

Determination of the Radon Emanation from Carbonate Rocks and Its Potential Hazard in Building Materials

By A. F. GABRYSH, N. D. McKEE, and H. EYRING

IT HAS BEEN found (1)¹ that increasing the temperature of concrete containing low-grade radium-bearing rock releases a large amount of radon gas from the expanded microfissures in the aggregate. A study of radon leakage from rock specimens having an average uranium concentration of about 0.008 per cent showed that in a room of a radiantly heated dwelling a concentration of about 4×10^{-9} curies of radon per cu ft of air could result. This is above the allowable value of 2.8×10^{-9} curies per cu ft adopted by the 1954 Hariman Tri-partite Conference on Radiation Protection. Thus, structures made of aggregate containing radioactive minerals are an increasing concern to the geneticist (2,3), and a laboratory analysis of the emanating power (4,5) of rocks used for aggregate seems essential to safeguard persons from unnecessary radiation hazards.

To determine the emanating power of a rock specimen one must eliminate those variables that are due to the solid structure of the specimen. Undesirable variations in radon-release characteristics are produced by such variables as difference in grain size, distribution of constituents within and between grains, porosity, specimen and microscopic fissure size, surface area, and other effects introduced during specimen preparation. The emanating power is calculated by dividing the emanation spontaneously escaping from a solid specimen by the total amount of emanation formed with the specimen in solution, where all the above variables are erased.

By any method, the complete dissolution of large rock specimens is cumbersome, slow, and costly, even for a practical-size (~ 2 g) specimen. The several dolomite rock specimens studied here

This paper presents an efficient technique to dissolve large rock specimens to (10 to 80 g) bearing small amounts of radium in order to determine their emanating power. A procedure is given for determining the small quantities of radon where alpha particles from the radon, radium A, and radium C are counted. The significance of radon leakage from microfissures in rock used as building material for homes or public buildings is described. The advisability of inquiring into the probable relation between air natural radioactivity and its biological importance is discussed briefly.

were selected from material readily available for building purposes. The specimens ranged from 12 to 78 g, and totaled about 726 g. It was soon established that several standard decomposing procedures were unsatisfactory. Some methods required 4 full days to gain complete decomposition of a 10-g specimen. From the various tests conducted to determine a method for efficiently decomposing such large specimens, the following method effected

complete decomposition in the shortest time.

Recommended Procedure for Dissolution

Grind the specimen to pass a 300-mesh sieve. Place into 1- or 2-liter beakers, depending on specimen weight. Add 1:1 HCl (sp gr 1.19) in the ratio of 60 ml of acid to 10 g of specimen. Digest until activity ceases and dilute with water while heating until soluble salts are in solution, then set aside to cool. After the

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¹The boldface numbers in parentheses refer to the list of references appended to this paper.

insoluble material has settled and the solution has become clear, pour off the clear liquid into another beaker.

The remaining solids of the larger specimens (greater than 30 g) should be treated again, using the above procedure, because saturation may have prevented² solubles from going into solution.

Transfer the remaining insoluble silicate residues to a 700-ml platinum dish and heat to dryness. Dampen with water and add 40 ml of HF (18 per cent) and 40 ml of HNO₃ (sp gr 1.42) for each 10 g of residue. Evaporate to dryness, then bake on a hot plate for about 15 min. Add 40 ml of HF and wash the sides of the dish with a little water. Heat to dryness and bake as before. Cool again, then add 40 ml of HF and 20 ml of HClO₄ for each 10 g of residue. Heat and fume until all the HClO₄ is evolved. Cool, then add 40 ml of 1:1 HCl (sp gr 1.19); digest and dilute with water as before. Heat until salts are in solution. Cool and pour off the clear solution after the remaining undissolved portion of the specimen has settled to the bottom. Heat residue to dryness.³

Use the sodium carbonate fusion method (6) to decompose the remaining material. Cool the mixture, then add 30 ml of 1:1 HCl (sp gr 1.19) to the fused material. Heat until the fusion mixture is decomposed. Cool and add water until all salts are in solution.

Complete decomposition of 1 to 3 g by sodium carbonate fusion ordinarily requires about 30 min at 1200 C, using a 10:1 ratio of Na₂CO₃ to residue.

Radon Determination and Results

Growth and Decay Law

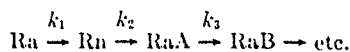
The buildup and decay of radon is essentially a problem in consecutive first-order reactions. The radon is formed from radium and decays into radium A, which transforms to radium B, hence is an intermediate. The instantaneous concentrations of such intermediates are given by equations of the form

$$C = a \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t})$$

where a , in this case, is a constant representing the radium concentration, k_1 is the rate constant for the formation of radon from radium, and k_2 is the rate constant for its subsequent decomposition into radium A, that is

² The proper amount of acid needed to hold the solubles in solution can be determined by heating the clear solution at moderate heat (70 to 85 C) until salts begin to crystallize out. Cool solution to room temperature, add water, and, if necessary, HCl until all salts are dissolved.

³ A semiquantitative spectrographic analysis of this remainder in one specimen revealed the following per cent amounts of the undissolvable constituents: Ag <0.0012; Ba = 0.5; Co <0.01; Li <0.02; Ni <0.01; Si = 0.16; U <0.3; Al = 0.07; Be <0.0024; Cr = 0.012; Mg = 0.01; P <0.156; Sn <0.0024; V <0.005; As <0.02; Bi <0.005; Cb <0.04; Mn <0.0024; Pb <0.0006; Sr = 20.0; Zn <0.01; Au <0.01; Ca = 0.06; Cu = 0.008; Mo <0.005; Ti <0.0012; Zr <0.16; B <0.0012; Cd <0.005; Fe = 0.02; K <0.015; Na <0.04; Sb <0.01.



Owing to the great difference in rate constants, the above equation can be simplified. The half-life of radium is 1590 years, while that of radon is 3.83 days. Under such circumstances, the equation becomes

$$C = a \left(\frac{k_1}{k_2} \right) (1 - e^{-k_2 t})$$

which indicates that the radon buildup is the complement curve for the decay curve. Figure 1 gives the curves and figures for these. The half-life equations give a daily decrease of activity of 16.5 per cent for radon. They also in-

dicate that the radon will build up again to over 99 per cent in about 30 days.

The significance of these figures is evident in the following example. Suppose a dwelling or school with heating coils imbedded in a concrete floor, made of aggregate bearing radioactive mineral, is not heated for a period of 30 or more days. The buildup of radon into the "closed" microfissures is then near maximum and is released into the room when the coils are heated, thus expanding the concrete and "opening" the microfissures. One should note that the greatest buildup of radon occurs during the first few days and that even a few days of no heat in the coils would result

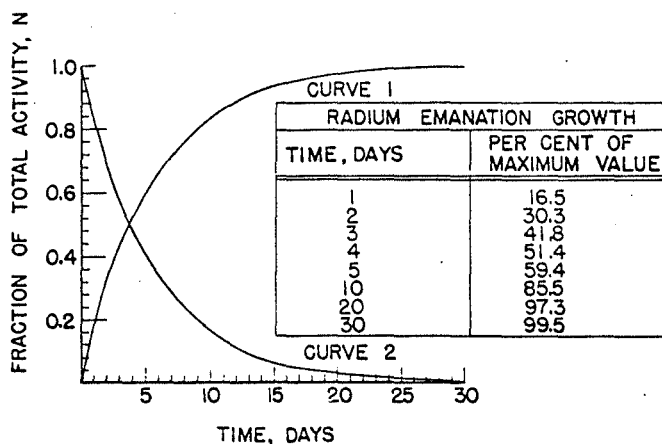


Fig. 1.—Curve 1 shows growth of radium emanation. Curve 2 shows its decay.

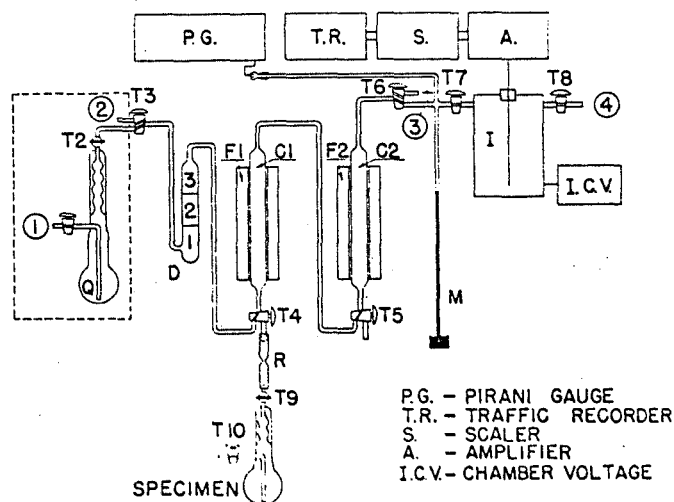


Fig. 2.—Diagrammatic sketch of apparatus: Q, standard; D, drying column; C₁ and C₂, reduced-copper columns; F₁ and F₂, electric furnaces; M, manometer; I, ionization chamber.

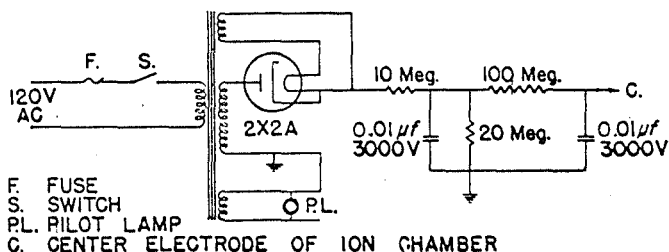


Fig. 3.—Schematic of high-voltage supply for central electrode of ionization chamber.

in a high content of radon stored in the microfissures.

Measurements

The quantity of radon given off by a specimen is measured by counting alpha particles emitted by the radon. Various methods for determining radioactive minerals have been used (7-10). A complete and detailed discussion of theory regarding ion-chamber calibration and counting statistics is given by Curtis (7).

A diagrammatic sketch of the system used here to count the alpha particles is shown in Fig. 2. A standard radium solution, used for calibrating the ion chambers, is stored in bulb *Q*. It is connected to a drying bulb *D* containing calcium chloride (1), ascarite (2), and magnesium perchlorate (3). The drying bulb is connected to two combustion tubes *C*₁ and *C*₂, which are filled with reduced copper and surrounded by furnaces *F*₁ and *F*₂. These in turn are connected to the ion chamber *I*, which is provided with a connection to a vacuum pump 4. The first step is to evacuate the chamber and system as far as stopcock *T*₃. With reduced copper in tubes *C*₁ and *C*₂, heated by variac-controlled electric furnaces (at about 500 C), *T*₃ is closed and *T*₃ is opened to admit a stream of dry nitrogen from a cylinder at 2. The rate of flow is controlled by a constriction in the glass tube (similar to *R*, which has about a 15-min period for filling, to atmospheric pressure, a 2-liter volume) so that the flow of nitrogen over the reduced copper, heated to a dull red, is slow, and all oxygen flowing with the incoming gas is completely removed by the copper. When the manometer *M* shows that the system is at atmospheric pressure, *T*₇ is closed. A high voltage (about 900 v) is supplied by a simple but very efficient source, schematically shown in Fig. 3, to the central electrode of the ion chamber and a background count is taken.

When a determination of the chamber background has been made, the chamber is calibrated by admitting a known quantity of radon from the standard radium solution *Q*. This is done by evacuating the system again up to stopcock *T*₂. Stopcock *T*₃ is then closed and nitrogen is admitted through a constriction tube at 1 through *T*₁ into bulb *Q* with *T*₂ and *T*₃ open to the chamber. At the same time heat is applied to the bulb, causing the radium solution to boil. With the nitrogen there is transferred to the ion chamber the quantity of radon that has accumulated in the standard solution since the radon was last removed. Atmospheric pressure in the chamber is regained by letting a sufficient amount of nitrogen pass through *T*₁, which is then closed and calibration data are taken. The chamber is then

emptied and allowed to return to background count before samples are introduced.

After the necessary background and calibration measurements have been obtained, the count for the unheated specimen is made by evacuating the system attaching the specimen. The restriction *R* connects *T*₃ to *T*₄. A flushing tube from the nitrogen tank is connected to *T*₁₀. With *T*₃ closed but *T*₁₀, *T*₉, and *T*₄ open the ion chamber is filled to atmospheric pressure with oxygen-free nitrogen-radon gas from the sample. *T*₇ is then closed and alpha particles from the sample are counted.

Computations

The average amount of radon, in curies, given up by a specimen is easily found. Disregarding the first few hours of the run it is then only necessary to calculate the average count per hour, subtract the background count, and divide by the chamber calibration which is obtained by counting the disintegrations of radon from a calibrated standard source. This gives the average amount of radon during a run. The initial amount of radon can be determined from

$$A_t = 1/t \int_0^t e^{-\lambda t} dt = \frac{1 - e^{-\lambda t}}{\lambda t}$$

where *A*, is the average of an exponential decay function, $e^{-\lambda t}$, for time *t*. The term λ is the decay constant (11). To correct for decaying of radon during the run (usually 10 to 12 hr), divide the

average radon by *A*, for the initial amount at the time of the first reading. A sample calculation follows:

The chamber used for these data was calibrated as having 209 counts per hr for radon from a solution containing 10^{-12} curies of radium. The record shown in Table II is for specimen No. 1, Table I, in acid solution. The solution was sealed for a total time of 434.5 hr. The subsequent average count rate per hour for a 10-hr period is shown as 11,035. The background for the chamber was 147 counts per hr, giving a net count of 10,888 per hr. Average correction due to decay of radon, during the period which begins when the chamber is filled and ends when the counting of disintegration is stopped, is 0.9730. The initial amount of radon is then readily calculated and is given as curies of radium per gram of specimen in solution (Table I).

Summary and Discussion

Details of an arrangement for determining the amount of radon emanating from a carbonate rock specimen are discussed and given schematically in Figs. 2 and 3. Analysis was first made with rock in solid form. An assay was then made with the material containing radium in a clear acid solution. The method described for decomposing rocks was found to be superior to several other methods since it enables efficient decomposition and dissolution of large dolomite rock specimens. The variables associated with a solid specimen are elimin-

TABLE I.—THE EMANATING POWER FOR SEVERAL SPECIMENS TAKEN FROM THE SAME VICINITY.

Specimen	Solid		Liquid		Emanating Power, per cent ^a
	Weight of Solid, g	Curies of Radon per Gram of Specimen	Weight in Solution, g	Curies of Radon per Gram of Specimen	
No. 1.....	50.74	0.18×10^{-12}	18.72	2.96×10^{-12}	6.1
No. 2.....	84.53	0.10	19.07	1.86	5.4
No. 3.....	73.59	0.20	18.72	1.58	12.7
No. 4.....	32.51	0.04	13.22	0.92	4.4
No. 5.....	56.72	0.06	24.85	1.36	4.4
No. 6.....	65.07	0.05	32.50	1.11	4.5
No. 7.....	67.50	0.03	32.05	0.23	13.0
No. 8.....	81.32	0.01	40.79	0.14	7.1
No. 9.....	83.95	0.02	40.95	0.17	11.8
No. 10.....	160.02	0.03	78.15	0.20	15.0

^a $\frac{\text{curies per gram (solid)}}{\text{curies per gram (liquid)}} \times 100.$

TABLE II.—RECORD FOR SPECIMEN NO. 1, TABLE I.

Date.....	12/17/1960	Calibration.....	209 counts per hr for 10^{-12} curies, radon
Specimen.....	No. 1		
Weight.....	18.72 g	Collection start, time and date.....	1200 (11/29/1960)
End count.....	56 799	Collection end, time and date.....	1500 (12/17/1960)
Start count.....	54 730	Collection time.....	434.5 hr
Sealer count.....	2 069	$1 - e^{-\lambda t}$	0.9625
Scale.....	64	Chamber filling start time.....	1430
Gross count.....	132 416	Chamber filling end time.....	1500
Hours.....	12	Decay time.....	10 hr
Count per hour.....	11 035	$e^{-\lambda t}$	0.9730
Background.....	147		
Net count per hour.....	10 888		
Initial amount of radon = $\frac{10.888 \times 10^{-12}}{209 \times 0.9652 \times 0.9730 \times 13.72} = 2.96 \times 10^{-12}$ curies per g			
Weight of solid			

ated, and the total amount of emanation formed in the rock can then readily be calculated. Complete results for several specimens are given in Table I. The large variations (for example, compare specimens 1, 3, and 10) in emanating power per gram for specimens taken from within a 200-yd radius of each other point up the need for controlled monitoring of building materials.

The results of an earlier study (1) showed the need of more extensive investigations concerning the analysis and the use of building material causing any type of abnormally high background radiation. The genetic significance of the dose received by the increasing number of persons engaged in radiological work is of more than academic interest. The added exposure of these and other individuals (such as young people attending the same school for many years) to building materials causing abnormally high background makes such hazards a serious and urgent problem. Investigators (12,13) recently reported that in those sections of Catania, Sicily, where building materials are naturally radioactive, the air radioactivity is greater than the allowable maximum dose; a probable relation between this air radioactivity and the frequency of cases of leukemia and bone cancer is suggested. The works of Sievert (2) and Hultqvist (14), in Sweden present observations of equal concern.

The transformation from radium (solid, in the rock) to radon (gas, escaping to the air) to radium A (solid, de-

posited in lungs) is a series of disintegrations which continue, possibly in the tissue of the respiratory system, with the atom of radium A emitting an alpha particle going to radium B (solid) which changes to radium C (solid) by the emission of beta and gamma rays. The results in Table I suggest that, if used as building materials in schools, homes, etc., such rocks could increase the long-range radiation doses received by the inhabitants and result in an unfavorable influence on genetic and health conditions.

Acknowledgment:

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Technical Note

Fatigue Gages of Aluminum Foil

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SMALL PIECES of aluminum foil show promise for anticipating fatigue failures in structural parts. They may prove useful in many applications where one wishes to know the susceptibility of critical areas to fatigue.

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² The boldface numbers in parentheses refer to the list of references appended to this paper.

The fatigue literature amply illustrates that all materials undergo microscopic plastic deformation under cyclic loading (1).² While these deformations are readily visible under the microscope when soft materials are being tested, they become increasingly difficult to observe as the material tested becomes stronger (2). In most structural materials, the deformations are so small that they cannot be readily observed in the light microscope. Although, in principle, the observation of fatigue-induced deformation of a part would enable one to evaluate its fatigue susceptibility in

service, the method cannot be used with most structural alloys.

It appears possible to circumvent this difficulty by bonding a soft material onto the area of interest. The soft material will undergo the same strains as the structural part, and, since fatigue-induced deformation is visible in the soft alloy, one can surmise what is happening in the structure. Just as the cladding of an clad aluminum-alloy product reveals incipient fatigue failures in the core material (3), the soft layer bonded to the structure acts as a gage in evaluating fatigue effects.