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2 possible disequilibrium in natural decay series

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10

11 Abstract

The determination of the activity concentration of naturally occurring radionuclides in construction 12 13 materials is based on the principles of gamma-spectrometry. Gamma spectrometry is a comparative 14 method and therefore includes many parameters that are specific to the test sample and 15 measurement circumstances. Consequently, several of the testing conditions must be verified prior 16 to testing and/or require correction to obtain accurate results. Besides problems encountered during 17 the measurement, the interpretation of the results and calculation of the activity indices, needed for 18 material classification, may lead to significant mistakes. Current regulation in the European Union 19 requires to calculate an activity concentration index (index I) using the activity concentration of ²²⁶Ra, 20 ²³²Th and ⁴⁰K. Not all of these radionuclides are directly measurable by gamma spectrometry and, to 21 determine the index, additional assumptions have to be made about secular equilibrium in uranium 22 and thorium decay series. These assumptions are often not valid in case of NORM (Naturally 23 Occurring Radioactive Materials) where long term lack of secular equilibrium in the uranium and/or 24 thorium decay series is often observed. As a consequence, this may result in an underestimation or 25 overestimation of the index. The article discusses specific disequilibrium situations in building 26 materials. Sources for potential inaccurate determinations and misinterpretation are identified and 27 practical mitigation options are proposed.

28

29 1. Introduction

30 Most construction materials are made from natural minerals. However currently many industrial 31 residues are also used for this purpose. Specific residues can contain increased concentrations of naturally occurring radionuclides and for some of these residues, classified as NORM (Naturally 32 33 Occurring Radioactive Materials), the related additional exposure to ionizing radiation is often not 34 negligible. This problem was elucidated recently, to a certain level, by requirements set in Directive 35 2013/59/EURATOM, the so called Euratom Basic Safety Standards (EU BSS) [EC, 2013]. This directive 36 contains an indicative list of building materials that might be of concern from the radiation 37 protection perspective and a general rule limiting additional exposure to ionizing radiation from 38 building materials (less than 1 mSv per year expressed as effective dose). As it is not possible (or 39 difficult, at least) to estimate the annual effective dose to members of the public caused by building 40 material directly, the EU BSS offers a possibility to comply with the dose limit by limiting the radionuclides activity concentration in building materials and introduces a screening tool, the index I, 41 42 to classify building materials from the radiation protection perspective. This index, in fact the first time proposed in Radiation Protection 112 [EC 1999], is expressed as a weighed sum of activity 43 44 concentration of the most important naturally occurring radionuclides:

45

$$I = \frac{C_{Ra-226}}{300} + \frac{C_{Th-232}}{200} + \frac{C_{K-40}}{3000} \le 1$$
(1)

46 where C_{Ra-226} , C_{Th-232} and C_{K-40} are the activity concentrations in Bq/kg of the corresponding 47 radionuclides.

The weighting factors applied were obtained based on generic assumptions: (i) a dose criterion of 1 48 49 mSv/y - taken as an excess to the average background originating from the Earth's crust -, (ii) an annual indoor occupancy factor of 7000 h, and (iii) a conversion coefficient 0.7 Sv/Gy. The calculation 50 51 of the weighting factors was based on a simplified room model i.e. room dimensions 4m x 5m x 2.8 m where surfaces (walls, floor and ceiling) were made of the same material (concrete of density = 2350 52 53 kgm⁻³ and thickness of 0.2 m) without the presence of windows or doors. These calculations do not 54 accurately reflect existing situations, instead the index I should be considered a conservative screening tool. This aspect is also underlined in the EU BSS by demanding a dose calculation that 55 assumes specific parameters adapted to the intended use of the materials in the case of an index I 56 larger than one. 57

58 Measurements of radionuclides are necessary to verify the compliance of building materials with the 59 requirements of the European BSS. Determination of the activity concentration of natural

radionuclides in construction materials is usually done by using gamma-spectrometry. This 60 spectrometric technique is a comparative method and therefore includes many parameters that are 61 62 specific to the test sample and measurement circumstances. Consequently, many of the testing 63 conditions must be verified prior to testing and/or require correction to obtain accurate results. 64 Moreover, not all radionuclides used for index I calculation are directly measurable by gamma spectrometry. That is why additional assumptions must me made about secular equilibrium in the 65 uranium and thorium decay series. These assumptions are difficult in case of NORM where long-term 66 67 lack of secular equilibrium in the uranium and/or thorium decay series is often observed and lack of 68 the proper interpretation of the results may lead to significant mistakes. In spite of the fact that the 69 system of differential equations describing sequential radioactive decay was already formulated by 70 Rutherford [1905] and relevant solution were proposed by Bateman [1910] more than 100 years ago 71 the possible effects of the phenomenon of secular equilibrium on the final exposure is rarely 72 considered when natural radionuclides are evaluated as a source of radiation risk.

73 In the current article ⁴⁰K is not discussed. The reason is that there is no problem to measure this 74 radionuclide by gamma spectrometry based on single, efficient gamma line at 1462 keV or by 75 classical chemical techniques assuming natural abundance of 0.0117% in natural potassium.

76 2. Disequilibrium in natural decay series

In raw materials, residues and building materials the members of the three natural decay chains, 77 starting from ²³⁸U, ²³⁵U and ²³²Th as well as ⁴⁰K can be present. As the ratio of ²³⁵U/ ²³⁸U activities in 78 79 natural uranium is very small (0.046 and this ratio can be changed only in the nuclear fuel 80 preparation process, that usually does not generate residues or waste useful for construction 81 purposes), in the *I* index calculation the contribution originating from ²³⁵U-decay series is assumed to be negligible. Moreover, other naturally occurring radionuclides (³H, ¹⁴C or ⁸⁷Rb) are generally 82 83 considered of no importance, considering their radiological impact, in this case. The presence of 84 artificial radionuclides, that can be incorporated into building materials due to environmental contamination caused by nuclear or radioactive accidents (e.g. ¹³⁷Cs), lays outside the scope of the I 85 86 index used in the EU BSS.

Finally, from the perspective of the possible radiation risk caused by construction materials, two
natural decay series (namely, the uranium and thorium series) are the most important (Figures 1 and
2).

90 The radionuclides constituting these decay series usually occur all together, but the ratio of their 91 activity concentrations depends on the origin and type of material of interest. In the natural state 92 and when the influence of external factors can be excluded, all the radionuclides in a decay series are in secular equilibrium (i.e. the activity concentration of each radionuclide is the same). In such a 93 situation, it is sufficient to measure the activity concentration of a single radionuclide for each decay 94 95 series (normally, the easiest one to measure) and to use the measured value for all the other 96 radionuclides. This situation is reflected in the criterion set by the EU BSS directive based on I index. Regrettably, this is a rather unusual situation and in practice secular equilibrium is frequently 97 98 disturbed due to the influence of external agents such as hydro-geological processes occurring in the 99 Earth's crust, or simply ambient weather conditions. In contrast to materials of natural origin, in 100 which secular equilibrium can sometimes be observed despite external influences, materials altered 101 by human activity (e.g. thermal processing, mining) almost always are characterised by the lack of secular equilibrium among members of the uranium and thorium series [Michalik et al., 2013]. 102

103 To avoid any mistakes with the interpretation of the index *I* value it is necessary to identify possible

104 disequilibrium states in material's decay series.



uranium decay series

105

106

- 107 Figure 1. Uranium decay series, in black boxes radionuclides emitting gamma radiation useful for
- 108 gamma spectrometry [Laboratoire National Henri Becquerel]
- 109



110

Figure 2. Thorium decay series, in black boxes radionuclides emitting gamma radiation useful forgamma spectrometry [Laboratoire National Henri Becquerel]

The half-life times of the nuclides within the natural decay chains are very different, from below milliseconds to billions of years. Although there are all together about 30 different radionuclides in the most important decay series, few of them have half-lives long enough to exist isolated from their parent nuclide. This means that only for those few radionuclides activity concentrations can differ from the activity concentrations of their parent radionuclide. The radionuclides from the uranium and thorium decay series that belong to this category are listed in table 1.

119 Factors other than the radioactive decay which influence the environmental behaviour of a 120 radionuclide are important only in the case when parent and decay product radionuclides are

121 different elements. Otherwise, when a parent radionuclide decays directly to another isotope of the same element (as in case of the uranium isotopes ²³⁸U and ²³⁴U) usually in any kind of abiotic 122 materials the isotopes remain in secular equilibrium. In nature, processes resulting in isotopic 123 124 fractionation of an element are very rare and the consequences, if exists, are negligible from the 125 radiation protection perspective, especially in the context of building materials [Koide and Goldberg, 126 1963; Grabowski and Bem, 2011; Kumar et al., 2016]. In contrast, human activity can significantly 127 change isotope ratios (for example, enrichment or depletion of uranium in the nuclear fuel cycle). Outside the nuclear fuel cycle, however, such processes are rare and are limited to specific cases, 128 129 such as in the medical sector.

130

Table 1. Natural radionuclides with half-life long enough to behave independently in theenvironment (half-lives taken from Laboratoire National Henri Becquerel data base).

Radionuclide	Half-life ($t_{1/2}$)	Gamma-emitting decay product			
²³⁸ U	4.468 × 10 ⁹ years	²³⁴ Th			
²³⁴ Th	2.5 × 10 ⁵ years	²³⁴ Th			
²³⁰ Th	7.538 × 10 ⁴ years	-			
²²⁶ Ra*	1600 years	²¹⁴ Bi, ²¹⁴ Pb			
²²² Rn	3.823 days	²¹⁴ Bi, ²¹⁴ Pb			
²¹⁰ Pb*	22.23 years	-			
²¹⁰ Po	138.3763 days	-			
²³² Th	1.402 × 10 ¹⁰ years	-			
²²⁸ Ra	5.75 years	²²⁸ Ac			
²²⁸ Th	1.9126 years	²¹² Pb, ²¹² Pb, ²⁰⁸ Tl			
²²⁴ Ra	3.64 days	²¹² Pb, ²¹² Pb, ²⁰⁸ Tl			

The solution for the system of differential equations formulated by Rutherford for an unlimited chain of radionuclides subject to sequential decay was provided by Bateman (2010). Limiting to two radionuclides A (parent) and B (decay product), the mutual relationship of their activity is described by the following equation:

138
$$\mathbf{B}_{t} = \frac{\lambda_{B}}{\lambda_{B} - \lambda_{A}} A_{0} \left(e^{-\lambda_{A}t} - e^{-\lambda_{B}t} \right) + B_{0} e^{-\lambda_{B}t}$$
(2)

139 where:

140 A_t and B_t are the activities of the different radionuclides at time t; A₀ and B₀ are the activities 141 at time t=0; decay constants $\lambda_A = \ln(2)/(T_{1/2,A})$ and $\lambda_B = \ln(2)/(T_{1/2,B})$; the half-life (T_{1/2}) is 142 provided for A and B, respectively.

143

144 Assuming that $B_0=0$ the equation (2) is simplified to:

145
$$\mathbf{B}_{t} = \frac{\lambda_{B}}{\lambda_{B} - \lambda_{A}} A_{0} \left(\mathbf{e}^{-\lambda_{A}t} - \mathbf{e}^{-\lambda_{B}t} \right)$$
(3)

146 Considering the half-lives ratio of both of these radionuclides subject to successive decay the 147 equation (2) implies three possible scenarios:

1481. If the half-life of the parent radionuclide is significantly longer than the decay product149 $(T_{1/2, A} >> T_{1/2, B}; \lambda_A << \lambda_B)$, the activity of this decay product increases during the time equal to150approximately five periods of its half-life and finally activities of both radionuclides, parent151and decay product become equal each other i.e. the secular equilibrium state is reached. So,152the secular equilibrium state *sine qua non* condition for two radionuclides is that half-life153 $(T_{1/2})$ of a parent radionuclide (A) must be significantly longer than $T_{1/2}$ of a decay product (B).

154

1552. In the case when the half-life of the parent nuclide A is only slightly longer than the half-156life of the decay product B, $(\lambda_A < \lambda_B)$. the activity of the decay product increases for a period157equal to about twice the half-life of the decay product and then decrease according to the158half-life of the parent radionuclide. It is the so called transient equilibrium state.

160 3. In the third case, when the half-life of the parent nuclide A is shorter than the half-life of 161 the daughter nuclide B ($\lambda_A > \lambda_B$), the situation is similar as in case 2, however, the activity of 162 the decay product decreases according to its own half-life.

163 Typical for scenario 2 and 3 is that the activity of the decay product can be bigger than the activity of 164 the parent radionuclide ($A_t < B_t$). Keeping in mind these rules, sub-series of radionuclides can be 165 distinguished in the uranium and thorium series.

Many processes in nature can lead to a disequilibrium in the natural decay series. A phenomenon causing the formation of or scales? containing only radium is observed during the production of of geothermal energy [Finster et al., 2015; Eggeling et al., 2013] and, to a lesser extent, during the treatment of water from underground sources [Fonollosa et al., 2015; Chmielewska et al., 2014; Kleinschmidt & Akber,2008; Szabo et al., 2008]. However, the best known industrial sector with sources of NORM with disrupted decay chains is the oil and gas industry [IAEA,2003; IAOGP,2008; Rowan et al.,2011].

173 2.1 Disequilibrium in uranium decay series

In the uranium series, a possible long-lasting disequilibrium state can be observed between uranium 174 isotopes thorium and radium (²³⁸U and ³⁰Th between ²³⁰Th and ²²⁶Ra), however these situations do 175 not influence the evaluation of the I index. The half-life of ²²⁶Ra is about 1600 years, hence about 10 176 177 000 years (a factor 5, analogue to scenario 1) is necessary to get secular equilibrium between any of ²²⁶Ra parent radionuclide and ²²⁶Ra. Considering that the oldest constructions still in use are normally 178 not older than a few hundred years the presence of ²³⁸U does not influence radium activity 179 concentration and, for calculation of the *I* index, the currently measured ²²⁶Ra activity concentration 180 181 can be used and considered as not changing over time.

On the other hand, ²²⁶Ra can create its own sub-series when it is isolated (Table 2). Although the presence of such sub-series is mostly of little significance when applied as a building material it is important when measuring the activity concentration. When applying gamma spectroscopy, usually no gamma emissions from radium are directly measured but instead the gamma emissions from radium decay products (table 1) are used. Hence, it is important to assure secular equilibrium between radium, radon and its short-lived progeny.

- 189 Table 2. Characteristics of radionuclides forming a sub-series starting from ²²⁶Ra in the ²³⁸U decay
- 190 series, (half-lives taken from Laboratoire National Henri Becquerel data base)

Radioactive nuclide	Half-life (T _{1/2})	$\lambda [s^{-1}]$
²²⁶ Ra	1600 years	1.374 × 10 ⁻¹¹
²²² Rn	3.823 days	$2.099 imes 10^{-06}$
²¹⁸ Po	3.071 minutes	3.762 × 10 ⁻⁰³
²¹⁴ Pb	26.916 minutes	4.29×10^{-4}
²¹⁴ Bi	19.8 minutes	5.834 × 10 ⁻⁴
²¹⁴ Po	162.3 milliseconds	4.271
²¹⁰ Pb**	22.23 years	9.860 × 10 ⁻¹⁰
²¹⁰ Bi**	5.012 days	1.6 × 10 ⁻⁶
²¹⁰ Po**	138.3763 days	5.8 × 10 ⁻⁸

^{191 **} long-lived decay products of radon

192 Actually, radium sub-series consist of two parts:

194 2) ²¹⁰Pb --> ²¹⁰Bi --> ²¹⁰Po

195

Additionally, the fact that the ²²²Rn is present in gaseous form, can lead to the separation of the
 subsequent sub-series starting from ²²²Rn:

199

Secular equilibrium between radium and radon is established after about three weeks, and between radon and radon progeny after about three hours (see ratios of relevant $T_{1/2}$ table 2). It means that radionuclides in ²²⁶Ra decay sub-series are expected to be in secular equilibrium after about 20 days, even in case when at the beginning only pure radium was present in material of concern. This is not

204 valid in case of another radionuclide that results from the short-lived decay products of radon, lead 205 isotope (²¹⁰Pb). Its half-life amounts to over 22 years (Table 2). This means that in case of a lack of 206 equilibrium, its growth process is relatively slow. Much earlier, before reaching secular equilibrium with radium, ²¹⁰Pb reaches secular radioactive equilibrium with ²¹⁰Bi (after about 1.5 months), and 207 208 then, after less than two years with ²¹⁰Po. The stabilization of secular radioactive equilibrium between ²²⁶Ra and its long-lived decay products (²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po), is reached after about 100 209 years. As the index formula was calculated assuming secular equilibrium in the whole uranium decay 210 211 series the lack of lead in the material means that the index I is a priori overestimated. However, the contribution to external gamma radiation from ²¹⁰Pb (and its progeny) is very low and therefore a 212 213 disequilibrium between ²²⁶Ra and ²¹⁰Pb does not influence the weighting factors in the index formula 214 significantly.

215 2.2. Disequilibrium in thorium decay series

216 When similar considerations are carried out for the thorium series the number of disequilibrium 217 situations and sub-series that may occur are smaller than in case of uranium. However, the 218 implications of disequilibrium on the index formula are much more severe than in case of uranium.

Table 3. Characteristics of radionuclides forming a sub-series starting from ²²⁸Ra in the ²³²Th series,

220

(half-lives taken from Laboratoire National Henri Becquerel data base)

Radioactive nuclide	Half-life(T _{1/2})	Decay constant λ In(2)/T _{1/2} [s ⁻¹]		
²²⁸ Ra	5.75 years	3.823 × 10 ⁻⁹		
²²⁸ Ac	6.25 hours	3.081×10^{-6}		
228Th	1.91 year	1.151 × 10 ⁻⁸		
²²⁴ Ra	3.63 days	$2.21 imes 10^{-6}$		
²²⁰ Rn	55.6 seconds	1.247×10^{-2}		
²¹⁶ Po	0.145 seconds	4.78		
²¹² Pb	²¹² Pb 10.64 hours			

²¹² Bi	60.55 minutes	$1.908 imes 10^{-4}$
²¹² Po	299 nanoseconds	$2.318 imes 10^6$
²⁰⁸ Tl	3.05 minutes	3.788 × 10 ^{−3}

The most important case to consider is the lack of equilibrium between ²³²Th and ²²⁸Ra. An isolated sub-series starting with ²²⁸Ra can be considered here (Table 3). Two situations may occur:

- (1) First, the material of concern may not contain ²²⁸Ra at the beginning of its life-cycle. In such
 case equilibrium between ²³²Th and ²²⁸Ra (as well as all remaining decay products since ²²⁸Ra
 has the longest half-life among them) is reached after about 30 years and always the activity of
 ²²⁸Ra is higher than the activity of its decay product ²²⁸Th (fig. 3).
- 228
- 229
- 230



Fig. 3. Projected changes in the activity of ²²⁸Ra and ²²⁸Th (with 7 short-lived decay products) related
to radioactive decay [Kovler et al., 2017]

(2) Another possible situation occurs when the material of concern does not contain ²³²Th at all
 and only ²²⁸Ra is present. Due to the different chemical properties of long lived ²²⁸Ra decay
 product - ²²⁸Th, the possibility of creation additional two sub-series should be taken into
 account:

238 ● ²²⁸Ra -> ²²⁸Ac

239

• ²²⁸Th - > ²²⁴Ra -> short-lived decay products (, ²²⁰Rn, ²¹⁶Po, ²¹²Pb, ²¹²Bi, ²¹²Po, ²⁰⁸Tl)

240 ²²⁸Ra reaches secular radioactive equilibrium almost immediately with its first decay product, ²²⁸Ac. On the other hand, due to the relatively small differences between the half-lives of ²²⁸Ra and ²²⁸Th, 241 242 the so-called transient radioactive equilibrium state (in which the concentration of the two isotopes 243 are temporary equal to each other, scenario 2) is reached after less than five years. But the activity of 244 thorium is constantly increasing and, after the next five years it is settled at a level equal to about 245 150% of ²²⁸Ra activity (fig.4). In the meantime, in about two weeks, the state of the secular radioactive equilibrium is achieved between ²²⁸Th and ²²⁴Ra and its six short-lived decay products 246 (Table 3). Such a situation i.e. when a higher activity is observed for ²²⁸Th relative to the activity of its 247 parent radionuclide (²²⁸Ra) after a time-period of about 5 years from the material of isolation is 248 249 possible only when in the material of concern there is no ²³²Th at all.

It should be mentioned that a third sub-series starting from ²²⁴Ra could be identified in the thorium
decay chain. This aspect is not overly important for building materials from longer time perspective,
however, one performing gamma spectrometry measurement must be aware about this.

When considering the ratio of ²²⁴Ra and its decay product with the longest half-life (²¹²Pb), the 253 254 secular equilibrium in the sub-chain starting from ²²⁴Ra is reached in about two days (tab. 4). Hence, 255 one can assume that in all cases the samples of natural origin (to some extend also in all samples 256 measured more than two days after sampling), the ²⁰⁸TI activity concentration reflects actually the activity concentration of ²²⁴Ra. However, taking into consideration that any process resulting in ²²⁸Ra 257 isolation will isolate ²²⁴Ra as well during the next 30 days after ²²⁸Ra sub-chain isolation, the 258 concentration of ²²⁴Ra (as measured from ²⁰⁸TI) does not reflect the concentration of ²²⁸Th..During 259 this period, unsupported ²²⁴Ra i.e. accumulated simultaneously together with ²²⁸Ra, is decaying and 260 261 total ²²⁴Ra activity must be calculated according to equation (2). After this period only the fraction of 262 this radionuclide created due to decay of ²²⁸Th remains in the material and activity of ²²⁴Ra reflects exactly activity of ²²⁸Th. This is important only when a sample has undergone chemical treatment 263 264 just before measurement (e.g. radium co-precipitation before liquid scintillation counting [Chałupnik and Lebecka, 1993) or when environmental process dynamics is being investigated. In most cases,
the time between sampling and sample measurement is long enough to cover these phenomena.
Possible relations among radionuclides constituting thorium decay series are well described by
Nelson et al. (2015) in the article discussing problems with natural radioactivity in the shale gas
industry.

²³²Th being a pure alpha emitter with a very long half-life does not contribute to external gamma 270 radiation and its presence is important in building materials only from the perspective of ²²⁸Ra 271 occurrence. If ²³²Th is not present in the material of concern, the activity of ²²⁸Ra and its progeny will 272 diminish during a fifty year period. Otherwise, ²³²Th creates a long lasting source of radiation; 273 however not directly but only as source of ²²⁸Ra and ²²⁸Th. In both situations, changes of activity of 274 275 ²²⁸Ra are going on during a few decades. The whole life cycle of building materials covers similar 276 periods. This is the reason why for a proper calculation of the I index, information about the activity 277 of both sub-series is required.

278



279

Fig. 4. Projected changes in the activity of ²²⁸Ra (+²²⁸Ac) and thorium ²²⁸Th (with 7 short-lived decay
products) related to radioactive decay [Kovler et al, 2017]

283 3. Measurements

All above discussed situations must be considered carefully during measurements focused on the 284 285 determination of the radionuclide concentrations needed for I index calculation. In addition, the 286 interpretation of the I index value depends on the actually existing equilibrium situations assessed 287 based on activity ratios of particular radionuclides. It is of equal importance to realise that currently 288 evaluated value of the I index might be subject to temporal changes. Considering the materials life 289 cycle these changes may not be negligible. Applying gamma spectroscopy, additional information 290 concerning the presence of almost all radionuclides constituting natural decay series can be 291 measured simultaneously which help one to solve the jigsaw when classifying the material.

292 3.1. Radium in uranium series

The formula for calculating the *I* index (1) needs the activity concentration of ²²⁶Ra. Methods for the determination of ²²⁶Ra in building materials of natural origin as well as NORM samples by gamma spectrometry can be based on either the direct measurement of the main ²²⁶Ra photopeak (186 keV) or an indirect measurement using the gamma emissions from ²²⁶Ra progeny (see table 1).

297 The advantage of the direct measurement method is that the sample can be prepared and measured 298 immediately without the need for progeny ingrowth. The disadvantages relate primarily to the 299 emission probability of this gamma photopeak (3.28 %) and the presence of the interfering primary gamma emission of ²³⁵U at 185.7 keV which has a higher photon emission probability (57.24 %). 300 While ²³⁵U is generally present at a much lower activity concentration than ²²⁶Ra in environmental 301 302 samples, it has an effective photon emission of ~ 2.6 % at this energy (assuming a natural U isotopic distribution). The energy resolution of currently available HPGe spectrometers is generally 303 considered insufficient to separate the two peaks. Hence, quantification of ²²⁶Ra via the 186 keV 304 gamma line must be conducted by attempting to quantify the contribution of ²³⁵U to the doublet 305 306 peak [Dowdall et al., 2004]. This problem is easily solved when uranium is not present at all or if the 307 activity of radium is equal to that of uranium¹. All intermediate states of disequilibrium between 308 uranium and ²²⁶Ra need additional information either on the uranium or radium concentration if the 309 activity of both radionuclides is to be measured simultaneously (or the standard samples used for a 310 spectrometer calibration reflect the uranium/radium ratio in the measured sample, what, in practice 311 is impossible).

¹ the case of enriched/depleted uranium is not considered here, but this makes the analysis more complex. 14

The isotope ²³⁵U may be measured via a low-intensity gamma line (143.8 keV) with an emission 312 313 probability of 11.0 %. But when one considers the very low isotopic abundance of ²³⁵U in natural uranium, a relatively high concentration of uranium is needed to obtain reliable results using this 314 approach (i.e. especially if ²³⁵U is to be measured with a low uncertainty). Alternatively, ²³⁸U can be 315 316 detected by gamma spectrometry using a gamma line emitted by ^{234m}Pa; however, this line has very 317 low emission probability (0.84%) and again, when the uranium activity concentration is low, this 318 photopeak may not be measurable with a good enough uncertainty. In both cases the concentration of uranium should be of the order of 100 Bq kg⁻¹ if reliable results are to be obtained in a reasonable 319 320 count time. Such quite high content of radioactivity is not common in building materials. A final 321 option for a uranium assay by gamma spectrometry is to use the ²³⁴Th line at 63 keV (see figure 1); in this case, however, the efficiency is again quite low (4.1%) and, due to its low energy, sample matrix 322 323 effects (e.g. including self-attenuation) need to be considered when conducting such measurements. Additionally, it needs to be considered that the ²³²Th line at 63,81 keV, even if it has a very low 324 325 emission probability of 0.263 %, overlaps this line.

A combination of the above described approaches usually does not improve the result significantly. Besides gamma spectrometry ²²⁶Ra may be measured by different techniques as either liquid scintillation or alpha spectrometry but both of them needs complex chemical sample preparation that in case of solid, mineral samples takes a lot of time, efforts and chemical reagents. Hence the applicability of these techniques to building materials is very limited [Jia and Jia, 2012].

In light of the above, the indirect method of ²²⁶Ra measurement using progeny radionuclides is 331 commonly applied. The determination of ²²⁶Ra in environmental samples by gamma spectrometry 332 has long been based on the detection of emissions of the ²²²Rn progeny (i.e. ²¹⁴Pb and ²¹⁴Bi after an 333 334 ingrowth period of at least 20 days, during which the sample has to be hermetically sealed to ensure secular equilibrium between ²²⁶Ra and its progeny). The main drawback of this approach is the long 335 336 time period necessary to obtain measurement results. But it is also very important to remember that radon isotopes, being in gaseous state, can permeate through some barriers. Therefore, to minimise 337 interfering effects associated with the loss of secular equilibrium between the ²²⁶Ra parent and 338 progeny radionuclides due to ²²²Rn exhalation, it is important that the seal of the sample container 339 340 used for gamma spectrometry is 'gas tight', and that the sample container itself is not permeable to 341 radon [Scholten et al., 2013]. There is a variety of containers that are suitable for solid samples. The specific types depend on the sample sizes and compositions or the applied method of sealing 342 343 [Mauring and Gäfvert, 2013]. For small volume crystalline samples, such as co-precipitated radium (e.g. Ba(Ra)SO₄), ²²²Rn emanation from the crystalline lattice is limited and therefore the sample 344 15

345 container specifications are less significant. For larger-volume samples, such as typically used for 346 building materials, permeability of the sample container and radon exhalation from the sample 347 should be assessed and avoided. This is especially important when standard samples for 348 spectrometric system efficiency calibration are prepared. When efficiency calibration is done 349 correctly, and any radon exhalation from the sample is addressed then a 20-day ingrowth period 350 should be sufficient to perform an adequate determination of the ²²⁶Ra concentration based on this 351 decay product.

The main advantage of the 'indirect method' is that results obtained via ²¹⁴Pb and ²¹⁴Bi will have a much lower uncertainty compared those ones obtained from the main ²²⁶Ra photopeak at 186 keV. This is due to the higher energy and emission probabilities of the gamma lines emitted by ²¹⁴Pb and ²¹⁴Bi and the fact that both have together at least 5 photopeaks that can be easily detected. For most gamma spectrometers, total uncertainties for ²²⁶Ra significantly lower than 1 Bq·kg⁻¹ should be achievable.

Following the measurement of the ²²⁶Ra activity, the uranium content may be calculated, if necessary.

360 3.2. Thorium and radium in thorium series

Direct measurement of ²³²Th by gamma spectrometry is impossible. All activity measurements of this radionuclide using gamma spectrometry must be based on its progeny activities. That is why all assumptions concerning equilibrium state in material of concern are extremely important. The most common approach is to assess ²³²Th by the first decay product ²²⁸Ra.

The radionuclide ²²⁸Ra is measured indirectly through its progeny, ²²⁸Ac. Due to the ratio of the half-365 lives of ²²⁸Ra and ²²⁸Ac, they are almost immediately (when considered from a perspective of typical 366 367 environmental conditions) in secular equilibrium. It is common practice to make this assumption for the measurement of building materials samples. The radionuclide ²²⁸Ac has few gamma lines with 368 369 high energy and emission probabilities; generally, the 911 keV gamma line is used for ²²⁸Ra 370 quantification. Sometimes, in samples of natural origin, when the assumption of secular equilibrium among all thorium decay series constituents is well justified, the activity concentration of ²²⁸Ra as 371 well as all its decay products, including ²²⁸Th can be evaluated based on the measurement of the 372 2614 keV photopeak of ²⁰⁸TI. Such situation is, however, guite rare in natural samples, and usually for 373 374 NORM samples a lack of equilibrium is observed and all situation describe in the previous section must be analysed i.e. conditions necessary to get equilibrium between, first ²²⁴Ra and ²²⁸Th, and then
 ²²⁸Th and ²²⁸Ra.

Often the measurement result of ²²⁸Th decay products is reported as the concentration of ²²⁴Ra (table 377 378 3). Under real it may be assumed that these nuclides are in the secular radioactive equilibrium, that is the activity of ²²⁴Ra is equal to activity of ²²⁸Th and one can asses the activity concentration both of 379 them based on ²²⁴Ra progenies. However, it must be especially remembered that any process 380 resulting in ²²⁸Ra isolation will also accumulate ²²⁴Ra. Hence, direct measurement of thallium during 381 the 30-days period after ²²⁸Ra isolation may not reflect neither ²²⁸Ra nor ²²⁸Th activity concentration 382 but the sum of activity of ²²⁴Ra resulted from ²²⁸Th decay and unsupported ²²⁴Ra. Actually, about 30 383 days are necessary for all of the unsupported ²²⁴Ra to decay and this is such a short time that this 384 385 situation may be important in case of an on-line measurements.

Radon isotope - ²²⁰Rn, present in thorium decay series, is characterized by a very short half-life.
 Therefore, its exhalation from solids is limited and in case of building materials samples does not lead
 to significant changes in ²²⁴Ra decay products measurement results.

Notwithstanding this, when using ²⁰⁸Tl for assessment of its parent radionuclides concentration it is crucial to remember that only 36% of ²¹²Bi decayed into thallium (see fig. 2) and a relevant correction is necessary to take this into account.

In summary, when one considers the possible disequilibrium in the ²²⁸Ra decay sub-series, directly 392 measured ²²⁸Ac reflects ²²⁸Ra whereas ²⁰⁸Tl (and other ²²⁰Rn progeny, e.g. ²¹²Pb and ²¹²Bi) reflect 393 ²²⁸Th. All these decay products have easily detectable non-conflicting photopeaks. When 394 a disequilibrium between these two radionuclides is measured, one cannot determine the ²³²Th 395 396 concentration by the gamma spectrometry technique. Alpha spectrometry or chemical analysis (mass 397 spectrometry) must be applied in such a case in order to get proper information about activity 398 concentration of this radionuclide. This is not required when the measured activity of ²²⁸Th is bigger 399 than ²²⁸Ra. Assuming that there are no other reasons for the observed phenomenon than radioactive 400 decay (e.g. mixing of different materials containing different radionuclides) one can be sure that in 401 this case no ²³²Th is present in the material of concern and a mid-term forecast (ca. 30-50 years) can be done for that material taking into consideration the ²²⁸Ra half-life and actual ²²⁸Ra/ ²²⁸Th ratio (fig. 402 403 4). Additional information regarding the origin and history of the tested material would help considerably to interpret measurements results showing a disequilibrium between ²²⁸Ra and ²²⁸Th. 404 Deriving relationships between the measured ²²⁸Ra ²²⁸Th and ²²⁶Ra and ²¹⁰Pb (which are usually 405 406 occur together) activities which originate from the decay law can be formulated to obtain a best 17

407 estimate of the ²³²Th concentration. However, this calculation requires so many assumptions that 408 results obtained in this way are questionable at best. It any way needs to be considered for the sub-409 chain starting with unsupported ²²⁸Ra, the ratio of ²²⁸Ra to its long-lived decay product, ²²⁸Th, is 410 changing significantly during the few years following sub-chain isolation (see Figure 2 and 4). This 411 leads to significant difficulties when material in which such a phenomenon is observed is subject to 412 classification according to whatever criterion derived from radiation protection requirements.

In summary, depending on a radionuclide measured directly and then used for activity index calculation the value of the index obtained either can vary significantly or do not reflect accurately the real exposure to radiation. In table 4 possible variations of activity index are presented considering only extreme conditions, radioactivity content close to the limits and keeping in the mind typical ratios of natural radionuclides observed in building materials

	Scenario	²²⁶ Ra	²²⁸ Ra	²²⁸ Th	²³² Th	⁴⁰ K	Index I	Index variation %	Real exposure assessment
1.	secular equilibrium (reference situation)	100	100	100	100	300	0.93	100	ok
	Index calculated	100	100	150	0	300	0.43	46	Underestimated – exposure from ²²⁸ Ra and ²²⁸ Th is not considered
2.	2. based on direct measurement of ²³² Th	100	0	0	100	300	0.93	100	Overestimated - exposure from not present or just growing ²²⁸ Ra and ²²⁸ Th is considered
3.	Index calculated based on direct measurement of ²²⁸ Ra	100	100	150	0	300	0.93	100	Underestimated - exposure from an excess of ²²⁸ Th is not considered
4.	Index calculated based on direct measurement of ²²⁸ Th	100	100	150	0	300	1.18	127	Overestimated - exposure from a lack of ²²⁸ Ra is not considered
5.	²²⁶ Ra underestimation due to typical radon escape from	80	100	100	100	300	0.87	93	underestimated

Table 4. Possible variations of activity index I caused by disequilibrium in a tested material

measurement beaker				

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422 4. Conclusions

Sequential decay of natural radionuclides constituting decay series of ²³⁸U and ²³²Th leads to significant changes in the activity concentrations and isotopic/elemental composition of the radionuclides suite present in building materials. In case of some building materials, especially building materials containing NORM, this phenomenon greatly affect the choice of measurement procedure used for activity concentration index *I* evaluation. When gamma spectrometry is applied, unjustified assumptions about the existing equilibrium state among specific radionuclides can influence the overall quality of the evaluated *I* index.

In particular, the decay of ²²⁸Ra leading to the formation of ²²⁸Th, occurring relatively rapidly can have a significant effect on the level of effective dose with no regard to the actual ²³²Th activity concentration. The test results from many building materials indicate that due to ²¹⁰Pb's long half-life the activity of this isotope often differs from the activity of ²²⁶Ra. However, from a dose perspective ²¹⁰Pb activity concentration over/under estimation is not as profound as for ²²⁸Th. Apart from the effects on the *I* index quality, for proper assessment of ²²⁶Ra also information concerning uranium is useful and the actual concentration of radon is extremely important.

As a consequence, for an accurate determination of the *I* index, the following radionuclides are ofimportance in addition to the directly used for calculation radionuclides:

- 439
- from uranium-radium decay chain: ²³⁸U, ²²²Rn, ²¹⁰Pb,

(from actinium decay chain: ²³⁵U, ²³¹Pa)

- from thorium decay chain: ²²⁸Ra, ²²⁸Th,
- 441

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The actinium decay chain is put into parentheses because generally it cannot be expected to have a deviation in the uranium isotopes (²³⁸U and ²³⁵U) ratio in building materials. The concentration of ²³⁵U in natural uranium is only 0.7% which means normally no radiological impact in case of building
 materials. However, ²³⁵U is a gamma emitter that disturb the direct ²²⁶Ra measurement hence it is
 useful to know (from somewhere else) its activity concentration and actual ratio between ²³⁸U and
 ²³⁵U

The most complex situation exists in the thorium decay series in the case when doubts may occur regarding the presence of ²³²Th in the sample. In this case, gamma spectrometry is not sufficient and other methods should be applied for exact ²³²Th activity assessment.

452 While different chemical analytical methods (atomic absorption, wet chemistry, fluorescence 453 methods, etc.) can be used to determine the chemical elements as U, Th, only mass spectroscopy 454 and radio-analytical methods can distinguish between the isotopes, what is a requirement in this 455 case.

All measurement difficulties discussed put into question mark the sense of the use of ²³²Th activity concentration as a criterion for building materials qualification. Moreover, ²³²Th as almost pure alpha emitter does not contribute to the external exposure to gamma radiation and its presence is only important from ²²⁸Ra and ²²⁸Th perspective, which both are efficient sources of gamma radiation.

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