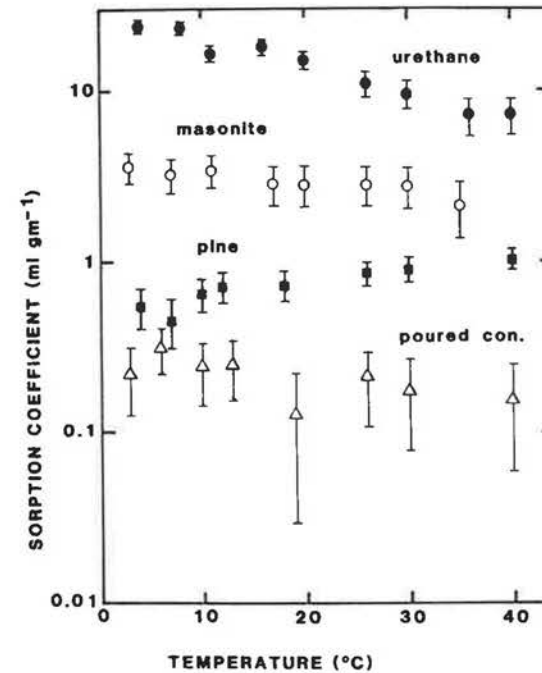$$k = k_o + k_t\,T + k_m M \qquad (1)$$

Figure 2.   Sorption coefficient versus temperature for dry (<0.2%) samples of urethane foam, masonite, pine lumber, and poured (slab) concrete.

where T is temperature in degrees Celsius and M is percent moisture by weight. This function is clearly a general low-order approximation and does not represent particularly well, for example, the apparent exponential dependence in some of the data when the temperature and moisture range is wide. However, the use of more sophisticated functional forms was considered presumptive without more complete knowledge about the specific sorption mechanisms involved.

The proportions between radon sorbed on grains and radon residing in the pore space for some selected conditions of moisture and humidity are tabulated in Table 2.

This proportion, labeled r, was calculated from

$$r = \frac{k\rho}{\varepsilon} \qquad (2)$$

where ρ is the density and ε the porosity of each sample. Values for k were determined by interpolation and use of Equation 1. The density or porosity of some materials (urethane foam, concrete, etc.) can be quite variable as used in the indoor environment. Due to this variability and the use of interpolation for k, the entries in Table 2, while representative, are less reliable than Table 1 and Figures 1 and 2 as primary reference data.
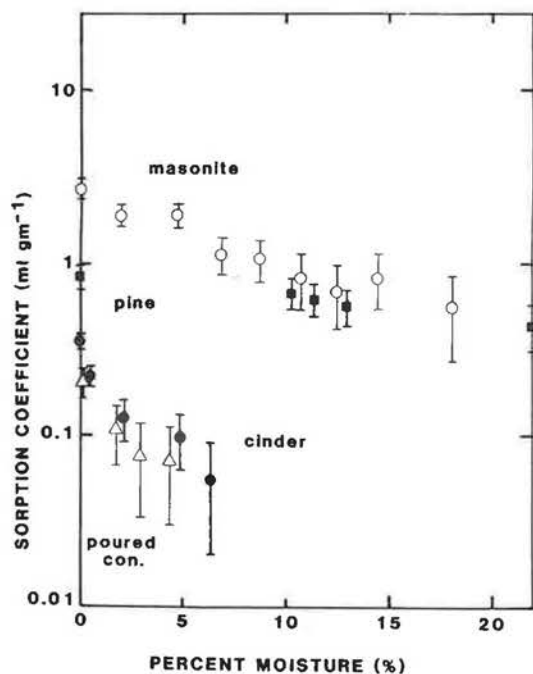
Figure 3.   Sorption coefficient at a temperature of 26°C vs. moisture for samples of masonite, pine lumber, concrete cinder block, and poured concrete.

Figure 4 shows a plot of sorption coefficients for dry samples at 0°C vs. internal surface area for samples for which measurements were available. Also shown (filled circles) are data for outdoor materials from Schery and Whittlestone[7] to provide a larger sample size for comparison and help in the interpretation of the data.

ANALYSIS

A wide variability in sorption coefficients, by a factor of 100 or more is indicated in Table 1. Even so, compared with well known high adsorbents such as activated charcoal, where sorption coefficients are often in the range of many thousands of milliliters per gram at room temperature, these sorption coefficients are generally small. Hence it is not obvious how important sorption is for control of radon in indoor air. It is necessary to take a closer look at specific mechanisms by which sorption could affect radon transport to indoor air.

One simple approach is to ask to what extent sorption is a significant reservoir or sink for radon compared with the radon stored in the bulk room air of a building. For example, consider a room 5 m × 5 m × 3 m with walls, ceiling, and floor of

Table 1.   Results of a Three Parameter Fit to the Sorption Data

Material	k_o ml g	k_T ml g·T	k_M ml g·M	Range T (°C)	Range M (%)	Comments
Concrete cinder block	0.37	−0.0006	−0.051	4–40	0–6.5	Porosity = 25%, cinders, gypsum, and concrete
Fired brick	0.096	0.001	−0.045	0–36	0–0.5	
Pumice concrete	0.25	−0.003	−0.049	0–36	0–3	Porosity = 21%, pumice, gypsum, and concrete
Sheetrock	0.19	−0.003	−0.012	2–36	0–5.5	Gypsum with paper binding
Oven dried pine	0.49	0.014	−0.019	2–40	0–25	Lumber sample
Urethane foam	27.1	−0.54	−1.20	4–40	0–9	
Particle board	2.05	−0.010	−0.086	3–40	0–14	Wood particles in cured resin binding
Masonite	3.95	−0.052	−0.13	2–39	019	Steam exploded wood fibers
Poured concrete	0.29	−0.004	−0.034	3–40	0–5	Gravel in cement binding, porosity = 17%
Oak	2.47	0.075	−0.045	0–30	0–9	Lumber sample
Celotex	9.21	−0.002	−0.084	0–30	0–20	Wood particles with asphalt binding
Fiberglass wall insulation	1.64	−0.012	−0.044	5–36	0–16	Glass fibers, most diameters 3 to 7 μm
Nylon carpet	1.55	0.006	−0.034	5–36	0–7	Fibers about 50 μm diameter, ANSO IV brand
Paper	5.3	0.06	−0.23	7–25	0–20	Newsprint

Table 2.   Values of r = kρ/ε for Different Conditions

|	Dry Warm Conditions (0%, 22°C)	Dry Cool Conditions (0%, 12°C)	Equilibrated in Air at 48% RH and T = 22°C	
	r	r	% Moisture	r
Concrete cinder block	2.8	2.8	0.8	2.5
Fired brick	1.9	1.7	0	1.9
Pumice concrete	1.6	1.9	0.9	1.2
Sheetrock	0.15	0.18	2.4	0.11
Oven dried pine	0.67	0.55	11.0	0.49
Urethane foam	0.32	0.44	0	0.32
Particle board	2.8	3.0	9.1	1.6
Masonite	5.6	6.7	8.1	3.5
Poured concrete	2.7	3.2	1.4	2.1
Oak	5.7	4.6	9.8	5.1
Celotex	3.2	3.2	6.9	3.0
Fiberglass wall insulation	0.23	0.25	0	0.23
Nylon carpet	0.16	0.16	1.9	0.16
Paper	9.0	8.2	12	5.3
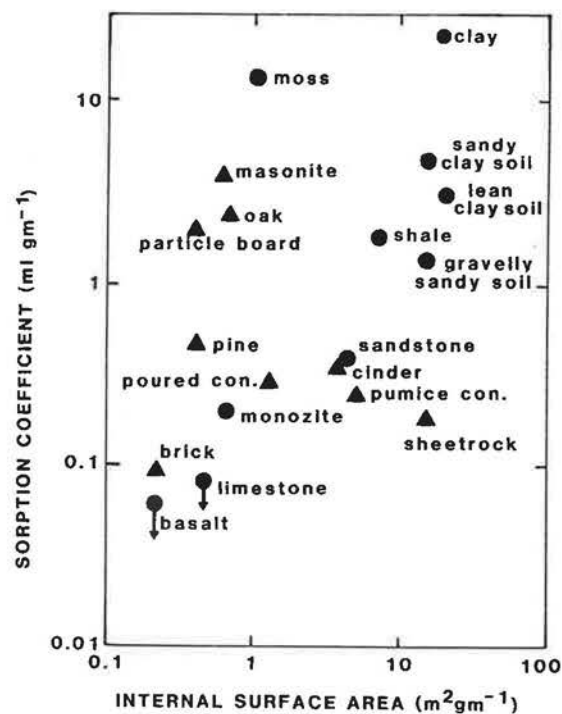
Figure 4. Internal surface area vs. sorption coefficients at 0°C and 0% moisture for samples for which surface area measurements were available. The filled circles are data from Schery and Whittlestone.[7]

concrete 0.05 m thick. Assume the concrete has a sorption coefficient of about 0.3 ml g^{-1} (a representative value, see Table 1) and a density of about 2 g ml^{-1}. The volume of the concrete is 5.5 m^3, so from the standpoint of sorption of radon it provides an equivalent reservoir volume of 5.5 m^3 × 2 g ml^{-1} × 0.3 ml g^{-1} = 3.3 m^3 compared with a bulk volume of room air of 75 m^3. Hence, assuming good radon exchange and steady-state conditions, most of the radon would reside in the room air (about 96%). The actual proportion in the concrete is likely to be even less than this estimate implies due to a reduction in the sorption coefficient because of moisture likely to be present and due to restricted penetration of radon through the concrete because of the finite diffusion length of radon. Calculations for standard sized rooms and the other materials from Table 1, for volumes of materials likely to be present in construction, generally also indicate a small role of sorption in creating a significant reservoir (e.g., masonite and urethane foam have much larger sorption coefficients but the mass of such materials used in construction would typically be much smaller, which would tend to compensate for the larger sorption coefficients). Special situations can be envisaged where sorption is more important. A small closet or cabinet filled with wood products (such as books or

paper) might well have sorption the dominant reservoir of radon. Dry soils, depending on clay content, can have significant sorption coefficients.[7] Thus, thick-walled adobe houses such as those that occur in the southwest U.S. might have sorption in the mud walls a more significant reservoir of radon. Situations have to be evaluated on a case-by-case basis. However, circumstances where sorption provides the dominant reservoir seem the exception, and the more general rule seems to be that usually sorption coefficients are too small and the volume-to-surface area of rooms too large for the building materials and furnishings to be a major reservoir of radon.

Another approach to analyzing the significance of sorption is to look at transport of radon within the porous materials themselves. Some important information is provided in Table 2. Even at the reduced sorption present with typical moisture in materials, the majority of materials have more radon in the sorbed state than in the pore air itself. The consequences can be indirect but potentially significant, for this situation indicates that diffusive transport may be controlled more by the properties of sorption than strictly by the physical laws for three-dimensional diffusion through the pore air itself (as sometimes assumed). Although diffusion can still be represented by a single effective diffusion coefficient, diffusion will tend to be slowed by sorption and have an altered temperature and moisture dependence. The above arguments can be quantified by looking at the results of a simplified model for the effective diffusion coefficient (D_e) when both pore diffusion (D_p) and surface diffusion (D_s) are present.[10] In our present context the result is

$$D_e = \frac{D_p + D_s \dfrac{k\rho}{\varepsilon}}{1 + \dfrac{k\rho}{\varepsilon}} \qquad (3)$$

Usually surface diffusion is much slower than pore diffusion ($D_s \ll D_p$) so

$$D_e = \frac{D_p}{1 + \dfrac{k\rho}{\varepsilon}} \qquad (4)$$

is a good approximation. Equation 4 highlights the sensitivity of the diffusion coefficient to the sorption coefficient. Large sorption coefficients will significantly reduce D_e. Furthermore, the dependence of k on temperature and moisture seen in much of the present data will cause stronger dependences of D_e on these variables than would otherwise be present with pure molecular pore diffusion. A porous slab possessing significant sorption could be a barrier to radon diffusion when dry but might become permeable to radon when moist due to rapid decrease in k with increasing moisture. For example, Equation 4 and the data of Figure 3 indicate the diffusion coefficient for cinder block could be reduced by a factor of over four when slightly moist compared with when dry.

Another consequence of the dependence of the effective diffusion coefficient on the sorption coefficient is the possibility of seeing pulsed releases of radon from building materials and furnishings upon change in temperature or moisture. Proper modeling of this situation requires analysis of changes in the concentration of radon in the pore space, and time dependence of the moisture and temperature penetration, as well as variation of D_e.[7] Such detailed modeling is outside the scope of this chapter, but there are a few simpler calculations that can provide insight. Consider an increase in indoor temperature of 10°C, say from 12 to 22°C, which might be a relatively feasible indoor event. For the room with concrete walls analyzed earlier, a representative sorption coefficient might change from of the order of 0.35 to 0.30 ml g^{-1}. If this change occurred instantaneously, and the desorbed radon was uniformly distributed throughout the indoor air, the increase in room air radon would only be of the order of 1%. Likewise, Table 2 indicates that such a 10°C temperature change is only sufficient to change most r-values by a small fraction, suggesting a rather small change in radon in the pore space and in the diffusive transport to the surface. Larger temperature changes, significant changes in moisture, or release into smaller air spaces would of course be capable of producing more noticeable changes in the radon level. If the instantaneous exhalation *rate* from a surface was measured, rather than the integrated effect on room air, effects could be more noticeable. On balance, though, it does not appear major pulsed releases would be common.

Detailed analysis of the physical mechanisms involved in radon sorption is outside the scope of this chapter. However, it is interesting to note that if organic materials are excluded (moss and wood products), as shown in Figure 4, there is a reasonable correlation between sorption coefficients and internal surface area as determined by the nitrogen adsorption procedure. This result might suggest the importance of simple adsorption for these inorganic materials. The fact that the organic materials form a separate grouping might reflect a different physical mechanism for sorption, or perhaps just some measurement artifact such as that resulting from internal surface area measurement at very cold temperatures.

CONCLUSIONS

Sorption coefficients have been measured for a cross section of materials common in the indoor environment. Coefficients vary widely, by a factor of 100 or greater, but compared with well-known adsorbents, such as activated charcoal, are relatively small. Coefficients generally decrease with increasing moisture and temperature. Given the generally dryer conditions in the indoor environment than outside, there appears a greater chance for sorption to play a significant role inside than outside.

Analysis indicated that the most likely effect of sorption is to change the

diffusion process through indoor materials from simple molecular diffusion through the pore space to a more complex process involving interaction between pore diffusion and sorption on grains. One likely consequence is that effective diffusion coefficients would have a stronger dependence on moisture and temperature than would otherwise be the case. Slabs that are barriers to radon at one temperature and moisture might not be barriers at other temperatures and moistures. This effect of sorption probably needs to be better taken into consideration in transport models and computer codes that are being developed.

Only in special situations did it appear sorption would be strong enough to give observable pulses of radon in the indoor air of rooms with changing temperature. Similarly, it appeared that generally sorption coefficients were too small, and the volume to surface ratio of rooms too big, for sorption to provide a major reservoir for radon compared with the bulk volume of the room air. Some exceptions were noted. Enclosures with high surface-to-volume ratios, for example closets or cabinets filled with paper products, might have sorption a significant reservoir of radon.

ACKNOWLEDGMENTS

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