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Removal of Radon-220 from HTGR Fuel Reprocessing and Refabrication Off-Gas Streams by Adsorption (Based on a Literature Survey)

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MASTER

OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

This report presents literature theory and data that are considered relevant to the removal of Rn-220 from HTGR fuel reprocessing and refabrication off-gas streams by adsorption. The data include equilibrium adsorption coefficients for radon on activated carbon (charcoal) and silica gel in the presence of air and other gases, and for radon on molecular sieve Type 5A in the presence of air. Also included are a few dynamic adsorption data (adsorption coefficients and values for the number of theoretical plates per foot) for radon on charcoal, with air as the carrier gas. These various data, which were obtained mainly at or near 25°C, are actually for Rn-222; however, they should also be applicable to Rn-220, provided the conditions are the same. Based on the available information, the radon adsorption coefficients decrease in the expected order: charcoal, molecular sieve Type 5A, and silica gel. Thus, charcoal should be the most effective of these adsorbents for Rn-220 removal; however, its use for this application cannot be recommended until the associated fire and explosion hazards, particularly those with regard to interaction with ozone, are resolved. Sorbent poisoning and particle penetration due to α-recoil are briefly treated. Adsorber design is discussed. Existing information appears adequate for sizing, albeit crudely, the sorbent bed for a Rn-220-charcoal-air (1-atm, < 10% relative humidity) system, and a suggested approach for doing this is outlined.

1.0 INTRODUCTION

Fertile ^{232}Th will be irradiated with neutrons in high-temperature gas-cooled reactors (HTGRs) to produce fissile ^{233}U. At the same time, a small but significant quantity of unwanted ^{232}U will also be produced. The ^{232}U decay chain includes ^{220}Rn as an intermediate daughter product. As a consequence, off-gas streams from those HTGR fuel reprocessing and refabrication operations involving ^{233}U will be contaminated with ^{220}Rn. And, as a further consequence, inclusion of some means for effective removal of ^{220}Rn in the corresponding off-gas cleanup systems will be required in order to satisfy, in part, the federal regulatory release criterion "As Low as Practicable."

One of the methods employed for removing short-lived krypton and xenon from reactor off-gas streams is based on their adsorptive-holdup and decay (mainly to stable or nonvolatile nuclides). Usually, the adsorbent is activated carbon (charcoal). Since ^{220}Rn has a half-life of only 55.3 sec and is less volatile than krypton or xenon, this method should also be feasible for the ^{220}Rn decontamination of off-gas streams. The principal objectives of this study were to review the available radon adsorption data and to identify a theoretical treatment that would be useful for adsorber design calculations.

2.0 THEORY

For a given noble-gas contaminant at the low concentrations as are usually encountered in these various off-gas streams and for temperatures of, say, $\geq 0°C$, the following equilibrium adsorption equation or its equivalent is generally assumed:

$$V_a = k_a p, \tag{1}$$

where

V_a = amount of the noble gas adsorbed per unit weight of sorbent [cm^3(STP)/g] (with STP referring to 0°C and 1 atm),

k_a = adsorption coefficient [cm^3(STP)/g atm], with its value depending on the noble gas, the temperature, the sorbent, and the nature and concentration(s) of any other gas(es) present,

and

p = partial pressure (atm) of the noble gas.

The performance of a radioactive noble gas adsorber operating under dynamic conditions depends, of course, to a large extent on its equilibrium adsorptive capacity. Other highly important factors are the flow rate (or velocity) of the carrier gas, the mass transfer characteristics of the system, and the half-life (or half-lives) of the noble gas(es).

The behavior of a small pulse of nonradioactive noble gas injected into a carrier gas flowing through an adsorbent bed of uniform cross section will first be considered. The process involved here is termed gas-solid chromatography. Use will be made, however, of certain theoretical considerations from gas-liquid chromatography; experimental justification for doing so will be cited subsequently. A theoretical plate treatment for a process approaching gas-liquid chromatography very closely and based on a linear distribution isotherm has been presented by Keulemans.[1] For use in treating radon (or other noble gas) removal by adsorptive-holdup, the elution curve equation corresponding to this treatment was converted to the following form, using Eq. (1) and the ideal gas law:

$$C_{N,t} = \frac{A(Ft)^{N-1}}{(km/N)^{N}(N - 1)!} e^{-NFt/km} \tag{2}$$

with

$$k = \frac{\varepsilon}{\rho} + \frac{T}{r} k_a , \tag{3}$$

where

$C_{N,t}$ = concentration [cm^3(STP)/cm^3] of noble gas at time t in the gas phase of plate N of a series of plates numbered 1, 2, 3 . . . (also regarded as the exit concentration if the total number of plates is N),

A = amount of noble gas injected as a small pulse [cm^3(STP)],

F = volumetric flow rate of the carrier gas (cm^3/min),

t = time after injection (min),

N = number of theoretical plates,

k = holdup coefficient (cm^3/g),

m = mass of sorbent (g) in adsorber (m/N is mass per plate),

ε = void fraction,

ρ = bulk density of sorbent (g/cm^3),

T = adsorber temperature (K)(adsorber considered isothermal),

and

r = b/R, where b is the molar volume [cm^3(STP)/mole] and R is the gas constant (cm^3 atm/K mole), i.e., r = 273.15 K cm^3(STP)/cm^3 atm.

For sufficiently large values of k_a,

$$k \simeq Tk_a/r. \tag{4}$$

An elution curve equation similar to Eq. (2) has been presented by Browning and Bolta.[2] It was developed to describe the behavior of a pulse of ^{85}Kr injected into a carrier gas flowing through a charcoal trap. Comparison of their equation with Eq. (2), making allowance for differences in units and assuming that Eq. (4) pertains, reveals that the two equations are equivalent even though the approaches employed in obtaining them were somewhat different. The Browning-Bolta equation was found to provide a reasonably good representation of experimental elution curves for pulses of ^{85}Kr injected into nitrogen or helium flowing through charcoal traps.[2]

The time corresponding to the maximum in the elution curve, t_{max}, is obtained in a manner similar to that of Browning and Bolta, i.e., by setting $dC_{N,t}/dt = 0$, yielding:

$$t_{max} = \frac{N - 1}{N} \frac{km}{F} . \qquad (5)$$

If the elution curve were symmetrical, t_{max} would be the average holdup time for the noble gas in the pulse. An experimental elution curve can be used to evaluate N, using the simple procedure described in various books on gas chromatography (e.g., ref. 1), and then k, assuming m and F are known and t_{max} has been measured.

In the preceding analysis, no allowance has been made for radioactive decay. However, Underhill[3] has extended the Browning-Bolta treatment to allow for radioactive decay and to provide an equation which permits the calculation of a decontamination factor corresponding to the holdup and decay of a pulse of radioactive noble gas when values for m, F, k, N, and the decay constant are available. A similar expression has been developed starting with Eq. (2) and using a mathematical procedure based on that presented by Underhill. (Details are given in the Appendix.) The expression is as follows:

$$DF = \left(\frac{1 + NF/km\lambda}{NF/km\lambda}\right)^N , \qquad (6)$$

where

DF = decontamination factor,

λ = decay constant (min^{-1}),

and the other terms are as already defined.

While Eq. (6) was developed for a single pulse of radioactive noble gas, it should apply equally well to the case of continuous injection of such gas, provided the concentrations involved are sufficiently low. That is, the continuously introduced noble gas may be regarded as consisting of a series of successive pulses for each of which Eq. (6) would be expected to apply within the limitations of the theory. Equation (6) has not, so far as is known, been tested experimentally.

The above treatment has mainly been concerned with the behavior of a pulse of noble gas. The relationship between the elution curve for a pulse and the breakthrough curve for a step--constant input (i.e., where the concentration rises abruptly from zero to a constant level) has been treated by Robell and Merrill.[4] For the case of linear adsorption, they showed that pulse-type data could be used to predict step--constant input breakthrough curves, and they indicated a method for evaluating N from the latter. The theoretical treatment of Browning and Bolta, together with certain of the theory and calculational techniques presented by Robell and Merrill, has recently been applied by Siegwarth et al.,[5] who investigated the dynamic adsorption of krypton and xenon by charcoal. The latter authors note that the time corresponding to the peak maximum for the pulse case can be equated to the time corresponding to the inflection point for the step--constant input case.

Included among other recent developments in the areas of gas-chromatographic theory and mathematical analysis of krypton-xenon holdup beds are those of Grubner[6] and Underhill.[7,8] The mathematical expressions involved are rather complex, and no particular effort was made to ascertain their usefulness with regard to the radon problem. There are numerous other papers of interest relative to noble gas adsorber theory and design. Of these, seven will be noted as follows: Burnette, Graham, and Morse,[9] Madey,[10] Glueckauf,[11] Kovach,[12], Underhill,[13] Underhill, Yusa, and Grubner,[14] and Kovach and Etheridge.[15]

3.0 RADON ADSORPTION DATA

3.1 Activated Carbon (Charcoal)

A fairly large variety of radon adsorption data was found for charcoal; however, for the purposes of this report, the examination of such data was restricted to a group of eight publications. In a few cases, the original papers were not readily available, but enough information was given in Chemical Abstracts to permit the evaluation of adsorption coefficients. With one exception, the indicated adsorption coefficients are in fair agreement. The available results are for ^{222}Rn rather than ^{220}Rn; however, their respective adsorption coefficients should be nearly identical for a given set of conditions. Except for the last of these eight papers to be treated (i.e., that of Thomas), the adsorption coefficients are equilibrium values. In most of these cases, circulation or transport of radon in a carrier gas was employed to aid in achieving equilibrium. The data are discussed, according to authors, in the subsections that follow.

3.1.1 Becker and Stehberger[16]

Radon adsorption results were obtained for a $ZnCl_2$-activated wood charcoal. The conditions were such that the adsorption coefficient at a given temperature was independent of the radon partial pressure. A small selection of their tabulated data was used to calculate representative k_a values for radon in the presence of air at a pressure of 75 or 76 cm Hg, as follows:

Temperature (°C)	Adsorption Coefficient, k_a [cm^3(STP)/g atm]
0	6400
17	2200
50	500

3.1.2 Gubeli and Stammbach[17]

The indicated k_a values for radon on charcoal as calculated from the data in this paper are higher, by some two orders of magnitude, than those from the other sources; thus they are not reported here. Whether this apparent discrepancy is due to some misinterpretation of the units employed or has some other explanation is not known.

3.1.3 Gubeli and Stori[18]

The data of Gubeli and Stori are in the form of adsorption isotherms for radon at low concentrations in the presence of various gases at atmospheric pressure. The sorbent was elm-wood charcoal. The radon partial pressures were $\leq 10^{-13}$ atm in cases where the predominant gas was air, N_2, or CO_2 and $< 10^{-12}$ atm in cases where the predominant gas was H_2. The adsorption coefficient values under these conditions are listed in Table 1. A puzzling aspect is that, whereas the k_a values estimated from their isotherms agree with those given in Table 1 for 0°C, the estimated values at higher temperatures tend to be lower than those tabulated; for example, the estimated values at 120°C are lower, on the average, by ~ 30%, suggesting that the temperature factor (273 + 120)/273 may be involved. The ratio of the adsorption coefficient at 20°C with air present to that with CO_2 present is of particular interest since both air and CO_2 off-gas streams will be generated in conjunction with HTGR fuel reprocessing and refabrication operations. This ratio is 5.0, which may be compared with a ratio of 3.5 for dynamic adsorption coefficients of krypton in O_2 and in CO_2 at 24°C for another type of charcoal.[19] Actually, one would expect the lower ratio to be associated with radon since CO_2 should interfere less with radon adsorption than with krypton adsorption.

3.1.4 Coleman et al.[20]

The equilibrium retention of radon by coconut charcoal was measured following exposure to flowing air containing radon at concentrations of 2×10^3 to 8×10^4 pCi/liter. Presumably, the temperature and pressure were ambient (i.e., those of the building). If the temperature was 25°C, the radon partial pressure range was 1.4×10^{-15} to 6×10^{-14} atm. The data of Coleman et al. indicate considerable deviation from linearity for the variation in adsorption with pressure. The ratio of the volume of radon adsorbed [cm^3(STP)/g] to the radon partial pressure (atm), as estimated from their graph, decreased from ~ 3×10^3 to ~ 9×10^2 over the above concentration range.

Table 1. Average radon adsorption coefficients[a,b] for elm-wood charcoal in the presence of various gases[c]

Temperature (°C)	Predominant gas			
	Air	N_2	CO_2	H_2
-18	-	-	1,585	-
-10	-	-	1,608	-
0	12,685	16,854	1,634	29,555
20	6,422	7,084	1,282	10,976
50	2,268	2,189	754	2,507
80	811	800	431	735
120	392	249	165	290

[a] Obtained by Gubeli and Stori.[18]

[b] The information in the original paper indicates that each of these values should be equivalent to k_a[cm^3(STP)/g atm] of Eq. (1).

[c] At atmospheric pressure.

3.1.5 Przytycka[21]

Radon adsorption was measured for three types of charcoal, at an indicated temperature of 20°C, in a closed circuit with air as the carrier gas. The k_a values calculated from the reported adsorption coefficients range from about 4600 to about 5600 [cm^3(STP)/g atm].

3.1.6 Fusamura, Kurosawa, and Ono[22]

An empirical equation was presented for radon adsorption on charcoal with air present and applicable to the temperature range 2 to 32°C. In terms of k_a [cm^3(STP)/g atm] for an absolute temperature T(K), this equation may be written as:

$$k_a = 6000 \left(\frac{273}{T}\right)\left(\frac{288}{T}\right)^{12.7} .$$

A k_a value of 3563 was calculated from this equation for a temperaure of 25°C.

3.1.7 Schroeder et al.[23]

Data were presented for the retention of radon from flowing air by coconut charcoal at 24°C. The results, expressed in terms of k_a values, are as follows:

Radon concentration (pCi/liter)	Adsorption coefficient, k_a [cm^3(STP)/g atm]
11,000	2500
5,000	1500
240	3800

3.1.8 Thomas[24]

This report is of particular interest because a fairly large variety of dynamic adsorption data was presented for the radon-charcoal system. The carrier gas was air at or near 1 atm; the temperatures involved were 20 to 25°C. Measurements were made on respiratory canisters containing beds of activated carbon. Two varieties of canisters were tested: the M11 and the Scott-Acme. (Types 184-OV and 184-OVWC of the latter were involved.) The Scott-Acme canister contained the larger bed, and most of Thomas' data that are reported herein were obtained using this variety of canister. Approximate values for the corresponding charcoal bed included a volume of 900 cm^3, a face area of 60 cm^2, and a 15-cm depth. The charcoal mesh size was listed as 6-16 (probably with reference to the U.S. Sieve Series).

In the tests of greatest interest, the canister was preequilibrated to flowing air at a definite humidity; the flow rates were 16, 32, or 64 liters/min. Then radon from a radium chloride solution was introduced at a concentration of 11,000 pCi/liter, which corresponds to a radon partial pressure of 8×10^{-15} atm at 25°C. Prior tests with an M11 canister had indicated no significant difference in the radon transmission (breakthrough) curves observed for 1600 and 38,000 pCi/liter. The transmission curve is a plot of the ratio of the exit concentration to the inlet concentration vs time. During the period of radon injection, the exit concentration was determined at 3-min intervals; the inlet concentration was determined both before and after the exposure of the canister to radon-containing air.

The two types of Scott-Acme canisters that were tested actually corresponded to three different types of activated carbon. One of the carbons was Witco type 337, which had a surface area of about 1300 m^2/g; another was Westvaco type WV-H, which had a surface area of about 1000 m^2/g. Analogous information was not available for the remaining carbon. The canister containing the Witco carbon exhibited the superior radon holdup performance; the performances of the other two were about the same. The carbon life to 2% transmission for the Witco carbon was the longer, by $\sim$ 45%, thus indicating the desirability of high surface area. This observation, however, appears to be in conflict with that of Kovach and Etheridge,[15] who found the optimum surface area for krypton holdup to be near 800 m^2/g for a series of similar carbons having surface areas of 525 to 1670 m^2/g. Obviously, more data are needed to specify with confidence a near-optimal type of activated carbon for ^{220}Rn adsorption.

The initially deleterious effect on radon adsorption of exposing dry charcoal to air containing an appreciable amount of moisture was observed and discussed. This effect, which was observed with the M11 canisters, results from the elevation in charcoal temperature that occurs when water is adsorbed. In the tests on the Scott-Acme canisters, this effect was avoided by preequilibrating the charcoal with flowing air at the same humidity as that which prevailed during radon injection.

Thomas investigated, in some detail, radon adsorption performance as a function of the moisture content of the air stream. The data to be summarized here are for the Scott-Acme canister containing Westvaco type WV-H activated carbon (about 1000 m^2/g) at 25°C (with preequilibration having been employed). In terms of the fraction of total input radon adsorbed during a 60-min test, the performance at a flow rate of 16, 32, or 64 liters/min for 39% relative humidity (R.H.) was poorer by only a few percent than that at the same flow rate for 6% R.H. (For most types of charcoal, the extent of water adsorption remains low up to about 30% R.H.) In terms of charcoal bed life to 2% radon transmission, the ratio of the performance at 48% R.H. to that at 6% R.H. averaged about 0.6 for 16, 32, and 64 liters/min; the analogous ratio for 61% R.H. (and 6% R.H.) was about 0.3.

The effect of changing the air flow rate, by a factor of 2, on bed life to 10% transmission was measured using M11 canisters (at 8 and 16 liters/min) and a Scott-Acme canister (at 16 and 32 liters/min and at 32 and 64 liters/min). The observed ratios of bed life (10%) at a given flow rate to that at twice the flow rate varied from 2.2 to 2.9. That these ratios are significantly higher than 2.0 is consistent with (1) the dependence of the shape of the breakthrough curves on N (the number of theoretical plates) and (2) the decrease in N with gas velocity that occurs in the velocity regime involved.

The breakthrough curve treatment of Robell and Merrill[4] was used to estimate values of k_a and N from two of the transmission curves presented by Thomas. These curves are for the Scott-Acme canister containing the Westvaco carbon and for air flow rates of 32 and 64 liters/min; other conditions were 6% R.H. and 25°C. Estimation of the k_a's also involved the use of Eq. (5), together with an assumed bulk density of 0.48 g/cm^3 for the carbon. The values obtained were as follows:

Air flow rate (liters/min)	Superficial velocity (fpm)	Adsorption coefficient, k_a [cm^3(STP)/g atm]	N/ft (ft^{-1})
32	17.5	3800	4.9
64	35.0	4600	3.7

The fact that these k_a and N values, as estimated, are somewhat crude is illustrated by the fairly large difference in the k_a values, which should be independent of gas velocity. The value of N is expected to decrease with velocity in this flow regime as based on the results from a previous investigation by Browning et al.[25] of the $^{85}Kr-O_2$-charcoal system. These results are shown in Fig. 1. The mesh size of the charcoal in the earlier study was 8 x 16 (U.S. Sieve Series) as contrasted with the 6 x 16 mesh size for the charcoal contained in the Scott-Acme canister. Despite the differences in noble gas, type of charcoal, and granule size (the difference in carrier gas is probably of lesser importance), one of the above N/ft-velocity data points practically falls on the curve of Fig. 1, while the other falls moderately above. The N values in the figure were evaluated from pulse-type elution curves by the method that is more commonly associated with gas-liquid chromatography. Although this method was at that time characterized as preliminary with regard to evaluating N from ^{85}Kr elution curves, its use for this purpose is now considered to be on a firmer basis.

The effect of temperature was investigated for the approximate range 20 to 25°C and was compared with that predicted by the equation of Fusamura, Kurosawa, and Ono.[22] The observed effect was about two-thirds the predicted effect; however, this apparent discrepancy may reflect differences in the charcoals and in the two sets of conditions.

The effect of 2 vol % CO_2 in the air stream was briefly investigated and found to be deleterious, especially at low humidity ($\leq$ 4% R.H.), where the indicated decrease in adsorption coefficient was about 25%. A much smaller effect (referring only to that due to the 2 vol % CO_2) was observed under the condition of $\sim$ 50% R.H., presumably because the adsorption of CO_2 was suppressed by the enhanced adsorption of H_2O at the higher relative humidity.

3.1.9 Other investigations relating to radon adsorption on charcoal

These investigations include the following (identified by authors): Nikitin and Ioffe,[26] Gubeli and Stori,[27] Rogalya,[28,29] Lucas,[30,31] Kapitanov et al.,[32] Thomas,[33] and Baetsle and Droissart.[34] A brief abstract indicates that the second paper of Rogalya is a review of the

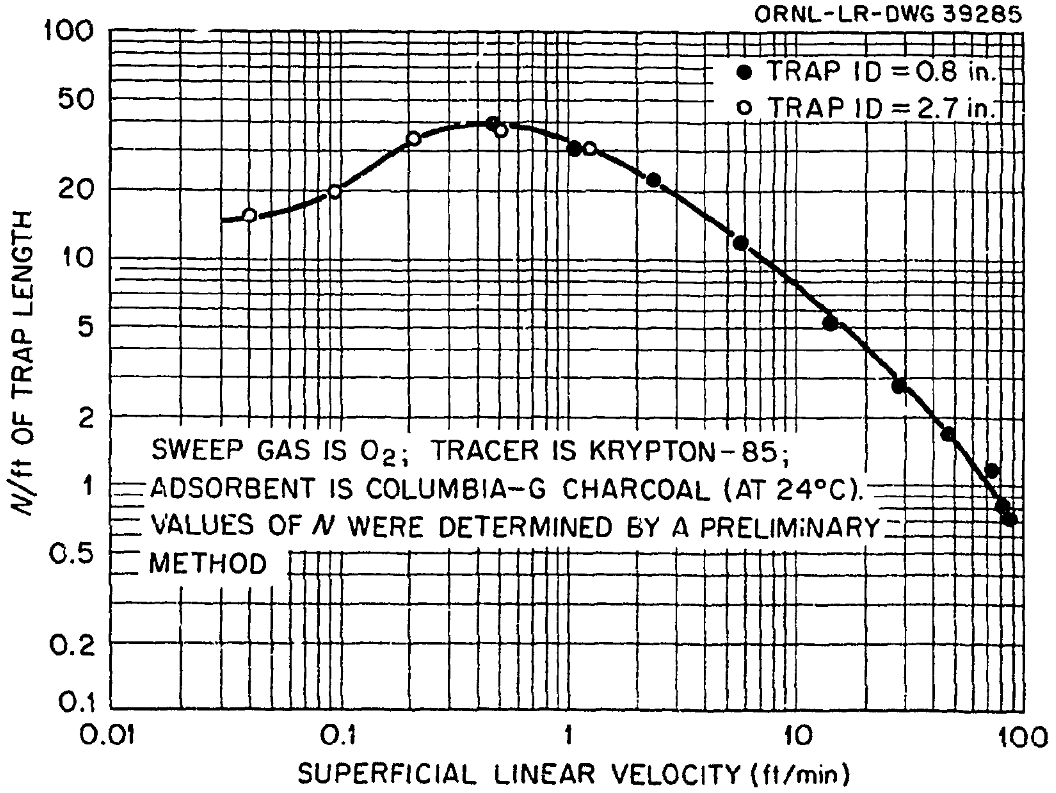

Fig. 1. Effect of linear velocity of the sweep gas on N, the number of theoretical plates.

adsorption of radioactive emanations (chiefly radon) on charcoal and other porous adsorbents. (The original paper was not readily available.)

3.2 Molecular Sieves

Only a small amount of radon adsorption data was found for molecular sieve adsorbent. Coleman et al.[20] measured the equilibrium retention of radon from flowing air by molecular sieve Type 5A in a manner similar to that employed for their measurements with charcoal. For the same radon concentration range (2×10^3 to 8×10^4 pCi/liter), the indicated ratio of the volume of radon adsorbed [cm^3(STP)/g] to the radon partial pressure (atm) increased from $\sim 5 \times 10^2$ to $\sim 8 \times 10^2$. Thus, the observed direction of change in this ratio with concentration for molecular sieve Type 5A was opposite to that which they observed with charcoal. They also noted that the adsorptive capacity* of molecular sieve Type 4A for radon was too low to be of significance. This latter observation is in accord with a result from another investigation in which an apparent adsorption coefficient of ~ 1[cm^3(STP)/g atm] was obtained for ^{85}Kr in dynamic adsorption measurements on Linde Molecular Sieve Type 4A at 25°C with O_2 as the carrier gas.[19] On the other hand, an equilibrium adsorption coefficient of about 11 has been observed for krypton on Linde Molecular Sieve Type 4A at 25°C using equilibrium times of up to 4 hr.[35]

3.3 Silica Gel

A fairly large number of radon adsorption data for silica gel were found, and a selection of these data is presented in the subsections below.

3.3.1 Becker and Stehberger[16]

Representative k_a values were calculated from tabulated data of Becker and Stehberger for the adsorption of radon on silica gel in the presence of air at 1 atm. These k_a values and the corresponding temperatures are as follows:

---

*Referring to that which is readily accessible (to radon).

Temperature (°C)	Adsorption coefficient, k_a [cm^3(STP)/g atm]
-80	3223
5	65
14	46
35	22

3.3.2 Burtt and Kurbatov[36]

Various adsorption data, including those for radon on silica gel in the presence of air, argon, and CO_2, were reported by Burtt and Kurbatov. Their radon data, after being converted to pressures and k_a values, are presented in Table 2.

Table 2. Radon adsorption coefficients[a] at 25°C for silica gel in the presence of various gases

Predominant gas		Radon partial pressure (10^{-12} atm)	Adsorption coefficient, k_a [cm^3(STP)/g atm]
Identity	Pressure (atm)		
Air	0.967	17.1	25.4[b]
		9.8	26.1
		2.4	27.0
		1.7	27.5
Ar	0.900	17.1	39.3
		9.8	39.4
		2.4	39.4
		1.7	39.5
CO_2	0.926	17.1	21.6
		9.8	22.9
		2.4	24.7
		1.7	24.6

[a] Derived from data of Burtt and Kurbatov.[36]

[b] These values, which are ratios of the quantity of radon adsorbed to the radon partial pressure, exhibit some deviation from constancy; consequently, they are not, strictly speaking, true k_a values.

3.3.3 Other investigations relating to radon adsorption on silica gel

These investigations include the following: Francis,[37] Livingston and Reyerson,[38] Siebert,[39] and Gubeli and Stammbach.[17] Isotherms in the latter paper are indicative of higher radon adsorption capability than that indicated by the data presented above. However, since the accompanying data for charcoal indicated unusually high adsorption coefficients, as was noted earlier, values corresponding to the silica gel data also will not be reported here. The data of Siebert[39] have been briefly discussed by Brunauer[40] and by Bikerman.[41] They present certain of Siebert's data which show that radon adsorption on silica gel at -80°C is strongly suppressed by the presence of CO_2. In terms of the adsorption coefficient, the value with CO_2 present at 1 atm is only about 0.02 times that with air at 1 atm (for -80°C).

4.0 HAZARDS ASSOCIATED WITH CHARCOAL ADSORBERS

Evaluation of the potential hazards associated with the use of charcoal adsorbers for ^{220}Rn holdup and decay is beyond the scope of this particular study but very likely will receive detailed attention as work on the radon problem develops. A few of the presently recognized hazards will, however, be noted here, together with references which might aid in initiating the hazards evaluation.

A hazard of particular concern to those involved in radon adsorber design is that represented by the radiation-induced generation of ozone and its subsequent accumulation on and interaction with the charcoal. Because of this concern, the use of an inorganic sorbent (rather than charcoal) is being considered for at least one important application. However, based on the available adsorption data alone, charcoal would be the preferred sorbent by a wide margin. The interaction of ozone with charcoal has been investigated by Deitz and Bitner.[42,43] Under certain conditions, explosions of ozone-treated charcoal were encountered. The ozone-charcoal system has also been investigated by Boberg and Levine.[44]

The presence of oxides of nitrogen may result from fuel reprocessing operations and/or from radiation. Under certain conditions, the NO_x-charcoal combination constitutes a serious fire hazard. Rodger and

Reese,[45] in discussing fuel reprocessing off-gas systems, refer to the work of Welch and Ross[46] and comment to the effect that oxides of nitrogen levels must always be restricted to well below 3 vol % if charcoal is used.

Other situations posing potential problems include the presence of combustible gases and, in the case of refrigerated beds, the relatively high concentrations of oxygen in the charcoal that might thereby be encountered.

5.0 PROCESSES AFFECTING ADSORBER PERFORMANCE

The effective surface area of charcoal that is exposed to flowing gases decreases with time, mainly as the result of poisoning. Decreases ranging up to about 50% of the initial value have been observed over a six-month period, although the conditions corresponding to the larger decreases can probably be characterized as unusually severe.[47] In any event, when designing adsorbers, some allowance should be made for the loss in adsorption capability of the charcoal (or any other sorbent) that results from extended exposure to off-gas.

The phenomenon of aggregate recoil as a consequence of α-decay and its possible involvement in the enhanced penetration of filters by α-emitting aggregate particles have been reviewed and investigated by Ryan, Skrable, and Chabot.[48] Their work suggests that multiple particulate filters, both upstream and downstream of the sorbent bed(s), may be required in a ^{220}Rn removal system. The question naturally arises as to whether or not the retention of ^{220}Rn decay products in the sorbent bed would be adversely affected to a significant extent by α-recoil. In this case, the possibility of decay product aggregation would appear to be limited, as would the possibility of reentrainment of these decay products. Such suppositions, however, remain subject to verification. For this reason and others, the use of ^{220}Rn, rather than the 3.82-day ^{222}Rn, would be preferable in experimental investigations relating to the ^{220}Rn problem.

6.0 ADSORBER DESIGN

Obviously, in designing adsorbers for ^{220}Rn holdup and decay, it would be desirable to have considerably more information than is currently available. An attempt will be made, however, to outline what might be done using existing information. In this connection, it should perhaps be reemphasized that, although the sizing of adsorbers containing charcoal is discussed, the question of their safety for this application remains unresolved.

Since the radon adsorption and mass transfer characteristics of the charcoal-air system are more firmly established than those for the other systems of interest, it will be considered first. A bed temperature of 25°C, a carrier gas (air) pressure of 1 atm, a relative humidity of less than 10%, and an inlet ^{220}Rn concentration of $<8 \times 10^{-5}$ Ci/liter ($<1 \times 10^{-14}$ atm partial pressure) are assumed. It is also assumed that a good grade of granular gas adsorbent carbon with a surface area (initial) of ~ 1200 m^2/g and a mesh size of 6 x 16 (U.S.) is to be installed. The k_a value for fresh charcoal of this type under the assumed conditions would probably be at least as high as 5000 cm^3(STP)/g atm.

The nature of the agreement (as noted earlier) between N/ft values calculated from Thomas' radon data and those for the same air velocities in Fig. 1 provides some justification for using Fig. 1 in obtaining estimates of N/ft for the radon-air-charcoal system under consideration. In any event, a superior approach to the evaluation of N for this system using existing information is not readily apparent. Whether the reduction in adsorption capability due to poisoning is accompanied by a significant (and undesirable) reduction in N is not known. Therefore, some uncertainty exists with regard to both the initial estimation of N and its possible change during exposure.

One way to make allowance for the uncertainty regarding N and, also, for the effects of poisoning is to use a reduced value of k_a for design purposes. Assuming that the exposure conditions are not too severe, reduction of the above value of 5000 [cm^3(STP)/g atm] to 2500 should constitute an adequate allowance for these factors, at least for some undeterminable period of operation.

Referring to Fig. 1, it may be seen that a change in velocity from 10 fpm to 40 fpm was accompanied by a change in N/ft from 8 to 2. This implies that the ratio of bed length to bed diameter is not crucial for this particular region. However, beds designed on the basis of the data shown in Fig. 1 should be at least 1 ft long; in general, the use of a somewhat longer bed (e.g., 3 ft) is envisaged.

Equation (6) relates the decontamination factor (DF) to k (readily calculated from k_a if the bed temperature is known), N(total for bed), λ, m (mass of sorbent), and the volumetric flow rate of the carrier gas through the adsorber. Thus, it would appear that existing information is adequate for sizing a charcoal bed for the above described situation (air, 25°C, etc.), provided of course that optimal design of the adsorber is not required. For purposes of illustration, a calculation was made using the following assumed or derived quantities: 200 cfm of air (R.H.$<$10%); 25°C; $k_a = 2500$ cm^3(STP)/g atm; bed diameter of 2.523 ft; superficial velocity of 40 fpm; bed length of 3 ft; N/ft = 2, or N = 6; charcoal bulk density of 0.45 g/cm^3; 421 lb of charcoal; and $\lambda = 0.75206$ min^{-1} (for $t_{1/2}$ of 55.3 sec). The calculated DF as obtained using Eq. (6) was 3.9×10^6.

The radon-CO_2-charcoal system will be discussed only briefly. Based on the 20°C data of Gubeli and Stori,[18] the k_a value at 25°C for the 100% CO_2-charcoal system would be only $\sim$ 20% of the value for the air-charcoal system discussed above. Thus, if the 50% allowance for poisoning, etc., is imposed, the resulting k_a value is $\sim$ 500 cm^3(STP)/g atm. However, no directly relevant data are available to provide the basis for estimating N values for this system, although application of mass transfer theory might yield useful estimates.

Comparison of the limited amount of equilibrium radon adsorption data found for molecular sieve Type 5A adsorbent with the relevant data for charcoal indicates that about ten or more times as much, by weight, of sieve Type 5A as charcoal would be required to achieve the same DF for the case where the off-gas is air at 25°C. (Comparison on a volume basis would be somewhat more favorable.) For the case of an off-gas whose composition is predominantly CO_2, the factor relative to charcoal is even less certain. Conceivably, a molecular sieve type other than 5A might be more useful for ^{220}Rn holdup. Thus, considerably more information than is now available will be required before molecular sieve beds for ^{220}Rn disposal can be designed with a reasonable degree of confidence with respect to their performance or optimization. In connection with a different application, Pence, Duce, and Maeck[49] have observed that granular sorbents have better mass transfer characteristics than sorbents in the forms of pellets and beads (the usual forms of molecular sieve adsorbents). This observation has relevance here since it implies that using the sorbent as granules rather than pellets or beads would result in a higher value for N, the number of theoretical plates. Decreasing the sorbent particle size also results in a higher value for N; however, exploitation of this effect is limited by the higher pressure drop and by the mechanical difficulties associated with retaining the sorbent.

The capability of silica gel for adsorbing radon appears to be too low to be considered for this application; nevertheless, a few of the more promising types should probably be included in screening tests of possible sorbents.

The above discussion on adsorber design indicates, in a general way, the approach that might be followed in the analysis and application of dynamic adsorption data obtained with 3.82-day ^{222}Rn. On the other hand, if such data are obtained with ^{220}Rn in terms of DF vs bed depth, the results could be applied without actually evaluating k (or k_a) and N, although some allowance should be made for the effects of poisoning.

7.0 SUMMARY AND CONCLUSIONS

Off-gas streams from ^{233}U reprocessing and refabrication operations will be contaminated with ^{220}Rn, and, as a consequence, some effective means for its removal will be required. In view of the short half-life and relatively favorable volatility of ^{220}Rn, the method based on adsorptive-holdup and decay should be feasible for coping with this decontamination problem. This literature survey represents an effort to collect and summarize what is currently known relative to the use of adsorption for ^{220}Rn removal and disposal.

A treatment of dynamic adsorption theory, extracted from the literature and based on the assumption of a linear adsorption isotherm, is presented for possible use in data analysis and adsorber design. This treatment yields an equation relating DF with a holdup coefficient, the mass of sorbent, the volumetric flow rate of the carrier gas, the number of theoretical plates, and the decay constant. The holdup coefficient is, in turn, related to the adsorption coefficient k_a and the sorbent temperature.

A fairly large quantity of equilibrium data was found for the adsorption of ^{222}Rn on charcoal in the presence of air and other gases, including CO_2. Also, various dynamic adsorption data for ^{222}Rn on charcoal with air as the carrier gas have been presented in a recent report.[24] Based on the available data for the radon-charcoal-air (1-atm) system, the corresponding radon adsorption coefficient at 25°C would probably be at least 5000 cm^3(STP)/g atm (initially) if certain criteria regarding the radon concentration, the quality and humidity of the air, and the nature of the charcoal are met. If CO_2 rather than air is specified for the system, a reduction in the analogous coefficient to a value of about 1000 is indicated.

The small amount of equilibrium data found for molecular sieve Type 5A adsorbent indicates that its radon adsorption coefficient at ambient temperature in the presence of air (the humidity was unspecified) is about 600 cm^3(STP)/g atm.

Equilibrium data for silica gel indicate that its capability for adsorbing radon is relatively low. Radon adsorption coefficient values derived from one group of measurements on silica gel at 25°C are about 25 and about 21 cm^3(STP)/g atm, respectively, for air and for CO_2 present at 1 atm.

Of the potential hazards associated with the use of charcoal for this application, the hazard involving ozone perhaps represents the greatest concern and probably is most in need of evaluation.

The sorbent suffers a loss in adsorption capability during extended exposure to off-gas, and allowance should be made for this loss when performing adsorber design calculations.

The use of multiple particulate filters may be required in a ^{220}Rn removal system as a consequence of the α-recoil phenomenon. On the other hand, it does not appear that α-recoil would significantly affect the retention (in the sorbent) of decay products from adsorbed ^{220}Rn, although this supposition remains subject to experimental examination. This, together with other considerations, suggests the use of ^{220}Rn rather than ^{222}Rn in experimentation related to the ^{220}Rn problem.

With regard to adsorber design, existing information is perhaps adequate for sizing, albeit crudely, the sorbent bed for a ^{220}Rn-charcoal-air (1-atm, < 10% R.H.) system operating at ambient temperature, and a suggested approach for doing this has been outlined. For other ^{220}Rn-charcoal systems in which the carrier gas differs from nearly dry air, the situation is more uncertain; however, existing information, together with mass transfer theory, might provide a reasonable basis for sizing the adsorber bed. The available data for other sorbents (e.g., molecular sieves) are too limited to provide the basis for designing ^{220}Rn removal systems.

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9.0 APPENDIX: DEVELOPMENT OF DECONTAMINATION FACTOR EQUATION

As already noted, the following analysis is based on that originally presented by Underhill.[3] First,

$$C^*_{N,t} = \frac{AN^N F^{N-1}}{(km)^N} e^{-\lambda t} G(t),$$

where

$C^*_{N,t}$ = as for $C_{N,t}$ in Eq. (2) but with effect of decay imposed,

$$G(t) = \frac{t^{N-1} e^{-NFt/km}}{(N-1)!},$$

and the other terms are as already defined. In time dt, the amount of radioactive noble gas exiting is:

$$C^*_{N,t} F \, dt = \frac{AN^N F^N}{(km)^N} e^{-\lambda t} G(t) \, dt.$$

Next, integrating over infinite time and dividing by A,

$$\frac{1}{DF} = \frac{N^N F^N}{(km)^N} \int_0^\infty e^{-\lambda t} G(t) \, dt.$$

This integral is readily evaluated by using the Laplace transformation since a function having the form $t^{n-1} e^{at}/(n-1)!$ is listed in tables of Laplace transforms. The result is:

$$\frac{1}{DF} = \frac{N^N F^N}{(km)^N} \; \frac{1}{(\lambda + \frac{NF}{km})^N} = \left(\frac{NF/km\lambda}{1 + NF/km\lambda}\right)^N.$$