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Naturally Occurring Radioactive Materials in Construction

Integrating Radiation Protection in Reuse (COST Action Tu1301 NORM4BUILDING)

Edited by Wouter Schroeyers

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Dr. Harry Friedmann was born 1949 in Vienna and studied physics and mathematics at the University of Vienna (http://homepage.univie.ac.at/harry.friedmann/). He received his PhD (PhD "sub auspiciis praesidentis") in 1975 with a thesis in nuclear physics. He had a fruitful career as a scientist at the University of Vienna. He was Nuclear Physics group leader in 2008 and retired from University in 2015 but is still giving lectures and participating in research projects. His main research interests are Nuclear reactions, natural radioactivity and related software development.

Dr. Tibor Kovács is the Head of Institute of Radiochemistry and Radioecology at the University of Pannonia. His research activities include nuclear measurements, radon emanation capability of soil, water, construction materials, and industrial by-products, inspecting radionuclide concentration in NORM, TENORM materials. He has several years of experience in the fields of nuclear accident prevention, radioactive waste management, and placement. He has more than 100 papers published in high-impact journals and is the editor of several journals including "Scientific Reports," "Radiation Emergency Medicine."

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Dr. Hans van der Sloot has been a private consultant since 2010 after retiring from ECN (Petten, The Netherlands). He is involved in standardization of leaching tests for waste, soil, and construction products at national and international level (CEN, ISO, US EPA). van der Sloot is the associate editor for *Waste Management*. He is involved in environmental studies on alternative materials in cement production and soil amendment, hazardous and nuclear waste characterization for treatment and disposal. He is the codeveloper of LeachXS with ECN and Vanderbilt University (Nashville, United States).

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The COST Action NORM4Building

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Guide for the reader: Situating chapter "1":

Chapter 1 introduces the aims of the COST network NORM4Building. The experts from the COST network have created this book that deals with the use of NORM residues in construction.

Chapters 2 and 3 give an introduction to, respectively, the terminology and relevant parameters to be controlled when considering the use of NORM residues in construction.

In the following chapters the legislative aspects (Chapter 4) and relevant measurement protocols (Chapter 5) are discussed.

Chapters 6 and 7 deal with the properties of NORM residues and their use in construction materials.

Chapters 8 and 9 discuss leaching and nontechnical properties of the considered construction materials. Finally, Chapter 10 gives a general conclusion and outlook.

Naturally occurring radionuclides are present in the earth's crust and in the minerals and ores that are then used by industry. Throughout industrial processes naturally occurring radionuclides can become concentrated in by-products, such as fly ash produced in large quantities from coal burning, slags from steelworks and metal recycling industries, phosphogypsum of the phosphate industry and red mud of the aluminum processing industry. Depending of the activity concentration some of these by-products can be considered as naturally occurring radioactive materials (NORM).

When by-products are investigated for use in construction materials then many factors have to be evaluated, taking into account the presence of trace elements, such as metals and naturally occurring radionuclides. The study of safe use of by-products in construction requires the involvement of experts from many different fields (construction and chemical engineering, environmental sciences, natural radioactivity, economics, etc.). The COST Action NORM4Building brings together a large variety of experts with different backgrounds in order to handle this type of multidisciplinary research. In total the NORM4Building network currently (Jan. 2017) comprises more than 120 researchers, covering very different fields, from 30 different European countries plus the United States.

The main objective of the COST Action Tu1301 "NORM4Building" is the exchange of multidisciplinary knowledge and experience (radiological, technical, economical, legislative, and ecological) to investigate and evaluate the use of by-products, from industries that encounter NORM in their industrial processes, in construction. An important focus of this book is the radiological evaluation of the use of by-products in new types of construction materials that are currently under research. There are many factors (technical, chemical, economic, etc.) that determine

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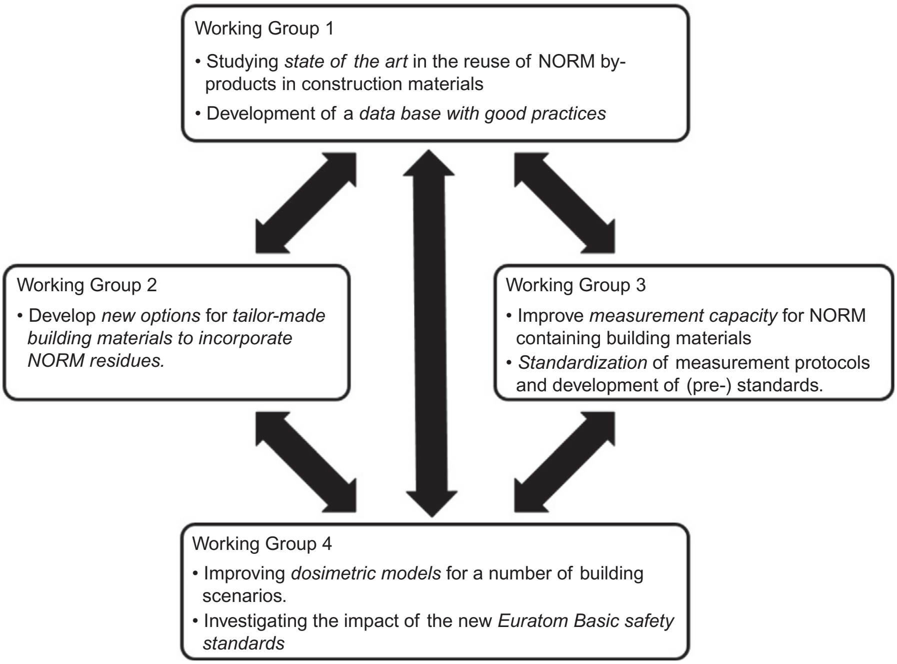

Fig. 1.1 Aims of the four working groups of the NORM4Building network.

if a by-product is actually going to be used in construction materials and these different factors are discussed throughout this book.

The COST network consists of four working groups and the aims of each working group are shown in Fig. 1.1. The central aims of the COST network are reflected in the content and the structure of this book.

The NORM4Building network develops strategies for the use of NORM residues in ceramics, concrete, and cement with a focus on the use of NORM residues in emerging building materials such as alkali-activated materials (i.e., inorganic polymers).

Working group 1 of the COST Action has developed the NORM4Building database with radiological information on raw materials, by-products, and construction materials. The data present in the database are discussed in more detail in Chapters 6 and 7.

Working group 2 provided a more in-depth discussion on the properties of the by-products that can enable or hinder the use in construction materials (Chapter 7).

Working group 3 investigates industrially useful measurement methodologies and protocols for the determination of the activity concentration of naturally occurring radionuclides in construction materials. More information on the relevant measurement methodologies can be found in Chapter 5. Working group 3 also organized intercomparisons between institutes using different measurement protocols and instruments.

Working group 4 develops new research on computational methodologies—room models to evaluate and predict indoor gamma dose rates and indoor radon concentrations on the basis of the activity concentration. The basis for the radiological evaluation of building materials is the new Council Directive 2013/59/EURATOM, laying down basic safety standards for protection against the dangers arising from exposure to ionizing radiation. The legislative aspects and room models used for the evaluation are discussed in Chapter 4. In addition, working group 4 considers the leaching aspects of naturally occurring radionuclides from construction materials to evaluate the end of life of NORM containing construction materials and these aspects are covered in Chapter 8.

The fact that this book is produced by experts from completely different fields is reflected in the contents of the different chapters. For example, Chapter 6 deals both with technical and radiological properties of the by-products. Chapter 7 links construction engineering with radiation protection in order to arrive at a realistic approach to the technical, chemical, and radiological evaluation of the use of the considered by-products in construction. Chapter 8 applies the know-how on leaching of metals to naturally occurring radionuclides. Chapter 9 involves many nontechnical aspects (such as marketing and cost-related aspects) in the discussion. This book was created by scientists in close collaboration with representatives from legislative authorities and industry who helped to assure the accuracy of the legislative aspects discussed in this book and to assure that the discussion (also the discussion on the nontechnical aspects) is industrially relevant.

The COST Action NORM4Building has prompted a lot of research in a field where information was lacking to assure that aspects regarding natural radioactivity are taking into consideration for new residue-based construction materials before they are introduced in the market. More information regarding the COST Action, its participants and the current status of the ongoing research, can be found at http://norm4building.org/.

Introduction

2

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Guide for the reader: Situating chapter "2":

Chapter 2 gives an introduction that focuses on finding the appropriate terminology to discuss the use of naturally occurring radioactive materials (NORM) in construction.

The main radiological parameters to be controlled in NORM and NORM containing building materials are discussed in Chapter 3. An in-depth discussion on the legislative aspects regarding natural radioactivity from building materials is given in Chapter 4. The methods for radiological characterization of construction materials are discussed extensively in Chapter 5.

The technical, chemical, and radiological properties of NORM by-products are considered in Chapter 6 with a focus on by-products that can be used in construction. Several applications of the considered NORM by-products in construction materials (cement, concrete, ceramics, and gypsum) are discussed in more detail in Chapter 7. In Chapter 8, an environmental leaching assessment of NORM containing construction materials is given. Nontechnical aspects that determine the reuse of NORM by-products are discussed in Chapter 9. Finally, Chapter 10 gives a general conclusion and outlook.

The depletion of energy resources and primary raw materials leads to the search for alternative pathways to produce construction materials. In the development of new synthetic construction materials, the use of by-products from several industrial sectors becomes more and more a necessity especially in a resource-poor continent such as Europe. By-products, such as slag and bottom ash from coal-fired power plants; unprocessed slag from primary iron production; lead, copper, and tin slags from primary and secondary production; and bauxite residue (red mud) from aluminum production, have interesting properties for use in construction but can in some cases, depending on the activity concentration, be considered as naturally occurring radioactive materials (NORM).

These by-products can be used in cement as alternative raw materials and supplementary cementitious materials (SCMs) or, in the case of by-products with a high caloric value, they can be introduced as an alternative fuel, the remaining ash being typically incorporated in the cement clinker (Guidelines on Co-processing Waste Materials in Cement Production, 2006; Hasanbeigi et al., 2012). In concrete several of these by-products are used or studied for use in increased amounts as SCMs (as partial cement replacement or as mineral additions in concrete) and as aggregates for concrete (Siddique and Khan, 2011). In ceramics, various types of metal slags were used, or investigated for use, as aggregates in for example clay-based ceramics (Pontikes and Angelopoulos, 2009). Alternatively, other types of by-products such as bauxite residue can be used in the bond system of clay ceramics (Pontikes and

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Angelopoulos, 2009). An emerging field in the construction industry is the development of alkali-activated materials (AAMs). The AAMs can contain calcium silicate or a more aluminosilicate-rich precursor, such as a metallurgical slag, natural pozzolan, fly ash or bottom ash as solid aluminosilicate source (Shi et al., 2006).

The terminology used to label a given material can inhibit or stimulate its application. Using the label “waste” for a given material creates the perception that these materials do not fit any application. Once a material is labeled as a “waste,” then reuse will not be easily accepted any more, both from a public and from a legislative perspective. The IAEA uses in its safety glossary as definition for waste “a material for which no further use is foreseen” (IAEA safety glossary, 2007). By this definition, once an application acceptable from a safety, societal, and engineering point of view is developed, then the material should not be considered (any more) as a waste. Since this book deals with the potential use of materials in construction, the term “waste” will not be further used unless justified from a legislative or safety perspective.

A common misperception, by the general public, is that primary raw materials are considered as “pure” and secondary raw materials as “impure.” The terms “pure” or “impure” should not be used due to the connotation of these terms but what is meant here is that the perception exists that secondary raw materials, when compared with primary raw materials, contain significantly more trace elements that can make them undesired for use in construction materials. When looking from a chemical, mineralogical point of view and comparing primary and secondary raw materials, with suitable properties for construction materials, then the presence of trace elements is strongly dependent on the type of primary raw material (e.g., limestone, clay, marl, or sand) or secondary raw material (e.g., blast-furnace slag, coal fly ash) that is used. It is not necessary true that secondary raw materials contain a higher concentration of trace elements compared with primary raw materials (Table 2.1). When comparing the average composition of clay, one of the oldest building materials on the Earth, to that of blast-furnace slag then it is clear from Table 2.1 that the concentration of trace elements such as As, Co, Cr, Cu, Ni, Pb, V, Zn can be higher in clay.

In addition to the considered chemical trace elements, all materials (ores, minerals) that are extracted from the Earth’s crust contain concentrations of natural occurring radionuclides (NOR) that are, due to their long decay times, already present since the birth of the Earth. Since radioactivity is present everywhere there is a need to define what is considered as a radioactive material. One definition used by the IAEA Safety Glossary for a radioactive material is “Material designated in national law or by a *regulatory body* as being subject to *regulatory control* because of its *radioactivity*.” The IAEA Safety Glossary defines NORM as a “Radioactive material containing no significant amounts of radionuclides other than naturally occurring radionuclides” where the exact definition of “significant amounts of naturally occurring radionuclides” would be a regulatory decision. In the IAEA glossary, NORM residue is defined as a “Material that remains from a process and comprises or is contaminated by NORM” and NORM waste is defined as “NORM for which no further use is foreseen” (IAEA safety glossary, 2007).

To establish what is NORM and what is not, the IAEA and Euratom Basic Safety Standards (IAEA- and EU-BSS) have selected a list of industrial sectors of concern (ANNEX VI of the Council Directive 2013/59/EURATOM, 2014). For these

Table 2.1 Average values (AV) of selected input materials that can be used in cement or concrete (Achternbosch et al., 2005)

Data in ppm		As	Cd	Co	Cr	Cu	Ni	Pb	Sb	Sn	V	Zn
Limestone	AV	3	0.2	3	14	11	18	18	1	4	26	30
Clay	AV	14	0.2	20	85	43	63	25	2	5	130	78
Marl	AV	6	0.3	5	28	12	16	12	4	3	20	48
Sand	AV	11	0.2	11	19	10	13	10	7	3	50	25
Iron works waste	xMin[a]	74	29	149	600	1076	254	481	10	81	229	2262
Iron ore	AV	37	6	144	495	1520	331	350	26	25	256	3288
Foundry sand	AV	3	0.3	90	290	28	92	62	0.8	40	150	75
Hard coal	AV	9	1.0	9	14	18	23	27	1	4	39	63
Brown coal	AV	0.8	0.2	1	3.6	1.8	3	3	0.8	4	10	10
Oil coke	AV	0.5	1	2.5	4.3	2.4	263	13	0.6	0.3	758	16
Used tyres	AV	1.6	7	30	137	68	90	125	136	15	19	6100
Waste oil	AV	2.4	0.8	1	12	51	20	151	1	6	2	700
Scrap wood	AV	3.4	1.2	10	27	24	13	222	8	6	3	440
MCIW fuel	AV	3	2.5	4	51	138	25	74	25	20	7	331
Blast-furnace slag	AV	0.8	0.7	4	25	5.2	5	6	2	5	30	38
Coal fly ash	AV	79	2.6	74	172	247	196	257	14	10	345	504

AV, average; *MCIW*, fuel, fractions from municipal, commercial, and industrial wastes.

[a] Average minimum values (xMin) were used (see Achternbosch et al., 2005).

Table 2.2 **Conversion of 1 kBq/kg to ppm**

Radionuclide	Activity concentration (kBq/kg)	Concentration (ppm)
^{238}U	1	81
^{232}Th	1	246
^{40}K	1	32,300

"industrial sectors involving NORM" the IAEA- and EU-BSS have defined an activity concentration of 1 kBq/kg of ^{238}U, ^{232}Th (or any of their decay products) and an activity concentration of 10 kBq/kg of ^{40}K as significant concentrations of these NOR. In other words, only if an activity concentration of more than 1 kBq/kg of ^{238}U, ^{232}Th (or any of their decay products) or more than 10 kBq/kg of ^{40}K is measured for a specific type of material from the industries mentioned in ANNEX VI, then this can be considered as NORM according to the EU- and IAEA-BSS (IAEA, 2014) and Council Directive 2013/59/EURATOM (2014). It is important to keep in mind that 1 kBq/kg of a given radionuclide represents a relatively low concentration (generally expressed in ppm) as is illustrated in Table 2.2 and that in many cases only radiological methods are sensitive enough to determine the activity concentration of several materials. Considering these aspects then a "NORM residue" is a material that remains from a process, which contains more than 1 kBq/kg of ^{238}U, ^{232}Th (or any of their decay products) or more than 10 kBq/kg of ^{40}K.

Modern production processes can be designed in such a way that no materials, or at least no large quantities of materials, remain any more after production. In such a production process all the output streams, or at least all output streams that contain large quantities of materials, are used. In this case, from a chemical point of view, all materials coming out of the process can be considered as the "product" of the reaction/production. From a (simplified) process technical point of view incoming materials can be considered as reagents and outgoing materials as (by-)products. In this terminology even filter dust or other materials that are the result of several emission control steps can be considered as a (by-)product. The term "product" has an economic connotation that indicates a material that can be sold. Modern processes are often designed in such a way with the intention to sell all products depending on the conditions on the market. Considering this discussion than the term "NORM residue" is not suitable in many situation and we could introduce the term "NORM by-product" meaning a by-product from an industrial process, which contains more than 1 kBq/kg of ^{238}U, ^{232}Th (or any of their decay products) or more than 10 kBq/kg of ^{40}K.

In this book both the terms "NORM by-product," which seems to be the most appropriate term, and "NORM residue," since it is formally defined in the IAEA glossary, are used. The term "NORM residue" can be in particular appropriate to also cover residues that remain from legacy sites. It can also be noted that if industrial processes are designed taking into account the NORM aspects that the term "NORM by-product" could in the future only apply to lower quantities of materials.

The term "NORM industries" will not be used in this book. There are no industries that "willingly" produce NORM, there are, however, industries that produce steel, metals, fertilizer, etc. In this book the terms "NORM processing industries" and "industries invoking NORM" will be used instead but the reader should keep in mind that most of the by-products produced in these industrial sectors are not NORM.

In addition to the NORM-related regulation, the EU-BSS requires the control of selected natural building materials and building materials "incorporating residues from industries processing naturally occurring radioactive material" (listed in annex XIII). For building materials, a reference level of 1 mSv per year is set for indoor external exposure to gamma radiation emitted by building materials, in addition to outdoor external exposure (Council Directive 2013/59/EURATOM, 2014). A term that will be used in this book is "NORM containing building materials," however, as noted earlier many of the by-products that are discussed are not necessarily NORM. This book focuses on NOR that enter the construction materials via the by-products and not specifically on natural building materials.

Regarding the terms "building materials" and "construction materials," the book uses both of them. The term "construction" in civil engineering includes a broader perspective than "buildings." A building is normally some structure used to enclose a space. Construction works is a term that is more general and includes construction of buildings, bridges, roads, railways, harbors, etc. It means that the term "construction materials" is valid not only for materials used in construction of buildings, but also for those used in other types of structures.

The purpose of setting controls on the radioactivity of building materials is to limit the radiation exposure due to materials with enhanced or elevated levels of natural radionuclides. The average annual exposure duration of the building occupants to natural ionizing radiation is 7000 h, while the exposure of the public to radiation from construction materials applied in other types of structures, such as tunnels, bridges, etc., is significantly shorter. Therefore, from the radiological perspective, the construction materials, which are used in building construction, are the focus of the discussion in the book chapters.

Finally, one more remark should be made on the differences between "materials" and "products," and between "materials" and their "constituents." The term "building materials" usually includes both "materials," which are produced and sold, but still do not have a final properties and shape as finished products, and "building products" (or "construction products"), which do have a well-defined geometry and properties (density, strength, thermal and acoustic insulation, etc.). "Construction product" means any product or kit which is produced and placed on the market for incorporation in a permanent manner in construction works or parts thereof and the performance of which has an effect on the performance of the construction works with respect to the basic requirements for construction works (Regulation (EU) No. 305/2011 of the European Parliament and of the Council, 2011).

The examples of building materials of the first type, which are called sometimes as "constituents" of building materials, are cement and concrete aggregates, while concrete, bricks, and tiles serve as examples of building materials of the second type, which are called as "construction products."

The legislation regulating radiation protection usually addresses "building materials" as a specific case of "construction products" and makes no distinction between "materials" and "products." For example, Council Directive 2013/59/EURATOM (2014) states that "building materials emitting radiation should be also regarded as construction products as defined in Regulation (EU) No. 305/2011, in the sense that the Regulation applies to construction works emitting dangerous substances or dangerous radiation." At the same time, there is a clear division in the norms between building materials of the first type (sometimes called "constituents of building materials") and those of the second type (finished products). For example, Council Directive 2013/59/EURATOM (2014) defines the index relating to the gamma radiation dose, in excess of typical outdoor exposure, in a building constructed from a specified building material, while this index applies to the building material, not to its constituents except when those constituents are building materials themselves and are separately assessed as such. For application of the index to such constituents, in particular, residues from industries processing NORM recycled into building materials, Council Directive 2013/59/EURATOM (2014) requires to apply an appropriate partitioning factor.

It is important to introduce these definitions and the nuances, related to overlapping and differences between the basic terms, that are used throughout the book at the start in order to make reading the book easy and smooth.

The book deals with chemical, technical, and radiological aspects that can influence the use of NORM by-products in building materials:

- First, the main parameters to be controlled are discussed (Chapter 3).
- Second, the legislative aspects are covered (Chapter 4).
- Third, the measurement methods are covered (Chapter 5).
- Then the properties of the by-products themselves are discussed (Chapter 6).
- In the next step construction materials based on NORM by-products are discussed (Chapter 7).
- Consecutively, an environmental leaching assessment of the construction materials is given (Chapter 8).
- Additionally, the nontechnical aspects are evaluated (Chapter 9).
- And finally, the conclusions and outlook are given (Chapter 10).

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Basic aspects of natural radioactivity

3

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Guide for the reader: Structure of chapter "3":

This chapter gives a basic introduction regarding radioactivity (Section 3.1), Naturally Occurring Radioactive Materials (NORMs) (Section 3.2), and the interaction of radiation with matter and the relevant doses and units (Section 3.3). An overview of the main natural sources for internal and external exposure is given in Section 3.4.

Section 3.5 gives a more in depth discussion of the principal radiation characteristics of NORM focusing on the properties of the individual radionuclides (^{238}U and ^{232}Th and their decay products and ^{40}K). This section deals with the activity concentration of the natural occurring radionuclides and with the concepts of radon emanation and exhalation.

3.1 Radioactivity

Radioactivity is a process by which nuclides spontaneously decay by the emission of radiation. The radiation consists of particles (α- and β-radiation) that in most cases are accompanied by electromagnetic waves (γ-radiation and X-rays). In the decay process, the so-called *parent nuclide* transforms to a nucleus of a different type, named the *daughter nuclide*. Thus a change in the chemical element occurs or an isotope is created according to the decay type. The SI derived unit of radioactivity is Becquerel (symbol Bq), which is defined as the activity of a quantity of radioactive material, in which one nucleus decays per second. The old unit is Curie (symbol Ci), which is still used in some countries (e.g., the United States). The conversion is $1\ \mathrm{Ci} = 3.7 \times 10^{10}$ Bq.

The energy of the emitted radiation is sufficient to ionize atoms by stripping electrons along the path of the radiation. This process occurs via either direct (α- and β-radiation) or indirect (γ- and X-rays).

Alpha (α-) radiation consists of α-particles containing 2 protons and 2 neutrons and it is identical to an ionized ^{4}He nuclei. An α-particle has a relatively big mass and twice elementary positive electric charge, hence has low penetrating power. Its path in biological tissues is no longer than a few tens of micrometers. Alpha radiation is densely ionizing, i.e., the number of produced ions per unit length, in the matter it travels

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through, is higher compared with other types of radiation. The reason for this is that the particles shed all their energy over a short distance. Alpha emitters are primarily responsible for internal exposure, which includes inhalation, ingestion, and skin contact.

Beta (β-) *radiation* is made up of β-particles that are electrons, with a negative elementary charge, or not so often, positrons both with positive elementary electric charge. The mass of an electron is significantly lower than an α-particle (about 8000 times), hence β-radiation has moderate penetrating power. Finally, exposure to beta particles will cause more external irradiation hazard and less internal radiation hazard than alpha particles. The external irradiation brought by beta particles is mostly confined to the epidermis and outer skin tissue but it can also have a harmful impact on the eye lens.

Gamma (γ-) *radiation* is composed of high-energy photons (electromagnetic waves) coming from the nucleus. This type of radiation is only weakly ionizing but has a high penetrating power and can travel through hundreds of meters of air. Usually, thick concrete or lead shielding is used to shield γ-radiation. It is primarily responsible for external exposure. As far as internal radiation exposure is concerned, the high penetrating power means that the energy released by gamma rays and taken up by a small volume of tissue is comparatively smaller relative to alpha and beta radiation. Therefore, the internal radiation exposure hazard caused by gamma rays is not as severe as that induced by other types of radiation (alpha and beta).

X-rays are also electromagnetic waves but emitted from the atomic shell. In general their energy is lower than the energy of the γ-radiation. As a result of the emission of α- and β-radiation or γ-radiation (with conversion electrons) the emitting nuclide often becomes ionized and in consequence also X-rays are released.

The probability for a radioactive decay is a constant for a certain nuclide. That means that the activity of nuclide (A), which expresses the number of decays per unit time, is proportional to the number of atoms or nucleus (N) of these nuclides. The proportional constant λ is called the decay constant.

$$A = \lambda N \tag{3.1}$$

Because every decay reduces the number of atoms of radioactive nuclides, the equation

$$A = -\frac{dN}{dt} \tag{3.2}$$

holds and the solution of the differential equation obtained from the combination of Eqs. (3.1) and (3.2) gives the well-known exponential decay law

$$A = A_o e^{-\lambda t} \quad \text{or} \quad N = N_o e^{-\lambda t} \tag{3.3}$$

with A_o or N_o the nuclide activity or the number of its atoms at the time $t = 0$. From Eq. (3.3) one can easily calculate the time $T_{1/2}$ (half-life time) after which the activity or the number of atoms has halved:

$$T_{1/2} = \frac{\ln 2}{\lambda} \tag{3.4}$$

3.2 Naturally occurring radioactive materials

Naturally occurring radioactive material (NORM) is defined in the IAEA Safety Glossary as a "Radioactive material containing no significant amounts of radionuclides other than *naturally occurring radionuclides* (NOR)" where the exact definition of "significant amounts of naturally occurring radionuclides" would be a regulatory decision.

Considering Eq. (3.4) one could wonder why NOR exist in nature. In principle, there are two possibilities: either the half-life time of the radioactive nuclide is comparable with the age of the Earth (approx. 4.5 billion years) or the radioactive nuclides are continuously created.

Member of the first group is called *primordial radionuclides* and typical representatives are uranium (^{238}U, ^{235}U), thorium (^{232}Th), and the potassium isotope ^{40}K. The decay of ^{238}U, ^{235}U, and ^{232}Th, however, forms again radioactive nuclides (*radiogenic nuclides or radionuclides*) creating chains of radionuclides, which finally end in stable lead isotopes (see Fig. 3.1). Within these chains of radioactive nuclides α-, β-, and γ-radiation can be observed. In contrast to these chains, the ^{40}K radionuclide decays forming the stable isotopes ^{40}Ca and ^{40}Ar.

Another type of radioactive nuclides comprises the *cosmogenic nuclides*. These nuclides are continuously formed mainly in the upper parts of the atmosphere by the interaction of the cosmic radiation with the atoms and molecules of the air. Typical representatives are radiocarbon (^{14}C), tritium (^{3}H), and isotopes of sodium (^{22}Na) and beryllium (^{7}Be).

When dealing with NORM issues, only the primordial natural radionuclides ^{238}U, ^{235}U, ^{232}Th, ^{40}K, and their radioactive progenies are of radiological interest.

Uranium, thorium, and potassium are present everywhere either as main constituents of some rock materials or as trace elements. This means NORM exists nearly everywhere and depending on its amount and use can cause radiological problems. Because of their geo-chemical behavior, some NOR can concentrate in certain minerals. Therefore, some important raw materials contain enhanced concentration of NOR. Processing such materials produces often NORM with higher concentrations of natural radionuclides, which the producer regards only as a waste. However, these materials often show excellent chemical properties for use in other industries sectors. The management or reuse of NORM is linked to some very important challenges:

- It is crucial to avoid waste disposals from where radioactive material can migrate uncontrolled in the environments.
- There is an important need to supply European industries, such as the building industry, with excellent and cheap raw materials.
- For all scenarios of management or reuse of NORM, assuring radiological safety for producers, customers, and end users is a key requirement.

3.3 Radiation physics

3.3.1 Interaction of radiation with matter

Only the interaction of α-, β-, and γ-radiation with material will be discussed here. The radiation of NORM can also cause the formation of neutrons by the interaction of

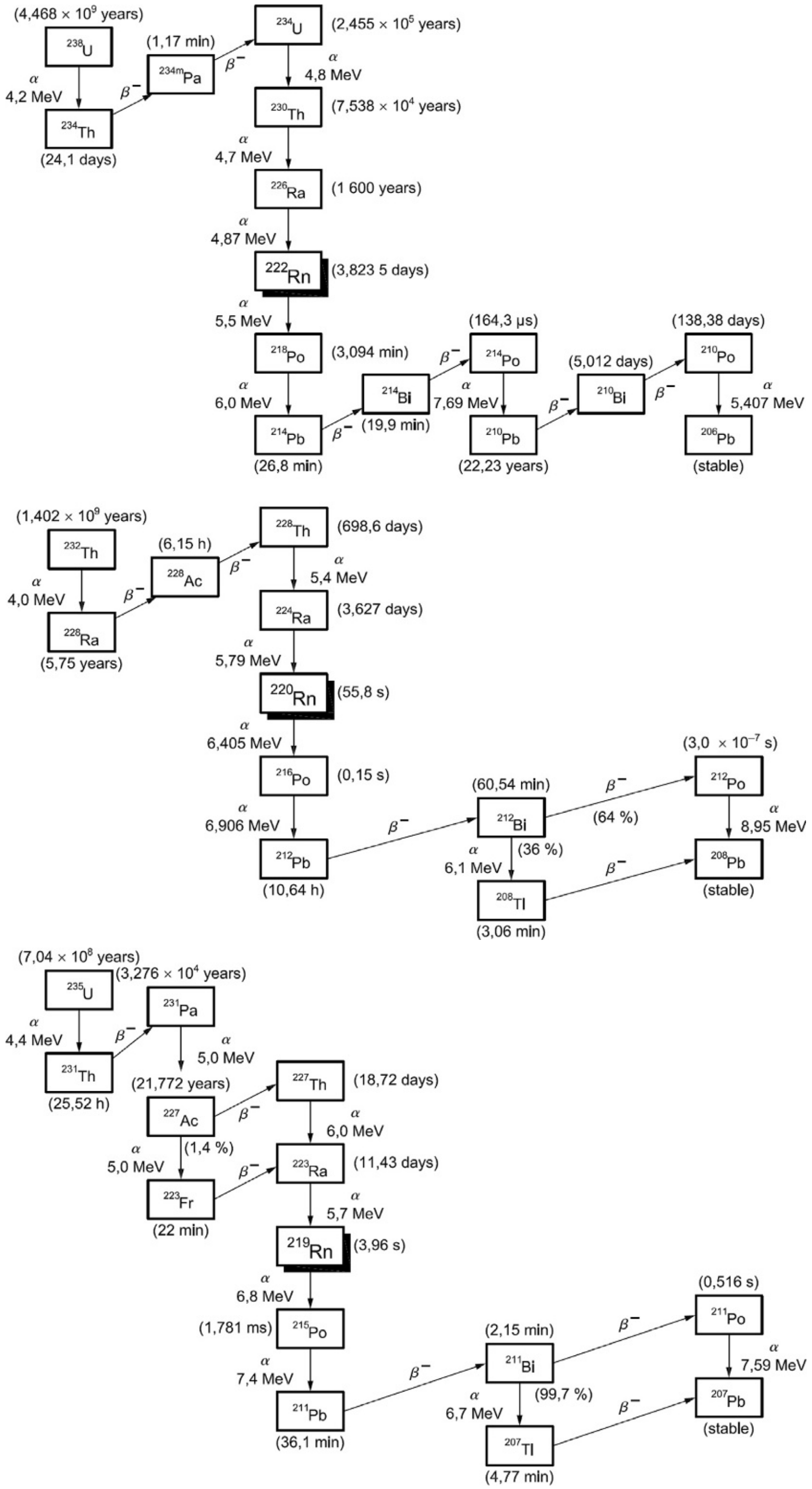

Fig. 3.1 Natural radioactive decay series, starting from ^{238}U, ^{232}Th and from ^{235}U.

α-particles with light elements, which exist in building material; however, this effect can be neglected nearly in all scenarios.

Alpha (α-) radiation is the emission of ^{4}He-nuclides, while β-radiation is the emission of electrons. Contrary to the emission of particles, γ-radiation is the emission of electromagnetic waves.

Particles transfer their energy to the absorbing material mainly by ionization. The Bethe-Bloch formula Eq. (3.5) (simplified version) describes the energy loss of charged particles by ionization (where n is the density of the decelerating particles, M is their mass, v is the velocity of the radiation particle, z is its charge, I is the mean ionization energy, e is the charge unit, ε_o is the electric field constant, $\beta = v/c$).

$$-\frac{dE}{dx} = \frac{4\pi n}{M}\left(\frac{ze^2}{4\pi\varepsilon_o v}\right)^2\left(\ln\left(\frac{2Mv^2}{I\left(1-\beta^2\right)}\right) - \beta^2\right) \tag{3.5}$$

Because the mass of α-particles is much higher than the mass of electrons, the velocity of α-particles is much lower than those of electrons with the same energy. From Eq. (3.5) it is clear that the energy loss per unit length of α-particles is much higher than that of electrons. That means that the range of α-radiation is substantially shorter than that of β-radiation with approximately the same energy. Because the energy loss is mainly due to ionization, α-particles are called *densely ionizing particles* while electrons are *weakly ionizing particles*. The typical range of α-radiation is 1 cm MeV^{-1} in air while in solids and liquids, with a density of approximately 1000 times of that of air, it is in the range of 10 μm MeV^{-1}. One can further deduct from Eq. (3.5) that the energy loss increases at the end of the particle track where the velocity decreases quickly. This effect is the most pronounced for α-particles (Bragg curve). Because α-particles are much heavier than electrons, they are not so much scattered away from their initial direction. Electrons, however, are strongly and multiple times scattered and lose their initial direction fast following more or less a zig-zag track. There is also another essential difference between α-radiation and β-radiation: α-radiation is monoenergetic which means that all α-particles have the same energy at the moment of emission, while β-radiation shows a continuous spectrum from zero to the maximum energy (which is the energy given in the decay schemes). Of course, radionuclides can have different ways of decay (different α- and/or β-decays), but in all cases the α-particles form groups of equal energy, while all the β-spectra superpose each other. These are the reasons why α-radiation shows a well-defined range, while the intensity of β-radiation decreases approximately exponentially with the thickness of the absorbing material.

In the case of electrons, a substantial energy loss can occur by bremsstrahlung too. For energies E up to some MeV and mean proton numbers Z of the absorber, the ionization energy loss is dominant and the ratio can be approximated by

$$\left(\frac{dE}{dx}\right)_{rad} \Big/ \left(\frac{dE}{dx}\right)_{ion} \approx \frac{EZ}{700} \tag{3.6}$$

In contrast to particle radiation, as discussed earlier, γ-radiation interacts quite differently with material. The γ-radiation is electromagnetic radiation, which means photons interact with the material. There are three possible effects: Compton scattering, photoelectric effect, and pair production. Scattering by free or only loosely bound electrons is called Compton scattering. In this case, only a part of the energy of the photon is transferred to the electron. Only when the electron is more strongly bound to a nucleus the energy of the photon can be fully transferred to the electron. This is true because energy and momentum can only be conserved if a part of the momentum is overtaken by the nucleus. This effect is called the *photoelectric effect* and it is the effect, which allows us to determine the energy of the γ-radiation and in consequence the emitting nucleus by γ-spectrometry. Finally, when the energy of the γ-radiation is above 1.022 MeV (twice the energy equivalent of the electron mass), then pair production is possible, which means the photon is converted into an electron and a positron (antielectron). Then the electron and the positron slow down in the material mainly by ionization. When the positron loses its kinetic energy then it annihilates with an electron by creating two 511 keV photons. If these two photons are detected together with the ionization caused by the slowdown of electron and positron, then the whole energy of the primary γ-radiation is deposited within the detector, then a single line will grow in the γ-spectrum. This allows the detection of the whole γ-energy and its emitting nucleus. However, if one of the two 511 keV photons leaves the detector, then another line will be formed 511 keV below the full energy line, which is called single escape line. If both 511 keV photons escape from the detector, the double escape line is formed 1022 keV below the full energy line. The typical high-resolution γ-spectrum can be seen in Chapter 5.

The probabilities for the three different effects depend on the energy of the γ-radiation and the atomic number of the absorbing material.

3.3.2 Radiation doses and units

The deposition of energy in material is called *energy imparted to matter* expressed directly in energy units (J) or *absorbed dose D* where its unit is 1 Gy (Gray), which is 1 J kg^{-1}. The biological effect depends on the type of radiation, which in the field of radiation protection is described by the *radiation weighting factor* w_R set for different kind of radiation and its energy (see Table 3.1). The reason for considering a difference in biological hazard caused by the same absorbed dose of different types of radiation is the ionization density. Radiation with dense ionization, opposed to sparse ionization, produces many more double-stranded DNA breaks which cannot be repaired. For this reason in the field of radiation protection the *equivalent dose H* is used. The *equivalent dose H* is the product of the radiation weighting factor with the absorbed dose *D* and its unit is 1 Sv (Sievert). In the field of radiation protection also the *effective dose E* is used that also considers the relative sensitivity of the irradiated organs. This is done by the *organ/tissue weighting factor* w_T (see Table 3.2). For a whole body exposure the tissue weighting factor is the sum of the weighting factors of the different organs and is per definition equal to 1. The effective dose *E* is calculated according to:

Table 3.1 Radiation weighting factors according to ICRP 103 (2007)

Radiation		w_R
x-rays, γ-rays, electrons, muons		1
Neutrons	<1 MeV	$2.5+18.2\times e^{-[\ln(E)]2/6}$
	1–50 MeV	$5.0+17.0\times e^{-[\ln(2\times E)]2/6}$
	>50 MeV	$2.5+3.25\times e^{-[\ln(0.04\times E)]2/6}$
Protons, charged pions		2
α-particles, fission products, heavy nuclei		20

It has to be noted that in many countries the weighting factors according to ICRP 60 (1991) are still in use and mandatory.

Table 3.2 Tissue weighting factors according to ICRP 103 (2007)

Organ/tissue	Number of tissues	w_T	Total contribution
Lung, stomach, colon, bone marrow, breast, remainder[a]	6	0.12	0.72
Gonades (mean testes and ovaries)	1	0.08	0.08
Thyroid, oesophagus, bladder, liver	4	0.04	0.16
Bone surface, skin, brain, salivary glands	4	0.01	0.04

In many countries the weighting factors according to ICRP 60 (1991) are still in use and mandatory.

[a] Adrenals, extrathoracic tissue, gall bladder, heart, kidneys, lymphatic nodes, muscle, oral mucosa, pancreas, small intestine, spleen, thymus, prostate—uterus/cervix (13 tissues in each sex).

$$E=\sum\nolimits_T w_T H_T=\sum\nolimits_T w_T\sum\nolimits_R w_R D_{T,R} \tag{3.7}$$

where H_T is the equivalent dose in the tissue T (organ dose) and $D_{T,R}$ is the absorbed dose in the tissue T deposited by the radiation R. The effective dose E is the dose, which generally is used to measure the radiation exposure. Its unit is again Sv.

Two types of radiation injuries are to be distinguished: stochastic and deterministic detriments. Deterministic effects are observable at relatively high doses (approx. >1 Sv) and include radiation burns, radiation decease, etc. Here only stochastic detriments are of interest, which means mainly an increase of probability for cancer with increasing effective dose.

The dose concept as explained earlier assumes a linear, no-threshold relation between effective dose and stochastic detriment (LNT theory) and has the advantage that different equivalent doses can linearly be added to calculate a final effective dose. This final effective dose can be multiplied by the detriment factor to calculate a risk either for cancer decease or cancer mortality.

3.4 Radiation exposure

3.4.1 Structure of radiation dose

The main radiation exposure of mankind is coming from natural radiation. The total annual dose varies strongly between different areas. For most people in Europe the annual effective dose lies between 2 and 5.5 mSv. The distribution of the sources can be seen from Fig. 3.2, but even the distribution of the sources of exposure differs from area to area and from person to person. It can be seen that more than 80% of the dose has natural origin and besides medicine, only about 1% comes from artificial radioactivity.

3.4.2 External radiation

The sources of external radiation are the cosmic and the telluric (or terrestrial) radiation. The telluric radiation is essentially caused by the uranium and thorium decay chains and by ^{40}K, i.e., what generally can be summarized as NORM. It is the gamma radiation from the soil, from rock material, and from the building materials, which causes the dose. Therefore, the contribution is strongly dependent on the concentration

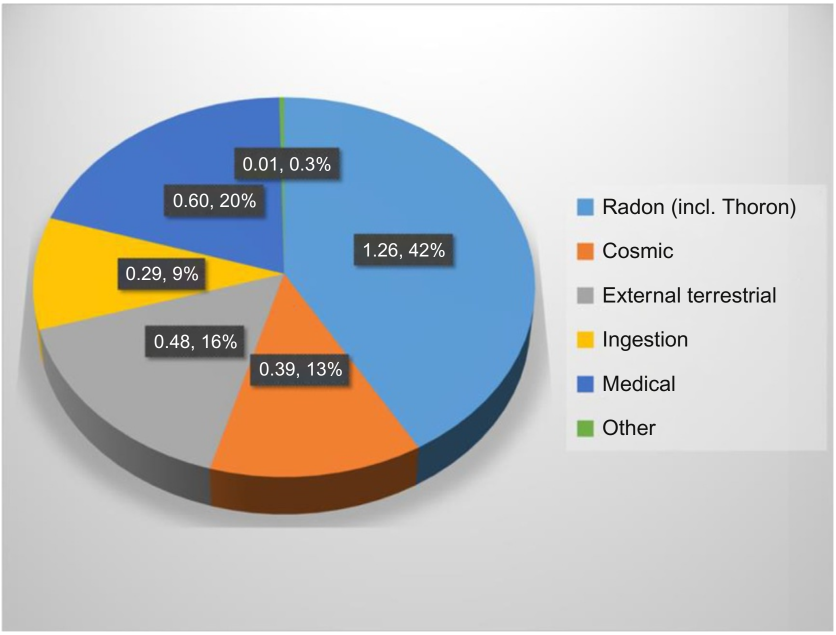

Fig. 3.2 Estimates of worldwide annual exposures and distribution of the sources of exposure, in both mSv and percentage of the total exposure (UNSCEAR, 2008). "Other" includes exposure due to fallout resulting from nuclear tests, to the Chernobyl accident, and to releases from nuclear power plants.

of NORM in the ground. The cosmic radiation consists mainly of high-energy protons (approx. 90%) which undergo nuclear reactions (spallation reactions) in the upper atmosphere with the atoms and molecules in air. In the upper atmosphere different new particles and photons are created, which can reach the Earth surface and cause the dose. Thus it is clear that the dose from cosmic radiation depends strongly on the height above the sea level. However, the dose also depends on the geographical latitude, because the Earth magnetic field deflects the primary cosmic radiation leading to higher doses in the polar-regions. The aurora borealis is also caused by interaction of the cosmic radiation, the Earth atmosphere, and its magnetic field.

3.4.3 Internal radiation

The internal radiation (without radon) is caused by radionuclides incorporated essentially by eating, drinking, and inhalation. Under normal conditions, there are, of course, contributions of the uranium and thorium decay chains, but the main sources are potassium, radiocarbon, and to a small extent tritium. In average, the activity of ^{40}K is 4.4 kBq and the activity of ^{14}C is 3.7 kBq in human body. The internal dose from ^{40}K arises mainly from the β-decay, because the electrons deposit all their energy within the body, while the γ-radiation leaves the body nearly unattenuated.

Intake by inhalation must be considered when particulate matter (PM) in air can contain an enhanced content of radionuclides.

As can be seen from Fig. 3.2, the primary dose (over 40%) is originating from radon, which is able to migrate from the soil or the building material to the outdoor or indoor atmosphere and result in internal exposure of the human body. There are three naturally occurring isotopes of radon, that is, ^{222}Rn (radon), ^{220}Rn (thoron), and ^{219}Rn (actinon) (see Fig. 3.1). The prevalence of the different radon isotopes in the atmosphere is significantly different—mainly, due to the difference in half-life. Actinon is not spread in the atmosphere, because it is hardly able to migrate after its formation due to very short lifetime. The half-life ($T_{1/2}$) of actinon does not exceed 4 s. The prevalence of thoron ($T_{1/2} = 55.6$ s) is very small, so it only accounts for 3.3% in the total dose (Fig. 3.2). The contribution of radon ^{222}Rn ($T_{1/2} = 3.82$ days) to the worldwide annual dose is the highest (38.3%, or 1.15 mSv on average around the globe), therefore radiation protection mainly focuses on radon, unless in specific cases thoron needs to be considered.

Radon its decay products (progeny) are primarily alpha-emitters. The mixture of short-lived radon progeny is a more powerful source of ionizing radiation than radon itself. The effective half-life of the mixture of short-lived radon daughters (about 40 min.) is significantly less than that of radon, which results in a relatively rapid removal of the progeny in the case of an instantaneous flow of radon. However, the accumulation of the mixture of the progeny can occur until the radioactive equilibrium with radon is achieved (can take two to three hours). Irradiation of humans by radon and its decay products occurs with the inhaled air. In contrast to the radon gas, which is inert, the radon progeny—radioactive metal isotopes of polonium (Po), lead (Pb), and bismuth (Bi)—can be deposited and accumulated in the bronchi and lungs, causing the internal radiation exposure. Thus the main radiation dose is formed not only by radon itself, but also by its decay products, while radon itself merely acts as a generator and transporter of the potential hazard.

Since the radon short-lived decay products are responsible for the main contribution to the radon exposure, the internal dose is calculated using the *equilibrium equivalent concentration* (EEC, expressed in Bq m^{-3}) of indoor radon. To understand the concept of equilibrium equivalent concentration it is important to take into account that in indoor air radioactive equilibrium between radon and its progeny is always broken. The EEC expresses a radon equivalent concentration at which the equilibrium mixture of radon with its daughter products allocates the same energy of alpha radiation, as a real nonequilibrium mixture in the room. The indoor activity of the radon daughter products is always lower than that of radon due to their precipitation and air exchange (natural or forced). The shift of radioactive equilibrium between radon and its mixture (expressed as EEC related to the radon concentration) is usually characterized by the equilibrium factor. Indoor measurements have shown that the equilibrium factor varies (within a 95% confidence interval) from 0.2 to 0.7 (Kokotti et al., 1992; Porstendörfer et al., 1994) around the mean value of 0.4 (UNSCEAR, 2006). Considering this, in many cases, especially when occupational risk must be controlled, it is much more accurate to measure the concentration of radon decay products in air, than to measure radon directly. Next to the EEC, the *potential alpha energy concentration* (PAEC), expressed in J m^{-3}, is often used for controlling the concentration of the progeny.

Based on the acceptable radiation risk, according to the recommendations of EU-BSS (Euratom-Basic safety standards), the EC countries have established permissible levels to control the maximum allowable average concentrations of indoor radon in the range from 100 to 300 Bq m^{-3} (Council Directive 2013/59/Euratom, 2014).

The outdoor radon (^{222}Rn or ^{220}Rn) concentration is usually 10 Bq m^{-3} (UNSCEAR 2006), which corresponds to a minimum possible level of indoor radon and is considered as very low. However, inside buildings, in confined spaces, radon is accumulated, which can create significant internal dose and pose a hazard to the population, given that the person stays usually inside buildings up to 80% of the time or ~7000 h per year (so-called occupancy time).

In most cases, the main source of radon is the ground below a house. Radon naturally exhales from the ground, but it can also exhales from mineral building materials, wherever traces of radium isotopes (which are daughter products of uranium and thorium decay series, according to Fig. 3.1) are present. Enhanced radon concentrations are particularly characteristic of the regions with soils containing granite or shale, which have higher radium concentrations, or in the zones of the tectonic breaks or zones with enhanced seismic activity.

Transport of radon from the soil into the building is explained primarily by a regular diffusion mechanism. The driving force for diffusion is a high radon concentration gradient at the soil-building boundary. In addition, the radon transport may periodically (inconstantly and irregularly) be significantly enhanced by convection of the soil gas that occurs when the pressure on the soil-building boundary changes.

Because of the uneven distribution of radium in soil, the air inside the soil (soil gas) has radon concentrations varying from several to tens or even hundreds of kBq m^{-3}.

Radon exhalation from the building materials and soil at the base of the building leads to annual indoor radon concentrations over 37 Bq m^{-3} (UNSCEAR 2006), which varies in the range from some tens of Bq m^{-3} to several kBq m^{-3} depending on the soil and foundation type.

The typical excess indoor radon concentration due to building materials is low: about 10–20 Bq m^{-3}, which is only 5%–10% of the design value introduced in the European Commission Recommendation (200 Bq m^{-3}) (RP-112, 1999). However, in some cases the building materials may also be an important source. For example, in Sweden, the radon emanating from building materials is a major problem. There are about 300,000 dwellings with walls made of lightweight concrete based on alum shale (so-called "blue concrete") (The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway, and Sweden, 2000).

It is clear that building materials contribute to the external dose by gamma radiation and to the internal dose by raising the indoor radon concentration. Usually the contribution to indoor radon from building materials is small compared with the inflow from the soil beneath the house; however, in some cases it has to be addressed. In this regard, the dose contribution of building materials to the internal and external radiation needs to be controlled and limited. In other words, the concentration of natural occurring radionuclides contained in building materials and products during their manufacture, creating a flow of penetrating ionizing radiation as well as the radon exhalation from building products, is an important issue in radiological protection of building occupants.

3.5 Principal radiation characteristics of NORM

3.5.1 Activity concentration of natural radionuclides

External exposure from construction materials of mineral origin is a result of the presence of radionuclides belonging to the natural radioactive decay series (Fig. 3.1), starting from ^{238}U ($T_{1/2} = 4.47 \times 10^9$ years), ^{232}Th ($T_{1/2} = 1.40 \times 10^{10}$ years) and from ^{235}U ($T_{1/2} = 7.04 \times 10^8$ years), and also from natural ^{40}K ($T_{1/2} = 1.25 \times 10^9$ years), as described before. The existence of these nuclides in the present era is explained by a very long half-life, which is over billions of years for all radionuclides except for ^{235}U. Because the current prevalence of ^{235}U in the Earth's crust is about 0.73% of ^{238}U [ISO 11665-1, 2012], the activity concentration of each element of the ^{235}U chain in secular equilibrium with ^{235}U, according to Eq. (3.1), is more than 20 times lower than that of the elements in the ^{238}U chain. Accordingly, the contribution of ^{235}U chain in the external dose, taking into account the ionization energy released per unit of equilibrium activity (due to penetrating gamma and beta radiation), can be neglected. Therefore, the activity concentration of the ^{235}U chain elements is not subject to control in case of materials intended to be used as a component of building materials.

Let us remind the reader that in contrast to ^{238}U and ^{232}Th, after the decay of ^{40}K the stable nuclides ^{40}Ca and ^{40}Ar are produced. In addition to the radioactive ^{40}K there are two isotopes in nature, ^{39}K and ^{41}K, which are stable and much more common than

^{40}K, which accounts only for 1% of the sum of abundances of ^{39}K and ^{41}K in the continental crust. At the same time, the content of ^{40}K in the Earth's crust is by one to two orders of magnitude higher than the rare nuclides ^{238}U or ^{232}Th. However, taking into account the value of the half-lives of ^{238}U, ^{232}Th, and ^{40}K, the ^{40}K activity concentration on average is about one order of magnitude higher than that of ^{238}U and ^{232}Th. UNSCEAR (2008) reports the following average (and maximum) values of activity concentrations of these nuclides in various subsurface soils around the globe: 33 (1000) Bq kg^{-1} for ^{238}U, 45 (360) Bq kg^{-1} for ^{232}Th, and 412 (3200) Bq kg^{-1} for ^{40}K. The data indicate relatively small differences between the average activity concentrations of ^{238}U and ^{232}Th in mineral materials, but also show high variation of activity concentrations of each of these nuclides.

The decay of ^{40}K is partly (89%) a β-decay and partly (11%) an electron capture followed by a gamma radiation with energy 1.460 MeV. This energy is large enough, but its release occurs in only one out of ten ^{40}K decays. However, taking into account a relatively high abundance of ^{40}K in the Earth's crust, its total contribution to the external radiation dose is considerable, so the activity concentration of ^{40}K present in construction materials should be subject to mandatory control.

Now let us determine which radionuclides in the ^{238}U and ^{232}Th disintegration chains are also able to generate significant external human exposure dose. In this connection, the relevant information is provided in Tables 3.3 and 3.4.

Table 3.3 shows that ^{214}Pb and ^{214}Bi are capable to produce significant external dose in the chain of ^{238}U nuclides. These nuclides are short-lived decay products of ^{222}Rn (radioactive equilibrium between these radionuclides occurs within 2–3 h in a closed system). Because inert radon actively migrates, especially in a nonclosed porous media, such as mineral construction materials or mined raw materials, the equilibrium between the radioactive parent nuclide ^{226}Ra and ^{222}Rn, and ^{214}Pb and ^{214}Bi is usually disturbed. However, in a closed environment that balance is restored quickly enough—already within 2–4 weeks, due to the relatively short half-life of ^{222}Rn (3.82 days), as compared with half-life of the parent ^{226}Ra (1600 years). Thus, in a closed environment the power of external radiation produced by the decay of ^{214}Pb and ^{214}Bi is determined by the activity concentration of ^{226}Ra in the material.

Hence, in order to ensure that testing of the material yields reliable results, the control has to be made in a closed system, where radioactive equilibrium between ^{226}Ra, ^{222}Rn, ^{214}Pb, and ^{214}Bi is provided. Because the half-life of ^{226}Ra is 1600 years, its noticeable decay or accumulation is possible only for a few centuries. Therefore, any shifts in radioactive equilibrium among all the elements in the chain of ^{238}U—parents to ^{226}Ra, cannot affect the external radiation of the material or product, if its service life does not exceed several centuries. In addition, UNSCEAR (2008) reports the average over the Globe activity concentrations of ^{238}U (33 Bq kg^{-1}) and ^{226}Ra (32 Bq kg^{-1}) in subsurface soils. The as good as equal activity concentrations indicate that a shift of radioactive equilibrium between ^{238}U and ^{226}Ra is virtually absent. Thus, in order to limit the contribution of the ^{238}U chain elements to the external radiation dose, created by the decay of ^{214}Pb and ^{214}Bi, the ^{226}Ra activity concentration in building materials, at radioactive equilibrium with the short-lived radon decay products, is subject to mandatory control.

Table 3.3 **Important properties of ^{238}U and its decay products and contribution to external dose**

		Major penetrating radiation energies, MeV (energy escape probability is given between brackets)		
Symbol	**Half-life**	**Beta (average)**	**Gamma**	**Contribution to external dose**
^{238}U	4.47×10^9 years	–	–	Absent
^{234}Th	24.10 days	0.024 (18.6%) 0.050 (72.5%)	0. 063 (3.81%) 0. 092 (2.69%)	Insignificant
^{234m}Pa	1.17 min	0.825 (98.3%)	–	Insignificant
^{234}Pa	6.7 h	0.141 (36.9%) 0.198 (15.9%)	0.131 (19.7%) 0.227 (5.50%) 0.733 (8.58%)	
^{234}U	244,500 years	–	–	Absent
^{230}Th	77,000 years	–	–	Absent
^{226}Ra	1600 years	–	0.186 (3.28%)	Insignificant
^{222}Rn	3.823 days	–	–	Absent
^{218}Po	3.05 min	–	–	Absent
^{214}Pb	26.8 min	0.207 (48.1%) 0.227 (42.1%)	0.295 (19.2%) 0.351 (37.1%)	Significant
^{214}Bi	19.9 min	0.491 (8.28%) 0.525 (17.6%) 0.539 (17.9%) 1.269 (17.7%)	0.609 (46.1%) 1.120 (15.0%) 1.765 (15.9%)	
^{214}Po	164.3 μs	–	–	Absent
^{210}Pb	22.3 years	0.016 (20%)	0.046 (4.05%)	Insignificant
^{210}Bi	5.012 days	0.388 (100%)	–	Insignificant
^{210}Po	138.38 days	–	–	Absent
^{206}Pb	Stable			

According to Table 3.4, ^{228}Ac and daughter decay products of ^{220}Rn, among which ^{208}Tl, are capable to create the considerable external dose in the chain of ^{232}Th. At the same time, unlike ^{222}Rn, a problem caused by the exhalation of ^{220}Rn from a material or product is not very much relevant, because of the significant limitations of the thoron transport inside the porous material, as reported in more detail in Section 3.5.2. It is therefore permissible to consider that ^{224}Ra is always in a radioactive equilibrium with all daughter products, including ^{212}Pb, ^{212}Bi, and ^{208}Tl. Thus, according to Table 3.4, most of the external radiation generated in the ^{232}Th chain is determined by the ^{224}Ra activity concentration, provided the radioactive equilibrium between ^{232}Th and ^{224}Ra. Violation of the radioactive equilibrium in the ^{232}Th chain can be

Table 3.4 Important properties of the ^{232}Th and its decay products and contribution to external dose

		Major penetrating radiation energies, MeV (energy escape probability)		
Symbol	**Half-life**	**Beta (average)**	**Gamma**	**Contribution to external dose**
^{232}Th	1.405×10^{10} years	–	–	Absent
^{228}Ra	5.75 years	0.865 (100%)	–	Insignificant
^{228}Ac	6.13 h	0.386 (40.4%) 0.610 (11.4%)	0.338 (12%) 0.911 (29%) 0.968 (17.5%)	Significant
^{228}Th	1.9131 years	–	–	Absent
^{224}Ra	3.66 days	–	–	Absent
^{220}Rn	55.6 s	–	–	Absent
^{216}Po	0.15 s	–	–	Absent
^{212}Pb	10.64 h	0.041 (5.21%) 0.094 (84.9%) 0.172 (9.89%)	0.238 (44.6%)	Significant
^{212}Bi	60.55 min	0.190 (3.44%) 0.228 (2.65%) 0.530 (7.9%) 0.831 (48.4%)	0.727 (11.8%)	
^{212}Po	0.305 μs	–	–	Absent
^{208}Tl	3.07 min	0.438 (22.8%) 0.532 (22%) 0.646 (50.9%)	0.510 (21.6%) 0.583 (85.8%) 0.860 (12%) 2.615 (99.8%)	Significant
^{208}Pb	Stable			

caused, primarily, by the shift between the activities of ^{232}Th and ^{228}Ra, since the latter nuclide has a relatively long half-life (5.75 years) and also an increased ability to take a part in various chemical and physical interactions. This shift can in particular occur in a natural environment untouched by man-made influence (although reports of such shifts in the natural geological environment are limited to ground waters as formation waters associated with fossil fuel, geothermal waters, etc. (Nelson et al., 2015, Bzowski and Michalik, 2015)). However, even in the case of disequilibrium between ^{232}Th and ^{228}Ra, the radioactive equilibrium between ^{228}Ra and ^{228}Ac ($T_{1/2} = 6.13$ h), which also contributes significantly to the dose, is usually kept. In the case of a significant shift of radioactive equilibrium between ^{228}Ra and ^{232}Th, taking place, for example, in the processing of raw materials, its restoration (including the entire chain of ^{232}Th) occurs within a few decades, as shown in Fig. 3.3.

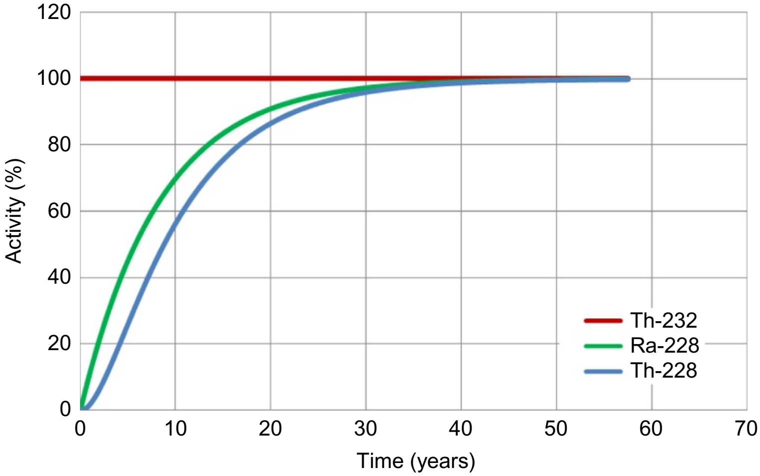

Fig. 3.3 The build-up of activity concentrations of ^{228}Ra and ^{228}Th in case of pure ^{232}Th.

To the contrary, an opposite situation must be considered in some specific NORM residues, when ^{232}Th is not present in material of concern. In Fig. 3.4 the relationship of activity concentration of two main contributors to gamma radiation in Th decay series is depicted, when ^{232}Th is not present at all, and at the beginning only ^{228}Ra occurs in material of concern. After about 4.5 years the so-called *transient equilibrium state* between ^{228}Ra and ^{228}Th is reached and then the activity concentration of ^{228}Th (i.e., in secular equilibrium with ^{224}Ra) is bigger than activity concentration of the parent radionuclide, ^{228}Ra, until both these radionuclides decay completely that happens in about 50 years (Michalik et al., 2013). NORM residues, in which this situation occurs, are rarely used for construction.

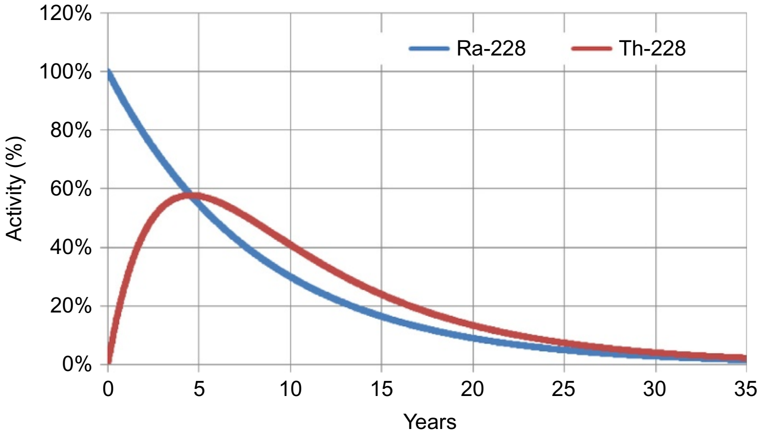

Fig. 3.4 Activity concentration of ^{228}Ra and build-up of ^{228}Th, when ^{232}Th does not exist.

The service life of building materials and products of mineral origin exceeds generally the given periods in both cases. Thus, in order to limit the contribution of the ^{232}Th chain elements to the external radiation dose, which is created by the decay of ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl, the activity concentration of ^{232}Th in building materials is subject to mandatory control. However, taking into account the above-mentioned radionuclides behavior patterns in the ^{232}Th chain and the fact that both extreme situations are unlikely in case of NORM used for construction purposes, actually the activity concentration of ^{228}Ra and ^{228}Th (^{224}Ra) must be controlled directly. When the disequilibrium between these two radionuclides is noticed, there is no equilibrium between ^{228}Ra and ^{232}Th and, in order to carry out an assessment of NORM from long-term perspective, ^{232}Th should be measured directly. This approach is reflected in practice, where more often activity concentration of ^{228}Ra and ^{228}Th (^{224}Ra) is easily measured by gamma spectrometry, than ^{232}Th by alpha spectrometry.

It can be concluded that the main parameter characterizing the external radiation dose, created solely by building materials of mineral origin, is the activity concentration of the three main natural radionuclides: ^{232}Th, ^{226}Ra (in a state of radioactive equilibrium with the short-lived radon decay products), and ^{40}K.

3.5.2 Radon emanation and exhalation

As shown earlier, the presence of radon in indoor air is the main factor that creates the internal human exposure. *Exhalation of radon* from soil and building (or other porous) materials into the air or into the building premises should be seen as a combination of two independent processes (IAEA, 2013):

- Emanation of radon, and more specifically—its generation in a solid-phase material and further removal from the bulk of the solid phase into the pore space by the recoil process, results from the alpha decay of the radium parent. Atoms of radon found in the pore space that have the ability to migrate into open pores are called free radon. Radon atoms held in the solid phase and which are not able to migrate are called bound radon.
- Transport of radon in the pore space of the material by diffusion, which may be enhanced by convection of gas in the pores.

There is often a confusion in the literature between the concepts of radon emanation and exhalation. This confusion will be discussed later on in more detail.

The process of emanation is quantitatively characterized by the emanation coefficient. The *radon emanation coefficient* can be defined as the ratio of free radon activity to the total activity (free and bound) of radon in the material under the radioactive equilibrium between radon and the radium parent. Radon emanation coefficient is determined through the following equations:

$$\varepsilon=\frac{C_{Rn}}{C_{Ra}}=1-\frac{C_{Ra}^{*}}{C_{Ra}},\quad C_{Ra}\geq C_{Ra}^{*}, \tag{3.8}$$

where C_{Rn} is the specific activity of free radon in the material (no flow of radon), Bq kg^{-1}; C_{Ra} is the specific activity of ^{226}Ra in the material ($C_{Ra} = C_{Rn}+C_{Ra}{}^{*}$), Bq kg^{-1}; and $C_{Ra}{}^{*}$ is the specific activity of bound radon in the material, Bq kg^{-1}.

The radon emanation coefficient is also called the emanating power, emanating fraction, release ratio, or escape-to-production ratio. The radon emanation coefficient is a dimensionless parameter and is represented as either a fraction or a percentage. The emanation coefficient ranges from 0 (no radon escapes) to 1 (all radon escapes). The rest of the produced radon (fraction $1-\varepsilon$) remains fixed in the solid structure of material. Table 3.5 presents an overview on the radium activity concentration and the radon emanation coefficient for several building materials.

Note that when studying/testing the radon exhalation of building materials, due solely to an internal radon source, the convective component of the transport is not considered. The effect of the convective process is usually minimized in the tests. Therefore, the radon flow inside a homogeneous building material (or soil) is characterized by the coefficient of radon diffusion in the material, as well as the radon concentration gradient according to the Fick's first law (in the most simple case, the transport can be considered as one-dimensional along a vertical axis x):

$$E(x) = -D \cdot \frac{\partial C(x)}{\partial x}, \tag{3.9}$$

Table 3.5 **Mean values and variation range (in brackets) of radium activity concentration and radon emanation coefficient for several popular building materials, according to Krisyuk (1989)**

Materials	**No. of samples**	**C_{Ra}, Bq kg^{-1}**	**ε (%)**
Clay	23	48 (10–255)	21 (13–39)
Soil	7	21 (15–28)	21 (5.7–44)
Coarse crushed aggregate	11	35 (14–81)	9.1 (3.0–17)
Sand–gravel mix	10	18 (8.1–41)	19 (7.4–35)
Mortar	4	15 (11–20)	24 (16–42)
Normal-weight concrete	15	27 (11–48)	11 (3.4–26)
Sand	14	9.6 (3.7–20)	20 (4.3–46)
Gravel	5	16 (5.6–23)	11 (7.1–14)
Lightweight concrete	5	23 (13–44)	9.5 (1.2–23)
Silicate brick	6	14 (6.3–30)	10 (6.9–14)
Plaster	3	9.6 (6.7–14)	12 (9.1–16)
Slag	17	104 (21–192)	0.9 (0.1–1.5)
Lime, chalk	6	26 (8.1–70)	3.5 (2.7–4.0)
Tuff	5	48 (37–67)	1.4 (0.5–2.4)
Red brick	16	36 (13–56)	1.5 (0.4–3.8)
Fly ash	8	107 (52–155)	0.8 (0.1–2.4)
Cement	13	41 (23–59)	1.3 (0.5–2.3)
LECA (lightweight expanded clay aggregate)	7	28 (23–74)	1.0 (0.3–1.7)
Gypsum plaster	4	8.9 (7.0–10)	4.4 (1.9–7.3)
Limestone	4	3.7 (3.7–4.1)	4.6 (1.4–13)

where $E(x)$ is the distribution function for vertical profile of radon exhalation rate within the bulk material, Bq m^{-2} s^{-1}; D is the radon diffusion coefficient in the material (bulk), m^2 s^{-1}; $C(x)$ is the distribution function for the vertical profile of free radon activity concentration in the bulk material, Bq m^{-3}, which is related to free radon activity concentration in the pores of the material (Bq m^{-3}) and the porosity η (rel) by the equation:

$$C = \eta \cdot C_p, \tag{3.10}$$

Thus the radon diffusion coefficient (bulk) expresses the radon activity permeating in a homogeneous media due to molecular diffusion through unit area of the elementary layer of unit thickness per unit time at unit radon activity concentration gradient on the boundaries of this layer (ISO/TS 11665-12, 2016).

To describe the radon diffusion transport in a heterogeneous medium (e.g., a multilayer structure made of different building materials), a concept of "equivalent radon diffusion coefficient"—radon diffusion coefficient of the particular heterogeneous (or multilayer consisting of several homogeneous single layers) material that numerically equals to the radon diffusion coefficient of a homogeneous material of the same thickness—is introduced (ISO/TS 11665-12, 2016).

A function $C(x)$ is defined by solving the system of Eqs. (3.11), (3.12) expressing the boundary problem of the radon diffusion transport in the steady state through the infinite horizontal layer of a homogenous material (which is consistent with the concrete slab thickness of 0.1–0.3 m and a width of not less than 1 m). The formation and transport of radon in a layer of material with a thickness d (m), specific activity of radium-226 C_{Ra} (Bq kg^{-1}), and density ρ (kg m^{-3}) is described by the equation

$$D \cdot \frac{\partial^2 C(x)}{\partial x^2} - \lambda \cdot C(x) + \lambda \cdot \rho \cdot \varepsilon \cdot C_{Ra} = 0, \tag{3.11}$$

considering the following boundary conditions on the upper and lower boundaries of the layer, respectively (it is possible to assume that the concentration of radon in the air is extremely small and close to zero compared with the concentration of free radon in the material):

$$C(x = d) = 0; \quad C(x = 0) = 0, \tag{3.12}$$

where λ is the radon decay constant, 2.09×10^{-6} s^{-1}.

According to Eq. (3.13), the radon surface exhalation rate (Bq m^{-2} s^{-1}) is a value of the activity concentration of radon atoms that leave a material per unit surface of the material per unit time (ISO 11665-1, 2012):

$$E_S = -D \cdot \frac{\partial C(x)}{\partial x}_{|x=0}, \tag{3.13}$$

Depending on the radon diffusion coefficient in the material sample (product) and its overall dimensions, not all free radon atoms generated in the sample are able to

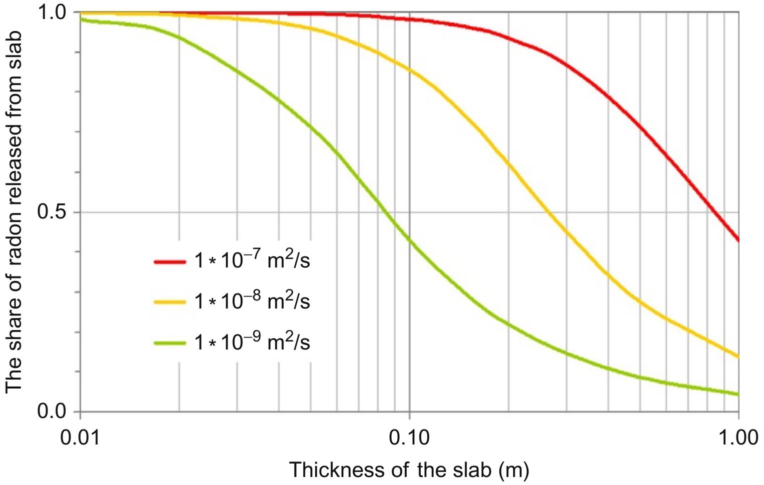

Fig. 3.5 The fraction of free radon released from an infinite plate (slab), depending on its thickness and radon diffusion coefficient in the material.

migrate into the air. Fig. 3.5 shows the fraction of free radon released from the slab (plate infinite in the horizontal plane) to the atmospheric air (up and down), depending on the plate thickness and radon diffusion coefficient in the homogenous material of the slab.

For certain values of D and d and, according to Fig. 3.5, when the percentage of free radon released from the plate is not less than 85%–90%, one can roughly assume that almost all of the free radon, which is formed in the plate due to radium-226 decay, is released in the surrounding space. Then the value of E_S can be determined by a simple equation:

$$E_S = \frac{1}{2} \cdot \lambda \cdot d \cdot \rho \cdot \varepsilon \cdot C_{Ra}, \tag{3.14}$$

Eqs. (3.8)–(3.14) are also valid for thoron given the activity concentration of thorium-232 in the material (instead of C_{Ra}) and $\lambda = 1.25 \times 10^{-2}\ \mathrm{s}^{-1}$, and in the absence of experimental data on D and ε values for thoron. The essential difference introduced in Eq. (3.14) when considering thoron is the value of d, for which the effective value of thoron is expected to lie in the range of from 3 to 5 mm, not exceeding 10 mm, and depending on the diffusion coefficient of thoron.

Kovler (2012) collected the literature data on the minimum and the maximum values of radium activity concentrations and radon surface exhalation rates for the main building materials. Table 3.6 reports these results in descending order by the radon exhalation rate.

It should be noted that, in addition to the values E_s and ε, radon exhalation rate from the sample of material (product) is sometimes expressed as the radon mass exhalation rate E_M (Bq kg^{-1} s^{-1}), which represents a value of the activity concentration of radon

Table 3.6 Minimum and maximum values of radium activity concentrations and radon surface exhalation rates for the popular building materials (Kovler, 2012)

Building material	C_{Ra}, Bq kg^{-1} Min	C_{Ra}, Bq kg^{-1} Max	E_S, Bq m^{-2} h^{-1} Min	E_S, Bq m^{-2} h^{-1} Max
Granite	<MDA[a]	297	<MDA	86
Wallboard (phosphogypsum)	470	700	1.5	42
Normal-weight concrete	11	75	1.1	32
Aerated concrete	6	22	0.4	32
Wallboard (natural gypsum)	<MDA	14	<MDA	21
Limestone	4	20	0.1	11
Tuff	40	70	<MDA	10
Clay brick	7	73	0.01	8
Pumice blocks	40	60	0.6	6
Silicate brick	7	73	1.9	5
Lightweight concrete	7	44	<MDA	3
Plaster	7	14	<MDA	0.2

[a] MDA—Minimum Detectable Activity (the smallest value that can be measured by a specific instrument) as given in the references.

atoms that leave a material per unit mass of the material per unit time (ISO 11665-1, 2012). In this case, the following equation holds:

$$E_M = \lambda \cdot \varepsilon \cdot C_{Ra}, \tag{3.15}$$

There is often a confusion in the literature between the radon emanation and the radon exhalation (expressed as surface or mass exhalation rate). The reason for this terminological confusion is discussed in Kovler (2012) and de Jong (2010). The thing is that usually the radon emanation coefficient is determined from the measured radon exhalation rate of some sample with a certain mass and geometry. While true radon emanation coefficient is determined from the production rate of radon per unit of interstitial space, the radon emanation coefficient (factor) on the other hand, which is often determined in practice by the measurement of exhalation rate, would be more accurately called the radon release factor (de Jong, 2010).

The radon emanation and radon diffusion in the material should be considered separately and independently of each other. Furthermore, until recently, neither there was standard terminology based on the corresponding Eqs. (3.8) and (3.13), Eqs. (3.14) and (3.15) available, nor there were limitations on their use in assessing radon emanation and exhalation.

In order to evaluate and compare radon diffusion permeability of the materials (mainly, radon-barriers), besides radon diffusion coefficient, another characteristic—radon diffusion length in the material L (m)—is often used in the literature in the last 10–20 years. Based on this parameter, it is possible to estimate the attenuation of radon exhalation rate E in the material, which does not contain radium, through the formula:

$$E(x) = E_0 \cdot \exp\left(-\frac{x}{L}\right), \quad \text{where } L = \sqrt{\frac{D}{\lambda}} \tag{3.16}$$

where E_0 is the initial radon exhalation rate, Bq $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$; x is the distance on which radon diffuses in the homogenous material, m.

The radon diffusion length, according to Eq. (3.16), is equal to the distance of radon transport in a homogeneous medium due to molecular diffusion, at which the radon exhalation rate or its activity concentration decreases to $1/e \approx 0.37$ (factor $e \approx 2.72$), while the transport is considered in conditionally infinite medium without the influence of edge effects. In contrast to the diffusion coefficient D, which is independent of the thickness of the material, the value of E through a sample decreases with the thickness. To get a thickness-independent parameter, which describes the permeability (or impermeability, i.e., tightness) of building products to radon gas, Keller et al. (1999) suggested to use the quotient of the sample thickness and the diffusion length.

The diffusion length is also the parameter, which characterizes a material used as radon barrier. According to Keller et al. (1999) a material is called radon-tight, if its thickness satisfies the condition $d > 3\ L$, which means a radon passage of less than 5% of the initial amount, that is, the radon exhalation rate is reduced nearly by 20 times, according to Eq. (3.16). Table 3.7 adapted from Keller et al. (1999) gives an overview of different materials and their capabilities to act as a radon barrier.

Tsapalov & Kovler (2016) recently studied the validity of the Keller criterion of radon tightness using simulation solutions of the boundary problem of radon diffusion through a structure consisting of two different layers with different properties, and obtained unsatisfactory results. It was found that the application of the Keller criterion leads to extremely high values of protective coating thickness d (more than 10–50 times, than practically accepted and justified values), especially when the difference of radon diffusion coefficients in different materials, such as a concrete slab and a protective coating, is high. The reasons of the inadequacy in the diffusion length criterion suggested by Keller are the following: (a) the diffusion properties of the material, from which radon is released, are not taken into account; (b) the radon transport is considered on the boundary of the medium excluding the boundary effects, which is contrary to the definition of the diffusion length. Thus it is recommended to use the value of radon diffusion length only for a qualitative comparison of the diffusive permeability of different homogenous materials. The real assessment of the attenuation value can be obtained only based on solving the boundary problem of steady-state diffusion of radon through the multilayered medium consisting of at least two layers of (Tsapalov & Kovler, 2016).

Table 3.7 **Experimental mean values of radon diffusion coefficient and radon diffusion length in popular building products and sealants**

Material	Thickness (mm)	Diffusion length (mm)	Remark
Gypsum	100	1100	Permeable
Pumice	150	850	Permeable
Limestone	150	400	Permeable
Brick	150	400	Permeable
Sandstone	100	1000	Permeable
Aerated concrete	100	800	Permeable
Heavy concrete	100	60	Permeable
Polymer concrete	40	7	Tight
Granite	30	160	Permeable
Glass foam plate	70	<0.7	Tight
Asphalt-asbestos	3	<0.7	Tight
Bitumen	3	<0.7	Tight
High-density polyethylene	1	<0.7	Tight
Silicone rubber	3	<0.7	Tight
Lead foil	0.1	<0.7	Tight
Butyl rubber	1.5	2	Permeable
Polyurethane coating	5	<0.7	Tight
Plastic foil	3	<0.7	Tight
Epoxy resin	3	<0.7	Tight

Data from Keller, G., Hoffmann, B., Feigenspan, T., 1999. Radon permeability and radon exhalation of building materials. Radon in the Living Environment, Athens, pp. 1271–1278.

In conclusion, the main parameters characterizing radon emanation and exhalation rate from building products are the radium activity concentration C_{Ra} (Bq kg^{-1}), the radon emanation coefficient, ε (rel), and the radon surface exhalation rate, E_s (Bq m^{-2} s^{-1}) or the radon mass exhalation rate, E_M (Bq kg^{-1} s^{-1}). Additional parameters characterizing the rate of radon release from the material are the radon diffusion coefficient D (m^2 s^{-1}), product thickness d (m), and its density ρ (kg m^{-3}).

3.6 Conclusions

External exposure from construction materials of mineral origin is a result of the presence of radionuclides belonging to the natural radioactive decay series, starting from ^{238}U, ^{232}Th and from ^{235}U, and also from natural ^{40}K.

Because the current prevalence of ^{235}U in the Earth's crust is about 0.73% of ^{238}U, the contribution of ^{235}U chain in the external dose can be neglected. Therefore, the activity concentration of the ^{235}U chain elements is not subject to control in case of materials intended for use in building products.

Taking into account a relatively high abundance of ^{40}K in the Earth's crust, its total contribution to the external radiation dose is considerable, in spite of the fact that release of gamma energy occurs in only one out of ten ^{40}K decays. Therefore, the activity concentration of ^{40}K present in construction materials should be subject to mandatory control.

Therefore, the main parameter characterizing the external radiation dose, created solely by building materials of mineral origin, is the activity concentration of the three main natural radionuclides: ^{232}Th, ^{226}Ra (in a state of radioactive equilibrium with the short-lived radon decay products), and ^{40}K.

The main parameters characterizing radon emanation and exhalation rate from building products are the radium activity concentration, the radon emanation coefficient and the radon exhalation rate. Additional parameters characterizing the rate of radon release from the material are the radon diffusion coefficient, product thickness, and density.

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Legislative aspects

4

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4.1 Introduction

Guide for the reader: Structure of chapter "4":

This chapter contains a lot of information on the new European approach to regulate natural radioactivity in building materials.

- The main Directive that deals with natural radioactivity in building materials is the Euratom-Basic Safety Standards Directive (EU-BSS) and its approach to regulate building materials is described in Section 4.3. Some additional information on the link with the Construction Products Regulation (CPR) is provided in Section 4.3.1.
- For the reader who wants to explore the history of the EU-BSS and several important earlier documents in greater depth we refer to Section 4.2.
- For the reader who wonders how the Euratom drinking water Directive might impact on building materials we refer to Section 4.4.
- In Sections 4.5 and 4.6 current national legislations on natural radioactivity in building materials are considered in more detail.
- Several tools are described for the screening of the radiological properties of building materials. These tools are discussed in Section 4.7.

It is well known that, owing to their natural radionuclide content, building materials give the most significant contribution to the indoor gamma dose (UNSCEAR, 2008). This is why for some 30 years researchers have investigated building materials from a radiological point of view and why, more recently, regulators have recognized building materials to be an important issue from the radiation protection (RP) point of view.

The recycling of NORM residues in building materials may be a sustainable option to counteract the further depletion of valuable raw materials. For the evaluation of

Naturally Occurring Radioactive Materials in Construction. http://dx.doi.org/10.1016/B978-0-08-102009-8.00004-9

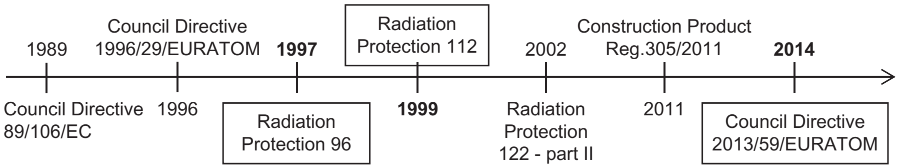

Fig. 4.1 Timeline of EU guidance and regulations concerning natural radioactivity in building materials. *Boxes* evidence the most important steps.

recycling options for NORM residues, it is, however, vital to carefully consider current legislation and recommendations.

Council Directive 2013/59/Euratom, laying down basic safety standards for protection against the dangers arising from exposure to ionizing radiation (EU, 2014), considers the gamma exposure from building materials. Article 75 and Annex VIII of the Directive are devoted to this issue. This Directive shall be transposed into national legislations of Member States and in force before Feb. 2018.

Fig. 4.1 gives a timeline sketching the development of EU legislation on building materials. This starts with Council Directive 1996/29/Euratom which was the first legislation in which RP from natural sources of ionizing radiations was considered.

In Section 4.2, the different steps of this development are presented. In Section 4.3, current EU legislation on this topic is described.

Section 4.4 gives a short presentation of the drinking water Directive 2013/51/Euratom. This legislation needs to be allowed for in case of disposal of NORM residues, which may eventually apply to building rubble as well. Section 4.5 gives a synthetic overview of regulations already in force in EU Member States and in some other countries.

In Section 4.6, examples of current national legislations in some EU Member States are presented in detail and also the legislative approach for reuse of NORM in construction in Australia is described.

Finally, Section 4.7 offers a review of different tools elaborated in different EU and non-EU countries in order to characterize the radioactivity content of building materials and to evaluate their radiological impact.

4.2 Evolution of the EU legislative approach to natural radioactivity in building materials

In this section, a short review of guidelines and regulations issued by EU to deal with RP problems determined by natural radioactivity in building materials is presented.

4.2.1 Radiation protection 96

In the 1990s the European Commission got interested in a possible common approach regarding exposure to enhanced natural radioactivity. Eventually, this resulted in a requirement in Council Directive 96/29/Euratom of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation (EU, 1996). The Directive merely required to identify work activities involving significantly increased levels of exposure for workers or members of the public to natural radiation sources which cannot be disregarded from a RP point of view. This requirement did, however, not consider explicitly natural radioactivity in building materials. Therefore, the European Commission contracted a study to the Finnish Radiation and Nuclear Safety Authority (STUK) with the aim “to provide the Commission with information about natural radioactivity in building materials and in industrial by-products used as raw materials for construction products and to enquire into existing relevant regulations in the Member States.” The results of this study were published in 1997 as RP 96 (EC, 1997) and provided for the first time a document treating the natural radioactivity in building materials from a broad perspective.

Indeed, the document presented interesting results, in particular:

- a survey of radioactivity levels in normal or commonly used building materials in Europe
- the examination of materials with enhanced radioactivity used in building industry
- a discussion of the economic and ecological benefit of recycling industrial by-products and wastes
- a discussion about the RP basis applicable to this special question and the corresponding framework
- an assessment of radiation doses caused by radioactivity in building materials with a room model developed at STUK
- a survey of existing regulations on natural radiation and radioactivity of building materials

Building materials may also be of concern as a radon source, but RP 96 affirmed that “It is very unlikely that building materials with ‘normal’ radium concentrations could cause indoor radon concentrations exceeding 200 Bq m^{-3}, which is the upper value for new dwellings, recommended by the European Commission” [see European Commission Recommendation 90/143/Euratom on the protection of the public against indoor exposure to radon (EC, 1990)].

Finally, a proposal for a common European approach to the regulation of the radioactivity of building materials was presented. A reference level of 1 mSv per year was proposed for the annual dose contribution of gamma radiation from building materials “in addition to the individual dose received from background gamma radiation from the undisturbed earth’s crust” (RP 96). The selected reference level, 1 mSv per year, is the same as the dose limit for public exposures to practices, including industrial sectors involving naturally occurring radioactive material. The “STUK model” (Markkanen, 1995) was introduced as a precautionary evaluation tool of the radiological impact of building materials according to their use (bulk or minor/superficial use).

4.2.2 Radiation protection 112

The information collected in the RP 96 publication was used as a basis for the elaboration of Community guidance in RP 112—“Radiological protection principles concerning the natural radioactivity of building materials” (RP 112), published in 1999 (EC, 1999). This guidance was adopted by the Article 31 Group of Experts and published by the European Commission to “be a useful reference document for the European Commission when considering possible regulatory initiatives at Community level” (EC, 1999).

In RP 112 the index I, already used in RP 96 to evaluate annual doses from building materials, was introduced as a conservative screening tool to identify materials that need supplementary investigations, starting from the basic assumption that “All building materials contain some natural radioactivity.” RP 112 noted that “small, unavoidable exposures need to be exempted from all possible controls” and considered that “a uniform exemption level within the European Union would allow free movement of most building materials within the EU” (EC, 1999).

The guidance RP 112 suggests basing the radioactivity control of building materials on a dose criterion and an exemption level. Therefore, “threshold” values for index I are calculated based on two dose criteria (0.3 and 1 mSv per year) and two categories to account for ways and amounts in which the material is used in a building (bulk or superficial). In this approach, the dose criterion is defined as the dose exceeding the mean environmental outdoor background in Europe of 50 nGy h^{-1} (~0.25 mSv per year with an indoor occupancy factor of 0.8) in 1999, as probably taken from the UNSCEAR 1993 Report (UNSCEAR, 1993).

RP 112 defines an index I in the following equation:

$$I = \frac{C_{\mathrm{Ra-226}}}{A_{\mathrm{Ra-226}}} + \frac{C_{\mathrm{Th-232}}}{A_{\mathrm{Th-232}}} + \frac{C_{\mathrm{K-40}}}{A_{\mathrm{K-40}}} \tag{4.1}$$

In RP 112 Eq. (4.1) $A_{\mathrm{Ra\text{-}226}}$, $A_{\mathrm{Th\text{-}232}}$, and $A_{\mathrm{K\text{-}40}}$ are 300, 200, and 3000 Bq kg^{-1}, respectively. $A_{\mathrm{Ra\text{-}226}}$, $A_{\mathrm{Th\text{-}232}}$, and $A_{\mathrm{K\text{-}40}}$ are calculated for a “standard room” with the following characteristics: size 4 m × 5 m × 2.8 m; walls, ceiling, and floor are made of concrete with density = 2300 kg m^{-3} and thickness = 0.2 m.

In particular, when materials are used in bulk amounts, indoor annual doses of 0.3 and 1 mSv correspond to an index I of 0.5 and 1, respectively. When materials are superficial or with restricted use (tiles, boards, etc.) the values of index I corresponding to the annual values of 0.3 and 1 mSv are 2 and 6, respectively. In Table 4.1 values of the index I corresponding to the dose criteria are summarized.

It is worth mentioning that the RP 112 (EC, 1999) addressed the “Rn issue” by stating that: “When gamma doses are limited to levels below 1 mSv per year, the ^{226}Ra concentrations in the materials are limited, in practice, to levels which are unlikely to cause indoor radon concentrations exceeding the design level of the Commission Recommendation (*in that time 200 Bq m*$^{-3}$) (EC, 1990).”

Table 4.1 **Values of index *I* for different dose criteria and uses**

Annual dose criterion	0.3 mSv	1 mSv
Materials used in bulk amounts, e.g., concrete	$I \leq 0.5$	$I \leq 1$
Superficial and other materials with restricted use: tiles, boards, etc.	$I \leq 2$	$I \leq 6$

4.2.3 Radiation protection 122 part II

The concepts of exemption of practices and clearance of materials containing artificial radioactivity were introduced in Council Directive 96/29/Euratom (EU, 1996). The general exemption and clearance criteria state that (1) the radiological risk to individuals is sufficiently low, (2) the practice is justified, and (3) the practice is inherently safe (EU, 1996, 2013). While for artificial radionuclides this general framework was translated into a dose criterion and into calculated exemption values, this was not the case for natural radioactive materials. The application of the framework to natural radioactive materials was addressed in later guidance—RP 122—part II (EC, 2002). RP 122 II deals with the handling, processing, use, and disposal of NORM residues and the relevant radiological consequences. The document considers ten exposure scenarios for workers and another three for the population, including dwellings built with NORM-containing building materials, in order to determine the activity concentrations to be used as general exemption or clearance levels (GCL) for NORM. The model applied in the "dwelling exposure scenario" uses parameters that differ from those of the RP 112 scenario (see Section 4.2.2). In this model, the room size is 3 m × 4 m × 2.5 m, the number of walls made of building material (concrete) containing NORM is 2, to consider the presence of doors and windows. The annual dose criterion applied is 300 μSv. Additionally, the dilution factor of NORM used as concrete component is taken normally as 30%, except for 10% for fly ash.

If the content of naturally occurring radionuclides is above the clearance level shown in Table 4.2 then a radiological impact assessment must be made to demonstrate that the dose increment for the members of the public, in addition to the prevailing background radiation, is not more than 300 μSv per year (EC, 2002).

Table 4.2 Rounded general clearance levels for naturally occurring radionuclides in all types of solid materials as proposed by radiation protection 122 II

Radionuclide	**Activity concentration (kBq kg^{-1})**
^{238}U*sec* incl. ^{235}U*sec*[a]	0.5
Natural U	5
^{230}Th	10
^{226}Ra+	0.5
^{210}Pb+	5
^{210}Po	5
^{232}Th*sec*	0.5
^{232}Th	5
^{228}Ra+	1
^{228}Th+	0.5
^{40}K	5

[a] ^{238}U*sec* and ^{235}U*sec* are in their fixed natural ratio (99.275% and 0.72% atomic fraction).
(From RP 122 II)

The General Clearance and Exemption levels as elaborated in RP 122 II were aimed to provide for clearance of NORM residues and for exemption of NORM activities. Hence the use of NORM residues as a component of building materials was considered but the specific radiological concern about building materials as a radiation source was not within the scope of RP 122 II.

4.3 Council Directive 2013/59/Euratom laying down basic safety standards for protection against the dangers arising from exposure to ionizing radiation

Different types of building materials are considered in Council Directive 2013/59/Euratom (EU, 2014) and in particular in article 75 of this Directive. Annex XIII provides an indicative list of building materials of concern—divided into natural materials and materials incorporating residues from NORM processing industries. In article 75 it is also stated that the reference level for the indoor external exposure to gamma radiation from building materials is 1 mSv per year, in addition to the outdoor external exposure. So, the Council Directive uses 1 mSv per year as a reference level instead of 300 μSv proposed in RP 122 II (EU, 2014; EC, 2002). Member States can make their legislation more stringent, however, as explicitly stated in the Directive.

Building materials as a radon source are dealt with in the Annex XVIII of this Directive, listing items to be considered in preparing the national action plan to address long-term risks from radon exposure.

Annex VIII is focused on the use of the activity concentration index *I*. The index is taken in the form as defined in the RP112 (EC, 1999), but only for bulk use, and introduced as a tool to identify materials that need supplementary investigations. Indeed, building materials are considered to be of concern from a RP point of view when the value of index *I* exceeds 1 (corresponding to a reference level of 1 mSv per year from calculations in RP 112 (EC, 1999)). Annex VIII states that the index *I* is a conservative screening tool, and for building materials of concern "the calculation of dose needs to take into account other factors such as density, thickness of the material as well as factors relating to the type of building and the intended use of the material (bulk or

Table 4.3 **Activity concentrations for exemption or clearance of naturally occurring radionuclides in solid materials in secular equilibrium with their progeny**

Radionuclide	Activity concentration (kBq kg^{-1})
Natural radionuclides from the ^{238}U series	1
Natural radionuclides from the ^{232}Th series	1
^{40}K	10

From Table A Part 2 of Annex VII of the Council Directive 2013/59/Euratom (EU, 2014).

superficial).” A detailed description of the index *I* and other tools to assess the gamma dose rate from building materials is reported in Section 4.7.

When recycling NORM residues in building materials is not a feasible option, the Annex VII of the Council Directive 2013/59/Euratom provides the exemption and clearance levels in terms of activity concentrations for naturally occurring radionuclides in solid materials (see Table 4.3) (EU, 2014). These values can be applied by default to any amount and any type of solid material to be cleared for reuse, recycling, conventional disposal, or incineration (EU, 2014). As the destination of the material is often not known in advance, these general clearance and exemption levels are defined as default minimum values. Member States may specify dose criteria (smaller than 1 mSv per year) for specific types of practices or specific pathways of exposure involving natural occurring radionuclide.

The activity concentrations listed in Table 4.3 apply to all radionuclides of the decay chain of ^{238}U or ^{232}Th in solid materials in secular equilibrium with their progeny. The EU-BSS does not exclude that for segments of the decay chain, which are not in equilibrium with the parent radionuclide, higher values may be applied, e.g., for ^{210}Po and ^{210}Pb.

4.3.1 Council Directive 2013/59/Euratom and CPR 305/2011

In Jul. 2013, the Construction Products Directive 89/106/EEC was replaced by a directly applicable CPR (305/2011/EU) laying down requirements for the marketing of construction products. Directive 89/106/EEC had put the “emission of dangerous radiation” in the list of the “essential requirements”—concerning hygiene, health, and the environment—to be satisfied by construction works. However, this generic statement was, so far, not translated in standards for the RP of workers of the public linked to general construction works. So, only Council Directive 2013/59/Euratom deals specifically with radioactivity in building materials

In the CPR, “dangerous radiation” is again mentioned in the “ANNEX I—Basic requirements for construction works,” hence giving the radiological characteristics of construction materials stronger emphasis. In fact, “dangerous radiation” together with other toxic and dangerous agents may not to become a “threat to the hygiene or health and safety of workers, occupants or neighbors, nor have an exceedingly high impact, over their entire life cycle, on the environmental quality or on the climate during their construction, use and demolition, etc.”

The intention of the CPR is

i. to provide for a system of harmonized technical specifications for construction products
ii. to establish harmonized rules on how to detail the performance of construction products in relation to certain essential characteristics
iii. to provide for the CE marking of products

As far as radiation is concerned, the construction works must be designed and built in such a way that the emission of dangerous radiation will not be a threat to the health of the occupant or neighbors.

It is important to emphasize that the CPR does not harmonize regulations and requirements concerning the actual construction product. It only harmonizes which product characteristics are relevant for consideration and it harmonizes the technical means of determining the product's performance in relation to these essential characteristics. Member States and public and private sector procurers are free to set their own requirements for the performance of the products and therefore on the performance level. The performance level of 1 mSv per year for building materials is laid down in the Council Directive 2013/59/Euratom.

The 2013/59 Euratom Directive refers to the CPR regulation (which was published three years earlier), stating (in the "preamble") that

> ***(19)*** *Building materials emitting gamma radiation should be within the scope of this Directive but should also be regarded as construction products as defined in Regulation (EU) No 305/2011, in the sense that Regulation applies to construction works emitting dangerous substances or dangerous radiation.*
>
> ***(20)*** *This Directive should be without prejudice to the provisions of Regulation (EU) No 305/2011 on the declaration of performance, the establishment of harmonized standards or the means and conditions for making available the declaration of performance or with regard to CE marking.*
>
> ***(21)*** *Regulation (EU) No 305/2011 requires information to be made available when products are placed on the market. This does not affect the right of Member States to specify in national legislation requirements for additional information they deem necessary to ensure radiation protection.*

Under the general rules of the Euratom Treaty, Members States are obliged to transform requirements of the Directive into national system of regulation by 6th of February 2018. To facilitate good implementation of the CPR, harmonized procedures for determining the radiological characteristics in construction products are required. The product information obtained through these procedures will be used in the declaration of performance or with regard to CE marking of building materials. For this purpose, the European Committee for Standardization (CEN)—mandated by the European Commission—has established the Technical Committee (TC351) in Nov. 2005 to develop horizontal standardized assessment methods for harmonized approaches relating to the release of dangerous substances under the CPR.

The development of harmonized methods in relation to radiation is carried out under Working Group 3 (WG3). The WG3 has drafted a Technical Specification (TS) for the determination of the activity concentrations from radium-226, thorium-232, and potassium-40 in construction products using gamma-ray spectrometry. The TS describes the sample preparation and the sample measurement and includes procedures for energy and efficiency calibration and analysis of the spectrum. The specification is based on the Dutch NEN 5697 (NEN, 2001). After completion of the TS the specification will be proposed for a European norm (EN). The WG3 has also drafted a technical report on the dose assessment of emitted gamma radiation from construction products. The report is intended to provide a harmonized dose assessment approach that accounts for factors such as density or thickness of the material as well as factors relating to the type of construction and the intended use of the material (bulk or superficial) (Hoffmann, 2014). This approach is especially needed for building materials with an index exceeding 1 but that nonetheless may still comply with the 1 mSv per year reference level.

4.4 Drinking water Directive

At first glance, there is no direct link between drinking water and building materials, but when their entire life cycle is considered, the possibility that they and/or their rubble can contaminate water by environmental pathways must be considered. This was intended to apply to NORM processing industries rather than construction works, as is pointed out in the article 25(3) of the Council Directive 2013/59/Euratom that states:

> *3. Notwithstanding the exemption criteria laid down in Article 26 (i.e. clearance levels, see tab 3), in situations identified by Member States where there is concern that a practice identified in accordance with Article 23 may lead to the presence of naturally-occurring radionuclides in water liable to affect the quality of drinking water supplies or affect any other exposure pathways, so as to be of concern from a radiation protection point of view, the competent authority may require that the practice be subject to notification.*

For the specific scenario in which one of the exposure pathways to natural or artificial radioactivity is through drinking water ingestion, dose to population is regulated by the Council Directive 2013/51/Euratom which lays down the requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption (EU, 2013). This Directive supersedes Directive 98/83/EC on the quality of water intended for human consumption "…as regards the requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption." Indeed, the Directive 98/83/EC dealt with all the pollutants in drinking water. Due to the Euratom Treaty competence in any situation of radiological exposure, Council Directive 2013/51/Euratom was issued specifically for radioactivity in drinking water.

Besides radon and tritium, considered separately, a special term was coined, indicative dose (ID). The indicative dose is defined as the effective committed dose obtained from all the radionuclides (natural and artificial) present/detected in drinking water but excluding tritium, radon, short-lived radon decay products, and ^{40}K. The parametric value for ID was set at 0.1 mSv per year. Based on this value, specific annual intake values, and dose per unit intake, a list of derived concentration values is provided for the most common natural (Table 4.4) and artificial radionuclides (but can also be calculated for other radionuclides that are not in the list). If a screening is performed for certain radionuclides and the activity concentration exceeds 20% of the corresponding derived value an analysis of additional radionuclides is required. When

Table 4.4 **Derived concentrations for naturally occurring radionuclides in drinking water**

Radionuclide	Derived concentration (Bq L^{-1})
^{238}U	3.0
^{234}U	2.8
^{226}Ra	0.5
^{228}Ra	0.2
^{210}Pb	0.2
^{210}Po	0.1

From Annex III of the Council Directive 2013/51/Euratom.

multiple radionuclides are present, the weighted sum of the concentrations of the individual radionuclides needs to be smaller or equal to 1 in order to be below the indicative dose of 0.1 mSv per year.

Instead of screening for individual radionuclides, it is also possible to measure gross alpha and beta activity with their corresponding screening levels of 0.1 Bq L^{-1} for gross alpha activity and 1.0 Bq L^{-1} for gross beta activity. If the measured activities are below their screening levels, it can be assumed that the indicative dose is less than 0.1 mSv per year; otherwise, a screening for specific radionuclides is required. The clearance levels set for NORM in solid materials and calculated according to RP 122 II (Table 4.2) are around three orders of magnitude higher than the derived concentration values in water (Table 4.4). This is why it is prudent to take into account the possibility of water contamination in case of long-term direct contact with rubble.

4.5 Analysis of national legislations

In Table 4.5 the legislation and recommendations currently (end of 2016) in use in EU and non-EU countries are summarized. These regulations have socio-economic consequences because they are used for banning the use and trade of materials exceeding the defined dose criteria. For screening and evaluation of construction materials several screening tools are in use that are summarized in Table 4.5 with the adopted screening tool reference values (decision values for a given index). The activity concentration index approach is widely used in different national legislations and recommendations. However, values of parameters and formula of indexes may significantly vary between countries. Other differences may arise due to considerations on activity concentration in typical building materials in each country and their final utilization,

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[1] The Ra_{eq} method, introduced by Beretka and Mathew (1985), is based on the definition of radium equivalent activity:

$$Ra_{eq} = C_{Ra-226} + 1.43C_{Th-232} + 0.077C_{K-40} \leq 370$$

Ra_{eq} uses dose criteria of 1.5 mGy per year, which corresponds to approximately 1 mSv per year and, approximately, to 370 Bq kg^{-1} of ^{226}Ra, 260 Bq kg^{-1} of ^{232}Th, and 4800 Bq kg^{-1} ^{40}K. In the Ra_{eq} equation, exposure to gamma radiation is controlled by limiting $Ra_{eq} \leq 370$ Bq kg^{-1}.

Table 4.5 **Summary of the legislation and recommendations still in use in EU and non-EU countries**

Country	Index	Decision values	End-use of building materials	Dose criterion (mSv per year)
EU countries				
Council Directive 2013/59/ Euratom (EU, 2014)	$I_1 = \frac{C_{\mathrm{Ra}}}{300} + \frac{C_{\mathrm{Th}}}{200} + \frac{C_{\mathrm{K}}}{3000}$	$I \leq 1$		1
Austria[a] (Austrian Standard Institute, 2009) ÖNORM S 5200: 2009	$I = \frac{C_{\mathrm{Ra-226}}}{880}(1 + 0.07\varepsilon pd) + \frac{C_{\mathrm{Th-232}}}{530} + \frac{C_{\mathrm{K-40}}}{8800}$	$I \leq 1$		1
Czech Republic (Hulka et al., 2008)	$I_1 = \frac{C_{\mathrm{Ra}}}{300} + \frac{C_{\mathrm{Th}}}{200} + \frac{C_{\mathrm{K}}}{3000}$; $C_{\mathrm{Ra}}\,\mathrm{Bq\ kg^{-1}}$	$I \leq 0.5$ $C_{\mathrm{Ra}} \leq 150$	Bulk material (e.g., brick, concrete, gypsum)	0.3
		$I \leq 1$ $C_{\mathrm{Ra}} \leq 300$	Raw material (e.g., sand)	
		$I \leq 2$ $C_{\mathrm{Ra}} \leq 300$	Superficial material (e.g., tiles)	
Finland (STUK, 2010)	$I_1 = \frac{C_{\mathrm{Ra}}}{300} + \frac{C_{\mathrm{Th}}}{200} + \frac{C_{\mathrm{K}}}{3000}$ $I_2 = \frac{C_{\mathrm{Ra}}}{700} + \frac{C_{\mathrm{Th}}}{500} + \frac{C_{\mathrm{K}}}{8000} + \frac{C_{\mathrm{Cs}}}{2000}$	$I_1 \leq 1$	Bulk material	1
		$I_1 \leq 6$	Superficial material	
		$I_2 \leq 1$	Bulk material for road constructions	0.1
		$I_2 \leq 1.5$	Superficial material for road constructions	

Continued

Table 4.5 **Continued**

Country	Index	Decision values	End-use of building materials	Dose criterion (mSv per year)
Poland (Poland Government, 2007)	$f_1 = \frac{S_{\mathrm{Ra}}}{300} + \frac{S_{\mathrm{Th}}}{200} + \frac{S_{\mathrm{K}}}{3000}$; $f_2 = S_{\mathrm{Ra}}\,\mathrm{Bq\,kg^{-1}}$	$f_1 + \Delta f_1 \leq 1.2$ $f_2 + \Delta f_2 \leq 220$	Dwelling: for civil engineering construction indexes can be multiplied up to four times	1
Non-EU countries				
Albania (Albania Government, 2011)	$I_1 = \frac{C_{\mathrm{Ra}}}{300} + \frac{C_{\mathrm{Th}}}{200} + \frac{C_{\mathrm{K}}}{3000}$	$I_1 \leq 1$	Bulk material	1
	$I_2 = \frac{C_{\mathrm{Ra}}}{700} + \frac{C_{\mathrm{Th}}}{500} + \frac{C_{\mathrm{K}}}{8000} + \frac{C_{\mathrm{Cs}}}{2000}$	$I_2 \leq 1$	Bulk material for road constructions	
China (Standardization Administration of the People's Republic of China, 2010) GB 6566-2010	$I_{\mathrm{r}} = \frac{C_{\mathrm{Ra}}}{370} + \frac{C_{\mathrm{Th}}}{260} + \frac{C_{\mathrm{K}}}{4200}$; $I_{\mathrm{Ra}} = \frac{C_{\mathrm{Ra}}}{200}$	$I_{\mathrm{Ra}} \leq 1.0$ $I_{\mathrm{r}} \leq 1.0$	Bulk material	1
		$I_{\mathrm{Ra}} \leq 1.0$ $I_{\mathrm{r}} \leq 1.3$	Superficial and 25% hollow bulk material for dwelling constructions	
		$I_{\mathrm{Ra}} \leq 1.3$ $I_{\mathrm{r}} \leq 1.9$	Superficial material for industrial constructions	
		$I_{\mathrm{r}} \leq 2.8$	Superficial material for outside use	

Israel[a,b] (Kovler, 2011)— SI_5098: 2009	$I=\frac{A_{\mathrm{Ra}}}{A_1}(1-\in)+\frac{A_{\mathrm{Ra}}}{A_2}\in+\frac{A_{\mathrm{Th}}}{A_3}+\frac{A_{\mathrm{K}}}{A_4}$	$I\leq 1$	Bulk material	0.3
		$I\leq 0.8$	Superficial material	
	$I_{\gamma}=\frac{A_{\mathrm{Ra}}}{A_1}+\frac{A_{\mathrm{Th}}}{A_3}+\frac{A_{\mathrm{K}}}{A_4}$	$I\leq 0.4$	Bulk material	
		$I\leq 0.32$	Superficial material	
Russia (State Committee for the Russian Federation for Standardization and Metrology, 1994) GOST 30,108-94	$A_{\mathrm{eff}}\,\mathrm{Bq\,kg^{-1}}=A_{\mathrm{Ra}}+1.3A_{\mathrm{Th}}+0.09A_{\mathrm{K}}$	$A_{\mathrm{eff}}+\Delta A_{\mathrm{eff}}$ ≤ 370	Dwelling/public constructions	1
		≤ 740	Industrial construction	
		≤ 1500	Road constructions	
Serbia Official Gazette of Serbia 86/2011[b]	$I_1=\frac{C_{\mathrm{Ra}}}{300}+\frac{C_{\mathrm{Th}}}{200}+\frac{C_{\mathrm{K}}}{3000}$	$I_1\leq 1$	Bulk material	1
	$I_1=\frac{C_{\mathrm{Ra}}}{400}+\frac{C_{\mathrm{Th}}}{300}+\frac{C_{\mathrm{K}}}{5000}$	$I_1\leq 1$	Bulk material for outside use	
	$I_1=\frac{C_{\mathrm{Ra}}}{700}+\frac{C_{\mathrm{Th}}}{500}+\frac{C_{\mathrm{K}}}{8000}$	$I_1\leq 1$	Bulk material for road constructions	

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[a] If emanation coefficient it is not known: in Austria $\varepsilon=10\%$ can be used; in Israel $\varepsilon=6\%$–7% for masonry block; and $\varepsilon=12\%$ for other building materials including concrete.

[b] The $A_{\text{K-40}}$, $A_{\text{Ra-226}}$, $A_{\text{Th-232}}$ values depend on the density and thickness of the building product.

different environmental background, and not the least the standard room model applied. The main differences are listed as follows.

- Many countries, e.g., Russia, use the radium equivalent activity concentration Ra_{eq} (see note[1]).
- In general, both EU and non-EU countries use 1 mSv per year as dose criteria. This annual dose is meant in excess to the average outdoor background which in the EU is 50 nGy h^{-1}. The Austrian legislation uses an average dose rate of approximately 240 nGy h^{-1} (Austrian Standard Institute, 2009). Israel uses a dose criterion of 0.3 mSv per year exceeding background which is "*the average dose which would be received in a house built from materials with* '*typical*' *activities*" (Markkanen, 2001). For the Finish legislation, an activity concentration index for "streets and playgrounds" (bulk material for road construction) larger than 1 indicates an effective gamma dose larger than 0.1 mSv per year while for the evaluation of building materials the dose criterion 1 mSv per year is used but both calculations are based on very different dose models (Markkanen, 1995).
- Regarding the activity concentration in building material it is worth highlighting that Nordic countries (like Finland) include also the presence of ^{137}Cs due to the Chernobyl accident.
- The screening indexes do not generally take radon emanation into account with the exception of Austria and Israel. On the other hand, many countries tried to account for radon exhalation by limiting the ^{226}Ra activity concentration, e.g., China, Czech Republic, and Poland.
- The determination of activity concentration is essential for accurately determining the activity concentration index; however, only the Russian and Polish legislations include the uncertainty in the determination of the index as: $A_{\text{eff}} + \Delta A_{\text{eff}} \leq 370\,\text{Bq/kg}$ and $\text{index}\, I + \Delta\text{index}\, I \leq 1.2$, respectively. In general, in different countries, it is only recommended that the relative uncertainty on the measurement should not be higher than 20%. As ^{232}Th does not contribute directly to gamma radiation, this is not the most relevant radionuclide to be considered in a screening index that is evaluating the gamma dose. The use of ^{232}Th in an index is only relevant in case of secular equilibrium in the whole thorium decay series. Moreover, ^{232}Th being an alpha emitter in not easily measurable and in practice, its decay products ^{228}Ra (by ^{228}Ac) and/or ^{228}Th (by ^{208}Tl) are measured by gamma spectrometry. As the equilibrium state is often disturbed in NORM and NORM-containing building materials the use of the considered decay products, instead of ^{232}Th, in relevant formulas is more appropriate. This aspect was accounted for in the Polish and Austrian regulations.

4.6 Examples of national legislations

In the next sections several examples of EU legislations and one example of a non-EU national legislation are discussed more in depth. For most EU Member States, as a result of the transposition of Council Directive 2013/59/Euratom, it is the first time that they are preparing national regulations dealing with the radioactivity in building materials.

4.6.1 Austria

In 1995, an index *I* that accounts for exposure from both gamma radiation and radon exhalation from building materials was established in the Austrian legislation (Austrian Standard Institute, 1995).

$$\begin{aligned} I = {} & (1+0.15k)C_{\mathrm{Ra-226}}/1000\,\mathrm{Bq\,kg^{-1}} + C_{\mathrm{Th-232}}/600\,\mathrm{Bq\,kg^{-1}} \\ & + C_{\mathrm{K-40}}/10{,}000\,\mathrm{Bq\,kg^{-1}} \le 1 \end{aligned} \tag{4.2}$$

where k is a constant which depends on some characteristics of the materials, i.e., density, thickness, and radon emanation power. The dose criterion used to calculate the A_x values for ^{226}Ra, ^{232}Th, and ^{40}K is 2.5 mSv per year.

In 2009 a new regulation was issued, which improved the radon contribution estimate to the excess indoor effective dose (Austrian Standard Institute, 2009) changing the index definition in this way:

$$\begin{aligned} I = {} & (1+0.07\varepsilon\rho\delta)C_{\mathrm{Ra-226}}/880\,\mathrm{Bq\,kg^{-1}} + C_{\mathrm{Th-232}}/530\,\mathrm{Bq\,kg^{-1}} \\ & + C_{\mathrm{K-40}}/8800\,\mathrm{Bq\,kg^{-1}} \le 1 \end{aligned} \tag{4.3}$$

where ε is the radon emanation power, ρ the wall density, d the wall thickness, and 0.07 is a constant, expressed in (m^2 kg^{-1}). When disequilibrium in thorium decay series is noticed then the ^{232}Th activity concentration is calculated as:

$$C_{\mathrm{Th-232}} = 0.5(C_{\mathrm{Ra-228}} + C_{\mathrm{Th-228}})$$

The dose criterion used to calculate the A_x values for ^{226}Ra, ^{232}Th, and ^{40}K is 1 mSv per year exceeding the assumed outdoor background dose of 1.2 mSv per year. More details on this Austrian index are reported in Section 4.7.5.

4.6.2 Belgium

For recycling NORM residues into building material, the activity concentration of a single batch of NORM residues should typically not exceed 10 kBq kg^{-1} and a control on the resulting activity concentration in the produced building material must be made by the operator. For building materials used in habitation, the activity index $I=1$ is used as a reference level. The clearance levels of Table 4.2 are used for other building materials, like materials used in road construction.

4.6.3 Czech Republic

Starting from 1970, the Czech Republic had to face a serious situation with several thousand houses built with material rich in radium or contaminated with residues from uranium paint and radium factories (with ^{226}Ra activity concentration up 1 MBq kg^{-1}). The Czech Republic is also one of the countries with the highest indoor radon concentration in the world (mean radon concentration = 140 Bq m^{-3}) (Hulka et al., 2008).

For the above reasons, in 1987 the Czech Republic had to introduce an ad hoc legislation stating interventional levels for already existing houses, which is the only example found in literature of the use of an index to identify existing dwellings of concern. For this purpose, the following index S was introduced, in order to limit both gamma and indoor radon exposures in dwellings:

Table 4.6 Limit values for ^{226}Ra in the Czech Republic legislation

Type of building material	^{226}Ra limit value (Bq kg^{-1})	
	Buildings where people live or stay	**Other constructions where people do not live or stay**
Material used in bulk amount (e.g., brick, concrete, gypsum)	150	500
Other material used in small amounts (e.g., tile, etc.) and raw material (sand, building stone, gravel aggregate, bottom ash, etc.)	300	1000

$$S = D/2\,\mu\mathrm{G}\gamma\,\mathrm{h}^{-1} + C_{\mathrm{Rn}}/400\,\mathrm{Bq\,m}^{-3} \tag{4.4}$$

where D is the gamma dose rate (μGy h^{-1}) and C_{Rn} the annual average radon concentration (Bq m^{-3}). This index results from the choice of a recommended value of 400 Bq m^{-3} for radon activity concentration, and 2 μGy h^{-1} for indoor gamma dose rate, to remediate existing buildings. “This sum rule (used only if $D > 2$ μGy h^{-1}) and value $S = 1$ were used for decision making on remedial measures with governmental support” (Hulka et al., 2008). For new houses, the limit value for ^{226}Ra was calculated in order to keep $\leq 30\%$ the building material contribution to the indoor radon limit value (200 Bq m^{-3}). With a room model under conservative conditions, the resulting limit value for ^{226}Ra was 120 Bq kg^{-1}. As reported by Hulka et al. (2008), “The other systems of regulation based on limitations for radon exhalation rate or emanation coefficient were discussed but rejected at the end because of sophisticated measurements of exhalation, long-term changes, and the complicated system of limitation proposed.”

The present Czech legislation concerning radioactivity in building materials is based on a two-step procedure to account for both gamma and radon exposure (Hulka et al., 2008): firstly, the index I, as defined by the RP 112 document (EC, 1999), is used as a screening tool. Producers and importers should ensure systematic measurements of natural radionuclides in building materials and submit the results to the State Office for Nuclear Safety. If the index I is higher than 0.5—a value corresponding to the exemption level of 0.3 mSv per year—a cost-benefit analysis should be done by the producer with a criterion aimed at reducing the public doses to a level as low as reasonably achievable (see details in Hulka et al., 2008). In the second step, in order to control radon exhalation from building materials, the producer must also apply the limit levels for ^{226}Ra activity concentrations of Table 4.6.

4.6.4 Example of a non-European approach: Australia

In Australia, materials containing natural radioactivity are generally subject to regulatory consideration dependent upon the radionuclide concentration and the radionuclide quantity. This is also the case for by-products or wastes from existing processes that may be used in construction materials.

The largest volumes of material that may be useful in construction are generated from mining and processing operations within Australia. While most of the material is disposed under appropriate mining regulation; in some case, the material may be used in activities such as road construction or as part of building materials. In these cases, it may only be used after approval from the appropriate authority.

Australia is a federation of states and territories and this has resulted in the development of different laws and regulations at a national level and also at individual State and territory level. Generally, the overall regulatory approach to NORM in Australia is guided by the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA), and the guidance is based on the International Atomic Energy Agency (IAEA) framework. State and territories then tend to adopt the guidance into regulation.

ARPANSA publishes a series of NORM-related documents as part of its Radiation Protection Series (http://www.arpansa.gov.au/) and these include

- Radiation Fundamentals: Fundamentals for Protection Against Ionizing Radiation (2014).
- Codes of Practice and Standards: These are detailed documents which are usually adopted in state-based regulation.
- Guides and Recommendations: General documents which provide practical advice and assistance for regulators or operators.

The primary ARPANSA NORM-related document is *Safety Guide for the Management of Naturally Occurring Radioactive Material* (*NORM*), published in 2008. The document essentially follows the guidance provided by the IAEA about the application of the concepts of exclusion, exemption, and clearance (IAEA, 2004a) and the IAEA Safety Guide about occupational RP in the mining and processing of raw materials (IAEA, 2004b).

4.7 Screening tools

4.7.1 Different approaches to modeling

In general, an index is used to estimate the gamma dose rate from the activity concentration in building material (EC, 1997). The index is the sum of the ratios of specific activities of various nuclides relative to reference values. In order that the material complies with the screening criterion, the index should not typically exceed the value of *I*:

$$I = \frac{C_{\mathrm{Ra-226}}}{A_{\mathrm{Ra-226}}} + \frac{C_{\mathrm{Th-232}}}{A_{\mathrm{Th-232}}} + \frac{C_{\mathrm{K-40}}}{A_{\mathrm{K-40}}} \leq 1 \tag{4.5}$$

where C_x (Bq kg^{-1}) is the measured activity concentration and A_x (Bq kg^{-1}) is the fixed reference value. The A_x values are calculated after assuming a dose criterion to be complied with and a background to be subtracted. These values also depend on the geometrical and structural characteristics of the indoor environment (room size, density, thickness of materials, etc.) and the dose rate coefficients per unit activity concentration (i.e., the room model) used. Finally, the outdoor background subtracted from the indoor dose rate might play a significant role. For this reason, A_x values might significantly vary among EU countries if the country-specific outdoor background were accounted to calculate A_x. These indexes are generally conservative tools, elaborated for screening purpose.

4.7.2 The EU BSS index

As mentioned already in Section 4.3, the EU BSS (Article 75, Annex XIII) (EU, 2014) introduces a screening index I_{BSS} in order to identify building materials that might be of concern from the RP point of view, "taking into account the indicative list of building materials set out in Annex XIII" of the EU BSS. This index, the first time proposed in RP 112 (EC, 1999), is the application of the "general index," shown in the previous paragraph, calculated in a specific case that will be described.

In the I_{BSS} formula

$$I_{\mathrm{BSS}} = \frac{C_{\mathrm{Ra-226}}}{300} + \frac{C_{\mathrm{Th-232}}}{200} + \frac{C_{\mathrm{K-40}}}{3000} \leq 1 \tag{4.6}$$

the A_x parametric values in generic index expression (1) calculated for Ra-226, Th-232, and K-40 are 300, 200, and 3000, respectively. These A_x values were obtained assuming: (i) a dose criterion of 1 mSv per year—as the excess to the average background originating from the Earth's crust, (ii) an annual occupancy factor of 7000 h, and (iii) a conversion coefficient 0.7 Sv Gy^{-1}. The background dose rate, corresponding to an average value outdoors in Europe, was assumed to be 50 nGy h^{-1}. With the cited hypotheses, 50 nGy h^{-1} correspond to about 0.25 mSv per year. Elaboration of A_x in I_{BSS} is based on specific prerequisites that do not always represent a given situation that is being evaluated. The following assumptions are linked to the I_{BSS}: (1) the room dimensions are 4 m × 5 m × 2.8 m, (2) all surfaces (walls, floor, and ceiling) are assumed to be made from the same material (concrete of density = 2350 kg m^{-3} and thickness of 0.2 m), (3) no presence of windows or doors, etc., is assumed. The room size is not a critical parameter, as demonstrated by Risica et al (2001)]. The assumption regarding the absence of windows and doors does not strongly influence the indoor gamma dose rate particularly considering its screening aim. On the contrary, thickness and density are the key characteristics of building materials that mostly affect the gamma irradiation indoors. A higher density and/or thickness results in a higher gamma irradiation. This aspect of $\mathrm{I_{BSS}}$ is also considered in the EU BSS. Indeed, Annex VIII states that when I_{BSS} of the considered building material exceeds 1 (corresponding to a reference level of 1 mSv per year), that "the calculation of dose needs to take into account other factors such as density, thickness of the material as well as factors relating to the type of building and the intended use of the material (bulk or superficial)." Considering that I_{BSS} parameters are calculated for a dense and thick building material, i.e., concrete of density = 2350 kg m^{-3} and thickness of 0.2 m, any other material of lower density and/or lower thickness is screened with a tool that is too conservative.

4.7.3 A new family of screening tools

In order to obtain a more realistic screening tool which better represents the gamma radiation properties of building materials, i.e., one that will allow for a conservative but realistic discrimination of building materials, in the last decade other tools accounting for density and thickness were developed. Confirming the need for this kind of tools, in the framework of the EU CPR No. 305/2011 (EU, 2011), the working group WG3 "Radiation from construction products" of the CEN/TC351 "Construction products: assessment of release of dangerous substances" received the mandate to screen possible ways for calculating the dose determined by gamma rays from building products with known concentrations of natural radionuclides (Hoffmann, 2014).

4.7.4 Israeli index

In 2009, Israel issued the standard SI 5098 for building materials radioactivity (Standards Institution of Israel, 2009). It should be pointed out, however, that this is not a screening tool, but a *standard*. This standard accounts for both gamma radiation and radon exhalation from building material, and introduces a total activity concentration index I:

$$I = \frac{C_{\mathrm{Ra-226}}}{A_1}(1-\varepsilon) + \frac{C_{\mathrm{Ra-226}}}{A_2}\varepsilon + \frac{C_{\mathrm{Th-232}}}{A_3} + \frac{C_{\mathrm{K-40}}}{A_4} \tag{4.7}$$

and the gamma activity concentration index I_γ

$$I_\gamma = \frac{C_{\mathrm{Ra-226}}}{A_1} + \frac{C_{\mathrm{Th-232}}}{A_3} + \frac{C_{\mathrm{K-40}}}{A_4} \tag{4.8}$$

As for the total index I in Eq. (4.7), the first, third, and fourth terms account for the excess indoor gamma dose; the second term, for the radon inhalation dose. The first term takes into account the gamma dose reduction from the ^{226}Ra chain due to emanation and exhalation of ^{222}Rn. Indeed, radioactive equilibrium disturbance in the material, due to radon emanation, results in activity contents of ^{214}Pb and ^{214}Bi in the material lower than that of ^{226}Ra.

A_x values depend on the typical specific area ρd (kg m^{-2}) of building material, i.e., density multiplied by thickness.

The A_x parameters are calculated assuming an excess dose of 0.3 mSv per year (dose criterion) above background, i.e., the typical levels of indoor exposure "which would be received in a room built from materials with typical activities." This dose criterion refers to the sum of gamma and radon exposure. Indeed, the building product must comply with both the total activity concentration index I and the gamma activity concentration index I_γ, which have two different series of reference values, e.-g., in the case of concrete, $I \leq 1$ and $I_\gamma \leq 0.4$.

In a similar way, the background dose accounts for both gamma radiation and radon and—like I and I_γ values—have been set for three classes of building products according to their density.

4.7.5 Austrian index

In Austria, the radioactivity in building material is regulated by the standard ÖNORM S5200 (Austrian Standard Institute, 2009). It is based on a similar index which, however, includes the exposure to Radon too:

$$I=\frac{C_{\mathrm{Ra-226}}}{880}(1+0.07\varepsilon\rho d)+\frac{C_{\mathrm{Th-232}}}{530}+\frac{C_{\mathrm{K-40}}}{8800}\leq 1 \tag{4.9}$$

with ρ is the density in kg m^{-3}, d is the thickness in m, and ε is the radon emanation coefficient in the building material. If these values are not known than the default values that listed below have to be used:

$$d=0.3\,m;\ \rho=2000\,\mathrm{kg}\,m^{-3};\ \rho d=600\,\mathrm{kg}\,m^{-2};\ \varepsilon=0.1.$$

The formula (4.9) is based on a dose criterion of 1.0 mSv per year exceeding an annual outdoor background of 1.2 mSv.

In case of a nonequilibrium in the thorium decay chain it is accepted to use

$$C_{\mathrm{Th-232}}=0.5(C_{\mathrm{Ra-228}}+C_{\mathrm{Th-228}}) \tag{4.10}$$

The simplified formula

$$I=\frac{\rho d}{250}\left[\frac{C_{\mathrm{Ra-226}}}{880}(1+18\varepsilon)+\frac{C_{\mathrm{Th-232}}}{530}+\frac{C_{\mathrm{K-40}}}{8800}\right]\leq 1 \tag{4.11}$$

can be used if the structural element has an areal density of below 250 kg m^{-2}.

When the index relation is fulfilled then the building material can be used without restriction. If the relation is not fulfilled then the (areal) weighted mean of all building materials of a room has to be used to check for compliance, however, the index of each contributing building material must stay below 2.

In addition, the surface β-activity must be below 2.0 Bq cm^{-2}. The measurement can be performed by a contamination monitor, which is calibrated for high-energy β-radiation.

4.7.6 Screening tool I(ρd)

Very recently a new tool to screen building materials as gamma ray source and accounting for density and thickness of building materials was published (Nuccetelli et al., 2015). Its structure is similar to the general expression (see Eq. 4.5) but terms A_x are dependent on density and thickness.

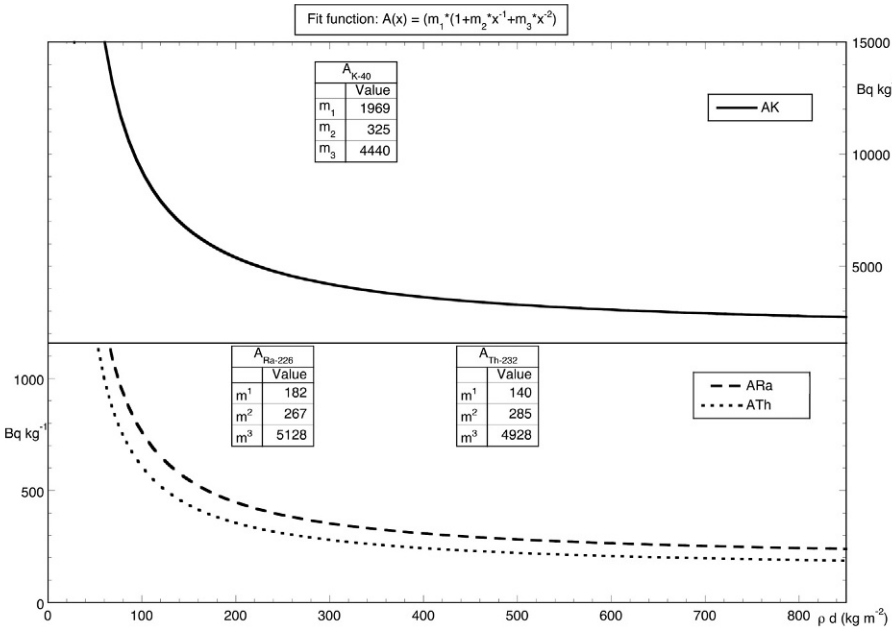

Fig. 4.2 Graphics of the $A(\rho d)_x$ for Ra-226, Th-232, and K-40.
Modified from Nuccetelli, C., Leonardi, F., Trevisi, R., 2015. A new accurate and flexible index to assess the contribution of building materials to indoor gamma exposure. J. Environ. Radioact. 143, 70–75.

$$I = \frac{C_{\mathrm{Ra-226}}}{A(\rho d)_{\mathrm{Ra-226}}} + \frac{C_{\mathrm{Th-232}}}{A(\rho d)_{\mathrm{Th-232}}} + \frac{C_{\mathrm{K-40}}}{A(\rho d)_{\mathrm{K-40}}} \leq 1 \tag{4.12}$$

where the general expression of $A(\rho d)_x$ is

$$A(\rho d)_x = m_1\left[1 + m_2(\rho d)^{-1} + m_3(\rho d)^{-2}\right] \tag{4.13}$$

It can be demonstrated that the I_{BSS} becomes a special application of Eq. (4.12). Indeed, when the factor (ρd) equals 470 kg m^{-2}, the typical value for concrete used in RP 112 (EC, 1999), the rounded values of $A(\rho d)_x$ become 300, 200, and 3000 for Ra-226, Th-232, and K-40, respectively (Fig. 4.2). The coefficients m_1, m_2, and m_3 have different values for Ra-226, Th-232, and K-40 and it can be shown that the m_1 values in Eq. (4.9) represent the asymptotic behavior of the $A(\rho d)_x$ when ρd tends to infinity, i.e., the lower limits of the activity concentrations of Ra-226, Th-232, and K-40 determining 1 mSv per year from any kind of building material (see Nuccetelli et al., 2015).

The idea is not to replace the index of the Euratom Directive; however, since this is merely a conventional expression of the radioactivity content. The term "I" in the equation is rather like a function correcting for density and thickness in order to evaluate the dose for comparison with the reference level of 1 mSv per year.

4.8 Conclusions and recommendations

In the development of EU technical guidelines and national regulations increasingly building materials were recognized as an important source of indoor gamma exposure. In the new EU Basic Safety Standards (EU, 2014), for the first time, building materials were included in the scope of application.

This fact sets the need to control activity concentrations of selected natural building materials and of NORM-containing building materials to comply with the new EU reference level defined in terms of 1 mSv per year (as effective gamma dose). It is important to note that compliance to the Directive 2013/59/Euratom should be without prejudice to the provisions of Regulation (EU) No. 305/2011 about construction products and the consequent CE marking. Therefore, harmonization of EU procedures is required to support the free movement of building materials in the EU internal market. To achieve this goal, harmonized methods for the determination of the activity concentrations and the dose assessment are under development by the Technical Committee 351—WG3 of the European Committee for Standardization (CEN). These harmonized methods are especially needed for building materials with an index exceeding 1 where it is important to verify whether they comply with the reference level of 1 mSv per year.

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Measurement of NORM

5

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5.1 Introduction

Guide for the reader: Aim of chapter "5":

The aim of this chapter is to discuss the necessary preparations for measurements and usually applied techniques for radioactivity measurements of NORM (naturally occurring radioactive materials), raw materials, and building products, taking into consideration their advantages and disadvantages in determining:

- The activity concentration of the considered natural occurring radionuclides (Section 5.2).
- The direct measurement of indoor dose rate (in dwellings) (Section 5.3).
- Radon gas exhalation (Section 5.4).
- Radon gas concentration in dwellings (also in Section 5.4, see especially in Section 5.4.3).

Measurements are necessary to verify the compliance of building materials with the requirements of the European Union (EU) Basic Safety Standards (EU-BSS) (EU, 2014; Chapter 4) and national regulations. There are two items concerning the radioactivity of building material which need to be verified:

(a) The application of a reference level for the external exposure to gamma radiation (<1 mSv per year). It has to be noted that in many cases it is not possible to estimate directly the annual gamma dose rate to a single person of the public as caused by building materials. For such cases the EU BSS offers the possibility to comply with the dose limit by regulating the building materials radionuclides concentration.

(b) The application of a reference level of radon (^{222}Rn) in indoor air (<300 Bqm^{-3}). This is usually achieved by determining the radon exhalation rate associated to the materials and subsequently controlling it to below the rate that leads to radon concentrations greater than the reference level. In some cases this could be alternatively accomplished by regulating the ^{226}Ra concentration in the materials.

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5.2 Measurements by gamma-ray spectrometry

The activity concentration of a radionuclide in NORM, raw materials, and building products is usually measured by gamma-ray spectrometry. The main advantages of this method are the possibility to measure many radionuclides simultaneously and the limited needs concerning sample preparation. Moreover, well developed software analyzing gamma-ray spectra are commercially available. Up to date gamma spectrometers, depending on configuration, can be widely applied for precise laboratory quantitative measurement as well as for qualitative screening or monitoring. However, this method does not allow the measurement of radionuclides which are pure alpha or beta emitters.

Gamma-ray spectrometry relies on the generation of a measurable pulse, either electrical or optical, by a photon (a gamma-ray) in a radiation detector. Independent of the detector type employed, the detector output signal must be converted into a current or voltage pulse that is proportional in magnitude to the gamma-ray emission energy produced by the decay of the radioactive material being measured. The amplitude of a registered pulse must be measured, usually by means of an analogue-to-digital converter (ADC) and the measured pulses are then sorted by their amplitude into the so-called channels of a multichannel analyzer (MCA). The number of channels necessary for the MCA should be as much as of the ADC resolution; common values include consecutive nonnegative powers of two (i.e., 512, 1024, 2048, 4096, 8192, or 16,384 channels). All pulses registered in channels create a sample spectrum with characteristic peaks (photopeaks) that reflect energies of gamma-rays emitted by radionuclides enclosed in a sample (Fig. 5.1). Each gamma-emitting radionuclide has its own characteristic gamma-ray energy emissions and these can be used both to establish the presence of the radionuclide in a sample and to quantitatively determine its activity concentration in the sample.

Modern systems are typically of the all-in-one design and operated via computer software applications. The advantage of these systems is that the package provides for the system control (high voltage for the detector system and amplifier settings and monitoring), MCA energy and efficiency calibration, photopeak detection and identification (including multiplet peak deconvolution), and provision of activity concentration and uncertainty calculations.

However, the spectrum analysis software available is not always up to the task and sometimes fails to detect radionuclides actually present in samples; therefore, some caution should be exercised when the spectrum analysis is performed fully automatically.

Generally, gamma-ray spectrometry does not allow for the absolute activity (concentration) determination. A calibration of the spectrometer is needed using a standard sample containing well-known activity concentration of some radionuclides. Moreover, results depend not only on detector types and parameters but also on electronics components, e.g., amplifier noise, ADC and MCA resolution and others. Measurement conditions, most notably sample shape and size (the measurement geometry), self-absorption of gamma-rays within the sample, and the gamma-rays radiation background, also influence the measurement results.

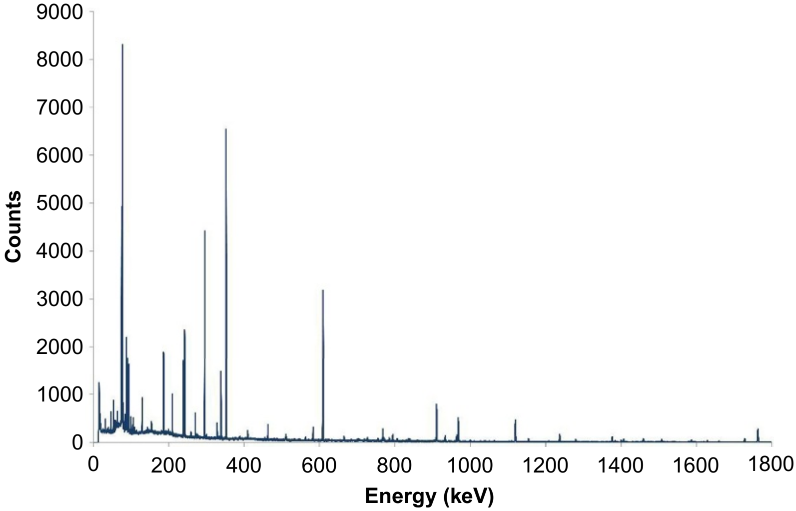

Fig. 5.1 An example of a spectrum obtained by a high-resolution semiconductor gamma-ray spectrometer. Each peak is associated with the energy of gamma radiation that reveals the presence of particular radionuclides in the measured sample.

A specific type of calibration methods are based on numerical calculations that allow the modeling of the interactions of gamma-ray radiation in the sample and detector mass and the theoretical calculation of adequate calibration factors.

Gamma-ray spectroscopy is a very useful tool for the measurement of natural radioactivity, which usually consists of several different radioactive nuclides. From the point of view of possible radiation risk, Potassium-40 and two natural decay series, namely, the Uranium and Thorium series are the most important (see Fig. 3.1 in Chapter 3).

5.2.1 Semiconductor spectrometry

To construct a semiconductor detector, it is necessary to form a connection between n-type (electron donor) and p-type (electron acceptor) semiconductor materials the so-called p-n junction. An n-type semiconductor has a higher concentration of electrons than a p-type semiconductor; consequently, diffusion of electrons from n-type to p-type materials is observed after formation of a p-n junction. This diffusion of electrons leaves positively-charged ions in the n-type material. In the p-type material, negative ions are formed respectively. This mechanism causes separation of electrical charge: negative charge concentrated in p-type semiconductor region and positive charge in the n-type region. Such a charge separation results in an electric field between the two types of semiconductor. This field helps to eliminate free charge carriers from the area around p-n junction. A layer with no free charge carriers results and is called "depletion layer." If some free charges are created in this volume, they are almost immediately removed by the electric field within a time scale of 10^{-12}–10^{-11} s. This removal is accompanied by a small electrical signal, a disruption of the electric field, which, in principle could be detected. This phenomenon can be used for the detection of ionizing radiation and gamma-rays in particular, due to the obvious fact that ionizing radiation traversing through depletion layer around a p-n junction could ionize atoms and create free electric charge carriers. However, the electric field of the p-n junction, alternatively called as the contact potential, is usually very small, being typically around 1 V. This field is not enough to effectively produce a detectable electric signal from the charge carriers created by ionization radiation. Within such a small field all ions will recombine and the crucial information about the ionizing radiation will be lost.

To eliminate this problem, the p-n junction is further polarized using an externally imposed potential. This also increases the size of the depletion layer to what is called the active volume. The potential in question depends on the type of detector and is typically in the order of a few kilovolts (kV). A simplified schematic of a p-n junction with and without external potential is given in Fig. 5.2.

The semiconductor detectors contemporarily used for gamma-ray spectrometry usually consist of pure germanium monocrystals (High Purity Germanium, or HPGe). The efficiency (i.e., the detection probability for a photon when passing through the detector) of such detectors depends much on the active volume size and the energy of the gamma-rays and it is generally lower than that of solid scintillation detectors of the

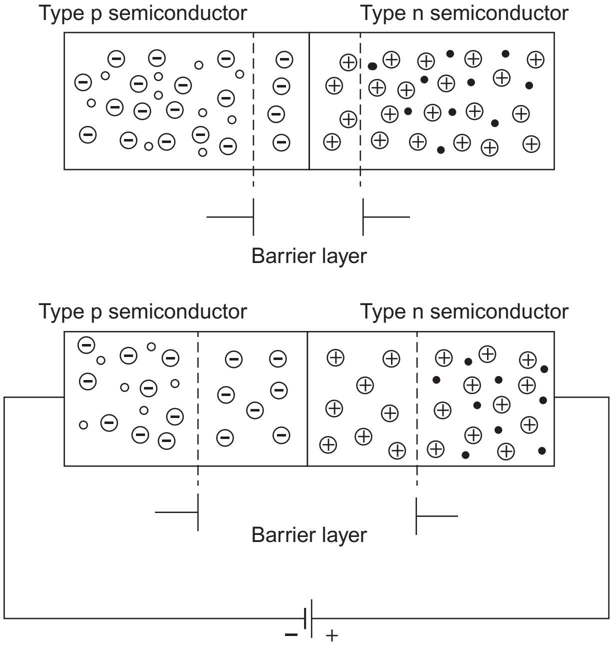

Fig. 5.2 Simplified schematic of a p-n junction.

same volume. It is, however, possible to make monocrystals with such a large volume that their efficiency may exceed the efficiency of a smaller scintillation detector.

Modern germanium detectors demonstrate very good energy resolution. Combined with an appropriate set of signal preamplifier, signal amplifier, ADC, and MCA, the collection of gamma-ray spectra with the ability to distinguish even very closely located gamma-ray photopeaks is enabled. Such detectors have typically a full width at half maximum (FWHM) resolution of approximately 2 keV at the 1332 keV photopeak of cobalt-60, and a few hundred eV at lower energies. This is far better than the 40–60 keV resolution of a typical NaI(Tl) detector. Therefore, high-resolution gamma-ray spectrometry with semiconductor detectors provides the detection of photopeaks that may not have been able to be resolved using scintillation detectors. Furthermore, modern germanium detectors have a useful energy range from around 5 keV to several MeV, and may have a relative detection efficiency, compared to the industry standard of the $3'' \times 3''$ sized NaI(Tl) detector, of greater than 100%.

5.2.1.1 Activity and uncertainty calculation

The determination of activity concentrations in samples comprises the preparation of the sample, the measurement and the calculation of activity concentration from the measurement results. In all these steps contribution to the uncertainty budget exist. This chapter deals with high resolution γ-spectrometry but some parts concern low resolution γ-spectrometry too.

The general sequence in this kind of analysis is shown in Fig. 5.3:

Therefore, the general approach is:

- Sample preparation: The sample has to be prepared homogeneous and in the same shape as the reference sample. The reference sample is either a real sample with known activity concentration or a virtual sample for which the detector efficiency for certain gammy peak energies is computed. Uncertainty contributions result from deviations from the reference sample which are not adjusted by correction factors involving detector efficiency and from the uncertainties of the correction factors. The correction factors concern mainly the density and the atomic composition of the sample compared with the reference sample. These correction factors are energy dependent.
- Measurement: Before starting a measurement the equipment should be checked, especially the electronic part should be adjusted for optimal resolution (time constant, baseline-restorer etc.). In NORM the determination of the activity concentration of a nuclide is often done indirectly by the determination of a progeny. In such a case it is essential to assure radioactive equilibrium between the relevant nuclides. This necessitates that intermediate decay products (such as ^{222}Rn or ^{220}Rn) remain in the sample. Any deviation from the radioactive equilibrium, if not corrected, will lead to an additional uncertainty. The aim of high resolution γ-spectrometry is to determine the counts within peaks that are only due to the investigated sample. Within the spectral interval which comprises the peak to be determined the following contributions must be considered and, where necessary, corrected: (1) unstructured background: counts from Compton scattered photons with higher energies, (2) structured background: counts from peaks from the surrounding radioactivity. This is especially relevant for the measurement of samples with natural radioactivity. Further corrections may be necessary for (3) coincident photon transitions (summing corrections), (4) for double

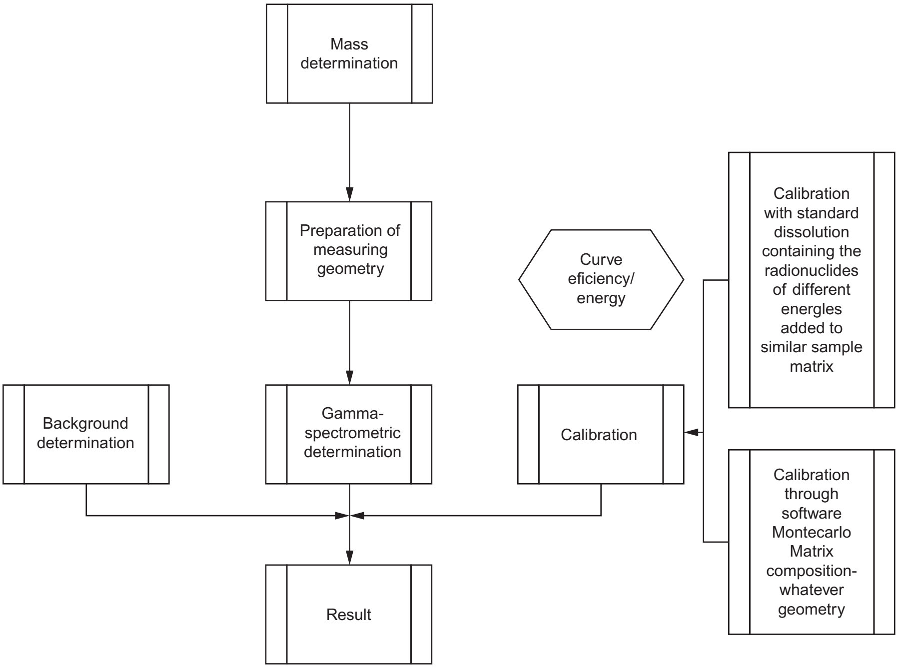

Fig. 5.3 The sequence in γ-spectrometry analysis.

peaks, and (5) for the dead-time of the ADC. The latter can usually be avoided when using live-time data acquisition which means the MCA stops the timer when the ADC is busy in a conversion and is not ready to accept an input signal.

- Calculation of the activity concentration:
  The measurand is the nuclide activity concentration C_{A_i} in Bq/kg based on the peak at energy E:

$$A_i = \frac{N_n}{\varepsilon \cdot t \cdot \gamma_d \cdot K} \tag{5.1}$$

$$C_{A_i} = \frac{A_i}{M} \tag{5.2}$$

where A_i = activity of nuclide i (Bq); N_n = background corrected net peak area; ε = detector efficiency; t = live time (s) (measurement time during which the digitally converted detector-pulses can be recorded); γ_d = branching ratio of this nuclide (γ conversion considered); M = mass of sample (kg); K = decay correction $K = e^{\frac{Ln2}{T_{1/2}} t_e}$ for the nuclide if it is applicable; $T_{1/2}$ = half-life time of the nuclide; t_e = elapsed time between the mid of acquisition and the time of sample collection.

The simplest way to determine the activity of the sample is to calculate the ratio of equivalent well separated peaks between the sample and a real reference sample. Then the activity of the sample at the time of the measurement can easily be calculated by:

$$A_i(\text{sample}) = \frac{r_{nn}(\text{sample})}{r_{nn}(\text{ reference})} A_i(\text{ reference}) \tag{5.3}$$

with r_{nn}… "net-net count rate" as defined in Annex A—Uncertainties, Decision Threshold (Decision Limit) and Detection Limit (Lower Limit of Detection), i.e., the net peak count rate of the sample (or reference) minus the net peak count rate in the background.

If necessary correction factors for density and atomic composition have to be applied. The uncertainty can be calculated in the usual way using the uncertainty propagation law. Only in case of high count rates ($\gg 10^4$ counts/s) a correction for random coincidences must be applied.

Often it makes sense to use more than one peak to determine an activity concentration. In such a case calculations for all used peaks should be performed and finally combined by a weighted mean with the inverse standard deviations as weights.

In case of calculated detector efficiencies several additional circumstances must be observed. For all peaks used for the determination of the activity concentration the gamma emission probabilities and the related uncertainties must be known. Further, coincident gamma transitions lead to summing peaks and consequently to a reduction in the peak areas of the single peaks. The size of this effect depends essentially on the geometry and efficiency, respectively, of the measurement setup. All the above-mentioned variables and effects are associated with uncertainties. In most cases the determination of these uncertainties is not easy and needs a lot of experience. All the uncertainties have to be combined by the uncertainty propagation law to the final uncertainty, which is an integral element of the final result.

Therefore, the estimation of uncertainties contains the following steps (see Fig. 5.23):

- Exploration of all factors influencing the measurement;
- Quantification of the uncertainty (standard uncertainty $s(x_j)$) connected to each factor x_j by measurement results or by expert judgment if applicable;
- Estimation of overall uncertainty of the measurement (standard uncertainty $s_c(C_{Ai})$).

$$\begin{aligned} s_c^2(C_{A_i}) &= \sum_{j=1} \left(\frac{\partial C_{A_i}}{\partial x_j}\right)^2 s^2(x_j) \\ &= C_{A_i}^2 \left(\frac{s^2(N_n)}{N_n^{\,2}} + \frac{s^2(\varepsilon)}{\varepsilon^2} + \frac{s^2(t)}{t^2} + \frac{s^2(\gamma_d)}{\gamma_d^2} + \frac{s^2(K)}{K^2} + \frac{s^2(M)}{M^2} + \cdots\right) \end{aligned} \tag{5.4}$$

The international standards (BIPM/ISO/IEC Guide 98-3, 2008; ISO, 11929, 2010) describe the methods for calculating these uncertainties in a practical way with some examples. The main components of uncertainty for the measurements using semiconductor detectors are listed in Annex A and Annex B.

5.2.1.2 *In situ spectrometry*

Strategy of measurements

In situ gamma spectroscopy is a well-known technique introduced by Beck et al. (1972) to determine the concentration of natural and artificial radionuclides in soil, the relevant ambient gamma dose rate in the air above, and the relative contribution of the radionuclides from the ^{238}U and ^{232}Th series and ^{40}K to the dose rate. This technique soon appeared to be a powerful tool to provide rapid and spatially representative estimates of environmental radioactivity. It basically consists of the elaboration of the full absorption peak areas multiplied by ad hoc calibration coefficients calculated according to two fundamental assumptions:

(1) the source—in this case the soil—can be modeled as an infinite half-space (so-called 2π geometry);

(2) the vertical distribution of radionuclides can be reasonably assumed (e.g., uniform distribution for natural radionuclides and exponential distribution for artificial ones).

Under these conditions it is possible to use a standard point source calibration performed in the laboratory (Beck et al., 1972; Cutshall and Larsen, 1986). With this calibration and the coefficients elaborated following Beck's method, the dose rate—produced by the unscattered and scattered fluence of gamma rays—can be estimated, and the radionuclide inventory calculated.

In view of the above features, in situ gamma spectroscopy can be a useful support to measure surface flat soils for many research or institutional activities, for example, to characterize sites in terms of natural background radiation or perform surveys to study sites contaminated by artificial radionuclides and/or NORM (ICRU, 1994; ISO, 18589-7, 2013) (Fig. 5.4). Further applications are the assessment of routine and accidental releases from nuclear facilities, and monitoring of soil contamination level in the different phases of environmental restoration projects. In short, in situ gamma spectroscopy is a very versatile and efficient tool for studying environmental radioactivity, but has some limits mainly associated to the need of a priori assumptions about the distribution of nuclides in the soil, an important source of uncertainties of activity concentration estimates and dose rate evaluations, since dose rate is obtained as a sum of different radionuclide contributions to unscattered and scattered gamma flux at the detector. Moreover, the original method cannot be used for all kinds of source geometry, e.g., indoors or urban outdoors, because it is not feasible to elaborate the build-up factors—taking into account the scattered gamma flux and necessity to determine the gamma dose rate from photopeaks in a recorded spectrum—or produce calibration curves from which to derive the radionuclide activity concentrations in the source. In the 1990s many studies were devoted to further widen the use of this method and overcome the above limitations, rendering in situ gamma spectrometry "independent" of source geometry. This research task yielded important outcomes such as indoor and outdoor build-up factors and the estimate of the actual radionuclide distribution in soil. These results have been obtained following two approaches: (1) Monte Carlo simulation and (2) the use of algorithms aimed to the

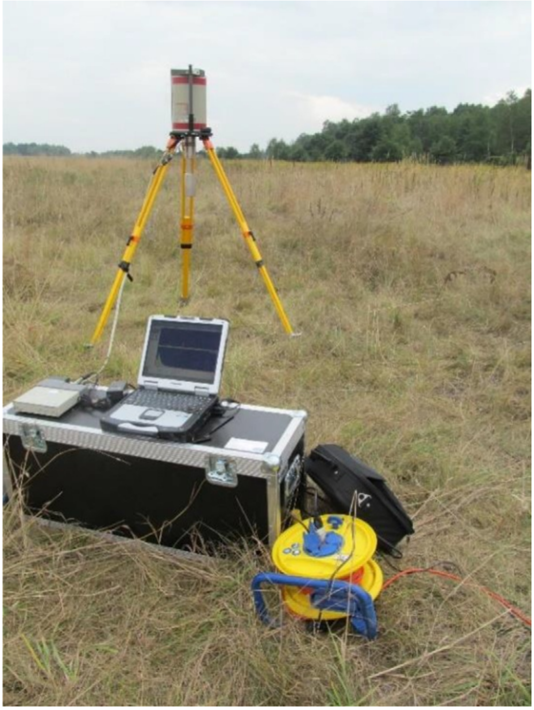

Fig. 5.4 Outdoor application of an in situ gamma spectrometer.

direct elaboration of spectra. With these new methodologies the applications of in situ gamma spectroscopy have been improved and/or extended to indoor environments, and to outdoor environments not easily represented with a model, such as forests (Gering et al., 2002), urban and industrial outdoor areas (Medeiros and Yoshimura, 2005), and large areas (Cresswell et al., 2006). In particular, indoor utilization provides interesting information on building material characteristics as source of population exposure to natural radionuclides. With different approaches—e.g., Monte Carlo (Clouvas et al., 2000), elaboration of spectra (Bochicchio et al., 1994), computation plus room model (Nuccetelli and Bolzan, 2001; Nuccetelli, 2008)—the use of in situ gamma spectroscopy indoors allows the evaluation of, and the relative contribution of the various nuclides to, the total gamma dose rates. In some countries an indoor methodology was also applied to perform surveys in order to get not only information on population exposure from building materials, but a more detailed description of the sources as well (Clouvas et al., 2004; Svoukis and Tsertos, 2007). Indoor applications of in situ gamma spectroscopy can also provide interesting information about building materials as sources of radon, thoron, and gamma rays (Nuccetelli and Bolzan, 2001; Clouvas et al., 2003) and provide quantitative estimates about the activity concentrations of radionuclides in building materials.

Fig. 5.5 Indoor application of an in situ gamma spectrometer.

Measurement results and uncertainty

The field-of-view of a detector, a parameter that is defined by the soil surface area from which 90% of the unscattered detected photons originate, limits the direct application of in situ gamma spectrometry in cases when the measured area cannot be modeled as an infinite half-space (Fig. 5.5). In these cases a correction factor (parameter) has to be applied. This parameter depends on the characteristics of the detector, the measurement height (distance from the source), and the distribution of the radionuclide of interest on the measured area. A gamma detector has a nearly 360° field-of-view, and can be used for 4π counting that needs a special calibration procedure which, when used indoor, must be prepared individually for almost each case of application (e.g., see differences in Fig. 5.5). However, the field-of-view can be reduced by adding a shield and collimators. A collimator can limit the field-of-view of the detector to the area of interest and to a certain size of this area. It allows filtering the flux of photons from outside of the measurement area of concern (Fig. 5.6). Finally, the calibration procedure either using calibration sources or mathematical calculation is easier and more accurate when the field-of-view is reduced.

5.2.1.3 Laboratory gamma-ray spectrometry

Sampling of NORM raw materials and by-products

The term NORM covers a wide variety of different materials that can either occur naturally in different forms or are created as a result of various technological processes. The final form of NORM occurrence is one of the most important parameters determining the sampling method that should be applied in order to collect laboratory samples representing the tested material properties at an acceptable level of confidence. Furthermore, sampling and measurement of NORM need to focus on different purposes depending on specific situations. When considering all possible situations, NORM could be sampled for:

- classification in the frame of regulatory control;
- identification of the contamination source or the contamination origin, including a contamination plume;
- identification of NORM related to high background areas;

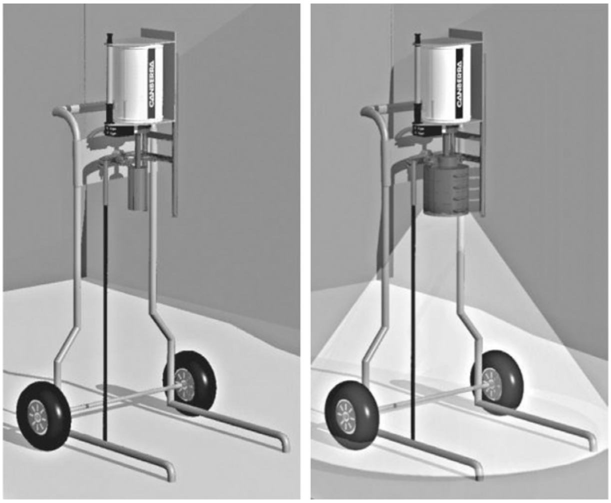

Fig. 5.6 The effect of a colimator application (Canberra, 2016).

- contamination inventory and NORM affected land classification including the risk assessment to humans and/or biota;
- land reclamation effectiveness assessment (in case of potential release from regulatory control); and
- existing exposure monitoring (e.g., in case of legacy sites).

All possible combinations of NORM occurrence forms and sampling and measurement purposes create a multiplicity of sampling and measurements scenarios. Therefore, it seems very difficult to develop a common and universal approach to sampling. At the moment as of 2017, there is no standard concerning NORM sampling; however, there often exists the possibility to apply sampling approaches developed for artificial radionuclides, e.g., like these described by Scott et al. (2008). In many cases existing contamination related to NORM can be monitored using principles set in standards dealing with soil sampling [see for example in ISO 18589-2 (ISO, 18589-2, 2015)] or methods developed for monitoring of soil general quality (Brus and de Gruijter, 1997; Judeza et al., 2006) and other relevant available standards like ISO 11074-2 (ISO, 11074-2, 2008), ISO 10381-1 (ISO, 10391-1, 2002), and ISO 10381-2 (ISO, 10381-2, 2002).

However, when applying these standards it is necessary to consider the differences existing between NORM and artificial radionuclides as well as classical pollutants, i.e., contamination source geometry, the location, the accumulation processes, and possible dispersion models. Actually, typical NORMs are either natural raw materials (ores) or, in case of residues, have the appearance of common waste dumps and in this case tend to have more in common with industrial waste than with wastes from the nuclear fuel cycle or the disposal of radioactive sources like those described in standard ISO 21238 (ISO, 21238, 2007). Moreover, natural radionuclides are chemical elements similar to other elements occurring naturally (e.g., heavy metals, noble gases) and their radioactivity does not significantly influence their behavior in the environment. Hence, due to the lack of specific recommendations and standards developed for NORM sampling, standards prepared for sampling of common waste can be applied [see for example PD CEN/TR 15310 (PD CEN/TR, 15310, Parts 1-5, 2006) and BS EN 14899 (BS EN, 14899, 2005)].

The sampling and measurement of NORM in order to release them from regulatory control towards their use in the construction industry is a specific aspect of the general regulatory overview. The screening levels of natural radioactivity content for NORM (despite the fact that these are not actually limits) intended to be used as an additive to building materials in construction industry as set in the EU-BSS (EU, 2014) are much more restrictive than the limits allowing release of NORM from regulatory control. This influences significantly the sampling procedures, which have to be more accurate than in the case of ordinary regulatory control. Considering that the content of natural radioactivity of NORM is only one parameter among many which are important from the point of view of the construction industry, NORMs that are intended for use in this industry must be well characterized and strict ways to prepare an appropriate characterisation are required. These requirements limit the variety of NORM available for consideration in construction industry to situations when their use could be justified from both, the economic and also from the technical point of view.

Therefore, the most suitable NORMs for this purpose are the residues created on regular basis as a result of a well-specified technological process or already accumulated in sufficient quantities (Fig. 5.7). Several typical cases are described in Chapter 6. In such cases initial data concerning the total quantities of NORM existing or expected along with homogeneity characteristics and relevant radionuclides content might be more readily available. Furthermore, usually there already exist sampling methods, used by the NORM processing industries, that could provide, besides their main purpose, also reliable information about the NORM properties for the construction industry. These sampling methods could be applied for the NORM radioactivity content identification and control as well. Moreover, standards developed either for quality monitoring of ordinary raw materials used in the construction industry or for final products can also be effectively adapted to radioactivity measurements. However, the presumable lack of homogeneity of NORM intended to be used as components for construction materials must be always taken into consideration when organizing a sampling campaign.

Fig. 5.7 Types of NORM residues created on regular basis as a result of a well specified technological process (left), or already accumulated (e.g., phosphogypsum, right) could be potential raw materials for the construction material industry.

Provided that initial data do exist to account for the:

- homogeneity characterization of NORM to be used as input in processes or NORM found in residues,
- expected suite of radionuclides, and
- the total amount of available or produced NORM

a sampling campaign could be organized.

Based on general rules of sampling the first step of a sampling campaign organization is to prepare a sampling strategy specifying the density and spatial distribution of sampling points. This process allows for the definition of a sampling unit. Sampling unit may be defined as a part of the sampling area or as a portion of the NORM of concern. The boundaries of a sampling unit could be either physical or even virtual (see Fig. 5.7). In turn, the sampling unit size may be defined using statistics or geostatistics in case of NORM as illustrated in Fig. 5.7, or it might depend on the homogeneity of the sampled material or, to some extent, on the technological process involved. For example, in the case of an existing NORM deposition the sampling size should be decided, taking into consideration if the deposition as a whole should be subject to sampling or if it is enough to check some portions according to the current use. Then the spatial distribution of the sampling area can be replaced by temporal distribution according to the actual use of the material to be exploited.

Having defined the sampling unit, a next step is to fix the sampling density. At this stage technical possibilities and financial restrictions should be considered as well as the sampling unit size, the number of sampling units and the required quality of results. In general, the sampling density should be defined according to the sampling method chosen, taking into consideration that the method should allow for a sound statistical analysis. The sampling method of choice could be:

- Random sampling: collecting samples from the sampling units at randomly selected sites in space and time.
- Systematic sampling: collecting samples from the sampling units by some systematic method in space and time.
- Random systematic sampling: collecting samples at random from each sampling unit from a set of systematically defined sampling units.

Finally, a sampling strategy must be formulated in a way that the collected samples sent to laboratory for analysis (laboratory samples) are representative of the whole material. This means that the distribution of the tested parameter (e.g., ^{232}Th-concentration) in the bulk material is mirrored in the laboratory samples. A sampling strategy presents a certain level of generality and can be applied to a particular type of NORM or for specific branches of industry. Specific applications of an adopted sampling strategy need an associated and precise protocol, which is usually called a sampling plan that, depending on the principles of the strategy, must include:

- Details of sampling method, such as:
  - The method of sample collection based on individual sampling action resulting in the final sample that is investigated:
    - Increment: the portion of material collected in a single action using a sampling device.

Fig. 5.8 Collection of single samples, systematic sampling.

        - Subsample: the sample in which the material of interest is randomly distributed in parts of equal or unequal size, a subsample may consist of one or more increments.
        - Single sample: the representative quantity of the material, presumed to be homogeneous, taken from a sampling unit (or at least from the borders of a sampling unit), kept and treated separately from all other samples (Fig. 5.8); a single sample may consist of one or more subsamples.
        - Composite sample—two or more increments or subsamples or single samples mixed in appropriate proportions, either discretely or continuously (blended composite sample), from which the average value representative of a desired characteristic may be obtained (Fig. 5.9).
    - The spatial distribution (i.e., sampling pattern—system of sampling locations based on the results of statistical procedures) and/or the temporal distribution (frequency), of individual sampling action.
    - The quantities sampled and the laboratory sample sizes preparation.
- The human and technical resources to be used for sampling.
- The necessary documentation (sampling report, sample identification and traceability, and Chain of Custody).
- The QA/QC procedures to be applied.

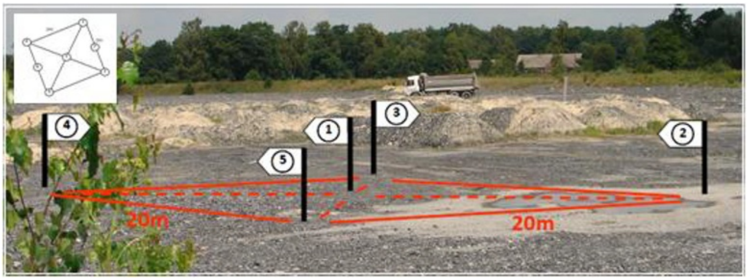

Fig. 5.9 Collection of a composite sample, the envelope method.

The preparation of a laboratory sample is one of the most important parts of a sampling plan and finally decides on the total number of samples intended to be analyzed. There is no strict recommendation concerning a laboratory sample preparation. Based on the previously defined sampling actions, an individual increment, a subsample as well as a composite sample can constitute a laboratory sample, providing that there is enough quantity of sampled material for the intended analysis. This means that in extreme cases the number of laboratory samples could be equal to the number of individual increments or on the other end there could exist only one composite sample as a representative of the whole tested NORM. Both approaches should give the same average quantity. However, limiting the number of laboratory samples reduces the direct information concerning the variability of the tested material.

The total number of laboratory samples is usually a compromise between the expected level of confidence of obtained results and available resources. In general, when sampled material is characterized by high variability in the parameter to be measured (such as natural radioactivity content), it is preferred to use a single sample as a laboratory sample, otherwise a composite sample obtained by mixing of some single samples could be representative enough. Apart from the expected quality of the analytical results that can be evaluated using a statistical procedure, other circumstances should be taken into account with regard to the technical feasibility of samples collection and the balance of costs related to samples collection and analysis.

Usually sampling does not involve very specific equipment and in the majority of cases a shovel can be good enough or other simple tools can be used (Fig. 5.10). However, it must be kept in mind that in some cases a sampling operation can be hindered by the conditions existing in a particular industry, e.g., access limitation

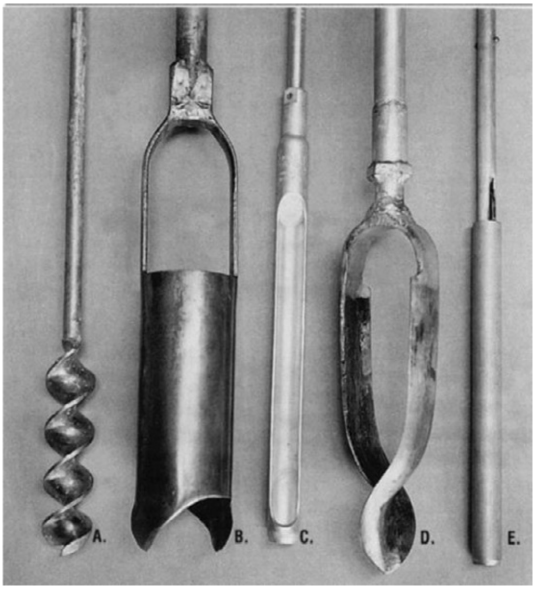

Fig. 5.10 Sampling tools: (A) screw or worm auger, (B) barrel auger, (C) sampling tube, (D) "Dutch mud" auger, and (E) peat sampler.

to the material during the technological process or the need for specialized sampling devices. A special case exists when a whole depository of NORM must be characterized. In such a situation deep core samples must be taken most often by using drilling rigs.

Each stage of a sampling operation must be properly documented in order to prove the sample representativeness and sample traceability. If the documentation system applied is specific to a particular case, it should be described in details in the sampling plan.

Sampling is a source of an additional uncertainty contributing significantly to the total uncertainty of planned analysis. Hence, relevant QA/QC procedures must be applied in order to provide all data necessary to evaluate the uncertainty related to sampling. The easiest and most commonly applied way to deal with this problem is the collection of duplicate or even multiple samples. However, this method, apart from extra cost, needs advanced statistics in order to be used effectively.

The afore described suggestions for conduct regarding NORM sampling, though not mature, seems constituting the general framework for a uniform approach to the preparation of sampling operations for NORM intended to be used as additives to building materials. In summary, when preparing a sampling strategy and a sampling plan, much consideration should be given to optimization and the balancing of costs and the risk of manufacturing unacceptable final products.

However, in the light of the lack of either direct regulations or recommendations concerning sampling of NORM dedicated for use in construction industry, not disputable sampling procedures trusted by all stakeholders, should be developed.

Application

An accurate activity concentration can be obtained by using gamma spectrometry under laboratory conditions. In the case of high-resolution semiconductor detector, a laboratory gamma spectrometry system consists of the high purity germanium detector (HPGe) mounted in a cryostat (maintained at approximately 83 K by either liquid nitrogen or electrically by Peltier thermoelectric cells) to reduce electronic noise, an integrated preamplifier, a high voltage supply, an amplifier, and a MCA. Modern systems tend to incorporate the high voltage supply, a digital amplifier, and MCA in a single unit operated via an external computer. The detector element in a basic system is enclosed by a passive environmental radiation shield to decrease interference from external radiation sources (such as natural background radiation). The shield is made from low background lead (typically a few centimeters thick, 5–15 cm) and may include an additional internal graded shield of tin and copper to attenuate the lead (and tin) fluorescent X-rays produced within the shield. Selected ultra-low background construction materials for the detector chassis, low background noise preamplifier, and low background environments (e.g., under damp walls, underground tunnels or caves) including efficient ventilation system eliminating radon progeny may also be used to further increase the sensitivity of a gamma spectrometry system (Fig. 5.11).

Fig. 5.11 High-resolution gamma spectrometry laboratory in the Silesian Centre for Environmental Radioactivity, Central Mining Institute, Katowice, Poland.

5.2.2 Scintillation spectrometry

A scintillation detector consists of a scintillator which emits light pulses when exposed to radiation and a device, usually a photomultiplier tube (PM), which transforms these light pulses into electrical signals. A scintillation spectrometer has a lower energy resolution than a semiconductor detector. However, despite the low energy resolution, scintillation detectors are widely used in routine monitoring tasks of building materials. The reason for this is a high sensitivity of the detector at a low cost and its ease of use—the detector does not require cooling to liquid nitrogen temperature, and the spectrometer generally has a lower weight and smaller dimensions (Fig. 5.12).

Still the most used type of scintillation detector for γ-spectrometry is the NaI(Tl) detector. The detector crystal with housing, photomultiplier, and base is relatively

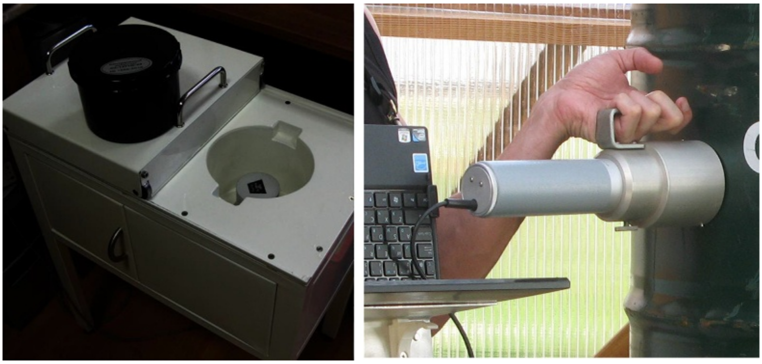

Fig. 5.12 Scintillation detector in laboratory (left) and in situ measurement (right).

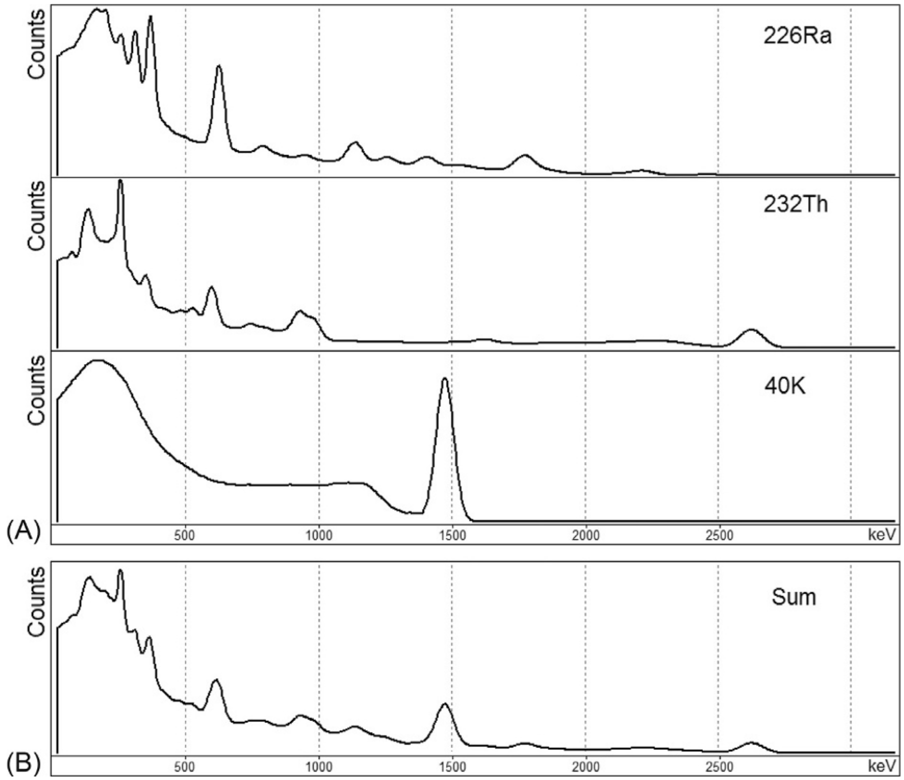

Fig. 5.13 Spectra of natural radionuclides registered by scintillation gamma-spectrometer: (A) spectra of mono-nuclide sources and (B) spectrum of a mixture of these radionuclides.

easily available even in large sizes. Portable versions with high voltage supply, amplifier, and MCA, all powered by batteries, can be purchased from several suppliers.

Fig. 5.13A shows spectra, registered by the scintillation detector from sources containing ^{40}K, ^{238}U, and ^{232}Th in radioactive equilibrium, while Fig. 5.13B shows the spectrum of a mixture of these radionuclides.

Special software was developed to overcome the drawbacks of low energy resolution of these detectors. It does not allocate single peaks for every radionuclide, but represents the whole measured spectrum as a sum of the images due to the contributions of these radionuclides. The spectra shown in Fig. 5.13A are determined during calibration of the spectrometer and represent the device response to radiation of unit activity of a radionuclide. The software automatically adjusts the image to the difference in densities of a test sample from the samples used in the calibration.

The conventional approach of spectra analysis is to calibrate broad spectral windows during the analysis for the main natural isotopes (Verdoya et al., 2009; Desbarats and Killeen, 1990). Generally, these windows are chosen around the photopeaks of ^{40}K (1460 keV), of ^{214}Bi (1765 keV), and of ^{208}Tl (2614 keV). Three typical energy intervals for in situ measurements are: 1370–1570 keV; 1660–1860 keV; and 2410–2810 keV (IAEA, 2003). The concentration of ^{238}U and ^{232}Th are then evaluated detecting the γ-rays produced by ^{214}Bi and ^{208}Tl respectively. The assumption of secular equilibrium of the decay chains is required in order to use this approach. In addition to the above-mentioned radionuclides, the three-windows method has been extended to the measurement of ^{137}Cs by Cresswell et al. (2006) and Sanderson et al. (1989).

The model of measurement assumes that the detected energy spectrum of gamma radiation is the sum of independent contributions due to background radiation and radiation of $j_{\max}$ radionuclides, which are present in the counting sample:

$$s(E) = b(E) + \sum_{j=1}^{j_{\max}} p_j(E) \cdot C_j \tag{5.5}$$

with $s(E)$, detected energy spectrum, imp/(s keV), (imp = impulses); $b(E)$, background energy spectrum, imp/(s·keV); $p_j(E)$, the fundamental energy spectra of the 1 Bq of element j, imp/(s·keV·Bq); C_j, the concentration of the element j, Bq; j, the index, which stands for K, Th, U, and eventually for ^{137}Cs (if this artificial radionuclide is of interest in building materials and products).

The integration of the Eq. (5.5) in $m_{\max}$ different energy intervals ($m_{\max} >= j_{\max}$) leads to a system of $m_{\max}$ equations

$$S_m = B_m + \sum_{j=1}^{j_{\max}} P_{j,m} \cdot C_j \quad m = 1 \ldots m_{\max} \tag{5.6}$$

where S_m (sample count rate in the energy interval m), B_m (background count rate in the energy interval m), and $P_{j,m}$ (sensitivity of the detector to irradiation of radionuclide j in the energy interval m) are the integral by energy within the interval m from the functions $s(E)$, $b(E)$, and $p_j(E)$, respectively.

The relation Eq. (5.6) can be written in matrix notation Eq. (5.7) with $R_m = S_m - B_m$ (net sample count rate i.e., sample count rate corrected for background) where $\vec{\mathrm{R}}$ is a vector with m components, $\vec{\mathrm{C}}$ is a vector with j components and $[P]$ is a $j_{\max} \times m_{\max}$ matrix.

$$\vec{\mathrm{R}} = [P]\,\vec{\mathrm{C}}\,. \tag{5.7}$$

In the simplest case, with only three energy intervals, as mentioned before, only about 5% of all impulses are registered. This low number of counts leads to an unnecessary large statistical uncertainty.

An example of the sensitivity matrix estimated for a 3″ × 3″ (cylindrical form: height 7.64 cm, diameter 7.64 cm) NaI(Tl) for pads used for ground measurements

Table 5.1 **Example for a sensitivity matrix [*P*]**

[*S*]	**Potassium window**	**Uranium window**	**Thorium window**
cps/%K	3.360	0.000	0.000
cps/ppm eU[a]	0.250	0.325	0.011
cps/ppm eTh[a]	0.062	0.075	0.128

[a] Because U and Th concentrations are estimated by their decay products, the results are reported in equivalent uranium (ppm eU) and equivalent thorium (ppm eTh).

(3 m in diameter, 50 cm thickness, and 2.25 g/cm^3 density) is given in Table 5.1 (IAEA, 2003). Because there is only one single line from potassium, no crossover occurs to the uranium and thorium window. Vice versa, uranium and thorium progeny produce γ-emission with many different energies causing also counts in the other windows.

It has become a conventional representation for in situ measurements, at least for geological purposes, to express the concentrations of natural radioisotopes in their respective abundances, where K is given in % weight while eU and eTh are given in ppm.

The unknown concentration of K, U, and Th in a sample then can be calculated by

$$\vec{\mathrm{C}} = [P]^{-1}\,\vec{\mathrm{R}} \tag{5.8}$$

with $[P]^{-1}$ the inverse matrix of the sensitivity matrix $[P]$. However, the inverse matrix is defined only for a quadratic matrix which means for three radionuclides only three windows can be chosen ($j_{\max} = m_{\max}$).

To increase the measurement accuracy more energy intervals can be used. A set of 12 energy intervals at the energy range 300–2800 keV proposed recently (Kovler et al, 2013) is listed in Table 5.2. To use this model either special software is necessary, or the software can be integrated in simpler computing facilities, such as in portable spectrometers.

In the extreme case, the energy intervals coincide with channels of the measured spectrum. In this case, the coefficient S_m is the value of the count rate recorded in channel m during the sample measurement and the number of equations in the system Eq. (5.6) is equal to the number of channels in the energy range used for processing. This method has been developed in different approaches (Maučec et al., 2009; Hendriks et al., 2001; Minty, 1992; Crossley and Reid, 1982; Smith et al., 1983) and was found to be a successful tool for spectrum analysis.

On one hand, the inclusion of as many channels as possible into the working range of the energy decreases the statistical measurement uncertainty. On the other hand, inclusion of the low energy region into the working area will increase the systematic component of the measurement uncertainty. Self-absorption of the radiation or of a portion of its energy in a sample substance by photoelectric effect or by Compton scattering at low energies contribute significantly to the shape of the spectrum $s(E)$. If the

Table 5.2 **Coefficient $\mu_{j,m}$ for the 1 L Marinelli geometry**

Interval index (m)	**Energy region (keV)**	**$\mu_{j,m}$ for nuclide j (cm^3/g)**			
		$j = {}^{137}$Cs	$j = {}^{40}$K	$j = {}^{226}$Ra	$j = {}^{232}$Th
1	300–400	1.00e−8	1.00e−8	2.17e−4	1.21e−4
2	400–580	1.00e−8	1.00e−8	4.20e−5	1.24e−4
3	580–630	1.85e−4	1.00e−8	2.46e−4	1.83e−4
4	630–720	2.60e−4	1.00e−8	1.64e−4	5.35e−5
5	720–800	–	1.00e−8	1.01e−4	1.24e−4
6	800–1030	–	1.00e−8	4.71e−5	1.77e−4
7	1030–1400	–	1.50e−5	1.00e−4	1.37e−5
8	1400–1580	–	1.50e−4	3.90e−5	3.00e−5
9	1580–1860	–	–	1.10e−4	3.00e−5
10	1860–2250	–	–	8.40e−5	1.00e−8
11	2250–2400	–	–	1.30e−4	1.00e−8
12	2400–2800	–	–	1.26e−4	1.10e−4

probability for Compton scattering slightly depends on the atomic numbers present in the sample, and is determined mainly by the density of the sample, the probability for the photoelectric effect depends strongly on the atomic numbers present in the sample, which in practice is not always possible to consider. Therefore, the spectrum usually is only analyzed above an energy of 300 keV.

To account for the self-absorption processes of gamma-radiation the detector sensitivity is expressed as a function of the sample density. For that purpose, volume sources with different density ρ and known activity are used.

For every source the value of sensitivity $P_{j,m}$ to the radiation of the radionuclide j in the interval m is

$$P_{j,m}(\rho) = \frac{S_{j,m}(\rho) - B_m}{A_j} \tag{5.9}$$

where $S_{j,m}$, count rate in the interval m registered from the source with density ρ; B_m, background count rate in the interval m; A_j, activity of nuclide j.

The function

$$P_{j,m}(\rho) = \frac{P^0_{j,m} \cdot \left(1 - e^{-\mu_{j,m} \cdot \rho}\right)}{\mu_{j,m} \cdot \rho} \tag{5.10}$$

is used to approximate the sensitivity depending on the sample mass.

$P_{j,m}^0$ is the sensitivity for a zero density sample. It is derived in the calibration process by extrapolation. $\mu_{j,m}$ characterizes the effect of absorption and scattering of gamma radiation in the sample. It depends on the measurement geometry and is used to calculate a correction factor to the sensitivity of the detector, taking into account the difference between the density of the sample and the density of the calibration source. Table 5.2 shows the values of coefficient $\mu_{j,m}$ for the 1 L Marinelli geometry.

The activity concentrations are deduced applying the least square algorithm by minimizing the reduced χ^2 according to Eq. (5.11):

$$\chi^2 = \frac{1}{(n-5)} \sum_{i=a}^{b} \frac{\left(S(i) - \sum_j S_j(i) C_j + B(i)\right)^2}{\sigma^2_{S(i)}} \tag{5.11}$$

where $S(i)$ are the counts in the channel i; C_j are the concentration of the element j; $P_j(i)$ are the associated counts to the fundamental spectrum of the element j in the channel i; $B(i)$ are the counts in the channel i due to the intrinsic background; and the index j stands for K, Th, U, and eventually for ^{137}Cs.

S(i) is considered Poisson distributed (then $\sigma_{N(i)} = \sqrt{N(i)}$) and $n = b - a$ is the number of channels in the spectrum used in the analysis (the selected energetic range is typically 300–2900 keV: There is a strong presence of backscattering events below 300 keV, which depend on the atomic number and density of the surrounding materials; while above 2900 keV only the cosmic ray contribution is present).

The χ^2 minimization without any further conditions can generate sensitive spectra having energy regions with negative events. To overcome this problem the NNLS (nonnegative least square) constraint was introduced. For details see (Lawson and Hanson, 1995; Désesquelles et al., 2009; Boutsidis and Drineas, 2009).

In the work of Kovler et al. (2013) the accuracy of activity determination by analyzing a spectrum by different methods is compared. For this purpose, different processing algorithms have been implemented for a certain detector. The algorithms differ by the number and width of energy ranges:

- energy intervals correspond to analyzer channels in energy range 300–2800 keV;
- 12 energy intervals according to Table 5.2;
- 4 intervals: 600–720; 1350–1560; 1640–1880; and 2500–2750 keV.

Measurements uncertainty values obtained for a coverage factor of $k = 2$ are given in Table 5.3 describing the results obtained for a NaI(Tl) $2.5 \times 2.5''$ scintillation detector, measurement duration of 1 h and Marinelli 1 L geometry.

Accuracy for all processing methods is sufficient to determine compliance of building materials with radiation safety criteria. Significantly lower cost makes this type of detector competitive in routine monitoring of large numbers and large volumes of construction materials.

The main advantage of the semiconductor detector, associated with its high-energy resolution, is the ability to identify the radionuclides in the samples with a complex radionuclide composition. This feature is not so relevant for the problem of measuring building materials—radionuclide composition of the sample is known a priori and is limited to natural radionuclides in a state of radioactive equilibrium. Exceptions are quite rare cases of imbalance (including in a chain of ^{232}Th) by chemical processing of

Table 5.3 Dependence of the expanded measurement uncertainty (twice the standard deviation of the measurement results) for low activity sample from processing method

No.	Processing method	Expanded uncertainty ($k = 2$), Bq ^{137}Cs	^{40}K	^{226}Ra	^{232}Th
1	Energy intervals correspond to analyzer channels in energy range 300–2800 keV (with more than 1000 intervals)	1.1	16.4	2.1	2.5
2	12 energy intervals in energy range 300–2800 keV	1.6	24.8	2.7	2.2
3	4 energy intervals	1.6	25.3	4.6	3.1

natural materials or ore dressing. Proper evaluation of the activity of individual radionuclides of ^{232}Th chain in the absence of radioactive equilibrium can be carried out only with the semiconductor detector.

The most important limit of this method is that it is blind to any unexpected signal (anthropic isotopes). Other limitations are the low accuracy for short time acquisitions and the physical restriction of poor intrinsic energetic resolution of the NaI(Tl) detector.

It should be noted that the scintillation spectrometer software allows revealing cases of presence of additional radionuclides in the sample or imbalance between daughter radionuclides of ^{232}Th chain. To do this, the software approximates the measured spectrum by a weighted sum of the fundamental spectra $P_j(E)$ (model spectrum). If the model spectrum differs from the measured spectrum, the software displays a warning that a more detailed study of the sample would be indicated, including a high energy resolution semiconductor analysis (Fig. 5.14).

Today, some newer scintillation detectors are available which generally show better energy resolutions, e.g., $LaCI_3$:Ce(0.9), $CeBr_3$, BGO, $CdWO_4$, and $PbWO_4$. To analyze the spectra of these detectors usually smaller windows around the main photopeaks can be chosen, thus the crosstalk between the different isotopes is substantially reduced. These detectors stand in the energy resolution and therefore in the analysis procedures between the NaI(Tl) and the semiconductor detectors. A problem for low-level measurements is in some cases the low but nevertheless existing intrinsic radioactivity of these newer scintillation detector materials.

5.2.3 Calibration and metrological assurance

To transfer the results of a measurement (e.g., counts/s) into activity or activity concentration a calibration of the spectrometer is necessary. Usually a linear relation between measurement result and the activity (concentration) exist. The proportionality factor is called efficiency which depends on the geometry of the measurement and the sample properties as density and composition. For semiconductor detectors usually the efficiency for the photopeak as a function of energy (efficiency curve) is

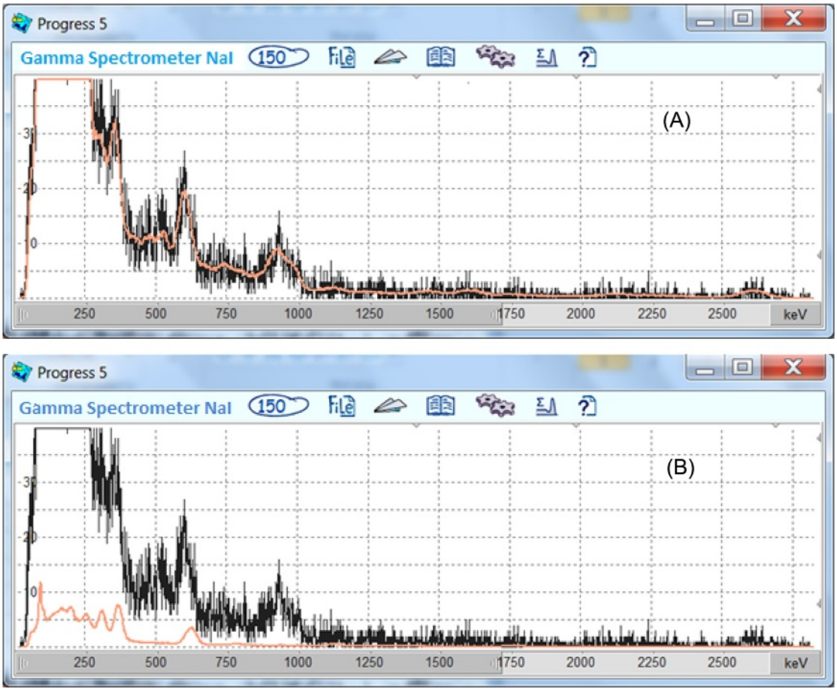

Fig. 5.14 (A) Displayed are the measured spectrum and the model spectrum; (B) Displayed are the measured spectrum and contribution from one radionuclide, in this case ^{226}Ra.

determined (see Annex B) for a specific geometry and sample properties. For scintillation detectors the sensitivity matrix [P] (Eq. 5.8) or matrix $P_{j,m}^{0}$ and $\mu_{j,m}$ (Eq. 5.10) are determined.

The calibration of semiconductor spectrometer can either be done by (1) using a reference source with known activity or (2) by a calculation using the detector characteristics as well as the foreseen measurement geometry and sample properties.

The first method allows metrological traceability which in some countries is demanded by law. The second method usually uses Monte Carlo codes but does not formally provide traceability of the results to a primary standard. The correct use of this method produces accurate results and in some cases (e.g., in certain situations of in situ measurements) it is the only possible method of calibration. Further details can be found in Annex B.

Calibration of a scintillation detector is usually a little more complicated, and includes not only the determination of the efficiency of the detector, but also the form of the Compton part of the spectrum. Unlike semiconductor detectors that are calibrated directly in the measurement laboratory, scintillation detectors are often calibrated by the equipment manufacturer. The user is supplied with a system of coefficients for different geometries or can directly adjust the used measurement geometry in the unit's software.

5.2.4 EU proposal of a harmonized standard for building products

5.2.4.1 Background

The European Commission decided to harmonize, promote, and consolidate the main recommendations concerning NORM, introducing them into a new Council Directive (EU, 2014) laying down basic safety standards for the protection against the dangers arising from exposure to ionizing radiation, the so called EU Basic Safety Standards, or EU-BSS. This BSS directive was officially issued in Jan. 2014 and is described in more detail in Chapter 4. Member States were given four years to transpose and implement this directive and according to the Euratom Treaty, members shall before then communicate to the Commission their existing and draft provisions. The Commission shall then make appropriate recommendations for harmonizing the provisions amongst member States.

Requirements of this directive dealing with building materials need to be taken into account along with the 2011 EU regulation laying down harmonized conditions for the marketing of construction products (EU, 2011) so called construction product regulation, or CPR, containing many relevant articles which complement the aforesaid BSS directive. Both EU regulatory documents constitute the new basis for building material radiation protection regulation and should be soon followed by more detailed EU guidance and standards (see Chapter 4). Subsequently, the European Commission (EC) has mandated the CEN to establish EU harmonized standards regarding the determination of the activity concentrations of natural nuclides in construction products using gamma-ray spectrometry. Such standards should be robust enough not to give a chance to be challenged in the future; and they should be adopted by all Member States as soon as the BSS will come into force.

5.2.4.2 Scope

Under this mandate (M/366) a Technical Specification (TS) has been prepared by Technical Committee CEN/TC 351 Construction products—Assessment of release of dangerous substances'. The TS provides a measurement (test) method for the determination of the activity concentrations of the radionuclides ^{226}Ra, ^{232}Th, and ^{40}K in construction products using gamma-ray spectrometry.

This TS describes the measurement method starting with the pretreatment of a laboratory sample, the test specimen preparation and the measurement by gamma-ray spectrometry. The description of measurement includes collection and analysis of a spectrum, background subtraction, energy and efficiency calibration, calculation of the activity concentrations with the associated uncertainties, the decision threshold and detection limit, and reporting of the results. Collection of product samples and the preparation of the laboratory sample from the initial product sample lie outside the scope of the TS. For that purpose rules described in product standards are suggested to be used. However, in case of NORM no strict recommendations exist and the adaptation of existing product standards is not always possible. Hence, individual approaches for NORM sampling based on general rules as described in the previous section are often required.

Authors of the TS have well identified major limitations and obstacles characteristic for gamma spectrometry and, additionally, this TS describes, in the normative part, the following:

- method for the determination of the radon-tightness of a test specimen container,
- preparation of standardized calibration sources,
- method for the determination of the activity concentration in a composite product, and
- determination of the dry matter content in the tested material and calculation of a related correction factor.

The TS is intended to be nonproduct-specific in scope, however, there are a limited number of product-specific elements such as the preparation of the test specimen and drying of the test sample that are not fitting to the generally requested procedures. The method is applicable to samples from products consisting of single or multiple material components, however special attention must be paid to proper preparation of representative test specimen when the testing material consists of more than one component.

Furthermore, the information within this TS is intended to be used for purposes of CE marking and evaluation/attestation of conformity. Product specification, standardization of representative sampling, and procedures for any product-specific laboratory sample preparation are the responsibility of product TCs and are not covered in this TS.

This TS supports existing regulations and standardized practices, and is based on methods described in standards, such as ISO 10703 (ISO, 10703, 2015), ISO 18589-2 (ISO, 18589-2, 2015), ISO 18589-3 (ISO, 18589-3, 2015), and NEN 5697 (NEN 5697, 2001).

5.2.4.3 The robustness testing

The draft of the TS 00351014 (Construction products—Assessment of release of dangerous substances—Determination of activity concentrations of radium-226, thorium-232, and potassium-40 in construction products using gamma-ray spectrometry) has undergone meticulous tests under real conditions in a gamma spectrometry laboratory according to the scenario developed by CEN/TC 351/WG 3 [“Revised work program for the robustness validation of draft TS 00351014” (N 116)]. The work program identified 14 parameters or measurement circumstances, respectively, that influence the results obtained by gamma spectrometry when applying the procedures set forth in the TS. However, all of these factors result from only a few physical phenomena and consequently the carried out tests were focused on:

- self-attenuation in an analyzed sample,
- radon leakage from measurement beakers,
- a temporary lack of secular equilibrium between radium and radon, and
- (long-term) lack of secular equilibrium inside uranium and/or thorium decay series.

All parameters influencing sample self-attenuation in all possible stages of the measurement process are presented in detail and one should give special consideration at any particular stage to these effects, which are summarized in Fig. 5.15.

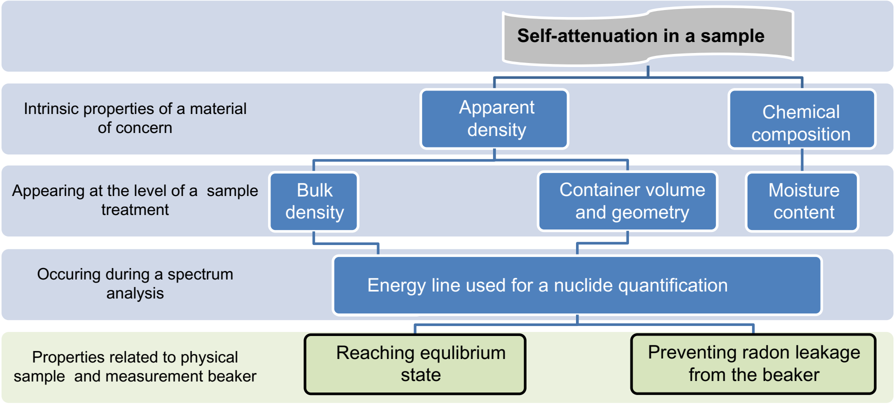

Fig. 5.15 Parameters influencing measurement results obtained by high-resolution gamma spectrometry considered by the TS.

The most important conclusions from the tests concerning the application of the TS are:

- According to the TS the activity concentrations of the gamma-emitting radionuclides in construction products should be determined by using high resolution gamma-ray spectrometry. A spectrometer with MCA with at least 4096 channels is required. This implies the use of high purity germanium detectors (HPGe), but this is not explicitly mentioned in the TS. That is why the question remains whether other detectors can be used without the risk not to comply with the standard requirements.
- As the TS requires, for ^{226}Ra and ^{232}Th the activity concentration should be determined using a progeny nuclide, while for ^{40}K the concentration is based on the photopeak from the nuclide itself. Despite the application of high-resolution gamma spectrometry the TS assumes that only the four (most intensive) photo peaks with the gamma-ray energies 352 keV (^{214}Pb, parent ^{226}Ra), 583 keV (^{208}Tl, parent ^{228}Th), 911 keV (^{228}Ac, parent ^{228}Ra), and 1461 keV (^{40}K) are used to determine the activity concentration of the radionuclides. However, when high resolution gamma spectrometry is applied, as required, there is no reason to use only one energy peak for the evaluation of a nuclide activity concentration. A weighted average from the use of more than one peak for the determination of the activity concentrations for a particular radionuclide will reduce the size of the uncertainty and will minimize the possibility of measurement errors. Existing practice showed that almost every professional gamma spectrometry laboratory is acting in this way.
- As was expected, all problems related to sample density, container shape, and volume can be solved by proper calibration using reference materials, which reflect the chemical and physical properties of the material, prepared as described in the standard. Separate standard samples are recommended for calibration of construction materials which are significantly different in chemical composition from materials of mineral origin commonly measured (e.g., for wooden materials). Therefore, the TS should not limit future user with materials made from raw materials of mineral origin for standard sample preparation as it is stated in the normative part of the current TS.

- In those cases, where the activity is determined using a progeny nuclide, a secular equilibrium between the progeny nuclide and its originating nuclide is necessary. To reach such equilibrium the test specimen is stored in a radon-tight container for a period of at least three weeks in order to ensure there is a secular equilibrium reached between ^{226}Ra, ^{214}Pb, and ^{214}Bi inside the container. Additionally, the TS requires that it must be proved that no degradation in the equilibrium due to a leakage of radon from a beaker has happened. For this purpose the TS includes in the normative part a test for the determination of the tightness of the sealed measurement beaker. This test and applied criteria are questionable and can be replaced by a much simpler test. Moreover, including this test in normative part of the future standard would seriously limit its application due to the fact that not so many gamma laboratories have the required resources to carry out this test. Obviously, the solution for this problem is to make the standard a sealed beaker used multiple times.
- Despite the required waiting time of three weeks a disequilibrium in the ^{232}Th decay chain can be present. Such disequilibrium is caused by different physio-chemical behavior between thorium and radium, the particular hydrogeological history and effects of industrial processes. Such disequilibrium is mirrored by a significant difference in the radioactivity concentrations of ^{228}Th and ^{228}Ra. In case of such a disequilibrium, the TS requires the use of available alternative measurement techniques or procedures for the determination of the ^{232}Th activity. But this is outside the scope of this document. However, taking into account the behavior patterns of the above-mentioned radionuclides in the ^{232}Th chain as described in Chapter 3, the specific observed ratio of ^{228}Ra and ^{228}Th radioactivity concentration, as well as supporting information concerning the origin of the NORM, allows the estimation of the ^{232}Th activity concentration. ^{232}Th does not contribute to the external dose because it is a pure α-emitter. But its direct progeny ^{228}Ra is of importance for the external gamma dose. Therefore, exact information about the activity concentration of ^{232}Th would be necessary when the observed ^{228}Ra to ^{228}Th ratio is bigger than one, otherwise it is almost sure that ^{228}Th is not present in the sample at all (see Figs. 3.3 and 3.4 from Chapter 3). This limits the necessity of direct measurement of ^{232}Th activity concentration significantly; however, this fact is not mentioned in the TS.

5.2.4.4 Summary

Currently (as of Jan. 2017) the relevant European standard is under development and the final form is still uncertain. However, experience collected by many gamma spectrometry laboratories involved in measurement of construction materials shows that the discussed version of Technical Specification presented by Technical Committee CEN/TC 351 "Construction products—Assessment of release of dangerous substances" for the determination of the activity concentrations of the radionuclides ^{226}Ra, ^{232}Th, and ^{40}K in construction products using gamma-ray spectrometry does not need significant changes. However, some part of the future standard, as discussed in the previous section, should allow users more flexibility in their choice of options provided by the state of the art in gamma spectrometry.

The full report from the robustness validation of draft TS 00351014, prepared by Silesian Centre for Environmental Radioactivity (GIG, Poland) will be available for the public on CEN web site.

5.3 Dose rate measurement

5.3.1 Preliminaries

According to the EU BSS the annual gamma dose rate to a single person of the public caused by building material should not exceed 1 mSv. Generally this cannot be measured directly and therefore several assumptions are necessary. These assumptions concern the personal habits and the construction of the dwelling, the person lives in. Investigations have shown that people spend about 80% of their life indoors. With this assumption ambient dose rate measurements can be used to estimate the annual dose inside a house and check it for compliance with annual dose reference level of 1 mSv. This rather easy-sounding procedure has several difficulties and drawbacks. The difficulties will be discussed in detail below while the drawback of the method is obvious: The measurement is done after building a house with certain building materials. Constant ambient dose-rates are usually measured by active dose-rate meters, based either on ionization-chambers, Geiger-counters, or scintillation counters. For legal purposes these devices must be calibrated and in some countries it is necessary to have them stamped by a national metrology institute. In such a certification the conditions for the use of the measurement device are specified and the uncertainty of the reading is given when used within the limits of the conditions of use. Often also correction factors are given for a use outside the limits of the conditions of use. Typical conditions concern ambient temperature, humidity, power supply voltage, air pressure, linearity etc. which usually are not problematic. Much more difficulties come with energy dependence and angle dependence which will be discussed below. In most cases it is not necessary to correct for the natural background because it can be assumed that the shielding of the building reduces the background to a nonsignificant level. However, this is not always the case, e.g., at the ground floor in areas with enhanced Uranium or Thorium concentration in the soil or bedrock.

5.3.2 Energy dependence

It is a good practice of the producer to supply dose-rate meters with a diagram concerning the dependence of the reading from the gamma energy (a typical example can be seen in Fig. 5.16). In other cases only the conditions for use are given, e.g., reading is valid within ±15% between 50 keV and 2 MeV. When dealing with radioactivity in building materials the three naturally occurring decay chains from ^{238}U, ^{235}U, and ^{232}Th as well as ^{40}K have to be regarded. ^{40}K is not a problem because there is only one gamma energy of about 1.4 MeV which usually is within the conditions of use for most gamma dose-rate meters. However, gamma energies below 50 keV exist in the decay schemes. In case of radioactive equilibrium the contribution of gamma rays with energies below 50 keV is negligible, but in building materials radioactive equilibrium cannot be assumed, particularly in materials containing NORM residues, and then gamma and X-rays with energies below 50 keV may contribute substantially to the dose-rate. Because of the relatively low energies the radiation is partly shielded by the building material itself. Therefore, it is of importance, if the radioactivity is part of

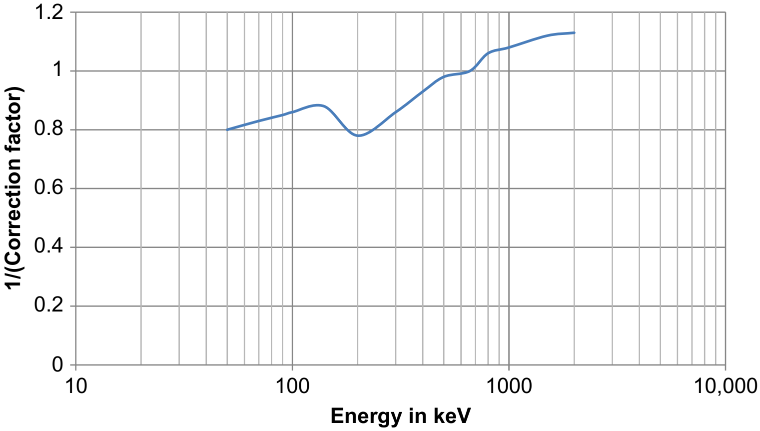

Fig. 5.16 Typical dependence of the relative efficiency as a function of energy [1/(energy correction factor)].

the bulk material or if it is part of a surface layer, e.g., tiles. It is not only the density which has to be considered but also the elemental composition which influences the self-absorption within the building material. If low energy radiation is essential, also the shielding by the person who measures can be a problem. Generally, when the interval of energies to be measured is known, then the correction factor can be taken as the mean between maximum and minimum of the correction factor within the energies of interest. For the uncertainty (coverage factor = 1 means one standard deviation) half of the difference between maximum and minimum of the correction factor is a good choice.

5.3.3 Angle dependence

Dose-rate detectors are calibrated for a certain direction and the conditions for a correct reading (within the given uncertainties) include a certain angle from this main direction. The efficiency of the detector and consequently the dose-rate reading decrease sometimes relatively fast (often to less than 30%) outside of this angle. This is especially important for the typical construction of hand-held dose-rate meters, which combine the detector and the electronics in one single box. The change in efficiency with angle is energy dependent too. In most cases, if at all, this dependence is only given for a certain energy (e.g., 662 keV). The angle dependence is caused by the construction of the device and, as mentioned above, there is also the effect of shielding by the person who measures the dose rate.

Thus, only in case of well-documented angle dependence it is possible to determine the ambient dose-rate by subsequent measurements in all directions. If this is not the case the dose rate must be determined for all parts of a building separately. The determination of the dose rate caused by one building product can be applied for building material control at the stage of production too. Taking into consideration that building material dose-rates are rather small, measurement devices with low detection limits are necessary which may be expensive. Many dose-rate meters can be switched to integrate the dose-rate over time, which allows extending the lower limit of detection (LLD) to lower values. Such an instrument can be used to quantify the dose-rate during the production of building materials without a specific determination of the isotopes contributing to the radioactivity. Moreover, the dose-rate will probably be more precise than that deduced from the concentration of the respective isotopes causing the gamma radiation. Thus, it can be imagined that if a measured dose rate from a building material extrapolated to a room construction (4π) remains below 1 mSv/y this building material can be used anywhere.

Another method for the measurement of ambient dose-rates is the use of specially developed integrating detectors, e.g., thermo-luminescence detectors (TLD). Such detectors may consist of more than one TLD crystal and may be calibrated for radiation from all angles. But even for these detectors it is necessary to observe the conditions of use (energy dependence).

5.4 Radon measurement

5.4.1 Basic information on radon and progeny

Radon is a radioactive noble gas formed by the decay of radium. As discussed in Chapter 3 two isotopes are relevant for the radioactive exposure, namely ^{222}Rn ("radon (Rn)") and ^{220}Rn ("thoron (Tn)"). The radon isotopes form chains of daughter decay products (or progeny), which have the properties of metals and release considerable energy by alpha, beta, and gamma radiation (see Fig. 3.1 and Tables 3.4 and 3.5).

Because of the different half-life times, the behaviors of ^{222}Rn ($T_{1/2}=3.82$ days) and ^{220}Rn ($T_{1/2}=55.8$ s) are different. Generally, when speaking of radon ^{222}Rn is assumed. The relative long half-life time allows ^{222}Rn to distribute more or less uniformly in closed rooms, producing the short living decay products ^{218}Po ($T_{1/2}=3.09$ min), ^{214}Pb ($T_{1/2}=26.8$ min), ^{214}Bi ($T_{1/2}=19.9$ min), and ^{214}Po ($T_{1/2}=164$ μs) anywhere in the rooms. In a sealed volume a satisfactory radioactive equilibrium between ^{222}Rn and its short-lived decay products (equilibrium factor), as well as their decay in the case of instantaneous removal of radon, is obtained within 2–3 h, because the effective half-life time of the mixture of the short-lived radon decay products is about 40 min. Therefore, the activity concentration of short-lived decay products in the air is in general controlled by the radon behavior. In real rooms, a part of the short-lived progeny is removed as a result of ventilation and plate-out on walls, furniture etc. but the rest remains in the air and is responsible for the internal dose. The indoor equilibrium factor generally ranges from 0.2 to 0.7 (see Chapter 3). The atmospheric content of the long-lived radon decay products ^{210}Pb ($T_{1/2}=22.3$ years), ^{210}Bi ($T_{1/2}=5.01$ days), ^{210}Po ($T_{1/2}=138$ days), and ^{206}Pb (stable) is extremely low due to the very long half-life of ^{210}Pb and the almost complete precipitation of this progeny from the atmosphere to some surfaces. The contribution of the long-lived radon progeny to the radiation dose is very small; and therefore will not be considered here.

^{220}Rn decays relatively quickly and shows its highest concentration close to its source, e.g., close to the walls. In radioactive equilibrium the formed decay products of ^{220}Rn, which are ^{216}Po ($T_{1/2} = 0.15$ s), ^{212}Pb ($T_{1/2} = 10.6$ h), ^{212}Bi ($T_{1/2} = 60.5$ min), ^{212}Po ($T_{1/2} = 0.30$ μs), and ^{208}Tl ($T_{1/2} = 3.06$ min) cause higher doses than the decay products of ^{222}Rn for the same concentration. Nevertheless, in many cases the contribution to the internal dose from ^{220}Rn can be neglected because its progeny often plate-out substantially on the walls from where ^{220}Rn is emitted and the exhalation rate of the ^{220}Rn from walls' surface usually is much less than that of ^{222}Rn (see Chapter 3).

In the internal dose formation by thoron decay chain, the decisive role belongs to ^{212}Pb, which has a half-life of more than 10 h—significantly longer than that of ^{220}Rn and all other progeny, and longer than usual air exchange rates. Besides deposition on walls, the remaining part of ^{212}Pb is removed from the room air due to ventilation. Therefore, there is a significant shift of radioactive equilibrium in this chain, indoors and outdoors, where the equilibrium factors drops to 0.01 or even lower values.

5.4.2 Radon and radon progeny measurement methods

Due to the significantly different lifetimes between ^{222}Rn and ^{220}Rn, an activity of 1 Bq corresponds to 476,600 ^{222}Rn atoms and 80 ^{220}Rn atoms. Therefore, usually the ^{220}Rn contribution to the internal dose can be neglected and the focus in this section is concentrated on ^{222}Rn measurements. However, if a substantial contribution of ^{220}Rn is expected, it is necessary to control ^{220}Rn or rather its progeny too. In addition, the presence of ^{220}Rn can significantly distort the measurement results, when continuous or integrated radon measurements are conducted, which do not take into account the contribution of thoron and its progeny.

5.4.2.1 Classification of the methods

The international standard of ISO (ISO, 11665-1, 2012) proposed a classification of radon and its progeny measurement methods (Table 5.4). According to this standard, the sampling duration is important for achieving the measurement objective and the required uncertainty. For the sake of presentation, the measurement methods can therefore be distinguished based on the duration of the sampling phase: (a) integrated measurement methods, (b) continuous measurement methods including measurements with registration periods from 1 to 6 h, and (c) spot measurement methods. The information that is provided by these three different types of measurement is described briefly below.

(a) Integrated measurement method

This method gives indications for measuring the average radon activity concentration or the average potential alpha energy concentration (PAEC) or the equilibrium equivalent concentration (EEC) of radon progeny in the air over periods varying from a few days to one year. Long-term integrated measurement methods are applicable in assessing human exposure to radon and its decay products.

Table 5.4 Classification of the methods to measure radon and its progeny

Radon detection principle		Measurement method (usual sampling duration)						
		Spot (<1 h)	Continuous (variable)		Integrated			
					Short-term (few days)		Long-term (several months)	
		Sampling characteristics						
		Active	Active	Passive	Active	Passive	Active	Passive
Ionization chamber		Rn,Tn[a]	Rn, Tn[a]	Rn	–	–	–	–
ZnS(Ag) scintillation		Rn,Tn[a]	Rn, Tn[a]	Rn	–	–	–	–
Gamma spectrometry (or gamma and beta radiometry) Liquid scintillation	Activated charcoal	Rn	–	–	–	Rn	–	–
Alpha spectrometry	Filter	RnP, TnP	RnP, TnP[a]	–	–	–	–	–
	Electrostatic precipitation	Rn, Tn[a]	Rn, Tn[a]	Rn	–	–	–	–
SSNTD+Filter		–	–	–	RnP, TnP		RnP, TnP	
Electret		–	–	–	–	Rn,Tn[a]	–	Rn,Tn[a]

Notations: *Rn*, measurement of radon activity concentration; *Tn*, measurement of thoron activity concentration; *RnP*, measurement of radon progeny activity concentration, as EEC or PAEC (conversion between EEC and PAEC can be found in the Glossary); *TnP*, measurement of thoron progeny activity concentration, as EEC or PAEC.

[a] Measurements are not supported by metrological assurance, so the uncertainty of measurement results is unknown.

(b) Continuous measurement method

This continuous monitoring enables the assessment of temporal changes in radon activity concentration in the environment, in public buildings, in homes and in workplaces, as a function of ventilation, and/or meteorological conditions.

(c) Spot measurement method

This method gives indications for spot measuring, at the scale of a few minutes at a given point, of the radon activity concentration or the PAEC or EEC radon progeny in open and confined atmospheres.

Table 5.4 addresses different types of sampling. Active sampling means continuously or intermittently forced pumping air through detector, filter, etc. Passive sampling does not use a forced pumping; in this case radon penetrates into measuring chamber, the sorption column, etc. by diffusion.

5.4.2.2 Radon detection principles

The radon detection principles mentioned in Table 5.4 are as follows ISO 11665-1 (ISO, 11665-1, 2012):

(a) Ionization chamber

When travelling through air, each alpha particle creates several tens of thousands of ion pairs which, under some experimental conditions, produces an ionization current. Although very low, this current may be measured using an ionization chamber that gives the activity concentration of radon and its decay products. When the sampling is performed through a filtering medium, only radon diffuses into the ionization chamber and the signal is proportional to the radon activity concentration.

(b) ZnS(Ag) scintillation (silver-activated zinc sulfide)

Some electrons in scintillating media, such as ZnS(Ag), have the particular feature of emitting light photons by returning to their ground state when they are excited by an alpha particle. These light photons can be detected using a photomultiplier. This is the principle adopted for scintillation cells, such as Lucas cells.

(c) Gamma spectrometry (or gamma and beta radiometry)

The radon, adsorbed on activated charcoal encapsulated in a container, is determined by gamma-ray spectrometry or gamma and beta radiometry of its short-lived decay products after their equilibrium is reached.

(d) Liquid scintillation

The radon, adsorbed on activated charcoal placed in a vial, is measured following the addition of a scintillation cocktail by counting alpha and beta particles emitted by the radon and its short-lived decay products after their equilibrium is reached

(e) Alpha spectrometry (based on the semiconductor detector)

A semiconductor detector (made of silicon) converts the energy from an incident alpha particle into electric charges. These are converted into pulses with amplitudes proportional to the energy of the alpha particles emitted by the radon or thoron decay products. This progeny is concentrated either near the front of the detector in case of sampling on a filter, or are precipitated directly onto the surface of the detector due to the electric field created specially in the measuring chamber.

(f) Solid-state nuclear track detectors (SSNTD)

An alpha particle triggers ionization as it passes through some polymer nuclear detectors (such as cellulose nitrate). Ion recombination is not complete after the particle has passed through. Appropriate etching acts as a developing agent. The detector then shows the tracks as etching holes or cones, in a quantity proportional to the number of alpha particles that have passed through the detector.

(g) Electret (discharge of polarized surface inside an expositional chamber)

A polytetrafluoroethylene (PTFE) disc with a positive electric potential is inserted into an ionization chamber, of a given volume, made of plastic conductive material. The electrostatic field, thus created inside the chamber, collects the ions formed during the disintegration of the radon and its decay products on this disc. After the ions have been collected, the electric potential of the disc decreases according to the radon activity concentration. An electrometer measures this potential difference, which is directly proportional to the radon activity concentration during the exposure period.

When thoron activity concentration is measured by SSNTD or Electret methods, two detectors are simultaneously exposed to thoron; one of them provides a diffusion barrier to eliminate the penetration of thoron in the exposition chamber. The difference between the measurement results obtained on these detectors is associated with the thoron activity concentration, but the uncertainty of this assessment is questionable due to the lack of metrological assurance for measurements of the thoron activity concentration.

5.4.3 Measurement of indoor radon concentration

The EU-BSS establishes reference levels for indoor radon concentrations. No distinction is made between building materials and the soil as sources of radon.

In this section the measurement of indoor radon concentration, as required by the EU-BSS, is discussed. Although the contribution of building materials to the indoor radon concentration is not regulated separately by the EU-BSS, and in spite of the fact, that it is indeed difficult to distinguish between building materials or the soil as sources of radon, but understanding how building materials contribute to the overall indoor radon, and how to limit this contribution by means of controlling radon exhalation from the surface of building materials, taking into account numerous different factors influencing indoor radon, is an important task, especially in the contest of the present book.

Indoor radon concentrations vary usually in a wide range, especially in rooms with high content of radon (relative to outdoor radon), as shown in Fig. 5.17. This is mainly due to the variations of air exchange rates caused by the ventilation mode, behavior of the inhabitants or workers, and changing weather conditions (mainly, temperature, wind).

This section does not deal with radon exhalation from the soil, its further transport into the dwelling and the resistance of building materials to the radon inflow from the soil into the living space, because this problem is rather complicated and is out of the scope of NORM4Building. At the same time, it is well known that in most cases the indoor radon concentration is mainly determined by the inflow of radon from the ground below a building. For that reason and because of the wide variability of the indoor radon concentration, the measurement of the indoor radon concentration is usually not appropriate to estimate the contribution from the building material.

Significant variability of the indoor radon concentration due to a large number of influencing factors is the main problem in the interpretation of measurement results and reliable prediction of annual average indoor radon concentration.

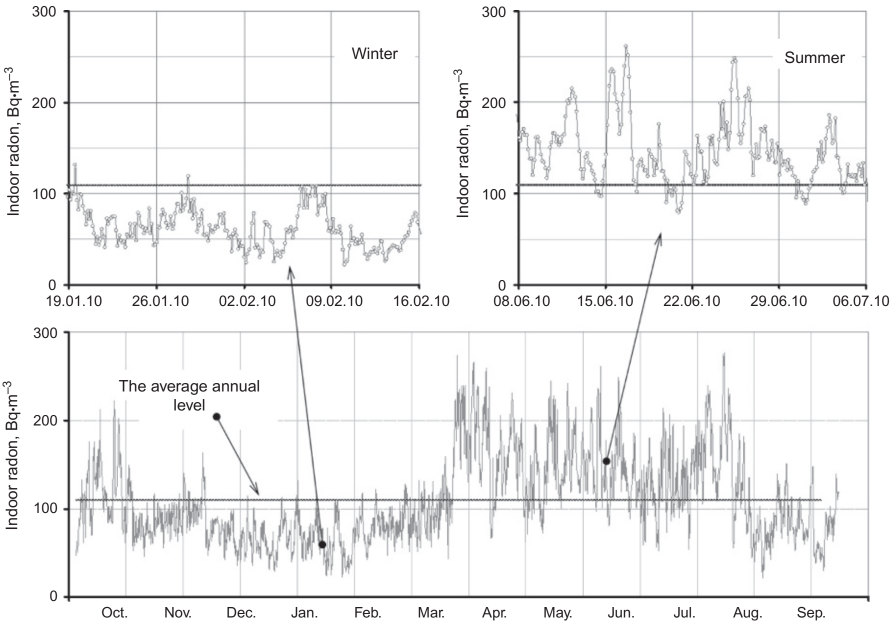

Fig. 5.17 Example of radon variations in enclosed room (natural ventilation and lack of people) on the ground floor of the multistory building.

When the average indoor radon concentration exceeds the level of outdoor radon by 5–10 times or more, usually both diurnal and seasonal variations of radon are observed. The amplitude of the temporal radon variation in buildings with a low radon concentration (at level of outdoor radon or slightly higher, but not more than 2–3 times higher) is significantly lower, and their regularity is less expressed.

Many researchers try to study the correlation between short-term and long-term measurement results. The unknown uncertainty of the annual average radon concentration using the measurements of different duration (both short- and long-term testing) prevents making reliable estimation. Obviously, the most accurate estimate of the average indoor radon concentration may be achieved, if the measurements were carried out during the whole year. However, only <2% of indoor radon measurements conducted, for example, in the US are made using long-term devices (George, 2015). The decrease of measurement duration will obviously tend to higher uncertainty of annual average estimates. In practice, the measurement duration varies usually from a few days to 1–2 weeks (short-term and continuous measurements), but sometimes can last 1–3 months and even longer (long-term and continuous measurements). Moreover, different countries use various measurement strategies and the corresponding traditional methods of estimating the annual average indoor radon concentration (WHO, 2009), including the measurement protocol for radon control applied in the USA. This protocol is based exclusively on a traditional experience approach (ANSI/AARST MAH, 2014). However, none of these methods, including those standardized by ISO (ISO, 11665-8, 2012), provides an estimate of the uncertainty of annual average indoor radon concentration.

An interesting method allowing to estimate quantitatively the uncertainty of measuring indoor radon is described in Annex C.

In most cases, indoor ^{220}Rn is not of importance, however when enhanced concentrations exist, then the building material can certainly be the source. Therefore, sometimes its measurement is necessary, if the research object contains materials with a high activity concentration of ^{232}Th or ^{228}Ra. To evaluate the contribution to the effective dose the PAEC or the EEC of thoron progeny concentration should be measured, because a significant shift of radioactive equilibrium within the thoron decay chain always occurs indoors and outdoors. Therefore, the relation between the thoron activity concentration and the EEC (or PAEC) is difficult to determine correctly.

5.4.4 Measurements of radon emanation and exhalation

The basic parameter characterizing the rate of radon release from the surface of materials is the radon surface exhalation rate E_S (Bq/m^2/s). Another parameter is the radon mass exhalation rate E_M (Bq/kg/s). But when only E_M is known, one should take into account that, depending on the dimensions of the product and diffusion coefficient of radon in the material, only a part of free radon generated in the product is able to escape into the ambient air. The values of E_S and E_M can be obtained either by direct measurement, or by calculation in accordance with (3.13)–(3.15), if the values of the ^{226}Ra activity concentration C_{Ra} (Bq/kg), the coefficient of emanation ε (rel), the density ρ (kg/m^3), and the radon diffusion coefficient in the material D (m^2/s) are known. Therefore, this section reports the methods of measurements of all of these three parameters: radon surface exhalation rate (E_S), radon mass exhalation rate (E_M), and radon emanation coefficient (ε). The value of C_{Ra} is determined by gamma spectrometry, as reported in detail before. Determination of D is a standard procedure, according to the future ISO standards ISO 11665-12 (ISO/TS, 11665-12, 2017) and ISO 11665-13 (ISO/TS, 11665-13, 2017). The standard (ISO 11665-12), in particular, proposed a rapid method for measuring the radon diffusion coefficient in various kinds of materials, which allows to reduce the duration of the test to 18 h. Further details about this method are available in Tsapalov et al. (2014).

The calculation formulas (3.8)–(3.15) describing the laws of emanation, transport, and exhalation of radon from materials are also valid to thoron, but have to consider the restrictions listed in Chapter 3 (Section 3.5.2).

5.4.4.1 Radon surface exhalation rate

The measurement of radon exhalation rates of building materials can be made by different methods (Kovler, 2012). Three fundamentally different methods of measuring radon surface exhalation rate are known. They are based on the analysis of radon release rate from the surface of the well-known area limited by sampling container (chamber). The features of the measurement principles depend on the different methods of sampling (passive or active), as well as on the design and composition of the sampling container (open or closed). Taking into account these differences, the measurement principles of the radon exhalation measurement have been suggested.

The Closed-Chamber Method (passive accumulation of radon in a closed container) is the most common method of measurement. It is based on the principle of radon accumulation in a closed container (usually of cylinder shape, with a diameter of 0.1–0.5 m and a volume of 1–10 L), which is mounted on the surface of the soil (IAEA, 2013) or the building material. The measurement of accumulating radon in the container is carried out in different ways, using (a) electrets (Kotrappa et al., 1993), (b) radon radiometers with either active (Lehmann et al., 2003) or passive (Lopez-Coto et al., 2009) sampling, or (c) activated charcoal, followed by measuring the activity of gamma radiation progeny of radon which accumulated in the activated charcoal (Duenas et al., 2007).

The international standard ISO 11665-7 (ISO, 11665-7, 2012) based on the Closed-Chamber Method gives guidelines for estimating the radon-222 surface exhalation rate over a short period (a few hours), at a given place, at the interface of the medium (soil, rock, laid building material, walls, etc.) and the atmosphere. The measurements are limited in time due to the growing influence of the closed chamber on the object of study with increasing duration of its exposure.

The essence of the Closed-Chamber Method, according to ISO 11665-7 (ISO, 11665-7, 2012), is to determine in the region of linear increase of the radon activity concentration, the rate of the increase in a closed container, which is purged by a clean atmospheric air (or better nitrogen) prior to the measurement after its installation on the investigated surface.

Starting from certain time after purging the container (depending on its height), the growth of radon activity concentration shows nearly a linear increase and later an asymptotic behavior: it slows down, ending in an equilibrium value. In this ideal steady-state mode (without leakage) the flow of radon into the container is practically absent. The calculation of E_S (Bq/m^2/s) is performed by measurements of radon activity concentration in the nonsteady state mode (during linear growth) by the formula:

$$E_S = \frac{V}{S} \cdot \frac{\Delta C}{\Delta t} \tag{5.12}$$

with ΔC, change in the radon activity concentration in the container in the linear region, Bq/m^3; Δt, time interval changes in the radon activity concentration, s; V, effective volume, m^3; S, container base area, m^2.

The ISO standard (ISO, 11665-7, 2012) addresses additional factors causing a disturbance in the free surface exhalation rate, which can significantly influence the final estimations:

(a) The variations in conditions (pressure, temperature, humidity) inside and outside the accumulation container: To minimize these effects, accumulation is specified in the standard to take place over a period of time with little variation in the external and internal container conditions (heavy rain and showers shall be avoided). However, the accumulation container may be thermally insulated.

(b) Inadequate air tightness (leakages) and back diffusion induce radon loss. To minimize the effect of leakages, improving air tightness is recommended. To minimize the effect of back diffusion, the container should be purged with radon-free air before beginning the accumulation process, and the calculation of the exhalation rate should be based on the initial slope of the curve of accumulation. It has to be clarified that the concept of "back diffusion" is often used in the professional literature and even in the ISO standard, although this term is not clearly defined and lacks the scientific basis. In this case, it should be understood that reduction of the radon diffusion into a closed container is due to the decrease of a gradient of radon activity concentration at the boundary, according to the Fick's law.

(c) The significant activity concentration of thoron in the soil pores.

Finally, the ISO standard ISO 11665-7 (ISO, 11665-7, 2012) provides the algorithms for estimating radon exhalation rate for different methods of measuring radon concentration in the container. However, as far as the implementation of these estimates is concerned, the standard procedure does not guarantee the reliability and accuracy of the measurements, because this standard does not define the calibration procedure of the measurements of radon surface exhalation rate.

The Open Charcoal Chamber Method (passive accumulation of radon in an open chamber with activated charcoal), in contrast to the Closed-Chamber Method, has a metrological assurance and passed the appropriate tests (Tsapalov et al, 2016a). However, this method is mainly used only for measuring the radon exhalation rate from the soil surface. Furthermore, this method is little known in the world, although is widespread in Russia and is used to control radon hazard of construction sites already for more than 20 years (Tsapalov et al, 2016a).

The Active Open-Chamber Method (continuous pumping of air through an open container) has not yet received wide practical application, because it is little known and rarely used in studies (Pearson at al., 1965; Pearson and Jones, 1966). Here, the measurement chamber is continuously purged with a fixed flow rate of the atmospheric or ambient air with a low radon concentration C_o. The radon concentration in the container (or pumped air) is given by

$$C(t) = C_o + \frac{SE_s(t)}{\omega} \tag{5.13}$$

with ω being the rate of air pumping in m^3/s (here the radioactive decay is neglected). The advantage of this method is that the influence of back diffusion as well as the influence of other factors, e.g., the change of vapor pressure inside a closed chamber is avoided. The disadvantage of this method is the necessary high sensitivity of the radon detector, especially when the radon exhalation rates are low. According to Jonassen (Jonassen, 1983), the difference between 2 in series connected chambers as described above can be applied for the determination of the exhalation rate for thoron [see e.g., (Tuccimei, et al., 2006; Ujic, et al., 2008; De With, et al., 2014)].

Generally, direct methods for measuring the thoron exhalation rate are more complex (Ujic et al., 2008) and not widespread, however the Dutch standard NEN 5699 (NEN 5699, 2001; De Jong et al., 2005) exists.

5.4.4.2 Radon mass exhalation rate

Two methods of measuring radon mass exhalation rate, which are different only in methods of sampling, as reported in (IAEA, 2013) are shown in Fig. 5.18.

In the option 1, the sample is kept in a sealed vessel at least 4 weeks to establish radioactive equilibrium between radon and radium parent. Then the activity of radon freely released from the sample is determined, for example, by measuring the radon activity concentration in the whole volume of the measuring system, including the vessel, the measuring chamber device, tubes, and other adaptations. Finally, E_M (Bq/kg/s) is calculated by the formula:

$$E_M = \frac{V}{M} \lambda C_\infty \tag{5.14}$$

where,C_∞ measured radon activity concentration, Bq/m^3; V effective volume, m^3; M sample weight, kg; λ radon decay constant, equal to 2.09×10^{-6} s^{-1}.

In the option 2 (similar to the Active Open-Chamber Method) air (or better nitrogen) with the low Rn concentration C_o is continuously pumped at a constant flow rate, through the vessel with a sample and the measuring device chamber. The radon activity concentration in the air flow is simultaneously measured, which corresponds to the rate of release of free radon activity from the sample per unit time taking into account the known volume rate of air flow and the radon concentration in the carrier gas.

Then, E_M (Bq/kg/s) can be calculated as:

$$E_M = \frac{(C - C_o) \cdot (\omega + \lambda \cdot V)}{M} \tag{5.15}$$

where ω is the volume rate of the pumped air, m^3/s. In most cases $\omega \gg \lambda V$ and λV can be neglected.

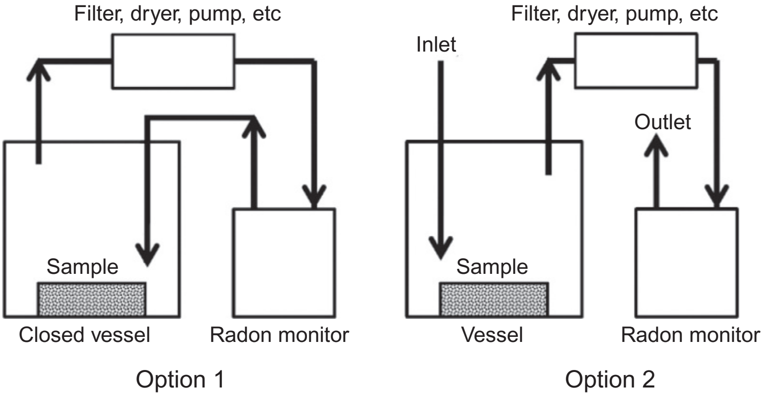

Fig. 5.18 The sampling option for measurement of the radon mass exhalation rate.

It should be noted that the option 2 allows for quickly obtaining the result, but the uncertainty of such result will be significantly higher, than in the option 1 because of the low radon concentration to be measured. Therefore, the most sensitive methods for measuring radon activity concentration, have to be used, e.g., activated charcoal with liquid scintillation counting. In this case, the radon released from the sample is absorbed by (cooled) activated charcoal for a certain time, and then the radon activity in this charcoal is measured, according to the ISO standard (ISO, 11665-9, 2016).

5.4.4.3 Radon emanation coefficient

The measurements of the emanation coefficient are always conducted in the laboratory. A sample of the test material must be crushed to a fraction of the single grains not exceeding 8–10 mm by size, in order to let the free radon to be completely released into the ambient air due to diffusion even at the lowest values of the radon diffusion coefficient in material, taking into account its thickness, according to Fig. 3.5. The crushed sample should be dried naturally to the air-dry state. For this purpose the sample is kept in a dispersed state under room conditions, while free radon is naturally removed—this stage is called "deemanation" of the sample.

Determination of the emanation coefficient, ε (rel), may be carried out by analogy with the measurement of the value of E_M (see the previous section). In this case, determination of the radium concentration C_{Ra} in the sample is additionally required, then the value of ε can be calculated from Eq. (3.15) taking into account Eqs. (5.14) and (5.15), respectively.

Another method to determine the emanation coefficient is achieved by means of gamma-spectrometry (IAEA, 2013). In principle two measurements are necessary: The first measurement concerns the sample at "deemanation state" that means all "free" radon and its progeny outside the sample are removed (kept in open air) so that only the activity concentration of the remaining "bond" radon and its progeny in the sample is measured and then converted to a virtual radium-concentration C^*_{Ra}. The second measurement is carried out after keeping the sample in a hermetically sealed condition for at least 4 weeks for determining the radium activity concentration C_{Ra} which corresponds to the total activity of the "free" and "bond" radon. The value of ε is determined by Eq. (3.8) or (5.16)

$$\varepsilon = 1 - \frac{C^*_{\mathrm{Ra}}}{C_{\mathrm{Ra}}} \tag{5.16}$$

Usually the determination of C^*_{Ra} and C_{Ra} is performed by repeated measurements (recommended are at least three) and the uncertainty of the radon emanation coefficient is calculated according to ISO/IEC Guide 98-3 (BIPM/ISO/IEC Guide 98-3, 2008).

The Gamma-Method can be also used to determine the thoron emanation coefficient too, but the sample of test material must be crushed to powder. Deemanation of such sample is carried out by keeping that powder at a layer not thicker than

2 mm during at least two days to free air. The second measurement is performed in at least two days after sealing the sample.

5.4.5 *Modeling indoor radon concentration from radon exhalation*

Given the radon surface exhalation rates E_i (corresponds to E_S in Bq/m^2/s) for different building materials in a room the total inflow of radon in Bq/s can be calculated as

$$F_M = \sum_i E_i S_i \tag{5.17}$$

with S_i (m^2) being the surface area of the building material with the exhalation surface rate E_i. The air exchange rate λ_{AE} (s^{-1}) is usually given as room volumes exchanged per hour. For example, $\lambda_{\mathrm{AE}} = 1\ \mathrm{h}^{-1} = 1/3600\ \mathrm{s}^{-1}$ means that the amount of external air equal to the volume of the room V (m^3) enters the room within 1 h (nowadays new houses with tight windows often have exchange rates of far below 1 h^{-1}). The balance of the indoor radon activity concentration C (Bq/m^3) in a nonsteady state mode is described by the equation

$$\frac{dC(t)}{dt} = \frac{1}{V}(F_M + F_S) - \lambda_{AE}C(t) - \lambda C(t) + \lambda_{AE}C_A \tag{5.18}$$

The first term at the right side is the total flux from building materials and soil (F_S, Bq/s) divided by the total volume of the room; the second term is the reduction of the radon concentration caused by the air exchange rate; the third term accounts for radon reduction due to the radon decay with the decay constant $\lambda = 2.09 \times 10^{-6}\ \mathrm{s}^{-1}$ and the last term accounts for radon inflow from atmospheric air C_A (Bq/m^3). In the steady state condition $C = \text{constant}$ for $t \rightarrow \infty$, then $\frac{dC}{dt} = 0$, and the Eq. (5.18) can be easily solved given that $\lambda \ll \lambda_{\mathrm{AE}}$:

$$C = \frac{1}{\lambda_{AE}V}(F_M + F_S) + C_A \tag{5.19}$$

One has to realize that in most cases the ground below the building is the main source of indoor radon. Still, it is necessary to assure that building material with NORM ingredients will not contribute substantially to the indoor radon concentration. This is achieved by controlling and limiting (if necessary) the value of $\mathrm{E_S}$.

5.4.6 *Estimation of the contribution from the building material to the indoor radon concentration*

To estimate the contribution of building material to the indoor radon concentration, Eqs. (5.17) and (5.19) can be used. The member of F_S in formula Eq. (5.19), considering the balance of radon only for the rooms of upper floors of buildings, will not be taken into account. The volume of the room and the area of the enclosing structures exhaling radon can be easily determined. Therefore, according to these formulas, the main components of uncertainty are the values of λ_{AE} and the surface exhalation rate E_S.

The uncertainty of the E_S-value can be estimated on the basis of formula (3.14), where the main sources of uncertainty are two quantities—ε and C_{Ra}, each of which can be determined in the lab with the accuracy of (30%–40%). Thus, the maximum uncertainty of the E_S-value does not exceed 60% (the square root from a sum of squares of components of the combined uncertainty). In the case of direct measurements of the E_S-value using the methods described in Section 5.4.4, even more accurate results can be obtained, if these methods have a reliable metrology assurance.

The value of λ_{AE} has an even larger uncertainty, but it does not exceed 100%. Indeed, taking into account the requirements for the design of modern buildings, most appropriately for modeling as the annual average would be to assume $\lambda_{AE}=0.5\ \mathrm{h}^{-1}$. Then, with a high probability one can expect that the confidence interval of the λ_{AE}-value will be equal to 0.25–1.0 h^{-1} (i.e., the uncertainty of guaranteeing the optimum air exchange rate in premises of modern buildings roughly corresponds to 100%). It has to be noted that in premises with the annual air exchange rate of lower than 0.25 h^{-1} it would be difficult to guarantee a good indoor air quality and comfortable environment for long-term stay of building occupants, because the necessary hygienic requirements are violated. For example, air humidity increases, as well as the concentration of carbon dioxide and other nonradioactive gases released from building materials and interior items. As far as the high annual air exchange rate—exceeding 1 h^{-1}, is concerned, it also does not provide a comfortable environment—differential pressures and powerful airflows in the rooms are developed. In addition, the energy efficiency of building is reduced.

Thus, the combined uncertainty of the evaluation of the annual indoor radon concentration obtained by modeling consists of two components (60% and 100%) and does not exceed 120%.

The obtained value of uncertainty exceeding 100% is generally perceived as unacceptably high. However, comparing the reference level of indoor radon (C_R) to the level of average contribution from building materials (C_M), it is quite acceptable that the modeling uncertainty may be so high. Indeed, according to the Eqs. (3.14), (5.17), and (5.19), and using the following parameter values: $S/V=1.4\ \mathrm{m}^{-1}$, $\lambda_{AE}=0.5\ \mathrm{h}^{-1}$, $d=0.2$ m, $\rho=2400\ \mathrm{kg/m^3}$, $\varepsilon=0.1$ (see Table 3.5), and $C_{Ra}=32$ Bq/kg[1] (the average concentration in the earth's crust), results in $C_M=16\ \mathrm{Bq/m^3}$. The reference values 300 or even 100 $\mathrm{Bq/m^3}$ are many times greater than the obtained value of C_M. Analogous calculation shows that the indicated reference levels of the annual indoor radon in the upper floors of buildings confirm with the contribution from building materials, if the value of C_{Ra} is equal to 600 or 200 Bq/kg, respectively. Note that popular building materials can have a high activity concentration of radium, as seen from Table 3.6.

Thus, based on the above presented considerations and quantitative assessments a principle of appropriate restriction (standardization) of radon exhalation from building materials is justified.

From the above example it can be seen that the determination of E_S could be important in case of an enhanced concentration of ^{226}Ra. In case of a ^{226}Ra concentration below, say 100 Bq/kg, and a nonhighly porous building material, radon from the building material should not lead to a radon concentration beyond the reference values.

5.5 Conclusions and recommendations

This chapter gives an overview on many aspects on measuring and how measurement results should be used to test the compliance of building materials (EU, 2011) with the EU Basic Safety Standards (BSS) (EU, 2014). However, all this information may be confusing to people who are not so familiar with radionuclide measurements, which is the case for the vast majority of people involved in either construction industry or construction materials manufacturing. Moreover, all parameters describing quality and expected mechanical properties crucial for construction materials (and hence controlled) have nothing in common with radioactivity.

Therefore, member states have not yet enforced requirements concerning radioactivity content in construction materials and seem not to be prepared to face the new challenges set in the directive. However, each member state has more or less well developed systems of nuclear safety and radiation protection with the relevant infrastructure as well as qualified personnel using all the measurement techniques discussed in this chapter. Therefore, it is not necessary to build a new measurement infrastructure from scratch. At the first stage, it is enough to introduce specific measurement procedures and engage existing resources. Such approach is justified also from an economic point of view because the necessary equipment is rather expensive and needs trained personnel. Taking into account the existing situation the concerns of the construction industry related to the technical and economic consequences of the introduction of the new measurement techniques are not well-founded.

A final *modus operandi* for monitoring radioactivity in building material will depend on the existing necessities and possibilities (i.e., number of construction materials types, number of samples, actually available resources, and related costs). It is not yet clear if the number of sample measurements with the demanded uncertainty of the results (measurement time related) can be managed by the existing laboratories as they do measurements for other purposes. One can imagine simplifying measurement of radioactivity of construction materials in comparison to the gamma spectrometry prepared for monitoring environmental radioactivity in all types of samples. Besides that certain laboratories can specialize in radioactivity measurements of construction materials. This approach is also supported by the state-of-the art requirements concerning quality management systems that have become obligatory in all laboratories involved in measurement of any parameter somehow related to the occupational or health risk assessment.

In principle it is possible for construction material producers to control themselves for all the used material in advance and during the production but the end product should be controlled by certified laboratories.

A slightly different situation exists when considering existing capabilities of radon measurement. The exposure to radon is significant in confined spaces, but existing measurement methods do not allow a known and sufficient accuracy to estimate the average annual indoor radon concentration if measurement duration of less than month, because the indoor radon concentration usually varies substantially in time. At the same time, the simulation based on the known radiation and physical properties of materials (defined under laboratory conditions) allows more accurate prediction of the contribution of the radon exhalation from building materials to the annual radon concentration in modern buildings. It is important that the accuracy of such assessment is practically not reduced, if the restriction of radon exhalation from building materials is mitigated only by setting the reference level of radium activity concentration (perhaps, considering also the thickness or dimensions of the end product). Thus, the control and restriction of the contribution of radon exhalation from building materials in the annual level of indoor radon can be provided by the results of the same laboratory gamma-ray measurements. In other words, it is not necessary to use a special equipment and measurement method.

NORM residues, which have radioactivity concentrations significantly exceeding the clearance level can be used for the production of construction materials as raw materials and other components are not subject to the requirements set in the EU directive. However, from a radiation protection point of view, occupational risk to workers involved in the process of construction materials manufacture is usually negligible, even if the concentration of natural radionuclides in raw materials exceeds either limits set for construction material or clearance level set for NORM. However, in some special situations when NORM is used as raw material then occupation exposure can be important. The reason can be either gamma radiation from large amounts of material or incorporation of dust or radon (progeny). Thus, several recommendations should be given for companies, which intend to process NORM above clearance level as set in the EU BSS directive.

Firstly, radiation protection concerns the workers in the production process and all people using the products. Usually, it should be possible by organizing provisions to avoid that workers become rated as radiation workers. This can be done by separating storage areas (large amounts of NORM) from working areas and/or limiting working time in areas with enhanced radiation. Cheap and simple measurement instruments are available to check for the ambient dose rate. In critical areas such dose-rate meters should be installed to survey these areas. According to the results of these measurements, the working time in such areas should be limited to assure less than a maximum effective dose of below 1 mSv/year to the workers. If radon concentration above 300 Bq/m^3 is measured in some working places, then increased ventilation should be provided or, if possible, the emanating materials should be moved to some other places, either outside or to the locations where the workers do not remain the whole working day. An initial investigation should be performed by a specialist, especially to check if the material used is the source of radon or if it is the soil/rock beneath the production areas. Later a permanent but cheap measurement system, e.g., by SSNTD, with exposure times of at least 1 month in cold and warm seasons of the year can be used. Finally, it should be checked, if incorporation of NORM via dust particles is possible. In such case, action has to be taken to mitigate exposure of workers. This can be a modification of storage areas or production procedures, increased ventilation or as a last solution the use of dust protection masks.

Besides the occupational risk issues companies processing NORM residues should pay special attention to control the end-product parameters before the final test in a laboratory. In order to assure the positive result of the final test of a construction material product the following recommendations can be followed:

- The concentration of natural radionuclides in the raw materials must be determined, or the information must be supplied by the producer/importer. Taking a representative sample is essential.
- From this information the radionuclide concentration can be calculated for the end product, taking into account the mixing ratios, as well as the mass changes according to chemical/physical procedures during the production processes. The resultant index should be significantly (about two standard deviations) below the limit to be sure that small variations in the mixing ratios will not lead to exceedance of the limit.
- As a final check, a dose-rate meter with an alarm level can be installed at the end of the production line. Such a measurement device must be installed in a way that the background radiation remains constant (no storage of raw materials or other products in the vicinity of the meter, shielding against other directions in a way that only the end product contributes to the measurement). A first calibration should be done by determining the index of the end product and comparing it with the background corrected reading of the dose-rate meter. In this way a cheap and reliable internal QA is possible.
- The measurement and the interpretation of the measurement results of the radon exhalation from the end product is a rather difficult job, however the control of radon exhalation from building materials can be carried out by the results of a laboratory measurements of the radium activity concentration. It should be noted that the problem of reliable sealing the measured sample is not completely solved yet, and more research is needed.
- Any equipment (for all types of measurements) must be adequate to the problem to be solved, e.g., the sensitivity must be sufficient to measure the low radiation levels, the device must be robust enough to be used in industrial workshops, etc. This seems self-evident, however, such quality characteristics have often been overseen especially when the problem is new to a company. In addition, the equipment and measurement methods should be a reliable metrological assurance and conform to international standards.
- All measurements and all measures in connection with radiation protection must be documented and the documents must be stored according to the national regulations. To some extent all of these recommendations are valid also for construction material manufacturers that do not process NORM with high content of radioactivity because the compliance with the requirements of the European BSS is in force and must be checked for all building materials.

Annex A Uncertainties, decision threshold (decision limit), and detection limit (lower limit of detection)

A1 Uncertainty in gamma-spectrometry

The result of a measurement is only an approximation or estimate of the value of the specific quantity subject to measurement. The result of every measurement consists of two values: the value of the measured quantity (measurand) and a quantitative statement of its uncertainty. The uncertainty is a value which characterizes the range within which the true or expected value of a measurand lies with a defined probability. It is inherently connected with the statistical behavior of the measurement process and the measurand. A comprehensive description of how to treat uncertainties can be found in the "Guide to express uncertainties in measurement" (BIPM/ISO/IEC Guide 98-3, 2008: GUM—Evaluation of measurement data—Guide to the expression of uncertainty in measurement.)

The uncertainties in the measurement process consist of several components that can be grouped into two categories:

(A) those which are evaluated by statistical methods (e.g., counting) and
(B) those which are evaluated by other means.

The evaluation of both components "A" and "B" may be based on any statistical method for treating data or scientific judgments using relevant information available, respectively. In the case of component "A": standard deviation of the mean of a series of independent observations or method of least squares to fit a curve and to estimate the parameters of the curve and their standard deviation or analysis of variance (ANOVA) to identify and quantify random effects in certain kinds of measurements. In the case of component "B": previous measurement data, general knowledge of the behavior and property of relevant materials and instruments, manufacturer's specifications, data provided in calibration, and uncertainties assigned to reference data taken from handbooks.

The final uncertainty of the measurement result could be a combination of several components of both kinds "A" and "B". When the measurand is not directly determined but is calculated through a function the law of propagation of uncertainty has to be used.

Let

$$y = f(x_1, x_2, \ldots, x_N) \tag{5.20}$$

be the outcome of a value derived from different inputs x_i with known uncertainties $u(x_i)$. Then combined uncertainty of the measurement result y, designed by $u_c^2(y)$ can be calculated as (Gaussian uncertainty propagation law)

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum\nolimits_{i=1}^{N-1} \sum\nolimits_{j=i+1}^{N} \frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j} u(x_i, x_j) \tag{5.21}$$

In case of uncorrelated inputs $\mathrm{x_i}$ the covariances $u(x_i, x_j)$ are zero and Eq. (5.21) reduces to

$$u_c^2(y) = \sum\nolimits_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) \tag{5.22}$$

Usually the uncertainties are given in standard deviations s_c, s_i multiplied with some coverage factor. If the probability density distribution for the result y follows a

Gaussian distribution then the probability for the true value of the result y lies between $y-s_c$ and $y+s_c$ is 68% (double-sided confidence level). If a higher probability is necessary a higher coverage factor has to be used, e.g., the probability is 95% for the range $y-2s_c$ to $y+2s_c$ (coverage factor $k=2$).

In contrast to the term "uncertainty", an error means a "wrong decision". For legal purposes it is often necessary to answer the question whether a sample contains a certain radionuclide. If a radioactivity measurement of the sample results in a value which is larger than the uncertainty of the measurement result then one decides that the sample contains a certain radioactivity. However, if this is not the case, then an error has been made. The size of the used uncertainty (the standard deviation and the used coverage factor) determines the probability for that error.

Besides statistical uncertainties there are a lot of possibilities for introducing additional uncertainties into the results of measurements. Fortunately many of them are small or can easily be compensated and some are not relevant in connection with the compliance for legal requirements. Especially for gamma spectrometry two points should be mentioned:

- Peak area determination: Generally, the background on both sides of a peak in the spectrum is used to estimate the background below the peak. Usually a linear extrapolation is used but in certain situations (e.g., adjacent to a Compton edge) a polynomial fit of the order 2 or 3 may simulate the background below the peak better. Additional attention must also be paid to overlapping peaks. Finally, HPGe detectors produce peaks with a relatively long tail at the low energy side. This is no problem if the sample peak is compared with a peak in a reference sample in an identical measurement situation. However, if only the efficiency of the detector is determined then one has to realize that outside the usually used interval for the determination of the peak area (usually 2–3 FWHM) approx. 2%–3% (depending of the size of the detector) of the peak area on the low energy side of the peak are not within the used interval (older Ge(Li) detectors do not show such effects). If the counting time is measured only when the MCA is ready to convert events (live-time measurement) no dead time correction is necessary.
- Sample effects: Generally a correction for sample density can be applied (the relevant correction factors should be determined during the calibration of the device), however also the atomic composition modifies the self-absorption in the sample because Compton scattering, photo effect, and (above 1 MeV) pairing effect are depending on some exponents of the atomic number Z. In most cases building material does not vary very much concerning the atomic numbers of its ingredients but in some cases (e.g., Ba-concrete) this may be of concern. Also the homogeneity of the samples can be of interest. A typical example is the measurement of liquid samples (e.g., leaching tests). Tiny solid parts, sometimes even invisible, can settle on the bottom of the sample container and this inhomogeneity of the radioactivity in the sample cannot be used to determine the activity by comparing with a homogeneous reference material.[1]

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[1] A simple method to avoid such sedimentation is to mix the sample with some glue (in aqueous solutions wall paper paste can be used) while stirring the sample as long as a sedimentation can occur. Then the solid parts are fixed homogeneously distributed in the sample.

In any measurement it is a good practice not to rely only on automatic analyzer systems but to think about all steps during the determination of an activity concentration and to realize what really happens and what uncertainties can be present in the process.

A2 Decision threshold and detection limit in gamma spectrometry

It is often necessary to decide if materials comply with legal requirements or not. However, all measurements are connected with uncertainties, thus, every decision may be erroneous. The only possibility is to limit such false decisions to a certain probability. To deal with such problems the decision threshold (or decision limit, DL) and detection limit (called hereafter LLD were introduced).

In case of low level measurements two decisions are of importance:

- to decide that a sample contains a certain radionuclide and
- to decide between the cases of radioactivity below or above a reference value.

Both decisions should be made with a certain low probability for a wrong decision which means low probabilities of error. It is obvious that the probability for an error essentially depends on the uncertainties of the measurements.

In the theory of statistics a certain hypothesis is called null-hypothesis (in the case to decide if a sample contains a certain radionuclide the null-hypothesis is usually the hypothesis that the sample does not contain the nuclide) while the other case is called antithesis. Then four possibilities exist and are shown in Table 5.5.

Thus, the “Error of the first kind” is a false accepted antithesis (false decision that the sample is radioactive), while the “Error of the second kind” is a false accepted null-hypothesis (false decision that the sample is not radioactive).

Now the question arises how to determine the probability of the error in the decision if a sample contains a certain radionuclide or vice versa, which net effect is necessary to decide that a sample contains that radionuclide and the probability of a wrong decision being lower than a required probability. To avoid the measurement time in the calculation only rates and their uncertainties are used below. The radioactivity determination comprises in principle two measurements: the measurements of the

Table 5.5 Definition of “Error of the first kind” and “Error of the second kind”

	Null-hypothesis is true: the sample does not contain the radionuclide	**Antithesis is true: the sample contains the radionuclide**
Decision: Sample does not contain the radionuclide (null-hypothesis is accepted)	Correct decision	Error of the second kind
Decision: Sample contains the radionuclide (antithesis is accepted)	Error of the first kind	Correct decision

sample (gross rate r_g with standard deviation s_g) and the measurement of the background (background rate r_b with standard deviation s_b). The required result is the net rate r_n with its standard deviation s_n which can easily be calculated:

$$r_n = r_g - r_b \quad \text{and} \quad s_n = \sqrt{s_g^2 + s_b^2} \tag{5.23}$$

Now we can introduce the decision limit DL (decision threshold): If the value of the result of a physical effect exceeds the decision threshold then one decides that the physical effect is present. At the limit of decision the probability for the error of the first kind is equal to α (e.g., Donn and Wolke, 1977).

In Fig. 5.19 the probability density distribution for r_n for a sample without the physical effect of radioactivity is shown. The decision limit will be chosen as $\mathrm{DL} = k_{1-\alpha} s_n$. e.g., a coverage factor $k_{1-\alpha} = 2$ leads to a (single-sided) probability $\alpha = 0.0228$ for r_n when assuming a Gaussian probability density distribution. With such a choice the error for a wrong decision is 2.28%. The choice of the value for the decision limit depends on the acceptable probability α for a wrong decision. (In earlier papers the DL was often called limit of detection or LLD, while today the LLD is defined differently (Altshuler and Pasternack, 1963)—see Table 5.6.)

Thus, the general expression for the decision limit can be written as

$$\mathrm{DL} = k_{1-\alpha} s_n^{\mathrm{DL}} = k_{1-\alpha} \cdot \sqrt{s_g^2 + s_b^2} \tag{5.24}$$

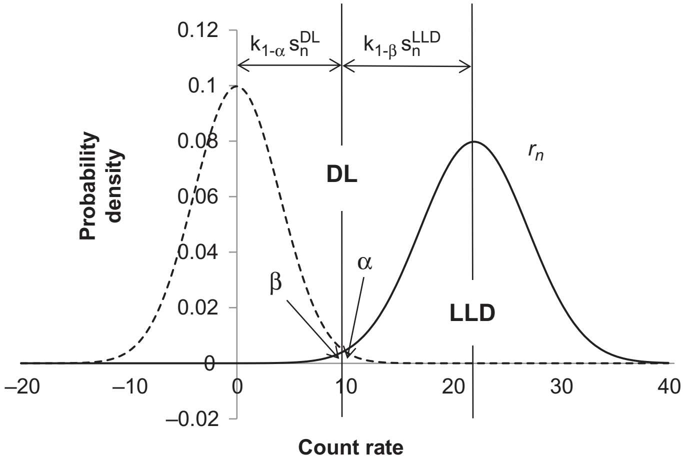

Fig. 5.19 Net rate density distribution for a sample without effect (dashed line) and a sample with a probability β that the sample shows an effect below the decision limit (solid line): the DL and the LLD are displayed as a function of the coverage factors $k_{1-\alpha}$, $k_{1-\beta}$ respectively and the standard deviations s_n. α is the probability for a wrong decision that the sample shows the effect.

Table 5.6 **Single-sided confidence level and single-sided significance level for different coverage factors for a Gaussian frequency density distribution**[a]

Coverage factor $k_{1-\alpha}$, $k_{1-\beta}$	Confidence level $1-\alpha$, $1-\beta$	Significance level α, β
1000	0.8414	0.1586
1282	0.9000	0.1000
1645	0.9500	0.0500
1960	0.9750	0.0250
2000	0.9772	0.0228
2326	0.9900	0.0100
2576	0.9950	0.0050
3000	0.9986	0.0014
3090	0.9990	0.0010

[a] For a very low number of counts the Poissonian distribution cannot be approximated by a Gaussian distribution and the difference between two Poissonian distributions is not a Poissonian distribution. Therefore, special tables have to be used (e.g., Helene, 1984).

with s_g the standard deviation of the gross measurement results for a sample at the decision limit and s_b the standard deviation of the background (which has to be subtracted from the gross measurement result). In most cases the approximation to compute s_g for the background is sufficient. In any case, the decision limit is—apart from the selected coverage factor-only dependent on the background (and the measurement circumstances, e.g., measurement time, etc.).

To achieve a value from the measurement which can be compared with a reference value or a limit it is not sufficient only to proof the existence of a radionuclide in a sample. For this task the LLD is introduced. The LLD is defined as the expectation value for the random variable (measured variable) with a given probability for a value below the decision limit (see Fig. 5.19).

The LLD can be written as

$$\mathrm{LLD} = \mathrm{DL} + k_{1-\beta} s_n^{\mathrm{LLD}} = \mathrm{DL} + k_{1-\beta} \cdot \sqrt{s_g^2 + s_b^2} \tag{5.25}$$

with s_g being the standard deviation of the gross measurement result for a sample at the LLD and s_b the standard deviation of the background.

What is the meaning of the LLD? Let us assume a sample with a true activity equal to the LLD. Then a single measurement will result in a value below the DL with a probability β. This means with a probability β it cannot be decided at a 1–α level that the sample shows any contribution of the radionuclide. Therefore, the LLD of the measurement procedure must be lower than the reference level or the limit to which the sample should be tested. If this is not the case the measurement procedure is not adequate to test the compliance with the reference value or limit.

In the case of a simple counting measurement, e.g., gross beta counting, the DL and LLD can be calculated according to

$$\mathrm{DL}=\frac{1}{2t_b}k_{1-\alpha}^2\left(1+\sqrt{1+\frac{4r_bt_b}{k_{1-\alpha}^2}\left(1+\frac{t_b}{t_g}\right)}\right) \tag{5.26}$$

$$\mathrm{LLD}=\left(k_{1-\alpha}+k_{1-\beta}\right)\sqrt{r_b\left(\frac{1}{t_b}+\frac{1}{t_g}\right)}+\frac{1}{4}\left(k_{1-\alpha}+k_{1-\beta}\right)^2\left(\frac{1}{t_b}+\frac{1}{t_g}\right) \tag{5.27}$$

where r_b is the background count rate, r_g is the gross count rate, and t_b and t_g the corresponding measuring times. For $r_bt_b>50$ one can use the following approximation:

$$\mathrm{DL}=k_{1-\alpha}\sqrt{r_b\left(\frac{1}{t_b}+\frac{1}{t_g}\right)} \tag{5.28}$$

$$\mathrm{LLD}=\left(k_{1-\alpha}+k_{1-\beta}\right)\sqrt{r_b\left(\frac{1}{t_b}+\frac{1}{t_g}\right)}=\frac{k_{1-\alpha}+k_{1-\beta}}{k_{1-\alpha}}\cdot\mathrm{DL} \tag{5.29}$$

A3 Application of DL and LLD in gamma-spectrometry

For a spectrometric measurement the determination of the DL and the LLD is more complicated [see ISO-11929 (ISO-11929, 2010) and ISO-28218 (ISO-28218, 2010)].

The simplest way to calculate the net count rate in a peak is a linear approximation of the background from the data left and right of the peak (Fig. 5.20). When using the

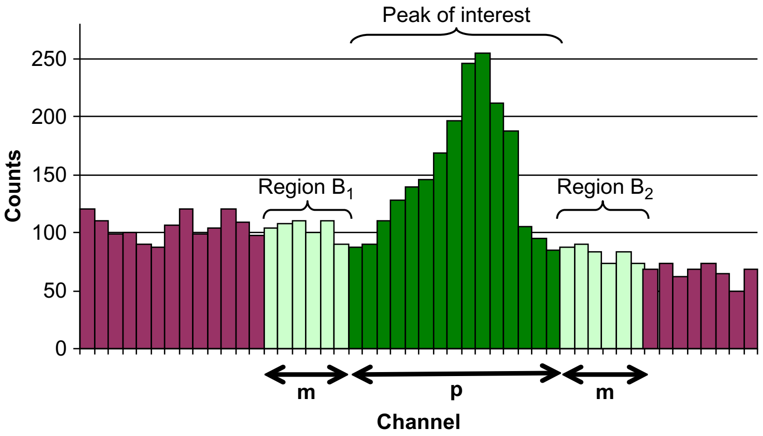

Fig. 5.20 Determination of the net peak area by using the background left and right of the peak of interest.

same number of channels (m) for the background on both sides of the peak, then the net peak rate (r_n) is

$$r_n = \frac{1}{t}\left(N_p - \frac{p}{2m}N_o\right) \tag{5.30}$$

with N_p being the number of counts in range p (channels) of the peak, N_o the sum of then number of counts in the background areas B_1 and B_2, and t the counting time. If it is not possible to select the same number of channels on both sides of the peak then Eq. (5.30) has to be slightly modified. Generally, from the counts in the range p the counts N_c of the pedestal below the peak have to be subtracted. Usually, N_c is computed by a linear fit from the background left and right from the peak, thus leading to equation (5.30).

Because counting statistics follows a Poissonian distribution the standard deviations of N_p and N_o are their square roots. With the uncertainty propagation law and considering that time and channel ratio has no significant uncertainty one gets

$$s(r_n) = \frac{1}{t}\sqrt{(N_p + N_c)} = \frac{1}{t}\sqrt{\left(N_p + \left(\frac{p}{2m}\right)^2 N_o\right)} \tag{5.31}$$

At the DL N_p can be calculated from Eqs. (5.30)and (5.31) and substituted in Eq. (5.24). This results in an implicit equation for DL with the result

$$\begin{aligned} \mathrm{DL} &= \frac{k_{1-\alpha}^2}{2t}\left(1 + \sqrt{1 + \frac{4N_c}{k_{1-\alpha}^2}\left(1 + \frac{N_c}{N_o}\right)}\right) \\ &= \frac{k_{1-\alpha}^2}{2t}\left(1 + \sqrt{1 + \frac{4\left(\frac{p}{2m}N_o\right)}{k_{1-\alpha}^2}\left(1 + \frac{p}{2m}\right)}\right) \end{aligned} \tag{5.32}$$

In case that there is no background peak below the analyzed peak the DL as determined according to Eq. (5.32) can be directly converted into a DL for the activity of the sample by dividing by the efficiency ε.

In the measurement of NORM the problem arises that in a separate background measurement usually peaks exist at the same position as those to be measured. Therefore, Eq. (5.32) cannot be used directly. Usual software supplied with the spectrometer often includes the determination of DL and LLD, however, these values concern only the situation with no background peak at the same position. The correct procedure to be applied is the following:

(a) Determination of the net count rate in the peak from the sample and its standard deviation;

(b) Determination of the net count rate in the peak in the background spectrum r_b (counting time t_b) at the same position and its standard deviation $s(r_b)$;

(c) Calculation of the "net-net-count" rate $r_{nn} = r_n - r_b$ (difference between net count rate from the sample and the net count rate from the background spectrum) and its (net–net) standard deviation;

(d) The (net–net) standard deviation $s(r_{nn})$ calculated this way can be used to calculate the DL according to Eq. (5.33). A measured net-net-count rate can then be compared with DL (and with LLD). To achieve the DL (and LLD) in units of activity a division by the efficiency (and other factors) is necessary.

$$\mathrm{DL} = \frac{k_{1-\alpha}^2}{2t}\left(1 + \sqrt{1 + \frac{4N_c}{k_{1-\alpha}^2}\left(1 + \frac{N_c}{N_o} + \frac{(t_b s(r_b))^2}{N_c}\right)}\right) \tag{5.33}$$

For $4N_c \gg k_{1-\alpha}^2$ which in most cases is fulfilled then Eq. (5.33) can be simplified to

$$\mathrm{DL} = \frac{k_{1-\alpha}}{t}\sqrt{N_c\left(1 + \frac{N_c}{N_o} + \frac{(t_b s(r_b))^2}{N_c}\right)} \tag{5.34}$$

In analogy to the formulas derived for the DL, the formula for the LLD can be found. The result is even more complicated but for $4N_c \gg k_{1-\alpha}^2$ one gets in good approximation

$$\mathrm{LLD} = \frac{k_{1-\alpha} + k_{1-\beta}}{k_{1-\alpha}} \cdot \mathrm{DL} \tag{5.35}$$

The above described methods are the correct procedures to determine DL and LLD. In case that the peak does not stick up considerably from the background (low-level measurement) then DL and LLD can be calculated as:

$$\mathrm{DL} = k_{1-\alpha} \cdot s(0)\,\mathrm{and}\,\mathrm{LLD} = k_{1-\alpha} \cdot s(0) + k_{1-\beta} \cdot s(0) \tag{5.36}$$

where $s(0)$ is the null measurement standard uncertainty which means the standard uncertainty of a measurement where the specified peak area is zero. For a coinciding peak in the background but a low contribution of the sample, then the calculation of $s(0)$ must include the peak in the background too.

The procedure to determine the DL and the LLD is in principle similar if more than one peak is used to determine the activity of a sample.

The DL and the LLD as derived in this chapter take only statistical uncertainties into account. Sample selection, preparation, etc. have to be separately analyzed and their uncertainties have to be included into the uncertainty budget of the result and used to determine the DL and LLD.

Another method to determine the activity of samples uses library spectra for single radionuclides with well-known activities and combines such spectra linearly with the background spectrum as in multivariate analysis. For this type of analyzes Pasternack and Harley (1971)) developed a method to compute the decision limits for different nuclides. Such methods are mainly applied when using detectors with lower energy resolution than Ge-detectors, e.g., NaI-detectors.

Because of some problems especially in sample selection, preparation etc. the ISO 11929 (ISO, 11929, 2010) does not use frequency statistics as derived above but the Bayesian statistics to determine DL and LLD (see ISO 11929 (ISO, 11929, 2010) and references therein (e.g., Weise, et al., 2006). In most cases there are no or only very small differences in DL and LLD between the different ways of calculation, thus, a determination of DL and LLD as explained above seems to be sufficient in practice.

Just to give an example for Bayesian statistics in radioactivity measurement: It is possible that the count rate of a sample is lower than the count rate in the background. This leads to a negative net-count rate which is physically not possible. An “a priori” information (radioactivity cannot be negative) can be used to cut the distribution of the net count rate at zero and to use the centroid of the tail of the distribution above zero to determine a positive net-count rate and its variance. This “a priori” information (only positive net-count rates are possible) is only one possibility (e.g., see Little, 1982).

A4 Example for the determination of peak area, DL and LLD

Commercial γ-spectrometry software usually includes the calculation of DL and LLD. Such software assumes that below the investigated peak no background peak exists. This is usually not the case when measuring NORM. An example for the procedure to calculate the net count rate in a peak with a peak at the same position in the background spectrum is shown below step by step (see Fig. 5.21), as well as the exact determination of DL and LLD.

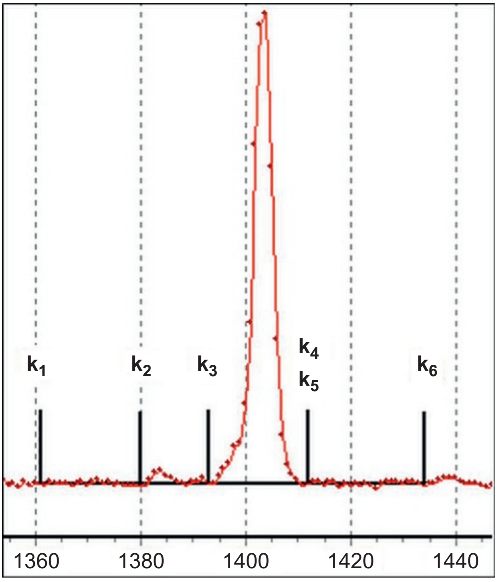

Fig. 5.21 Cutout of a sample spectrum with selected intervals for background and peak area and a linear fit to the background areas.

- The intervals for the determination of background and peak have to be defined. It is not always possible to define the intervals for the background determination back to back and equally sized on both sides of the peak interval as shown in Fig. 5.20. Thus, the channel numbers for the left background area (B_1) from k_1 to k_2, the peak interval should be from k_3 to k_4 and the right background (B_2) comprises the channels k_5 to k_6.
- The left background counts are $N_L = \Sigma n_i$ with i from k_1 to k_2, the right background counts are $N_R = \Sigma n_i$ with i from k_5 to k_6 and the counts in the peak area are $N_P = \Sigma n_i$ with i from k_3 to k_4.
- The computed background below the peak N_C area is determined by a linear fit based on the left and right background areas.
- Then the net peat area is $N_n = N_P - N_C$.
- The standard uncertainty is $s(N_n) = \sqrt{s(N_P)^2 + s(N_C)^2}$. Because of the Poissonian distribution and the assumption that the relative uncertainty of N_C is approximately equal to the relative uncertainty of $N_L + N_R$, this can be written as $s(N_n) = \sqrt{N_P + \frac{N_C^2}{N_L + N_R}}$.
- The net count-rate and its uncertainty are then calculated by a division by the measured (live) time t: $r_n = N_n/t$ and $s(r_n) = s(N_n)/t$.

In NORM it can be assumed that below the observed peak from the sample the same nuclide from the environment causes a peak in the background at the identical position. A structured background can be neglected only in case of an extremely good shielding. Therefore, the same procedure as described above should be applied for the background. Thus, the count rate in a peak which is due only to the sample (r_{nn}) is the difference between the net count rates from the sample and the count rate from the background.

- $r_{nn} = r_n(\text{sample}) - r_n(\text{background})$ and $s(r_{nn}) = \sqrt{r_n(\text{sample})^2 + r_n(\text{background})^2}$.
- According to Eqs. (5.33) or (5.34) and (5.35) the DL and the LLD can be determined.

Numerical realization: Sample measurement time $t = 20{,}000$ s.

- Selected intervals: $k_1 = 1361$, $k_2 = 1380$, $k_3 = 1393$, $k_4 = 1412$, $k_5 = 1412$, $k_6 = 1434$. The left background area was selected not directly adjacent to the peak interval because of a possible additional peak.
- The background counts from k_1 to k_2 ($N_L = 9966$) and from k_5 to k_6 ($N_R = 11{,}538$) are used to calculate the unstructured background within the interval k_3 to k_4. The total counts in the peak interval are $N_P = 32{,}793$ counts and in the background intervals $N_o = N_L + N_R = 9966 + 11{,}538 = 21{,}504$ counts.
- The linear fit results in $N_C = 10005.2$ counts.
- The net peak area is $N_n = 32{,}793\text{-}10005.2 = 22787.8$ counts.
- The standard uncertainty computes to

$$s(N_n) = \sqrt{N_P + \frac{N_C^2}{N_L + N_R}} = \sqrt{32{,}793 + \frac{10005.2^2}{9966 + 11{,}538}} = 193.5$$

- Thus, the net count rate and its uncertainty is $r_n(\text{sample}) = 1.14$ counts/s and $s(r_n) = 0.01$ counts/s.

A measurement (measurement time $t_b = 40{,}000$ s) without the sample shows a peak at the same position as the peak to be investigated. The same procedure as above gives $r_n(\text{background}) = (0.02 \pm 0.01)$counts/s.

- $r_{nn} = r_n(\text{sample}) - r_n(\text{background}) = 1.14 - 0.02 = 1.12$ counts/s and $s(r_{nn}) = \sqrt{s(r_n(\text{sample}))^2 + s(r_n(\text{background}))^2} = \sqrt{0.01^2 + 0.01^2} = 0.014$. In this case the peak in the background spectrum does not really change the uncertainty in the net peak count rate.
- $$DL = \frac{k_{1-\alpha}}{t}\sqrt{N_c\left(1 + \frac{N_c}{N_o} + \frac{(t_b s(r_b))^2}{N_c}\right)} = \frac{k_{1-\alpha}}{20000}\sqrt{10005.2\left(1 + \frac{10005.2}{21504} + \frac{(20000 \times 0.01)^2}{10005.2}\right)}$$
  For $k_{1-\alpha} = 2$ we get $\text{DL} = 0.02_3$ counts/s and with $k_{1-\beta} = 2$ we have LDD = 0.05 counts/s.
- The uncertainty in the net count rate is in the order of 1% which means that in such a case this statistical uncertainty (uncertainty of category A) usually can be neglected in comparison with all other uncertainties appearing during the determination of the activity concentration in a sample.
- When using the simplified Eq. (5.36) then $s(0)$ must be determined: From $r_{nn} = r_n(\text{sample}) - r_n(\text{background}) = r_P(\text{sample}) - r_C(\text{sample}) - r_n(\text{background})$ we get $s(0) = \sqrt{s^2(r_C(\text{sample})) + s^2(r_n(\text{background}))} = \sqrt{\frac{10005.2^2}{21{,}504 \cdot 20{,}000^2} + 0.01^2} = 0.0106$.
  For $k_{1-\alpha} = 2$ we get $\text{DL} = 0.02_1$ counts/s and with $k_{1-\beta} = 2$ we have LDD = 0.04 counts/s. Thus, DL and LLD do not differ much compared with the exact formulas.

Fig. 5.22 shows a general scheme for identifying possible sources of uncertainties in γ-spectrometry and estimating their size.

A general test for the integrity of the measurement equipment which can be applied to all types of counting measurements relies on the comparison of the results of repeated measurements and the result of an analysis of summing up the data of all measurements: Any results of counting measurements should follow a Poissonian distribution. This means that the number of counts is equal to the variance of the measurement result. Thus, the uncertainty of repeated measurements with the same counting time can be determined by calculating the standard uncertainty of the mean in the usual way (outer uncertainty s_{out}) and compare this standard uncertainty with the standard uncertainty of the sum of all measurements (inner uncertainty s_{in}). The standard deviations should agree within

$$\left|\frac{s_{\text{int}} - s_{\text{out}}}{(s_{\text{int}} + s_{\text{out}})/2}\right| < \frac{1}{\sqrt{2(n-1)}} \tag{5.37}$$

with n being the number of measurements (comparison of inner and outer uncertainty). A similar procedure can be applied when more than one gamma peak are used to determine the concentration of a radionuclide in a sample.

A5 Uncertainties in dosimetry

The ambient dose H or dose rate $\dot{H}$ can be calculated from the reading of a measurement device M, its calibration factor N and correction factors k_j for the different influencing quantities which do not modify the reading but the result of the measurement:

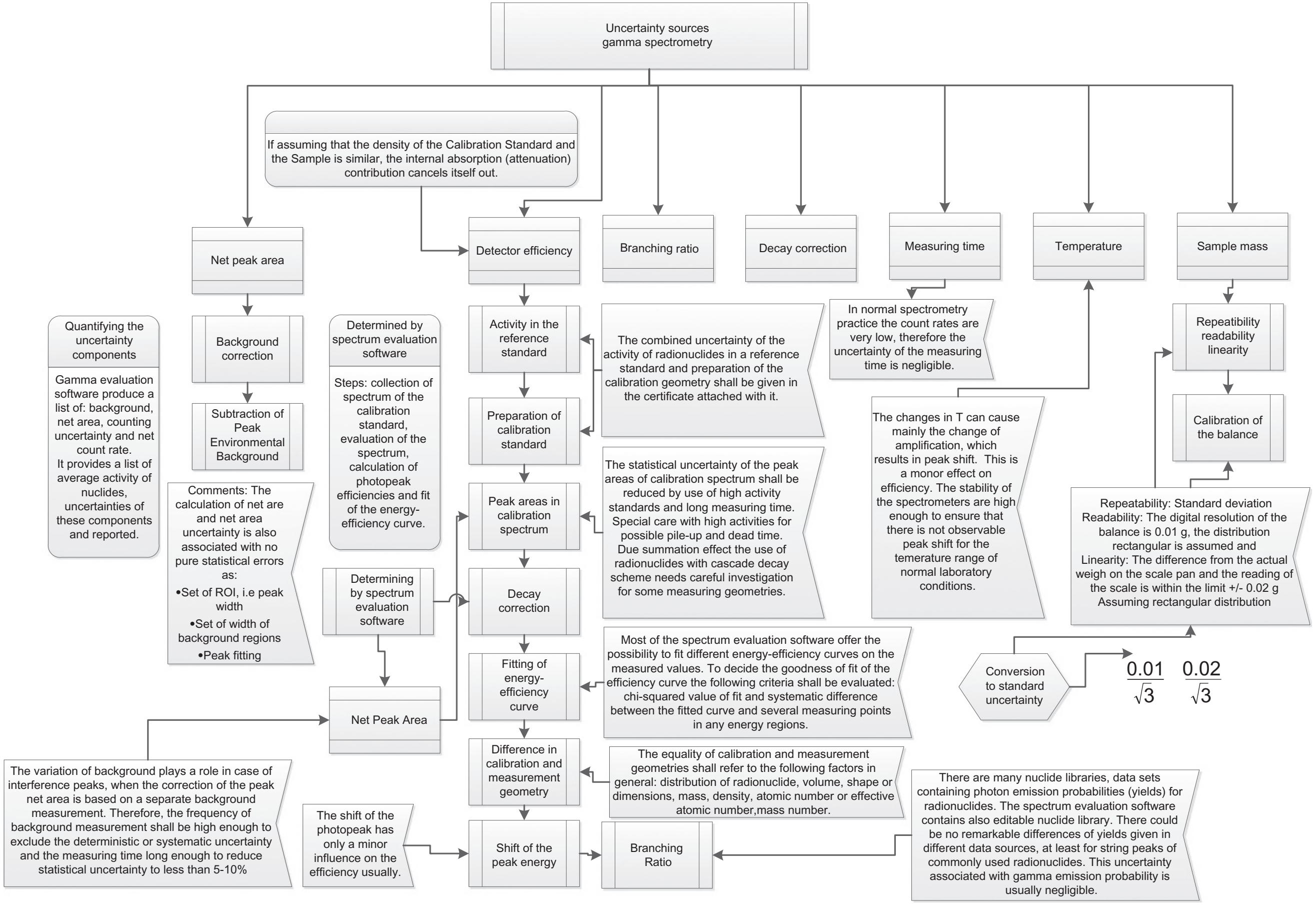

Fig. 5.22 Scheme of identifying and estimating the uncertainties in γ-spectrometry.

Table 5.7 **Influencing parameters and correction factors for ambient dose-rate measurements**

Influencing parameter	Correction factor
Photon energy	k_E
Direction of incidence	k_R
Supply voltage	k_U
Ambient temperature	k_T
Relative humidity	k_W
Air pressure	k_p
Electromagnetic disturbances	k_{EM}
Linearity	k_L

$$\dot{H} = \dot{M} N k_E k_R k_U k_T k_W k_p k_{EM} k_L \tag{5.38}$$

Correction factors k_j are necessary to correct measurements which are not made under the reference conditions (conditions for calibration). Main correction factors are listed in Table 5.7.

The calculation of the standard uncertainty must include all uncertainties from the correction factors too. The simplest case is a measurement with a calibrated device at reference conditions. Then the calibration factor is $N = 1$ and all correction factors are unity. If a national metrology institute has verified the calibration, it usually testifies the compliance with the national standard within e.g., 20% assuming a rectangle probability density distribution.[2] This means a standard uncertainty of $0.2/\sqrt{3} = 0.115$. Let us assume repeated measurements at reference conditions with a mean and a standard uncertainty for the reading $M = (15.28 \pm 0.17)$ μSv/h then the measurement result and its standard uncertainty becomes $\dot{H} = (15.3 \pm 1.8)$ μSv/h (coverage factor $k = 1$) by using the uncertainty propagation law.

If the instrument was calibrated a calibration factor with an uncertainty is given, e.g., $N = 1.05 \pm 0.20$. If the reading is about 15 μSv/h but the calibration was performed at 25 μSv/h then estimation of the uncertainty of k_L is necessary. The correction factor for the linearity should not exceed the interval between 0.95 and 1.05 (rectangle distribution). This gives a standard uncertainty for k_L as $0.05/\sqrt{3} = 0.03$. More important is the uncertainty for the correction factor for the photon energy k_E. Fig. 5.16 shows a typical behavior for k_E when the reference energy was

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[2] Rectangle distribution: $f(x) = 1/2a$ for $m - a < x < m + a$, $= 0$ for all other x. Standard deviation $s^2 = \mathrm{Var}(x) = <x^2> - <x>^2 = \int_{-\infty}^{\infty} f(x) x^2 dx - \left(\int_{-\infty}^{\infty} f(x) x dx \right)^2$ - $\frac{1}{2a} \cdot \frac{x^3}{3} \Big|_{m-a}^{m+a} - \left(\frac{1}{2a} \cdot \frac{x^2}{2} \Big|_{m-a}^{m+a} \right)^2 = m^2 + \frac{a^2}{3} - m^2 = \frac{a^2}{3} \rightarrow s = \frac{a}{\sqrt{3}}$ Probability within $m - s$ to $m + s$: $P = \frac{1}{2a} \cdot \frac{2a}{\sqrt{3}} = \frac{1}{\sqrt{3}} \approx 0.58$ (different compared with a Gaussian distribution!)

662 keV (^{137}Cs). Let the actually measured energy vary between 50 and 1000 keV. Then the mean correction factor is $k_E = 0.95$ and it varies between 0.8 and 1.1. Thus a good choice would be a rectangle distribution with a width of ±0.15. This means that the standard deviation for k_E is $0.15/\sqrt{3} = 0.087$ and with $k_E = 0.95 \pm 0.09$ and $k_L = 1.00 \pm 0.03$ the final result and its standard deviation can be computed. In the case of $M = (15.28 \pm 0.17)$ μSv/h, $N = 1.05 \pm 0.20$, $k_E = 0.95 \pm 0.09$, and $k_L = 1.00 \pm 0.03$ and all other correction factors are unity then the result becomes $\dot{H} = (15.2 \pm 3.3)$ μSv/h (coverage factor $k = 1$).

For a measurement outside the reference conditions all correction factors with their uncertainties have to be considered. For most ambient dose rate monitors the correction factor for the direction of incidence is of main importance and its uncertainty becomes the largest of all correction factors. Even in the example above which represents a typical situation the standard uncertainty is about 20%. When the direction of gamma radiation incidence is not clearly known as it is usually the case in ambient dose-rate measurements then the standard uncertainty becomes even larger. This should always be kept in mind when ambient dose-rate measurement results are used to check for compliance with legal requirements.

The circumstances are much better when dose-rate measurements are made in a standard situation (geometry and energy) which can easily be corrected to the reference conditions or when only relative measurements are necessary. Such a situation is possible when the same type of product is surveyed at the end of a production process.

Annex B Calibration and metrological assurance for semiconductor detectors

The most common way of detector efficiency calibration in gamma spectrometry is experimentally using certified mixed radionuclide solutions. These calibration solutions typically contain a series of radionuclides emitting photons to cover the energy region 59—1836 keV, where photons emitted by most of the radionuclides usually found in the environmental samples can be registered. The mixed radionuclide solution is used for the preparation of a calibration source having the same geometry as the sample to be analyzed. If samples of different geometries are to be analyzed, more calibration sources have to be prepared. It is therefore possible to calculate the detector full energy peak efficiency for each photon energy emitted by the calibration source and for the specific source-to-detector geometry by the formula:

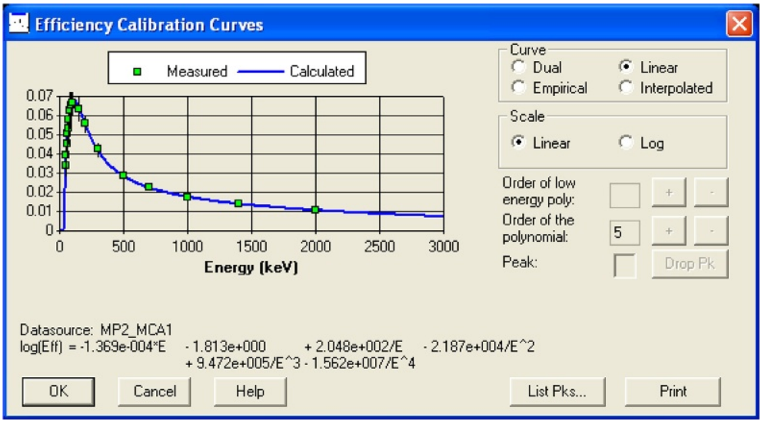
$$\text{efficiency} = \frac{\text{area}}{\text{time} \times \text{yield} \times \text{activity}} \tag{5.39}$$

where *yield* is the specific photon emission probability and *activity* is the corresponding radionuclide radioactivity at the day of the analysis. A series of correction factors may be required further for the efficiency calibration to take into consideration self-attenuation of low energy photons, coincidence summing corrections etc.

Unfortunately reality often shows that radionuclides other than those ones actually present in a standard sample available need to be measured. In this case calibration coefficients obtained for radionuclides present in a standard sample are used to calculate a detector efficiency curve, which is a function of energy. Obtained efficiency curves can be used for the evaluation of calibration coefficients for radionuclides that were not present in a standard sample but need to be measured in a test sample (Canberra, 2016) (Fig. 5.23).

Besides the calibration of the detector done using a standard sample containing well known content of some radionuclides, the most important aspect is self-attenuation of gamma radiation within a sample. According to the interaction of radiation with matter part of the radiation is attenuated in the sample. This phenomenon depends of radiation energy, sample density, and chemical composition. Its impact on measurement results is included in the efficiency curve obtained during calibration and there is no problem when a tested sample has the same properties as the reference sample. As it is unlikely that separate standard (and calibration curve) is available for each and every kind of sample intended to be measured, additional correction is necessary for a sample that significantly differs from the used standard. A practical approach to solve this problem is to prepare a set of standards reflecting a range of typical samples measured. With a sufficiently large set of different calibration standards it is possible to calculate correction factors for a sample with particular properties. It is important to note that the calculated correction factors should cover the entire spectral range of gamma energies measured.

The radiation self-absorption in a sample can also be determined by the "transmission method": An additional source containing the radionuclide of concern is placed directly on the tested sample to enable direct measurement of the self-attenuation in the sample (when compared with the measurement made without the tested sample). This method is mainly used for measurement of radionuclides emitting low energy radiation, as for this method not only the sample density is important but



Curve
○ Dual ● Linear
○ Empirical ○ Interpolated

Scale
● Linear ○ Log

Order of low energy poly:
Order of the polynomial: 5
Peak: ☐

Datasource: MP2_MCA1
log(Eff) = -1.369e-004*E - 1.813e+000 + 2.048e+002/E - 2.187e+004/E^2
+ 9.472e+005/E^3 - 1.562e+007/E^4

Fig. 5.23 An example of a semiconductor detector efficiency calibration curve.

also its chemical composition. In practice this method is used mainly for the measurement of ^{210}Pb (Cutshall et al., 1983; Bonczyk et al., 2016).

Over the last few years an extensive use of computational methods—often combined with experimental ones—for efficiency calibration has been observed. Most of them are based on Monte Carlo simulation. Progress in computational calibration was mainly due to the development of powerful computers—including parallel processing—and user-friendly graphical interfaces. Two types of Monte Carlo computer codes are used for computational calibrations:

A. General-purpose Monte Carlo (M-C) simulation computer codes that can be also used for detector calibrations. Typical codes are: MCNP, GEANT, ETRAN, PENELOPE, EGS4, etc. For these codes to be used for detector efficiency calibration, the user has to describe as accurately as possible the source-to-detector geometry, using a series of mathematically described surfaces. By using these surfaces, the detector, source, shielding and all other bodies existing in the detector system can be described. The existence of user-friendly graphical interfaces and computer programs like *gview3d* allow the user to display the geometry on the computer screen. After the geometry has been described the code simulates a large amount of "histories" that may reach or exceed 10^9, each of them corresponding to a single photon emitted by the source and its interaction with the source material and the detector. The software ensures that the photons are emitted randomly inside the source. Simulation codes normally incorporate "virtual detectors" that are used for recording several parameters during the simulation, the most important being the energy deposition detector (EDD). By defining an EDD with the same geometry as the actual detector under calibration, it is possible to record the amount of energy which is deposited in the detector for each simulated photon of energy E emitted by the source. For this purpose the energy region from zero to E is divided in energy windows (bins) of user-defined width. The simulation of a large amount of photons results in the probability distribution function of the photon energy deposited on the detector, which corresponds to the actual spectrum collected by the detector. It is therefore possible to use information from this probability distribution function to calculate the full energy peak efficiency or the total efficiency of the detector.

Though the whole procedure seems rather straightforward, there are some details that may significantly affect the quality of the simulation results. One of them is detector geometry. Only part of the detector geometry is accurately known or can be directly determined by the user. In most cases the user relies on the geometrical characteristics provided by the detector manufacturer which may not be entirely accurate. A typical case is that of HPGe detectors, where the user cannot actually see the detector as it is enclosed inside the detector housing. The detector manufacturer provides some of the external geometrical characteristics of the detector (e.g., height, diameter, etc.) and an estimation of the thickness of the detector's insensitive layer (dead layer), which however cannot be measured. Furthermore, the detector and the dead layer may not be homogenous. Another issue is the inhomogeneity of the electric field inside the detector which may affect the charge collection and the corresponding signal produced in the detector. It is clear that these problems should be taken into consideration for the simulation results to be meaningful and accurate.

The way to deal with these problems is the experimental determination of the detector geometrical characteristics, a process described as "detector characterization". For this purpose an iterative procedure is introduced, consisting of the following steps: (i) The full energy peak efficiency for the detector is experimentally determined using sources emitting various photon energies. (ii) Monte Carlo simulations of these experiments are conducted using the best available detector geometrical characteristics, subsequently calculating full energy peak efficiencies using the simulation results. (iii) Experimental and simulation results are compared and simulations are repeated with slightly modified geometrical characteristics aiming at the convergence between experimental and simulation results. The whole procedure is repeated until acceptable convergence is reached (e.g., an error margin of 2%–3%). As a result, a set of new detector geometrical characteristics is obtained which are then used for the determination of detector efficiency for energies and geometries where no experimental data exist. It should be noted that: (i) this set of geometrical characteristics is not necessarily the actual detector geometrical characteristics, (ii) this set of geometrical characteristics may strongly depend on the source geometry and distance from detector, and (iii) the whole process introduces a systematic (Type B) uncertainty, originating from the difference between experimental and simulation results, which should be further taken into consideration during efficiency uncertainty determination.

Another important issue is the simulation results interpretation. This was clearly demonstrated in an International Intercomparison of Monte Carlo codes in gamma spectrometry (Vidmar, et al., 2008), where the efficiency calibration of an HPGe detector for three well-defined source-to-detector-geometries was required. It was found that, even when the same computer code was used, significant differences in the full energy peak efficiencies were observed, depending on the selection of various simulation parameters—mainly the cut-off energies—and the interpretation of the simulation results. In a real spectrum, the photopeaks do not contain the full energy of all photons that contribute to a given photopeak. Some of these photons may have lost a small part of their energy content as a result of prior interaction (e.g., small angle Compton scattering inside the source) and deliver a reduced amount of energy to the detector. Additionally, the charge collection can marginally be incomplete. This is particularly important for low energy photons (e.g., 46.5 keV of ^{210}Pb) where a distortion of the photopeak and a low energy tail are occasionally observed. It is therefore of great importance for the simulation to select an energy bin width that will record all of the photon energies that are actually recorded under the real photopeak in the corresponding gamma spectrum. For this purpose the detector energy resolution should be taken into consideration.

B. Dedicated computer codes for detector efficiency calibration. Several such codes have been developed over the last few years for the calibration of Germanium detectors, some of which are based on analytical calculations, others on M-C simulation and still others on a combination of both. Besides the efficiency calibration some of the codes are also calculating correction factors for self-absorption or true coincidence. A list of such codes include:

  i. ANGLE is commercially available software for the efficiency calibration of Ge detectors. The program uses a technique called "efficiency transfer". ANGLE calculates a transfer function between the absolute efficiency data for a detector-sample-matrix geometry which is experimentally determined (the "reference geometry") and the new detector-sample geometry (the "sample"). The semiempirical approach used in ANGLE differs from absolute methods, in that ANGLE starts from a measured calibration which is then "transferred" to the new geometry by calculation of the transfer function, rather than starting with a Monte Carlo model of the detector and then correcting the model via measurement (detector characterization). Obviously, the closer the calibration source is to the sample geometry, the better the result.

  ii. GESPECOR is a Monte Carlo based software developed for the calculation of full energy and total efficiency, as well as correction factors to take into consideration matrix effects (self-attenuation) and coincidence summing. The code can be used for coaxial, well-type HPGe or Ge(Li) detectors, and for various types of sources, including point, cylindrical, spherical sources or Marinelli beakers. Since the exact geometrical characteristics of the detector may not be accurately known, the users are advised to check the calculated values of the full energy peak efficiency for some geometry against experimental values. It is also possible to use the efficiency transfer method for the calculation of the full energy peak efficiency. The results obtained using the efficiency transfer method are less sensitive to the uncertainty of the detector geometrical characteristics than the results obtained by a direct computation of the efficiency. Therefore, if the reference measurement was made using high quality standard sources, the efficiency transfer method should be preferred. The code is capable of using the results of transmission experiments carried out with uncollimated point sources for the estimation of the linear attenuation coefficient which is needed for self-attenuation correction.

iii. ETNA is a computer code that has been developed at the Laboratoire National Henri Becquerel for computing the efficiency transfer and coincidence summing corrections for gamma-ray spectrometry. The code uses a numerical method and requires the decay scheme of the radionuclide emitting the photons of interest, as well as the experimentally determined full energy and total efficiency for the corresponding photon energy for at least one source-to-detector geometry. The code is available from the developer upon request.

iv. LabSOCS (Laboratory Sourceless Calibration System) is a commercially available computer code for the calculation of the full energy peak efficiency of voluminous sources. Efficiency for a specific source is calculated by integrating the response over the volume of the source. For this purpose the detector is previously characterized by the manufacturer, the detector model is determined using the MCNP code and compared to experimental results using five different traceable sources of different geometries. A large number of efficiency data sets for point sources in vacuum at various positions around the detector is then obtained and a calibration grid of the detector is created. It should be mentioned however that the user has to rely on a factory calibrated detector and therefore experimental verification of detector calibration should be conducted.

v. EFFTRAN (EFFiciency TRANsfer) is a computer code for the transfer of full energy peak efficiency from one geometry to another and for coincidence summing correction calculations in gamma ray spectrometry. It is limited to coaxial detectors and cylindrical sources including point sources. The program calculates the total efficiencies for the required source geometry and a reference point source geometry applying the Monte-Carlo integration method. For this purpose the detector geometrical characteristics provided by the detector manufacturer are used. For the calculation of the full energy peak efficiency for the required source geometry the efficiency for the reference point source geometry must experimentally be determined.

For example ISOCS (In Situ Object Counting System) provided by CANBERRA has been designed in order to limit the field-of-view of a detector to 30, 90, and nearly 180 degrees by simply sliding the appropriate shield components on the mounting rails (Canberra, 2016) (Fig. 5.24).

The ISOCS is connected with a calibration software package making gamma in situ assay simpler and more effective by eliminating the need for traditional calibration sources during the efficiency calibration process. The detector characterization produced by the MCNP (Monte Carlo N-Particle; https://mcnp.lanl.govc/, accessed 02.11.16) modeling code, mathematical geometry templates, physical (shape and size)

Fig. 5.24 ISOCS shield systems (Canberra, 2016).

parameters of measured objects, and its chemical composition are necessary. Using these data, the ISOCS Calibration Software provides the ability to get accurate calibration of a spectrometric system used for most any object type and size (Canberra, 2016) (Fig. 5.25).

Despite the principal possibility of in situ measurements, HPGe gamma spectrometry is traditionally used in a laboratory environment to determine the activity concentrations in sample materials using a predefined geometry. Rather to the contrary, the

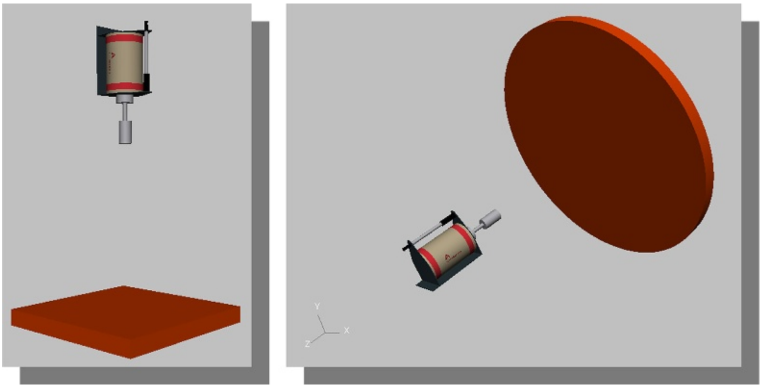


Fig. 5.25 Examples of simple applications of the ISOCS software, useful for in situ measurement of construction materials.

use of low resolution scintillation techniques as an alternative to HPGe gamma spectrometry in field applications is even more often met than its laboratory use. The main advantage of scintillation-based techniques is its simple ability to perform measurements on site as well as the purchase and operational costs that are considerably lower when compared against HPGe, which needs to be cooled during operation to a temperature about liquid nitrogen (Kovler et al., 2013). The drawback of scintillation detectors such as NaI(Tl), CeBr, or LaBr is their low energy resolution. The energy resolution is expressed in terms of a FWHM. For scintillation detectors the FWHM in the energy regions of interest is in the order of 5%–10%; in comparison the FWHM for an HPGe detector is well below 1%. As a result, the energy peaks in the spectrum do not appear as discrete lines but show a more diffuse and wider peak instead. When dealing with NORM the spectrum is characterized by many individual peaks coming from the photons emitted by radium, thorium, and its progeny at many different energy. As a consequence, the individual energy peaks in the spectrum will interfere with each other making it difficult to achieve an accurate assessment of the peak content and its associated activity concentration in the sample.

Annex C Uncertainties in estimation of annual average indoor radon concentration

The absence of information about the measurement uncertainty of annual average indoor radon concentration does not allow performing correctly its comparison with the normative (control, or action) level, as well as to optimize the measurement duration. For example, it is extremely inefficient to carry out the measurements in houses with a radon concentration far below the reference value for several months for checking compliance with the reference. Moreover, in cases where the upper limit of confidence interval does not differ from the normative level, the measurement should be continued longer, even beyond the three months of continuous monitoring. Furthermore, the results of repeated measurements with certain confidence intervals can be correctly averaged, using the inverse uncertainties as weights, which is particularly important in the development of radon hazard maps.

An interesting and promising method of estimating the confidence interval of the average annual indoor radon concentration, depending on the duration of the measurement, has been recently suggested through the following expression (Tsapalov et al., 2016b):

$$\frac{C(t) \pm \sqrt{(K_V(t) \cdot C(t))^2 + s^2(C)}}{K_T(\Delta T_R) + 1} \tag{5.40}$$

where $C(t)$ …average indoor radon activity concentration measured for a sampling duration time t, Bq/m^3; $s(C)$ …instrumental standard uncertainty of radon concentration measurement, Bq/m^3; $K_V(t)$ …radon variation coefficient depending on a sampling duration, (rel); $K_T(\Delta T_R)$ …the thermal influence function, (rel).

Table 5.8 **The values of radon variation coefficient depending on the measurement duration**

Measurement duration (days)	2	3	4	5	6	8	10	12	14	Minimum duration of one of the two long-term measurements[a]			Continuous measurement during 1 year
										1 month	2 months	3 months	
K_V (*t*), %	240	220	200	180	160	150	140	140	140	40	30	20	0

[a] Two measurements are performed in different seasons—cold and warm.

The coefficients $K_V(t)$ and $K_T(\Delta T_R)$ are determined by statistical processing of the results of annual continuous monitoring of the radon activity concentration and temperature in rooms with enhanced radon concentrations at typical ventilation mode. These coefficients have been defined for the premises of the buildings located in Russia (Moscow region), and their values are given in Tsapalov and Marennyy (2014). However, for buildings located in other climatic zones and geological conditions, the values of the coefficients may vary. Therefore, there is a need to conduct appropriate studies in order to clarify the values of these coefficients.

As already reported in Section 5.4.3, the uncertainty of assessment of the annual average indoor radon depends on the measurement duration. The longer the measurements are, the more accurate the assessment is. For example, Table 5.8 provides the values of radon variation coefficient for the rooms, which are equipped with systems of natural ventilation and operating without any restrictions. In this table the values of variation coefficient, according to Eq. (5.39) for the measurement duration of no longer than several weeks, correspond to the combined uncertainty of the annual average indoor radon.

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From raw materials to NORM by-products

6

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6.1 Introduction

Guide for the reader: Structure of Chapter 6:

This chapter gives information on NORM by-products and each section contains two parts: (1) Technical properties (a part that also deals on chemical properties of the by-products) and (2) Radiological properties. This chapter focuses on NORM by-products with suitable properties for construction.

Chapter 7 deals with the properties of the construction materials (cements, concretes, and ceramics) that can be produced on the basis of the considered by-products.

Article 23 of the Council Directive 2013/59/EURATOM (EU, 2014) deals with the "Identification of practices involving naturally occurring radioactive material (NORM)." According to Article 23 "Member States shall ensure the identification of classes or types of practice involving naturally occurring radioactive material and leading to exposure of workers or members of the public which cannot be disregarded from a radiation protection point of view. Such identification shall be carried out by appropriate means taking into account industrial sectors listed in Annex VI."

Naturally Occurring Radioactive Materials in Construction. http://dx.doi.org/10.1016/B978-0-08-102009-8.00006-2

ANNEX VI of the Council Directive 2013/59/EURATOM:

List of industrial sectors involving naturally occurring radioactive material as referred to in Article 23

When applying Article 23 the following list of industrial sectors involving naturally occurring radioactive material, including research and relevant secondary processes, shall be taken into account:

- Extraction of rare earths from monazite
- Production of thorium compounds and manufacture of thorium-containing products
- Processing of niobium/tantalum ore
- Oil and gas production
- Geothermal energy production
- TiO_2 pigment production
- Thermal phosphorus production
- Zircon and zirconium industry
- Production of phosphate fertilizers
- Cement production, maintenance of clinker ovens
- Coal-fired power plants, maintenance of boilers
- Phosphoric acid production,
- Primary iron production,
- Tin/lead/copper smelting,
- Ground water filtration facilities,
- Mining of ores other than uranium ore.

The Annex VII (Table 6.1) of the Council Directive 2013/59/EURATOM provides the exemption and clearance levels in terms of activity concentrations for naturally occurring radionuclides in solid materials. For industrial sectors involving naturally occurring radioactive material these values can be applied by default to any amount and any type of solid material to be cleared for reuse, recycling, conventional disposal, or incineration.

All the activity concentrations reported in this chapter can be considered in light of the exemption or clearance levels (Table 6.1). However, when considering the use of specific by-products from NORM processing industries in building materials then additional criteria for evaluation (the 1 mSv/y reference level for indoor external exposure to gamma radiation from building materials; the activity concentration index as screening parameter) need to be taken into account. Chapter 4 gives a detailed overview regarding the legislation regarding NORM and the reuse of NORM by-products in building materials. The additional criteria for evaluation of building materials

Table 6.1 Activity concentrations for exemption or clearance of naturally occurring radionuclides in solid materials in secular equilibrium with their progeny

Radionuclide	Activity concentration (kBq/kg)
Natural radionuclides from the ^{238}U series	1
Natural radionuclides from the ^{232}Th series	1
^{40}K	10

From Table A Part 2 of Annex VII of the Council Directive 2013/59/EURATOM (EU, 2014).

(1 mSv/y reference level and the activity concentration index) are discussed in Chapter 7.

The focus of the current chapter is specifically on NORM by-products that find application in construction materials (cement, concrete, and ceramics). Therefore, the current chapter does not discuss all industrial sectors considered by Annex VI but focuses only on by-products with interesting properties for use in construction materials. The construction materials (cement, concrete, and ceramics) that can be produced on the basis of these by-products are discussed in more detail in Chapter 7.

6.2 NORM4Building database

An important goal of the COST Action Tu1301 "NORM4Building" (2014–2017) was to develop a database with best practices for reuse of NORM residues. To automate the accurate collection of data, text mining methodology was applied. Text mining is the process of analyzing collections of textual materials in order to capture and extract key concepts and themes and to uncover hidden relationships and trends from scientific papers without requiring that the precise words or terms that authors have used to express those concepts, is known (Zaki and Wagner, 2013). After retrieving structured information from textual data mining was used to load in the extracted measurement data.

The main milestones of the data mining process were the following:

- automatic keyword-driven selection of papers;
- building and applying the filter based on selected keywords;
- handling different types of publications into the IBM SPSS Modeler software to extract information by means of natural language processing (NLP);
- extracting complete measurement results and the origin (country) from relevant publications in different formats such as Microsoft Word, Microsoft Excel, and Microsoft PowerPoint, as well as Adobe PDF, XML, HTML,
- applying Text Link Analysis (TLA) to define pattern rules and to compare these to relationships found in the text; and
- structuring the collected data.

6.2.1 Collection of data

Input has been gathered from multiple sources:

- A huge amount of publications (More than 39,000 filtered publications have been processed up to the Jan. 6, 2017) have been processed from different e-journals collected from the available materials on Science Direct and Web of Science and others (IAEA and ICRP documents, National Surveys, etc.). The number of investigated publications keeps increasing by the hundreds monthly. The information in several tables provided in this chapter originates from data mining (after manual verification of the results) and the references from which the data were extracted are mentioned.
- A large fraction of the reported data is not coming from the original sources but from papers in which, besides original measurements a review of measurements is also reported. Efforts were made to avoid, also in this case, that data was reported in double, however, in a limited amount of cases this could not be excluded.

6.2.2 Structure of the built database

The database can be divided into several smaller parts, easing decision making by providing multiple options. The main role of the system itself is to provide a large amount of scientific data, from which statistical outputs can be derived. The data can be accessed in the datastore menu, where all the records are simultaneously displayed with all associated data points. Currently the database contains, besides identification and supplementary data (e.g., References, etc.), mainly measurement results obtained from the original scientific article such as the minimum, maximum, and mean values of individual measurements of the ^{226}Ra, ^{232}Th, and ^{40}K radionuclides. In addition the database system also uses the mentioned activity concentrations to generate and store the activity concentration index values calculated on the basis of Radiation Protection 112 (EC, 1999). More information on the activity concentration indexes is given in Chapter 4. The activity concentration indexes are discussed in Chapter 7.

Because of the large number of records stored in the database, some filtering is required to access more sophisticated data. The radiological features option makes the user able to select the region of interest and the type of source material of interest. A simple wizard-like list of options aids the selection. Eventually only the relevant part of the datastore can be shown in Fig. 6.1.

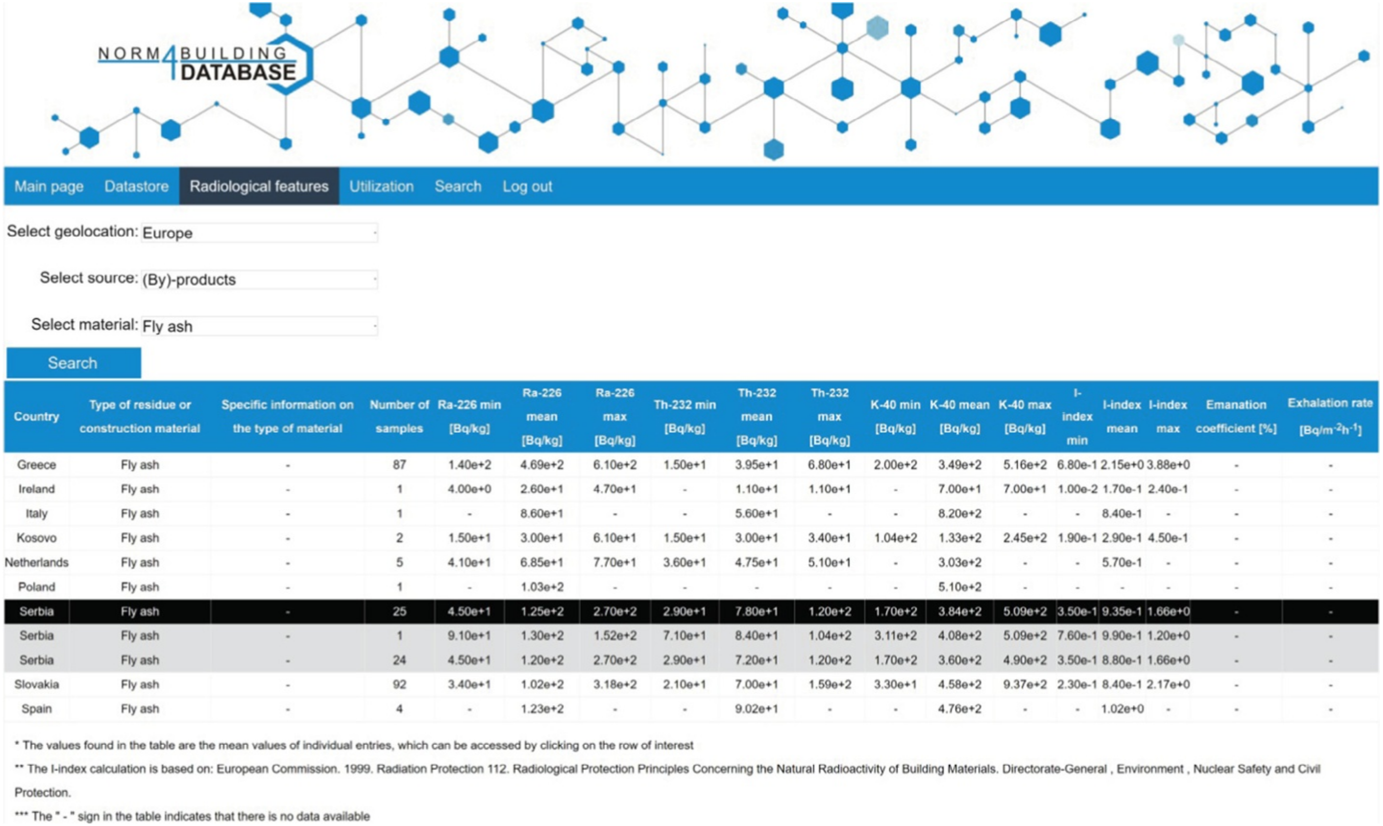
The geological origin of the studied materials is very relevant for the radiological properties of the studied materials. Since country-specific circumstances (legislation, dominant industrial sectors, accessible resources, etc.) determine the use of materials the database aims at providing country-specific information. Therefore the country of origin of the investigated materials is mentioned and visualized for the various entries (Fig. 6.2). The depicted results consist out of averaged results for a given country of origin. As the depicted average is not necessarily representative for all samples for a specific country, clicking on the averaged row displays the list of records with all associated data, from which the averaged values were generated.

Utilization of the database is also facilitated by a simple method to calculate the radiation dose from the building material. The system contains such a calculator, with which the user can make dose calculation (based on Radiation Protection 112 (EC, 1999)) using a simple form submission. The data needed to make the calculation are stored individually in the system, while the activity data are retrieved from the greater datastore. To help decision making, a simple graphical chart is displayed with notable dose limits, thus demonstrating the radiation dose absorbed by an individual (Fig. 6.3).

Another option that can support the processing of the data by the user is the "comparison" feature (Fig. 6.4). This feature enables the user to compare a by-product to be utilized with the raw material where it was produced from (if the data are available in the database). As it is known that some processes enrich radioactive material in the produced residue, this feature allows one to see the enrichment ratio.

6.2.3 Utilizing the built database

Several NORM residues, partially deposited in landfills and representing a continuous cost (land-use monitoring, active prevention measures, risk management, etc.), can be a valuable resource for the construction industry. In order to achieve a safe reuse of



Select geolocation: Europe

Select source: (By)-products

Select material: Fly ash

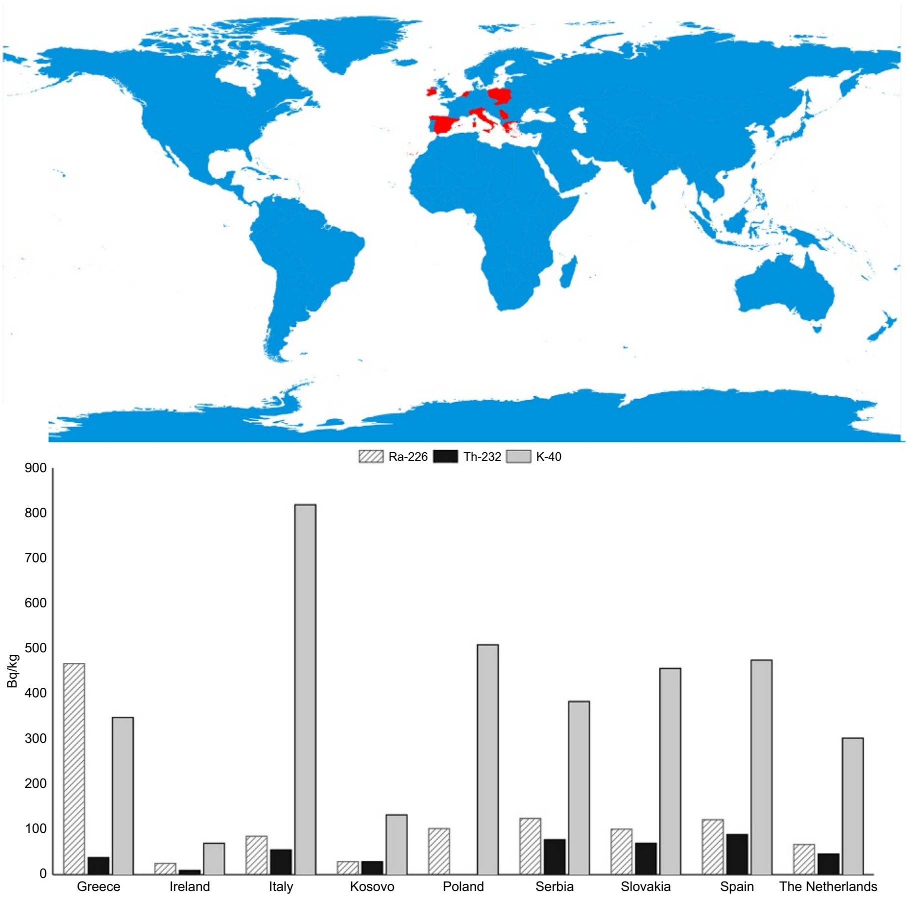
Country	Type of residue or construction material	Specific information on the type of material	Number of samples	Ra-226 min [Bq/kg]	Ra-226 mean [Bq/kg]	Ra-226 max [Bq/kg]	Th-232 min [Bq/kg]	Th-232 mean [Bq/kg]	Th-232 max [Bq/kg]	K-40 min [Bq/kg]	K-40 mean [Bq/kg]	K-40 max [Bq/kg]	I-index min	I-index mean	I-index max	Emanation coefficient [%]	Exhalation rate [Bq/m^{-2}h^{-1}]
Greece	Fly ash	-	87	1.40e+2	4.69e+2	6.10e+2	1.50e+1	3.95e+1	6.80e+1	2.00e+2	3.49e+2	5.16e+2	6.80e-1	2.15e+0	3.88e+0	-	-
Ireland	Fly ash	-	1	4.00e+0	2.60e+1	4.70e+1	-	1.10e+1	1.10e+1	-	7.00e+1	7.00e+1	1.00e-2	1.70e-1	2.40e-1	-	-
Italy	Fly ash	-	1	-	8.60e+1	-	-	5.60e+1	-	-	8.20e+2	-	-	8.40e-1	-	-	-
Kosovo	Fly ash	-	2	1.50e+1	3.00e+1	6.10e+1	1.50e+1	3.00e+1	3.40e+1	1.04e+2	1.33e+2	2.45e+2	1.90e-1	2.90e-1	4.50e-1	-	-
Netherlands	Fly ash	-	5	4.10e+1	6.85e+1	7.70e+1	3.60e+1	4.75e+1	5.10e+1	-	3.03e+2	-	-	5.70e-1	-	-	-
Poland	Fly ash	-	1	-	1.03e+2	-	-	-	-	-	5.10e+2	-	-	-	-	-	-
Serbia	Fly ash	-	25	4.50e+1	1.25e+2	2.70e+2	2.90e+1	7.80e+1	1.20e+2	1.70e+2	3.84e+2	5.09e+2	3.50e-1	9.35e-1	1.66e+0	-	-
Serbia	Fly ash	-	1	9.10e+1	1.30e+2	1.52e+2	7.10e+1	8.40e+1	1.04e+2	3.11e+2	4.08e+2	5.09e+2	7.60e-1	9.90e-1	1.20e+0	-	-
Serbia	Fly ash	-	24	4.50e+1	1.20e+2	2.70e+2	2.90e+1	7.20e+1	1.20e+2	1.70e+2	3.60e+2	4.90e+2	3.50e-1	8.80e-1	1.66e+0	-	-
Slovakia	Fly ash	-	92	3.40e+1	1.02e+2	3.18e+2	2.10e+1	7.00e+1	1.59e+2	3.30e+1	4.58e+2	9.37e+2	2.30e-1	8.40e-1	2.17e+0	-	-
Spain	Fly ash	-	4	-	1.23e+2	-	-	9.02e+1	-	-	4.76e+2	-	-	1.02e+0	-	-	-

* The values found in the table are the mean values of individual entries, which can be accessed by clicking on the row of interest

** The I-index calculation is based on: European Commission. 1999. Radiation Protection 112. Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials. Directorate-General , Environment , Nuclear Safety and Civil Protection.

*** The " - " sign in the table indicates that there is no data available

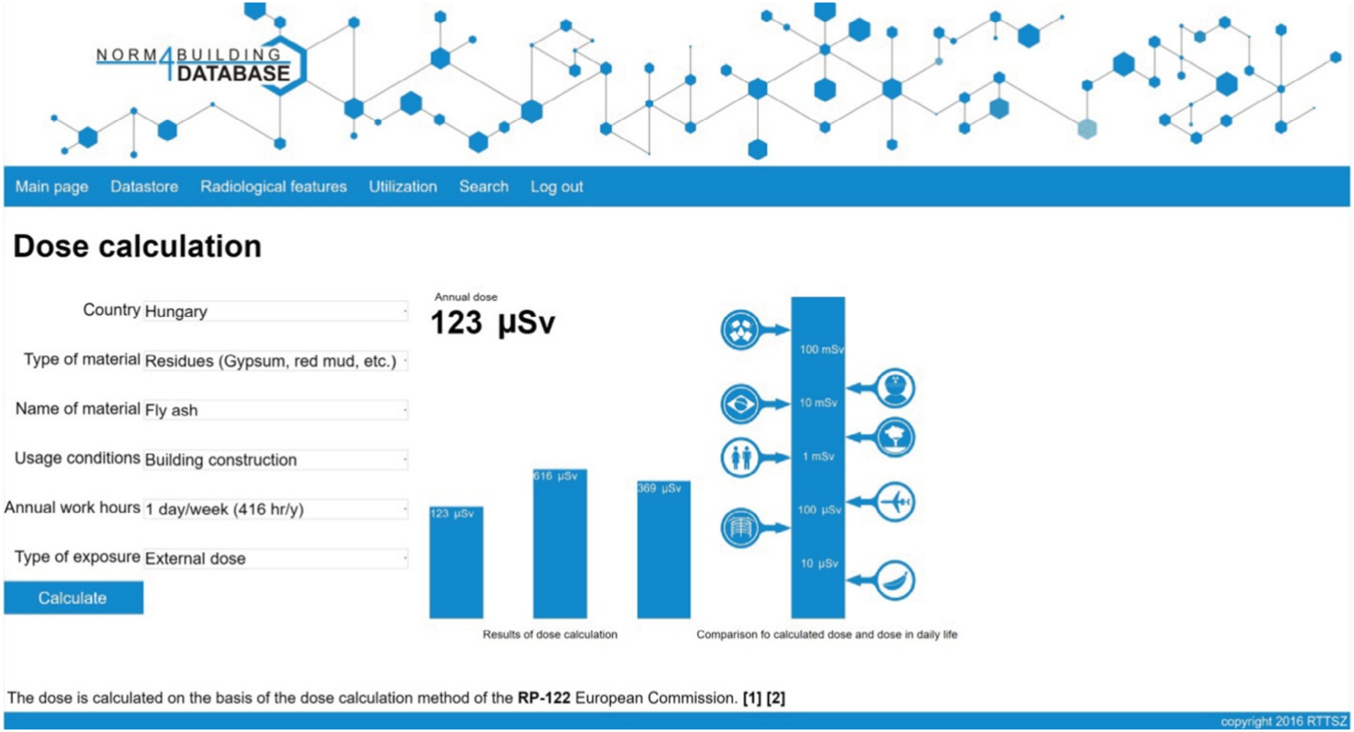
Fig. 6.1 The user interface of the NORM4Building database in work.



The values found in the histogram are the mean values from the table

Fig. 6.2 Built-in visualization methods of the NORM4Building database, geographical distribution, and comparison of average activity levels by country.

by-products in construction, numerous concerns have to be addressed. The physical, chemical, and radiological aspects of the construction materials containing by-products have to be considered and evaluated. The legislators and regulators need reliable information in order to implement adequate rules to assure the safety of the population while as much as possible allowing the recycling of by-products. In order to meet these requirements the construction products must be safe and environmental friendly, meet every requirement as a construction material and the application has to be economically viable. Numerous experiments, surveys, and research programs were undertaken to study the safety and the impact of by-product containing construction materials on the environment. A vast quantity of data is available that needs to be processed so that the information can reach the stakeholders. The NORM4Building



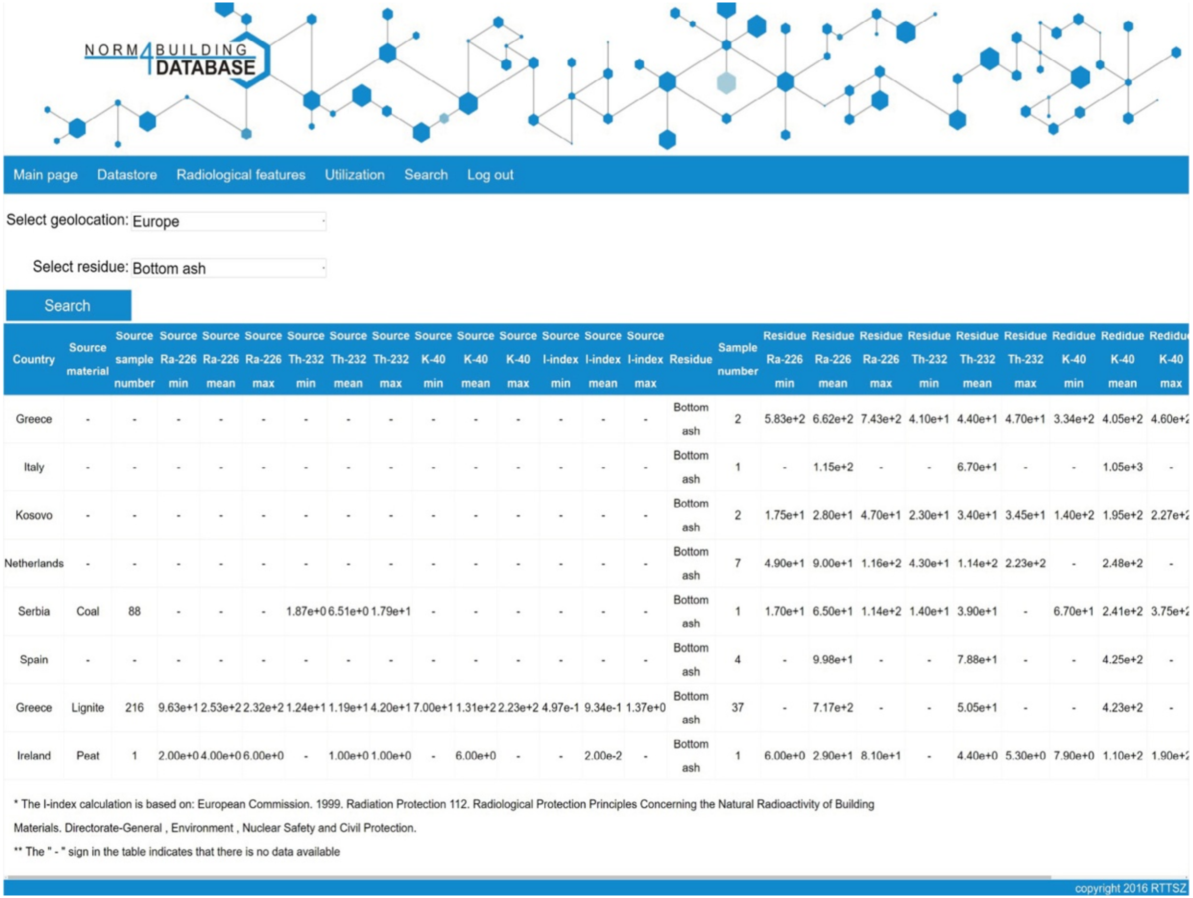
Dose calculation

Country Hungary
Type of material Residues (Gypsum, red mud, etc.)
Name of material Fly ash
Usage conditions Building construction
Annual work hours 1 day/week (416 hr/y)
Type of exposure External dose

Annual dose
123 µSv

The dose is calculated on the basis of the dose calculation method of the **RP-122** European Commission. **[1] [2]**

Fig. 6.3 Dose calculation panel on the database system.



Select geolocation: Europe

Select residue: Bottom ash

Country	Source material	Source sample number	Source Ra-226 min	Source Ra-226 mean	Source Ra-226 max	Source Th-232 min	Source Th-232 mean	Source Th-232 max	Source K-40 min	Source K-40 mean	Source K-40 max	Source I-index min	Source I-index mean	Source I-index max	Residue	Sample number	Residue Ra-226 min	Residue Ra-226 mean	Residue Ra-226 max	Residue Th-232 min	Residue Th-232 mean	Residue Th-232 max	Redidue K-40 min	Redidue K-40 mean	Redidue K-40 max
Greece	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Bottom ash	2	5.83e+2	6.62e+2	7.43e+2	4.10e+1	4.40e+1	4.70e+1	3.34e+2	4.05e+2	4.60e+2
Italy	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Bottom ash	1	-	1.15e+2	-	-	6.70e+1	-	-	1.05e+3	-
Kosovo	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Bottom ash	2	1.75e+1	2.80e+1	4.70e+1	2.30e+1	3.40e+1	3.45e+1	1.40e+2	1.95e+2	2.27e+2
Netherlands	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Bottom ash	7	4.90e+1	9.00e+1	1.16e+2	4.30e+1	1.14e+2	2.23e+2	-	2.48e+2	-
Serbia	Coal	88	-	-	-	1.87e+0	6.51e+0	1.79e+1	-	-	-	-	-	-	Bottom ash	1	1.70e+1	6.50e+1	1.14e+2	1.40e+1	3.90e+1	-	6.70e+1	2.41e+2	3.75e+2
Spain	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Bottom ash	4	-	9.98e+1	-	-	7.88e+1	-	-	4.25e+2	-
Greece	Lignite	216	9.63e+1	2.53e+2	2.32e+2	1.24e+1	1.19e+1	4.20e+1	7.00e+1	1.31e+2	2.23e+2	4.97e-1	9.34e-1	1.37e+0	Bottom ash	37	-	7.17e+2	-	-	5.05e+1	-	-	4.23e+2	-
Ireland	Peat	1	2.00e+0	4.00e+0	6.00e+0	-	1.00e+0	1.00e+0	-	6.00e+0	-	-	2.00e-2	-	Bottom ash	1	6.00e+0	2.90e+1	8.10e+1	-	4.40e+0	5.30e+0	7.90e+0	1.10e+2	1.90e+2

* The I-index calculation is based on: European Commission. 1999. Radiation Protection 112. Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials. Directorate-General , Environment , Nuclear Safety and Civil Protection.

** The " - " sign in the table indicates that there is no data available

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Fig. 6.4 Built-in comparison feature of the NORM4Building database.

database aims to provide an efficient tool to support the transfer of information on radiological aspects to the professional stakeholders. By using the technique of data mining the NORM4Building database can be automatically updated in the future and also data mining allows that in the future new criteria can be used for the (re-) evaluation of data. More advanced tools for comparison and visualization of data are in preparation.

In the next sections the data from the database (extract from the NORM4Building Database) are discussed for different by-products from NORM processing industries. In Chapter 7 the data of the database are then used to discuss the radiological aspect of the construction materials that can be produced on the basis of the considered by-products.

6.3 Coal mining and combustion

The world hard coal production in 2011 was 7678 million tons whereas the world lignite production covered only 1041 million tons. Given that coal provides about 30% of world primary energy demand. It is expected that coal production will continue to increase (Reddy, 2013).

During the energy production process based on coal firing, ranging from the mining to the burning of the coals, in every step issues arise related to the presence of naturally occurring radionuclides. The raw material originates from either underground mines or open pits.

The mined coal generally contains ^{238}U and ^{232}Th as well as their decay products and ^{40}K. The concentration of these radionuclides varies by the geology of the area, but generally the radioactivity of the coal and the surrounding rocks are the same. Moreover, the activity concentration of these materials is generally not high (Table 6.2) in comparison to the average concentration in the Earth crust. Generally the world average concentrations of radium, thorium, and potassium in the Earth's crust are about 40 Bq/kg, 40 Bq/kg, and 400 Bq/kg, respectively (EC, 1999). The concentration of naturally occurring radionuclides is related to the sulfur and heavy metal content of the coal. Table 6.2 shows a summary of activity concentrations found in coals of various origin.

Both underground mining and open pits generate a huge amount of residues, which, if not managed properly, can cause an environmental threat in itself. Stockpiled residues can be affected by the weather conditions like rain and wind, and if not managed properly the naturally occurring radionuclides can be released into the atmosphere or to groundwater bodies. Specifically in the case of underground mining, there is always the possibility that the radon concentration in poorly ventilated spaces can increase, affecting the health of the miners. Other naturally occurring radionuclides, predominantly ^{226}Ra, can be found in the waste rock and water streams in these facilities. Studies show that in some cases the ^{226}Ra activity concentration of these waste streams can reach values up to 55 kBq/kg (IAEA, 2003).

After the mining process the coal is transported to the power plants, where the material is fired to generate electricity and in some cases heat.

In a typical coal-fired power plant, pulverized coal is burnt in a boiler and the heat is extracted as steam. The finely powdered coal is introduced into the combustion

Table 6.2 ^{226}Ra, ^{232}Th, and ^{40}K activity concentrations in different types of coal

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Australia	–	27.5	20	–	6	Cooper (2005), IAEA (2003)
Brazil	130	62	340	–	49	IAEA (2003)
Canada	–	7.5	26	–	1	Tracy and Prantl (1985)
China	17.7	24.5	70.5	0.2	15	Lu et al. (2006), Parami et al. (2010), and Tso and Leung (1996)
Germany	32	21	225	0.3	1	IAEA (2013a)
Hungary	–	–	–	–	1	IAEA (2013a)
India	24	44	111	–	41	Kazahaya et al. (2015), Mahur et al. (2008), Mandal and Sengupta (2005), and Shukla et al. (2005)
Indonesia	7	2.9	47	0.1	2	Parami et al. (2010)
Romania	126	62	–	–	1	IAEA (2013a)
Russian Federation	28	12	120	–	401	Arbuzov et al. (2011), Lissachenko and Obuchova (1982)
Serbia	–	6.5	–	–	88	Zivotic et al. (2008)
South Africa	27.2	20.4	111	0.2	19	Baeza et al. (2012)
The United Kingdom	14	11.3	136	–	21	Salmon et al. (1984)

These values are the mean values of individual entries.

The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.

Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.

The "–" sign in the table indicates that there is no data available.

chamber as a mixture of coal and hot air. Steam is used to drive a turbine, which in turn, drives an electrical generator.

The fired coals contain naturally occurring radionuclides, so it is logic to assume that in the effluent streams of such facilities also show certain levels of naturally occurring radionuclides depending on specific stream and process conditions during firing.

6.3.1 Coal fly ash

6.3.1.1 Technical properties

Coal typically contains 5%–30% inert mineral material that remains as ash after burning (Cooper, 2005).

Coal fly ash is a fine, powdery material that is produced by burning coal to produce electricity, primarily in pulverized coal combustion boilers. It is composed mainly of noncombustible inorganic material but also contains some carbon that is a leftover from partially combusted coal. Although fly ash particles are generally largely spherical in shape, there are usually also irregularly shaped particles present, such as angular particles of quartz. The spherical shape of the fly ash particles results from the formation of tiny molten droplets as the ash travels through the boiler. The droplets form spheres because this shape minimizes the surface area relative to the volume.

Fine ash is collected by the electrostatic precipitators, fabric filters, and flue gas scrubbers. Due to the fineness of the fly ash, removal and collection from combustion gases (flue gas) requires this type of specialized equipment (Cooper, 2005).

By-products from coal firing, coal combustion products (CCPs), are produced in coal-fired power plants all over the world. The production of these CCPs is increasing worldwide by the higher demand for electricity due to growing population and economic development. In Europe, an additional factor that increases the volume and mass of CCP are the legal requirements for flue gas cleaning. The utilization of CCPs is an accepted practice in several countries of the world, based on a long-term experience and both technical as well as environmental benefits (Cooper, 2005).

Next to naturally occurring radionuclides also other components, such as Cd, Cr, Zn, and Pb, are present in the ashes that in some cases may induce an environmental risk (Jiao et al., 2016).

6.3.1.2 Radiological properties

The main NORM-related problem of coal firing is occurring during the combustion process, naturally occurring radionuclides can concentrate in the ashes. Because the radionuclides are, under given conditions, inert a significant amount will remain in the ash, thus enriching it. Typically the enrichment of naturally occurring radionuclides in the fly ash (Table 6.3) is more pronounced than in the bottom ash (Table 6.5). In some cases the ^{238}U and ^{232}Th activity concentrations in fly ash can be tenfold higher than in the used coal.

Most of the data presented in Table 6.3 are obtained in coal-producing countries. However, similar data are also available in coal-importing countries, which monitor

Table 6.3 **NORM radionuclide activity in coal fly ash**

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Australia	96	170	200	1.2	1	Beretka and Mathew (1985)
Canada	–	58	200	–	1	Tracy and Prantl (1985)
China	120	75	195	0.6	27	Lu et al. (2006), Tso and Leung (1996)
Greece	468.7	39.5	349	2.2	87	Dimotakis et al. (1988), Hasani et al. (2014), Manolopoulou and Papastefanou (1992), Papaefthymiou et al. (2007), Papastefanou (2010), Papastefanou and Charalambous (n.d.), and Simopoulos and Angelopoulos (1987)
India	93.6	122.7	352.5	1	91	Gupta et al. (2013), Kant et al. (2010), Kumar et al. (1999), Mahur et al. (2008), and Shukla et al. (2005)
Ireland	26	11	70	0.2	1	Organo et al. (2005)
Italy	86	56	820	0.8	1	Hasani et al. (2014)
Philippines	87	86.5	305	0.8	5	Parami et al. (2010)
Poland	103	–	510	–	1	Zieliński (2015)
Russian Federation	93	–	360	–	400	Lissachenko and Obuchova (1982)

Table 6.3 Continued

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Serbia	125	78	384	0.9	25	Hasani et al. (2014), Janković et al. (2011)
Slovakia	102	70	458	0.8	92	Vladar and Cabanekova (1998)
Spain	123	90.2	476	1	4	Baeza et al. (2012), Dewar et al. (2014), and Hasani et al. (2014)
Syria	52.5	–	–	–	14	Al-Masri and Haddad (2012)
The Netherlands	68.5	47.5	303	0.6	5	Ackers et al. (1985)
Turkey	349	76.4	236	1.6	26	Ayçik and Ercan (1997), Cevik et al. (2008), Hasani et al. (2014), Turhan (2008), and Turhan et al. (2011)
The United States	–	77	370	–	39	Roper et al. (2013)

These values are the mean values of individual entries.
The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.
The "–" sign in the table indicates that there is no data available.

continuously the content of radionuclides in coal fly ash, such as in Israel (NCAB, 2017). The data assembled in Table 6.4 are more updated than those reported in Table 6.3, and also present interesting information about statistical variation of activity concentrations in coal fly ash imported from different countries. The samples of fly ash were tested continuously by the same laboratory for the long period of follow-up (10 years).

Table 6.4 **Statistical variation of activity concentrations in fly ash from the main sources of coal imported to Israel for the years 2005–15 (NCAB, 2017)**

Country	Radionuclide concentration (Bq/kg)		
	^{226}Ra	^{232}Th	^{40}K
Australia	88–109	84–101	117–214
Columbia	78–159	46–132	250–628
Indonesia	55–142	47–128	105–510
South Africa	98–264	56–240	123–368
Russian Federation	85–161	60–131	264–563
Weighted average	155	134	291

In fly ash and bottom ash from coal-burning plants significant disruption of radioactive equilibrium is observed among the radionuclides of ^{238}U and ^{232}Th, due to the different physicochemical properties of the respective elements. Lead-210 is enriched in fly-ash and depleted in bottom ash mainly due to the volatilization of lead in the combustion chamber. It is furthermore observed that ^{210}Pb is especially enriched in the finer ash particles collected at the electrostatic precipitators toward the end of the flue gas pathway (Karangelos et al., 2004). As a result, the ratio of ^{210}Pb/^{226}Ra may be as much as 3 in finer fractions of fly ash and as much as 0.5 in bottom ash. Enrichment of other radionuclides such as ^{226}Ra is also observed, though not so significant. It is worth noting that other elements follow the same behavior and their concentration is enriched in the finer fly ash fractions (Peppas et al., 2010).

The end-of-pipe filtering systems of these plants can efficiently remove solid contaminants containing naturally occurring radionuclides as they behave similar to the nonradiological chemical analogs. However, the volatile compounds like polonium and lead can escape these filtering systems. Mora et al (2011) reported airborne releases of ~3000 Bq/kg ^{210}Po for a coal-fired power plant. Coal-fired power plants were also identified as contributing to the elevated levels of atmospheric radon (Parami et al., 2010).

In the case of a modern power plant, where more than 99% of the fly ash is filtered, most of the radioactive material remains within the bottom ash and fly ash. Upon monitoring the activity concentration of other radionuclides, such as ^{210}Pb and ^{40}K, even more pronounced enrichment can be observed in this case (IAEA, 2013a).

6.3.2 Coal bottom ash

6.3.2.1 Technical properties

The heavier, more refractory mineral matter settles at the bottom of the boiler as bottom ash or slag (Cooper, 2005). Coal bottom ash is primarily comprised of fused coarser ash particles. Frequently, these particles are quite porous and look like volcanic lava.

6.3.2.2 Radiological properties

Table 6.5 presents an overview of the concentrations of naturally occurring radionuclides in coal bottom ash for several countries. More information regarding the comparison of the radiological properties with coal fly ash can also be found in Section 6.3.1.2.

The information about statistical variation of activity concentrations in coal bottom ash imported in Israel is presented in Table 6.6.

What is important—the activity concentrations of both coal fly ash and bottom ash vary in rather wide range (the coal in each country is produced usually in different mines and, as a result, the properties of ash, including the content of radionuclides, are expected to differ as well), although the maximum values never exceeded the activity concentrations accepted for exemption or clearance of naturally occurring radionuclides (see Table 6.1), which were far away from the measured values in both types of coal ash, fly and bottom.

It can be seen also that the weighted average of the population of bottom ash is slightly lower (by about 10% for each radionuclide measured), than that of fly ash (Table 6.4). At the same time, the difference between the two populations is not significant, taking into account a quite wide range of variation.

6.4 Ferrous industry: iron and steel production

The primary material for the iron and steel industry, mainly consists of a combination of iron oxides, coal and limestone (Cooper, 2005).

The blast furnaces (Fig. 6.5) produce iron by the reduction of various iron containing materials with a hot gas. The furnace is fed with iron ore, pellets, and/or sinter, flux and slag producing material such as limestone or dolomite, and coke for fuel. The blast air causes the iron oxides, flux, and coke to react and iron, carbon monoxide and blast-furnace slag is produced. The molten iron and blast-furnace slag is collected at the base of the furnace, while the gases are recirculated for fuel in the sinter process, after separation of particulate material (Cooper, 2005).

To produce 1 ton iron, 1.4 tons of ore, 0.5–0.65 tons of coke, 0.25 tons of flux, and 1.8–2 tons of air are necessary, while 0.2–0.4 tons of slag and 2.5–3.5 tons of blast-furnace gas are created as by-product (US EPA, 1995).

You can see the activity concentrations of several materials typically found in iron and steel production in Table 6.7.

6.4.1 Slag from iron and steel

6.4.1.1 Technical properties

Slag is a by-product generated by the purification, casting, and alloying of metals. Namely, the metal ores (such as iron, copper, lead, and aluminum) in nature are found in an impure state, often oxidized and mixed with other metal silicates. During ore melting, when ore is exposed to high temperatures, such impurities are separated from the molten metal and can be removed. The collected and removed compounds consist

Table 6.5 NORM radionuclide activity in coal bottom ash

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Australia	110	120	80	0.99	3	Cooper (2005)
Canada	–	61	250	–	1	Tracy and Prantl (1985)
China	85	110	270	0.95	13	Lu et al. (2006), Tso and Leung (1996)
Greece	703	48.3	419	2.9	38	Hasani et al. (2014), Papaefthymiou et al. (2007), and Simopoulos and Angelopoulos (1987)
Ireland	29	4.4	110	0.16	1	Organo et al. (2005)
Italy	115	67	1050	1.07	1	Hasani et al. (2014)
Philippines	63.3	64	270	0.64	6	Parami et al. (2010), Sahoo et al. (2011)
Serbia	65	39	241	0.49	1	Hasani et al. (2014)
Spain	99.8	78.8	425	0.87	4	Baeza et al. (2012)
Syria	115	–	–	–	4	Al-Masri and Haddad (2012)
The Netherlands	90	114	248	0.96	7	Ackers et al. (1985)
Turkey	341	39.5	179	1.39	4	Ayçik and Ercan (1997) Hasani et al. (2014)

These values are the mean values of individual entries.

The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.

Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.

The “–” sign in the table indicates that there is no data available.

Table 6.6 **Statistical variation of activity concentrations in bottom ash from the main sources of coal imported to Israel for the years 2005–15 (NCAB, 2017)**

Country	Radionuclide concentration (Bq/kg)		
	^{226}Ra	^{232}Th	^{40}K
Australia	69–88	63–85	97–179
Columbia	45–103	28–81	145–465
Indonesia	37–65	29–66	231–375
South Africa	89–237	80–212	66–138
Russian Federation	59–109	35–93	180–519
Weighted average	143	121	269

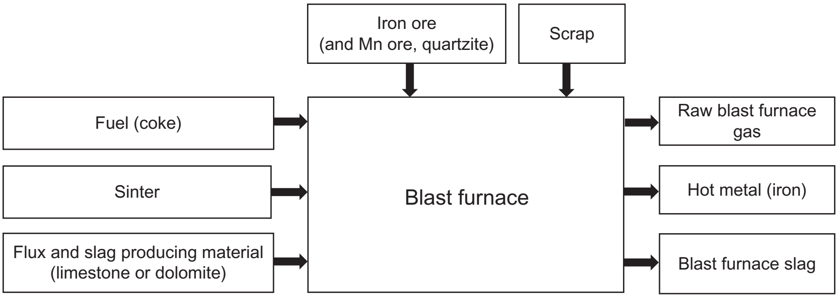

Fig. 6.5 Iron production in a blast furnace.

of slag. With once-purified metal, during further processing (casting and alloying), substances are added to melt and enrich it, with reformed slag as a by-product in which all impurities are concentrated. Therefore, slag mainly consists of ore impurities (mainly silicon and aluminum) combined with calcium and magnesium from various supplements (Cooper, 2005).

The composition and properties of slags depend on the kind of iron and steelmaking process in which they are produced and on the type of ores that are used (Table 6.8). Different types of slags are generated in several stages of iron and steel production:

(1) during the pig iron production;
(2) in the blast furnace (see Fig. 6.5); and
(3) during the later steps of the steel production.

Blast-furnace slag (BFS) is “developed” in a molten condition simultaneously with iron in a blast furnace (Lewis, 1982). Such slag consists primarily of impurities of iron ore (mainly silica and alumina). The composition of slag depends on the composition of iron ore, fuel, flux stones, and mixing ratios required for efficient furnace operation.

Table 6.7 Radionuclide concentrations of input materials and produced dusts in iron and steel production (Cooper, 2005)

Material	Radionuclide concentration (Bq/kg)			
	U-238	^{226}Ra	^{210}Pb	^{210}Po
Iron ore	31	42	16	39
Limestone	<20	14	7	92
Coke	26	26	26	61
Sinter	57	6	5	19
Fugitive dust (indirect dust emissions during the processing steps)	30		100	1670
Ductwork dust	<30	24	18,900	15,600

Different types of BFS can be produced that often find applications in construction (see Chapter 7):

(1) *Ground granulated blast-furnace slag,* obtained by quenching of molten iron slag in water or steam, is the main by-product from iron production used in construction (Lewis, 1982).
(2) *Air-cooled blast-furnace slag* is naturally cooled with moderate sprinkling.
(3) *Pelletized blast-furnace slag* is produced by means of a pelletizer with a spinning drum to cool the slag quickly (in dispersed form) with air and water (Virgalitte et al., 2000).

Steel slag is a by-product of the steel-making process formed from the reaction of flux such as calcium oxide with the inorganic nonmetallic components present in the steel scrap. Two types of steel slag can be distinguished:

(1) *Basic oxygen furnace (BOF)* steel slag.
(2) *Electric arc furnace (EAF)* steel slag.

The BOF process uses 25%–35% old steel (scrap), while the EAF process uses virtually 100% scrap to make new steel. In 2015, in the United States, BOF makes up ~40% and EAF makes up about 60% of the steel production.

After completion of the primary steel-making operations, steel produced by the BOF or EAF processes can be further refined to obtain the desired chemical composition. These refining processes are called secondary steel-making operations. Refining processes are common in the production of high-grade steels. The most important functions of secondary refining processes are final desulfurization; degassing of oxygen, nitrogen, and hydrogen; removal of impurities; and final decarburization (done for ultralow carbon steels). The final carburization takes place in a Ladle Furnace (LF) for refining. An LD (Linz and Donawitz) refining process can be carried out in an LD vessel and in this process LD converter slag is produced. Depending on the quality of the desired steel, molten steel produced in the EAF and BOF process goes through some or all of the above-mentioned refining processes (Brand and Roesler, 2015).

Table 6.8 Chemical composition of distinct slag generated by the primary steel making (Puertas, 1993; Brand and Roesler, 2015)

Oxides, wt%	CaO	SiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	MnO	P_2O_5	S	Free lime
BFS	32	33	19	0.4	–	10	0.2	–	0.8	–
BOF slag	45–60	10–15	1–5	7–20	3–9	3–13	2–6	1–4	–	–
EAF slag	30–50	11–20	10–18	8–22	5–6	8–13	5–10	2–5	–	–
LD converter slag	48	14	1	23		10	0.57	2.34	0.03	7–8

6.4.1.2 Radiological properties

An overview of naturally occurring radionuclides found in metallurgical slags in different countries is shown in Fig. 6.6.

Three potential sources (from the ores, sinter, or scrap) of naturally occurring radionuclides in the slag are discussed.

Iron ores due to their geochemical properties scavenge radionuclides and heavy metals resulting in only trace levels of uranium in the main raw materials for iron-making; iron ore and coke ranging of 20–30 Bq/kg and 5 Bq/kg for limestone (Cooper, 2005).

Another source of radioactivity in the slag is its accumulation of Pb and Po in the sinter plant. Due to the recycling of the waste gases through the sinter plant in order to reduce dust emissions, concentrations of ^{210}Pb and ^{210}Po become further enhanced in the exhaust (Cooper, 2005).

Natural and artificial radioactive materials are present in the metal scrap and could potentially be a source of natural and artificial radionuclides in the steel-making process (Sofilić et al., 2010). However, portal monitors are used intensively by scrap yard and steelworks in particular to avoid the melting of an artificial radioactive source and to avoid that as a result the steel might be contaminated by artificial radionuclides. As a consequence of the intense use of portal monitors also NORM is also often removed from the scrap.

Besides the dependence of the raw material used, the concentration of naturally occurring radionuclides in the BFS is also dependent on the industrial process (e.g., type of furnace) as discussed by Puch et al. (2005).

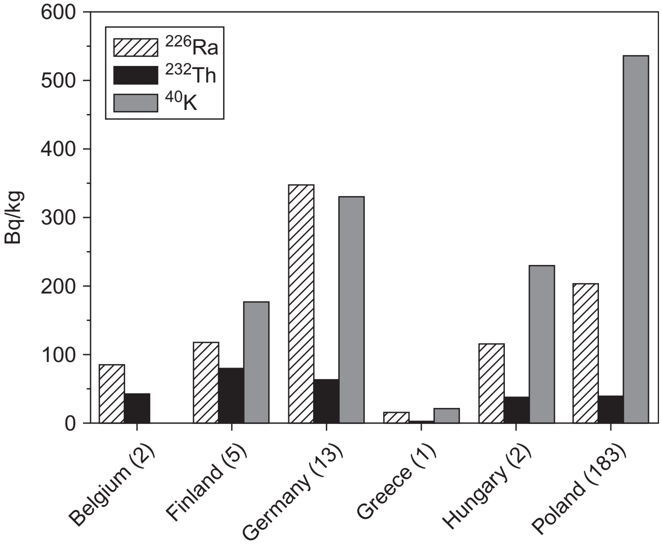

Fig. 6.6 Natural radionuclides concentrations in metallurgical slags (Nuccetelli et al., 2015).

The activity concentration measurements for air-cooled blast-furnace slag and granulated blast-furnace slag underline the same magnitude for the mean values of both materials. The large range between the minimum and maximum values originates from the use of different raw materials in the different plants. The mean activity concentrations for the considered radionuclides are below or around 200 Bq/kg as presented in Table 6.9 (Puch et al., 2005). Table 6.9 demonstrates that blast-furnace slag contains relatively low levels of long-lived radionuclides from the uranium and thorium series. It was also reported that the ^{210}Pb and ^{210}Po levels in dust collected from the off-gases in the blast furnace are generally lower than those of the sinter plant. For more information regarding this aspect we refer to Puch et al. (2005).

In Table 6.10 data are gathered from several studies on BFS in different European countries and larger ranges in activity concentrations are reported here for ^{226}Ra, ^{232}Th, and ^{40}K.

6.5 Nonferrous industry

The nonferrous metals industry is of economic and strategic importance greater than its employment, capital, and turnover statistics indicate. Nonferrous metals and their alloys lie at the heart of modern life and many high-technology developments, particularly in the energy generation, computing, electronic, telecommunications, and transport industries, depend upon them.

This industrial sector aims mainly at the production of copper, aluminum, lead, tin, zinc, cadmium, nickel, cobalt, carbon and graphite, zircon, ferro-alloys, and phosphates. Both primary and secondary raw materials are used as input streams.

The output of the industry is either refined metal or what is known as semi-manufactures, that is, metal and metal alloy cast ingots or wrought shapes, extruded shapes, foils, strips, rods, etc.

6.5.1 Nonferrous slag

6.5.1.1 Technical properties

Nonferrous slags are produced during the recovery and processing of nonferrous metal from primary and secondary raw materials. The nonferrous slags are molten by-products of high-temperature processes that are used to separate the nonferrous metal from other constituents. As a result of the melting of nonferrous metals, iron and silicon are separated to form a silicon-based slag. The resulting slag contains a high proportion of steel. When cooled, the molten slag converts to a rocklike or granular material.

The most common nonferrous slags are those originating from the processing of copper, nickel, phosphorus, lead, and zinc.

Copper production begins with ore milling and copper separation by flotation in order to produce a concentrate with a copper content of about 30%. The produced concentrates are smelted to remove volatile and other impurities and by further purification of the copper melt from the smelter, a primary form of the metal, known as blister copper is derived. Higher purity copper is then produced by electro-refining (Cooper,

Table 6.9 Activity concentration in different types of slag (in Bq/kg) (Puch et al., 2005)

Slag	^{226}Ra			^{232}Th			^{40}K		
	Min	**Max**	**Mean value**	**Min**	**Max**	**Mean value**	**Min**	**Max**	**Mean value**
Air-cooled blast-furnace slag	66	145	99.3	28	129	58.6	60	405	205
Granulated blast-furnace slag	81	360	150.2	30	125	64.8	70	320	141.9

Table 6.10 Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in blast-furnace slag

Country	Radionuclide concentration (Bq/kg)			I-index[a]	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Croatia	251.2	24.8	214.2	1.03	–	Sofilić et al. (2011)
Finland	117	78.1	176	0.84	5	Mustonen (1984)
Hungary	115.2	36.4	228.5	0.64	2	Gallyas and Torok (1984)
Poland	115.33	34.55	192.33	0.62	368	Żak et al. (2008)
Spain	166	47.6	232.3	0.87	1	Chinchon-Paya et al. (2011)
Turkey	177.9	147.8	242.5	1.41	12	Turhan (2008)

The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.

Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.

The "–" sign in the table indicates that there is no data available.

[a] These values are the mean values of individual entries.

2005). The main waste materials within this process are the tailings from the flotation stage and the furnace slags from the smelting stage.

Copper slag is produced during matte smelting and converting steps of pyrometallurgical production of copper from copper ores, when silica is added. It combines with the oxides to form silicates phases. The chemical composition of slag varies with the types of furnace or process of treatment (Cooper, 2005).

The origin of copper and nickel slag can be seen as the result of a multistep process, as shown in Fig. 6.7, and lead and zinc slags are formed in a very similar way. After initial processing (grinding), minerals are exposed to temperatures below their melting point. This process, called roasting, converts sulfur to sulfur dioxide. Then, reduction of the metal ion via the process of smelting is accomplished with the roasted product dissolved in siliceous flux. This melt is then desulfurized with lime flux, iron ore, or basic slag during the process of conversion, and then oxygen is lanced to remove other impurities.

Lead, lead-zinc, and zinc slag are formed during pyrometallurgical treatment of the sulfide ores. This process is similar to the production of copper and nickel slag, including roasting, smelting, and conversion.

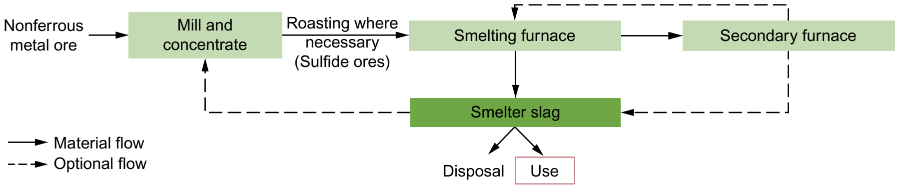

Fig. 6.7 Production process of copper, nickel, lead, lead-zinc, and zinc slag (Lewis, 1982).

Phosphorous slag is a by-product of the elemental phosphorus refining process. Elemental phosphorus in the EAF is added to flux materials to separate it from the phosphate-bearing rock. The flux additives, whose role during this process is the removal of impurities, are mainly silica and carbon. In addition to silica and carbon, iron can be added in the furnace, which combines with phosphorus to form ferrophosphorus. By the removal of ferrophosphorus (or only phosphorus, if iron is not added), slag is also created.

The amount of nonferrous slag produced in these processes is not as large as ferrous slag. Therefore, researchers have tended to focus their investigations on the larger-volume waste materials. Depending on the production process, the quantity of slag per produced quantity of metal can vary. It was estimated by Gorai et al. that for every ton of copper 2.2 ton of slag is produced (Gorai and Jana, 2003). Proctor et al. estimated that 220–370 kg blast-furnace slag is produced per ton of produced iron (Proctor et al., 2000).

6.5.1.2 Radiological properties

A lot of information regarding the radiological properties of nonferrous slags is included in the IAEA Safety Report Series 49, 2006. Information regarding the following types of nonferrous slag can be found here:

- Copper and Nickel Slags
- Phosphorus Slag
- Lead, Lead-Zinc, and Zinc Slags

In Table 6.11 an overview is given of the activity concentrations (^{226}Ra, ^{232}Th, and ^{40}K) reported for different types of nonferrous slags.

Specifically, for the copper production partitioning of ^{210}Pb and ^{210}Po from uranium occurs into the copper concentrate during the smelting process. These radionuclides are vaporized at the smelting stage and may accumulate in dusts collected from off gases. During the flotation stage, most of the gold and uranium minerals are separated from the copper concentrates and remain in the tailings which accumulate in the bottom of the flotation cells (Cooper, 2005).

Uranium and thorium may be present in significant quantities in the copper minerals. Where the uranium content of the original ore is sufficiently high to the level of commercial exploitation, additional treatment and processing of tailings should take

Table 6.11 Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in nonferrous slag

Slag type	Country	Radionuclide concentration (Bq/kg)			I-index[a]	Number of samples	References
		^{226}Ra	^{232}Th	^{40}K			
Tin slag	Germany	1100	300	330	5.28	–	Lehmann (1996)
Nickel slag	Poland	234.57	44.9	604.7	1.21	3	Żak et al. (2008)
Nickel slag	Germany	52	78	76	0.59	–	Lehmann (1996)
Lead slag	Germany	270	36	200	1.15	–	Lehmann (1996)
Copper slag	Poland	316.78	54.16	886.46	1.62	80	Żak et al. (2008)
Copper slag	Germany	770	52	650	3.04	–	Lehmann (1996)

The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.

Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.

The "–" sign in the table indicates that there is no data available.

[a] These values are the mean values of individual entries.

place using hydrometallurgy (mainly acid leaching) to recover uranium concentrates. Otherwise the uranium minerals will remain within the tailings (Cooper, 2005).

6.5.2 Bauxite residue also known as red mud

6.5.2.1 Technical properties

Red mud is a waste produced during the Bayer method in bauxite refining, where digestion of pulverized bauxite with sodium hydroxide at elevated temperatures and pressures takes place. It is a highly alkaline (pH = 10–12.5) slurry with 15–30 wt% of solids. After drying, the material produced is also found in literature as bauxite residue (Gu et al., 2012).

Red mud is composed mainly of fine particles of silica, aluminum, iron, calcium, and titanium oxides in different proportions dependent upon the bauxite ore, aluminum extraction conditions, and quality control. Table 6.12 shows the constituent differences which are attributed to the type of bauxite ores and process conditions (Gu et al., 2012). Iron oxides (typically hematite) provide the red color to the mud.

Table 6.13 shows approximate estimations of bauxite residue quantities produced per year and the size of bauxite residue disposal area (BRDA) for Western European alumina refineries. These estimations are based on the assumption that ~1.5 tons of residues are produced per ton of alumina (Bonomi et al., 2016). It should be noted, however, that the ratio of bauxite residue per ton of alumina can vary significantly. It can be as little as 0.3 ton of residue per 1 ton of alumina or up to 2.5 tons of residue per 1 ton of alumina in case of low-grade ores. Western European refineries tend to use higher-grade bauxites so the resulting residue quantity is probably relatively smaller (European Aluminium Association, 2014).

There is an annual 90–120 million tons bauxite residue production in the alumina industry. The existing size of world by-products so far is over 2.7 billion tons (Nuccetelli et al., 2015; Ruyters et al., 2011). Bauxite residues are being produced in a number of EU countries (e.g., France, Germany, Greece, Ireland, Romania, Spain) in addition to a great number of legacy sites in countries that no longer are producing aluminum (Nuccetelli et al., 2015). Traditionally these by-products are stockpiled by wet or dry methods. The sea discharge method has been abandoned due to its environmental effects. The factors causing problems during deposition of red mud using wet or dry methods are mainly related to the physical mass disposed and deposition field sizes required. Other problems regarding the use relate to the alkalinity, presence of trace toxic compounds, the presence of trace heavy metals, and radioactivity content. Depending on aspects as mentioned earlier, these legacy sites can pose a significant problem to the environment and society as a whole (Hegedus et al., 2016).

6.5.2.2 Radiological properties

The activity concentration (^{226}Ra, ^{232}Th, and ^{40}K) of the bauxite ores, depending of its country of origin, is given in Table 6.14.

Table 6.12 Main chemical composition (wt%) of red mud from different countries (Gu et al., 2012)

Components	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_3	Na_3O	K_3O	MgO	LOI	Other	Total
Spanish red mud	20.2	7.5	47.8	6.2	9.9	8.4	0.1	0.3	5.1	–	100.5
Greek red mud	19.9	6.8	40.8	12.6	5.8	2.7	0.1	0.2	10.5	0.5	100.1
Greek red mud	17	7.8	44.3	11.6	5.1	3.2	0	0.5	9.8	–	99.5
Italian red mud	20	11.6	35.2	6.7	9.2	7.5	0	0.4	7.3	2.1	100
Birac red mud	14.1	11.5	48.5	3.9	5.4	7.5	0	0	7.2	0.6	99

Table 6.13 **Approximate estimations of bauxite residue quantities produced per year and bauxite residue disposal area**

Refinery	Disposal period	Disposal method	Residue production rate (kton/year)	BRDA (ha)
Stade	For 1973	Ponds disposal	1500	150
Gardanne	1893–2012	Sea discharge	690	
	2012–14	Sea discharge/ dry stacking	n.d.	29.4
San Ciprian	1981–2014	Dry stacking	2175	84
Aughinish	For 1983	Dry stacking	3000	121
Aluminium of Greece	1966–2012	Sea discharge/ dry stacking	1200	19
	2012–14	Dry stacking	749	
Eurallumina	1977–2009	Ponds disposal	1200	120

For bauxite residue, red mud, the activity concentration (^{226}Ra, ^{232}Th and ^{40}K), depending of its country of origin, is given in Table 6.15.

There have been several accidents involving red mud depositories, such as the Ajka accident in October 2010, Hungary, and the Luoyang incident in August 2016, China. In the case of the Ajka incident it has been estimated that 800 ha of agricultural land has been contaminated by a 5–10 cm red mud cover layer (Ruyters et al., 2011). The ^{238}U and ^{232}Th activities present in the red mud were 5–10-fold above the soil background values and through the EU project INTAILRISK the radiation risks from red mud has been estimated. The main dose contributor as for the surrounding population has been identified as the indoor radon. The gas phase of Hungarian red mud deposits may contain radon up to 300 kBq/m^3, roughly 10 times the background values. A mixture of red mud with normal soil yields increased radon concentration in the soil, causing additional indoor radon exposure (Ruyters et al., 2011).

6.5.3 Aluminum dross

6.5.3.1 Technical properties

The recycling of aluminum generates slag and *dross*, both normally classed as hazardous wastes. Dross, as solid impurities floating on the molten metal, can be distinguished from slag.

Aluminum dross is formed on the surface of molten aluminum or its alloys, by oxidation. Typical dross generation from a primary operation can be from 0.8 wt% to 1.3 wt% of aluminum output, while from secondary smelters it can reach up to 10% (Galindo et al., 2015). There are two forms of dross: (a) white dross and (b) black dross. White dross is formed during refining of primary Al, while black dross is formed when secondary/recycled aluminum is refined, where a relatively large amount of chloride salt flux is used. Subsequently, the dross is processed in rotary kilns to recover the Al, and the

Table 6.14 **Activity concentrations for ^{226}Ra, ^{232}Th, and ^{40}K in Bauxite (Bq/kg)**

Country	**Radionuclide concentration (Bq/kg)**			**I-index**	**Number of samples**	**References**
	^{226}Ra	**^{232}Th**	**^{40}K**			
Australia	57	421	28	0.62	4	Hassan et al. (2011), Iwaoka et al. (2009), and O'connor et al. (2013)
Brazil	769	98	13	0.68	2	Georgescu et al. (2005), Righi et al. (2009)
China	370	420	91	3.36	5	Righi et al. (2009)
Guinea	159	175	–	–	5	Abbady and El-Arabi (2006), Georgescu et al. (2005)
Guyana	68	230	24	1.38	3	Righi et al. (2009)
Hungary	419	256	47	2.69	46	Somlai et al. (2008)
India	68	510	–	–	5	Abbady and El-Arabi (2006)
Indonesia	56	170	27	1.05	1	Iwaoka et al. (2009)
Turkey	17.1	19.8	43.2	0.17	2	Turhan (2008)

These values are the mean values of individual entries.
The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.
The "–" sign in the table indicates that there is no data available.

resultant salt cake is sent to landfills (Chen, 2012). As a whole, the aluminum industry produces ~3.2 million tons of dross annually from domestic aluminum smelting (Taylor et al., 2009). Chemical and mineralogical compositions of raw aluminum dross wastes produced in Turkey are given in Tables 6.16 and 6.17 (Gunay et al., 2008).

6.5.3.2 Radiological properties

Regarding aluminum dross only a limited amount of information on the radiological properties is available. Abbady and El-arabi (2006) discussed the NORM aspects of Egyptian aluminum dross tailings. For the tailings they found average activity concentrations (9 investigated samples) of 8.5 ± 0.8 Bq/kg and 10.7 ± 1.2 Bq/kg for, respectively, ^{226}Ra and ^{232}Th (Abbady and El-Arabi, 2006). These activity concentrations

Table 6.15 NORM radionuclide activity in Red mud

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Australia	318	1320	190	7.3	5	Nuccetelli et al. (2015), O'connor et al. (2013)
Belgium	550	640	–	–	1	Xhixha et al. (2013)
Brazil	139	350	45	2.2	1	Nuccetelli et al. (2015)
China	380	507	361	3.9	5	Nuccetelli et al. (2015)
Germany	156	216	–	–	2	Nuccetelli et al. (2015), Xhixha et al. (2013)
Greece	306	408	33	3.1	3	Nuccetelli et al. (2015), Xhixha et al. (2013)
Hungary	289	285	121	2.3	64	Hasani et al. (2014), Nuccetelli et al. (2015), Somlai et al. (2008), and Xhixha et al. (2013)
Italy	97	118	15	0.9	1	Nuccetelli et al. (2015)
Jamaica	708	339	300	4.2	2	Nuccetelli et al. (2015)
Romania	566	434	–	–	4	Georgescu et al. (2005), Xhixha et al. (2013)
Turkey	210	539	112	3.4	2	Nuccetelli et al. (2015), Xhixha et al. (2013)
Ukraine	165	328	53	2.2	1	(U.D.C. 691.5)

These values are the mean values of individual entries.
The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.
The "–" sign in the table indicates that there is no data available.

Table 6.16 **Chemical analysis of dross from different foundries in Turkey (Gunay et al., 2008)**

Component (wt%)	Dross A	Dross B	Dross C
F	1.74	0.47	1.95
NaCl	0.12	0.27	1.38
MgO	0.98	9.09	0.61
Al_2O_3	89.2	85.4	87.9
SiO_2	1.90	1.81	0.52
SO_3	0.04	0.80	0.08
KCl	4.52	0.31	6.31
CaO	0.62	0.87	0.50
TiO_2	0.27	0.33	0.22
MnO_2	0.21	0.05	0.17
Fe_2O_3	0.26	0.39	0.20
BaO	0.01	0.14	–

Table 6.17 **Mineralogical analysis of dross from different foundries in Turkey (Gunay et al., 2007)**

Sample code	Mineral
A	α-Al_2O_3, AlN, β-Al_2O_3
B	Al (metal), MgO, Ca_2SiO_4
C	α-Al_2O_3, β-Al_2O_3, KCl, NaCl, K_2SiF_6

are very low in comparison to the world average concentrations of radium (40 Bq/kg) and thorium (40 Bq/kg) in the Earth's crust (EC, 1999) or in the European soil (Table 6.20).

6.5.4 Zircon and zirconia

6.5.4.1 Technical properties

Zirconium (chemical element with symbol Zr) is relatively abundant within the Earth's crust (it is the 18th most abundant element, three times more abundant than copper) and is mined from mineral sands. In mineral sands it is primarily present as the mineral *zircon* (=$ZrSiO_4$) and more rarely as the mineral baddeleyite. The mineral baddeleyite is the naturally occurring form of the compound *zirconia* (=ZrO_2). Most commercial zirconium minerals are produced in Australia, South Africa, and the United States. Zircon is by far the leading zirconium ore; baddeleyite is much more rare and is currently mined only in Russian Federation, while caldasite, a mixture of baddeleyite and zircon can be found in Brazil (IAEA, 2007a).

The typical density of the mineral zircon is between 4200 and 4800 kg/m^3. The mineral has a low chemical reactivity, a melting point well over 2000°C, a high-refractive index (1.80–1.98), and a hardness higher than quartz (Mohs hardness of 7) (IAEA, 2007a).

Considering mineral sands that are commercially used then the typical premium grade commercial "zircon sand" consists of 66% ZrO_2 (including ~2% HfO_2), 32% SiO_2, 0.1% TiO_2, 0.5% Al_2O_3, and 0.05% Fe_2O_3. Most commercial zircon sands have a median diameter of 110–130 μm with a typical range in particle diameter of 100–200 μm. For many applications, this has to be reduced by milling to create zircon flour or micronized zircon (IAEA, 2007a).

Several processes (also shown in Fig. 6.8) are used to convert zircon (=$ZrSiO_4$) into zirconia (=ZrO_2) and other compounds:

(a) In a thermal process zircon is melted with coke at 2800°C in an EAF. The carbon reduces the zircon to zirconia (commercial name: "fused zirconia") and silicon monoxide. Silicon monoxide, being unstable, is rapidly oxidized to silica, which comes off the process as a silica fume. Stabilizing elements are added to the melt to produce the desired composition. The molten product is tapped from the furnace, cast into blocks and crushed to the desired particle size range (IAEA, 2007b).

(b) Heating zircon at 1800°C or more results in the breaking of zircon into its components ZrO_2 and SiO_2. In a next step the zirconia component is purified chemically and a zirconia of higher purity is produced (IAEA, 2007a).

(c) Reaction of zircon with sodium hydroxide at 700°C (caustic fusion) and dissolution in hydrochloric acid to form octahydrate ($ZrOCl_2 \cdot 8H_2O$), for high-purity zirconia and zirconium chemical production (IAEA, 2007a).

(d) Chlorination of zircon at 1200°C in the presence of carbon in order to produce zirconium tetrachloride. Zirconium tetrachloride is then used for zirconium metal manufacture by reduction with magnesium or for the production of other chemicals (IAEA, 2007a).

For more detailed information the IAEA Safety Series No. 51, 2007 can be consulted.

6.5.4.2 Radiological properties

All zircon sands contain low levels of natural occurring radionuclides; however, these are significantly higher than average concentrations in normal rocks and soil. Activity concentrations in the natural zircon sands and the mineral zircon are shown in Table 6.18.

The activity concentrations of ^{238}U and ^{232}Th series radionuclides in commercially available zircon are between 2–4 and 0.4–1 kBq/kg, respectively. Baddeleyite shows a greater variation, the activity concentrations of ^{238}U and ^{232}Th series radionuclides vary between 3–13 and 0.1–26 kBq/kg, respectively. Data for ^{210}Po suggest a possible disequilibrium at the lower end of the uranium decay chain in some cases, especially for baddeleyite samples (IAEA, 2007a).

The data collected in the NORM4Building database (Table 6.18) correspond to the data discussed in IAEA Safety Series No. 51, 2007. The activity concentrations exceeding 1 kBq/kg cause all activities involving zircon or baddeleyite in Member States of the European Union to be considered for regulation under the EU-BSS.

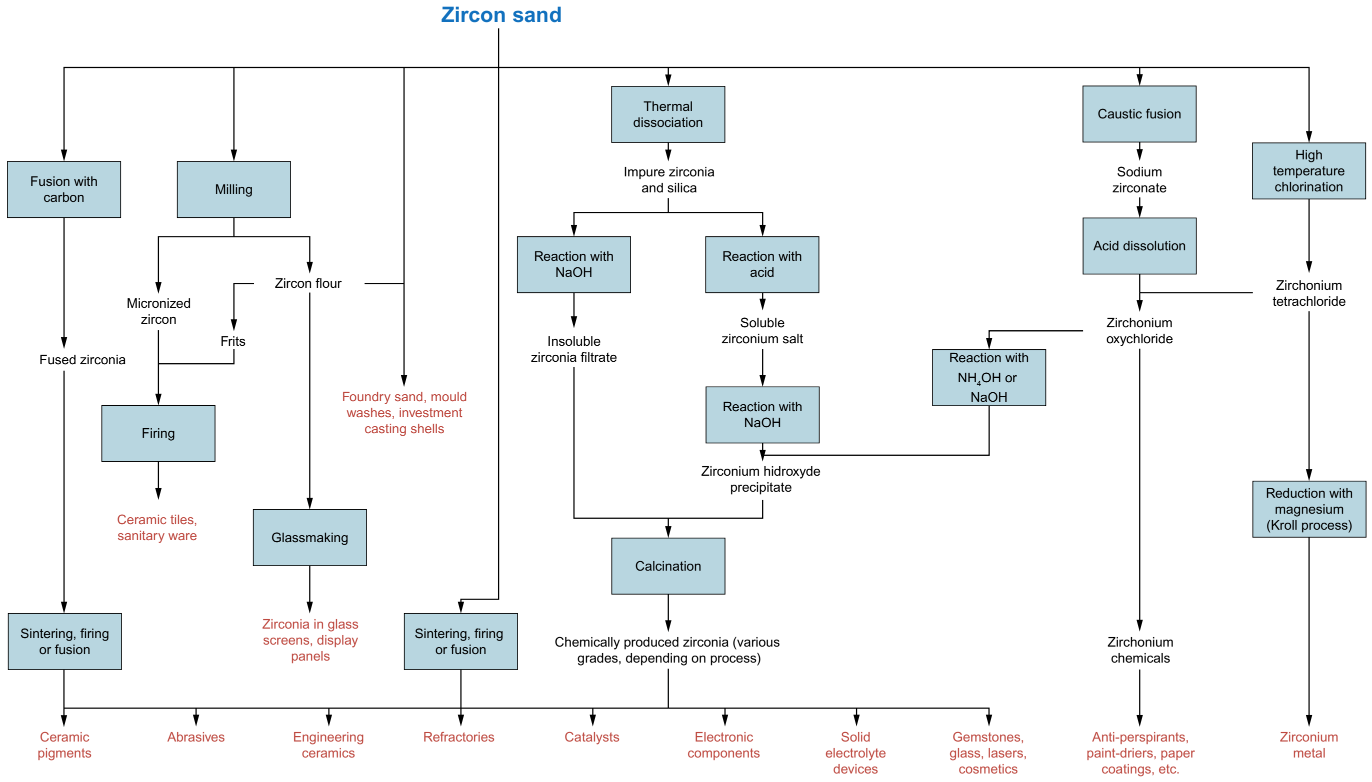

Fig. 6.8 A simplified schematic of zircon and zirconia industry (IAEA, 2007a).

Table 6.18 NORM radionuclide activity in Zircon (A) and Zircon sand (B)

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Zircon (A)						
Australia	2600	682	39.6	–	6	Bruzzi et al. (2000), Iwaoka et al. (2009), and Johnston (1991)
Egypt	4900	1200	190	22.4	10	El Afifi et al. (2006)
Germany	4100	620	–	–	1	Jankovic and Todorovic (2011)
India	3600	1210	140	15.2	6	Mohanty et al. (2004), Sartandel et al. (2012)
Italy	3400	620	–	–	11	Jankovic and Todorovic (2011)
Slovakia	4100	550	–	–	1	Jankovic and Todorovic (2011)
Slovenia	1800	360	–	–	3	Jankovic and Todorovic (2011)
Spain	3000	600	–	–	1	Jankovic and Todorovic (2011)
Sweden	2900	570	–	–	1	Jankovic and Todorovic (2011)
The United Kingdom	3100	480	–	–	3	Jankovic and Todorovic (2011)
Zircon sand (B)						
Australia	3030	682	35.6	14.1	5	Iwaoka et al. (2013), Righi et al. (2005)
Belgium	–	570	77	–	2	Fathivand et al. (2007)
Germany	–	590	65	–	3	Fathivand et al. (2007)
Italy	2400	570	47.5	11	9	Fathivand et al. (2007), Righi et al. (2009)
South Africa	3700	656	51.2	17.9	8	Ballesteros et al. (2008), Iwaoka et al. (2013), Rajamma et al. (2009), and Righi et al. (2005)
Ukraine	–	403	36	–	5	Fathivand et al. (2007), Righi et al. (2005)

These values are the mean values of individual entries.
The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.
The "–" sign in the table indicates that there is no data available.

The milling of zircon is used by more than 70% of zircon users. The main exposure pathways from this process are external exposures from storage of raw materials and products, inhalation exposures from plant leaks, bagging operations, and process cleanups (IAEA, 2007b).

In a thermal process (such as process "(a)" as discussed before), when zircon is melted at 2800°C in an EAF, typical radionuclide activity concentrations found are 3–4.5 Bq/g for ^{238}U in the raw zircon, 4.5–6.8 Bq/g for ^{238}U in the zirconia, and about 6 Bq/g for ^{226}Ra in the silica fume. The high temperatures used in this process destroy the crystal structure and allow the more volatile elements to be partially removed into the silica fume. Consequently, the fume may be enriched in ^{226}Ra, ^{210}Po, and ^{210}Pb. The zirconia phase retains the high-boiling point elements such as uranium and thorium. In this way the radiological equilibrium between radionuclides in the ^{238}U and ^{232}Th decay chain is disturbed for the different (by-)products. Exposure pathways in this process are (a) external radiation from the raw material, from product storage, and from maintenance of the silica fume collector systems and (b) inhalation exposure from silica fume and zirconia dust during the milling and bagging operations. Radon exposure is usually insignificant with well-ventilated storage. Typical annual effective doses received by workers in a thermal zirconia plant are 70–260 μSv from external exposure and 600–3000 μSv from dust inhalation, giving a total annual effective dose of 700–3100 μSv (IAEA, 2007b).

The annual effective dose received by a worker in a chemical zirconia processing plant (using processes such as "(c)" and "(d)" as described above) is usually less than 1 mSv. However, because of the possibility of reaching the 1 mSv level and also because of the potential public exposure from radionuclide containing wastes, it is likely that these plants would require registration (IAEA, 2007b).

6.6 Phosphate industry

The phosphate industry has a crucial role in providing the world with food through supporting intensive agriculture, namely the phosphate fertilizer production.

Safety report No. 78 "Radiation protection and Management of NORM residues in the Phosphate Industry," published by the IAEA in 2013, gives a very extensive overview regarding the radiological properties and the management of NORM residues from the phosphate industry.

Three main production steps are used to convert phosphate ore into commercial products (IAEA, 2013b):

(1) Mining and initial treatment (reduction) of the phosphate ore to produce phosphate rock.
(2) Predominately, two types of processes are used for further processing of the phosphate rock:
  (a) Wet acid digestion processes are used to convert 85% of phosphate rock into intermediate or final products.
  (b) An EAF is used for direct thermal conversion of the phosphate rock into elemental phosphorus. This "thermal process" is only applied on a minor fraction of the phosphate rock.

(3) After further chemical processing the produced phosphoric acid, that is produced in case of a wet acid digestion process, is converted into fertilizer products, animal feed supplements, and a variety of other products.

The phosphate ores (mainly various types of apatite), especially the sedimentary types, contain a wide range of contaminants, such as uranium, radium, polonium, thorium, and lead radioisotopes. Typical radionuclide activity concentrations in phosphate ores are in the range of less than 1 up to several Bq/g. The UNSCEAR indicates an average of 1500 Bq/kg for ^{238}U in sedimentary phosphate ore deposits (UNSCEAR, 1988, 1993).

6.6.1 Phosphogypsum

6.6.1.1 Technical properties

Considering the processing of the phosphate rock (IAEA, 2013b):

(1) For 71% of the phosphate rock processing, a wet process, involving the production of phosphoric acid, is used for the acid digestion and in most cases large amounts of phosphogypsum are produced as a by-product.
(2) 24% of the phosphate rock is processed directly into fertilizer (so not by means of indirect processing via phosphoric acid).
(3) 5% of the phosphate rock is converted directly into other types of products.

During the wet production process, the contaminants are distributed between the different (by-)products depending on the type of acid (sulfuric acid, hydrochloric acid, or nitric acid) used for digestion. In the case of sulfuric acid digestion, which is frequently used for fertilizer production, one processing road leads via the production of phosphoric acid and phosphogypsum and the following reaction can occur (IAEA, 2013b):

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$

For a complete overview of the different production streams that result from phosphate rock processing, we refer to IAEA (2013b).

6.6.1.2 Radiological properties

During the wet production process involving the production of phosphoric acid, the amount of radionuclide going into each fraction can vary depending on the used technology. In general most of the uranium eventually remains in the fertilizer, radium is more evenly distributed between the (by-)products and can partly remain (be precipitated) inside the plant, while most of polonium is removed with the phosphogypsum fraction (IAEA, 2013b).

The specific concentrations of naturally occurring radionuclides in the phosphogypsum depend on the origin and the chemical treatment of the phosphate ore (IAEA, 2013b).

An overview of the average activity concentrations of naturally occurring radionuclides in phosphogypsum from several countries, extracted from the NORM4Building database, is given in Table 6.19.

In the NORM4Building database, for phosphogypsum in particular, there is less data available for fewer countries in comparison with natural gypsum. Concerning natural gypsum, the database contains measurements relevant to 502 samples from 16 EU Member States. The mean value (and ranges) for natural gypsum is 15 (1–70) Bq/kg for ^{226}Ra, 9 (1–100) Bq/kg for ^{232}Th, and 91 (5–279) Bq/kg for

Table 6.19 **NORM radionuclide activity in Phosphogypsum**

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Australia	246	50	340	1.2	28	Beretka and Mathew (1985), Cooper (2005), and Msila et al. (2016)
Bangladesh	234	21	108	0.9	1	Gezer et al. (2012)
Belgium	431	11	–	–	30	Trevisi et al. (2012)
Brazil	410	182	33.5	1.6	268	da Conceicao and Bonotto (2006), Mazzilli and Saueia (1999), Santos et al. (2006), Saueia et al. (2005), Saueia and Mazzilli (2006), Silva et al. (2001), and Xhixha et al. (2013)
Bulgaria	209	17	3	0.8	2	Trevisi et al. (2012)
Czech Republic	115	31	95	0.6	22	Trevisi et al. (2012)
Egypt	322	18.4	116	0.8	27	El Afifi et al. (2006), Gezer et al. (2012), Hussein (1994), Matiullah and Hussein (1998),

Continued

Table 6.19 Continued

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
						Medhat (2009), Moharram et al. (2012), Msila et al. (2016), and Xhixha et al. (2013)
Finland	306	23	17	1.2	17	Trevisi et al. (2012)
Germany	305	20	110	1.2	2	Trevisi et al. (2012)
Greece	440	12.4	235	1.5	31	Trevisi et al. (2012)
India	233	30.3	323	0.4	24	Haridasan et al. (2009), Msila et al. (2016), and Shukla et al. (2005)
Iran	250	–	–	–	1	Fathabadi et al. (2012)
Israel	747	14	63	2.6	1	Gezer et al. (2012)
Jordan	378	4	40	1.3	16	Al-Jundi et al. (2008), Gezer et al. (2012)
Korea	618	9	24	2.1	1	Gezer et al. (2012)
Morocco	1420	–	–	–	1	Xhixha et al. (2013)
Nigeria	340	4	200	1.2	3	Okeji et al. (2012)
Norway	104	62	1060	1	6	Msila et al. (2016)
Poland	390	17	90.5	1	29	Trevisi et al. (2012)
Portugal	–	–	–	–	1	Xhixha et al. (2013)
Romania	496	42.1	95.1	1.9	75	Trevisi et al. (2012)
Serbia	439	8.7	8.7	1.5	1	Msila et al. (2016)
Slovenia	500	10	41	1.7	1	Trevisi et al. (2012)

Table 6.19 Continued

Country	Radionuclide concentration (Bq/kg)			I-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
Spain	491	31.1	68.4	1.5	54	Bolívar et al. (2009), Gezer et al. (2012), and Mantero et al. (2013)
Sri Lanka	35	72	585	0.7	25	Msila et al. (2016)
Syria	320	2.1	–	–	12	Al Attar et al. (2011)
Tanzania	–	140	–	–	1	Makweba and Holm (1993)
The Netherlands	131	32.5	305	0.7	34	Trevisi et al. (2012)
Turkey	375	13.1	10.3	1.3	22	Cooper (2005), Gezer et al., 2012, and Turhan (2008)
The United Kingdom	1020	33	130	3.6	91	Trevisi et al. (2012)
The United States	750	1	14	–	95	Hull and Burnett (1996), Roper et al. (2013)

These values are the mean values of individual entries.
The I-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the I-index, as proposed by Council Directive 2013/59/EURATOM, is only used for building materials. An I-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material, however, this assumption can be useful as starting point for dilution calculations.
The "–" sign in the table indicates that there is no data available.

^{40}K. The activity concentration of natural gypsum is generally lower than the average level in European soil (Table 6.20); therefore, this material is not the most relevant from a radiation protection point of view.

Phosphogypsum, however, is slightly more radioactive than natural gypsum. The radium is found in the latticework of gypsum crystals in the form of radium sulfate, the salt of extremely low solubility (Kovler et al., 2005). Radium naturally associated with phosphate rock becomes associated with the phosphogypsum after the rock is reacted with sulfuric acid.

Regarding phosphogypsum, it is known that, due to its origin, it contains high levels of ^{226}Ra and low levels of ^{232}Th and ^{40}K (see Table 6.19). All ^{226}Ra national averages range from one to several hundred Bq/kg, UK heading them all with an

Table 6.20 **^{226}Ra, ^{232}Th, and ^{40}K activity concentrations in European natural gypsum and comparison with the European soil (Trevisi et al., 2012)**

	^{226}Ra	^{232}Th	^{40}K
Natural gypsum	15 (1–70)	9 (1–100)	91 (5–279)
European soil	36 (0–1000)	34 (1–258)	483 (0–3200)

Average activity concentrations in natural gypsum are much lower than in average European soil.

average higher than one thousand, and the maximum value higher than that of concrete made with alum shale (Trevisi et al., 2012). Concerning ^{40}K, both national averages and maximum values are in many cases lower than those of brick, concrete, and cement (Trevisi et al., 2012).

6.7 Conclusions

This chapter gives a concise overview about the technical, chemical, and radiological properties of by-products from coal mining and combustion, ferrous and nonferrous industries, and from the phosphate industry. The focus is in particular on by-products with interesting properties for use in construction.

The main part of the data given and discussed in this chapter was extracted from the NORM4Building database, after manual verification. The database is being constructed with the aid of an automated data mining by the COST network Tu1301 “NORM4Building.”

The activity concentrations for several of the by-products considered in this chapter are higher than the exemption/clearance levels (1 kBq/kg for natural radionuclides from the ^{238}U and ^{232}Th series and 10 kBq/kg) proposed by the EU-BSS. Several of these by-products can therefore be considered as NORM and care needs to be taken to assure that upon application the dose to workers and the public is below 1 mSv/y.

In Chapter 7 the considered by-products are further evaluated for the use in buildings taking into account the activity concentration index and the 1 mSv/y reference level for indoor external exposure to gamma radiation from building materials and radon.

ANNEX A Crystalline, granulated and expanded of foamed slag

Depending on the cooling and solidification method of the molten masses (those from the processing of ferrous and nonferrous metals), there are a few basic types of slag, as shown in Fig. 6.9.

Crystalline slag is obtained by casting in a trench and cooling to ambient conditions. Upon mass solidification, cooling can be accelerated by sprays of water, which results in the formation of cracks within the mass and thus facilitates subsequent crushing. This

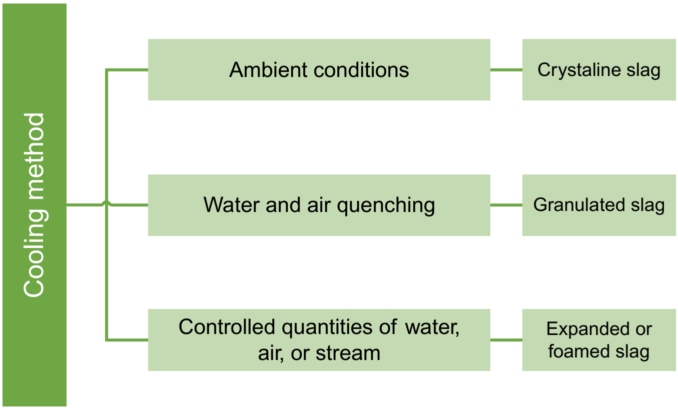

Fig. 6.9 Types of slag, according to the cooling method.

product is mainly crystalline (as indicated by the name), with a cellular or vesicular structure as a result of gas bubbles that formed in the molten mass (Lewis, 1982).

Granulated slag is formed by quickly quenching (chilling) molten slag with water or air to produce a glassy state, with little or no crystallization. After the granulated blast-furnace slag is formed, it must be dewatered, dried, and ground up before it is used as a cementitious material. Magnets are often used before and after grinding to remove residual metallic iron (Virgalitte et al., 2000). As a result of this process, sand-size particles and friable material like clinker are formed. The physical structure and gradation of the resulting slag depend on the chemical composition and temperature of the molten mass during cooling. Sand-size grains resembling dense glass are produced, and they contain oxides that are found in Portland cement, with a significant difference in the proportion of calcium and silicon. Like Portland cement, it has excellent hydraulic properties and, with a suitable activator (such as calcium hydroxide), it will set in a similar manner (Lewis, 1982). The rate of reaction increases with the fineness. Typically, this slag is ground to an air-permeability (Blaine) fineness exceeding that of Portland cement to obtain increased activity at early ages (Virgalitte et al., 2000).

Expanded or foamed slag results from the treatment of molten slag with controlled quantities of water, air, or foam. Variations in the amount of coolant and the cooling rate will result in variations in the properties of the cooled mass. However, in general, this is a product of a more porous and vesicular nature than air-cooled slag, and thus is much lighter in weight. Due to the variation in properties, the research literature often cites pelletized slag as a subtype of expanded slag. This slag is generated by a cooling method that involves cooling the molten mass using a limited amount of water, followed by chilling slag droplets thrown through the air by a rapidly revolving finned drum. Depending on the cooling process, the resulting slag particles may be angular and roughly cubical in shape, and thus more appropriate as aggregate, or they may be spherical and smooth, and therefore more suitable for use as a cement additive (Lewis, 1982).

Use of a pelletizer, also referred to as air granulation, involves molten slag passing over a vibrating feed plate, where it is expanded and cooled by water sprays. It then passes onto a rotating, finned drum, which throws it into the air, where it rapidly solidifies into spherical pellets. This slag may also have a high-glass content and can be used either as a cementitious material or, for larger particle sizes, as a lightweight aggregate (Virgalitte et al., 2000).

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From NORM by-products to building materials

7

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7.1 Introduction

Guide for the Reader: Structure of Chapter 7:

Within this chapter, four main groups of construction materials that allow the reuse of large quantities of by-products are considered: (1) those based on Portland cements (both as cement itself and as concrete), (2) those based on the alkali activation of different industrial products (mainly ground-granulated blast-furnace slag and fly ash), (3) ceramics and glass-ceramics, and (4) gypsum, in particular phosphogypsum.

Particular emphasis is placed upon the types of by-product that could be used in the preparation of these construction materials and on the technical and chemical aspects that govern the reuse. For each by-product a separate section deals on (1) the technical (and chemical) aspects of the use as a construction material and on (2) the resulting radiological properties of the construction material.

The considered by-products themselves and their radiological properties are discussed more in detail in Chapter 6.

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7.1.1 Recycling of industrial by-products in building materials

The cementitious materials and ceramics industries are excellent targets for the recycling and valorization of some wastes, residues, and by-products, from a wide variety of industries.

Given the environmental challenges inherent in Portland cement manufacture (high thermal and electrical energy demand, need to quarry large quantities of limestone and clay and the emission of greenhouse gases, especially CO_2), the study and development of cements based on the reuse of waste of varying origin is a priority line of research and technological innovation in the pursuit of industry sustainability. A broad range of types of waste can be used in blends with Portland cements, representing an environmentally friendly and clinker-saving way of production.

Of the 27 types of cement listed in the European Standard EN 197-1:2011 (Sanjuán and Argiz, 2011), 26 contain some manner of mineral addition which can include industrial residues such as siliceous or calcareous fly ash, blast-furnace slag, or silica fume. All of the aforementioned additions are industrial by-products and dependent on the content of natural radionuclides some of them are listed as naturally occurring radioactive materials (NORMs). The trend of industrial by-product recycling is expected to continue. The draft of the common cements standard prEN 197-1:2016 includes five new cement subtypes with higher amounts of by-products; in particular, siliceous fly ash and blast-furnace slag. In addition to the earlier, new potential cement constituents are being explored, such as ground coal bottom ash, paper sludge ash, silicon-manganese slag, copper slag, and so on (Argiz et al., 2013; Vegas et al., 2006; Sabador et al., 2007; Frias et al., 2006; García Medina et al., 2006; Siddique, 2003).

Industrial waste and by-products are used not in blends with Portland cement, but may also be added during clinkerization itself, partially or totally replacing the virgin raw materials in the raw meal (limestone in particular) or contributing as secondary fuel. Very different types of waste or by-products can be used as partial raw meal replacements, including crystallized blast-furnace slag (Puertas et al., 1988), waste from the manufacture of clay-based products (Puertas et al., 2010), aluminum recycling (Paval) (Blanco-Varela et al., 2000), etc. Efforts are also being made to use alternative fuels in OPC production: in countries such as the Netherlands, Austria, Germany, and Norway, these fuels account for over 60% of the total. The sources vary widely in nature, including shredded tires, solvents, water treatment plant sludge and used oil, among others (Pontikes and Snellings, 2014).

Another avenue for manufacturing eco-efficient cements is the development of new materials wholly different from ordinary Portland cement. Due to their mechanical and durability properties, versatility alkali-activated cements (also known as geopolymers) are among the most prominent of these new materials (Palomo et al., 2014). These cements are defined as the binders resulting from the chemical interaction between alkaline solutions and natural (clay; possibly thermally treated) or the result of human activity (industrial waste or by-products) aluminosilicates with a high- or low-Ca content, possibly having also Fe. Alkaline activation calls for two basic components: (1) a solid precursor that is prone to dissolution (most often amorphous or vitreous) and (2) an alkaline activator. The aluminosilicates may be natural products such as metakaolin or industrial by-products such as blast-furnace slag or aluminosiliceous fly ash. The alkaline solutions able to interact with aluminosilicates to generate such new binders include alkaline metal or alkaline-earth hydroxides (ROH, $X(OH)_2$), weak acid salts (R_2CO_3, R_2S, RF), strong acid salts (Na_2SO_4, $CaSO_4 \cdot 2H_2O$), and $R_2O(n)SiO_2$-type siliceous salts known as waterglass (where R is an alkaline ion such as N, K, or Li). From the standpoint of end product strength and other properties, the most effective of these activators are NaOH, Na_2CO_3, and sodium silicate hydrate (waterglass). Industrial by-products are presently also being studied for use as possible alkaline activators. Patents have been awarded for the use of industrial waste or by-products such as ash from rice husks, silica fume, and urban and industrial vitreous waste as potential alkaline activators to replace the family of substances known as water glass (Puertas and Torres-Carrasco, 2014). Here also, the main components of these cements may be NORMs.

The foregoing is indicative of the high potential for reuse and valorization of industrial waste and by-products in the manufacturing of cement and other construction materials. To be apt for such purposes, the waste must exhibit certain chemical, physical, and microstructural characteristics that favor their reactivity and behavior. Next to the binder described so far, the aggregates to be used for mortar and concrete production can also be residues and NORM in particular. Considering that they could be used in a proportion close to 80% in concrete volume, they might have a substantial contribution in the concentration of radionuclides in the final building materials.

The main ceramics which are produced using raw materials that can contain enhanced concentrations of natural radionuclides are refractories as well as tiles in which zirconia (the main source of natural radionuclides) is mixed with other constituents. In refractories, the applications cover the production of either prefabricated units (bricks) or the use as a mortar for in situ applications, for example, in kilns. Not every zirconia can be considered as NORM and in some cases only smaller amounts of zirconia are used, hence, not every refractory has enhanced levels of natural radionuclides. This is controlled by the composition of the refractory, which depends on the required properties in terms of temperature, chemical corrosive circumstances, and whether abrasion is an issue. Refractories with enhanced levels of natural radionuclides can be found in the glass industry (kilns) and sometimes in the ceramic brick or tiles kilns. Zirconium is also a common opacifier of ceramic glazes. In general, the glazes show activity concentrations below 1 kBq/kg for the main natural radionuclides, and only their production deserves control.

Other areas where significant amounts of by-products, such as fly ash, mining tailings, etc., are incorporated are clay-based formulations, ceramic bricks for example. Despite the often notable amount of by-products employed, the concentration of natural radionuclides in such ceramic materials is, in general, similar to that of common ceramic bricks.

7.1.2 Radiological consideration for recycling of industrial by-products in building materials

As discussed in Chapter 4, in Council Directive 2013/59/Euratom a reference level of 1 mSv/year is applied to indoor external exposure to gamma radiation emitted by building materials, in addition to outdoor external exposure (EU, 2014). Therefore, Member States shall ensure that the activity concentrations of the radionuclides are determined (control the external exposure with respect to the reference level) before the materials listed below are placed on the market for use in buildings:

(1) Natural materials
  (a) Alum-shale.
  (b) Building materials or additives of natural igneous origin, such as:
    - granitoides (such as granites, syenite, and orthogneiss);
    - porphyries;
    - tuff;
    - pozzolana (pozzolanic ash); and
    - lava.

(2) Materials incorporating residues from industries processing NORM, such as:
  - fly ash;
  - phosphogypsum;
  - phosphorus slag;
  - tin slag;
  - copper slag;
  - red mud (residue from aluminum production); and
  - residues from steel production.

To comply with the Council Directive 2013/59/Euratom requirements Member States shall arrange control measures with regard to their emitted gamma radiation. For screening and evaluation of building materials the Council Directive 2013/59/Euratom uses an activity concentration index (I_{BSS}):

$$I_{\mathrm{BSS}} = \frac{C_{\mathrm{Ra-226}}}{300} + \frac{C_{\mathrm{Th-232}}}{200} + \frac{C_{\mathrm{K-40}}}{3000} \leq 1 \qquad (7.1)$$

where $C_{\mathrm{Ra\text{-}226}}$, $C_{\mathrm{Th\text{-}232}}$, and $C_{\mathrm{K\text{-}40}}$ are the measured activity concentrations (Bq/kg) for, respectively, ^{226}Ra, ^{232}Th, and ^{40}K (EU, 2014).

The activity concentration index and the legislative aspects are discussed in more detail in Chapter 4. It needs to be kept in mind that the activity concentration index is only a screening parameter. In case a value of $I_{\mathrm{BSS}} > 1$ is found for a given building material, then it needs to be verified that, upon use in a building, the exposure to gamma radiation is less than the reference level of 1 mSv/year (which is the real criterion for evaluation of building materials). In this chapter the activity concentration index proposed by the Council Directive is used to screen the content of natural radionuclides in several building materials.

The activity concentration index is used only for building materials (or for their constituents if the constituents are also building materials) (EU, 2014). In this chapter (and in Chapter 6) also the "activity concentration index for by-products" is considered, but this purely for the purpose of dilution calculations in order to support the discussion of building materials incorporating a given by-product. Using an "activity concentration index for by-products" would in theory mean that the by-product itself is used (for 100%) as a building material which for most by-products is an unrealistic scenario. In this way the extreme case of NORM by-product incorporation in building materials is discussed. The reported activity concentration indexes are calculated on the basis of the activity concentration for ^{226}Ra, ^{232}Th, and ^{40}K from different literature references. The original values for these activity concentrations are also reported in Chapter 6.

The overall radiation hazard due to ionizing radiation from building materials includes both a gamma radiation component, which depends on their radionuclides content, and a component caused by their radon exhalation. However, most of the standards in the world, which regulate radioactivity of building materials, address the gamma radiation only, and do not require even to test the product for radon exhalation. The evaluation of the excess dose caused by building materials for the radon pathway is indeed rather complicated (Markkanen, 2011). One of the reasons is that the actual correlation between the monitored quantity and radon exhalation rate measured in laboratory and the excess indoor radon concentration on site might be rather poor. Numerous factors, such as temperature (both indoors and outdoors), air pressure and humidity fluctuations, total porosity, pore distribution and pore type (open or close), surface treating done at the building site or type of the coating material applied, influence significantly radon exhalation in dwellings. Finally, it is extremely difficult to take into account the effect of the inhabitant behavior influencing directly air exchange rate in living spaces. That is why most of the standards regulating radioactivity of building materials address the radon exhalation in a very simplified form—through the limitation of ^{226}Ra—the precursor of ^{222}Rn in the ^{238}U radioactivity chain (Kovler, 2011). At present only two national standards (Austrian Standard ÖNORM S 5200 and Israeli Standard SI 5098) address radon exhalation from building products, considering ^{226}Ra activity concentrations, radon emanation coefficient, density and thickness of the product. The detailed review of the standards regulating natural radioactivity of building materials is available in Chapter 4.

In reality, typical excess indoor radon concentration due to building materials is low: not higher than 20 Bq/m^3 (Kovler, 2009), which is only 7% of the reference value introduced in the Council Directive 2013/59/Euratom (300 Bq/m^3). In other words, radon cannot "compete" by its contribution with the underlying soil, which is correctly considered the most important source of indoor radon. At the same time, the building materials may also be an important source. For example, about 300,000 dwellings with walls made of lightweight concrete based on alum shale (the so-called "blue concrete") were built between 1929 and 1975 in Sweden (Mjoenes and Aakerblom, 2001). The radon concentrations in these houses can reach 1000 Bq/m^3 under low ventilation rate, while the building occupants can get an annual effective dose of 4 mSv/year—only from building material. In addition, the main part of indoor radon at the upper floors of a building originates also from building materials.

The Council Directive 2013/59/Euratom does not provide a guideline that deals separately with the radon exhalation/emanation from only the building materials. In Article 74, dealing with indoor exposure to radon, member states are expected to "promote action to identify dwellings, with radon concentrations (as an annual average) exceeding the reference level" (300 Bq/m^3). In other words, radon is regulated at the level of dwellings and no distinction is made between the building materials and the soil as sources of radon. Radon exhalation/emanation is dealt with in this chapter when information is available.

7.2 Portland cement and concretes

7.2.1 Introduction

The beneficial utilization of some industrial by-products in improving the technical, environmental, and cost profiles of fresh and hardened concrete is recognized. By-products such as coal fly and bottom ash, silica fume, and ground-granulated blast-furnace slag are well-known cement constituents in blended cements and also can be added in different proportions to concrete as mineral admixtures. Some others, such as copper slag and coal bottom ash, are being used mainly as concrete aggregates.

New by-products and waste materials are being generated by various industries and the disposal of these residues raises sustainability questions. The use of some waste materials in the cement and concrete industry is a promising alternative.

7.2.2 Coal fly ash

7.2.2.1 Technical properties

The recycling of fly ash (in particular, in concrete construction) has become increasingly important in recent years due to increasing landfill costs and current interest in sustainable development. Coal fly ash is a well-known cement constituent and concrete additive (Argiz et al., 2015; Kovler, 2017). A lot of information can be found at the website of the ECOBA (European Fly Ash Association): Fly ash was successfully used in concrete around the world for the last 50 years. In the United States more than six million tons and in Europe more than nine million tons are used annually in cement and concrete.

Coal fly ash is classified into two main groups: class F and class C fly ash. When the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is higher than 70 wt% they are classed as F-type. If not, then they belong to class C (Argiz et al., 2015). In both cases, fly ash consists of fine particles that could contain some heavy metals and natural occurring radionuclides. Its management remains a major challenge all over the world. However, the utilization of fly ash is technically feasible in the cement industry. There are essentially two main applications for fly ash in cement production, (1) first as a raw material to produce Portland clinker and (2) second as a mineral or pozzolana addition. Fly ash can be added to the Portland cement clinker as a pozzolanic constituent in the production of CEM II, Portland-composite cement, CEM IV, Pozzolanic cement or CEM V, Composite cement. Table 7.1 shows the ten cement types according to the European Standard EN 197-1:2011, which are CEM II/A-V, CEM II/B-V, CEM IV/A, CEM IV/B, CEM V/A, and CEM V/B, the amount of fly ash in the cement goes from 6% to 55% (6%–20%, 21%–35%, 11%–35%, 36%–55%, 18%–30%, and 31%–49%, respectively). Incorporation of high amounts of fly ash leads to a decrease in the early strength of cement due to the early low reactivity of fly ash, which could be improved by grinding.

The use of coal fly ash in blended cements is increasing because it improves some properties of concrete (Argiz et al., 2015). The pozzolanic activity of coal fly ash contributes to increased strength at later ages when the concrete is kept moist. In addition,

Table 7.1 Fly ash in common Portland cements with *K*, Clinker; *S*, Slag; *D*, Silica Fume; *P*, Natural Pozzolan; *Q*, Industrial Pozzolan; *V*, Siliceous fly ash; *W*, Calcareous fly ash; *T*, Burnt Shale; *L* and *LL*, Limestone (in LL TOC content ≤0.20 wt% and in L TOC content ≤ 0.50 wt%)

Main types	Designation		Composition (wt%)										
			Main constituents										
						Pozzolan		Fly ash			Limestone		Minor constituents
			Clinker K	S	D	P	Q	siliceous V	calcareous W	T	L	LL	
CEM II	Portland-fly ash cement	CEM II/A-V	80–94	–	–	–	–	6–20	–	–	–	–	0–5
		CEM II/B-V	65–79	–	–	–	–	21–35	–	–	–	–	0–5
		CEM II/A-W	80–94	–	–	–	–	–	6–20	–	–	–	0–5
		CEM II/B-W	65–79	–	–	–	–	–	21–35	–	–	–	0–5
	Portland-composite cement	CEM II/A-M	80–94	<- - - - - - - - - - - - - - 6–20 - - - - - - - - - - - - - ->									0–5
		CEM II/B-M	65–79	<- - - - - - - - - - - -21–35 - - - - - - - - - - - - - - - ->									0–5
CEM IV	Pozzolanic cement	CEM IV/A	65–89	–	<- - - - - - - 11–35 - - - - - - - - ->					–	–	–	0–5
		CEM IV/B	45–64	–	<- - - - - - - - 36–55 - - - - - - - ->					–	–	–	0–5
CEM V	Composite cement	CEM V/A	40–64	18–30	–	<- - - - 18–30 - - - ->			–	–	–	–	0–5
		CEM V/B	20–38	31–50	–	<- - - - 31–50 - - - ->			–	–	–	–	0–5

it leads in general to a lower water demand of the concrete for a given workability. This means a decrease in the water-cement ratio and capillary porosity and reduces bleeding. It also provides a low heat of hydration which is recommended in mass concrete applications to minimize cracking at early ages. Finally, coal fly ash cement in concrete means less concrete permeability as a result of producing a dense material. Given that, it provides a high-concrete resistance to sulfate ions attack, chloride ingress into the concrete, frost-thaw cycles, and alkali-silica reaction.

Typical applications of concretes made of coal fly ash cements are roller compacted concrete (RCC), which is a wide spread practice, such as in roads and dams' construction, road subbase, and soil stabilization. Also, coal fly ash has been employed as a lightweight aggregate in construction, an aggregate filler, a bituminous pavement additive, and a mineral filler for bituminous concrete (Blanco-Varela et al., 2000).

Some concrete plants produce concrete with coal fly ash as a mineral additive replacing partially Portland cement (because of pozzolanic properties of fly ash contributing in strength and durability of concrete). European Standard EN 206-1 regulates the replacement of cement with fly ash. For example, 1 kg of cement can be replaced by 2.5 kg of fly ash keeping the durability-related properties (or strength) of concrete unchanged. At the same time, the standard sets a maximum limit for such replacement, because pozzolanic reaction of fly ash occurs only, if calcium hydroxide, which is one of the products of cement hydration, is available. In other words, a presence of a minimum content of cement to trigger pozzolanic reaction of fly ash is vital. EN 206-1 allows replacing maximum 33% and 25% of cements CEM I and CEM II, respectively. If a greater amount of fly ash is used, the excess shall not be taken into account for the calculation of the replacement of cement.

Except a part of cement, fly ash can successfully replace also a part of sand, namely—its fine fraction. The partial replacement of sand in concrete becomes especially important nowadays for several countries, which suffer from the lack of high-quality quartz sand. Fly ash as a replacement of fine sand improves workability and pumpability of fresh concrete mixes. As a partial replacement of sand, fly ash can be introduced in normal-weight concrete mixes by much larger amount, than replacement of cement.

The total content of fly ash in normal-weight concrete mix at the level of 120 kg/m^3 is typical, although high-volume fly ash (HVFA) concrete compositions, which were introduced in order to maximize recycling of fly ash in concrete construction, are known (ACI, 2014). LEED (the abbreviation of Leadership in Energy and Environmental Design) promotes the use of HVFA concrete, which contains up to 40% of fly ash in cement or concrete (PCA, 2005).

The following example adapted from Kovler (2011) demonstrates a typical replacement of both cement and sand by fly ash. Two concrete mixes, the reference concrete and concrete containing 120 kg/m^3 of fly ash as a partial replacement of both cement and fine aggregates, are manufactured in the same concrete plant from the same raw materials—Portland cement and aggregates. Concrete compositions are shown in Table 7.2. In this example 30 kg/m^3 of cement is replaced with $30 \times 2.5 = 75$ kg/m^3 of fly ash, while the rest of fly ash ($120–75 = 45$ kg/m^3) replaces a part of sand. Total content of fine materials (cement + fly ash) in this concrete mix remains constant, which guarantees the same consistency of fresh concrete at the given water content. With this

Table 7.2 **Example of mix design for concrete with and without fly ash (kg/m^3)**

Raw materials	Reference concrete	Concrete with fly ash
Cement	300	270
Coarse aggregates	1200	1200
Fine aggregates	700	610
Fly ash	–	120
Water	150	150
Total	2350	2350

replacement the main properties of concrete in both fresh and hardened states are assumed to perfectly meet the design specifications.

A clear trend is observed in the last years in construction field: the concrete grade gradually increases, because of the need to design buildings and structures for higher loads (e.g., high-rise buildings, bridges, public buildings with large span, etc.), while economizing raw materials, which results in selecting thinner cross-sections for load-bearing elements. This trend results in a gradual increase in the content of cementitious materials. These materials contain often supplementary cementitious materials, such as coal fly ash. In parallel, the uses of coal fly ash in concrete mixes as a partial replacement of either cement or sand (or both) become more and more versatile. Considering this trend, the following typical compositions seem to serve as better basis for estimating the radiological properties of modern concrete.

In Table 7.3 a typical mix design for different modern concrete compositions with and without fly ash is given. This example will be further discussed in the discussion of the radiological aspects.

7.2.2.2 Radiological properties

Coal fly ash acts as a source of gamma radiation in concrete due to the presence of the radionuclides ^{226}Ra, ^{232}Th, and, to a lesser extent, ^{40}K. An overview of the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in coal fly ashes produced in several countries is given in Chapter 6. Several authors (Kovler, 2012; Kovler et al., 2005; Chinchón-Payá et al., 2011) measured relatively higher levels of natural occurring radionuclides in coal fly ash, which is currently used in Portland cements and concretes. By contrast, the radon exhalation is controversial because of the low emanation coefficient from the coal fly ash particles, which are generated under high temperatures in coal-firing thermal plants at the process of coal combustion (Kovler et al., 2004). The coal fly ash particles have dense glassy structure, which prevents radon atoms from escaping into the surrounding cement matrix. In spite of the fact that coal fly ash participates slowly in pozzolanic reaction, and then may contribute in radon emanation, like the resulting calcium silicate hydrates, this is neutralized by the strengthening of the overall structure of cementitious matrix, which is accompanied by lowering density and reduction of radon exhalation rate of concrete with time. Drying of concrete in time is another factor reducing radon exhalation of Portland cement—fly ash concrete. These processes are described and discussed in detail by Kovler (2012).

Table 7.3 Example of mix design for modern concrete compositions with and without fly ash (kg/m^3)

Raw materials	Reference concrete (no FA)	Concrete containing FA as partial replacement of sand	Concrete containing FA as partial replacement of cement and sand	HVFA (high-volume fly ash) concrete
Cement	400	360	320	160
Coarse and fine aggregates	1850	1800	1750	1700
Fly ash as a partial replacement of cement	0	0	50	40
Fly ash as a partial replacement of sand	0	90	80	180
Water	150	150	150	140
Total	2400	2350	2350	2220

The concentration of natural radionuclides in the resulting Portland cement will be decreased (relative to the material of origin the coal fly ash) since depended on the type of Portland cement (see Table 7.1) only a limited percentage of fly ash (up to 55 wt% of fly ash for pozzolanic cement) can be used. Therefore, recycling of coal fly ash in blended cements can have high environmental and safety advantages.

For estimating the values of *I*-index calculated by Eq. (7.1) of typical concrete compositions containing coal fly ash, typical activity concentrations reported by Trevisi et al. (2012) for Portland cement and European average soil (as the first approximation of the aggregates, both coarse and fine) are used. As far as coal fly ash is concerned, the minimum and maximum *I*-indexes (reported for coal fly ash in Chapter 6) will serve as a good assumption representing the variability of the radiological properties of this by-product.

As clearly stated in the Council Directive 2013/59/Euratom, the index should apply to the building material (concrete in our case), and not to its constituents (unless the constituents are also building materials), such as cement, aggregates, or coal fly ash. At the same time, *I*-index values for concrete constituents calculated by Eq. (7.2) make calculation of the overall *I*-index of concrete easier. Typical activity concentrations of concrete constituents for the calculation of the *I*-index value of modern concrete compositions containing coal fly ash are given in Table 7.4.

The activity concentration index of the hydrated Portland cement-based concrete is slightly lower than in the anhydrous form because of the presence of water (Puertas et al., 2015a,b).

Table 7.4 **Typical activity concentration index for concrete constituents in modern concrete compositions containing coal fly ash**

Raw materials	Typical activity concentrations [^{226}Ra; ^{232}Th; ^{40}K] (Bq/kg)	*I*-index	Reference
Cement	[45; 31; 216]	0.38	Trevisi et al. (2012)
Aggregates	[36; 34; 483]	0.45	Trevisi et al. (2012)
Coal fly ash (Ireland)	[26, 11, 70]	0.2	Minimum value (Table 3 of Chapter 6)
Coal fly ash (Greece)	[469; 40; 349]	2.2	Maximum value (Table 3 of Chapter 6)

The *I*-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the *I*-index, as proposed by Council Directive 2013/59/Euratom, is only used for building materials or for their constituents if the constituents are also building materials: An *I*-index given for a by-product or cement makes the unrealistic assumption that 100% of the by-product or cement is used as a building material.

The results of the *I*-index calculation of modern concrete compositions containing coal fly ash are given in Table 7.5.

Taking into account that HVFA concrete is mainly used in infrastructure, but rarely applied in dwellings and other inhabited buildings, we can conclude that the *I*-index unlikely exceeds half of the control value ($I=1$). In other words, the introduction of coal fly ash into concrete mix does not lead to significant increase of gamma doses. In parallel, radon emanation of concrete, especially in the mixes containing coal fly ash

Table 7.5 ***I*-index of modern concrete compositions containing coal fly ash**

Raw materials	Reference concrete (no FA)	Concrete containing FA as partial replacement of sand	Concrete containing FA as partial replacement of cement and sand	HVFA (high-volume fly ash) concrete
Maximum activity of fly ash ($I=2.2$)	0.41	0.48	0.51	0.59
Minimum activity of fly ash ($I=0.2$)	0.41	0.40	0.40	0.39

as a partial replacement of sand, is usually reduced, compared with the reference concrete (Kovler, 2012, 2017). Therefore, recycling of coal fly ash in concrete construction does not represent a radiological concern.

7.2.3 Coal bottom ash

7.2.3.1 Technical properties

Coal bottom ash is generated together with fly ash in the boiler of coal-fired power plants. Therefore, its chemical composition is in many cases quite similar. However, as discussed in Chapter 6, there are important differences related to the concentrations of the incorporated trace elements, such as the naturally occurring radionuclides of concern. In addition, there are important differences in the concentrations of (partly-) volatile species, for example, alkali metals.

Most of the scientific papers published regarding studies performed on coal bottom ashes suggest its use as artificial aggregates in road bases (Churcill and Amirkhanian, 1999) and only few attempts deal with their pozzolanic properties in blended cements (Cheriaf et al., 1999; Argiz et al., 2013; Bajare et al., 2013; Bumanis et al., 2013).

7.2.3.2 Radiological properties

For the use of coal fly ash as an aggregate in road bases currently (Jan. 2017), no European directives exist. Therefore, there are no limitations from a radiological point of view in most European Member States.

In some member states, like in Sweden, a specific index for bulk incorporation in construction materials for roads and play grounds is defined (Markkanen, 1995). More information on this specific index can be found in Section 4.5.

In the unlikely case of the use of coal bottom ash in building materials then the tables with activity concentrations given in Section 6.3.1.2 can be used for the evaluation for this specific application.

7.2.4 Slags from iron and steel production

7.2.4.1 Technical properties

Slag is a by-product from the pyrometallurgical processing of various ores. The characteristics of both ferrous (steel and blast-furnace Fe) and nonferrous (Ag, Cu, Ni, Pb, Sn, and Zn) slag must be known in order to assess its possible reuse as building material. The characteristics of slag depend on the metallurgical processes that form the material and will influence its classification as waste or as a reusable product. The properties of different types of slag are discussed in detail in Chapter 6.

Ground-granulated blast-furnace slag (GGBFS) is the main by-product from iron production used in construction. Ground-granulated blast-furnace slag is also a well-known cement constituent and concrete addition. Table 7.6 shows the nine cement types according to the European Standard EN 197-1:2011.

Table 7.6 Use of blast-furnace slag in the common Portland cements

Main types	Designation		Composition (wt%)										
			Main constituents										Minor constituents
			Clinker			Pozzolan		Fly ash			Limestone		
			K	S	D	P	Q	V	W	T	L	LL	
CEM II	Portland-slag cement	CEM II/A-S	80–94	6–20	–	–	–	–	–	–	–	–	0–5
		CEM II/B-S	65–79	21–35	–	–	–	–	–	–	–	–	0–5
	Composite cement	CEM II/A-M	80–94	<- - - - - - - - - - - - - 6–20 - - - - - - - - - - - ->									0–5
		CEM II/B-M	65–79	<- - - - - - - - - - - - - 21–35 - - - - - - - - - - - ->									0–5
CEM III	Blast-furnace cement	CEM III/A	35–64	36–65	–	–	–	–	–	–	–	–	0–5
		CEM III/B	20–34	66–80	–	–	–	–	–	–	–	–	0–5
		CEM III/C	5–19	81–95	–	–	–	–	–	–	–	–	0–5
CEM V	Composite cement	CEM V/A	40–64	18–30	–	<- - - 18–30 - - ->			–	–	–	–	0–5
		CEM V/B	20–38	31–50	–	<- - - 31–50 - - ->			–	–	–	–	0–5

Pelletized blast-furnace slag resulted from cooled blast-furnace slag. It has a vesicular texture and it is used as a lightweight aggregate and finely grounded as cementitious material.

Air-cooled blast-furnace slag is naturally cooled with moderate sprinkling. The crystallized slag, after crushing, sieving, and removing magnetic matter, can be used as construction aggregate, concrete bricks, road bases, and surface and Portland clinker production raw material.

Steel slag is a by-product of the steel-making process formed from the reaction of flux such as calcium oxide with the inorganic nonmetallic components present in the steel scrap. The two main types of steel slag which can be used for construction are basic oxygen furnace (BOF) steel slag and electric arc furnace (EAF) steel slag. Both types of steel slag are commonly blended with ground-granulated blast-furnace slag, coal fly ash and lime to form pavement material, skid resistant asphalt aggregate and unconfined construction fill.

BOF slags have variable compositions depending on the particularities of the metallurgical process followed and the iron ores used. In general, these slags are being used in low-end applications as their management is typically not a priority. In more detail, the main fields of application of BOF slag are aggregates for road construction (Guttm et al., 1967; Everett and Gutt, 1967) (in bound and unbound mixtures), structural fills, hydraulic engineering, fertilizers, waste water treatment, and internal use in the blast furnace.

Apart from the low-end applications, BOF slags are also used as hydraulic binders in combination with other materials. In Europe, BOF slags are mixed with GGBFS and hydraulic road binder are delivered for the stabilization of the road surfacing and upper and lower layers of the roadbed.

Studies into utilizing slag as concrete aggregates, carried out by several researchers, have shown that these slag-aggregate concretes were stronger in compressive strength than plain concrete. However, slag-aggregate concrete was found to be more vulnerable to sulfate attack in aggressive environments.

The possible utilization of slag as a building material has to be explored and the radiological impact of steel slag should be examined carefully as well during all the stages of its life cycle.

In Table 7.7 a typical mix design for different modern concrete compositions with and without blast-furnace slag is given. This example will be further discussed in the discussion of the radiological aspects.

7.2.4.2 Radiological properties

Residues from iron and steel production that are used in Portland cement and concretes can contain elevated levels of natural occurring radionuclides (Puertas et al., 2015a,b; Trevisi et al., 2012; Piedecausa et al., 2011a,b). An overview of the radiological properties of the residues is given in Chapter 6. As mentioned before ground-granulated blast-furnace slag is the main by-product from iron production that is currently used as a well-known cement constituent and concrete additive.

In Portland cement, depending of the type of cement larger percentages (up to 95% for blast-furnace cement) can be used (Table 7.6).

Table 7.7 Example of mix design for modern concrete compositions with and without blast-furnace slag (kg/m^3)

Raw materials	Reference concrete (no FA)	Concrete containing slag as partial replacement of cement	Concrete containing slag[a] as a partial replacement of cement and concrete
Cement	400	80	80
Slag as partial replacement of cement	0	320	320
Coarse and fine aggregates	1850	1850	1450
Slag as partial replacement of aggregates	0	0	400
Water	150	150	150
Total	2400	2400	2400

[a] In this assumption, for a realistic replacement, two different types of slag are to be used in order to replace both cement and aggregates.

For concrete, containing blast-furnace slag, a possible mixing design is given in Table 7.7. For this mixing design, dilution calculations were made in order to calculate the *I*-index of blast-furnace slag containing concrete, based on the values of the *I*-index for the constituents (Table 7.8). The result of the *I*-index calculations is given in Table 7.9.

7.2.5 Copper slag

7.2.5.1 Technical properties

The physico-mechanical characteristics of copper slag suggest that it can be utilized in the cement and concrete industry (Shi et al., 2008). Granulated copper slag exhibits pozzolanic properties, and then, it could be used as a constituent for common Portland cement.

When slowly cooled and milled to be used as fine or coarse aggregate in high-strength concrete, the concrete showed comparable or even superior mechanical properties compared with conventional OPC. Depending of the composition and characteristics of copper slags, they can be used as ballast, abrasive material, fine aggregate in concrete, aggregates in hot mix asphalt pavements, cement raw material, roofing granules, glass, tiles, and so on (Al-Jabri et al., 2006, 2009; Arino-Moreno and Mobasher, 1999; Shi and Qian, 2000; Khanzadi and Behnood, 2009).

In Table 7.10 a typical mix design for different concrete compositions with and without copper slag is given. This example will be further discussed in the discussion of the radiological aspects.

Table 7.8 **Typical activity concentration indexes for concrete constituents in modern concrete compositions containing blast-furnace slag**

Raw materials	Typical activity concentrations [^{226}Ra; ^{232}Th; ^{40}K] (Bq/kg)	*I*-index	Reference
Cement	[45; 31; 216]	0.38	Trevisi et al. (2012)
Aggregates	[36; 34; 483]	0.45	Trevisi et al. (2012)
Blast-furnace slag (Poland)	[115; 35; 192]	0.62	Minimum value (Table 10 of Chapter 6)
Blast-furnace slag (Turkey)	[178; 148; 242]	1.41	Maximum value (Table 10 of Chapter 6)

The *I*-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the *I*-index, as proposed by Council Directive 2013/59/Euratom, is only used for building materials or for their constituents if the constituents are also building materials: An *I*-index given for a by-product or cement makes the unrealistic assumption that 100% of the by-product or cement is used as a building material.

Table 7.9 ***I*-index of modern concrete compositions containing blast-furnace slag**

Raw materials	Reference concrete (no blast-furnace slag)	Concrete containing slag as partial replacement of cement	Concrete containing slag as a partial replacement of cement and concrete
Maximum activity of blast furnace ($I = 1.41$)	0.41	0.55	0.71
Minimum activity of blast-furnace slag ($I = 0.62$)	0.41	0.44	0.47

7.2.5.2 Radiological properties

For concrete, containing copper slag, a possible mixing design is given in Table 7.10. For this mixing design, dilution calculations were made in order to calculate the *I*-index of copper slag containing concrete, based on the values of the *I*-index for the constituents (Table 7.11). The result of the *I*-index calculations is given in Table 7.12.

Table 7.10 Example of mix design for modern concrete compositions with and without copper slag (kg/m^3)

Raw materials	Reference concrete (no FA)	Concrete containing slag as a partial replacement of concrete
Cement	400	400
Coarse and fine aggregates	1850	1450
Slag as partial replacement of aggregates	0	400
Water	150	150
Total	2400	2400

Table 7.11 Typical activity concentration indexes for concrete constituents in modern concrete compositions containing copper slag

Raw materials	Typical activity concentrations [^{226}Ra; ^{232}Th; ^{40}K] (Bq/kg)	*I*-index	Reference
Cement	[45; 31; 216]	0.38	Trevisi et al. (2012)
Aggregates	[36; 34; 483]	0.45	Trevisi et al. (2012)
Copper slag (Poland)	[317; 54; 886]	1.62	Minimum value (Table 11 of Chapter 6)
Copper slag (Germany)	[770; 52; 650]	3.04	Maximum value (Table 11 of Chapter 6)

The *I*-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.
Note that the *I*-index, as proposed by Council Directive 2013/59/Euratom, is only used for building materials or for their constituents if the constituents are also building materials: An *I*-index given for a by-product or cement makes the unrealistic assumption that 100% of the by-product or cement is used as a building material.

7.2.6 Red mud

7.2.6.1 Technical properties

The potential uses of red mud can be classified into recovery of major or minor constituents and direct uses or incorporation into products such as concrete, tiles, and so on. Within the first group, recovery of iron, vanadium, chromium, titanium dioxide, rare earths, and aluminum oxide has been reported in the literature. With regard to applications in building materials, red mud can be used as a raw material in cement,

Table 7.12 ***I*-index of modern concrete compositions containing copper slag**

Raw materials	Reference concrete (no copper slag)	Concrete containing slag as a partial replacement of cement and concrete
Maximum activity of copper slag ($I = 3.04$)	0.41	0.84
Minimum activity of copper slag ($I = 1.62$)	0.41	0.61

bricks, roofing tiles, and glass-ceramics production (Thakur and Sant, 1983; Tsakiridis et al., 2004; Vangelatos et al., 2009; Singh et al., 1997; Yang and Xiao, 2008; Romero and Rincón, 2000; Vincenzo et al., 2000; Pontikes and Angelopoulos, 2013).

The use of bauxite residue in Portland cement production has been the subject of some research projects from as early as 1936 (Thakur and Sant, 1983). The iron and alumina contents of the residue are beneficial in the mix raw material to produce clinker. The residue must be pressured before its incorporation to the raw mix in a proportion below 5% (Tsakiridis et al., 2004; Vangelatos et al., 2009). Also, some special cement has been investigated in the past using of mixtures of gypsum and bauxite residue. In particular, the titanium content of the mud was found to be beneficial to cement compressive strength (Singh et al., 1997; Yang and Xiao, 2008).

Artificial aggregates made of red mud require a number of processing steps, including drying, pelletizing, and calcinations. Therefore, it is unlikely that such type of artificial aggregate could be competitive with other types due to the processing cost (Romero and Rincón, 2000).

7.2.6.2 Radiological properties

The radiological properties of red mud are discussed in detail in Chapter 6. On the basis of the activity concentration of naturally occurring radionuclides in red mud calculations can be made regarding the resulting activity concentration index of the concrete.

Especially the production of alkali-activated cement and concretes could enable the incorporation of larger percentages of red mud in concrete. This aspect is discussed in more detail in Section 7.3.5.

7.2.7 Overall discussion of radiological aspects of Portland cements and concretes

Commonly, the concentration of radionuclides, originating from residues, is decreased in the produced Portland cements and concretes due to a dilution effect. This is illustrated in Table 7.13 where the radiological properties of some investigated concretes are given.

Table 7.13 **Radiological properties of investigated concrete samples (extracted from NORM4Building database)**

Country	Radionuclide concentration (Bq/kg)			*I*-index	Number of samples	References
	^{226}Ra	^{232}Th	^{40}K			
China	25.8	26.8	852	0.5	13	Xinwei (2005)
Estonia	35.1	11.3	207	0.2	1	Lust and Realo (2012)
Hungary	11	6	142	0.1	2	Szabó et al. (2013)
Lithuania	32	17	426	0.3	1	Trevisi et al. (2012)
Luxembourg	93	92	110	0.8	2	Trevisi et al. (2012)
Poland	18.5	16.5	350	0.3	2	Zalewski et al. (2001)
Slovakia	17.1	19.7	351	0.3	34	Michael (2010), Vladar and Cabanekova (1998)
Spain	23.2	21	278	0.3	9	Chinchon-Paya et al. (2011)
Syria	24.5	4.8	70	0.1	6	Shweikani et al. (2013)

These values are the mean values of individual entries.
The *I*-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.

Generally, the uranium series radionuclide concentration in the cement-based materials, in descending order is: Fly ash > Anhydrous calcium aluminate cement > Slags > Anhydrous Portland cement > Limestone = Silica fume (Puertas et al., 2015a,b).

Aggregates often have the greatest influence in the concrete radioactivity because they account for more than 80% of the concrete volume. Radium-rich and thorium-rich materials, for instance, granites and gneiss or others used as aggregates in concrete may enhance the indoor gamma radiation from the walls in buildings (Ackers et al., 1985; Botezatu et al., 2002). In a similar way, some industrial wastes such as blast-furnace slag, coal fly ash, and coal bottom, among others, can cause enhanced activity concentrations of concrete when they are used as aggregates (Kominek et al, 1992: Nuccetelli et al., 2015b; Skowronek and Dulewski, 2001). By contrast, natural stone of sedimentary origin such as limestone or dolomite does not enhance the radionuclide content of concrete mix. From a recent update of Trevisi et al. (2012), reporting summarized data of radioactivity concentrations of building materials in EU countries, some information can be obtained. For ^{226}Ra, ^{232}Th, and ^{40}K averages (and ranges) of EU national values, expressed in Bq/kg, are 60 (14–272), 34 (8–138), and 345 (17–685), respectively (Trevisi et al., 2016). By a detailed analysis of the database it is possible to see that the highest activity concentrations are generally relevant to concretes containing NORM residues.

With regard to the radon production in concrete as a result of the presence of ^{226}Ra, it is well-known that it depends on some characteristics of the concrete such as moisture content, porosity, tortuosity, permeability, cracks formation, and thickness of the concrete element. In general, high-moisture content in porous materials increases the radon exhalation rate (Kovler et al., 2005; Stranden et al., 1984; Yu et al., 1996). On the contrary, dehydration of concrete due to aging of materials determines a decrease of the radon exhalation rate.

7.3 Alkali-activated cement and concretes (geopolymers)

7.3.1 Introduction

In 1895 and 1908, for the first time patents demonstrated that the combination of a vitreous slag and different alkaline solutions could be used to develop a material with a performance similar to Portland cement. In the 1960s and the 1970s of the last century, relevant contributions were given by Glukhovsky (1959) at the Institute for Binders and Materials of Kyiv National University of Construction and Architecture, focusing on the alkali-carbonate activation of metallurgical slags. In early 1980s (Davidovits, 1982), in France, patented several aluminosilicate-based formulations and introduced the name “geopolymers” for these alkaline materials. Since the 1990s several research groups are working on the development of such alternative construction materials, attempting to optimize the formulations and final (mechanical, chemical, physical, and microstructural) properties. More recently, pilot-scale and industrial trials on the application of alkali-activated binders (concrete, mortars, and related materials) were conducted, and recommendations to the national and international standardization bodies were given for the practical implementations of these alternative building materials.

The alkali-activated materials (AAMs) are derived by the reaction of an alkali metal source (solid or dissolved) with a solid silicoaluminate powder (binder or precursor). This solid can be metakaolin, metallurgical slag, natural pozzolan, fly ash, or bottom ash. The alkali sources used can include alkali hydroxides, silicates, carbonates, sulfates, aluminates, or oxides (Provis and van Deventer, 2014).

According to the chemical composition of the binder, we can distinguish two main systems of AAMs:

(1) High-calcium AAMs [where the binder is mainly blast-furnace slag (BFS)].
(2) Low-calcium AAMs [where the binder is mainly fly ash (FA)].

7.3.2 Blast-furnace slag

7.3.2.1 Technical properties

In the second half of the 20th century alkali-activate slag (AAS) concretes have been successfully applied in different fields of civil engineering, particularly in Eastern Europe: Ukraine, Russia, and Poland (Shi et al., 2006). A historical study of more than 50 years old AAS concrete in Belgium was recently presented (Buchwald et al., 2015). Valuable experience for further development and applications of alkali-activated binders and concretes has been gathered from the existing applications. The lack of uniformly accepted standards is probably the major obstacle toward broader application in the construction industry. The recommendation of RILEM Technical Committee 224-AAM is that a performance-based standards regime should be implemented to provide description and regulation for alkali-activated binders and concretes (Provis and van Deventer, 2014).

Ground-granulated blast-furnace slag is the most frequently used metallurgical slag for the production of alkali-activated slag mortars, and concretes. During the alkali activation process, the vitreous phase of BFS dissolves, forming, mainly, calcium aluminosilicate hydrates (C-A-S-H) afterwards. This reaction depends on a whole series of parameters such as physical and chemical properties of BFS, properties of alkali activator (the nature, concentration, and pH of the activators), and conditions of the reaction (temperature, relative humidity, and curing time). The influence of all of these factors on the structure and properties of alkali-activated blast-furnace slag (AAS) pastes, mortars, and concretes is thoroughly presented in some other publications (Shi et al., 2006; Davidovits, 2008; Provis and van Deventer, 2014; Provis et al., 2015; Pacheco-Torgal et al., 2015).

Properties of AAS are highly affected by the activator nature (type) and concentration. The earliest binder made from BFS was lime-activated BFS. Alkali hydroxides, silicates, sulfates, and carbonates or their mixtures can successfully activate BFS.

The activator is normally used as a solution. On the other hand, one part of the binder can be produced by mixing or intergrinding solid-state activator with the BFS. However, this might cause problems due to the hygroscopic nature of the activator. Furthermore, the heat of hydration released during dissolution of solid activator may enhance the reactivity of BFS. Optimal concentration and dosage strongly depend on the nature of slag, alkali activators used, and curing conditions.

The highest strength is most commonly developed when BFS was activated with sodium silicate (water glass) as demonstrated in Fig. 7.1 (Puertas and Torres-Carrasco, 2014). However, undesirable side effects, such as fast setting and/or high-drying shrinkage, usually accompany the high strength. Such problems might be solved by extending the mixing time. The activation of BFS with NaOH or KOH results in a high-early strength, but when considering the strength at 7 days or later ages, it is usually lower in comparison to BFS activated with sodium silicate.

The selection of a suitable alkali activator most probably has the largest economic and environmental impact on the production of alkali-activated binders or concretes. The large-scale utilization of commercially produced sodium silicate as an activator

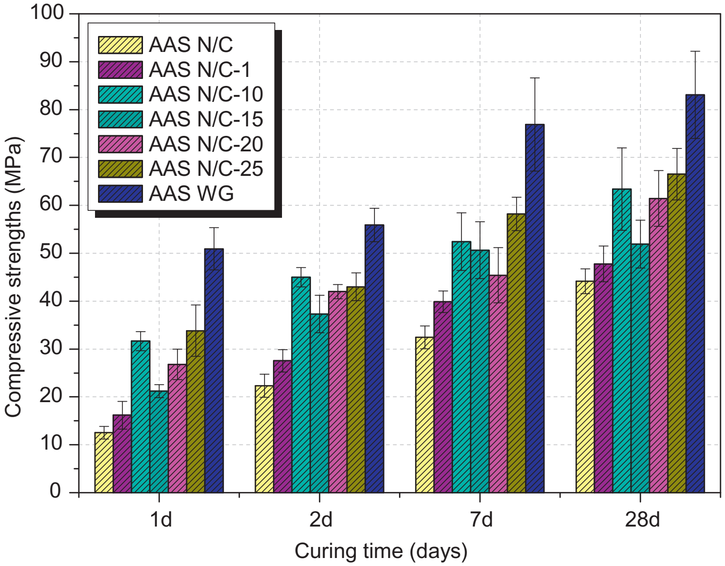

Fig. 7.1 Compressive Strength behavior of AAS cement pastes prepared with different activators (N/C: $NaOH/Na_2CO_3$; WG: sodium silicate hydrate); N/C-*x*: Content in *x* g waste glass/100 mL (Puertas and Torres-Carrasco, 2014).

will face limitations in terms of scalability, cost, practical handling issues, and the environmental cost of this product (Provis et al., 2015). New activators should be investigated in order to contribute to the fabrication of inexpensive binder systems, sustainable processes, and nonhazardous handling. Sodium sulfate, $NaOH/Na_2CO_3$ mixture, and the glass waste mixed solution or NaOH/silica fume also proved to be effective as alkali activators for BFS—see Fig. 7.1 (Puertas and Torres-Carrasco, 2014).

Curing conditions have a significant impact on the mechanical properties of AAS, as the provision of proper curing proved to be essential for high-strength development. Curing in water, the most common curing procedure for Portland cement is not recommended, as it might lead to premature leaching and unavoidable loss of strength. More appropriate options of curing at room temperature are sealed curing (in a sealed container) or curing in a humid chamber (Relative humidity > 90%). Curing at elevated temperature (heat or steam curing) increases the rate of alkali activation reaction and strength development, whereby irreversible loss of water should be prevented as it might lead to the high-drying shrinkage, micro cracks formation, and strength loss (Marjanović et al., 2015). Steam and autoclave curing are significantly effective in reducing the drying shrinkage of AAS mortars. Unconventional curing by ultrasound or microwaves also has some potential (Komljenović, 2015).

The water/binder ratio plays a dominant role in strength development of AAS. Generally, a lower water/binder ratio induces higher strength. However, it depends on the activator concentration and dosage as well (Fernández-Jimenez et al., 1999). Standard water reducing admixtures, which were developed for the Portland cement systems, usually do not work properly in the alkali activation process due to high-alkaline conditions present (Palacios et al., 2009). The setting time of AAS primarily depends on the dissolution rate of the precursor material and precipitation of the reaction products. The setting time can vary significantly as a function of curing conditions and the type, concentration, and dosage of the activator used. The heat of hydration of AAS is usually lower than OPC (Križan and Živanović, 2002).

The mechanical properties of AAS concrete, such as compressive strength, flexural and splitting tensile strengths, drying shrinkage, etc., are normally assessed by using the standards of ordinary Portland cement concrete. However, some of those methods may be inappropriate for geopolymers (Provis and van Deventer, 2014).

AAS concrete has some advantages with respect to the OPC concrete, such as a low heat of hydration, a high-early strength, and an increased durability in aggressive environments. AAS concrete also shows a greater tensile strain capacity than OPC concrete due to the greater creep, the lower elastic modulus, and the higher tensile strength. Drying shrinkage and tendency to microcrack formation of AAS concrete is usually higher than OPC, particularly under dry conditions. The problem of efflorescence is also frequently present in AAS concrete, due to the high concentration and mobility of alkalis present in the pore solution, and the porosity of hardened AAS (Puertas et al., 2003). The efflorescence is rarely harmful to the product performance, but its avoiding is highly desirable due to the undesirable visual effects. The elastic properties of AAS under applied force, which are of particular importance for construction applications, can be improved by introducing fiber reinforcement such as short fibers or unidirectional long fibers into the AAS matrix. The addition of different types of fibers (polypropylene, polyvinyl alcohol, alkali-resistant glass, steel, carbon, etc.) usually increases flexural and splitting tensile strength, reducing drying shrinkage as well. Some adverse effects on workability and compressive strength were also reported (Puertas et al., 2003).

Concrete durability during long-term exploitation is of key importance for its safe and efficient functioning and it is determined by its ability to resist chemical attacks, abrasion, weathering action, or any other process of deterioration.

AAS usually contains a large amount of alkalis, which means that if AAS is being used in structural applications, an important precondition is met for the alkali-aggregate reaction (AAR) to occur. The role of calcium is known to be important in determining the rate and extent of the alkali silica reaction (ASR). AAS concrete is probably more resistant to ASR than Portland cement concrete due to the lower availability of alkalis and calcium (C-A-S-H with a lower Ca/Si ratio) (Puertas et al., 2009). However, the opposite, a lower resistant to ASR in comparison with Portland cement was also reported (Bakharev et al., 2001; Shi et al., 2015).

Carbonation is one of the most important degradation processes that can significantly affect the long-term durability of concrete infrastructures. The carbonation rate of AAS depends on the properties of BFS. For example, higher amount of MgO present in BFS reduces the carbonation rate (Bernal et al., 2014). The type and concentration of the activator used also influences the carbonation rates, as well as the water/binder ratio, the amount of BFS present in the concrete mixture, and curing conditions.

Frost resistance of AAS becomes important in cold climates when the concrete construction is exposed to freeze-thaw cycling. Deterioration of concrete can appear in two principal forms: internal cracking due to freezing and thawing cycles and surface scaling due to freezing in the presence of deicing salts (usually NaCl). However, the available literature is mainly focused on issues related to internal cracking (Cyr and Pouhet, 2015).

Different methods for testing the frost resistance of Portland cement concretes are available. However, these methods are based on different experimental conditions such as the temperatures of freezing and thawing, cycle count and duration, etc. The curing procedure prior to this or any other type of alkali-activated BFS testing is particularly important, as the proposed curing methods for Portland cement systems might not be appropriate for AAS. Generally, AAS shows very good frost resistance due to favorable characteristics of the air-void/bubble network system (Cyr and Pouhet, 2015). Sodium silicate-activated BFS concrete usually has the least porous structure, highest strength, and best frost resistance.

Chloride penetration through concrete can cause corrosion of the reinforcing steel and deterioration of reinforced concrete structures. This type of deterioration is quite common in concrete structures exposed to deicing salts or sea water. Therefore, the resistance of reinforced concrete structures to chloride penetration is quite important for designing, producing, and maintaining durable concrete structures. A great number of methods for chloride penetration testing developed for Portland cement concretes are available. The RILEM Technical Committee TC 178-TMC: "Testing and Modeling Chloride Penetration in Concrete" has tested four different groups of methods for determining chloride transport parameters in concrete: (1) natural diffusion methods, (2) migration methods, (3) resistivity methods, and (4) colorimetric methods. The RILEM Technical Committee TC 224 AAM (Provis and van Deventer, 2014) suggested that chloride ponding tests such as ASTM C1543, or rapid migration tests such as the Nord Test method NT Build 492, might be more suitable for AAMs testing. Compared with OPC, alkali-activated binders demonstrate better performance against chloride ingress, according to both accelerated (Fig. 7.2) (NordTest NT Build 492) and ponding (ASTM C1543) methods. The NordTest method is considered more reliable as an accelerated way to assess chloride durability of AAMs (Torres-Carrasco et al., 2015).

Corrosion of reinforcing steel in AAS is strongly influenced by the specific BFS chemistry (presence of sulfide). Therefore, the predictions designed for Portland cement concretes may not be applicable to the AAS concretes. Despite the fact that some reports for corrosion of reinforcing steel testing in AAS already exist, the method specifically adapted to the complex chemistry of AAS is yet to be developed.

External sulfate attack is the consequence of impact of sulfate ions present in soils, underground waters, sea water, or industrial waste waters on hardened concrete. Sulfates generally cause harmful effects on cement, depending on the type of cement used, the nature and concentration of aggressive sulfate solution, the presence of different cations and/or salts in sulfate solution, the quality of concrete, as well as concrete exposure conditions. Different methods and criteria were also used to assess the resistance of AAS mortar or concrete to external sulfate attack, most commonly based

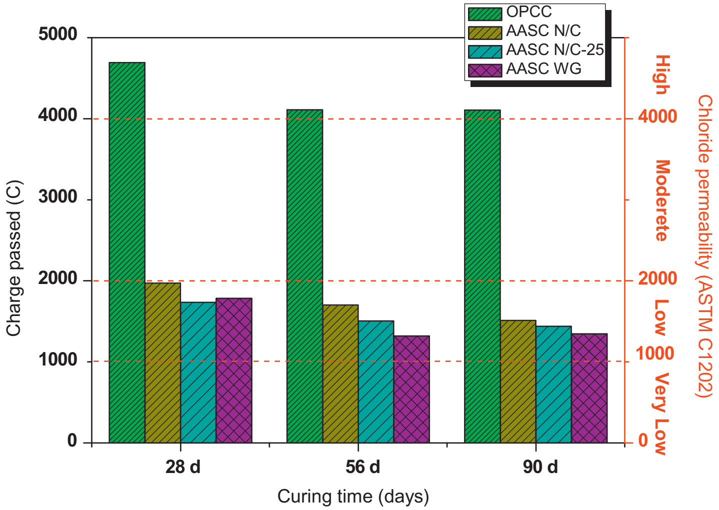

Fig. 7.2 Rapid chloride permeability test results for 28, 56, and 90 days cured activated slag and OPC concretes with different activators, performed according to the ASTM C1202 (Torres-Carrasco et al., 2015).

on (1) expansion, (2) flexural and/or compressive strength, and (3) the strength loss index (Komljenović et al., 2013). More detailed reports are given elsewhere (Shi et al., 2006; Provis and van Deventer, 2014; Pacheco-Torgal et al., 2015). Generally, AAS performs better in sulfate environment than Portland cement systems. However, this performance depends also on the properties of BFS, the type and concentration of the activator, concentration of sulfate solution, and cations present in the solution.

Despite the fact that most of the concrete structures are not exposed to acidic conditions, some concrete structures can be exposed to acidic aggressive environments such as specific industrial processes, acid rains, acid sulfate soils, animal husbandry, or biogenic sulfuric acid corrosion (present in sewage pipes). AAS is expected to demonstrate similar or even better acid corrosion resistance in comparison with Portland cement, due to the significant differences in the reaction products (absence of Portlandite in and low Ca/Si ratio of the BFS-based binder). According to the available literature, AAS generally shows good performance in acidic environments (Komljenovic et al., 2012; Varga et al., 2015).

7.3.2.2 Radiological properties

The radiological properties of blast-furnace slag are discussed in Chapter 6. These data can be used to assess the activity concentration of an alkali-activated cements and concrete based on blast-furnace slag.

Radiological properties of alkali-activated cements and concretes produced on the basis of blast-furnace slag and coal fly ash are discussed in Section 7.3.3.2.

7.3.3 Coal fly ash

7.3.3.1 Technical properties

Development of alkali-activated cements allows using fly ash as an aluminosilicate component (Krivenko, 1992). A specific feature of these systems is the high-initial pH value. When being appropriately used, the alkalis accelerate the first stage of destruction of the initial aluminosilicate structure, and then take an active part in the formation of compounds responsible for the strength characteristics of the material.

An important component of fly ash alkali-activated (AAFA) cement is low-calcium coal ash (up to 10% of CaO by mass, class F according to ASTM classification). In addition, also Class C ash can be used as is the case for several applications in the United States.

Curing conditions of AAFA cements also differ depending on the required properties for tailored applications: (i) special applications require autoclave curing, steam curing, and drying; (ii) common cements are cured in normal conditions (steam curing).

According to the Ukrainian Standard DSTU B V.2.7-181:2009 “Alkaline cements. Specifications” (DSTU B.V. 2.7-181, 2009), AAFA cements can be divided three classes, as shown in Table 7.14.

Table 7.14 **Fly ash in the alkali-activated cements**

<table>
<tr><th rowspan="3">Class</th><th rowspan="3">Designation</th><th colspan="4">Composition (% by mass)</th></tr>
<tr><th colspan="3">Main constituents (aluminosilicates)</th><th rowspan="2">Alkali (Na or K) metal compounds (over 100%)</th></tr>
<tr><th>Granulated blast-furnace slag</th><th>Clinker</th><th>Fly ash</th></tr>
<tr><td>AAC I—ASH</td><td>Alkali-activated cement with addition of fly ash</td><td>55–90</td><td>0–10</td><td>10–35</td><td>1.5–12</td></tr>
<tr><td>AAC III</td><td>Alkali-activated pozzolanic cement</td><td colspan="2">20–64</td><td>36–80</td><td>1.5–12</td></tr>
<tr><td>AAC V</td><td>Alkali-activated composite cement</td><td>30–50</td><td>5–10</td><td>40–65</td><td>1.5–12</td></tr>
</table>

Based on DSTU B.V. 2.7-181, 2009. Alkaline Cements, Specifications. National Standard of Ukraine, Kyiv.

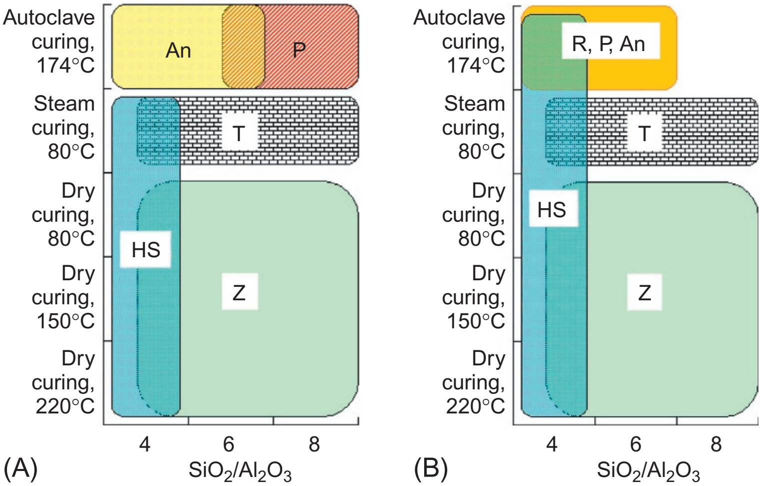

Fig. 7.3 Composition of reaction products vs. cement composition: (A) fly ash 1; (B) fly ash 2; and curing conditions. *An*, analcime; *P*, zeolite P; *R*, zeolite R; *HS*, hydroxysodalite; *Z*, trona; *T*, sodium carbonate hydrate. Note that Trona and Sodium carbonate hydrate are not alkali activation products but that they result from the carbonation of excess alkali. The alkali-activation results in a disordered aluminosilicate gel as primary reaction product. More information on the type of zeolites P and R can be found in Palomo et al. (2014).

The main reaction products according the curing conditions are shown in Fig. 7.3 (Krivenko and Kovalchuk, 2002; Krivenko et al., 2006).

The mechanical strength of AAFA cements is similar to OPC or AAS. Their evolution with curing age is shown in Fig. 7.4. Compositions and properties of the cements are given in Table 7.15. Remarkable is the strength gain at older ages: after

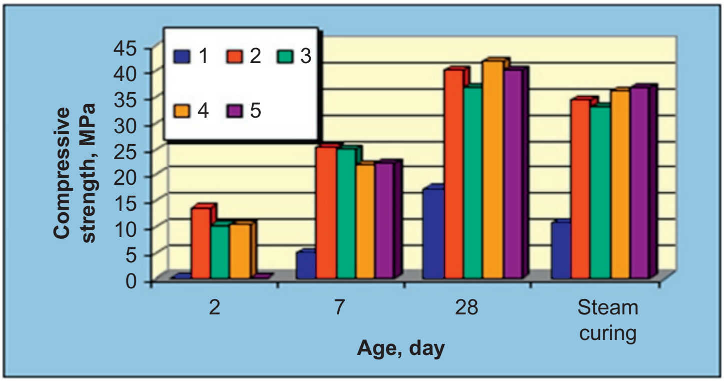

Fig. 7.4 Strength development of AAFA cements. 1–4—AAFA cements with clinker content 0–10–20–30 wt% and fly ash content 60–80 wt%, 5—OPC CEM II/A-400 (Grade 42.5).

Table 7.15 Characteristics of alkali-activated cements

No.	Cement composition, % by mass					Properties		Flow (cone), mm (W/C)
	Clinker	Fly ash	Granulated blast-furnace slag (S)	Na_2CO_3	Plasticizer	Paste of normal consistency, %	Initial setting time, min	
1	–	60	40	5	1	25.7	75	115/0.34
2	10	60	30	5	1	25.5	70	112/0.34
3	20	80	–	5	1	26.7	80	108/0.31
4	30	70	–	5	1	26.0	75	110/0.32
5	OPC CEM II/A-400 (reference)					27.8	85	112/0.38

three years curing samples might harden over 150% of the strength obtained after 28 days.

At the same time, AAFA concrete shows other interesting properties (Grabovchak, 2013; Krivenko et al., 2014; Krivenko et al., 2005; Kovalchuk and Grabovchak, 2013; Krivenko et al., 2010): (i) high-corrosion resistance in sea water, in Na_2SO_4 (10% concentration) and $MgSO_4$ (up to 4% concentration) solutions; (ii) low shrinkage; (iii) high freeze-thaw resistance. These concretes are highly advantageous in massive structures prepared in situ; and (iv) high-temperature resistance (heat- and fire-resistant concretes). Residual strength of such materials after burning at 800°C could reach 500% comparing with the strength in normal conditions.

The durability of AAFA concretes is similar to that of previously presented AAS concretes. Sulfate resistance is outstanding and has no analogs among the traditional materials. There were obtaining concretes with strength classes C15–C40. Frost resistance, weather resistance, water impermeability, and other service properties are similar to those of traditional concretes (Kovalchuk and Grabovchak, 2013; Krivenko et al., 2010).

7.3.3.2 Radiological properties

The discussion below deals both with the radiological properties of alkali-activated cements and concretes produced on the basis of blast-furnace slag and coal fly ash since in most cases AAMs will merge several by-products that contain naturally occurring radionuclides.

The radiological properties of geopolymers or alkali-activated cement pastes have been recently studied in detail by Puertas et al. (2015a,b). Sample preparation and activation conditions used are shown in Table 7.16.

The radionuclide activity concentrations in alkaline cement pastes (Wg-AAS, Glass-AAS, N/15Wg-AAFA, and Glass-AAFA) (see Table 7.17) have been calculated considering the percentage of slag or fly ash in the anhydrous geopolymers and in the activated end products. It needs to be noted that the ^{40}K concentration

Table 7.16 Sample preparation and activation conditions of geopolymers used to study radiological features (Puertas et al., 2015a,b)

Sample	**Solution**	**liquid-to-solid ratio**	**SiO_2/ Na_2O**
Water glass-AA Slag	Sodium silicate	0.4	0.86
Glass-AASlag	$NaOH/Na_2CO_3$ + glass waste	0.4	0.86
N/15Wg-AA fly ash	NaOH 10 M + sodium silicate	0.3	0.19
Glass-AA fly ash	NaOH 10 M + glass waste	0.3	0.11

Table 7.17 **Activity concentrations in raw materials (fly ash, BFS, and waste glass) and cements after alkaline activation (in Bq/kg) (uncertainty, $k = 2$) (Puertas et al., 2015a,b)**

Series	^{238}U		^{232}Th			^{40}K	Index[a]
Material	^{234}Th	^{214}Pb	^{228}Ac	^{212}Pb	^{208}Tl		
Fly ash	130 ± 7.1	127.4 ± 1.3	130.3 ± 1.5	133.8 ± 1.3	41.33 ± 0.57	316.4 ± 5.9	1.1815 ± 0.0089
BFS	156.4 ± 6.8	147.2 ± 1.4	45.7 ± 0.86	42.9 ± 1.2	14.71 ± 0.30	76.3 ± 2.7	0.7448 ± 0.0065
Waste Glass	11.4 ± 1.1	8.73 ± 0.19	5.83 ± 0.22	6.28 ± 0.12	1.867 ± 0.075	226.8 ± 4.4	0.1338 ± 0.0020
Wg-AAS	91.5 ± 5.6	48.7 ± 1.1	22.84 ± 0.71	23.3 ± 0.69	7.7 ± 0.39	77.0 ± 5.0	0.3022 ± 0.0054
Waste Glass-AAS	94.4 ± 6.7	54.5 ± 1.4	23.78 ± 0.81	24.99 ± 0.83	8.04 ± 0.41	89.2 ± 4.8	0.3303 ± 0.0064
N/15Wg-AAFA	56.4 ± 5.7	36.44 ± 0.97	67.8 ± 1.4	75.1 ± 1.8	21.57 ± 0.59	578 ± 15	0.6531 ± 0.0092
Waste Glass-AAFA	57.4 ± 3.2	37.9 ± 1.1	62.2 ± 1.2	75.1 ± 1.2	22.62 ± 0.63	550 ± 14	0.6207 ± 0.0084

[a] Note that the *I*-index, as proposed by Council Directive 2013/59/Euratom, is only used for building materials or for their constituents if the constituents are also building materials: An *I*-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material.

increases in such activated materials because the potassium impurities, that are often present in the NaOH activator, result in an increased ^{40}K potassium content in the end product.

A paper of the radiological characterization and impact of alkali-activated concretes has been recently published (Nuccetelli et al., 2017). The publication reports results of a study on five different types of fly ash from Serbian coal burning power plants and their potential use as a binder in alkali-activated concrete (AAC), depending on their radiological and mechanical properties. Five AAC mixtures with different types of coal burning fly ash and one type of blast-furnace slag were designed. Measurements of the activity concentrations of ^{40}K, ^{226}Ra, and ^{232}Th were done both on concrete constituents (fly ash, blast-furnace slag, and aggregate) (see Table 7.18) and on the five solid AAC samples (see Table 7.19). Experimental results were compared by using the activity concentration assessment tool for building materials—the activity concentration index I, as introduced by the RP 112 and EU Basic Safety Standards [RP 122, 1999;24] and in Chapter 4. All five designed alkali-activated concretes comply with EU BSS screening requirements for indoor building materials. Finally, the index I values were compared with the results of the application of a more accurate index-I (ρd), which accounts for thickness and density of building materials (Nuccetelli et al., 2015a) and the annual dose, evaluated with an accurate formula accounting for the actual density and thickness of the AAFAC concrete sample, was also calculated. Considering the actual density and thickness of each concrete sample index-I (ρd) values are lower than index-I values and the annual dose resulted negative, once the background is subtracted, in three cases

Table 7.18 **Natural radionuclide activity concentrations in Serbian fly ash and blast-furnace slag samples used in alkali-activated concretes (Nuccetelli et al., 2017)**

	^{232}Th	^{226}Ra	^{40}K	index I[a]
	(Bq/kg)			
Fly ash-1	90.9 ± 1.7	123 ± 5	445 ± 7	1.01
Fly ash-2	112 ± 2	163 ± 5	416 ± 7	1.24
Fly ash-3	42.7 ± 0.8	56.2 ± 2.1	199 ± 3	0.47
Fly ash-4	66.0 ± 1.2	151 ± 5	393 ± 6	0.96
Fly ash-5	78.3 ± 1.5	152 ± 4	369 ± 6	1.02
Blast-furnace slag	26.5 ± 0.5	108 ± 3	122 ± 2	0.54
Fly ash from RP112 (EC, 1999)	100	180	650	
Fly ash (Nuccetelli et al, 2015b)	80	207	546	
Slag from RP112 (EC, 1999)	70	270	240	
Slag[b]	63	147	246	

[a] Note that the *I*-index, as proposed by COUNCIL DIRECTIVE, 2013/59/EURATOM, is only used for building materials or for their constituents if the constituents are also building materials: An *I*-index given for a by-product makes the unrealistic assumption that 100% of the by-product is used as a building material.
[b] Based on new elaboration of national values given in the EU database.

Table 7.19 **Natural radionuclide activity concentrations of alkali-activated concretes (AAC) samples: calculation of index *I*, index *I* (*ρd*), and gamma dose**

AAC samples	**^{232}Th**	**^{226}Ra**	**^{40}K**	**index I**	**I (*ρd*)**	**D(*ρd*) (mSv/year)**
		(Bq/kg)				
AAC-1	18.4 ± 0.4	28.5 ± 1.5	232 ± 4	0.26 ± 0.01	0.23 ± 0.01	0.8E-02 ± 1.0E-02
AAC-2	18.6 ± 0.4	28.8 ± 1.3	225 ± 4	0.26 ± 0.01	0.24 ± 0.01	1.4E-02 ± 0.9E-02
AAC-3	12.5 ± 0.2	21.2 ± 0.9	196 ± 3	0.20 ± 0.01	0.18 ± 0.01	−6.4E-02 ± 0.6E-02
AAC-4	14.9 ± 0.3	27.7 ± 1.7	218 ± 3	0.24 ± 0.01	0.21 ± 0.01	−1.6E-02 ± 1.0E-02
AAC-5	16.1 ± 0.3	28.3 ± 1.2	197 ± 3	0.24 ± 0.01	0.21 ± 0.01	−1.9E-02 ± 0.8E-02

and less than 2.3E-02 mSv, with uncertainties, in the other two cases. In the paper, a synthesis of main results concerning mechanical and chemical properties has also been provided.

7.3.4 Steel-melting slags

7.3.4.1 Technical properties

The chemical-mineralogical composition of steel-melting slags varies within wide ranges, and this is the major drawback for recycling (Krivenko, 1986).

Alkali-activated cements made from basic steel-melting slags cured for 28 days in normal conditions show compressive strengths of 15–20 or 20–30 MPa when sodium carbonate or sodium di- and metasilicate are used as activators, respectively. Appreciable hardening is observed at later ages (Kavalerova et al., 2000): 30–42 MPa with sodium carbonate and 46–58 MPa with sodium metasilicate after 1 year; 40–50 and 60–70 MPa, respectively, for the same activators, after 4 years.

Mixtures formulated with low-basic glassy steel-melting slags tend to show slower hardening rates: only by the third day of normal curing the material acquires the resistance achieved after 24 h by the cements made from basic slags. The high-basic steel-melting slags are even less reactive and 14 days curing are required to get the strength of a basic slag formulation after 24 h.

One way to accelerate the hardening rate of such slow reactive systems is mixing with granulated blast-furnace slag. When properly combined with a high-basic crystallized steel-melting slag the obtained mixture acts as a quick-hardening cement: compressive strengths of 52–62, 66–80, and 90–110 MPa after 3, 7, and 28 days curing. The use of these slags also as aggregates in concrete mixtures can increase their consumption rates to up to 90 wt% of the final composition of the construction material (Kavalerova et al., 2000).

7.3.4.2 Radiological properties

The radiological properties for different types of steel-melting slag are reported in Chapter 6. These properties can be used for screening of these residues for use in building materials.

No publications with radiological information on alkali-activated cements or alkali-activated concretes containing steel-melting slags were found.

7.3.5 Red mud

7.3.5.1 Technical properties

The use of red mud in alkali-activated cements was studied in detail by Rostovskaya (1994). Well-succeeded attempts to incorporate high-mass percentages in the formulations (between 25% and 60% by total bindermass) were conducted, by the proper combination of red mud with glassy low-basic aluminosilicate compounds (blast-furnace slag, steel-melting slags) and high-basic Ca-containing additives (nepheline sludge, OPC), which are known to hydrate intensively in a highly alkaline environment. The alkali-activated cement containing red mud (60% by mass), ground-granulated blast-furnace slag (30% by mass), and OPC (10% by mass), using sodium silicate ($Ms = 2.8$, $\rho = 1300\ \mathrm{kg/m^3}$) as alkaline activator, showed compressive strengths of 6.2, 30.3, and 60.0 MPa at 2, 7, and 28 days curing ages, respectively. Hydration products phase composition depends on the constituent composition but in general is constituted by a low-basic calcium hydrosilicate crystalline phase and an aluminosilicate and ferrosilicate gel phase. The concretes made using these cement formulations have high-frost resistance (200–500 cycles) and reduced shrinkage (0.16–0.20 mm/m).

There are substantial works done in incorporating bauxite reside in geopolymer composites formation (Dimas et al., 2009; He et al., 2013; Ye et al., 2014; Badanoiu et al., 2015). Different compositions and precursors (metakaolin, blast-furnace slag) were used with different activator conditions and preparations. Some authors (Ye et al., 2014) obtained mixing granulated blast-furnace slag in varying proportions with calcined red mud (800°C) specimens with 50 MPa after 28 days in a 50–50 wt% mix. In general terms, all of described inorganic polymers are characterized by a significant decrease in compressive strength with an increasing content of bauxite residue.

More chemical activity was found when the bauxite residue is thermally activated. More recently Hertel et al. (2016) treated the bauxite residue at 1100°C with carbon and silica. The resulting material was activated with K-silicate solution and was cured at 60°C for 72 h. The final material obtained with around 88.6 wt% bauxite red mud, 1.4 wt% carbon, and 10.0 wt% SiO_2 reached more than 40 MPa compressive strength. A potential application of these construction materials should be pavements tiles or floor/roofing tiles.

In addition, the results (Rostovskaya, 1994) showed that red mud can also be used as an aggregate in concrete products produced by semidry pressing. This allows reaching incorporation rates of the red mud up to 75 wt%. Compressive strength of these products ranges from 20 to 40 MPa.

An example for a mix design for geopolymer concrete incorporating red mud and ggbs (compared with regular concrete) is given in Table 7.20.

7.3.5.2 Radiological properties

The content of naturally occurring radionuclides in red mud is discussed in Chapter 6. This section deals with the resulting radiological properties of AAMs incorporating higher percentages of red mud.

By knowing that cumulative radiation activity of the red mud used is 599 Bq/kg, according to Ukrainian legislation the designed concrete products containing 60 wt% red muds can be used without restrictions in all fields of construction. Those formulated with 60–75 wt% waste can be used in road and airfield construction including in residential areas, while the concretes incorporating 90 wt% red muds can only be used in road, hydro engineering, and industrial constructions (Rostovskaya, 1994).

Table 7.20 **Example of mix design for reference concrete and an alkali-activated concrete with red mud and ggbs (kg/m^3)**

Raw materials	Reference concrete	Concrete containing red mud as a partial replacement of cement and concrete
Portland cement	400	
Alkaline cement included ggbs—400; alkaline component —50	0	450
Coarse and fine aggregates	1850	0
Red mud as partial replacement of aggregates	0	1800
Water	150	150
Total	2400	2400

The study by Croymans et al. (2017) involves the radiological characterization of different types of alkali-activated concretes containing (up to 90 wt%) red mud from Ukraine. The authors measured activity concentrations of natural radionuclides, used different types of indexes (the index proposed by the EU-BSS and the index proposed by Markkanen (1995) for "materials used for constructing streets and playgrounds") to evaluate the public exposure and RP122 to evaluate the occupational exposure.

Based on the mixing design in Table 7.20 and the activity concentrations given in Table 7.21, an *I*-index calculation for geopolymer concrete containing red mud and ggbs was made and the result is given in Table 7.22.

7.3.6 Nonferrous slag

7.3.6.1 Technical properties

In this section the technical properties of nonferrous slags (such as lead, nickel, and copper slag) that determine its use in construction materials are discussed.

Modulus of basicity ($Mb=(CaO+MgO)/(Al_2O_3+SiO_2)$) of the nonferrous slags under study by Krivenko et al. (1984) varied from 0.30 to 0.60, while the crystalline phase content was 1–5 wt%. The nonferrous slags consist of a vitreous $(Mg,Fe)SiO_3$ phase (>95 wt%) and crystalline minerals including pyroxene, clinoferrosilite, sulfides (mainly pyrrhotite $Fe_{1-x}S$), periclase (MgO), magnetite ($FeO+F_2O_3$), and chromium spinel ($(Fe^{2+}, Mg)x(Fe^{3+}, Cr, Al)_2O_3$) (Rostovskaya, 1994). Since the iron content might strongly affect the alkaline activation of such slags, a so-called quality index (K) has been introduced (Krivenko et al., 1984):

$$K=\frac{CaO+MgO+Al_2O_3+Fe_2O_3+1/2FeO}{SiO_2+1/2FeO} \tag{7.2}$$

Table 7.21 Typical activity concentration index for concrete constituents in concrete compositions containing red mud in Europe

Raw materials	Typical activity concentrations [^{226}Ra, ^{232}Th, ^{40}K] (Bq/kg)	*I*-index	Reference
Portland cement	[45; 31; 216]	0.38	Trevisi et al. (2012)
Aggregates	[36; 34; 483]	0.45	Trevisi et al. (2012)
Blast-furnace slag (Poland)	[115.33; 34.55; 192.33]	0.62	Żak et al. (2008)
Red mud (Italy)	[97; 118; 15]	0.9	Minimum EU value (Table 15 of Chapter 6)
Red mud (Turkey)	[210; 539; 112]	3.4	Maximum EU value (Table 15 of Chapter 6)

The *I*-index calculation is based on European Commission 1999; Radiation Protection 112; Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials; and Directorate-General, Environment, Nuclear Safety and Civil Protection.

Note that the *I*-index, as proposed by Council Directive 2013/59/Euratom, is only used for building materials or for their constituents if the constituents are also building materials: An *I*-index given for a by-product or cement makes the unrealistic assumption that 100% of the by-product or cement is used as a building material.

Table 7.22 *I*-index for regular concrete and geopolymer concrete compositions containing red mud.

Raw materials	Reference concrete	Alkali-activated concrete containing red mud and blast-furnace slag
Maximum activity of red mud ($I = 3.4$)	0.41	2.67
Minimum activity of red mud ($I = 0.9$)	0.41	0.79

According to this quality index, nonferrous slags can be classified into three types as shown in Table 7.23 (TU 67–648-84, 1984).

Expected compressive strength values of the alkali-activated nonferrous slag cements hardened in normal conditions versus quality index and type of alkaline activator used in the process is given in Table 7.24 (Sultanov, 1985). Strength of optimal formulations can reach 100 MPa, depending on the cement type and its content, type of alkaline activator, and curing conditions. The concretes obtained by using such cements show low heat evolution, high-freeze-thaw resistance, high-abrasion resistance and can assure nuclear radiation protection.

Table 7.23 **Characterization of nonferrous slags in terms of chemical composition and according to the activity quality index**

Characteristics	Compositional classes		
	I	II	III
Quality index	>1.0	0.7–1.0	<0.7
Content of silicon oxide (SiO_2), wt%	26.0–32.0	33.0–52.0	33.0–52.0
Calcium oxide (CaO) and magnesium oxide (MgO) contents, wt%, no more than	>20.0	>17.0	>8.0
Content of iron (II) oxide (FeO), no more than	<30.0	<30.0	<35.0

Table 7.24 **Compressive strength (MPa) of the alkali-activated nonferrous slag cements hardened in natural conditions vs. quality index and type of alkaline activator**

Alkaline activator	Values of quality index		
	$K>1$	$0.7 \leq K \leq 1$	$K<0.7$
Sodium carbonate	30–40	10–30	–
Soda-alkali melt (waste of chemical industry)	30–40	10–30	–
Sodium silicate (Ms = 2.8)	30–40	20–30	10–20
Sodium disilicate (Ms = 2.0)	50–80	30–50	20–30
Sodium metasilicate (Ms = 1.0)	50–80	30–50	20–40
Caustic alkali	20–30	10–20	–

7.3.6.2 Radiological properties

The activity concentrations of naturally occurring radionuclides in nonferrous slag are discussed in Chapter 6. These values can be used for the evaluation of concretes depending of the percentage of nonferrous slag incorporation.

No publications with radiological information on alkali-activated cements or alkali-activated concretes containing nonferrous slags were found.

7.3.7 Granulated phosphorus slag

7.3.7.1 Technical properties

Granulated phosphorus slag is a latent cementitious material but less reactive than granulated blast-furnace slag at early age due to the lower Al_2O_3 content and the presence of P_2O_5 and F. A hydraulic index of phosphorus slag is defined as follows (Shi et al., 2006; RCT 5024-83, 1983):

$$K = \frac{CaO + MgO + Al_2O_3}{SiO_2 + P_2O_5} \tag{7.3}$$

Latent cementitious properties of granulated phosphorus slag can be very effectively triggered by alkaline activation.

The phase composition of cement hydration products is chiefly represented by tobermorite 1.13 nm. With addition of Portland cement, the intensity of tobermorite occurrence is higher and lines (peaks) characteristic of truscottite $(Ca,Mn)14Si_2 4O_{58}(OH)_8 \cdot 2H_2O$—a mineral of the reyerite *group* and wenkite—$Ba_4Ca_6(Si,Al)_{20}O_{41}(OH)_2(SO_4)_3 \cdot H_2O$—a mineral of the cancrinite-sodalite *group* appears in the X-ray diffraction patterns (Sanserbaev, 1987).

Experience obtained from the use of concrete and reinforced concrete structures from these cements in industrial, hydro engineering, and agricultural construction coincides well with assumption on the higher durability compared with those made from Portland cement concretes (Krivenko et al., 1993).

7.3.7.2 Radiological properties

No publications with radiological information on alkali-activated cements or alkali-activated concretes containing granulated phosphorus were found.

7.3.8 Overall discussion of radiological aspects of alkali-activated cements and concretes

The legislation and the methodology used for the evaluation of the radiological aspects of construction materials is discussed in, respectively, Chapters 4 and 5. The radiological properties of the by-products themselves are given in Chapter 6.

It is clear from the literature that currently (Jan. 2017) there is very little information on the radiological properties of alkali-activated cements and concretes. This is a logic situation since this type of materials is still in the research stage and there are only a limited amount of commercial applications. Alkali-activated cements and concretes can allow the incorporation of larger percentages of by-products (in comparison to Portland cements and concretes). This is one of the features that makes alkali-activated cements and concretes attractive for future applications, but also implies the requirement to control these materials from a radiological point of view. This aspect was illustrated by studies on fly ash, slag, and red mud containing alkali-activated concretes.

A good assessment regarding the activity concentration index of alkali-activated concretes can be obtained via dilution calculations if the activity concentrations of the natural occurring radionuclides in the by-products are known. Much harder is to make an assessment regarding radon exhalation/emanation from alkali-activated concretes, this will require additional measurements.

7.4 Ceramics

7.4.1 Introduction

Many industrial by-products and wastes are utilizable in the ceramic technology to substitute raw materials. The most used by-products are (i) fly ashes from power plants, incinerator of municipal wastes, and pyro metallurgical plants on the condition that they do not contain high percentages of lead or zinc; (ii) synthetic gypsum arising from sulfur decontamination of gaseous effluents; (iii) red mud from the Bayer process; (iv) foundry slags; (v) residues from the flotation process employed in the enrichment of metal containing ores; (vi) mining tails; and (vii) asbestos containing residues or asbestos fibers.

Several organic materials can usefully be employed in the ceramic technology to produce porous ceramics, while their burning is a source of energy. They mainly are (i) paper production sludges; (ii) fertilizer residues; (iii) sludge from domestic wastewater or sewage treatment; and (iv) plastics.

Literature reports several ceramic products containing wastes (Pelino, 1997; Dondi et al., 1997; Perez et al., 1996; Lee et al., 2007; VII Conference of the European Ceramic Society, 2001). They include dense and lightweight bricks, roofing tiles, paving tiles, filters, refractories, and glass-ceramics. Recycling by the ceramic technology has several advantages: (i) Possibility of substituting mining raw materials whose cost is growing due to the increasing cost of mining and land restoration; (ii) simple processes using mature technologies; (iii) fast firing cycles with high-energetic efficiency; (iv) controlled/standardized production; and (v) possibility of commercial exploitation in the large market of building materials.

The main disadvantages are related to constrains in the use of hazardous wastes and this aspect is linked to the residual porous microstructure of the ceramic material. If the microstructure is too porous, the ceramic might show low chemical resistance and enhanced leachability. On the other hand, dense products require higher temperatures and/or longer firing cycles, so the energy demand on processing is higher and final product is heavier. This goes against the sustainability principles that recommend the production/use of light materials showing less embodied energy.

The ceramic industry itself also uses zircon and zirconia (in glazes, refractories, etc.), and radiological consequences of their production, further use/manipulation by other industrial sectors (e.g., ceramic glazes and frits production), and on the final costumers also deserve a brief analysis at the end of this chapter.

7.4.2 Coal fly ash

7.4.2.1 Technical properties

The similarity in chemical (mainly SiO_2 and Al_2O_3) and granulometric composition of fly ash and traditional raw materials makes fly ash suitable to be used in certain ceramic formulations. The marginal presence of residual carbon and heavy metals in fly ash are tolerated without problems due to the fact that the temperature employed for ceramics production is in general above 1000°C and promotes an effective incorporation of those elements in the ceramic matrix.

In the fabrication of dense ceramics, distinct fly ash samples collected at different zones of the electro filter (fly ash particle morphology in Fig. 7.5A) were mixed with clay. Fig. 7.5B shows the typical microstructure of the ceramic presenting optimal properties: porosity = 2.96 ± 0.5%, bending strength = 47 ± 2 MPa, and compressive strength = 170 ± 5 MPa. This sample was fabricated by using fly ash taken from the fourth zone of electro filter, showing particle size below 0.063 mm. The material was pressed at 133 MPa and then fired at 1100°C, using heating rate of 10°C/min. Upon sintering, diopside [$Ca(Mg,Al)(SiAl)_2O_6$] was formed and this phase is the main responsible for the properties, due to the interlocking microstructure of the crystals (Angusheva et al., 2012). Fly ash-clay blends containing distinct fly ash contents (from 10 to 90 wt%) were prepared and fired at 900–1100°C for 1 h. Fig. 7.5C exemplifies the microstructure of 40 wt% fly ash—60 wt% clay blend, pressed at 45 MPa and then fired at 1100°C for 1 h. This material shows optimal properties, i.e., density = 2.09 g/cm^3, water absorption = 7.02%, bending strength = 50.47 MPa, and E-modulus = 25.35 GPa (Fidancevska et al., 2014).

Jung et al. (2001) report the fabrication of low dense (63% of theoretical density) mullite ceramics from the mixture of coal fly ash and alumina. A mixture was formulated aiming to obtain the stoichiometric mullite (71.8 wt% Al_2O_3 and 28.2 wt% SiO_2). The shape and size of mullite particles control the relevant properties of the fired material, namely the pore structure and fracture strength. The addition of 3Y-PSZ particles (globular-shaped) inhibited grain growth of mullite particles and enhanced densification and the mechanical resistance: bending strength = 395 MPa was obtained for samples sintered at 1500°C for 2 h.

Lightweight building bricks (Cicek and Cincin, 2015) obtained by mixing fly ash (88 wt%) with lime (12 wt%) were produced in a pilot-scale autoclave (cured for 6 h at 12 bars of steam pressure). Samples show water absorption = 60.9%, compressive strength = 7.65 MPa, and flexural strength = 0.56 MPa. Their thermal conductivity was 0.225 W/mK, which is comparable to an aerated cellular concrete and much lower than of common clay bricks.

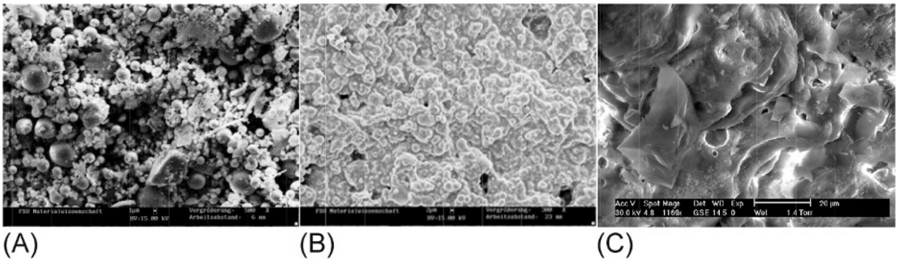

Fig. 7.5 (A) Fly ash particle morphology; (B) dense fly ash compacts sintered at 1100°C for 1 h; (C) dense fly ash-clay blend also sintered at 1100°C for 1 h.

Further studies on the effect of fly ash milling on the properties of dry pressed ceramics composed of 70 wt% fly ash and 30 wt% stoneware clay are reported by Sokolar and Smetanova (2010). In the Netherlands one company is producing over decades a ceramic brick which contains ca 30 wt% of fly ash, 30 wt% of mine stone and clay (Roelofs and Wiegers, 1995). From measurements conducted in the 1990s, it was found that the level of radionuclides does not differ much from the one of common ceramic bricks produced in the Netherlands.

Another option for utilization of coal fly ash is production of glass-ceramics (Rawlings et al., 2006; Leroy et al., 2001; Lyer and Scott, 2001). According to Kim and Kim (2004) there are several ways to modify the composition of the fly ash for this application: (i) combination with other inorganic wastes such as glass cullet (composed by SiO_2, CaO, and Na_2O); (ii) addition of CaO and MgO as a float dolomite to promote the formation of amorphous materials; (iii) by adding TiO_2 as nucleating agent, (iv) by adding CaO and Na_2O as fluxing additives. Coal fly ash-containing glass-ceramics were produced by melting/quenching + thermal treatment (Deguire and Risbud, 1984). The material was melted (at 1500°C when no fluxing additives are used) and the glass was poured into graphite molds. Unusual two-stage nucleation treatment was then used: (a) 2 h at temperature between 650°C and 750°C + (b) 5–10 h at 800–950°C. Finally, the crystallization stage was done at temperature ranging from 1000°C to 1150°C. Further studies conducted by the same authors led to the conclusion that a single nucleation stage might be used instead. Some other authors (Barbieri et al., 1990) reported the development of glass-ceramics from coal fly ash, guided by the phase diagrams to anticipate the phase composition and properties of the material.

Bossert et al. (2004) reported the production of dense and porous glass-ceramics through the powder processing technology. Fly ash and waste glass (from TV monitors, windows, and flasks) were used as starting raw materials. Mixtures composed of 50 wt% fly ash and 50 wt% glass properly processed show bending strength of about 56 MPa and E-modulus near 26 GPa. Porous glass-ceramics was obtained by adding polyurethane foam (Fig. 7.6A) or C-fibers (Fig. 7.6B). E-modulus and bending strength values of the porous glass-ceramic samples were 2.7 ± 0.5 GPa and 4.5 ± 1 MPa when polyurethane foam is used; 7.1 ± 1 GPa and 9.3 ± 2 MPa for C-fibers.

Similar studies were conducted by Wu et al. (2006) but using ≤ 5 wt% fine SiC particles (5–25 μm) as pore creator. Wollastonite was the major crystalline phase detected while the porosity ranged from 70% to 90%. Pore size varied between 0.2 and 1.5 mm, depending on the sintering temperature.

7.4.2.2 Radiological properties

Fly ash (see Fig. 7.5A) from the thermal power plant REK Bitola, Republic of Macedonia, shows the following concentration of natural radionuclides: ^{266}Ra: 59 ± 6 Bq/kg; ^{232}Th: 76 ± 8 Bq/kg; and ^{40}K: 376 ± 29 Bq/kg. Depending on the wt % of incorporation and the activity concentration of the other constituents, the resulting activity concentration index for the fly ash containing ceramics can be calculated.

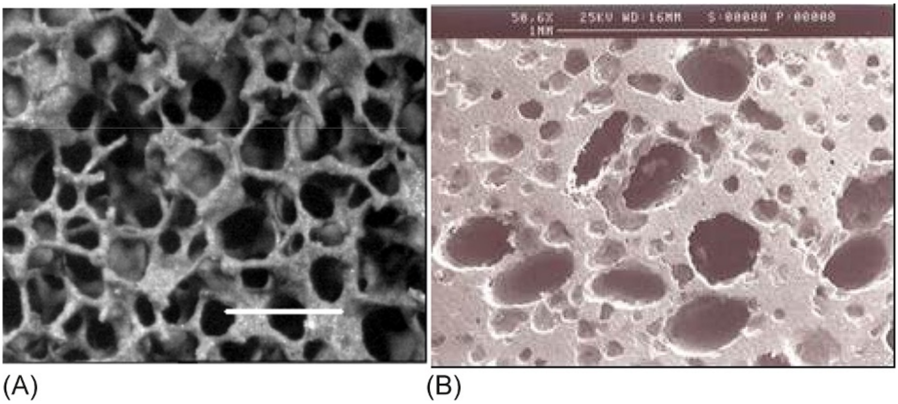

Fig. 7.6 Macrostructures of porous glass-ceramics obtained by using polyurethane foam (A) or C-fibers (B) as pore forming agents. The bar corresponds to 1 mm.

The data from Chapter 6 can be used to calculate the activity concentration index when other types of fly ash are used.

7.4.3 Steel slag

7.4.3.1 Technical properties

Guo et al. (2011) and Khater (2002) used steel slag into the preparation of glass-ceramics. Shih et al. (2004) found that an appropriate addition of such slag could reduce the firing temperature of clay bricks. The waste was also used to produce colored paving bricks and tiles (Chen et al., 2010), and Lianyuan steel invented steel slag baking-free load-bearing tiles (Shinkai et al., 1997). The recycling of Ladle Slag (from secondary metallurgy) in the production of bricks was reported by Shinkai et al. (1997). The granulation of slag particles was introduced by Kojimori et al. (2003).

7.4.3.2 Radiological properties

In all cases, limited incorporation levels might be applied, without deleterious effects on the final properties of the products. No radiological features were reported for ceramics based on steel slag. The data from Chapter 6 on steel slag (Section 6.4.1.2) can be used to evaluate the activity concentration index for ceramics containing steel slag.

7.4.4 Aluminum-rich by-products

7.4.4.1 Technical properties

The recycling of aluminum generates slag and *dross*, both normally classed as hazardous wastes, can occur via ceramics products. The properties of by-product aluminum dross are discussed in Chapter 6.

Despite its potential hazardous character, alumina richness is an attractive aspect favoring its recycling. The two reutilization areas mostly explored are (Yoshimura et al., 2008): (i) refractories and (ii) composites (Al-alumina composites).

Lightweight expanded clay aggregates were produced from natural plastic clay and aluminum scrap recycling waste (ASRW), which were obtained as a result of recovering Al metal from black dross by using conventional metallurgical process (Bajare et al., 2012). ASRW contains aluminum nitride (AlN—on average 5 wt%), aluminum chloride ($AlCl_3$—on average 3 wt%), potassium and sodium chlorides (total 5 wt%), and iron sulfite ($FeSO_3$—on average 1 wt%). Its average chemical composition is given in Table 7.25, while the elemental analysis is shown in Table 7.26.

The decomposition of volatile elements, present in the nitride, sulfite, and chlorides, will generate gases upon firing and the aluminum scrap recycling waste might act as a pore forming agent. The ceramic aggregates were produced from mixtures of carbonaceous clay and ASRW in distinct proportions (ASRW ranging from 9 to 37.5 wt%). The prepared aggregates were dried for 3 h at 105°C and then calcined for 5 min at various temperatures, ranging from 1150°C to 1270°C. Heating rate was kept constant (15°C/min). Physical and microstructural properties of sintered aggregates were then evaluated.

Apparent density of the aggregates ranged from 0.4 to 0.6 g/cm^3. The pore structure is shown in Fig. 7.7, consisting of macropores with 1 mm mean diameter and micropores (size below 0.2 μm).

According to Pereira et al. (2000a), the salt slag generated from the smelting of secondary aluminum can be used in refractory bricks. Typical industrial processing conditions were followed. The incorporation of slag tends to improve the physical and mechanical characteristics of the ceramic material, due to its fluxing action. Higher incorporation levels (ca. 10 mass-%) are admissible. The same authors tested the incorporation of Al-rich salt slag in bauxitic-type refractories (Pereira et al., 2000b). It was concluded that it is possible to incorporate washed aluminum salt slags in bauxitic-type refractories. In general, the physical properties of the fired material

Table 7.25 **Average chemical composition of aluminum scrap recycling waste (wt%) (Bajare et al., 2012)**

LOI, 1000°C	Al_2O_3	SiO_2	CaO	SO_3	TiO_2	Na_2O	K_2O	MgO	Fe_2O_3	Others
6.21	63.19	7.92	2.57	0.36	0.53	3.84	3.81	4.43	4.54	>2.6

Table 7.26 **Elemental analysis of aluminum scrap recycling waste (wt%) (Bajare et al., 2012)**

Al	Si	Ca	Mg	Fe	Na	K	Cl	S	Cu	Pb	Zn
34.4	4.4	1.32	2.44	3.60	1.69	2.31	4.23	0.07	0.99	0.14	0.6

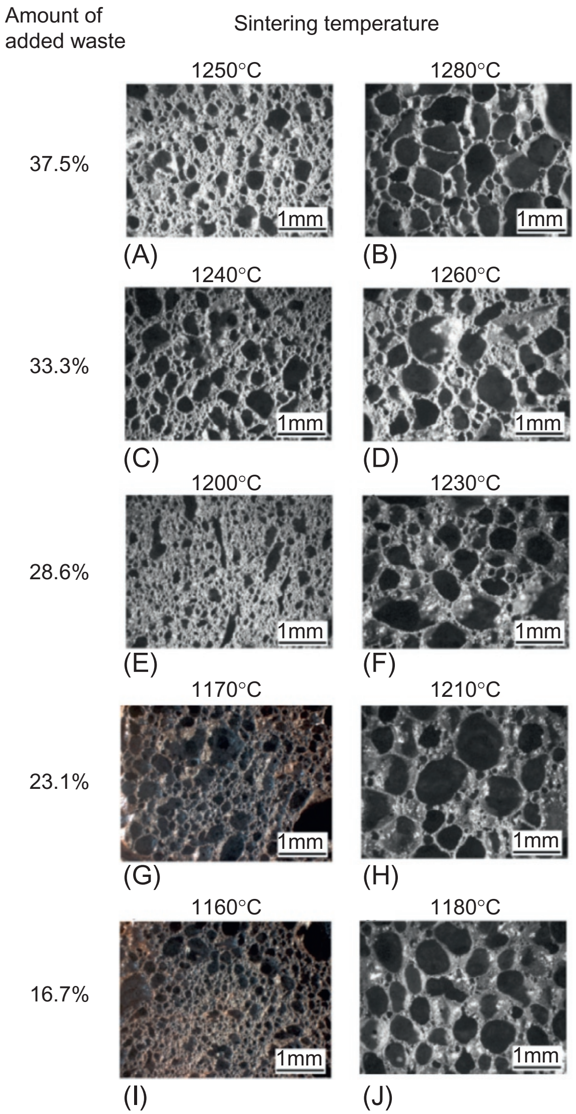

Fig. 7.7 Pore structure of aggregates produced from blends of clay and ground and aluminum scrap recycling waste (wt% is shown) and fired at distinct (given) temperatures (Bajare et al., 2012).

tend to be improved with increasing slag contents (e.g., higher flexural strength). The fluxing characteristics of the slag might explain this effect. From a functional point of view, significant incorporation levels (18 wt%) are permitted.

Anodizing and powder surface coating processes are highly water consuming, not only in each consecutive chemical batch, but also to properly wash the pieces in between. As a direct consequence, a huge amount of wastewater is generated and, after proper treatments, it results in clean water and a high amount of solid waste, denominated aluminum sludge (BREF, 2006; Magalhães et al., 2005).

The clay brick ceramic industry might constitute an interesting alternative to land disposal of sludge. Marques et al. (2012) aimed to develop a thermal-resistant brick via the recycling of the aluminum sludge in bricks production. They used the production cycle of the brick plant and tried a full-scale test in brickwork, producing 10 tons of real bricks. As a conclusion anodizing sludge addition enhances the thermal behavior of bricks by 26%, without increasing the brick production cost, leading to a clear improvement of buildings' thermal comfort. The remaining physical-mechanical properties (water absorption and compression strength) of bricks still present suitable values (Marques et al., 2012).

The goal of Khezri et al. (2010) was to find an application for utilizing the sludge cake of aluminum anodizing units in order to prevent environmental pollution and finding economic profit for the factories. For this purpose, bricks with different combination of sludge, clay, and sand were made and tested with available standard. The result showed that bricks containing 40 wt% sludge have best and nearest quality standardized parameters of ordinary inner bricks. These bricks have lighter weight than the bricks in same bulk and cheaper price and also prevent sludge spreading in the environment.

Ozturk (2014) studied the utilization of anodizing sludge which is produced at high tonnages in one of the aluminum company in Turkey (Table 7.27). The research goal was the production of mullite ceramics from Al-rich sludge which contains 15–30 wt% of solid matter (90 wt% of the solid matter is boehmite (AlOOH) and the remaining is thenardite (Na_2SO_4) and barite ($BaSO_4$)).

Mullite is the stable crystalline alumino-silicate phase in the Al_2O_3-SiO_2 system and contributes to high-performance strength, creep resistance, chemical inertness, and thermal stability in ceramic materials (Martins et al., 2004).

Ozturk (2014) applied a washing, filtering, and drying process to the anodizing sludge in order to remove sodium before the production of mullite ceramics. The sodium removal cycle was repeated until sodium was completely removed from the sludge. Then, the sodium-free powder is calcined at 1400°C for 1 h at a heating rate of 5°C/min to obtain a powder with alpha alumina (α-Al_2O_3) phase. The produced α-Al_2O_3 powder was mixed (42 wt%) with kaolin, diatomite, and clay at proportions 15%, 28%, and 15 wt%, respectively. The mixture was dry pressed and sintered at 1450–1550°C for 1–5-h (Sample code M1). The results are compared with other mixture which is prepared by using Alcoa commercial α-Al_2O_3 powder (Sample code M2). As a conclusion of the work it was found that if appropriately treated and mixed with natural mineral additives, the anodizing sludge can be utilized in the production of mullite-based ceramic materials (Table 7.28) (Ozturk, 2014).

Table 7.27 Chemical composition of Al-rich anodizing sludge (wt%, XRF) (Ozturk, 2014)

Al-rich sludge	Al_2O_3	SiO_2	Fe_2O_3	CaO	SO_3	Na_2O	K_2O	MgO	BaO
	70.9	0.78	0.31	2.06	20.2	2.95	0.03	0.97	1.20

Table 7.28 **Physical and mechanical properties of sintered M1 and M2 samples**

Composition	Sintering conditions	Bending strength (MPa)	Density (g/cm^3)	Porosity (%)	Water absorption (%)	Densification (%)
M1	1450°C—1 h	53	2.02	26.1	12.88	63.9
	1500°C—1 h	54	2.27	13.1	5.76	71.8
	1550°C—1 h	80	2.47	0.72	0.29	78.2
	1550°C—3 h	81	2.49	0.71	0.29	78.8
	1550°C—5 h	84	2.49	0.72	0.29	78.8
M2	1450°C—1 h	72	2.15	0.81	0.81	70.3
	1500°C—1 h	80	2.13	1.02	1.02	68.7
	1550°C—1 h	75	2.11	1.69	1.69	66.8
	1550°C—3 h	72	2.11	1.75	1.75	66.8
	1550°C—5 h	72	2.10	6.36	2.36	66.5

Ribeiro et al. (2004a,b, 2006), Ribeiro and Labrincha (2008) and Labrincha et al. (2006) performed detailed studies on the use of Al-anodizing sludge in the production of refractory and electrical insulating ceramics. Mullite- and cordierite-based refractory ceramic materials were produced from formulations containing 42 and 25 wt% sludge, respectively. Kaolin, ball-clay, diatomite, and talc completed the formulations. Cylindrical samples processed by uniaxial dry pressing were sintered at different temperatures. The fired properties of materials were evaluated (firing shrinkage, water absorption, bending strength, thermal expansion coefficient, refractoriness, and SEM microstructure) and demonstrated that optimal properties were obtained at 1650°C for mullite and 1350°C for cordierite bodies (Ribeiro and Labrincha, 2008). The last ones can be used up to 1300°C as refractory bricks.

Sludge-fully composed formulations were also produced and tested, revealing the formation of α-alumina and β-alumina ($NaAl_{11}O_{37}$) on samples sintered at 1450°C or above (Ribeiro et al., 2004a,b). Their electrical insulating characteristics are reported in distinct works (Labrincha et al, 2006; Ribeiro et al., 2004a,b). Mullite-based formulations (containing 42 wt% sludge) show electrical conductivity about four orders of magnitude higher than alumina-based ones (100% sludge). The last ones show

Fig. 7.8 Al-sludge-based bodies processed by extrusion and slip casting (Ribeiro et al., 2004a).

insulating characteristics comparable to 90% purity alumina samples. Fig. 7.8 shows bodies processed during those works.

The same sludge was also explored in the formulation of inorganic pigments (Leite et al., 2009; Hajjaji et al., 2009), in some cases combined with other wastes (e.g., Fe-wire drawing and Cr/Ni plating sludges, marble cutting/polishing sludge/fines). Wastes-fully based formulations form stable structures at lower temperatures than commercial (chemically pure reagents) pigments, and distinct colors can be obtained, as shown in Fig. 7.9 (Hajjaji et al., 2012; Costa et al., 2007).

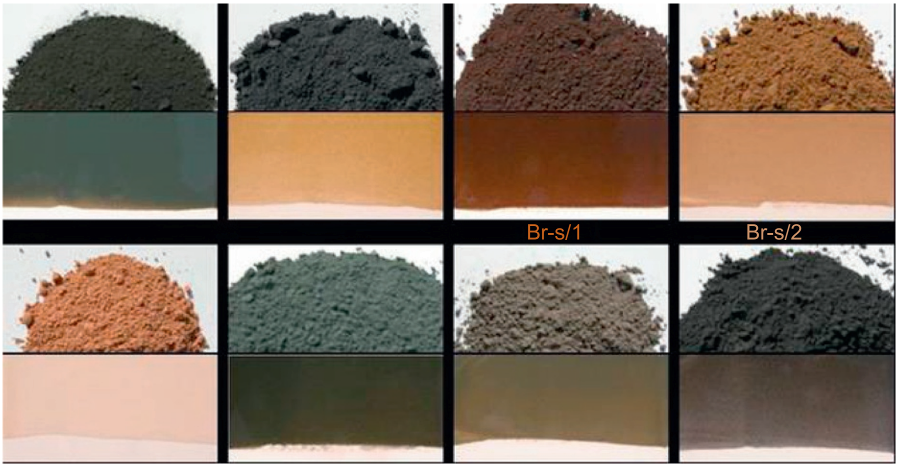

Fig. 7.9 Distinct pigments formulated from wastes (Hajjaji et al., 2012).

7.4.4.2 Radiological properties

In all these cases, no radiological studies on the considered by-products and ceramics were found. As discussed in Chapter 6 a lot of information is available on bauxite and bauxite residue but only a limited amount of radiological information is available on other aluminum-rich by-products such as aluminum dross tailings. A possible reason for this absence of information is because the activity concentration of most aluminum rich by-products, such as aluminum dross, is very low and this makes it hard to publish this type of results. The activity concentration of Egyptian aluminum dross tailings was found to be very low (Abbady and El-Arabi, 2006, see also in Section 6.5.3.2).

7.4.5 Zircon and zirconia ceramic products

7.4.5.1 Technical properties

In a wide review published in 2007 (Selby, 2007) the ceramics sector is analyzed considering its different products as glazed tiles, porcelain tiles, sanitary ware such as baths and wash basins, frits, ceramic pigments, and engineering ceramics. The main ceramics using NORM raw materials are refractories as well as tiles in which zirconia (the NORM raw material) is mixed with other constituents. In 2005, about 54 wt% of the zircon produced was consumed in ceramics production, while refractories required about 14%. In the same year, 39% of produced zirconia was used in refractories, while 33% was consumed in pigments, and 12% in advanced ceramics and catalysts (Selby, 2007).

Refractories are materials that are designed to maintain strength, dimensional stability, and chemical resistance at high temperature. They are manufactured in the form of bricks, fibers, nozzles, slide gates, valves, and grouts. One of the largest uses of zircon and zirconia in refractories is in the glass industry, where the linings of glass furnaces are made from a combination of zircon and zirconia bricks. The zircon bricks for glass furnaces typically contain 30%–40% zircon. Zirconia is commonly used for nozzles, slide gates, filters, and ceramic linings, where the zirconia content approaches 94%. Refractories are typically made from alumina, magnesia, clays, binders, and zircon or zirconia. There are two methods of fabrication: (a) mixing of the ingredients, pressing into the desired shapes, drying, and kiln firing and (b) mixing of ingredients, melting in a furnace and casting the molten mass into the desired shapes (Selby, 2007).

The main application in the ceramics field is in *glazed tiles and sanitary ware*. In this application the ceramic has a two-piece body—a clay-based ceramic body is covered with a silicate/borate glaze to provide waterproofing, durability, and decoration. Zircon is added to the glaze for opacification and to provide a white color. The zircon may be added in the milled form as micronized zircon or as a frit. The concentration of milled zircon in the glaze is up to 20% (Selby, 2007).

Frits are ceramic glasses containing silica and boric acid and are manufactured by melting all constituents together and then quenching in water, followed by milling. Their use allows a water-soluble constituent to be added to the glaze and converted into an insoluble form and also to control the vitrification point of the glaze. The zircon content of frits is usually 10%–20% (Selby, 2007).

In contrast to the glazed ceramics, *porcelains* have a one-piece ceramic body; however, they may also be glazed for decorative purposes. Porcelain ceramic tiles are more resistant to wear than the glazed variety and they are composed of clays, quartz, feldspars, and nepheline syenite together with zircon. In this application the zircon is used in the milled form at concentrations of up to 15% (Selby, 2007).

Ceramic pigments are manufactured by mixing zirconia, quartz, sodium fluoride, and an appropriate chromophore. After firing, the product is milled (Selby, 2007).

There are many *"high tech" uses for zirconia* in the engineering field such as coatings, grinding media, and cutting tools. Zirconia coatings are applied by plasma spraying, while grinding media are manufactured by high-pressure forming and sintering. Zirconia contents are 60%–95%. Cutting tools are made by fusion of zirconia with alumina, with a ZrO_2 content of 5%–10% (Selby, 2007).

7.4.5.2 Radiological properties

Several studies were carried out about the radiological impact of ceramics industries, mainly as regard zircon and zirconia use. An overview of several studies is given in this section.

The exposure pathways in *refractories* are external exposure from raw materials and products, inhalation exposure from mixing and blending of components and final shaping of products, especially where this is done by grinding. Inhalation exposure can also occur from furnace dusts where enrichment in polonium and lead can occur to levels of 20–30 kBq/kg. The activity concentration of ^{238}U in refractory products ranges from about 2.5 kBq/kg for glass refractories to about 5 kBq/kg for the more specialized zirconia products (Selby, 2007). The refractory industry could be a case for exemption from regulation, but the regulatory body would probably need to be convinced on a case-by-case basis (Selby, 2007).

Serradell et al. (2007) reported a radiological study of the ceramics industry, carried out by the Environmental Radioactivity Laboratory at the Universidad Politécnica de Valencia. The study covered three types of plant: *zircon sand milling, ceramic frit production, and ceramic tile production, all of which use zircon as a raw material*. These industrial activities include those that use zircon (zirconium silicate) sand as a raw material. This sand is milled for use directly by the ceramics industry or as an intermediate step for producing milled frits that are also used in the production of ceramics (see Fig. 7.10).

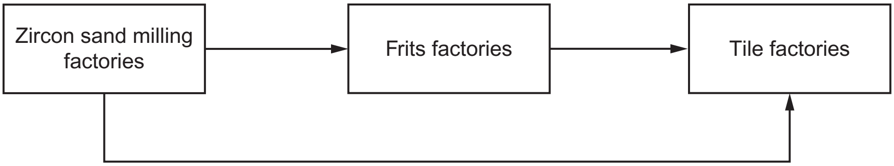

Fig. 7.10 Manufacturing processes using zircon sand (Serradell et al., 2007).

The *milling plant* studied has two lines, corresponding to dry and wet milling processes. The dry process consists of a ball mill (silex or alumina balls) and a dynamic classification system that feeds back the largest particles and produces "zircon flour." The wet process also consists of a ball mill, followed by a dynamic size classifier and a dryer at the end of the process that produces "micronized zircon."

Frits are also analyzed in this paper. They are intermediate materials for use in other factories producing end products. They comprise a wide variety of raw materials, of which only zircon is of radiological interest. Most of the raw material mix formulations do not contain zircon, but when they do the ZrO_2 content rarely exceeds 18%. This type of plant therefore generally represents no significant radiological risk, either for the employees or for the environment (Serradell et al., 2007).

The *manufacture of ceramic tiles* includes a great variety of processes. The radiological study therefore focused only on those manufacturing lines in the factory that used zircon. It concluded that some values of total annual effective dose exceed the annual dose limit of 1 mSv for members of the public, mainly in the milling plants, indicating that this type of industry needs to be carefully monitored. Some areas show quite high-external dose values. Therefore, shielding walls are recommended and workers' occupancy of these areas needs to be controlled. Also, the internal dose makes an important contribution to the total dose, so it is very important to set up a highly efficient air cleaning system. Factories manufacturing frits and tiles show lower values of total effective dose—in both cases, only the zircon silo gives an effective dose exceeding 1 mSv, mainly due to external exposure (Serradell et al., 2007).

Bruzzi et al. (2000) reported on the radioactivity in *raw materials and end products in the Italian ceramics industry*. The natural radioactivity due to the presence of ^{238}U, ^{232}Th, and ^{40}K in zirconium minerals (zircon and baddeleyite) used in the Italian ceramics industry, in tiles and in waste sludge's resulting from ceramic processes, has been measured. The average concentrations of ^{238}U and ^{232}Th observed in the mineral samples (>3000 and >500 Bq/kg, respectively) are higher than the concentrations found in the Earth's crust by one or two orders of magnitude. The specific activities of tiles and sludges are much lower than in zirconium minerals. The ^{238}U and ^{232}Th concentrations in tiles (50–79 and 52–66 Bq/kg, respectively) are not higher than in other building materials. The ^{238}U concentration of sludges (116–193 Bq/kg) is 4–6 times higher than the mean value for the Earth's crust. In general, the data obtained confirm once more that ceramic tiles usually contain small amounts of zirconium compounds and therefore are not a cause of concern from the radioprotection point of view for members of the public; in fact, they produce negligible additional dose values. A similar conclusion was obtained by Turhan et al., from their study on radiometric analysis of raw materials and end products in the Turkish ceramics industry (Turhan et al., 2011).

7.4.6 Overall discussion of the radiological aspects of ceramics

The exposure pathways are very similar for all of the above applications in the ceramics field. The clays and zircon contribute ^{238}U, while the feldspars and syenites contribute ^{40}K. External exposure may arise from raw material storage and materials handling, while inhalation exposure may arise from mixing and blending, or from firing of products. For occupational exposure, the manufacture of ceramics leads to an annual effective dose of 30–200 μSv from external radiation and 10–400 μSv from inhalation, with a total annual effective dose of 10–500 μSv. Public exposure pathways occur with glazed and porcelain ceramics where the dominant pathway is external exposure. Radon in homes is also a possible pathway for these applications. The typical annual effective dose received by a member of the public from glazed ceramics amounts to 7–50 μSv from external radiation, together with an increase of 3–5 Bq/m^3 in indoor radon concentration. By contrast, porcelain tiles give rise to an annual effective dose of 3–150 μSv from external radiation and an increase in radon concentration of 10–46 Bq/m^3. Frits, ceramic pigments, and engineering ceramics are used only in industrial applications, so do not result in any significant public exposure pathways (Selby, 2007).

Wastes related to raw materials are recycled internally and a typical waste from a ceramic plant has an activity concentration of about 0.6 Bq/g, while waste glaze slurry has an activity concentration of less than 2 Bq/g. There are no processes in the ceramics industries for enhancing the radionuclide levels above the natural levels in the zircon or the zirconia (Selby, 2007).

On basis of doses generally found in ceramics industry, Selby proposes that this industrial sector could be a candidate for a generic exemption from regulation since the annual effective dose received by a worker is less than 1 mSv and that received by a member of the public from the use of the products is of the order of 100 μSv (Selby, 2007).

Information about tile activity concentrations in EU countries is collected in a recent update of Trevisi et al. (2012, 2016) presenting the summary of a database of building material activity concentrations in EU collected mainly by international literature. Unfortunately, information about components, in particular zircon sands, is not generally available in the papers used to build the database. In Table 7.29 a summary of tile information is reported. From analysis of the table a comment emerges: generally, values are not high, also when maximum values are considered. However, the superficial use of tiles must be taken into account to evaluate their radiological impact. For example, the application of the index I from the Council Directive 2013/59/Euratom to tiles can bring to wrong conclusions because I is appropriate to screen materials used in bulk amount, typically concrete (see Chapter 4), and not materials a few centimeters thick. For tiles a more precise screening tool accounting for thickness and density should be used, like the method reported in Section 4.7.6. Application of this type of index can show that all tiles are far from determining doses close to 1 mSv.

7.5 Gypsum

7.5.1 Introduction

Gypsum (hydrous calcium sulfate) is a popular raw material for manufacturing various construction products, such as plasters, drywall (wallboard or plasterboard), ceiling tiles, partitions, and building blocks. In addition, Portland cement industry consumes up to 4%–5% of gypsum as a retarder to meet the standard requirements

Table 7.29 Activity concentrations of tiles used in EU countries

Country	No. of samples	Ra-226 (Bq/kg)			Th-232 (Bq/kg)			K-40 (Bq/kg)		
		Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Austria	5	48	91	18	56	135	13	528	819	343
Bulgaria	2	65	110	19	31	52	9	120	140	100
Cyprus	2	23	34	12	9	16	2	191	377	4
Estonia	2	56	64	49	84	86	82	314	344	285
France	35	66	180	1	44	85	2	27	68	1
Germany	7	71	88	50	62	70	55	433	560	310
Greece	53	55	81	3	42	95	2	538	1200	23
Italy	54	61	190	12	46	68	9	627	1026	150
Luxembourg	13	85	100	70	66	74	58	645	669	620
The Netherlands	15	51	61	43	55	66	43	553	600	480
Poland	1190	52	190	1	49	120	1	724	1410	60
Romania	4	46			58			792		
Slovakia	1	31	41	20	37	41	19	507	770	271

related to the setting times of cement. However, from the radiological perspective the uses of gypsum in plasters and finished gypsum products, which can contain up to 100% of gypsum, can be important.

The advancement of gypsum construction is due to its reduced time and cost. Gypsum and gypsum construction products are known for their excellent workability in fresh state, fast setting and hardening, excellent finish, increased fire resistance, lightweight, white color, acoustic properties for noise insulation, etc.

Gypsum raw materials are available in two forms: as a natural gypsum stone (or anhydrite—anhydrous calcium sulfate) and as a byproduct of many industrial processes, which is called chemical or synthetic gypsum (or anhydrite). The modern gypsum industry uses chemical gypsum to substitute natural gypsum whenever possible, in order to reduce the pressure on natural resources.

Flue-gas desulfurization (FGD) gypsum is a by-product of coal-firing power industry and is the most popular supplement to the supply of natural gypsum. This synthetic gypsum has a higher purity than most natural gypsum. Other types of chemical gypsum include phosphogypsum, fluorogypsum, citrogypsum, and titanogypsum, which are by-products from manufacturing phosphoric acid, hydrofluoric acid, citric acid, and titanium dioxide, respectively.

Among all kinds of gypsum, only phosphogypsum is considered as a raw material of radiological concern.

7.5.2 Phosphogypsum

7.5.2.1 Technical properties

Phosphogypsum is contaminated by chemical and radioactive materials and, therefore, in the world is mostly dumped in stockpiled in controlled areas and only about 15% is recycled; mostly as setting time retarder and in some construction elements (Tayibi et al., 2009; Yang et al., 2009).

Phosphogypsum contains, next to naturally occurring radionuclides, some trace elements such as arsenic, lead, cadmium, chromium, fluoride, zinc, antimony, copper (U.S. Environmental Protection Agency, 1990), which may be leached. Therefore, phosphogypsum is mostly dumped in stockpiled in controlled areas and only a minor part of it is recycled; mostly as setting time retarder and in some construction elements, which include the production of bricks, blocks, tiles, and artificial stone (Kumar, 2000, 2003; Weiguo et al., 2007; Tayibi et al., 2009; Yang et al., 2009). Degirmenci (2008) and some other researchers studied a possibility of the phosphogypsum utilization in combination with fly ash and lime, to produce a cementitious binder. The recent comprehensive publication of IAEA (2013) estimates that recycling rate of phosphogypsum is still very low: less than 5%.

Unfortunately, many valuable materials, which can serve future generations as raw materials in producing electrical energy, chemical, building, and other useful products, are lost in this industrial by-product. The building materials industry seems to be the largest among all the industries, which is able to reprocess the greatest amount of this industrial by-product and benefit man. However, the key problem restraining the utilization of phosphogypsum in construction is radiological effect on the human population.

Recent developments in the phosphate industry in China, India, and some other countries with rapidly developing economies have led to a major increase in the production of phosphogypsum, which in turn has stimulated interest in its use in construction and other fields. As a result, the relevant authorities have taken a greater interest in establishing the necessary conditions for the safe use of phosphogypsum (Hilton, 2008).

7.5.2.2 Radiological properties

The radium (^{226}Ra) concentration in phosphogypsum is 200–3000 Bq/kg (U.S. Environmental Protection Agency, 1990). Building elements made of phosphogypsum, such as wallboards and similar construction elements, give yield to high values of radon emanation together with the mentioned elevated concentrations of ^{226}Ra. Phosphogypsum can be used in Portland cement as a setting time retarder in amounts below 4–5 wt%; then, it is diluted in the concrete and normally does not influence the ^{226}Ra activity concentration, but it increases the radon flux (Kovler et al., 2004).

Exposure levels from building materials incorporating phosphogypsum depend strongly on how the phosphogypsum is used. For example, exposure from finished building products made of phosphogypsum depends on their thickness and density, as well as on radium-226 concentration in phosphogypsum. O’Brien (1997) assumed a ^{226}Ra activity concentration of 400 Bq/kg in phosphogypsum and calculated the annual effective dose from gamma radiation for a person continually occupying the room of dimensions up to 5 m × 5 m × 3 m lined from all the walls and ceiling by 10-mm wallboard, and found that it does not exceed 0.13 mSv. For the comparison, a measured annual average effective dose from gamma radiation in Australian homes is 0.9 mSv. In other words, such exposure levels are not likely to be of serious concern.

At the same time, experience suggests that the use of phosphogypsum in building materials is not being given the attention that it perhaps deserves (IAEA, 2013). In particular, relatively open microstructure and high porosity of gypsum wallboards, ceilings, masonry blocks, and other building products promotes radon exhalation. For example, Bossew (2003) and Stoulos et al. (2004) estimated radon emanation power of gypsum as 30%, while Kovler (2007) found it even higher—around 50%. Kovler (2007) explains that the reason of such high-radon emanation of gypsum is in its very special microstructure and its high-open porosity. The shape of gypsum crystals is usually longitudinal (fibroid), with well-developed surface area, while the overall density of gypsum product is low—usually 800–1200 kg m^3 (Fig. 7.11). These features make radon release from gypsum relatively easy.

The final answer about the safe exposure dose can be obtained only after calculation of the total dose, not only from gamma radiation, but also from radon. O’Brien et al. (1995) estimated the contribution to the annual effective dose due to airborne contamination from phosphogypsum wallboard with enhanced radium content used as an internal lining. For ventilation rates greater than 0.5–1/h, the contribution to

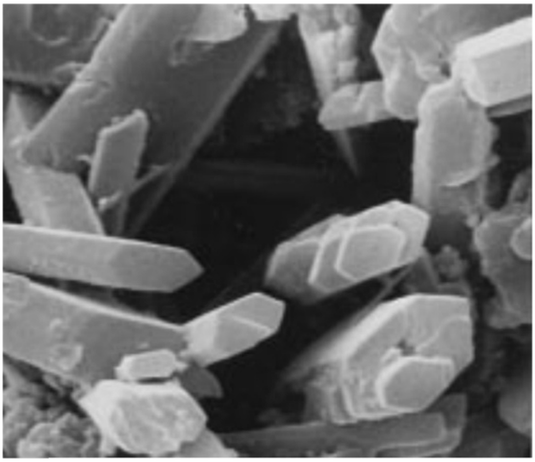

Fig. 7.11 Typical appearance of gypsum crystals (width of the photograph is ~0.01 mm).

the total annual effective dose from inhalation of ^{222}Rn and its progeny exhaled from the wallboard was below 1 mSv. This contribution was reduced, when the surface of the wallboard was painted or coated by cardboard, or if the very fine particles were removed from the phosphogypsum during manufacture of the wallboard (a type of phosphogypsum purification, because it is known that fine fractions are usually more contaminated). The effective doses arising from dust generation during the installation of the wallboard were also estimated to be below 1 mSv.

Unfortunately, no industrial implementation is known so far for phosphogypsum processing and utilization in construction. The central problem of recycling of phosphogypsum in construction is its slightly elevated radioactivity—mainly because of enhanced ^{226}Ra concentration, because other chemical impurities can be extracted relatively easily, for example, by using phase transformations between different kinds of calcium sulfate hydrate and subsequent filtering of the obtained solution. Traditional technologies of purification of phosphogypsum from radium are usually not effective, because of the similarity of chemical properties of radium sulfate and calcium sulfate, when the contaminant salt is isomorphously introduced in the gypsum crystals, and therefore, cannot be washed out from the crystal surface.

In principle, there are three ways of making phosphogypsum free of radium and/or heavy metals (Weterings, 1982), viz.:

- starting from clean phosphate rock, i.e., phosphate rock which is free of heavy metals and radium;
- using a clean process, i.e., a process which yields clean gypsum; and
- purifying the gypsum.

Much research has been done on methods of purifying phosphogypsum during the manufacture of phosphoric acid, to obtain grades, which are acceptable for use as plaster or as setting retarder in cement. With all the methods developed, it is mainly the phosphate content, which is decreased; the content of radium and heavy metals is hardly reduced, if at all. The purification technology is based on rearrangement of the crystal lattice during the transition to calcium sulfate hemihydrate (HH) or dihydrate (DH). There are two main variations: HH-DH processes (e.g., Nissan) and DH-HH processes (e.g., Prayon). Radium could be removed by suitable measures during the gypsum purification. Apart from the partial removal of radium, which is part of the wet gypsum purification, no procedures for the removal of radium are operative at present. In the patent literature Ra is removed by a recrystallization of the gypsum in nitric acid or in sulfuric acid with an addition of Ba-ions. Nothing is known about patent-literature concerning the removal of heavy metals from gypsum. However, none of the three alternatives, i.e., the use of clean phosphate rock, a clean phosphoric acid process, or purified gypsum, is at present practicable, and a nonstandard approach has to be used to lead to the desired result: obtaining of gypsum, which is free of ^{226}Ra and heavy metals, provided that it is economically feasible.

Principally new technological approach has been developed recently (Kovler et al., 2015). It was found that the main contaminant of phosphogypsum is radium sulfate, the salt of extremely low solubility (2×10^{-4}). The method is based on mixing hot phosphogypsum suspension containing special chemical reagents to extract the impurities and transition of insoluble radium salt to a soluble compound, which is successfully filtered out from the suspension. The best results demonstrated reduction of ^{226}Ra content by an order of magnitude.

7.5.3 Overall discussion of the radiological aspects of phosphogypsum

The production cost of the environment-conscious gypsum binders can be lower than that of natural gypsum stone, because (a) the raw material is a by-product phosphogypsum, which is widely available in many countries in large quantities; (b) the following technological expenses are excluded: for mining gypsum rock, its transportation, storage, grinding, extraction of silicates, calcite, dolomite, clay, and other impurities containing in rock, with losses of a part of the ground gypsum with these impurities. At the same time, pretreatment increases the process costs.

It has to be emphasized that phosphogypsum recycling would be economically feasible, if industrial installations for the production of environmentally friendly gypsum binders and finished building products are located near phosphate plants, providing the minimum expenses for phosphogypsum transportation and for removing the small amount of the solution of the extracted impurities to the operating neutralization installations of the phosphate plant together with large amount of acidic and radioactive flows of this plant.

In spite of the fact that the problem of purification of phosphogypsum can be adequately solved on technical level, it has to be emphasized that there have been nevertheless a few attempts in different countries to produce gypsum wallboards and masonry blocks from phosphogypsum, which has been purified by simple washing and neutralized by lime (to reduce its pH and remove some acidic compounds). Such simplified treatment is certainly not sufficient to meet the environmental standards, which are getting stricter year by year.

In view of this, there is a need in parallel to develop new environmentally friendly and economically feasible technologies of purification, and also to introduce environmentally safe and economically reasonable standard regulations, which should be based on justified radiological, social, economic, and legislative concepts.

7.6 General conclusion

This chapter provided technical, chemical, and radiological information to support a safe recycling of by-products in four groups of construction materials: (1) construction materials based on Portland cements (both as cement itself and as concrete), (2) construction materials based on alkali-activated binders, (3) ceramics and glass-ceramics, and (4) gypsum.

For most of the construction materials discussed here the recycling of by-products is not a problem from a radiological perspective when taking into consideration the approach of the Council Directive 2013/59/Euratom. Several of the evaluated building materials have an *I*-index < 1 (e.g., coal fly ash or blast-furnace slag recycling in Portland cement-based concretes) meaning that these building materials meet the gamma dose reference level set by the Council Directive 2013/59/Euratom. For only a limited amount of cases (e.g., when using 75 wt% of specific types of red mud in alkali-activated concretes) an index higher than one was found and there is a need to further verify the gamma dose reference level of 1 mSv/year. For the radiological screening of ceramics, that can be used as a layer of only a few centimeters thick and where the density can be quite different from concrete, the use of a density and thickness corrected index is recommended.

As a result of dilution, in general, the concentration of radionuclides, originating from residues, is decreased in the produced construction materials. Aggregates have the greatest influence in the concrete radioactivity because they account for the main fraction of the concrete volume. The relative fraction of by-products that can be incorporated as aggregates in construction materials is very by-product dependent and this parameter will strongly determine the resulting concentration of naturally occurring radionuclides in the construction material. This aspect was demonstrated by means of appropriate mix designs for concretes in order to make a realistic dilution calculation.

Knowing the radiological properties of by-products (Chapter 6) and resulting construction materials (this chapter) facilitates the design of new types of construction materials that are safe considering the recommendations of Council Directive 2013/59/Euratom.

For many construction materials only a limited amount, or no information at all, is available regarding the radiological aspects of these materials. New studies, many of them initiated by the COST network NORM4Building, are in preparation to tackle the gap in the knowledge.

Appendix A Toxic and radioactive waste immobilization by alkali-activated cement and concretes

Materials processed by the alkali activation technique might show strong capability to immobilize a large variety of hazardous and radioactive species (Krivenko et al., 1993; Palomo and López de la Fuente, 2003). The effectiveness level of stabilization is basically controlled by two parameters—mechanical strength and leaching resistance (Jaarsveld et al., 1998). In more detail, parameters such as the setting time (5–72 h), compressive strength ($>$0.35 MPa), and metal concentration in leachates (mg/L): $Cd < 0.5$, $Cr < 5$, $Pb < 5$, and $Zn < 300$ are important (Palomo and López de la Fuente, 2003; Jaarsveld et al., 1998). Metal bearing waste can have either a positive or a negative effect on the strength development. Palomo and Lopez (Krivenko et al., 1993) have concluded that boron negatively affects Portland cement hydration while it does interfere in the alkali activation process of fly ash. Boron could then be immobilized in the structure of alkali-activated fly ash-lime materials and its leaching rate can be reduced up to 100 times comparing to Portland cement- or lime-based systems.

The resistance of heavy-metal-containing AAMs to leaching in different environments strongly depends on the nature of the heavy metal and on the aggressive components of the leaching solution. Pb could be immobilized effectively by a chemical binding mechanism in AAMs, meaning that its addition in a soluble chemical form is actually preferable (Zhang et al., 2008). Heavy metals in the form of ions, such as Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{6+}, can be effectively stabilized in slag cements activated by NaOH, Na_2CO_3, and sodium silicate solution (Zhang et al., 2008; Malolepszy and Deja, 1995; Deja, 2002). The results also show that up to 2 wt% Hg^{2+} ions can be effectively immobilized in the alkali-activated slag cement matrix (Qian et al., 2003).

Wastes show much less interference upon the hydration process of alkali-activated cements than that of PC. However, alkali-activated cements usually exhibit higher shrinkage than PC upon hydration at room temperatures, and cracking risks of the waste-containing monolithic geopolymeric structure are higher. Some alkalis may leach out of the material structure and enter into the environment if the material is immersed (Shi and Fernández-Jiménez, 2006).

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Leaching assessment as a component of environmental safety and durability analyses for NORM containing building materials

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8.1 Introduction

Guide for the reader: Structure of chapter "8":

- The goals of the environmental leaching assessment of NORM containing construction materials and the naturally occurring radionuclides of potential concern for leaching are discussed in Section 8.2.
- Section 8.3 deals with the selection of the appropriate leaching test for NORM containing construction materials, while in Section 8.4 leaching test results for specific constituents are given.
- Section 8.5 handles the modeling of radionuclide release behavior from NORM containing construction materials and the influence of the redox conditions and carbonation.
- Section 8.6 gives broader scenarios to assess the impact of the leaching of natural occurring radionuclides on the environment.

NORMs (naturally occurring radioactive materials) may be considered for use as construction material if, in the form that they are used, they meet appropriate standards for protection of human health and the environment. When evaluating construction materials, it is important to consider the full life cycle of the material, including the use scenario as well as the potential for reuse and disposal. If demonstrated to be safe, then use of NORM offers potential sustainability benefits through reduction in energy use and reduction in mining or use of virgin natural resources for production of construction materials (e.g., aggregate, cement, concrete, paving block, tiles, filler for road works, etc.). Important pathways to be evaluated for potential human health and environmental

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impacts include (i) direct exposure to radiation, (ii) emission of radon, (iii) potential exposures through ingestion and inhalation, and (iv) waterborne pathways through leaching of radionuclides or other contaminants of potential concern (COPCs). Additionally, the potential benefits derived from the use of NORM require demonstration of durable products with acceptable environmental safety.

An important reason to focus on natural radioactivity is that alternative materials (by-products) used in construction as part of the new circular economy targets set by the European Commission may contain natural radioactivity in elevated levels compared with traditional materials used in construction. However, many traditional materials (e.g., granites) also may contain elevated levels of radionuclides depending on their origin and therefore, both traditional and alternative materials require consideration of radiation exposure as part of the determination of their suitability for use (as was already discussed in Chapters 3–7).

As of Jul. 2013, the Construction Products Regulation (CPR) (EU, 2011), provides the regulatory and logistic framework for management of products prepared with waste-derived materials as well as pristine materials used for construction purposes. Although the CPR, which replaced the Construction Products Directive (CPD) (EU, 1989) in 2013, extends the considerations of environment and health from only the service life to the entire lifecycle, the actual criteria to be met by construction products are still a matter for the individual Member States. Only the Netherlands and Germany have set leaching limit values for COPCs in a broad range of construction products to be used for applications with potential for impact of soil and groundwater.

Discussions are ongoing to be able to declare an end of waste (EoW) status to make easier the use of alternative materials that otherwise may be considered waste. The options to define a simple test to declare a waste as EoW (Delgado et al., 2009), have been shown to be more complicated than was initially foreseen (Saveyn et al., 2014). When a material obtains EoW status it becomes a product and is no longer regulated by waste legislation. When it is used for construction purposes, its potential impact on the environment will be regulated by the Essential Requirement 3: Health, Hygiene, and the Environment in Council Directive 89/106 (EU, 1989) and its replacement, Construction Products Regulation 305/2011 (EU, 2011). Although the test methods are being harmonized at the European level, only the Netherlands has set specific criteria on the release (leaching) of substances from construction products regardless of their origin (SQD, 2007). In Germany the main focus is on the alternative materials with potential for use in construction (German Federal Regulation—Mantelverordnunug, 2007). In most other EU Member States, a waste-derived aggregate which has obtained EoW status at EU level will not be subject to testing and compliance with environmental quality criteria. For release of radionuclides to groundwater, the criteria for radionuclides as specified in the Euratom Water Directive (EU, 2013) apply. The results from leaching tests can be applied directly for comparison with these water quality objectives for initial screening purposes. A source-path-receptor approach similar to that used for inorganic substances needs to be applied to realistically account for dilution and attenuation from the source (construction product) to the receptor (e.g., groundwater used for drinking water) when initial screening indicates leaching results to greater than criteria.

When considering end of life (EoL) for a material used in a construction application, one may expect in most circumstances that the material to be judged will be oxidized and largely carbonated (neutral to near neutral pH) due to contact with the atmosphere. For durable metallurgical slags, this relates to the surface of the particles, where the core may still be alkaline. This implies that to evaluate material performance in EoL condition, the pH dependence test (EN 14429, 2015 or EPA 1313, Garrabrants et al., 2012) is an appropriate tool, as it will indicate what changes in leaching behavior to expect starting from the materials initial pH to a final assumed pH condition in EoL status.

In the United States, beneficial use of secondary materials is governed by state regulations, with the US EPA providing guidance to the states with respect to evaluation approaches (US EPA, 2013). However, each state may choose not to follow the EPA guidance and issue their own regulations.

This chapter focuses on the waterborne pathway of potential impacts through leaching[1] of radionuclides and other COPCs. Many of the historic leaching tests were based on a simulation-based approach to testing whereby the laboratory test method seeks to mimic specific field scenarios, such as attempting to mimic co-disposal with municipal solid waste as the basis for the toxicity characteristic leaching procedure (TCLP, 1992).[2] Even though the percolation test (EN 14405, 2017) was used in developing the criteria in Annex 2 of the European Landfill Directive (2003), the single batch test EN 12457 (2002) or related tests (Laili et al., 2012) are used too often to address questions that are beyond their scope. Single batch test approaches do not provide a basis for comparing estimated leaching performance under different scenarios and have been shown to provide misleading results under a range of circumstance (Van Zomeren et al., 2015). More recently, there is a shift toward measurement of intrinsic leaching characteristics (i.e., characterization of leaching as a function of key release controlling parameters such as pH, liquid-to-solid ratio (L/S), or time) of a material over a range of conditions as a basis for comparison between materials, and using mass transport relationships to estimate anticipated leaching under the range of likely field conditions (Kosson et al., 2002). The implementation of characterization leaching tests has occurred through coordinated development in the United States and the European Union and is referred to by the US EPA as the Leaching Environmental Assessment Framework (LEAF; Kosson et al., 2014). The LEAF is fundamentally different from the simulation-based approach to test methods because it focuses on characterization of intrinsic material-specific leaching behaviors controlling the release of COPCs from solid materials over a broad range of test and environmental conditions, with application of the resulting leaching data to specific disposal or use conditions (Kosson et al., 2002) The LEAF approach will be used as the basis for discussion of leaching from naturally occurring radionuclides (NOR) here, based on similarities in leaching behavior between radionuclides and the corresponding stable isotopes.

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[1] Leaching is defined as the release of constituents from a solid material to the aqueous phase when contacted with water.

[2] TCLP was designed to simulate a plausible mismanagement scenario of co-disposal in a municipal solid waste landfill.

Leaching of inorganic elements and naturally occurring radionuclides are controlled by the same set of chemical and physical processes and therefore can be evaluated using a common approach, including leaching test methods and descriptions of use or disposal scenarios. Leaching test results are used in conjunction with simple or detailed mass transfer models to provide a "source term" for evaluating constituent fate and transport from a source to a receptor based on the scenario to be considered. Exposure-based risk assessment or preestablished thresholds for each COPC are then used to determine if the proposed material use or disposal scenario is acceptable. For NORM, thresholds need to consider COPCs both from chemical and radiation perspectives. A tiered approach allows for simplified evaluations to be used for screening purposes, while allowing for more detailed evaluations when warranted. For all materials, including NORM, important considerations include (1) hydrogeologic setting, (2) the full lifecycle of the material (from initial production through use, reuse, and final disposition), and (3) the potential for changing material properties and local environmental conditions over time (e.g., changes in oxidation/reduction state, carbon dioxide uptake by alkaline materials, establishment of preferential flow pathways). Furthermore, the materials may change their leaching behavior in response to blending with other materials (resulting in changes in chemistry from changes in primary constituent composition) or at interfaces between dissimilar materials.

The same tools used for evaluating environmental safety associated with leaching can also play an important role in understanding the durability of many construction materials. Durability may be described in a holistic way as how a building material resists to external physical and chemical attacks, including at the interfaces with other building materials, or to internal interactions between different constituents of the building material itself. LEAF testing may be used to evaluate the susceptibility of materials to loss of primary constituents (e.g., decalcification of cements), and ingress of reactive species through contacting water (e.g., sulfate and chloride attack) or through the gas phase (e.g., carbon dioxide) (Sarkar et al., 2010; Branch et al., 2016).

Such interactions may result in changes of the principal physical properties of the building material such as its mechanical properties (e.g., elastic, flexural, tensile, compressive strength) and shape (e.g., by swelling, cracking) and of its response to subsequent physicochemical attack such as observed in freeze-thaw cycles, exposure to the atmosphere (CO_2, O_2), infiltration (e.g., salts from deicing), or interaction with aggressive groundwater (e.g., high sulfate concentrations leading to sulfate attack). These principal physical characteristics of building materials are described in a vast amount of literature (Hewlett, 1998; Scrivener and Young, 1995), and not repeated here. In this chapter we rather focus on the release of COPCs emphasis on naturally occurring radionuclides, recognizing that physical degradation of a material may lead to increased leaching of COPCs. However, the mechanisms underlying the responses to chemical and physical processes may predict the durability of materials, and should therefore be well understood.

Basically the same processes that affect leaching from traditional materials will influence the release of natural radionuclides from NORM. This implies that all observations on long-term leaching behavior comparing laboratory testing and field leaching (Kosson et al., 2014) apply. In addition, long-term stresses (e.g., sulfate attack, chloride attack, carbonation, oxidation) as studied in the context of the Cement Barriers Partnership (CBP) on cementitious materials used for containment of nuclear waste are also of relevance (http://www.cementbarriers.org). Studies into release behavior from masonry, geopolymers, and cement-stabilized materials are of direct relevance as well.

The leaching behavior of stable elements is not fundamentally different from that of radionuclides, which means that the leaching behavior of stable elements can be used to understand and estimate the leaching of radionuclides. Previously reported total elemental leaching (e.g., for uranium) can be used to estimate the appropriate radioactive isotopes based on naturally occurring isotopic ratios. In addition, the leaching behavior of stable isotopes can be used to estimate the behavior of radioactive isotopes present as decay products and chemical analogs can be used as a first indication of the possible behavior of specific radionuclides.

8.2 Leaching assessment

The goal of environmental leaching assessment is to provide an estimate of constituent leaching potential for materials under possible management scenarios. The approach is as accurate as practically needed, but also does not underestimate the release of COPCs, here naturally occurring radionuclides. The intended use of assessments may be to evaluate the environmental safety of specific use or disposal options for a class of materials, to evaluate effectiveness of material treatment options, or to characterize EoW conditions for materials with potential for beneficial use. The constituents identified as COPCs will be specific to the material being evaluated. With regard to naturally occurring materials, the history of the materials used will determine which radionuclides are present. This is determined by the original natural resource and the way it is processed. In particular, chemical separation processes, including thermal treatment, can result in differential separation of daughter elements from radioactive decay that behaves chemically differently. Radionuclides are therefore not necessarily in secular equilibrium, and therefore care must be taken in assuming the concentrations of daughter radionuclide relative to the initial radionuclide (Titayeva, 2000). For example, in the Bayer process, to extract aluminum from Bauxite, the process affects the secular equilibrium due to the different chemical behavior of the decay chain elements related to uranium decay (Cuccia, et al., 2011). In addition, red mud is sometimes defined as the sum of the sand and red mud residues, but in fact these are two different residues in the Bayer Process which might be mixed or used separately. Depending on the origin of the ores, the red mud may have quite different radiological composition as shown in Chapter 6.

The broad range of potential uses of environmental leaching assessment implies that there is a need for a graded or tiered approach. This approach needs to provide flexible, scenario-based assessments and allow tailoring of the needed testing and information based on the type of intended use of the assessment and the available prior or related information. Often, an initial screening assessment, using simplified testing and very conservative leaching estimates,[3] can be used to eliminate specific COPCs and/or entire materials from further concern and evaluation. It is important to include such initial screening options in regulation, to limit the burden to industry without jeopardizing impact to health and environment.

Only some radionuclides from the natural decay chains may be of potential concern with respect to leaching. According to Gellerman et al. (2002), it may be stated that radionuclides like Pb-210, Po-210, and Ra-228 do not have a significant potential for groundwater contamination as long as only isolated migration is considered and hence the focus should be mainly on the long-lived Ra-226 and U isotopes, which show in practice significant migration distances in soils. On the other hand, Po-210 has similarities to the behavior of Se and thus can be mobile in the mildly alkaline pH domain. For Pb-210 and Th, the interaction with dissolved organic carbon (DOC, generated by degradation of organic matter) can lead to formation of mobile element-DOC complexes. So the environmental context needs to be considered before limiting the COPC to be considered.

Leaching of COPCs most often is strongly influenced by the general chemical state (e.g., pH, oxidation-reduction potential, and ionic strength) of the leachant in contact with the solid, the leaching of major and minor constituents, and the physical characteristics of the material that influence the degree of water contact. The extent and rate of leaching can be determined by constituent liquid-solid partitioning (including consideration of solubility, adsorption to solid phases, available content for leaching, aqueous complexation, etc.), the physical properties of the material that limit mass transport, the degree to which equilibrium is achieved, and the properties of the contacting liquid. Examples of intrinsic physicochemical characteristics are the chemical composition (including elemental speciation and molecular composition, type of mineral phases and their surface chemistry, ionic character of chemical bonds determining ion exchange capacity, type of charge-balancing ions, redox conditions, the presence of hydrophobic additives or coatings, etc.), and also the physical state of the material (crystallinity, porosity, tortuosity, and particle size). Material aging, for example, through pozzolanic reactions or ingress of reactive species (e.g., oxygen, carbon dioxide, sulfate), also may impact material chemical and physical characteristics. Thus observed leaching is the result of the chemistry and mass transfer characteristics (e.g., physical properties, water contact, diffusivity, capillarity) of the system.

Leaching chemistry is primarily controlled by the behavior of the leaching element. It may present cationic behavior (Ni, Cu, Zn, Cd, Pb, Al, Fe), oxyanionic behavior (Mo, Cr(VI), As, Se, Sb, SO_4), or soluble salt behavior. The leaching behavior of different elements can be classified into groups, leading to roughly the leaching patterns as a function of pH as shown in Fig. 8.1. We restrict discussion here to the elements of concern related to NORM.

The alkali metals, group I (Na, K, and Cs), are very soluble. K-40 is an important naturally occurring radionuclide, which can leach easily in most cases, and the high

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[3] Herein, the term "conservative" is used to imply bias in assumptions that result in overestimation of leaching when precise information is unavailable. A conservative leaching estimate should insure protection of resources and health but assumptions may be refined to result in a more precise leaching estimate, and therefore less conservative, leaching estimate.

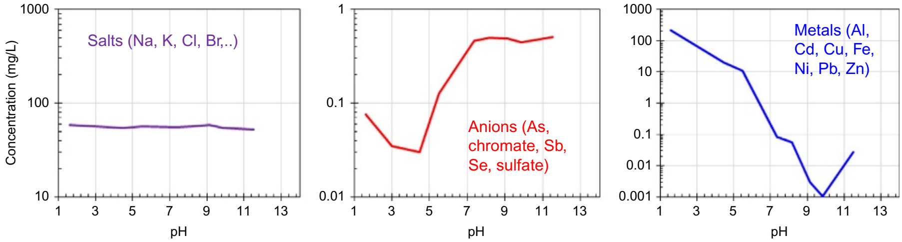

Fig. 8.1 General leaching behavior of three groups of constituents as a function of pH. Cations, anions, and soluble salts have a distinct leach pattern, caused by their chemical speciation, and vary orders of magnitude as a function of pH.

predominance of the stable isotopes of these elements make them available as a charge balancing ion in aluminosilicate materials, where Al^{3+} is present in tetrahedral coordination. Some fraction of the Group I elements such as K^+ also can be immobilized within the 3D alumino-silicate network and not present on surfaces, and thus not readily subject to ion exchange and leaching. The difference between available and nonavailable counterbalancing ions can be determined by analyzing the cation exchange capacity.

From the natural uranium and thorium decay series, the most important radionuclides with significant potential for groundwater contamination are radium and uranium if limiting the discussion to isolated migration (Gellerman et al., 2002). We therefore highlight the speciation of Ra and U that may be of concern in cementitious or alkali-activated materials.

The heaviest element of the alkaline earth metals group 2 is Ra, which is of relevance to NORM as Ra-226 and Ra-228. The environmental behavior of radium is reviewed in the IAEA Technical Report Series No. 476 (2014). We highlight from this report that radium (hydrated ionic radius of 3.98 Å) behaves similar to barium (hydrated ionic radius of 4.04 Å), and therefore, when data for radium leaching are missing, barium can be used as a surrogate element for preliminary evaluation. Ra^{2+} forms insoluble sulfate, carbonate, and chromate salts, mostly in co-precipitation with barium, another group 2 element, as the radium concentrations rarely approach the solubility limit. However, hydroxide salts of radium are soluble. An extensive study on radium-barium co-precipitation and potential near-field impact has been provided by Grandia et al. (2008).

Uranium is a redox-sensitive element. In sufficiently oxidizing conditions to stabilize the uranyl ion ($UO_2{}^{2+}$) uranium can migrate kilometers from its source (Merkel and Hasche-Berger, 2008). At $pH \leq 2.5$ the uranyl ion is very stable. Near pH 7, the uranyl ion forms stable complexes with phosphate and carbonate. Uranium sulfate and carbonate complexes are soluble and can migrate with ground water. Uranium may be precipitated by reduction to U(IV), or as phosphates, silicates, arsenates, vanadates, and oxyhydroxides. Tetravalent uranium forms stable hydroxides, hydrated fluorides, and phosphates of low solubility (Závodská et al., 2008).

The above explanation only takes into account the leaching element itself in combination with its complex or salt forming capacities. The way these elements are bound in the matrix may also play a crucial role in their behavior, as far as leaching or environmental stresses do not decompose the matrices themselves. Van Deventer et al. (2007) noted that in geopolymers, every s- and p-group element listed in a study of Bankowski et al. (2004) can be immobilized by the geopolymerization reaction of fly ash, while transition metals either show no immobilization or increased leachability in the metakaolin-based geopolymer, compared with the untreated fly ash. Hermann et al. (1999) demonstrated an optimized two-step technology, in which wastes from former uranium production mines in East Germany were premixed with ordinary Portland cement (PC), and successively mixed with a geopolymeric binder. Immobilizing uranium mine tailing also have been reported by Davidovits and Davidovits (1999), Gatzweiler et al. (2001), Davidovits et al. (1990), Hermann et al. (1999), and Kunze (2003).

In general, it is useful to use leaching tests to (1) characterize equilibrium partitioning between the solid and liquid phases as a function of pH and L/S and (2) determine the rate of mass transport. The materials of interest may be natural aggregates, secondary materials under consideration for beneficial use (e.g., industrial slags, flue gas desulfurization gypsum, coal fly ash, red mud), alkali-activated materials including geopolymers and construction materials containing alternative materials. The contacting water may be from percolation through porous materials, flow around porous or nonporous (or fractured) monolithic materials, or from condensation processes. The material may be water-saturated or unsaturated. The source and fate of the water (and any leached constituents) may include precipitation, runoff, groundwater, surface water, or collected leachate.

8.3 Standard leaching tests and analysis

The leaching test methods developed in EU and the United States (LEAF) are presented in Table 8.1 by type and standard reference. Both the EU and the United States provide comparable results and are designed to measure fundamental leaching parameters including:

- Liquid-solid partitioning (LSP) as a function of eluate pH;
- LSP as a function of L/S under percolation (column flow) or batch extraction testing;
- Mass transport rates of COPCs leaching from monolithic or compacted granular materials; and
- Additional parameters for assessing special conditions, such as redox status, acid generation potential and parameters for geochemical reaction and transport modeling.

EPA Method 1313 and EPA Method 1316 are parallel batch procedures intended to characterize the LSP at conditions approaching equilibrium as a function of final extract pH and L/S, respectively. Method 1314 and Method 1315 are test methods intended to measure the rate of constituent release under percolation or diffusive/dissolution mass transport conditions, respectively. The test parameters and values specified in these methods have been described in a background information document on the LEAF leaching methods with fully validated methods available (Garrabrants et al., 2010, 2011, 2012).

Table 8.1 **Leaching test types corresponding across different fields and jurisdictions (EU and the United States)**

	CEN/TC 345 soil ISO/TC 190 soil	**CEN/TC 292 waste**	**CEN/TC 292 WG8**	**CEN/TC 351+ 60 product TC′s**
Matrix Test	**Soil, sediments, compost, and sludge**	**Waste**	**Mining waste**	**Construction products**
pH dependence test	ISO/TS21268-4 EPA 1313[a]	EN14429 EN14497 EPA 1313	EN14429 EN14497 EPA 1313	EN14429[c] EPA 1313
Percolation test	ISO/TS21268-3 EPA 1314[a]	EN14405 NEN7373 EPA 1314	EN14405 EPA 1314	FprCENTS 16637-3 NEN7373 EPA 1314
Monolith test	EPA 1315[a]	EN15863 NEN7375 EPA 1315	EPA 1315	FprCENTS 16637-2 NEN7375 EPA 1315
Compacted granular test	EPA 1315	NEN7347 EPA 1315	EPA 1315	FprCENTS 16637-2 EPA 1315
Redox capacity		CEN/TS 16660[b]		CEN/TS 16660[b]
Acid rock drainage			EN15875	
Reactive surfaces	ISO 12782 Parts 1–5	EN-ISO 12782 Parts 1–5		

[a] EPA methods included in SW846.
[b] Based on NEN 7348.
[c] Not yet adopted in CEN/TC 351 (very relevant for CPR).

8.3.1 *Characterization leaching tests*

Below a short description of the characterization leaching tests is given with an indication of how simplified testing can be carried out, once the release behavior of a material has been sufficiently established.

8.3.1.1 pH dependence

This test provides information about the pH sensitivity on the COPC leaching from the material (EN 14429, 2015; EN 14997, 2015; EPA Method 1313, Garrabrants et al., 2011). The listed methods lead to very comparable results (Garrabrants et al., 2011). The test consists of a number of parallel batch extractions of a material at L/S = 10 mL/g (dry weight basis) during 48 h at a series of preset target pH values. The pH is adjusted at the start of the experiment with acid or base (HNO_3, NaOH, or KOH) to achieve targeted endpoint pH values. After 48 h of equilibration by end-over-end rotation in polyethylene containers, the suspensions are filtered (0.45 μm) and analyzed. The test provides the response of a material to imposed pH changes and an acid-base titration to understand the response of the material to acid or base reactions under environmental scenarios (e.g., carbonation, infiltration, sulfide oxidation, soil interfaces). Results also are used to determine the available content of constituents (Kosson et al., 2014) and can be used to estimate the amount of carbonate present in cementitious materials (Branch et al., 2016).

8.3.1.2 Percolation test

The column leaching test provides information on the leaching behavior of the material as a function of the L/S (expressed in L/kg or mL/g on a dry weight basis) (EN 14405, 2017; CEN/TS16637-3, 2016; EPA Method 1314, Garrabrants et al., 2012). The listed methods lead to very comparable results (Garrabrants et al., 2012). Seven eluate fractions are collected over the L/S range 0.1–10 L/kg, with the total test duration being approx. 10 days. The eluent is demineralized water, or 1 mM $CaCl_2$ when deflocculation of clays or organic matter is a concern. The material is tested as received, unless the particle size does not conform to the test requirements or a noncrushable material needs to be removed, and upflow (14 mL/h EN 14405; 28 mL/h CEN/TS16637-3; EPA 1314 specifies a flow rate to achieve a residence time of 0.75–1.0 day) is applied through a column with a height of about 25 cm and a diameter of 5 cm. L/S can be related to a timescale through the infiltration rate, density, and height of the application (Hjelmar, 1990; Sanchez and Kosson, 2005).

8.3.1.3 Monolith leach test

The monolith leach test provides information on the release per unit surface as a function of time and it is performed on regular shaped product samples according to standardized procedures (EN 15863, 2015; CEN/TS 16637-2, 2015; EPA Method 1315, Garrabrants et al., 2012). The listed methods lead to very comparable results (Garrabrants et al., 2012). The specimen is subjected to leaching in a closed tank. Demineralized water is used as the leaching solution at an eluent-to-product volume ratio (L/V) of approx. 5. The leaching solution is renewed after 8 h, 1, 2.25, 4, 9, 16, 36, and 64 days. The pH, electrical conductivity (EC), and, if needed, the redox potential (Eh) are measured in all eluates before filtration (0.45 μm) and chemical analysis. From this method, information about the predominant release mechanism can be obtained. The results can also be used to estimate diffusion tortuosity and observed diffusivities for specific COPCs.

8.3.1.4 Compacted granular leach test

For fine-grained materials, such as clays, that are granular, but have a very low permeability when compacted, the release is based on exposed surface area rather than percolation. The compacted granular leach test has been developed for such materials (CEN/TS16637-2 Annex, 2015; EPA Method 1315, Garrabrants et al., 2012). With the exception of the inner vessel with compacted material, the test is performed in the same manner as the monolith leach test.

8.3.1.5 Redox capacity test

The redox behavior and redox capacity test is not yet validated at the international level (CEN/TS 16660, 2015). However, it allows identification of whether a material has the potential to impose reducing properties on its leachate. Since the release behavior under reducing conditions can be very different from the materials behavior under oxidized conditions, it is important to be aware of the oxidation state of a material. In particular, industrial slags can exhibit such behavior. For example, uranium typically is more soluble under oxidizing conditions than reducing conditions.

8.3.1.6 Sorptive phase parameters

The quantities of "reactive" organic carbon in the solid phase (e.g., humic acid [HA] and fulvic acid [FA]) can be estimated by a batch procedure (van Zomeren and Comans, 2007). In short, the procedure is based on the solubility behavior of HA (flocculation at $\mathrm{pH} < 1$) and the adsorption of FA to a polymer resin (DAX-8). When test data are not available, an estimate can be made based on measured DOC in eluates from the pH dependence test. The amount of amorphous and crystalline iron (hydr) oxides in the waste mixture can be estimated by a dithionite extraction (Kostka and Luther III, 1994). The amount of amorphous aluminum (hydr)oxides can be estimated by an oxalate extraction (Blakemore et al., 1987). The extracted amounts of Fe and Al can be summed and used as a surrogate for hydrous ferric oxides (HFO) in geochemical speciation modeling (Meima & Comans, 1998). The methods have been standardized in ISO/TC 190 (Soil) under series ISO TS 12782, 2010 parts 1–5 (2010). An estimate of Fe and Al (hydr)oxides also can be taken from the available content as obtained from the pH dependence test (e.g., EPA Method 1313).

8.3.1.7 Chemical analysis

The eluates from laboratory tests and leachates from field scale studies are preferably analyzed for major, minor, and trace elements by ICP (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, TI, V, Zn). DOC and TIC (total inorganic carbon) can be analyzed by a Shimadzu TOC 5000a analyzer (combustion to CO_2 and analysis by an infrared gas analyzer) or a similar instrument. Cl, F, phosphate, nitrate, and sulfate can be analyzed by ion-chromatography. The multielement methods are highly preferred, as the major elements dictate the chemical environment that controls release of many substances. Although the leaching methods after some modification in equipment used are suitable for organic contaminants as well, this is not further of relevance here in the context of NORM. It is important that the COPCs, analytical methods, and associated detection and quantification limits selected are consistent with applicable regulatory thresholds.

Different analytical methods are required for specific radionuclides in leaching test eluates, as generally the concentrations are too low to be determined by traditional analytical methods. Direct gamma spectrometry of eluates, although easiest to perform, often is not possible due to too low concentrations. Methods applied in the work reported below comprise the following:

- Po-210—Eluates are acidified to 0.5 N HCl. Po-209 or Po-208 is added as tracer for recovery, while stable Pb and Bi are added as nitrate salts. Ascorbic acid is added and the solution is heated to 80°C for 2 h while in contact with a small metal Ag plate. Po208 or Po-209 and Po-210 are quantified by alpha spectrometry of the Ag plate (Fleer and Bacon, 1984; van Weers and Groothuis, 1990).
- Pb-210—Acidified eluate solutions from the Po-210 measurement are evaporated to dryness and the residue subsequently dissolved in 1.5 N HCl. This solution is passed over an anion exchanger. Pb-210, Pb and Bi are eluted with demineralized water and 8 N HNO_3, respectively. Pb is precipitated as $PbCrO_4$, filtered and dried. After evaporation of the Bi containing fraction, Bi is precipitated as BiOCl and filtered, dried, and weighed. The weight is used to quantify the recovery and the self-absorption for the beta counting of Bi-210. The Pb-210 is obtained after ingrowth of Bi-210 and decay of Bi-210 in the isolated Bi fraction. Beta counting is carried out in a low background GM counter with continuous gas flow (Fleer and Bacon, 1984; van Weers and Groothuis, 1990).
- Ra-226—The concentration of Ra-226 is determined by allowing ingrowth of Rn-222 in a closed system and subsequent extraction on active carbon with He at – 60°C. At 500°C the Rn-gas is evacuated from the active carbon with He in a Lucas cell and subsequently measured by scintillation counting (Matieu et al., 1980).

8.3.2 Intercomparability of EPA and EU methods

LEAF—methods and corresponding methods from the EU (shown in Table 8.1) are similar in structure and intent. The LEAF and EU methods have only minor deviations in test structure (e.g., the number of test fractions taken) or in test parameters (e.g., specified targets or time durations). This means that the results obtained are equivalent as was demonstrated in parallel validation (Garrabrants et al., 2012). Documentation supporting the development and use of the US and EU test methods is available (Garrabrants et al., 2010; van der Sloot et al., 1997; Hjelmar et al., 2013). In Fig. 8.2 the comparability of data for Cr and Mo between the EU and the LEAF methods for pH dependence in three different materials is illustrated.

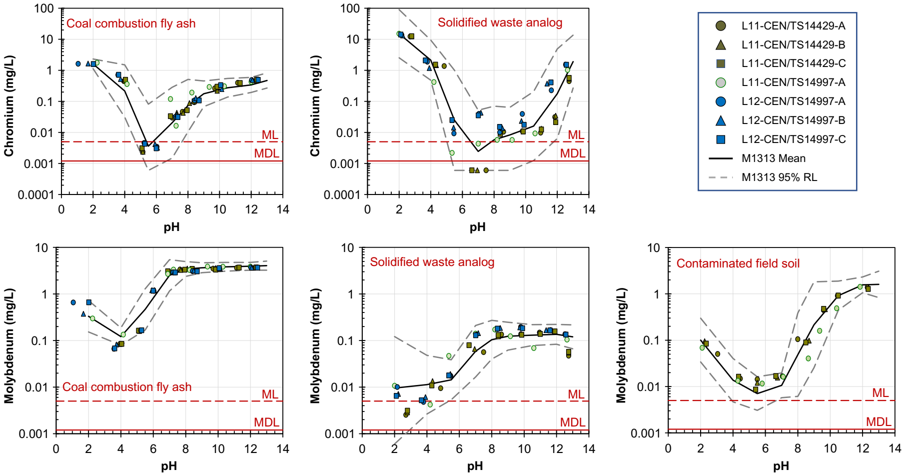

Fig. 8.2 Comparison of CEN TS14429 results with EPA Method 1313 results for pH-dependent leaching (Garrabrants et al., 2011).

8.3.3 *Uncertainty*

The uncertainty associated with leaching test results is comprised of uncertainties in sample representativeness of the material for which a decision is needed, uncertainty in leaching test performance and uncertainties associated with chemical analysis of eluates. The uncertainty of testing (including analysis) is covered by the intercomparison validation carried out (Garrabrants et al., 2012). Generally, the analytical uncertainty is on the order of <10%–20% depending on laboratory specifications, provided that the measurements are not close to the method detection limit. Typical performance data for the characterization leaching tests are given in Table 8.2.

Uncertainties associated with the prediction of release under field conditions are of approximately an order of magnitude, and are influenced by choices in the assumed

Table 8.2 **Typical performance data for characterization leaching tests including analytical uncertainty specified at less than 10% (Garrabrants et al., 2012)**

Method	Repeatability (%)	Reproducibility (%)
pH dependence test[a]	13	28
Percolation test[b]	6	16
Monolith leach test[b]	8	21

[a] Based on eluate concentration.
[b] Based on cumulative release.

exposure conditions (e.g., water infiltration/contact, wet/dry cycles, temperature, dimensions of the application, interaction of released substances with the near field soil system, the distance to a relevant point of compliance). A comparison of laboratory test results to field measurement of leaching is provided in Kosson et al. (2014).

8.4 Leaching test results for specific constituents and materials

8.4.1 Leaching data for U, Th, K, Po-210, Pb-210, Ra-226, and others from materials of interest

Limited data are available for the release of radionuclides from NORM with the above-mentioned characterization tests. In Fig. 8.3 results are given for Pb-210, Po-210, Ra-226, Th, and U release from granular phosphate slag by percolation (PrEN 14405, 2016). The total content, available content, relevant test conditions, and derived effective diffusion coefficients are given in Table 8.3 (Hoede et al., 1991). The eluate concentrations of Pb-201, Po-210, and Th are virtually constant, which is indicative of solubility limited release. For Ra-226 and U, the release appears sensitive to the pH change from pH 8.5 to almost 10, but still solubility limited.

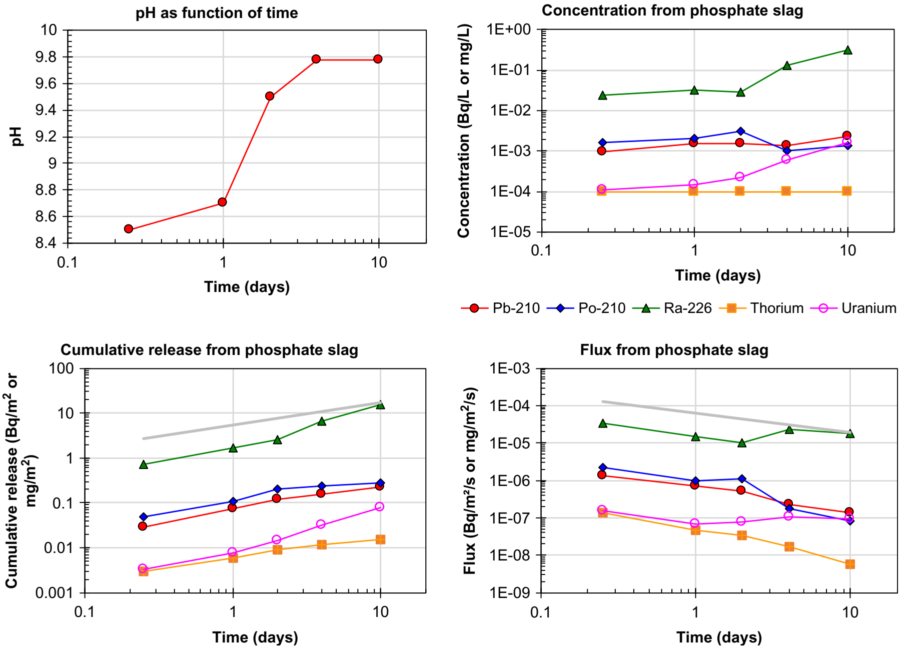

Fig. 8.3 Pb-210, Po-210, Ra-226, Th, and U concentrations in eluates from leaching of granular phosphorus slag by percolation using NEN 7343 (similar to EPA 1314 and PrEN 14405). Gray lines show slope 0.5 (left) and slope −0.5 (right) indicative of diffusion-controlled release.

Table 8.3 **Total content, available content, test conditions, and observed diffusivities (D_e) for phosphorous slag (5 pieces of slag; surface area 0.2 m^2; mass 5.8 kg; water volume 5 times total volume of slag)**

	Total		Available content		pD_e ($-\log(D_e)$)
	mg/kg	Bq/kg	mg/kg	Bq/kg	(D_e in m^2/s)
U	127		16.5		16.6
Th	50		<0.01		>11.7
Po-210		35		<0.02	9.8
Pb-210		70		2.66	14.4
Ra-226		1576		70	13.2

The leachability of Po-210 was measured from a monolithic cement-stabilized gypsum (van der Sloot et al., 1987) using a monolith leach test NEN 7345 (1995) similar to EN15863 and EPA Method 1315. In Fig. 8.4, the flux of Po-210 from the stabilized product is given, which indicates diffusion-controlled release (slope 0.5 in cumulative release graph and slope −0.5 in flux graph). Based on total content, the effective diffusion coefficient derived from the data is 8.2×10^{-15} m^2/s. This seems a very low value, but when corrected based on available content the value becomes 6.0×10^{-12} m^2/s, which is less than an order of magnitude lower than Na mobility in this matrix (3.2×10^{-11} m^2/s). So a fraction of the Po-210 is retained in the matrix more effectively and thus the key question is whether the release remains the same when the "mobile fraction" has been depleted.

For the stable elements much more data are available for NORM as well as construction products containing NORM. In Fig. 8.5 data on U and Pb from coal fly ash

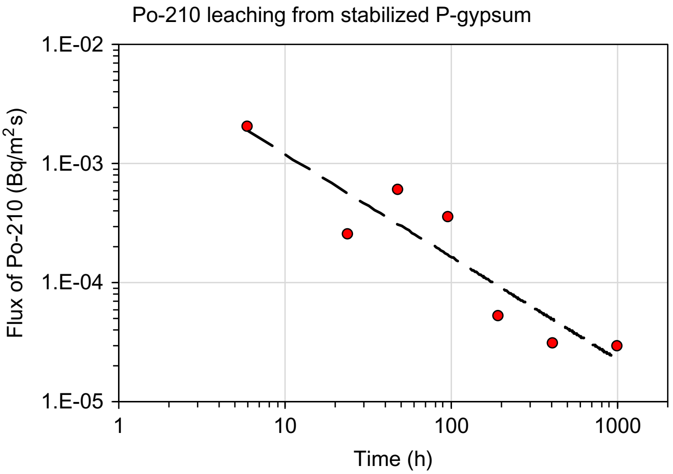

Fig. 8.4 Po-210 leaching from a monolith of cement-stabilized phosphogypsum by NEN 7345.

(Kosson et al., 2009) are given, which illustrates for most coal fly ashes the same behavior, with a few coal ashes showing increased U leachability in the pH range 6–11, likely caused by carbonate complexation.

For K and hence for K-40, the release behavior from a range of NORM is mostly independent of pH and K (and K-40) are depleted from the granular material within an L/S of 1 during percolation column testing (Fig. 8.6). The activity of U-238 (30–217 Bq/kg), Th-232 (10–120 Bq/kg), and K-40 (87–303 Bq/kg) series for the same fly ashes has been reported in Roper et al. (2013). In Fig. 8.7 leaching data for U and Th are given for a selection of materials. Natural rocks generally have low leaching levels, whereas phosphogypsum and related phosphate processing wastes show elevated levels of U and Th.

In Fig. 8.8, the leaching of U from a range of monolithic NORM and monolithic products containing NORM is given for the tank leaching test (NEN 7375, similar to

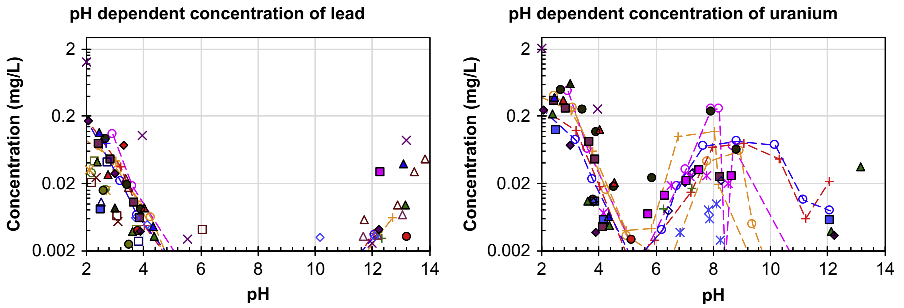

Fig. 8.5 U and Pb pH-dependent leaching concentrations from a wide range of coal fly ash samples obtained by EN14429 and EPA 1313 (Kosson et al., 2009); detection limit for Pb and U 0.002 mg/l.

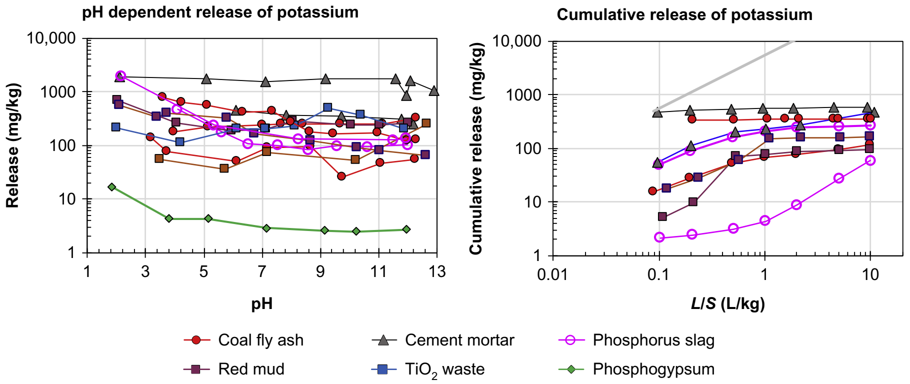

Fig. 8.6 K leaching from a range of NORM based on pH dependence and percolation column leaching test results. Horizontal lines reflect total composition data. The gray line (slope 0.5) in the cumulative release graph indicates diffusion-controlled release.

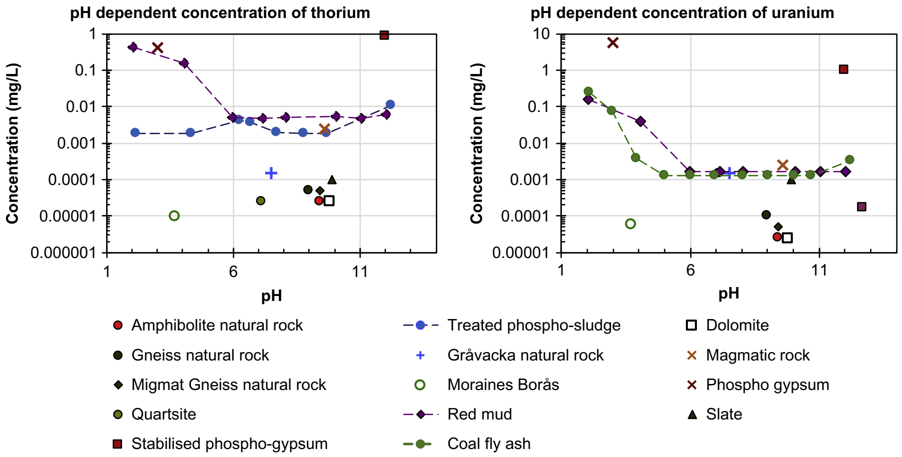

Fig. 8.7 U and Th leaching from a range of NORM based on pH dependence leaching test results.

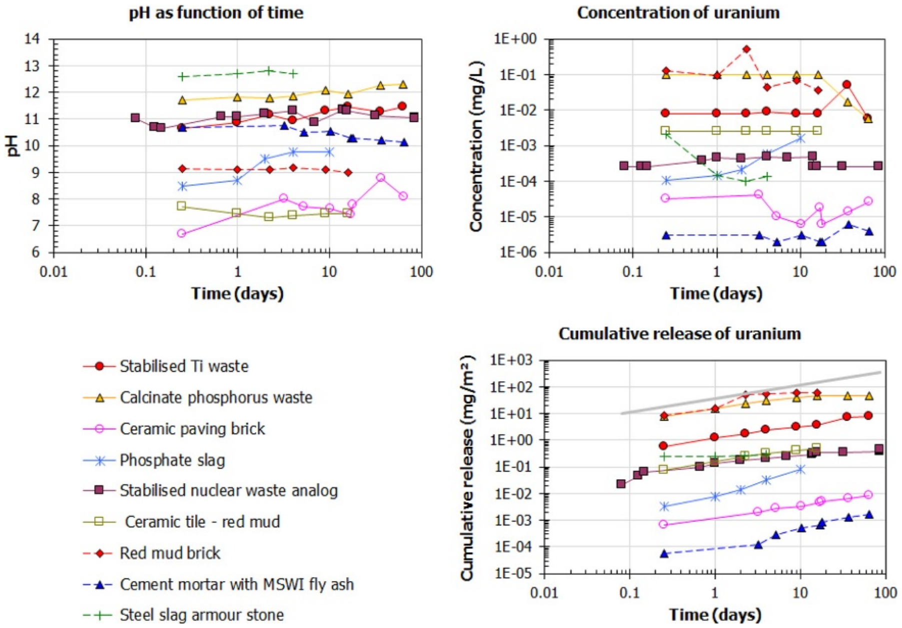

Fig. 8.8 U release from possible NORM and monolithic products containing NORM based on monolith leaching test results (ECN, 2016). The gray line (slope 0.5) in the cumulative release graph indicates diffusion-controlled release.

EN 15683 and EPA 1315). The concentration of U is more or less constant for almost all materials (except phosphate slag and steel slag armor stone), which implies diffusion-controlled release.

As discussed earlier, chemical analogs can be used to provide an initial understanding of the leaching behavior of some radionuclides. Ba and Ra have many similarities. Therefore the leaching behavior of Ba can give an indication of what to expect for Ra-228 and Ra-226 release. In Fig. 8.9, Ba release as a function of pH is given for a range of NORM.

8.4.2 Leaching behavior of alkali-activated cements and cements with coal fly ash

The leaching behavior of alkali-activated cements (AACs) (i.e., geopolymers) and PCs containing coal fly ash is of interest because these construction materials are made from NORM components. In addition, geopolymers have been used to reduce release of natural radioactivity (Hermann et al., 1999; Rafiza et al., 2013).

For deeper understanding of alkali-activated materials, we refer to Provis and van Deventer (2014). In addition, a comprehensive review has been written by Provis et al. (2015) on the understanding of alkali-activated materials, including comparisons between cements which are basically a calcium silicate structure, and alkali-activated materials that are aluminosilicate structures (see Chapter 7).

Differences in leaching between AAC and a regular PC mortar are determined by the mineral and sorptive phases controlling leachability. In AAC aluminosilicate hydrate is the primary matrix phase that is present, whereas in PC calcium silicate hydrate predominates as matrix phase. The primary identified mineral phases in

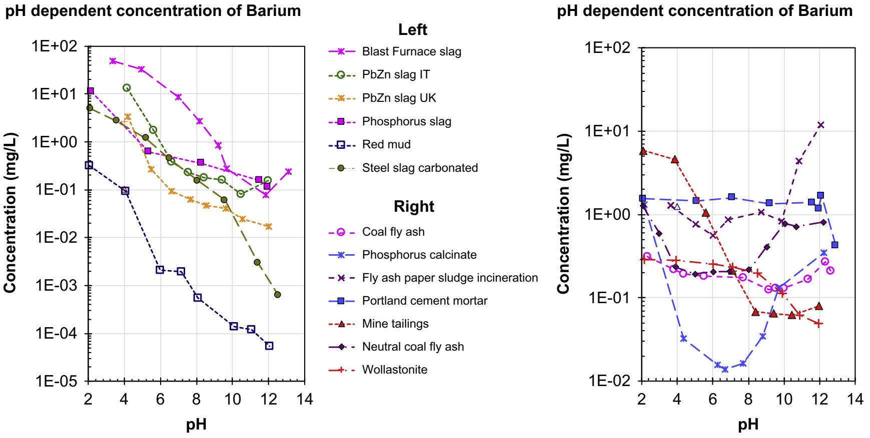

Fig. 8.9 Ba release from NORM as surrogate information for Ra-228 and Ra-226 release behavior.

the bulk matrix may be less important with respect to leaching than minor phases present on the mineral and pore surfaces within the material. On the other hand the bulk composition will mainly predict the porewater chemistry at the interface of liquid and solid within the pores. In Fig. 8.10 a comparison between AAC and PC is provided, which shows that an important difference is the lack of ettringite in AAC, where for PC ettringite is responsible for retention of several anions by substitution with sulfate

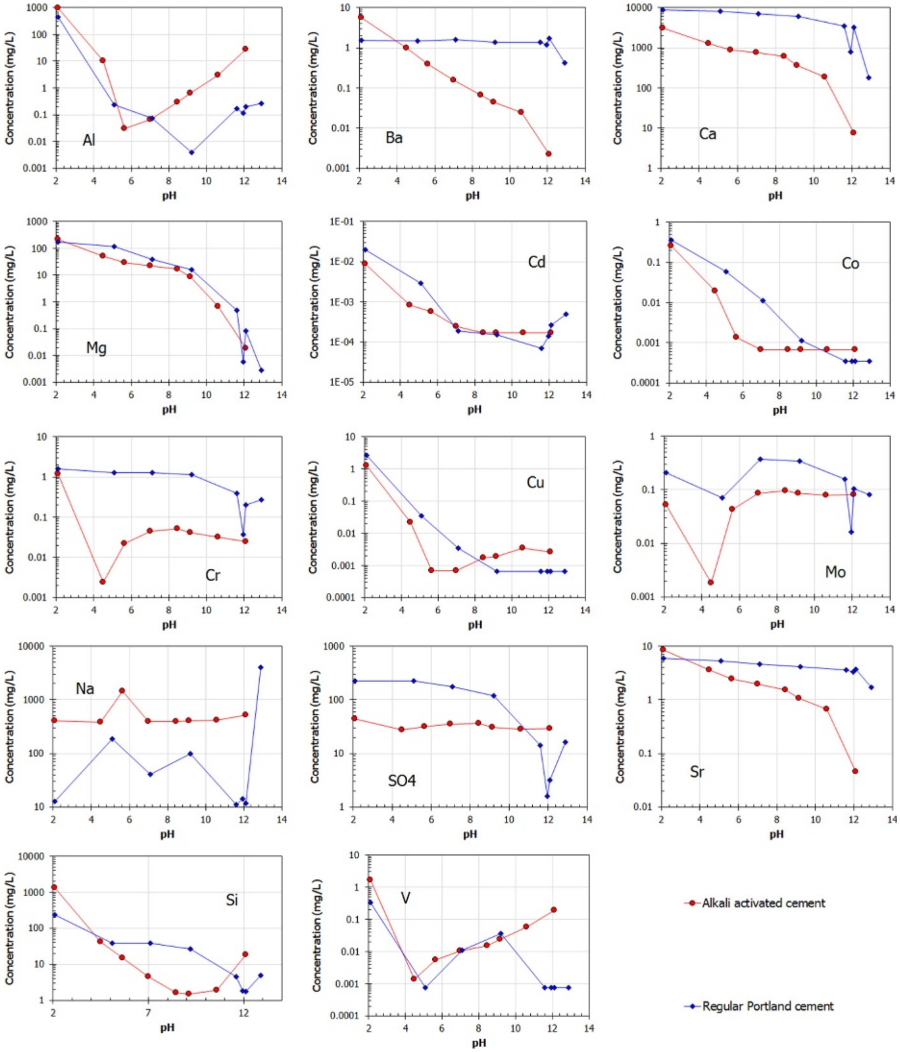

Fig. 8.10 Comparison of leaching characteristics of alkali-activated cement (AAC) (based on blast-furnace slag and coal fly ash) and Portland cement.

at alkaline pH (see sulfate, Cr, Mo, and V). However, less Cr is leachable in AAC at alkali pH than from PC mortar because a greater proportion of Cr is present as Cr^{3+} than Cr^{6+}. In PC, about 11% of the total Cr content is present as Cr^{6+} (van der Sloot et al., 2011). In AAC, Al concentration is increasing from pH 6 indicating different phases control Al solubility for AAC and PC. Ca solubility is lower over the entire pH range in AAC compared with PC. Also, Ba and Sr have a strong decrease in concentration with increasing pH. The behavior of these Group IIa elements in AAC, i.e., very good immobilization at alkaline pH, is in line with Van Deventer et al. (2007). In the neutral to mildly alkaline pH range (pH 5–11) silicon solubility from AAC is substantially less than for PC. Cr leaching is less in AAC and looks more like a blended cement (van der Sloot et al., 2011). Na leaching is considerably higher in AAC compared with PC because of the use of NaOH in AAC activation. Metals like Co, Cu, and Ni show increased retention for AAC than PC at pH 5–8. All other measured elements (Cd, Fe, K, Mg, Mn, P, Pb, Sb, and Zn) show very similar release behavior in level and shape indicating very similar release controlling phases. For Th no comparison data in PC are available, although the release behavior is not likely to be very different (Fig. 8.11).

Surface chemistry and interphase chemistry between different phases within the building material itself, but also at the interface with other materials in the building during its lifetime (e.g., steel reinforcement) and at EoL (e.g., in contact with other wastes, acid rain, soil, milling/erosion, freeze-thaw, or other weather conditions) may influence the response to physicochemical attacks.

Chemical and physical attack will have an effect on the release through leaching. In addition, mass transfer processes analogous (but inverse) to leaching are responsible for ingress of reactive species such as chloride, carbon dioxide. The latter lowers material pH and can lead to corrosion of reinforcement steel. Sulfate attack leads

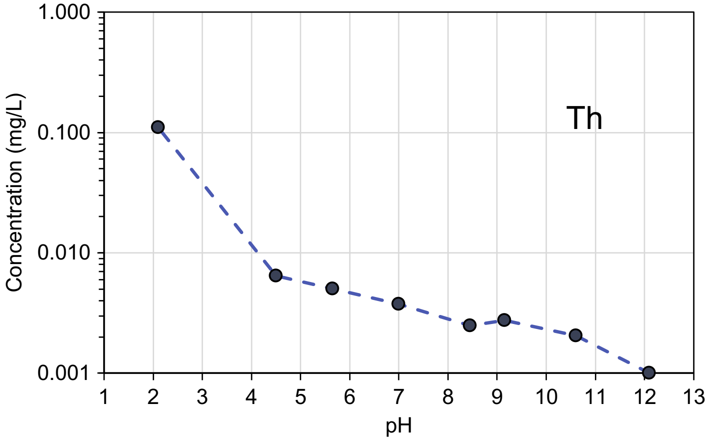

Fig. 8.11 pH-dependent Th release from AAC (same as Fig. 8.10).

to physical deterioration. The use of leaching assessment to understand and calibrate reactive transport models to simulate these phenomena has been described elsewhere (Branch et al., 2016; Sarkar et al., 2010).

We refer to Chapter 7 for the description of the different types of alkali-activated materials and cements and the applicability of the standardized durability tests developed for PC to the different materials is critically reviewed. We selected here some examples of durability tests to highlight the important impact of durability to leaching.

For cement, standardized durability tests have been developed to determine deterioration by chloride ingress, carbonation, sulfate attack, and acid attack to assess the response of the material from external chemical stressors. In addition, intrinsic deterioration by hydration of reactive minerals (free lime) and alkali-aggregate reactions inside the material is another characteristic studied for cement and alkali-activated materials. However, durability tests which have originally been set up for PC mortar or concrete do not necessarily reflect durability if applied to alkali-activated materials (Bernall et al., 2012). For example, standard carbonation tests (ISO-1920-12, 2015 and EN 13295:2004) setup for PC-based materials, are based on elevated CO_2 concentrations to increase the rate of aging. In conventional concrete carbonation may lead to reduced pH in the pore water, which can induce corrosion of the steel reinforcement (Chi et al., 2002). Application of this test to aluminosilicates would result in phase changes, which do not reflect the durability toward CO_2 under realistic conditions (Bernal et al., 2010). It is expected that under natural CO_2 conditions, the pore solution pH may be maintained longer by the excess of alkalis present. Understanding the impacts of aging on AAC materials, including long-term carbonation, requires further study.

A mechanistic understanding of the processes leading to leaching or chemical attack is needed to understand the macroscopic behavior of building materials and the validity of testing methods. The example of sulfuric acid attack toward a geopolymer-based product with high alkali content and a molecular ratio of Na-Si of 0.6 is used as an illustration. An extensive study was performed by Allahverdi and Skvara (2006). At a pH of 1, 2, and 3, different behavior of the geopolymer has been observed. Sulfate attack as tested with the ASTM C1012 may lead to opposite effects when applied to a geopolymer or to a PC-based concrete: whereas PC may expand under these test conditions, the geopolymer tested by Davidovits and Davidovits (1999) shrank. This difference might be related to the presence and absence of sulfate-containing AFm phases in PC and geopolymers, respectively. An extensive review on sulfate resistance in different alkali-activated materials is given in Provis and van Deventer (2014). Clearly, different responses to sulfate attack will lead to different secondary leaching behavior.

Moreover, significant differences in behavior have been observed within the different subtypes of alkali-activated materials. For instance, the type of alkali used as activator of the aluminosilicate source (metakaolin or other clay materials, Ca-rich blast-furnace slag, fly ash with high or low calcium content, red mud or other NORM residues), and the specific combination of alkali type and aluminosilicate source used, may influence the durability.

8.5 Use of geochemical speciation and reactive transport modeling

8.5.1 Modeling of radionuclide release behavior

Geochemical speciation and reactive transport modeling of radionuclides is carried out with the same modeling tools as used for stable elements. Based on the test results from the pH dependence test a chemical speciation fingerprint can be derived or used from prior work (van der Sloot and van Zomeren, 2012; van der Sloot et al., 2010). For instance, when radionuclides need to be assessed in a cement mortar (hydrated cement with only fine aggregate) or concrete the chemical speciation fingerprint established for ordinary PC or blended cements can be used (Kosson et al., 2014) with the addition of the thermodynamic data for the radionuclide(s) of interest. Figs. 8.12 and 8.13 show the use of geochemical speciation modeling to simulate pH-dependent leaching test results and the mineral phases and reactions controlling the observed leaching for several cementitious materials.

8.5.2 Influence of redox conditions and carbonation

Release behavior is strongly influenced by pH, so when alkaline materials (cement-based products and many slag types) are exposed to the atmosphere, the materials will be carbonated and hence the pH decreases and the release behavior of many substances may change drastically. In Fig. 8.14 this is illustrated for Ca through measurement of field exposed material (PC concrete, recycled concrete aggregate, and Roman cement together with modeling results of increasing degree of carbonation). Ba and Sr have been shown to be affected by carbonation similarly to Ca and therefore it can be expected that Ra-226 will also be affected.

8.6 Scenario-based approach to leaching assessment

8.6.1 Overview of scenario approach

Characterization of leaching behavior using the LEAF testing approach along with scenario-specific information can be used to assemble a leaching "source term" for many environmental scenarios or levels of environmental assessment including:

- screening-level assessments at a site-specific, regional or national scale;
- detailed site-specific evaluations;
- performance comparisons between different materials or treatment processes under specific use scenarios; and
- development of chemical speciation-based models to evaluate potential material leaching behavior under field conditions that may be difficult or impossible to reproduce in the laboratory.

Assessment of the applicability and accuracy of any predictive leaching assessment approach, however, requires evaluation through the use of pilot- and full-scale field studies in which leaching predictions for a particular material based on laboratory

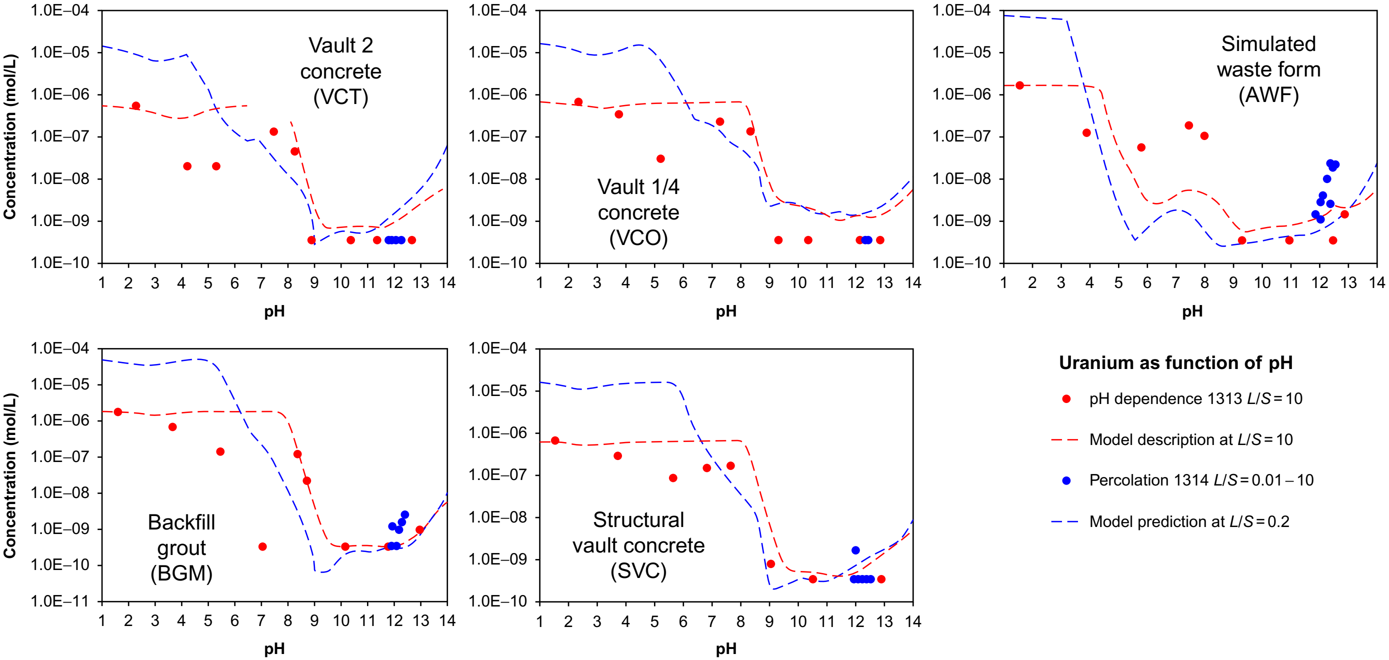

Fig. 8.12 Geochemical modeling of U release as a function of pH in cementitious materials.

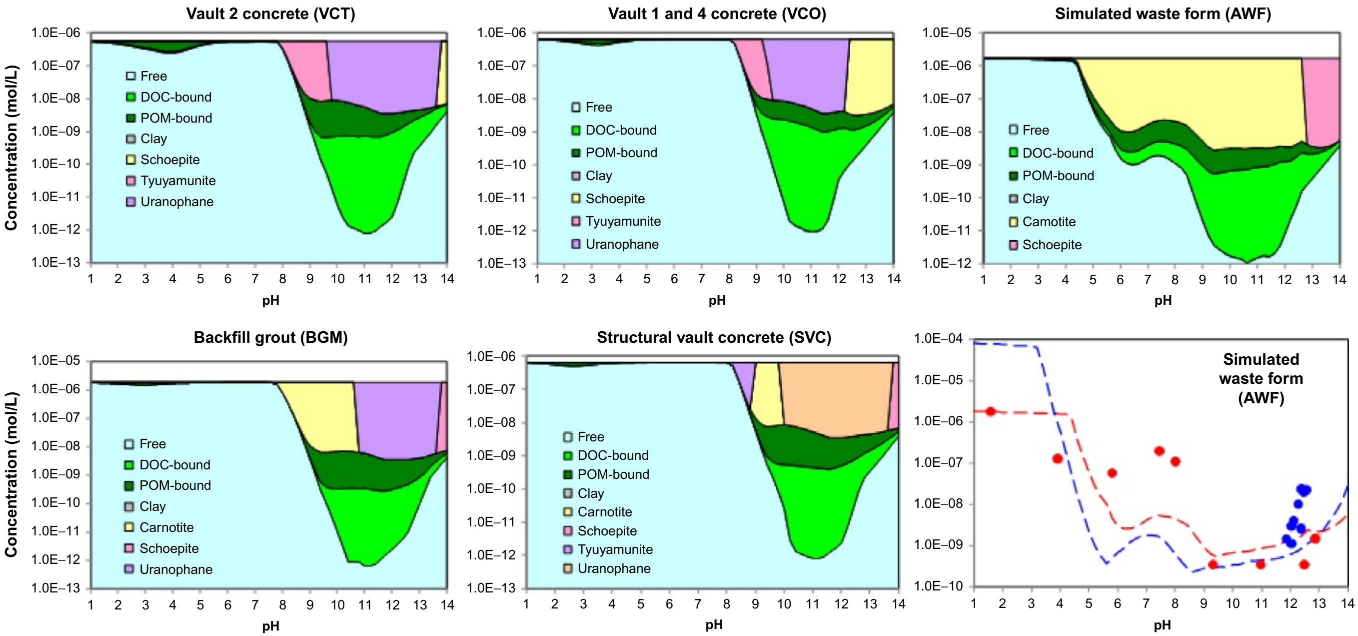

Fig. 8.13 Partitioning of U release behavior over dissolved and particulate phases.

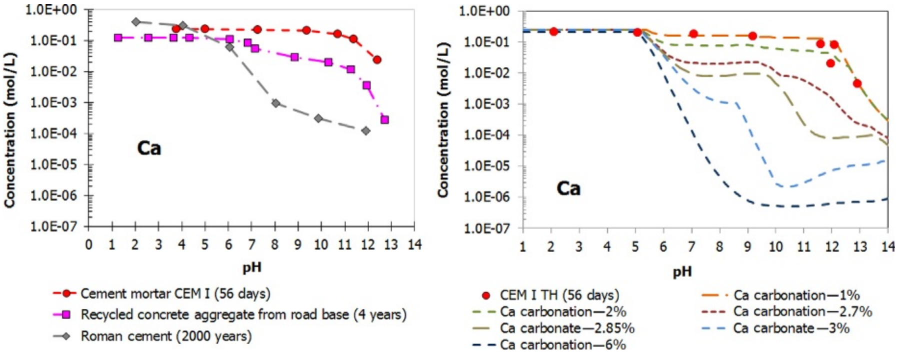

Fig. 8.14 Measured Ca leaching as a function of pH in comparison with modeling of the degree of carbonation through geochemical modeling (Kosson et al., 2014).

testing may be compared to measured leachate concentrations for that material collected under field conditions. Field studies also provide information regarding the relative importance of natural processes on leaching of COPCs including water flow patterns, extent of local chemical equilibrium, and chemical changes due to aging or exposure to the environment (Fig. 8.15).

In Kosson et al. (2002), leaching assessment using a performance or "impact-based approach" was proposed, that subsequently has been referred to as LEAF. The LEAF testing methodology allows for both empirical use of testing data for specific scenarios as part of a screening assessment, and use of the leaching test data in conjunction with chemical speciation and mass transport models to provide a more realistic and refined, scenario-specific estimate of constituent leaching that can be used as a source term for risk assessment. While the screening assessment is a bounding estimate of leaching potential, consideration of waste and scenario-specific information allows many conservative assumptions to be refined with further testing data and mass transport

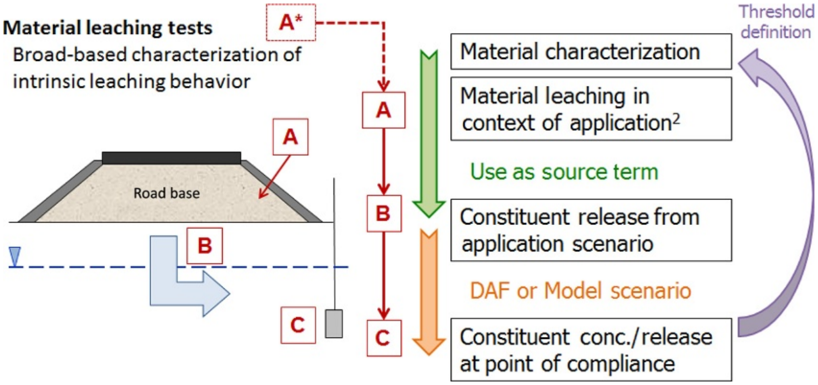

Fig. 8.15 Assessment approach to derive acceptance criteria based on source-path-target impact modeling. DAF stands for dilution-attenuation factor.

modeling results. A tiered-approach was proposed for developing the leaching source term, considering the type of evaluation being carried out, the level of information available, and the extent of conservatism embedded in the estimate. Subsequently, the EPA published its *Methodology for Evaluating Encapsulated Beneficial Uses of Coal Combustion Residuals* (US EPA, 2013), which describes a tiered approach that can be applied to a more limited set of uses of two secondary materials (i.e., coal fly ash use as a cement replacement in concrete and FGD (flue gas desulfurization) gypsum use in gypsum board).

The observations and information gathered in Kosson et al. (2014) provides a basis for more detailed recommendations provided on the use of LEAF test methods, consistent with the initially proposed methodology by Kosson et al. (2002) and the EPA methodology (US EPA, 2013). These recommendations for use of leach test data only provide the approach for estimating the leaching source term (i.e., concentrations and amounts of a constituents leaching from the material under a specific scenario). Additional determinations are needed to define or account for (i) the location that serves as the basis for exposure assessment following constituent leaching release from a source scenario (e.g., point of compliance), (ii) dilution and attenuation in the vadose zone and groundwater or surface water from the point of release to the point of compliance, and (iii) appropriate exposure scenarios or reference thresholds (e.g., human health or ecological thresholds). These evaluations can be incorporated into a model of constituent fate and transport leading to possible receptor exposure (e.g., groundwater transport to a drinking water well, with water ingestion as the exposure pathway).

Defining the material use scenario is the first step to selecting the appropriate leaching tests and basis for interpreting the resulting data. The extent of information needed as part of the scenario definition increases as the evaluation seeks to achieve a more detailed and refined estimate of constituent leaching. The initial scenario definition should at a minimum include determination of the applicable pH domain, range of oxidation-reduction conditions, and the primary mode and amount of water contact (see Fig. 8.16).

8.6.2 Case study radiological impact assessment

The following scenario is presented in order to further illustrate the modeling approach used to estimate the radiological dose to a member of the public. A total of 2×10^8 kg of NORM-containing building waste is dumped on a waste heap (~20 m in height). The material is sandwiched between two layers of low permeability clay (0.5 m at the top and bottom of the material) to reduce infiltration and leaching to the local groundwater. Radionuclides from the U-238 and Th-232 decay chains are assumed to be in secular equilibrium, and their activity concentrations in the building waste material correspond to an activity concentration index for the gamma radiation emitted by building materials of 1 (EU, 2014). As such, first an activity concentration of 300 Bq/kg is considered for U-238 and its daughters, based on the Ra-226 limit in the activity concentration index. Second, an activity concentration of 200 Bq/kg is considered for Th-232 and its daughters (direct limit from the activity concentration index). The dose is estimated for the following two cases:

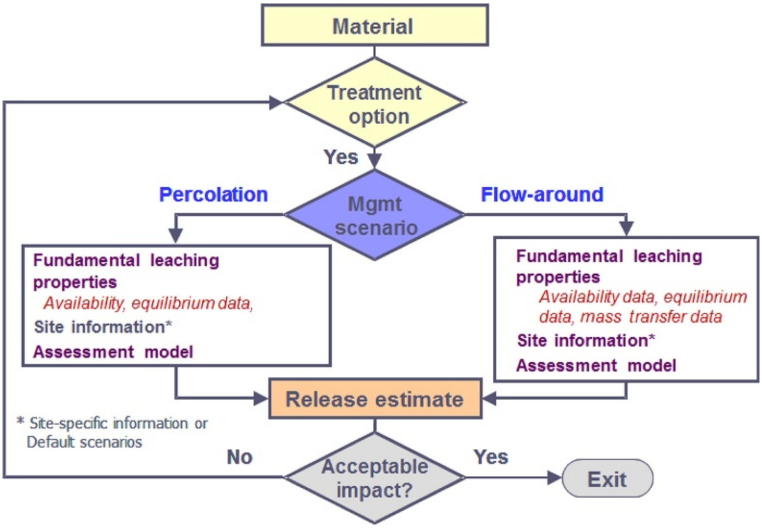

Fig. 8.16 Decision scheme for selection of test method and type of impact assessment.

(1) Intact, fully functional clay (both hydrologically and chemically) and best estimate sorption (reference case)
(2) Degraded clay (i.e., clay has lost its hydraulic integrity) and decreased sorption

For the reference case, typical hydraulic properties for clay and best estimate sorption parameters (i.e., the solid-liquid distribution coefficient, K_d) are used as inputs into the calculations. For the degraded clay and reduced sorption case, the clay hydraulic conductivity is increased whereas the K_d values are decreased (by a factor of 10) to simulate increased infiltration and leaching.

Leaching of NOR from the building waste material is simulated using the one-dimensional transport code HYDRUS-1D (Šimůnek et al., 2013). For the setup of the model, the following profile is assumed: a 20 m thick NORM layer separated from the local water table by 0.5 m of low permeable clay and 1.5 m of native sand. The water flux through the waste (i.e., the upper boundary) is set to 30 mm/year for the intact clay case and to 270 mm/year for the degraded case. The sorption parameter K_d used in the simulations is nuclide-specific to represent the different geochemical behavior of NORs in the profile materials and hence their different mobility. The simulation is performed over a time frame of 10,000 years. It should be noted, however, that during the simulation period of 10,000 years, the maximum concentration in the leachate was only reached in the worst case scenario runs (i.e., degraded clay and reduced sorption). The lower infiltration rate through the intact clay layers combined with the high sorption of the NORs considerably delayed the time to reach the maximum leachate concentration in the reference scenario. Nevertheless, the results from the worst case scenario illustrate the maximum radiological impact of the leaching NORs. The fractions of NOR leached to the aquifer in case of degraded clay and decreased sorption are presented in Table 8.4. The calculations with respect to leaching indicate that the effect of increased infiltration due to the degraded clay is secondary to the effect of decreased sorption.

Table 8.4 Percentage [%] of the total waste inventory leached for conditions of degraded clay and decreased sorption (worst case scenario)

	U-238 series							Th-232 series		
	U-238	**U-234**	**Th-230**	**Ra-226**	**Rn-222**	**Pb-210**	**Po-210**	**Th-232**	**Ra-228**	**Th-228**
1000 y	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
10,000 y	65	64	87	3	<1	1	<1	90	<1	<1

After leaching to the groundwater, the radionuclides are assumed to migrate to a nearby water well, 50 m downgradient, through a sandy aquifer. For radionuclide transport in the groundwater, the maximum activity concentration below the waste heap is assumed. A dilution factor is applied to the maximum concentration in the groundwater below the disposal site taking into account the area of the disposal site, the average groundwater velocity, the thickness of the aquifer, and the discharge rate.

In the next phase, a biosphere model is used to calculate the activities of the NOR in different biosphere compartments and the subsequent dose to humans. The biosphere model represents the transfer mechanisms of radionuclides in the biosphere, along with related assumptions and simplifications. Within the model, transfer is considered rapid with respect to the modeling scale and equilibrium can be assumed between the different media (e.g., soil-to-plant, uptake by animals). Radioactive decay and ingrowth are also considered in the model. To calculate the dose to man, conservative human habits are assumed. In this case study, the water in the well is used by a self-sustaining farmer. It is assumed that the farmer uses the maximum activity concentration in the well water for irrigation of food crops and pasture and livestock watering and only uses food products coming from the contaminated area. Several transfer pathways are considered in this scenario such as transfer of radionuclides from irrigated water to plants, transfer of radionuclides from irrigated water to soil, and transfer from plant to animal through watering and feed. To calculate the dose to the self-sustaining farmer, exposure pathways such as ingestion of well water, ingestion of food products (e.g., vegetables, meat, eggs, milk), external radiation from soil and inhalation of dust (ingestion), and radon when working on the field are taken into account. When considering all these transfer and exposure pathways, a maximum annual dose can be calculated, albeit this is only a very simplified scenario for illustration and there are great uncertainties with respect to the radionuclide transport assumptions. The doses a farmer could get after 10,000 years in case of the reference scenario and for the worst case scenario are presented in Table 8.5.

These calculations suggest that the annual dose to a member of the public following leaching of radionuclides from a waste heap with NORM containing building waste is below the maximum exposure limit of 1 mSv/year.

Table 8.5 **Maximal dose rates [mSv/year] to self-sustaining farmer after 10,000 years**

	Reference scenario with intact clay and best sorption	**Scenario with degraded clay and reduced sorption (K_d/10)**
U-238 series (U-238, U-234, Th-230, Ra-226, Rn-222, Pb-210, Po-210)	1.30×10^{-16}	0.0143
Th-232 series (Th-232, Ra-228, Th-228)	1.43×10^{-21}	0.0376

In addition to the dose-calculation for humans, a radiological impact assessment is also conducted for wildlife. Based on the concentration of NOR in the soil after irrigation, which is considered the peak concentration, an assessment is done using the ERICA tool for terrestrial ecosystems (Brown et al., 2008). With the ERICA tool, calculations can be performed to estimate the risks to selected animals and plants (e.g., mammal, worm, bird, grass, tree, etc.). A dose and risk quotient are calculated based on a 10 μGy h^{-1} no-effect-dose-rate (a risk quotient of 1 means no risk). For the worst-case scenario, in which degraded clay and increased leaching are considered, the risk quotient is $\sim 10^{-6}$.

8.7 Conclusions and recommendations for evaluation of norm

Use of NORM residues, including use as aggregates and addition to PCs and AACs, is being considered more extensively to reduce waste management requirements and to reduce energy and natural resources usage through replacement of traditional materials. Leaching and durability assessment are important components of evaluating environmental safety and protection of human health.

The leaching of radionuclides present in NORM is controlled by the same physical-chemical processes that control leaching of stable inorganic elements. Thus leaching data from total elemental analysis of elements with radioactive isotopes (e.g., K, U, Th, Pb) can be used to gain an initial understanding of the leaching of the corresponding radioisotopes. In addition, chemical analogs can be used to provide an initial understanding of the leaching behavior of some naturally occurring radionuclides (e.g., Ba as an analog for Ra). However, there are only very limited data available on the leaching of specific radionuclides from NORM and further testing and assessments should be supported.

The leaching of specific constituents from NORM is a function of the primary material matrix, the mechanism by which each radionuclide is retained in the primary matrix (e.g., by incorporation into the matrix network structure, adsorption onto pore surfaces, co-precipitation with a distinct mineral phase, or association with solid organic matter), and the contacting water chemistry (e.g., pH, redox, carbonate concentration).

Leaching and durability of materials are closely linked for some material degradation processes. Leaching of primary components and ingress of reactive species (e.g., chloride, sulfate, carbon dioxide) through liquid or gas phase transport during aging may change the physical durability and leaching characteristics of NORM and NORM containing construction materials. Standardized tests developed for assessing aging and durability of ordinary PC materials may provide misleading results and may not be applicable for alternative cementitious binder chemistries such as AACs and mortars and concretes produced from such cements. Further evaluation of the aging processes and long-term leaching of alternative binder chemistries is needed.

The leaching assessment framework LEAF and its underlying leaching methods are applicable to a wide range of materials, field scenarios, and treatment process decisions for NORM and construction products containing NORM. CEN and US EPA leaching methods produce the same results as shown in intercomparison studies, thereby facilitating exchangeability and comparability of results. Use of these methods in characterization testing also will provide very detailed insight in controls and possible difference in release behavior of stable elements and radioisotopes and between stable elements acting as surrogates (e.g., Ba for Ra-226 and Ra-228).

> For granular materials, the pH dependence test and the percolation test should be used.
> For monolithic materials, the pH dependence test and monolith leach test or compacted granular leach test should be used.

For major sources and types of NORM, parallel measurements of stable and radionuclides of relevance would be highly revealing to understand release controlling phases and thereby provide better means to deal with changes occurring in the long term (carbonation, oxidation, physical degradation, etc.).

By focusing on fundamental leaching properties a single data set can be used for evaluation of multiple use and disposal options. Accumulation and comparison of data provides basis for defining material classes through ranges in release and characteristic behavior of material types, thereby reducing the need for and intensity of testing as part of quality control by the NORM residue provider. After characterization and demonstration of compatibility between stable element behavior and radioisotopes much more simple testing will suffice for regular control, if needed. Simplified testing after characterization in a tiered approach allows for cost-effective applications.

As in EoL material is likely to become size reduced and fully oxidized due to exposure to the atmosphere, the pH dependence test provides a very useful means to assess behavior under such conditions provided a realistic pH domain is selected for the final evaluation (mostly near neutral pH as a result of carbonation or exposure to the natural environment).

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Nontechnical aspects that influence the reuse of NORM in construction industry

9

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9.1 Introduction

Guide for the reader: Structure of chapter "9":

This chapter is nontechnical in nature.

- It focuses on nontechnical issues (Section 9.2) that have to be addressed before use of NORM by-products can be considered in construction materials.
- In Section 9.3 an overview is given of key steps in the product development that need to be undertaken before use of an NORM by-product in construction is achieved.

In the previous chapters all kinds of information is given about the types of NORM (naturally occurring radioactive material), the potential application, and all kind of relevant ecological and health issues as well as measurement methods. However, when developing a new building product or to use a NORM by-product in an existing application also other aspects are of relevance and are sometimes more restricting then the already mentioned issues. Aim of this chapter will be to discuss nontechnical aspects and to explain how these aspects interact not only between themselves, but also with the issues discussed in the previous chapters. Therefore, first a short introduction in product development is given in case of the use of by-products for the building industry and in that framework the most important aspects will be addressed. Finally a generic approach will be discussed, which could be used to set up a product development project.

9.2 The issues

When trying to find a use for a NORM by-product in the building industry several aspects have to be assessed:

- Size of the by-product stream
- Properties and status of the by-product
- Product process interaction

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- Environmental and health issues
- Type of recycling
- Potential market and acceptance/perception aspects
- Cost aspects throughout the chain
- Competition with other by-products
- CE marking and other certification aspects

In the following paragraphs a concise description of each of these aspects is given showing the complexity of both the aspects themselves and the interaction between them. Furthermore, this complexity is one of the main reasons that it is rather difficult to bring a new building product on the market, which complexity is only enhanced in case some of its constituents are NORM or considered as waste materials.

9.2.1 Size of by-product stream

The building industry is a bulk industry, which has as a consequence that they use large quantities of raw materials. In practice this can range from a few hundred Mg per year for a specific application of a small-sized installation up to hundreds of thousands of Mg per year for bulk application such as the concrete industry. Therefore, it generally does not make much sense to try to develop a building product when the amount of by-products is less than a few hundred Mg a year. On the other hand, if the by-product stream is large, basically the building industry is the only industry capable to process huge amounts of nonspecific raw materials.

9.2.2 Properties and status of the by-product

What properties are required and/or accepted from a by-product depends to a great extend on the intended use. In case the required properties are based on the requirements of an existing process then the properties will be compared to that of the component it replaces. On the other hand, in case of product development the specific properties of a given by-product will be used to make first assessments on potential applications. In the first case it is rather clear which properties are required and, hence, have to be measured. In the latter case, when developing a construction product specifically based on the properties of a given by-product, it is a bit more complicated. Basically, first the main components of the by-product are measured and then in subsequent steps further information is gained as far as deemed relevant at that moment. For this kind of investigation both physical (such as granule size distribution and porosity) and chemical (main components and environmentally relevant substituents) properties are relevant. Also other aspects can be of relevance such as odor, color, and rheology depending on the foreseen application. These properties are not only relevant for considering the end product properties, but also for assessing the potential suitable production processes. For example, such a property is the rheology, which is not only relevant for (internal) storage and transport but also for assessing whether existing installations can process a given by-product or (in case of a new process) what the demands are for the installations.

One other aspect related to the properties of the by-product (and up to some extend the process/industry where it is set free) is the status. The status relates the perception of industry, authorities, and the public Being considered as a (hazardous) waste requires different actions and permits then being regarded as a by-product. The next paragraph gives a description of the current situation in the EU and (although regulation will change over the time) an interesting example how one single issue can be very complex on one hand and be of great practical importance on the other hand.

"Discussions about how to resolve the issues resulting from implementing the classification, labelling and packaging (EU, 2008) rules as part of the list of waste (EU, 2000) in the EU Hazardous Waste Directive (WFD EU, 2008) are still ongoing and, as of today, have not led to a satisfactory solution for (waste) materials with potential for beneficial use. This is particularly true for residues from thermal processes (Hjelmar et al, 2013; Hennebert et al, 2014). Classifying a material unjustly as a hazardous waste will seriously hamper beneficial use of such a material and result in increased use of primary materials. If there is a real hazard, then this is obviously fully justified, but when a material is classified as a hazardous waste when adverse human and environmental impacts are unlikely, then steps should be undertaken to find a proper solution for such materials. The requirement to use the total content of substances, even if they are chemically tied up in the matrix and are not accessible for release even under extreme exposure conditions, precludes the possibility to beneficially use materials that would otherwise be suitable. In the process of evaluating alternative options to provide a more relevant classification of residues from thermal processes, the recently fully validated pH dependence test can be considered as replacement for total content in the foreseen classification schemes (the waste classification rules are currently under revision by the European Commission: DG ENV 2012a, b; Garcia Burgués, 2013)."

Concentrations of stable elements exceeding 1000 mg/kg may result in hazard classification independent of the consideration of NORM. There is a potential risk of noncompliance, even when criteria for safe use of NORM are met.

9.2.3 Product process interaction

One aspect of the product development is, of course, to generate a product with the required properties. However, only if this product can also be made on an industrial scale (and not only in the laboratory) a potential reuse of the by-product is given. This means that during the product development always the aspect of the production must be addressed and generally this is done on an iterative basis. This can result in adjustment of the raw material composition or the process design or types of equipment. As an example it is known that puzzolanic material, when mixed with a CaO-containing binder, will react forming clumps in the mixture. These clumps can cause bridging in storage facilities or influence the mixing procedure. Either this can be solved by choosing other binders or to adjust the process with equipment capable to handle sticky materials. Furthermore, also (generally in a later stage of the development process) aspects such as costs and eventually required (additional) permits must be looked upon.

9.2.4 Environmental and health issues

It is already mentioned in previous chapters that all kinds of environmental and health issues have to be met (including the related legal and regulatory aspects), but it is also important to realize that this does not only concern the (use) of the product but also the production itself. The environmental issues can address aspects such as transport, (intermediate) storage, the production process itself (e.g., dust or discharges), and end storage of the material. The health aspects are, as far as production-related aspects are concerned, commonly workers related and for a minor part to the public (due to eventual discharges). These aspects, as well as perceptions they cause, are very important to address properly and timely in order to avoid all kinds of regulatory time (and money)-consuming processes delaying the development and implementation process or even causing production disruption in case legal actions are undertaken by authorities once the new NORM product is produced. One last aspect which should be mentioned in this paragraph is the fact that the elapsed time between first development steps and the moment a product is put on the market can take quite a long time and sometimes up to 10 years (and more). In this period legislation may change and/or thresholds may be lowered which implies that in some cases the development process has to be partially repeated or the development might be stopped in case of inability to comply with the contemporary legislation at the moment of market introduction.

9.2.5 Type of recycling

Depending on the size of the waste stream several strategies might be considered for finding a new product. In case of small amounts, the first aim will be to try to replace a component in an existing production process for the simple reason that it is unlikely that all kinds of development and investments costs (just to name some types of costs) will be covered by producing small amounts of a product. Although the definition of small amounts is fluid depending on both the properties of the waste stream and the available production options generally an amount less than 1000 Mg/year can be seen as a small amount and when looking at infrastructural applications even over 10,000 Mg/year can be considered to be too small for turning the waste in a new product. On the other hand also for large amounts replacement of the main component in an existing product/process could be of interest, but this means that the NORM by-product stream must fit rather precisely in the framework given by the material it replaces. This is because it becomes the main component of an existing product which has to meet the same technical and environmental requirements as the original product does. This can be very limiting for the application in such an existing product. An alternative for large(r) NORM by-product streams is, therefore, to develop a new product based on its own specific properties and thus the application can be chosen based on the achieved product properties. An example for both situations is the use of fly ash in cement. On one hand this is the replacement of cement clinker by given fly ash and thus the type and amount are limited by the requirements, cements have to meet. On the other hand new cement types were developed using the specific qualities of fly ash as substituent in cement and, therefore, opened new markets for cement. It must be stated that this was in both cases a time-consuming and expensive approach in which besides all kinds of technical test in the development phase numerous tests had to be carried out just to convince the market of the applicability and reliability of the use of fly ash. Moreover, in several cases also the building codes had to be adjusted, as well as new certificates had to be applied (which are neither simple nor cheap activities).

9.2.6 Potential market and acceptance/perception aspects

Even though NORM by-products are in many cases as good as other by-products and raw materials, the fact that it is related to radioactivity does pose a potential problem. Although generally the public (as well as the industry) embraces reuse when it comes to C2C (cradle to cradle) or reduction of the CO_2 emission, once they have to make the choice for their own dwelling, they tend to choose for "natural" building products. At least that is the perception of many of the producers of building products. As long as this perception exists, building industry will remain reluctant in using NORM by-product or even assessing this option. The fact that some NORM processing industries as well as NORM by-products are mentioned in the annexes of the Euratom BSS 2014 (EU, 2014; see also Chapter 4) is not helping toward a public acceptance of using by-products in general and NORM by-products specifically for reasons of a negative perception this invokes. Hence, depending on the given situation, in advance of approaching a potential user of NORM by-products, a good strategy should be elaborated, in which both the doubts of the potential user are addressed and the positive sides are stressed like saving of natural resources, reducing energy consumption, or reducing the CO_2 emission as far as applicable on given situation and foreseen application. As is expressed elsewhere in this chapter, it is of crucial importance to build up trust between the partners and this only can be achieved by transparency. However, it is equally important to think about the presentation of information and the relevant moment when to share it with whom.

In case of a new product its (foreseen) place in the market will dictate the financial, logistical, and technical demands. As in marketing the three P's (people, planet, and profit) are essential, nonetheless the price of a new product is the first and main aspect to assess whether a product will have any change. Moreover, other cost aspects (such as mentioned in the next paragraph) are also essential: does the user need to invest in order to be able to use the new product, what guarantees can be given by the producer in terms of durability, availability (both delivery and quantity related) to name only a few. The best this can be explained by comparing this to the developing of products which have to compete with existing bulk building materials like concrete. These are very cheap materials which are very well known. This means that over time a lot of knowledge was build up on numerous applications. Construction companies know exactly how to work with them and they are aware of its durability aspects and are thus capable to address these aspects and subsequently can guarantee the safety without any additional (financial) risk for the client. Moreover, these materials are available on any required spot in any quantity required by the customer. As you can see, it is a very demanding existing market in which a new product has to find its application.

Hence, in this case developing a new product should address these challenges by, for example, looking to a very specific applications where the new product is capable in competing with the existing materials, only smaller amounts of products are required and addressing the relevant specific aspects as described earlier.

9.2.7 Cost aspects throughout the chain

Generally, using a by-product may cause costs throughout the chain starting at the site where the NORM by-product is set free to the application of the NORM-based end product. The first costs could be involved due to process and storage adjustments of the existing infrastructure to meet the requirements for the reuse of the NORM by-product. In this category the quality control and assurance on the NORM by-product as well as separated storage capacity could cause extra costs due to the use (instead of landfill) of a by-product. Furthermore, it could be necessary to conduct pretreatment activities (such as dewatering, grinding, sieving, etc.) in order to meet the requirements of the foreseen customer. Next there is the transport issue which generally is an important issue for reasons that this can be a major part of the cost structure. This is not only influenced by the transport distance but also by eventual demands on the transport itself (specific containers, required cleaning of the containers after transport, etc.). For the user of the NORM by-product, also some extra costs may occur; some addition to or adjustments of the process equipment might be necessary in order to be able to process given NORM by-products. Examples are the necessity of special storage facilities to prevent leaching into the soil or special equipment to handle materials in case the rheology of the by-products differs from the existing raw materials. Depending on the situation and the radionuclide content of the NORM by-product, specific permits may be required and potentially personal has to be informed and instructed accordingly. In some cases, due to the use of the NORM by-products, also QA and certification systems for the end product have to be adjusted. These aspects are partly direct related to the use of given by-product but can, for a part, also be influenced during the development phase, for example by using additives to enhance the handling properties.

As already pointed out, the product development including building a production facility, marketing, etc. can take quite a long period. In this period not only legislation may change but also prices and markets can change. For example, in the 1980s several new technologies were introduced on the Dutch market for the reuse of fly ash. During the second half of the 1980s the quality of the coal fly ash was improved (lower carbon content), which was a show stopper for the Lytage technology which required high amounts of carbon due to its production process in which granules were fired to aggregates. Also due to the enhanced quality of the fly ash it became more and more applicable in the cement industry where it is a valuable component with accordingly interesting prices instead of the gate fee the power stations had to pay in earlier years. Technologies like Aardelite (granules) and KALDIN (circulating fluidized bed combustion technology) were only economic feasible when gate fees were paid. Hence this development caused the untimely termination of both projects in which millions of Euros were invested, in R&D as well as in the production sites, to achieve the market introduction of fly ash. In the 1990s, the IBR company developed a sewage sludge stabilization binder based on fly ash. However, in the mean period the sewage sludge plant operators decided to incinerate the sewage sludges instead of, as had been done for many years, to deposit them on landfills. Hence, they had no need any more for stabilization binders and the IBR product was never put on the market although all tests showed it fulfilled all the demands for landfilling and was cheaper than the current binders like lime and cement.

9.2.8 Competition with other by-products

Some producers in the building material industry are interested in using by-products and others want to use only "natural" raw materials. In case a producer is open for the use of by-products, he has the choice from many types of by-products. The requirements on the (environmental) properties of his product, as well as the limitations of his existing process, form a first basis for screening the options. In most cases the screening results in more than one option and, therefore, each by-product will have to compete with several other by-products. In most cases this competition is not based on the quality of the by-product (it already has been assessed that all the competing by-products are applicable) but on the financial benefit for the producer. From the previous paragraph on cost aspects, it can be derived that the use of an NORM by-product may cause costs, which have to be covered by its raw material value. In cases the by-product has specific gains for the user (for example replacing a valuable raw material or supplying the product with specific interesting properties) this can result in selling the NORM by-product with a gain. In almost all other circumstances a so-called "gate fee" is required to make the reuse, also in economic terms, an interesting proposition for the potential customer. This basically means that a NORM by-product has to compete with the gate fee of other competitors. This also implicates that in many cases the concrete use of the NORM by-product is subject to regular reassessment concerning its price and therefor can be terminated after each end of the contract period. The specific use will be subject to renegotiating the price at a regular basis. The less specific the advantages of using the given NORM by-product are, the more easily it can be replaced by another by-product for reasons that more by-products will fullfill generic demands and thus qualify as a (potential) replacement. Hence, developing applications with the highest added value (in technical and economic terms) generally pays off on the longer term even though this requires more R&D effort in the development phase. In some cases it also can be seen that a previously required gate fee turns over the years into a selling price. A good example is fly ash where in the Netherlands there was a gate fee in the 1980s and nowadays prices up to €40/ton is paid for a good quality. The latter suggests that in the meantime not only a lot of product development, but also quality enhancing investments were done. One aspect which sometimes seems to be forgotten is the requirement to keep ahead of the competitors once an application has been realized which means that after some time reassessment and further optimizing of the current application is vital for long-term application of the by-product.

A last basis for competition is the availability of the by-product, which is a specific aspect of a by-product since a by-product is not always intentionally produced. Hence, both quantity and quality depend on the choices made for the main process in which (economical) optimization is the central aim of a given producer. An important question in this matter is whether there is a match between the availability of required amounts of by-products and the demands of the client in which besides the available amounts also aspects as storage capacity and supply guarantee are of importance in case the NORM by-product has specific (wanted) properties. This caused by the fact that once the customer adjusted its process to the use of the by-product, he therefor cannot simply switch to another supplier for reasons that most of the by-products are rather unique and therefor if the supplier is not capable to deliver, the user has a major problem. Moreover, if the NORM-based product turns out to be a success and increasing amounts of the NORM by-product are required, the demand can exceed the available quantities. Also if changes in the main process of the supplier occur, this will also influence the properties of the by-product. These aspects are essential whether a NORM by-product is used even if based on all other aspects the use would be favorable.

9.2.9 CE marking and other certification aspects

In Europe (as in many countries throughout the world) building materials and products are subject to all kinds of regulations of technical, environmental, and health nature. Especially following regulation is relevant for the European market: Regulation No. 305/2011 (Construction Products Regulation [CPR]) (EU, 2011). This is a regulation from 2011 that lays down harmonized conditions for introducing construction products on the market. The EU regulation is aiming to simplify and clarify the framework for the introducing of construction products on the market.

This regulation aims to

- clarify the affixing of CE marking to construction products for which the producer has made a declaration of performance;
- introduce simplified procedures enabling cost reductions for businesses, especially SMEs; and
- impose stricter designation for organizations responsible for assessing the performance of construction products and verifying their consistency.

According to the CPR (articles 4, 11, and 24), before placing construction products on the market, these products should comply first with some EU harmonized standards and should be accompanied by a “declaration of performance” which includes health and safety aspects (CPR articles 15 and 16). This declaration of performance and related standards are needed to get the CE marking. This marking confirms indeed that the construction product complies with the declared “performance” and the EU harmonized standards. However, CE marking is only available and at the same time obligatory for those products were a harmonized CEN standard is available. For most of the (major) product groups harmonization of the standards is envisaged and will be published over the next years.

In this respect the CEN is preparing several standards for measuring the required properties such as the radionuclide concentration of building materials. In order to prove that given product fulfils continuously the relevant requirements, products can be (or must be) certificated. Moreover, a producer can claim certain properties for his product and can add this aspect to his certification system. Generally, the certification is based on both an internal and an external quality assurance system which, based on protocols, requires certain measurements as well as a structure in which the quality assurance is incorporated in the daily production. Setting up such a system and acquiring a certificate can be very time consuming and costly. Hence, if the intended use of an NORM by-product requires adjustments and/or additions to the certification system, this can add to the costs and efforts involved with using the by-product.

9.3 Generic approach in product development

As discussed in previous chapters and earlier, a wide range of technical and nontechnical aspects is involved in developing a reuse for NORM by-products. For reasons that they are partially interdependent and for another part are a result of previous choices, these aspects cannot be addressed at the same moment. Therefore, a tailor made product development strategy has to be chosen based on the specific situation. Nonetheless, some generic guidelines can be given to structure the development process and to enhance the changes of finding a sound solution with a good market prospect. In this approach the first step is to gather all relevant information on properties, amounts, and other relevant parameters. This includes also logistic aspects and cost aspects. Combined with the knowledge of the relevant market (depending on the situation this can be either local, regional, or (inter)national) a first set of potential applications should be selected for screening. This screening involves basic application test per envisaged application and should result in a short list of potentially interesting (and technical possible) options. Once an interesting option is selected, it could be considered to try to involve the envisaged potential users of the NORM by-products. Being involved at an early stage not only enhances their commitment, but in this way also their specific demands can be addressed in the development process which increases both efficiency as well as the change for actual application. As always, this advantage has also disadvantages. For example by focusing on one prospect, one tends to oversee other interesting options or becomes dependent on this specific user at an early stage. After a shortlist of interesting options is made some more in depth development work has to be carried out looking into the specific demands of the envisaged application and, once a final application has been selected, working on optimization of both product and process and their interaction. At the beginning of this stage at the latest also nontechnical aspects such as costs and marketing should be involved. Process aspects should be involved, once the development is in a stage where it is clear what (raw) materials (binders, fillers, additives) will be used and what shaping and hardening technologies are required. In case of an existing production process (e.g., when the NORM by-product is used as replacement of one of the existing raw materials) the required product properties are clear and the choice of the combination of materials should be adjusted to the needs of the existing process. Also in case a new facility will be set up in order to produce a novel product, close contact between product developer and the process engineers is favorable in order to set up a basic design in an early stage of the development process. The development process does not only consist of looking how basic product properties can be achieved (which are often relative simple to measure) but also measuring more complicated properties which are in general more expensive and time-consuming tests. Examples of the latter are the environmental tests, fire resisting tests, or durability tests. Generally, for reasons of both costs and time, these tests are performed once a certain product is chosen and first optimization tests are performed and turned out to be successful. Of course, from the more specific test the outcome could be that the developed product does not meet the requirements and, as a consequence, part of the development process has to be repeated. On the other hand, to perform these (expensive) tests in a too early stage should be avoided since these tests might very well be performed on options which will be rejected for other reasons.

Once the development process comes in the phase where the technical and economic aspects are addressed satisfactory, the core product development evolves into a series of activities which ranges from the certification of the (new) product to permits for the production process as well as marketing activities and the upscaling of the (laboratory) test results into a full size production facility. In all these phases problems (or challenges) can occur which require to return to the product development phase in order to assess given problem by adjusting either the (raw) materials mix or the required process conditions or (in most cases) a combination of both.

As can be seen, during the process from the first screening tests to the full size production, a lot of different expertise is required in order to support the transition from a by-product into a commercial product. Hence, in many cases a team of experts is involved to ensure that at the right time the right experts are involved which reduces the change of developing nonfeasible products and enhances as efficient as possible product development process.

The above-mentioned approach can be summarized in the following stages:

- Gathering all available and relevant information to set up the first screening tests.
- Screening test in order to select technical realistic options.
- Based on results screening tests and first other relevant feasibility aspects selecting a short list of applications.
- In this stage at the latest all kind of other relevant aspects (process, nontechnical aspects, etc.) should be involved in the development process and accordingly a team of experts should be formed.
- Optimization per application in several stages and finally selecting the most promising option. At this stage involvement of potential users should be considered (if not already involved).
- Performing all relevant (specific application) tests on the selected product option.
- In each stage, due to the outcome of tests or results or the studies on the nontechnical aspects further optimization or even returning to previous phases could be necessary.
- If all previous phases were successful the final issues such as upscaling, engineering, investment decisions, marketing, and permits should be addressed.

Finally, only when all these phases are succeeded successfully, a real solution for an NORM by-product is established.

9.4 Conclusion

In the paragraphs of this chapter we chose to point out all the potential traps and problems involved in trying to achieve a reuse for NORM by-products. Our intention is not to deter potential users or to demotivate them before they are starting the process. On the contrary, many NORM by-products are already used in a wide range of applications over the last decades saving both natural raw materials as well as energy and having other (economical) advantages. To our opinion, for adding successful applications to these already existing ones, it is important to have a realistic view on all aspects involved including potential draw backs and show stoppers. This is the aim of this chapter, to raise awareness of interested researchers and also potential users of NORM by-products on all the aspects which have to be addressed and which could cause either delay or even termination of a solution only for reasons of nonawareness of given aspect.

Furthermore, it should be stated that each aspect poses both a challenge and an opportunity, in case the product developer is aware of this aspect in due time. In this case this matter can be addressed at the proper moment and is not raised it in a (too) late phase of the product development process causing delay or unnecessary termination of the project.

Last but not least, once a potential client for the NORM by-product is envisaged, it is our opinion as well as experience that an open communication addressing all the involved aspects and suggesting pragmatic solutions will only enhance the change to turn a by-product into a sound and in many ways interesting (new) building material. Moreover, an open exchange of information enhances the trust between partners, which is a condition sine qua non when a lasting relationship has to be built as basis for a long-term use of NORM by-products.

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General conclusion and the way forward

10

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Content for the reader: Chapter 10:

This chapter gives the main conclusions and perspectives of the COST Action NORM4Building regarding the radiological analysis of the use of by-products in construction materials.

In the radiological evaluation of building materials, the main parameters characterizing the external radiation dose and radon surface exhalation are discussed in Chapter 3. For the discussion of the external exposure, the focus is on the activity concentration of the three main natural radionuclides: ^{232}Th, ^{226}Ra (and their respective chains), and ^{40}K. It is shown that the main parameters characterizing radon emanation and exhalation rate from building products are the radon emanation coefficient and the radon exhalation rate. Additional parameters characterizing the rate of radon release from a building material are the radium activity concentration, the radon diffusion coefficient, and product thickness and density.

Considering these parameters, building materials are more and more recognized as a potential source of indoor radiation exposure. In the new Euratom Basic Safety Standards (EU-BSS), for the first time, building materials were included in the application field. The new directive, described in Chapter 4, establishes reference levels for indoor radon concentrations and for indoor gamma radiation emitted from building materials, and sets requirements on the recycling of residues from industries processing naturally occurring radioactive materials (NORMs) into building materials. The EU-BSS requires that Member States shall establish a national radon action plan for indoor radon exposure to address risks related to radon exposure for any source of radon ingress, whether from soil, building materials, or water.

The free movement of building materials in the EU internal market can benefit from harmonized methods for the determination of the activity concentrations, annual indoor radon, and the dose assessment. There is especially a strong need for harmonized methods for the evaluation of building materials with an I-index exceeding one

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in order to verify compliance with the reference level of 1 mSv per year. In Jan. 2017, methods for the determination of the building material activity concentrations and the relevant gamma dose evaluation are under finalization by the Technical Committee 351—WG3 of the European Committee for Standardization (CEN). A lot of useful information that can support the development of new measurement procedures for NORM-containing construction materials and evaluation of occupational exposure is presented in Chapter 5.

Several studies were undertaken to study the NORM aspects of by-products. An overview of the information collected in the NORM4Building database, can be found in Chapter 6. In order to use this information to evaluate industrial processes, it is important to take into account that the properties of by-products are changing over time. An example: in a metal processing plant the extraction of the metals of interest becomes more efficient over time and this will have an impact on the properties of the produced slag. Owing to the changing properties of the by-products, a suitable frequency of measurements is required to monitor the changes in chemical, technical, and radiological properties of the by-products over time. This also means that it is important that the production process/plant for the production of the construction materials, can handle the changes that occur in the input materials. The data mining approach that is used for the construction of the NORM4Building database can, provided that it will be continuously operated also after the end of the COST Action, be a very useful tool also for the radiological evaluation of future building materials. To increase its usability, it will be important to further expand the sources of information on which the database is build. By incorporating more results from national studies in the database and by regularly updating these national studies, it is the opinion of the COST Action that the database can become a very useful tool that can support regulators and industry regarding the exploration and assessing of reuse options.

For most of the construction materials (cement, concrete, ceramics, and gypsum), discussed in Chapter 7, the recycling of by-products is not a problem from a radiological perspective when taking into consideration the EU-BSS. The I-index of the evaluated building materials is in many cases <1 (for example, coal fly ash or blast furnace slag recycling in Portland cement based concretes) meaning that these building materials meet the EU-BSS gamma dose reference level. An I-index >1 was only found in a limited amount of cases (for example, when using 75 wt% of specific types of red mud in alkali activated concretes). For these cases there is a need to further verify the gamma dose reference level of 1 mSv/y. Aggregates have the greatest influence on the concrete radioactivity because they account for the main fraction of the concrete volume. For products such as ceramics, where both geometry of the application and the density can be quite different from concrete (which is used as the standard material in the index calculation), the use of a density and thickness corrected index can facilitate a more realistic screening.

As is demonstrated in Chapter 7, the information on the radiological features of construction materials, in particular values of radon exhalation and emanation, is scarce or absent. Regarding the external radiation dose it is often only possible to draw conclusions based on information regarding the activity concentration of naturally occurring radionuclides in the by-products. But in many cases this information is not available for all constituents of a construction material. The COST Action has initiated new research to assess the radiological properties of construction materials. The data gathered here will be further incorporated in the database, increasing its usability. In our evaluation of construction materials, the aim is to link radiological, chemical, and technical properties in order to go for a realistic approach and avoid too conservative approximations.

In Chapter 8 a Leaching Assessment Framework (LEAF) consisting of validated US EPA and corresponding European methods (pH dependence, percolation, monolith leaching) is proposed for long-term release of naturally occurring radionuclides from NORM by-products in construction and to assure the protection of human health and the environment via waterborne pathways. The same physical-chemical processes that control the leaching of stable inorganic elements will also control the leaching of naturally occurring radionuclides. Thus, leaching data from total elemental analysis of elements (or chemical analogs) with radioactive isotopes (e.g., K, U, Th, Pb) was used to gain an initial understanding of the leaching of the corresponding radioisotopes. Available leaching data on naturally occurring radionuclides is very limited. The mechanisms by which radionuclides are retained and the contacting water chemistry that determine the leaching behavior from NORM-containing construction materials, including degradation mechanisms, are discussed in Chapter 8. For new types of granular construction materials, the pH dependence test and the percolation test should be used. For monolithic materials, the pH dependence test and monolith leach test or compacted granular leach test should be used. For major sources and types of NORM, parallel measurements of stable and radionuclides of relevance would be highly revealing to understand release controlling phases and thereby provide better means to deal with changes occurring in the long-term (carbonation, oxidation, physical degradation, etc.).

Chapter 9 points out potential traps and problems involved in the use of NORM by-products. It can be concluded that in order to add successful applications to the already existing ones, it is important to have a realistic view on all aspects involved, including potential drawbacks and show stoppers. Chapter 9 tries to raise awareness among interested researchers and also potential users of NORM by-products on all the aspects which have to be addressed and which could cause either delay or even termination of a solution only for reasons of nonawareness of a given aspect.

Once a potential client for the NORM by-product is envisaged, it is our opinion as well as experience, that an open communication addressing all the involved aspects and suggesting pragmatic solutions will only enhance the change to turn a by-product into a sound and in many ways interesting (new) building material. With this book, we hope to support a further open exchange of information that enhances the trust between partners, which is a condition sine qua non when a lasting relationship has to be built as basis for a long term safe use of NORM by-products.

The main conclusion of this book is that naturally occurring radioactive materials can generally be used in a safe and sustainable way in construction products for which this book supplies the user with many relevant aspects to be considered as well as guidance on how to address this specific topic. Therefore we hope that this books contributes to facilitate the use of many kinds of NORM (by)products and thus strengthen given industries whilst maintaining a high standard of product quality and safety for both users and environment. Furthermore, a sound use of NORM (by)products also supports the requirements of efficient use of materials as well as reducing the use of virgin materials both of which are of imminent importance for our society.

Glossary of terms

A

Acid neutralization capacity The amount of acid, expressed in mol/kg, required to neutralize a given weight of material to a stable neutral pH.

Activity Number of radioactive decays per unit time. Unit: 1 Bq (Becquerel) = 1 decay/s; Old unit: 1 Ci (Curie) = 3.7×10^{10} Bq.

Activity concentration Activity per unit mass.

ADC Analog-to-digital converter.

Alpha (α-) radiation Radiation, which consists of α-particles containing two protons and two neutrons and is identical to an ionized ^{4}He nuclei.

Anion An ion with a negative charge.

Available content The quantity of a constituent that can be leached from a material under conditions that under extreme conditions could be reached in the environment or in the very long term.

B

Base neutralization capacity The amount of base, expressed in mol/kg, required to neutralize a given weight of material to a stable neutral pH.

Batch tests Leaching tests which are carried out on a single portion of material using a single portion of leachant, i.e., there is no renewal of leachant during the test.

Beta (β-) radiation Radiation made up of β-particles that are electrons, with a negative elementary charge, or not so often, positrons both with positive elementary electric charge.

Branching ratio The probability that a nucleus will decay by a certain process (compared to all possible decay processes).

BSS Basic Safety Standard.

Buffer A solution containing both a weak acid and its conjugate weak base whose pH changes only slightly on addition of acid or alkali.

Building A structure, which encloses a space.

Building material Material used in a construction work for the construction of a building

Building product Construction product for incorporation in a permanent manner in a building or parts thereof

C

Carbonation Uptake of carbon dioxide in an alkaline material.

Cation An ion with a positive charge.

Complexation The formation of an ion into a molecular structure consisting of a central atom bonded to other atoms by coordinate covalent bonds.

Construction material Material used in a construction work.

Construction product Any product or kit which is produced and placed in the market for incorporation in a permanent manner in construction works or parts thereof and the performance of which has an effect on the performance of the construction works with respect to the basic requirements for construction works.

Construction work Any work carried out in connection with the construction, alteration, conversion, fitting-out, commissioning, renovation, repair, maintenance, refurbishment, demolition, decommissioning or dismantling of a structure.

Correction factor Factor by which the reading of a measurement device must be corrected when the measurement is not performed at the conditions at calibration.

D

DIC See *dissolved inorganic carbon*

Diffusion Transfer of matter due to the thermal energy of molecules (a particular case of diffusion is the spontaneous mixing of one substance with another when in contact or separated by a permeable membrane or microporous barrier).

Dissolution Molecular dispersion of a solid in a liquid.

Dissolved inorganic carbon This usually represents carbonate species.

Dissolved organic carbon (or DOC) Natural or artificial organic matter remaining in dissolved state in solution (e.g., humic and fulvic acids).

DL Decision limit.

Dose conversion factor (for radon) Factor by which the radon exposure can be converted into a dose.

E

Effective dose Absorbed radiation energy in tissue weighted by the kind of radiation (radiation weighting factor w_R) and targeted tissues/organs (tissue weighting factor w_T); the effective dose can be used for the radiation risk estimation.

Effective dose rate Effective dose per unit time.

Efficiency Probability for detecting radiation per unit decay or per unit radiation particle or photon.

Eluate As *leachate* but usually in the context of a laboratory test.

Emission Release of substances from one environment, medium, or phase to another.

Equilibrium (chemical and physical) Chemical equilibrium is a condition in which a reaction and its opposite or reverse reaction occur at the same rate resulting in a constant concentration of reactants. Physical equilibrium is exhibited when two or more phases of a system are changing at the same rate so the net change in the system is zero.

Equilibrium (secular) The activity of a shorter lived progeny is the same as the activity of the longer lived mother nuclide. Thus, the activity of the progeny decreases with the half-life of the mother nuclide. In case of ^{222}Rn radioactive equilibrium means that the activity of each short-lived progeny is the same as the activity of the longer-lived radon gas.

Equilibrium equivalent concentration (EEC) Computed radon concentration in radioactive equilibrium with the same potential alpha energy concentration (PAEC) as observed:

$$\mathrm{EEC(Rn-222)} = 0.106c_{\mathrm{Po-218}} + 0.513c_{\mathrm{Pb-214}} + 0.381c_{\mathrm{Bi-214}}$$
$$\mathrm{EEC(Rn-220)} = 0.913c_{\mathrm{Pb-212}} + 0.087c_{\mathrm{Bi-212}}$$

Equilibrium factor Ratio of the EEC to the radon activity concentration (or ratio of the potential alpha energy concentration of short-lived radon decay products in a given volume of air to the potential alpha energy concentration of these decay products if these are in radioactive equilibrium with radon in the same volume of air).

Exhalation rate, *E* Radon activity transferred from either a mass (E_m—free mass radon exhalation rate, unit: Bq/kg/s) or a surface (E_s—free surface radon exhalation rate, unit: Bq/m^2/s) to the ambient air per unit time.

Exposure Contact to radiation, either measured in dose units (or equivalent units) or as a product of activity's concentration and time.

Extraction A separation operation that may involve three types of mixture: (1) a mixture composed of two or more solids (2) a mixture composed of a solid and a liquid—as in this context (3) a mixture of two or more liquids. One or more components of such a mixture are removed (extracted) by exposing the mixture to the action of a solution or solvent in which the component to be removed is soluble.

F

Fluence Number of particles or photons passing through unit area.

FWHM Full width at half maximum.

G

Gamma (γ-) radiation Radiation composed of high-energy photons (electromagnetic waves) coming from the nucleus.

H

Half-life Time until a nuclide has reduced to half its initial value when no further production of this nuclide take place (e.g., in radioactive decay chains).

HPGe High-purity germanium (detector).

I

Index I or I-index Activity concentration index

Infiltration The movement of water (usually rainwater) into and through a solid material.

Inorganic Chemicals that are generally considered to include all substances except hydrocarbons and their derivatives or all substances which are not compounds of carbon with the exception of carbon oxides and carbon disulfide.

Ionic strength A measure of the concentration of ions in solution.

Isotopes Nuclides with equal number of protons but different numbers of neutrons. Most chemical elements consist of different isotopes. These isotopes behave chemically (nearly) identically.

L

Leachant Liquid in contact with or which will be brought in contact with a solid which extracts soluble components of the solid.

Leachate Liquid containing soluble components extracted from a solid (usually linked to field conditions, e.g., landfill leachate).

Leaching The process by which the soluble components of one phase (usually a solid) are transferred to another phase (usually a liquid).

Liquid to solid ratio The liquid to solid ratio relates to the amount of liquid used in a batch leaching test to extract a given amount of solid. Abbreviation: L/S Unit: L/kg.

LLD Lower level of detection.

M

Marinelli beaker A plastic container with a cylindrical recess in the bottom for detector installation for analyzing moderate to low activity level of radioactive samples in powder or liquid form directly for gamma ray emitting isotopes.

MCA Multichannel analyzer.

Montecarlo calculation A technique used to model the probability of different outcomes in a process that cannot easily be predicted due to the intervention of random variables.

MS Members states (of the EU)

N

Naturally occurring radioactive material (or NORM) Radioactive material containing no significant amounts of radionuclides other than naturally occurring radionuclides (NOR), for a detailed discussion of the concept see Chapter 2.

NOR Naturally occurring radionuclides.

NORM by-product By-products from a process and either comprises or is contaminated by NORM.

NORM residue Material that remains from a process and comprises or is contaminated by NORM.

NORM waste NORM for which no further use is foreseen.

O

Organic Chemicals that are generally considered to include all compounds of carbon except carbon oxides and sulfides.

Oxidation/reduction potential A measure of the ability of a system to cause oxidation or reduction reactions. Oxidation and reduction are reactions in which electrons are transferred. Oxidation and reduction always occur simultaneously (redox reactions). The substance that gains the electrons is termed the oxidizing agent and the substance that loses the electrons is termed the reducing agent.

P

Partitioning The distribution of molecules in different states or phases in a system for example as solid, liquid, or gas.

pE A measure of the redox potential

Percolation The movement of a liquid through a solid.

pH A value taken to represent the acidity or alkalinity of an aqueous solution.

Photopeak Relative maximum in the energy spectrum of a gamma emitter which is caused by the deposition of the full energy of a photon (full energy peak).

pH static leach test A leaching test consisting of a number of individual extractions of subsamples of the same material at pH values fixed by addition of acid or base as required.

Porosity The relative volume of void space to the total volume occupied by a material.

Potential alpha energy concentration (PAEC) Sum of all α-energies from the short living Rn-progeny deposited in unity air volume. Units: J/m^3 or MeV/m^3. PAEC can be converted into EEC and vice versa.

Precipitation The settlement of small particles out of a liquid or gaseous suspension by gravity or as the result of a chemical reaction.

Progeny Chain of decay products (of radon)—formerly called radon daughter products.

Q

QA Quality assurance.

QC Quality control.

R

Radiation The emission of energy as electromagnetic waves or as moving subatomic particles, especially high-energy particles that cause ionization.

Radioactive equilibrium The activity of a short-lived progeny is the same as the activity of the longer living mother nuclide.

Radioactive material Material designated under national law or by a *regulatory body* as being subject to *regulatory control* because of its *radioactivity*.

Radioactivity A process by which nuclides spontaneously decay by the emission of radiation.

Radionuclide Isotope which undergoes radioactive decay

Radon diffusion coefficient The radon activity permeating in a homogeneous media due to molecular diffusion through unit area of the elementary layer of unit thickness per unit time at unit radon activity concentration gradient on the boundaries of this layer.

Radon diffusion length The distance of radon transport in a homogeneous medium due to molecular diffusion, at which the radon flow rate or its activity concentration decreases to $1/e \approx 0.37$ (factor $e \approx 2.72$), while the transport is considered in conditionally infinite medium without the influence of edge effects.

Radon emanation The process of radon generation and further removal from the bulk of the solid phase into the pore space by the recoil process resulting from the alpha decay of the radium parent. Atoms of radon found in the pore space that have the ability to migrate into open pores are called free radon. Radon atoms held in the solid phase and which are not able to migrate are called bound radon.

Radon emanation coefficient The ratio of free radon activity to the total activity (free and bound) of radon in the material under the radioactive equilibrium between radon and the radium parent.

Radon exhalation The process of releasing a free radon from the material surface into the surrounding medium (air).

Radon exhalation rate The activity of radon atoms that leave a material per unit surface (or mass) of the material per unit time (also see *exhalation rate*, *E*).

Radon exposure Radon activity concentration multiplied by the time of exposure.

Redox See *oxidation/reduction potential*.

Redox potential (E_H) A measure of the oxidation reduction potential. See *oxidation/reduction*.

S

Scintillator A material that fluoresces when struck by a charged particle or high-energy photon.

Self-attenuation Radiation shielding inside of a sample caused by the sample itself.

Short-lived decay products (short-lived progeny) Radioactive progeny of radon (218Po, 214Pb, 214Bi, 214Po) and thoron (216Po, 212Pb, 212Bi, 212Po, 208Tl).

Solubility The ability or tendency of one substance to blend uniformly with another, e.g., solid in liquid, liquid in liquid, gas in liquid, gas in gas. Solids vary from 0% to 100% in their degree of solubility in liquids depending on the chemical nature of the substances.

Sorption A surface phenomenon that may be either absorption, adsorption, or a combination of the two. The term is often used when the specific mechanism is not known.

Speciation Determination of the precise chemical form of a substance present in a solid material, in a liquid, or in a gas.

Standard A documented method or specification to which activities should conform.

Structure Anything that is constructed.

Structures include buildings, towers, pipelines, structures for transport/communication infrastructure (roads, overpasses, tunnels, parkings), any component and part of a structure.

T

Traceability The ability to refer to a primary standard by an unbroken chain of comparisons.

TS Technical specification.

U

Uncertainty (of measurement) A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

W

Waste A material for which no further use is foreseen

Working level (WL) Any combination of short-lived radon decay products in 1 L of air that will result in the ultimate emission of 130,000 MeV of potential alpha energy. (Old definition: total alpha energy released from the short-lived decay products in equilibrium with 100 pCi of ^{222}Rn per liter of air.)

Working level month (WLM) 170 h exposure to 1 WL.

Conversion tables

Concentration

	J/m^3 (PEAC)	**MeV/m^3 (PAEC)**	**Bq/m^3 (EEC)**	**WL**
1 J/m^3	1	$6.2 \cdot 10^{12}$	$1.8 \cdot 10^{8}$	$4.9 \cdot 10^{4}$
1 MeV/m^3	$1.6 \cdot 10^{-13}$	1	$2.9 \cdot 10^{-5}$	$7.6 \cdot 10^{-9}$
1 Bq/m^3	$5.6 \cdot 10^{-9}$	$3.5 \cdot 10^{4}$	1	$2.7 \cdot 10^{-4}$
1 WL	$2.1 \cdot 10^{-5}$	$1.3 \cdot 10^{8}$	$3.7 \cdot 10^{3}$	1

Exposure

	Jh/m^3 (PEAC)	**$MeVh/m^3$ (PAEC)**	**Bqh/m^3 (EEC)**	**WLM**
1 Jh/m^3	1	$6.2 \cdot 10^{12}$	$1.8 \cdot 10^{8}$	$2.9 \cdot 10^{2}$
1 $MeVh/m^3$	$1.6 \cdot 10^{-13}$	1	$2.9 \cdot 10^{-5}$	$4.6 \cdot 10^{-11}$
1 Bqh/m^3	$5.6 \cdot 10^{-9}$	$3.5 \cdot 10^{4}$	1	$1.6 \cdot 10^{-6}$
1 WLM	$3.5 \cdot 10^{-3}$	$2.2 \cdot 10^{10}$	$6.3 \cdot 10^{5}$	1

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Note: Page numbers followed by *f* indicate figures, and *t* indicate tables.

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The depletion of energy resources and raw materials has a huge impact on the building market and in the development of new synthetic building materials, whereby the reuse of various (waste) residue streams becomes a necessity. Based on the outcome of COST Action TU 1301, scientists, regulators, and representatives from the industry have come together presenting new findings and data, sharing knowledge, experiences, and technologies, to stimulate research on the reuse of naturally occuring radioactive materials (NORMs) in tailor-made building materials, whilst considering the impact on both external gamma exposure of building materials to occupants and indoor air quality requirements. The reuse of NORM residues can also decrease an environmental detriment caused by its accumulation at landfills.

Naturally Occurring Radioactive Materials in Construction addresses legislative issues, measurement, and assessment of building materials, physical and chemical aspects, from raw materials to residues with enhanced concentrations of NORM, processes and building products containing NORM as well as end of life and reuse requirements. By improving radiological impact assessment models for the reuse of NORM residues in building materials, the authors hope to further stimulate justified uses of NORM residues in different types of newly developed building materials.

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