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# Measurement of radioactivity in building materials – problems encountered caused by possible disequilibrium in natural decay series

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## Abstract

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

## 1. Introduction

Most construction materials are made from natural minerals. However currently many industrial 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 Occurring Radioactive Materials), the related additional exposure to ionizing radiation is often not negligible. This problem was elucidated recently, to a certain level, by requirements set in Directive 2013/59/EURATOM, the so called Euratom Basic Safety Standards (EU BSS) [EC, 2013]. This directive contains an indicative list of building materials that might be of concern from the radiation protection perspective and a general rule limiting additional exposure to ionizing radiation from building materials (less than 1 mSv per year expressed as effective dose). As it is not possible (or difficult, at least) to estimate the annual effective dose to members of the public caused by building 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  $I$ , 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 concentration of the most important naturally occurring radionuclides:

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

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

The weighting factors applied were obtained based on generic assumptions: (i) a dose criterion of 1 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 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 kgm<sup>-3</sup> and thickness of 0.2 m) without the presence of windows or doors. These calculations do not 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 assumes specific parameters adapted to the intended use of the materials in the case of an index  $I$  larger than one.

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

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

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

## 2. Disequilibrium in natural decay series

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

The radionuclides constituting these decay series usually occur all together, but the ratio of their activity concentrations depends on the origin and type of material of interest. In the natural state 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 situation, it is sufficient to measure the activity concentration of a single radionuclide for each decay series (normally, the easiest one to measure) and to use the measured value for all the other 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 disturbed due to the influence of external agents such as hydro-geological processes occurring in the Earth's crust, or simply ambient weather conditions. In contrast to materials of natural origin, in which secular equilibrium can sometimes be observed despite external influences, materials altered 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].

To avoid any mistakes with the interpretation of the index  $I$  value it is necessary to identify possible disequilibrium states in material's decay series.

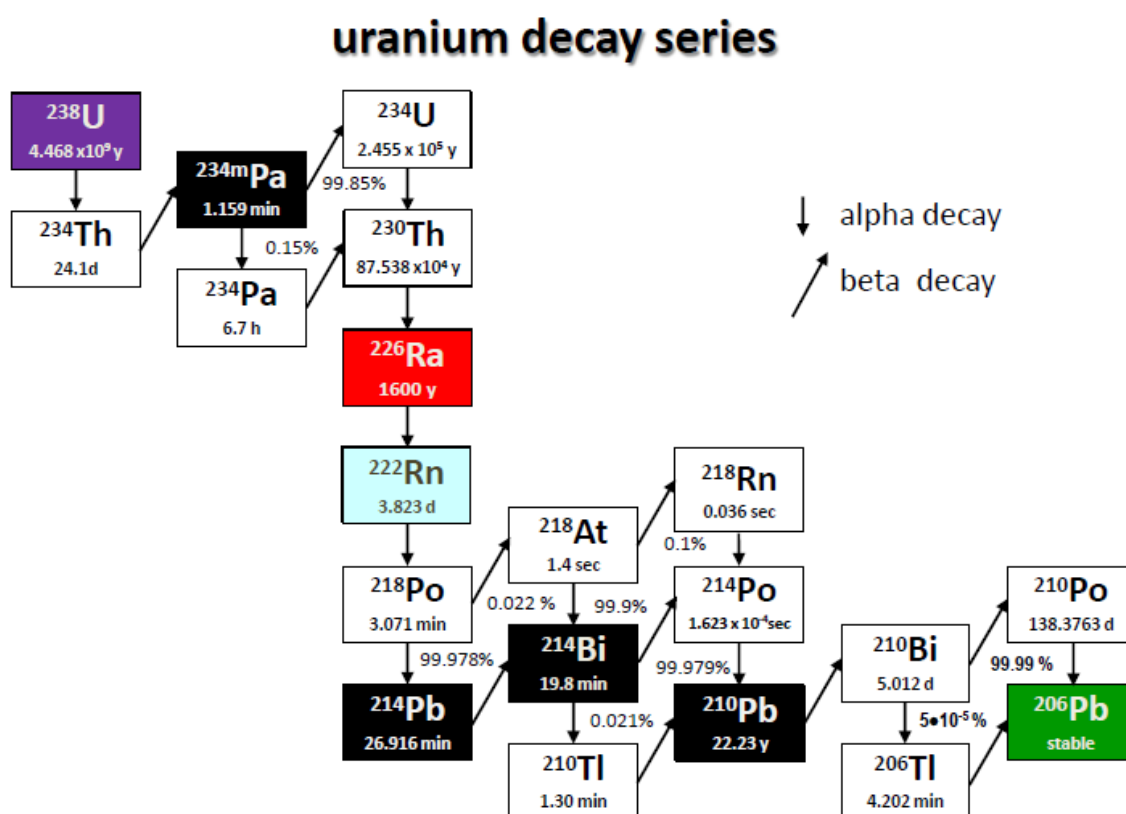


Figure 1. Uranium decay series, in black boxes radionuclides emitting gamma radiation useful for gamma spectrometry [Laboratoire National Henri Becquerel]

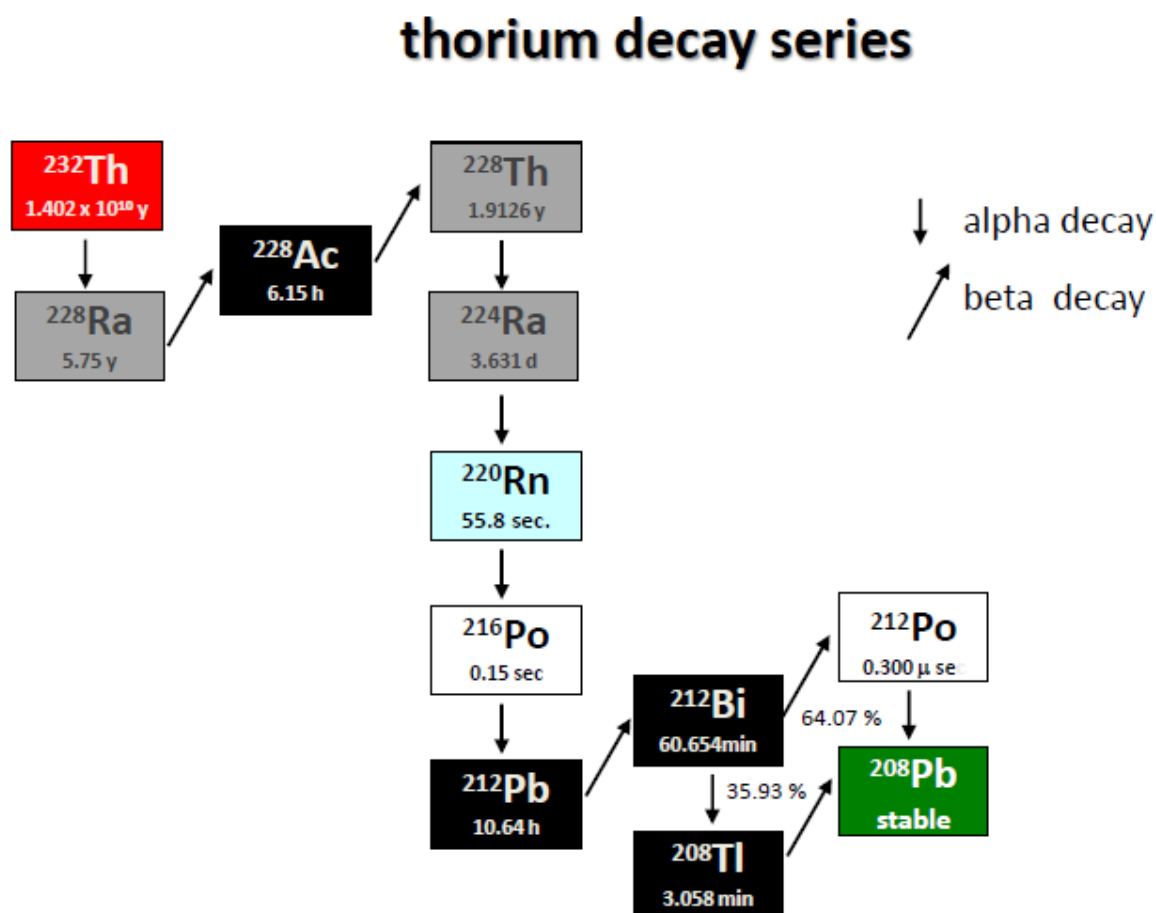


Figure 2. Thorium decay series, in black boxes radionuclides emitting gamma radiation useful for gamma spectrometry [Laboratoire National Henri Becquerel]

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.

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

different elements. Otherwise, when a parent radionuclide decays directly to another isotope of the same element (as in case of the uranium isotopes  $^{238}\text{U}$  and  $^{234}\text{U}$ ) usually in any kind of abiotic materials the isotopes remain in secular equilibrium. In nature, processes resulting in isotopic fractionation of an element are very rare and the consequences, if exists, are negligible from the radiation protection perspective, especially in the context of building materials [Koide and Goldberg, 1963; Grabowski and Bem, 2011; Kumar et al., 2016]. In contrast, human activity can significantly 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, such as in the medical sector.

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

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

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:

$$B_t = \frac{\lambda_B}{\lambda_B - \lambda_A} A_0 (e^{-\lambda_A t} - e^{-\lambda_B t}) + B_0 e^{-\lambda_B t} \quad (2)$$

where:

$A_t$  and  $B_t$  are the activities of the different radionuclides at time  $t$ ;  $A_0$  and  $B_0$  are the activities 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 provided for A and B, respectively.

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

$$B_t = \frac{\lambda_B}{\lambda_B - \lambda_A} A_0 (e^{-\lambda_A t} - e^{-\lambda_B t}) \quad (3)$$

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

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

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



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

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

## 2.1 Disequilibrium in uranium decay series

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

On the other hand,  $^{226}\text{Ra}$  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  $^{226}\text{Ra}$  in the  $^{238}\text{U}$  decay  
190 series, (half-lives taken from Laboratoire National Henri Becquerel data base)

Radioactive nuclide	Half-life ( $T_{1/2}$ )	$\lambda$ [ $\text{s}^{-1}$ ]
$^{226}\text{Ra}$	1600 years	$1.374 \times 10^{-11}$
$^{222}\text{Rn}$	3.823 days	$2.099 \times 10^{-6}$
$^{218}\text{Po}$	3.071 minutes	$3.762 \times 10^{-3}$
$^{214}\text{Pb}$	26.916 minutes	$4.29 \times 10^{-4}$
$^{214}\text{Bi}$	19.8 minutes	$5.834 \times 10^{-4}$
$^{214}\text{Po}$	162.3 milliseconds	4.271
$^{210}\text{Pb}^{**}$	22.23 years	$9.860 \times 10^{-10}$
$^{210}\text{Bi}^{**}$	5.012 days	$1.6 \times 10^{-6}$
$^{210}\text{Po}^{**}$	138.3763 days	$5.8 \times 10^{-8}$

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

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

193 1)  $^{226}\text{Ra} \rightarrow ^{222}\text{Rn} \rightarrow$  short-lived decay products ( $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ,  $^{214}\text{Po}$ ,  $^{218}\text{Po}$ )

194 2)  $^{210}\text{Pb} \rightarrow ^{210}\text{Bi} \rightarrow ^{210}\text{Po}$

195

196 Additionally, the fact that the  $^{222}\text{Rn}$  is present in gaseous form, can lead to the separation of the  
197 subsequent sub-series starting from  $^{222}\text{Rn}$ :

198  $^{222}\text{Rn} \rightarrow$  short-lived decay products ( $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ,  $^{214}\text{Po}$ ,  $^{218}\text{Po}$ )  $\rightarrow ^{210}\text{Pb} \rightarrow ^{210}\text{Bi} \rightarrow ^{210}\text{Po}$

199

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

valid in case of another radionuclide that results from the short-lived decay products of radon, lead isotope ( $^{210}\text{Pb}$ ). Its half-life amounts to over 22 years (Table 2). This means that in case of a lack of equilibrium, its growth process is relatively slow. Much earlier, before reaching secular equilibrium with radium,  $^{210}\text{Pb}$  reaches secular radioactive equilibrium with  $^{210}\text{Bi}$  (after about 1.5 months), and then, after less than two years with  $^{210}\text{Po}$ . The stabilization of secular radioactive equilibrium between  $^{226}\text{Ra}$  and its long-lived decay products ( $^{210}\text{Pb}$ ,  $^{210}\text{Bi}$  and  $^{210}\text{Po}$ ), is reached after about 100 years. As the index formula was calculated assuming secular equilibrium in the whole uranium decay 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  $^{210}\text{Pb}$  (and its progeny) is very low and therefore a disequilibrium between  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  does not influence the weighting factors in the index formula significantly.

## 2.2. Disequilibrium in thorium decay series

When similar considerations are carried out for the thorium series the number of disequilibrium situations and sub-series that may occur are smaller than in case of uranium. However, the 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  $^{228}\text{Ra}$  in the  $^{232}\text{Th}$  series, (half-lives taken from Laboratoire National Henri Becquerel data base)

Radioactive nuclide	Half-life( $T_{1/2}$ )	Decay constant $\lambda$ $\ln(2)/T_{1/2}$ [ $\text{s}^{-1}$ ]
$^{228}\text{Ra}$	5.75 years	$3.823 \times 10^{-9}$
$^{228}\text{Ac}$	6.25 hours	$3.081 \times 10^{-6}$
$^{228}\text{Th}$	1.91 year	$1.151 \times 10^{-8}$
$^{224}\text{Ra}$	3.63 days	$2.21 \times 10^{-6}$
$^{220}\text{Rn}$	55.6 seconds	$1.247 \times 10^{-2}$
$^{216}\text{Po}$	0.145 seconds	4.78
$^{212}\text{Pb}$	10.64 hours	$1.810 \times 10^{-5}$

$^{212}\text{Bi}$	60.55 minutes	$1.908 \times 10^{-4}$
$^{212}\text{Po}$	299 nanoseconds	$2.318 \times 10^6$
$^{208}\text{Tl}$	3.05 minutes	$3.788 \times 10^{-3}$

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

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

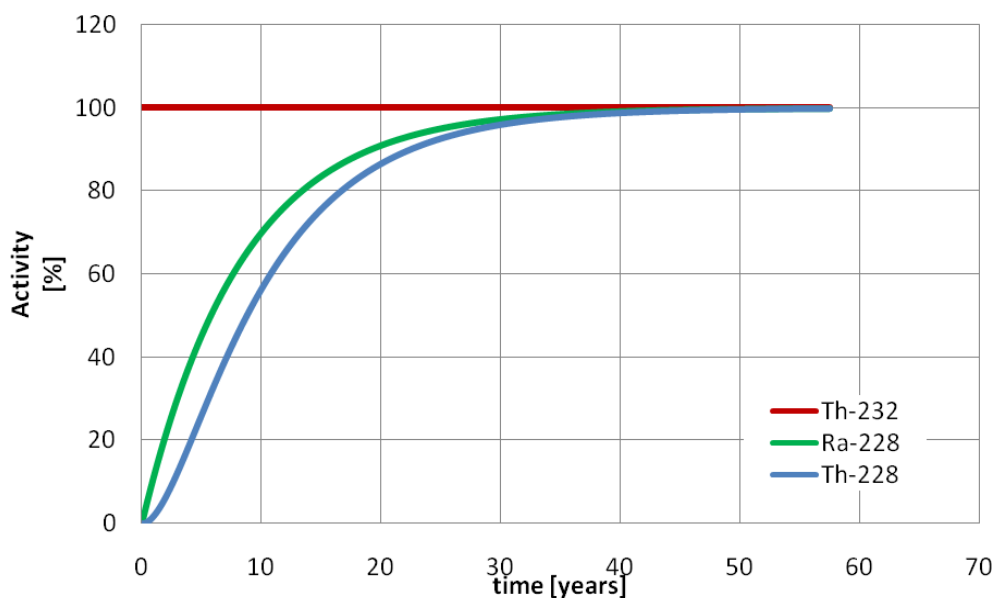


Fig. 3. Projected changes in the activity of  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  (with 7 short-lived decay products) related to radioactive decay [Kovler et al., 2017]

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

- $^{228}\text{Ra} \rightarrow ^{228}\text{Ac}$
- $^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow$  short-lived decay products ( $^{220}\text{Rn}$ ,  $^{216}\text{Po}$ ,  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{212}\text{Po}$ ,  $^{208}\text{Tl}$ )

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

It should be mentioned that a third sub-series starting from  $^{224}\text{Ra}$  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  $^{224}\text{Ra}$  and its decay product with the longest half-life ( $^{212}\text{Pb}$ ), the secular equilibrium in the sub-chain starting from  $^{224}\text{Ra}$  is reached in about two days (tab. 4). Hence, one can assume that in all cases the samples of natural origin (to some extend also in all samples measured more than two days after sampling), the  $^{208}\text{Tl}$  activity concentration reflects actually the activity concentration of  $^{224}\text{Ra}$ . However, taking into consideration that any process resulting in  $^{228}\text{Ra}$  isolation will isolate  $^{224}\text{Ra}$  as well during the next 30 days after  $^{228}\text{Ra}$  sub-chain isolation, the concentration of  $^{224}\text{Ra}$  (as measured from  $^{208}\text{Tl}$ ) does not reflect the concentration of  $^{228}\text{Th}$ . During this period, unsupported  $^{224}\text{Ra}$  i.e. accumulated simultaneously together with  $^{228}\text{Ra}$ , is decaying and total  $^{224}\text{Ra}$  activity must be calculated according to equation (2). After this period only the fraction of this radionuclide created due to decay of  $^{228}\text{Th}$  remains in the material and activity of  $^{224}\text{Ra}$  reflects exactly activity of  $^{228}\text{Th}$ . This is important only when a sample has undergone chemical treatment just before measurement (e.g. radium co-precipitation before liquid scintillation counting [Chalupnik

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.

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

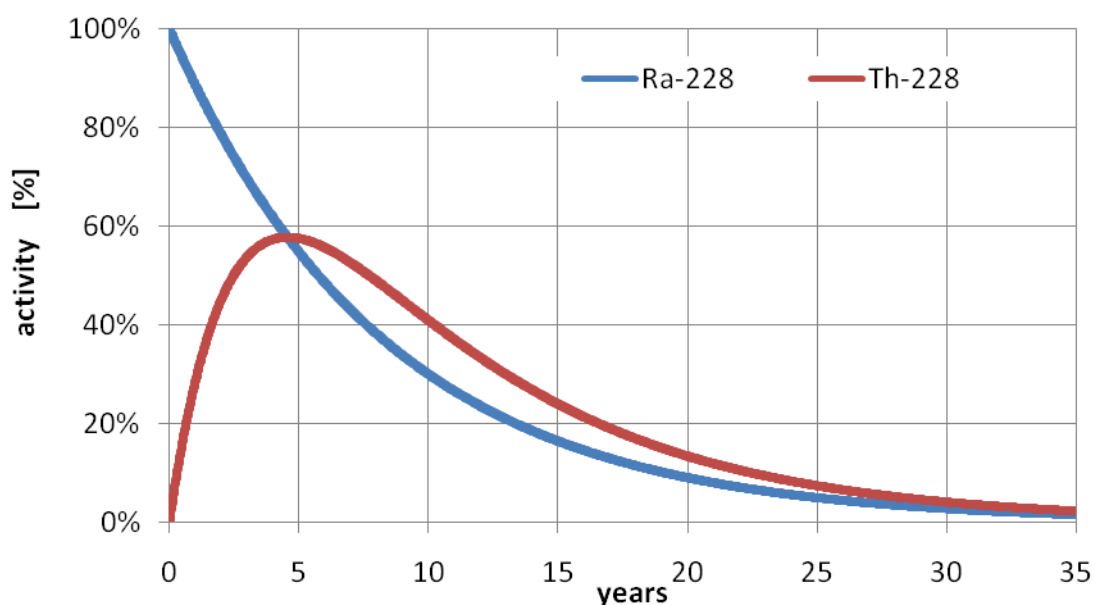


Fig. 4. Projected changes in the activity of  $^{228}\text{Ra}$  (+ $^{228}\text{Ac}$ ) and thorium  $^{228}\text{Th}$  (with 7 short-lived decay products) related to radioactive decay [Kovler et al, 2017]

### 3. Measurements

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

#### 3.1. Radium in uranium series

The formula for calculating the  $I$  index (1) needs the activity concentration of  $^{226}\text{Ra}$ . Methods for the determination of  $^{226}\text{Ra}$  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  $^{226}\text{Ra}$  photopeak (186 keV) or an indirect measurement using the gamma emissions from  $^{226}\text{Ra}$  progeny (see table 1).

The advantage of the direct measurement method is that the sample can be prepared and measured immediately without the need for progeny ingrowth. The disadvantages relate primarily to the emission probability of this gamma photopeak (3.28 %) and the presence of the interfering primary gamma emission of  $^{235}\text{U}$  at 185.7 keV which has a higher photon emission probability (57.24 %). While  $^{235}\text{U}$  is generally present at a much lower activity concentration than  $^{226}\text{Ra}$  in environmental samples, it has an effective photon emission of  $\sim 2.6$  % at this energy (assuming a natural U isotopic distribution). The energy resolution of currently available HPGe spectrometers is generally considered insufficient to separate the two peaks. Hence, quantification of  $^{226}\text{Ra}$  via the 186 keV gamma line must be conducted by attempting to quantify the contribution of  $^{235}\text{U}$  to the doublet peak [Dowdall et al., 2004]. This problem is easily solved when uranium is not present at all or if the activity of radium is equal to that of uranium<sup>1</sup>. All intermediate states of disequilibrium between uranium and  $^{226}\text{Ra}$  need additional information either on the uranium or radium concentration if the activity of both radionuclides is to be measured simultaneously (or the standard samples used for a spectrometer calibration reflect the uranium/radium ratio in the measured sample, what, in practice is impossible).

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

The isotope  $^{235}\text{U}$  may be measured via a low-intensity gamma line (143.8 keV) with an emission probability of 11.0 %. But when one considers the very low isotopic abundance of  $^{235}\text{U}$  in natural uranium, a relatively high concentration of uranium is needed to obtain reliable results using this approach (i.e. especially if  $^{235}\text{U}$  is to be measured with a low uncertainty). Alternatively,  $^{238}\text{U}$  can be detected by gamma spectrometry using a gamma line emitted by  $^{234\text{m}}\text{Pa}$ ; however, this line has very low emission probability (0.84%) and again, when the uranium activity concentration is low, this photopeak may not be measurable with a good enough uncertainty. In both cases the concentration of uranium should be of the order of  $100 \text{ Bq kg}^{-1}$  if reliable results are to be obtained in a reasonable count time. Such quite high content of radioactivity is not common in building materials. A final option for a uranium assay by gamma spectrometry is to use the  $^{234}\text{Th}$  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 effects (e.g. including self-attenuation) need to be considered when conducting such measurements. Additionally, it needs to be considered that the  $^{232}\text{Th}$  line at 63,81 keV, even if it has a very low 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  $^{226}\text{Ra}$  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  $^{226}\text{Ra}$  measurement using progeny radionuclides is commonly applied. The determination of  $^{226}\text{Ra}$  in environmental samples by gamma spectrometry has long been based on the detection of emissions of the  $^{222}\text{Rn}$  progeny (i.e.  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  after an ingrowth period of at least 20 days, during which the sample has to be hermetically sealed to ensure secular equilibrium between  $^{226}\text{Ra}$  and its progeny). The main drawback of this approach is the long 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 interfering effects associated with the loss of secular equilibrium between the  $^{226}\text{Ra}$  parent and progeny radionuclides due to  $^{222}\text{Rn}$  exhalation, it is important that the seal of the sample container used for gamma spectrometry is 'gas tight', and that the sample container itself is not permeable to 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 [Mauring and Gäfvert, 2013]. For small volume crystalline samples, such as co-precipitated radium (e.g.  $\text{Ba}(\text{Ra})\text{SO}_4$ ),  $^{222}\text{Rn}$  emanation from the crystalline lattice is limited and therefore the sample



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

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

Following the measurement of the  $^{226}\text{Ra}$  activity, the uranium content may be calculated, if necessary.

### 3.2. Thorium and radium in thorium series

Direct measurement of  $^{232}\text{Th}$  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  $^{232}\text{Th}$  by the first decay product  $^{228}\text{Ra}$ .

The radionuclide  $^{228}\text{Ra}$  is measured indirectly through its progeny,  $^{228}\text{Ac}$ . Due to the ratio of the half-lives of  $^{228}\text{Ra}$  and  $^{228}\text{Ac}$ , they are almost immediately (when considered from a perspective of typical environmental conditions) in secular equilibrium. It is common practice to make this assumption for the measurement of building materials samples. The radionuclide  $^{228}\text{Ac}$  has few gamma lines with high energy and emission probabilities; generally, the 911 keV gamma line is used for  $^{228}\text{Ra}$  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  $^{228}\text{Ra}$  as well as all its decay products, including  $^{228}\text{Th}$  can be evaluated based on the measurement of the 2614 keV photopeak of  $^{208}\text{Tl}$ . Such situation is, however, quite rare in natural samples, and usually for 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  $^{224}\text{Ra}$  and  $^{228}\text{Th}$ , and then  $^{228}\text{Th}$  and  $^{228}\text{Ra}$ .

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

Radon isotope -  $^{220}\text{Rn}$ , 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  $^{224}\text{Ra}$  decay products measurement results.

Notwithstanding this, when using  $^{208}\text{Tl}$  for assessment of its parent radionuclides concentration it is crucial to remember that only 36% of  $^{212}\text{Bi}$  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  $^{228}\text{Ra}$  decay sub-series, directly measured  $^{228}\text{Ac}$  reflects  $^{228}\text{Ra}$  whereas  $^{208}\text{Tl}$  (and other  $^{220}\text{Rn}$  progeny, e.g.  $^{212}\text{Pb}$  and  $^{212}\text{Bi}$ ) reflect  $^{228}\text{Th}$ . All these decay products have easily detectable non-conflicting photopeaks. When a disequilibrium between these two radionuclides is measured, one cannot determine the  $^{232}\text{Th}$  concentration by the gamma spectrometry technique. Alpha spectrometry or chemical analysis (mass spectrometry) must be applied in such a case in order to get proper information about activity concentration of this radionuclide. This is not required when the measured activity of  $^{228}\text{Th}$  is bigger than  $^{228}\text{Ra}$ . Assuming that there are no other reasons for the observed phenomenon than radioactive decay (e.g. mixing of different materials containing different radionuclides) one can be sure that in this case no  $^{232}\text{Th}$  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  $^{228}\text{Ra}$  half-life and actual  $^{228}\text{Ra}/^{228}\text{Th}$  ratio (fig. 4). Additional information regarding the origin and history of the tested material would help considerably to interpret measurements results showing a disequilibrium between  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ . Deriving relationships between the measured  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$  and  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  (which are usually occur together) activities which originate from the decay law can be formulated to obtain a best

estimate of the  $^{232}\text{Th}$  concentration. However, this calculation requires so many assumptions that results obtained in this way are questionable at best. It any way needs to be considered for the sub-chain starting with unsupported  $^{228}\text{Ra}$ , the ratio of  $^{228}\text{Ra}$  to its long-lived decay product,  $^{228}\text{Th}$ , is changing significantly during the few years following sub-chain isolation (see Figure 2 and 4). This leads to significant difficulties when material in which such a phenomenon is observed is subject to 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

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

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

	measurement beaker								
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## 422 4. Conclusions

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

430 In particular, the decay of  $^{228}\text{Ra}$  leading to the formation of  $^{228}\text{Th}$ , occurring relatively rapidly can have  
 431 a significant effect on the level of effective dose with no regard to the actual  $^{232}\text{Th}$  activity  
 432 concentration. The test results from many building materials indicate that due to  $^{210}\text{Pb}$ 's long half-life  
 433 the activity of this isotope often differs from the activity of  $^{226}\text{Ra}$ . However, from a dose perspective  
 434  $^{210}\text{Pb}$  activity concentration over/under estimation is not as profound as for  $^{228}\text{Th}$ . Apart from the  
 435 effects on the / index quality, for proper assessment of  $^{226}\text{Ra}$  also information concerning uranium is  
 436 useful and the actual concentration of radon is extremely important.

437 As a consequence, for an accurate determination of the / index, the following radionuclides are of  
 438 importance in addition to the directly used for calculation radionuclides:

- 439 • from uranium-radium decay chain:  $^{238}\text{U}$ ,  $^{222}\text{Rn}$ ,  $^{210}\text{Pb}$ ,
- 440 • from thorium decay chain:  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$ ,
- 441 • (from actinium decay chain:  $^{235}\text{U}$ ,  $^{231}\text{Pa}$ )

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443 The actinium decay chain is put into parentheses because generally it cannot be expected to have a  
 444 deviation in the uranium isotopes (  $^{238}\text{U}$  and  $^{235}\text{U}$  ) ratio in building materials. The concentration of

$^{235}\text{U}$  in natural uranium is only 0.7% which means normally no radiological impact in case of building materials. However,  $^{235}\text{U}$  is a gamma emitter that disturb the direct  $^{226}\text{Ra}$  measurement hence it is useful to know (from somewhere else) its activity concentration and actual ratio between  $^{238}\text{U}$  and  $^{235}\text{U}$

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

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

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

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