In: Building Materials
Editor: Donald N. Cornejo and Jason L. Haro, pp.

ISBN 978-1-60741-082-9

Chapter 7

RADON EXHALATION RATES OF BUILDING MATERIALS: EXPERIMENTAL, ANALYTICAL PROTOCOL AND CLASSIFICATION CRITERIA

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ABSTRACT

The strict correlation between indoor radon exposure and potential health hazard to occupants is well known. The indoor radon concentrations mainly depend on radon exhalation from surrounding soil, but also on exhalation from building materials and radon in domestic water supply. The radon emanating from building materials achieves a larger relevance in some areas of the world, where rocks enriched in radon precursors, are used in construction industry, either as cut-stone or in a granular form to prepare cements. The parameter that better expresses the indoor accumulation of radon released by geological materials is the radon exhalation rate. With a view to this, it is very important to study factors that influence the phenomenon and to standardise the experimental procedure to measure radon exhalation rates. An experimental set-up to measure simultaneously ^{222}Rn and ^{220}Rn release from building material is presented. The method makes use of a continuous monitor equipped with a solid-state alpha detector, in-line connected to a small accumulation chamber. Parameters controlling exhalation rates are discussed: temperature, air mixing, humidity and particle size. Guidelines for a standard experimental protocol are advanced and a tentative classification of building materials is proposed on the basis of radon exhalation rates required to reach legal indoor radon action levels.

INTRODUCTION

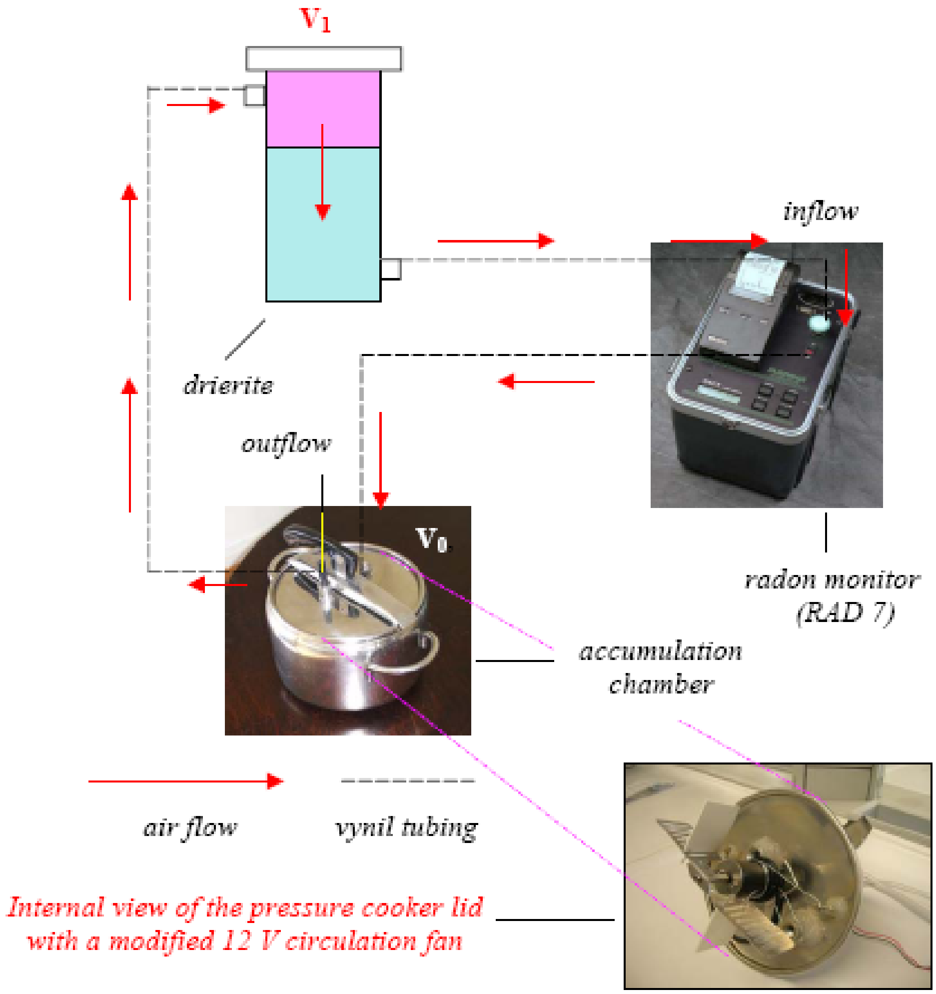
European Commission has examined the issue of regulatory control of building materials with regard to their content of naturally occurring radionuclides (EC-Radiation Protection, 1999). The purpose of setting regulatory controls on the radioactivity of building materials is to limit the radiation exposure due to materials with enhanced or elevated levels of natural radionuclides. Nonetheless, human exposure to radioactivity is at a large extent (55 %) due to radon (UNSCEAR, 2000) and the activity of naturally occurring radionuclides, expressed as activity concentration index (I) or radium equivalent activity (Ra-eq, Kovler et al., 2005), is not able to predict satisfactorily radon indoor concentrations due to the exhalation of radon from surrounding soil or from building materials. A parameter that better expresses the indoor accumulation of radon released by geological materials is the radon exhalation rate (Carrera et al., 1997). With a view to this, it is very important to study the parameters that influence the phenomenon and to standardise the experimental procedure to measure radon exhalation rates (Quindos et al., 1994; Chao et al., 1997; De Martino et al., 1998; Keller et al., 2001; Petropolous et al., 2001; Ferry et al., 2002; Gutiérrez et al., 2004; Kovler et al., 2005; Tuccimei et al., 2006).

This chapter reports on the simultaneous measurements of ^{222}Rn and ^{220}Rn (also known as thoron) exhalation rates from building materials using a small stainless steel accumulation chamber, in line connected to a radon monitor. Validation tests of the experimental set-up are presented in order to support the method; mixing and temperature-control facilities are also illustrated. The influence of temperature, particle size and humidity on radon exhalation rates is discussed. On this basis, a standard analytical protocol is proposed and data of radon exhalation rates of volcanic cut-stone and cements commercialised in central Italy are listed. Finally the basic of classification criteria to apply to building materials is advanced.

EXPERIMENTAL SET-UP

The experimental set-up reported in this section is the development of a previous apparatus described in Tuccimei et al. (2006). The old system, consisting of a small PVC accumulation chamber, sealed with silicon, was affected by gas leakage out of the container and radon back-diffusion to the material due to radon building up in the chamber. These phenomena produced a reduction of the accumulated radon and lead to the determination of exhalation rates about 30 % lower than true values. Proper corrections to evaluate free exhalation rates were however proposed. On the basis of the gained experience, the previous experimental set-up was modified and the PVC accumulation chamber was replaced with a modified pressure cooker to remove leakage and back-diffusion.

The new method makes use of a continuous monitor equipped with a solid state alpha detector, in line connected to an accumulation chamber, consisting of a 5.1 L modified stainless steel pressure cooker with a mechanical tightness system, supplied with a 12 V circulation fan (17-cm diameter) for mixing purposes (Figure 1). The chamber is connected via vinyl tubing to a gas-drying unit filled with a desiccant ($CaSO_4$, 3% $CoCl_2$, as indicator) and to the RAD7 radon monitor (Durridge Company Inc). The instrument draws air from the chamber, through the desiccant and an inlet filter, into the monitor.



V_0 = free volume of accumulation chamber
V_1 = volume between outflow of accumulation chamber and inflow of the radon monitor
V = total volume of the analytical system

Figure 1. Experimental set-up to measure ^{222}Rn and ^{220}Rn exhalation rates.

The air is then returned to the enclosure from the RAD7 outlet. The filtered air decays inside the monitor chamber, producing detectable alpha emitting progeny, particularly the polonium isotopes. A high voltage of 2500 V is applied to the chamber walls. The solid state silicon detector converts alpha radiation directly to an electrical signal discriminating the electrical pulses generated by α-particles from the polonium isotopes (^{218}Po, ^{216}Po, ^{214}Po, ^{212}Po) with energies of 6.0, 6.7, 7.7 and 8.8 MeV, respectively. Using this approach, it is possible to use only the ^{218}Po peak for ^{222}Rn and ^{216}Po for ^{220}Rn, obtaining a rapid equilibrium between polonium and radon nuclides, because the equilibrium between ^{218}Po and ^{222}Rn is achieved in about 15 min (about five times the half-life of ^{218}Po), and between ^{216}Po and ^{220}Rn in a few seconds. The ^{222}Rn growth curve is monitored with cycle times from 15 minutes up to 2 hours for a day in order to calculate the exhalation rate that is proportional to the slope of the growth curve. The measurement allows the simultaneous determination of

^{222}Rn and ^{220}Rn exhalation rates that can be referred to the mass or the surface of the material. The detection limit of the experimental apparatus is equal to 0.01 Bq h^{-1} for ^{222}Rn and to 6 Bq h^{-1} for ^{220}Rn.

VALIDATION TEST

In order to test the experimental set-up and samples preparation procedures, validation tests have been carried out using “Tufo Rosso a Scorie Nere” (TRSN) pyroclastic flow as standard material. This tuff, emitted from Vico volcanic apparatus (50 km north-east of Roma, Italy), is commonly used in cut-stone and concrete masonry because of its lightness, tenacity and machinability. TRSN standard, crushed and sieved between 2 and 1 mm, has been always dried at 110°C for 24 hours and weighed (800 g), before the beginning of experiments. Validation tests have been performed with air mixing and temperature has been kept constant at 20 °C, unless indicated otherwise.

The first test was aimed at demonstrating that the new apparatus was not affected by leakage and back diffusion phenomena so that ^{222}Rn concentration increase in the closed loop configuration is effectively described by ^{222}Rn decay constant. A 24-hour experiment was performed and ^{222}Rn activity concentration was measured with cycles of 15 minutes in order to have enough data to process and fit according to the following conventional equation (Petropoulos et al., 2001):

$$C = C_0 \cdot e^{(-\lambda \cdot t)} + \frac{E \cdot \left(1 - e^{-\lambda \cdot t}\right)}{\lambda \cdot V} \qquad (1)$$

where C is ^{222}Rn activity concentration [Bq m^{-3}], C_0 is the initial concentration [Bq m^{-3}], λ is the decay constant [h^{-1}], t is time [h], E is ^{222}Rn exhalation rate [Bq h^{-1}] and V is the free total volume of the analytical system [m^3]. The first term of the equation takes into account the decrease of radon initially present in the measuring apparatus, whereas the second represents radon exponential increase in the closed circuit up to equilibrium conditions. The purpose of this procedure is to estimate the values of C_0, λ and E that better describe the data, choosing the parameters that would minimise the deviations of the theoretical curve from the experimental points.

This experiment (test 1-1) was compared with a second test (test 1-2) performed under the same conditions, but using the PVC accumulation chamber (Figure 2) in order to prove that present set-up is better in terms of radon loss. Best-fitting parameters of experimental data are: $C_0 = 20$ Bq m^{-3} in both cases; $\lambda = 0.0076$ and 0.018 h^{-1} for stainless steel and PVC test, respectively and E = 0.07 and 0.04 Bq h^{-1}, correspondingly for test 1-1 and 1-2. Curve fitting provided a value of $C_{0,}$ which is actually the average indoor radon value in the laboratory and an estimation of λ in test 1-1 which is equal to ^{222}Rn decay constant, significantly lower than that from test 1-2.. The goodness of the fit (R^2) is about 0.98. Test 1-1 was repeated several times in order to verify the outcomes, demonstrating the repeatability of the measurements with the new experimental design.

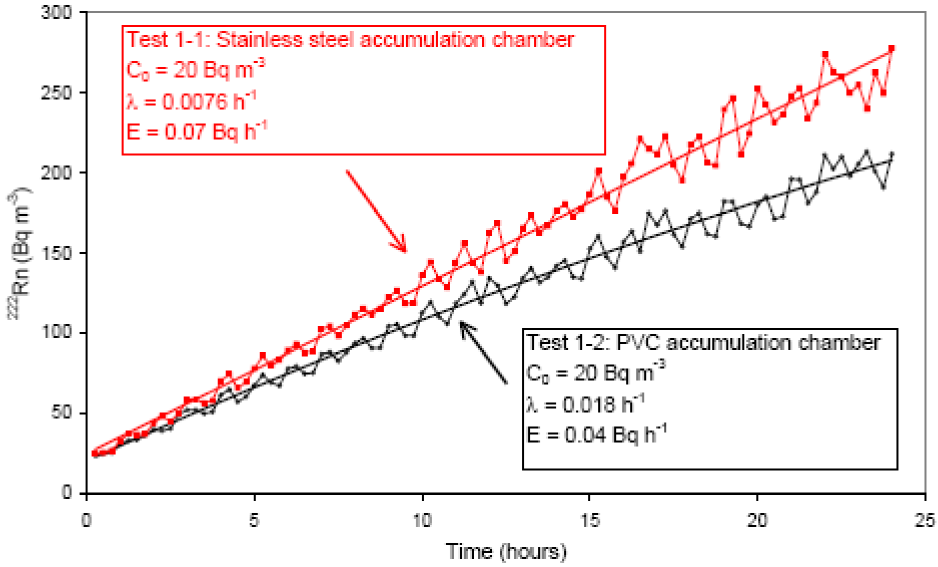


Figure 2. Experimental ^{222}Rn concentration growth of TRSN standard over a 24-hour experiment using the stainless steel (test 1-1, red squares) and the PVC (test 1-2, black circles) accumulation chambers. Least-squares fitting curves described by equation 1 provided values of C_0, λ and E for both experiments. Errors are around 5 %.

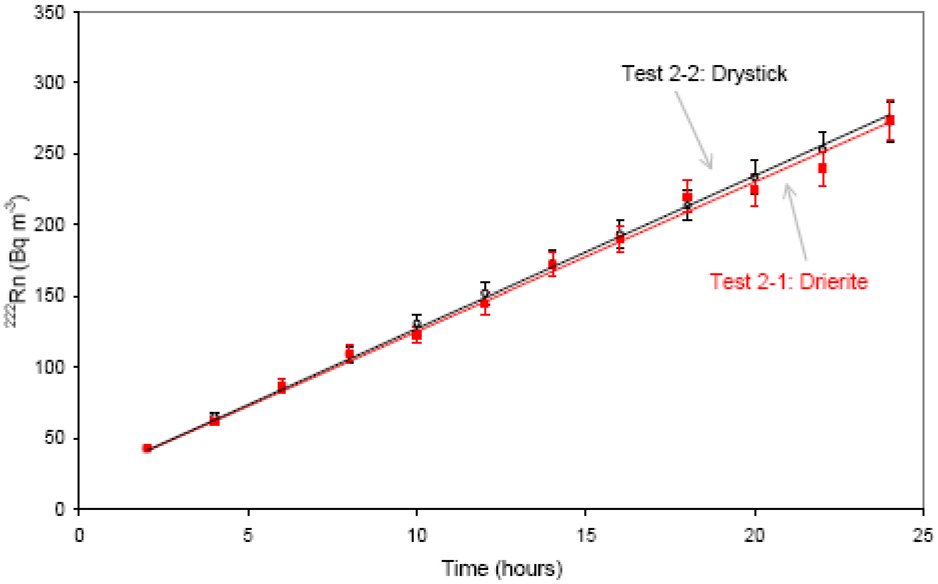


Figure 3. Experimental ^{222}Rn growth curves of TRSN standard over a 24-hour experiment using the stainless steel accumulation chamber equipped with the drierite (test 2-1, red squares) or the drystick (test 2-2, black circles) device.

A second set of experiments was performed to demonstrate that $CaSO_4$ grains, used as desiccant, did not absorb radon, reducing exhalation rate. In order to prove that, two tests were conducted using TRSN standard under the same experimental conditions described for previous experiments, with the exception of the device used to capture moisture: $CaSO_4$ (drierite, test 2-1) and a large drystick (test 2-2). Drystick is commercialised by Durridge Company Inc. (www.durridge.com) and consists of a set of tubes made of NAFION, a Teflon based material that allows removing water molecule, without absorbing radon. Before starting test 2-2, the system was run using the drierite to reduce humidity down to 1-2 %. Drierite was then removed and replaced with a large drystick, capable to maintain constant the moisture content during the 24-hour test and dried TRSN standard was put in the chamber. Results of tests 2-1 and 2-2 are reported in Figure 3 and show that data overlap within the error range, showing a negligible effect of gas sorption by $CaSO_4$ grains.

EXHALATION RATES CALCULATION

Radon Exhalation Calculation

Conventionally, ^{222}Rn exhalation rate, E_{222}, [Bq h^{-1}] is calculated according to the following equation, which is equation 1 solved with respect to E:

$$E_{222} = \frac{\left(C - C_0 e^{-\lambda_{222} \cdot t} \right)}{1 - e^{-\lambda_{222} \cdot t}} \cdot \lambda_{222} \cdot V \qquad (2)$$

where C is the equilibrium concentration [Bq m^{-3}], C_0 is the initial radon concentration [Bq m^{-3}], λ_{222} is ^{222}Rn decay constant [h^{-1}], V is the free total volume of the analytical system [m^3] and t is time [h].

However, a simplified formula is routinely used and provides comparable results when applied to 24-hour experiments:

$$E_{222} = \left(m + \lambda_{222.} \cdot C_0 \right) \cdot V \qquad (3)$$

where m [Bq m^{-3} h^{-1}], is the initial slope of the radon growth curve. The equivalence of equation 2 and 3 is here demonstrated (Table 1) by comparing ^{222}Rn exhalation rate of TRSN standard obtained from a 19-day experiment (test 3) according to equation 2 with that determined from data collected during the first 24 hours of the test and calculated using equation 3. Duration of 19 days was chosen because ^{222}Rn reaches equilibrium conditions between exhaled and decayed radon just after that time (Figure 4). In conclusion, it is worth noting that exhalation rates can be refereed to the unity of surface [Bq m^{-2} h^{-1}] or that of mass [Bq kg^{-1} h^{-1}].

The latter is probably more suitable for granular materials where a precise calculation of the exhaling surface is difficult and strongly depends on grain size. Surface or mass exhalation rates are simply obtained by equation 3 (or 2) dividing the value of E_{222} [Bq h^{-1}] by the surface [m^2] or the mass [kg] of the sample.

Table 1. ^{222}Rn and ^{220}Rn exhalation rates of a TRSN standard (2-1 mm) and a selection of volcanic rocks and cements used in cut-stone and concrete masonry in Italy

Material	Description	E_{222} (a) Bq m^{-2} h^{-1}	E_{222} (b) Bq m^{-2} h^{-1}	E_{222} (c) Bq kg^{-1} h^{-1}	E_{220} (d) Bq m^{-2} h^{-1}	E_{220} (e) Bq kg^{-1} h^{-1}	Classification on the basis of E
TRSN standard	Pyroclastic flow - granular	1.58 ± 0.06	1.57 ± 0.07	0.047 ± 0.002	5282 ± 264	158 ± 8	C2
TRSN standard	Pyroclastic flow - granular	-	2.68 ± 0.13 (f)	0.080 ± 0.004 (f)	8979 ± 449 (f)	269 ± 13 (f)	D3 (f)
Tufo Lionato	Pyroclastic flow - slab	-	0.86 ± 0.04	0.026 ± 0.001	972 ± 49	29 ± 1	B1
Peperino from Marino	Pyroclastic flow - slab	-	1.33 ± 0.06	0.040 ± 0.002	896 ± 49	27 ± 1	C1
Peperino from Albano	Pyroclastic flow -slab	-	1.55 ± 0.07	0.046 ± 0.002	389 ± 19	12 ± 1	C1
Peperino from Via Flaminia	Pyroclastic flow - slab	-	0.83 ± 0.04	0.026 ± 0.001	1537 ± 77	46 ± 2	B1
Tufo Giallo Napoletano	Pyroclastic flow - slab	-	2.66 ± 0.13	0.080 ± 0.004	583 ± 29	17 ± 1	D1
Lava from Nemi	Pyroclastic flow - slab	-	2.23 ± 0.11	0.067 ± 0.003	292 ± 15	9 ± 1	D1
Black Pozzolan	Siliceoeus volcanic ash - granular	-	37.08 ± 1.32	1.112 ± 0.056	22644 ± 1132	670 ± 34	D4
Lapilli	Fragments of Pyroclastic flow - granular	-	2.41 ± 0.12	0.072 ± 0.004	3150 ± 157	94 ± 5	D2
Cement (Cementerie A. Barbetti)	I 52,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Cementerie A. Barbetti)	II/A-LL 42,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Buzzi Unicem)	II/B-LL 32,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Micron Mineral)	III/A 32,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Cementerie A. Barbetti)	IV/B (P) 32,5 R	-	0.49 ± 0.12	0.015 ± 0.001	1175 ± 22	35 ± 2	B1
Cement (Colacem)	IV/B (P) 32,5 R	-	0.72 ± 0.12	0.022 ± 0.001	2190 ± 17	66 ± 3	B1
Cement (Italcementi)	IV/B (P) 32,5 R	-	0.75 ± 0.13	0.022 ± 0.001	2014 ± 20	60 ± 3	B1
Cement (Italcementi)	V/A (S-P) 32,5 R	-	bdl	bdl	bdl	bdl	A1

(a) calculated according to equation 2 (19-day long experiment) and divided by sample surface.

(b) calculated according to equation 3 (24-hour long experiment) and divided by sample exhaling surface.

(c) calculated according to equation 3 (24-hour long experiment) and divided by sample mass.

(d) calculated according to equation 5 (24-hour long experiment) and divided by sample exhaling surface.

(e) calculated according to equation 5 (24-hour long experiment), divided by sample mass.

(f) experiment at 30°C.

bdl stands for below detection limit.

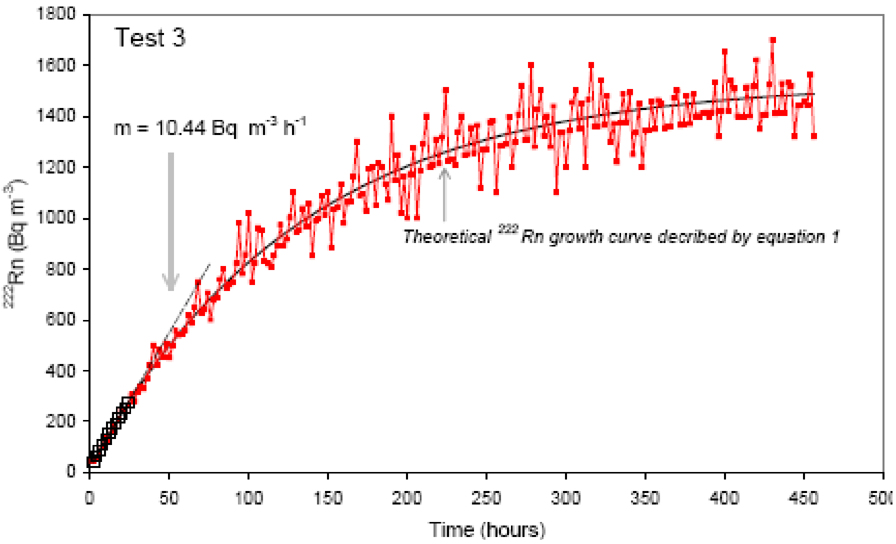


Figure 4. Experimental ^{222}Rn growth curve of TRSN standard (red squares) over a 19-day experiment (test 3) compared with a theoretical curve described by equation 1. The angular coefficient (m) of linear fitting performed on data from first 24 hours is reported. Errors are around 5 %.

Thoron Exhalation Calculations

As demonstrated by validation tests based on non-linear fitting of experimental data, ^{222}Rn growth curve in the closed loop set-up is actually described by ^{222}Rn decay constant and is not affected by leakage, back-diffusion and absorption at the desiccant. The same approach is not applicable to ^{220}Rn because of its short half-life and consequently it is necessary to hypothesise that no thoron loss other than decay occurs within the measuring apparatus, by analogy with ^{222}Rn.

The ^{220}Rn exhalation rate, E_{220} [Bq h^{-1}], can be calculated according to the following equation:

$$E_{220} = (\lambda_{220} \cdot V_0) \cdot \frac{C_m}{e^{-\lambda 220 \cdot (V_1 / Q)}} \tag{4}$$

where λ_{220} is ^{220}Rn decay constant (h^{-1}), V_0 is the volume of the accumulation chamber (m^3), C_m is the measured ^{220}Rn concentration [Bq m^{-3}], V_1 is the volume between the outflow of the accumulation chamber and the inflow of the radon monitor (see also Figure 1) and Q is the flow rate in the system. The second term of the equation corrects for the decay of ^{220}Rn during the transport in the closed system, because thoron half-life (55.61 s) is comparable with time required to complete a whole loop, causing the underestimation of thoron activity concentration.

An alternative approach to determine thoron exhalation rate with the present set-up is to use a calibrated thoron source, measure its activity concentration and calculate a correction factor (f_c) from the ratio between certified and measured value. This factor is then used to correct values of thoron concentration activities (C_m), obtained with the same experimental configuration and conditions, and to calculate E_{220} according to the following simplified equation:

$$E_{220} = \lambda_{220} \cdot V_0 \cdot C_m \cdot f_c \tag{5}$$

This second approach is preferable because the calibration factor summarises different points, like detector efficiency and effective duration of gas transport from exhalation to detection. The latter is extremely variable and difficult to determine because it strongly depends on experimental conditions, like for example air mixing. In order to show the influence of air circulation on detected ^{220}Rn concentration activity, two different 24-hour tests (Figure 5), have been performed on TRSN standard using the same analytical conditions and configuration except for circulation fan on (test 4-1) or off (4-2). Thoron equilibrium value is significantly reduced without air circulation because of easier stratification at the bottom of the accumulation chamber and presumably longer transport to the radon monitor. Conversely, ^{222}Rn data from the two experiments overlap within the error range because radon half-life (3.82 days) is about two orders of magnitude higher than duration of transport within the measuring apparatus, showing that air mixing is not discriminative for ^{222}Rn exhalation rate.

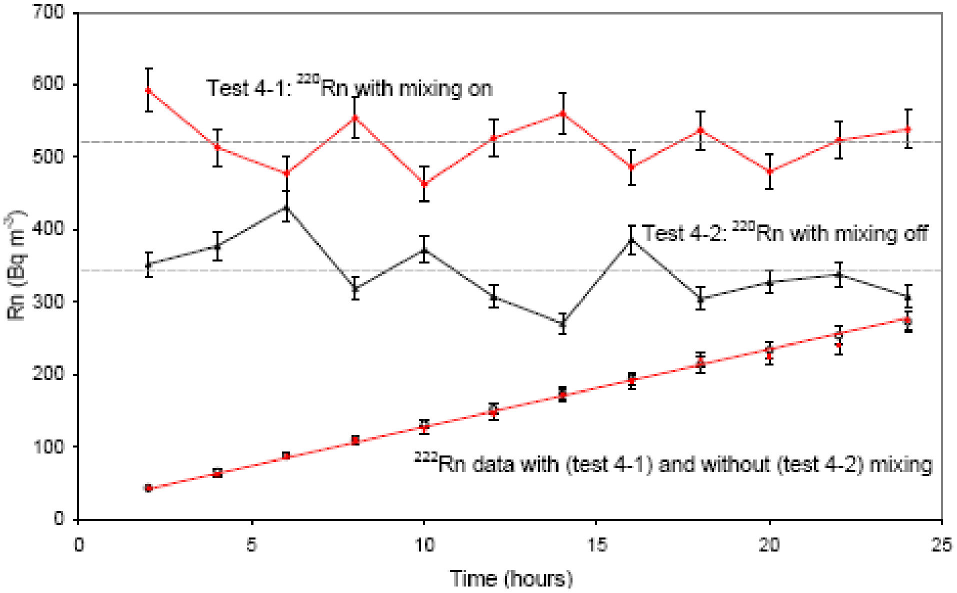


Figure 5. Experimental ^{222}Rn growth curves and ^{220}Rn activity concentration data of TRSN standard over a 24-hour experiment using the stainless steel accumulation chamber with mixing device on (test 4-1) or off (test 4-2). Closed squares and open circles refer to ^{222}Rn data collected respectively with or without mixing; red diamonds and black triangles stand for ^{220}Rn activity concentrations measured under both experimental configuration. Average thoron concentrations are indicated with dashed horizontal lines.

^{220}Rn exhalation rate can be referred to the unit of surface [Bq m^{-2} h^{-1}] or that of mass [Bq kg^{-1} h^{-1}], as stated for ^{222}Rn, dividing the value of E_{220} [Bq h^{-1}] from equation 5 by the surface [m^2] or the mass [kg] of the sample.

THE INFLUENCE OF TEMPERATURE ON RADON EXHALATION RATES

Among parameters affecting radon exhalation rate, temperature is undoubtedly relevant and deserves special attention. Its influence can be visualized from a 19-day experiment (test 5) performed on TRSN standard (Figure 6), allowed to undergo ambient temperature fluctuations. ^{222}Rn growth curve from test 5 is compared with the theoretical curve that well describes experimental data from test 3 (Figure 4), where temperature was set and kept at 20°C.

It is evident that during the first segment of test 5 (about 250-hour long), when temperature changes were not relevant (less than 2°C), ^{222}Rn experimental data approached the theoretical curve described by equation 1 (Figure 6). Successively, and up to 370 hours after the beginning of the test (segment 2), significant and rapid temperature fluctuations were recorded along with corresponding changes of radon concentration. In general, this segment of the experiment is characterised by a general temperature decrease up to 360 hours from the start, with radon data falling below the theoretical curve, but during the last 10-12 hours of the segment, an abrupt temperature increase of 12°C makes radon concentration rise up to the curve. Throughout the last section of the experiment (segment 3), temperature fluctuations are accompanied by parallel oscillations of radon data in the frame of a general decrease of both variables, with radon concentrations always below the curve.

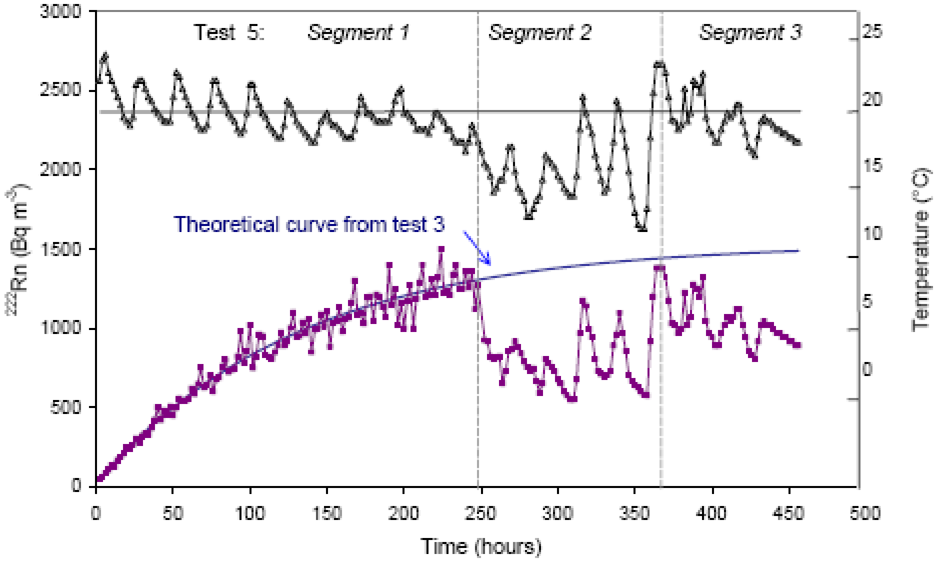


Figure 6. Experimental ^{222}Rn growth curve of TRSN standard (purple squares) over a 19-day experiment (test 5) performed at ambient conditions (variable temperature) compared with theoretical radon curve from test 3 conducted at a constant temperature of 20°C. Temperature data are indicated with black triangles. The reference temperature of 20°C is indicated with a full horizontal line. Errors are around 5 %.

Test 5 clearly shows a direct correlation between large temperature changes and variations of radon concentration within the experimental set-up, the latter being realistically due to a change of radon release from the standard. This is simply demonstrated by two 24-hour experiments carried out on TRSN standard under the same experimental condition, except for temperature, kept constant at 20 and 30°C. Results show that radon exhalation rates are different within the error range (see first and second lines of Table 1).

A similar finding on the effect of rapid temperature increases on radon exhalation rate (as in the last 10 hours of segment 2 – test 5) was reported in Kovler (2006a, b) where peaks of radon exhalation rates coincide with those of temperature measured on the surface of cement pastes, due to hydration heat development during the shrinkage phase. The author states that heating of the material weakens physical adsorption of radon gas atoms on the newly formed solid surfaces, enhancing radon release. Slighter temperature changes during longer periods (as in segment 1 of test 5) do not seem to affect significantly ^{222}Rn exhalation rates.

GUIDELINES TO SET A STANDARD PROTOCOL TO MEASURE RADON EXHALATION RATES

On the basis of validation experiments reported above, guidelines for an experimental protocol to measure simultaneously ^{222}Rn and ^{220}Rn exhalation rates are proposed. A special attention is devoted to minimise factors influencing values of exhalation rates: temperature, air mixing, humidity and grain size. The development of a specific protocol to certify building materials, evaluating their attitude to release radon gas, meets the statements of EC directive 89/106/EEC concerning construction products. This regulation reports the requirements applicable to building materials for their use in construction, among which that they should not emit dangerous radiations nor develop toxic gases. The protocol can be used alone or in conjunction with the activity concentration index (EC-Radiation Protection, 1999) to better determine the exhalation rates of building materials.

The protocol can be applied to cut-stone or granular material, grounded and sieved according to specific use, taking into account that grain size strongly influences exhalation rates, the smaller the grain size, the larger the exhaling surface (De Martino et al., 1998; Kovler et al., 2005; Tuccimei et al., 2006). In addition, when analysing a cut-stone, it should be considered that its exhalation rate increases considerably if the block is grounded. A reference grain size (if a granular material is analysed) and sample weight and volume should be introduced.

Samples have to be weighed (from 0.5 to 1 Kg) and dried at 110°C for 24 hours. The last operation is essential because of the lower recoil distance of radon in water-filled pores than in air-filled pores, resulting in a higher probability of the recoiled radon atoms to stay into the water-filled pores and not be reabsorbed by other grains and, in turn, determining larger exhalation rates from humid samples (Carrera et al., 1997, Wiegand, 2001; Tuccimei et al., 2006).

The analysis is to be performed for 24 hours and the activity concentration of radon isotopes is recorded hourly or every two hours, along with the humidity content and the temperature in the radon monitor inner chamber. The circulation fan should be on, to reach higher equilibrium concentration of thoron and thus determine the relative exhalation rate with better precision. ^{222}Rn and ^{220}Rn exhalation rates are calculated according to equation 3 and 5, respectively. It is advisable to perform experiments at constant temperature because rapid and strong variations of this parameter affect the ^{222}Rn exhalation rate, as demonstrated previously. A reference temperature could be 20 °C, because it corresponds to average temperature in air-conditioned environments. Good operation of the experimental apparatus should be checked periodically by measuring a standard and certified material. This is particularly useful in order to control if the circulation fan works properly and air mixing in the accumulation chamber is guaranteed. A slowing down of the ventilator rotation is likely to occur over time if it is powered to a voltage lower than the proper functioning value. This circumstance could occur if the operator had to reduce the speed of the fan during the analyses of very fine samples that could spread out and being pumped up along the tubing. With a view to this, it is advisable to choose a light and two-blade ventilator (see Figure 1) to have a correct rotation speed, powered at the correct operating voltage. Finally, filters and tubing should be cleaned regularly to keep airflow constant within the experimental apparatus and drierite (tending to release a fine powder) should be sieved and periodically replaced.

Exhalation Rates of Building Materials and Proposal of a Classification Scheme

This section reports on the results of some analyses carried out on six blocks of pyroclastic flows used as cut-stone, two loose volcanic products and eight different unhydrated cements traded in Italy, according to the previously described standard protocol (Table 1). Results are discussed and a proposal of a classification scheme to apply to building materials is advanced.

The blocks of tuff are quarried in Colli Albani and Sabatini districts near Roma (central Italy) and in the area of Napoli (southern Italy). Black pozzolan (a siliceous volcanic ash) and lapilli tuffs (fragments of pyroclastic rocks measuring between 2 and 64 mm), both from Colli Albani area, are used to produce grout, mortar and hydraulic cement. A selection of cements is presented, choosing at least one sample from each of the types that the European Committee for Standardization (CEN, 2000) has established in EN 197-1: 2000. Briefly, type I is Portland cement, consisting of at least 95 % of clinker (hydraulic material consisting of calcium silicates, aluminium- and iron-containing oxides); type II is Portland cement (at least 79 %) mixed with other components (e.g. granulated blast furnace slag, limestone or pozzolan); type III is slag cement with variable contents of clinker; type IV is pozzolan cement with different percentage of clinker; type V is composite cement with a reduced proportion of clinker added with a mixture of slag, pozzolan, coal fly ash and silica fume.

^{222}Rn exhalation rates of pyroclastic rocks resulted generally relevant, whereas ^{220}Rn release becomes significant only for granular samples, like pozzolan or lapilli tuffs, characterised by a larger exhaling surface. Cements belonging to classes I and II (see details in Table 1), being a mixture of clinker and limestone, provided exhalation rates lower than detection limits of the experimental apparatus. Also cements of classes III and V, essentially a mixture of clinker and slag, gave the same results, whereas pozzolan cements (type IV) presented higher ^{222}Rn and ^{220}Rn exhalation rate. These results are consistent with the high abundance of radium and thorium (radon precursors) in volcanic products from Italian districts.

On this basis, a classification scheme of building materials, applicable to rocks and cements, is proposed (Table 2). An alphanumeric codex that labels the exhalation rate classes (with letters from A to D for ^{222}Rn and numbers from 1 to 4 for ^{220}Rn) supports the classification. From A to D (codex 222 in Table 2) and from 1 to 4 (codex 220 in Table 2), radon exhalation rates progressively increase. The limits between classes are chosen as a function of radon exhalation rates required to reach predetermined equilibrium activity concentrations in a standard confined environment (the model room of 56 m^3, reported in EC-Radiation Protection, 1999), completely covered with the investigated material. The preset values of radon equilibrium concentrations are 200 and 400 Bq m^{-3}, suggested by the EC recommendation 90/143/Euratom, as action levels in the new and old houses, respectively. These activity concentrations correspond to reference levels of 10 and 20 mSv per year effective dose equivalent, respectively. The choice of setting a class between 100 and 200 Bq m^{-3} is due to significant ^{220}Rn exhalation rates from some building materials, whose contribution adds to indoor ^{222}Rn gas. This additional input is generally neglected, but needs to be accounted for, otherwise its potential risk is underestimated. This view is clearly expressed in Steinhauser et al. (1994) who underlined that the existing database on ^{220}Rn in the environment, the experimental validation of dosimetric models and potential health effects are scarce, but identifies circumstances where the ^{220}Rn dose becomes relevant, as in the indoor environment if building materials with high concentrations of ^{220}Rn precursor are present.

Table 2. Proposal of a classification scheme for building materials. Codex 222 and codex 220 are attributed to samples on the basis of their ^{222}Rn and ^{220}Rn exhalation rates, respectively. The combination of Codex 222 and Codex 220 (in this order) identifies the class of material (see text for explanation)

Codex 222	Equilibrium ^{222}Rn Bq m^{-3}	E_{222} Bq m^{-2} h^{-1}	E_{222} Bq kg^{-1} h^{-1}	Codex 220	Equilibrium ^{220}Rn Bq m^{-3}	E_{220} Bq m^{-2} h^{-1}	E_{220} Bq kg^{-1} h^{-1}
A	< 100	< 0.49	< 0.015	1	< 100	< 2849	< 85
B	100-200	0.49 - 0.97	0.015 - 0.029	2	100-200	2849 - 5697	85 - 171
C	200 - 400	0.97- 1.94	0.029 - 0.058	3	200 - 400	5697 - 11394	171 - 342
D	> 400	> 1.94	> 0.058	4	> 400	> 11394	> 342

According to this classification, blocks of pyroclastic rocks are to be referred to subclass B to D, but mainly to the latter (> 400 Bq m^{-3} due to ^{222}Rn), whereas granular volcanics are classified as D, with the additional contribution of ^{220}Rn (subclass 2 to 4). TRSN standard, which is a pyroclastic rock grounded and sieved between 2 and 1 mm, is coherently referred to class C2 when measured at 20°C and to class D3 if the test is conducted at 30°C (Table 1). This difference shows how important the introduction of a reference temperature is, in terms of building materials classification. Generally speaking, it is evident that pyroclastic rocks deserve special attention when used in construction, because they can produce indoor radon concentration beyond the action limits recommended by the European legislation.

As far as unhydrated cements of class I, II, III and V are concerned, our analyses show that most of them are classified as A1 material and are not a potential source of risk. However, cements of type IV (pozzolan cement), belonging to class B1, show an higher radon exhalation rate, even if lower than action levels reported by EC recommendation 90/143/Euratom. Finally, it is worth noting that our analyses and classification are referred to unhydrated cements, without taking into consideration the possible effect of cement hydration on the increase of radon exhalation rate (Kovler, 2006a, b).

CONCLUSION

The main conclusion of this chapter can be summarised as follows:

1) The experimental apparatus permits the determination of radon free exhalation rates, as shown by validation tests based on non-linear fitting of experimental data. This is clearly shown by the obtained time constant that minimise the deviations from the theoretical curve. Phenomena like sorption of radon by $CaSO_4$ grains used as desiccant are negligible.
2) The experimental set-up makes possible to measure simultaneously ^{222}Rn and ^{220}Rn exhalation rates, taking into account the decay of ^{220}Rn during the transport within the measurement closed-loop from the accumulation chamber to the radon monitor.

3) Air circulation during the test affects considerably thoron activity concentration and the use of a certified thoron source is chosen to calibrate the set-up either with air mixing or without it, providing specific thoron calibration factors for both experimental procedures.
4) Major and rapid temperature fluctuations are positively correlated with ^{222}Rn activity concentration detected during the measurement. This is probably due to changed exhalation rates as a function of temperature, as shown by the results of two experiments carried out at 20 and 30 °C. Such outcome implies the need to keep the temperature constant during the experiment.
5) A standard protocol to measure radon and thoron exhalation rate is proposed and basic maintenance procedures are advanced with the aim of keeping constant airflow within the experimental apparatus.
6) Samples of cut-stones and cements used in central Italy as building materials have been analysed and classified according to a tentative scheme on the basis of exhalation rates required to reach the indoor radon action levels recommend by European Community in a model room completely covered with the investigated material.
7) Pyroclastic rocks, mainly in granular form, can produce indoor radon concentration beyond the action limits recommended by the European legislation. When added to clinker to prepare pozzolan cement, they contribute to increase radon exhalation rate.
8) The role of ^{220}Rn, generally underestimated, is to be considered when evaluating indoor radon risk due to building materials because its contribution can supply a significant amount of radon in a confined environment, as in the case of pozzolan and lapilli tuffs used to prepare grouts, mortar and cements.

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