# Natural Radioactivity and Hazard Level Assessment of Cements and Cement Raw Materials

**Naim Sezgin, Bektas Karakelle, Ugur Emre Temelli, and Semih Nemlioğlu**

**Abstract** Cement is a composite material and it consists of different raw materials. The raw materials which are used in the cement production industry are commonly obtained from rocks such as limestone, gypsum, clay, and iron ore. In addition, the cement raw materials may also include natural radionuclides such as $^{226}$Ra, $^{232}$Th, and $^{40}$K, which may have an adverse effect on human health. Hence, determination of natural radioactivity level is very important for human health safety. In this study, natural activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K are investigated in cement and cement raw materials in Turkey as a case study. In addition, eight different radiological parameters and indices were calculated from activity concentrations. The natural radioactivity due to the presence of $^{226}$Ra, $^{232}$Th, and $^{40}$K was measured using the gamma spectrometer coupled with HPGe detector. The mean measured activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K in the raw materials were 38.14, 92.66, and 636.63 Bq kg$^{-1}$, respectively, with higher activity concentrations in coal for $^{226}$Ra and trass for $^{232}$Th and $^{40}$K. Mean activity concentrations of natural radionuclides ($^{226}$Ra, $^{232}$Th, and $^{40}$K) in cement samples were found as 34.26, 58.2, and 512, respectively. The results showed that coal and fly ash are the principal contributors for the presence of $^{226}$Ra activity concentration, trass and iron ore materials for the presence of $^{232}$Th, and clay and trass raw materials for the presence of $^{40}$K in cements.

**Keywords** Natural radioactivity · Radiation hazard · Cement raw materials · Cement

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## Introduction

Cement is one of the leading construction materials applied across the globe. Without cement, structures such as bridges, tunnels, and residences could not be fabricated. Of these, the latter consumes the highest volume of cement due to plastering and cement bricks [1]. The construction sector has a very important part in Turkey's economy, like many other countries of the world in the last years. The growth of Turkey's economy is almost dependent on the growth of the construction sector and the urban transformation studies performed in many cities of the country. Therefore, there are many building raw material production plants like cement and cement raw materials in Turkey.

Cement, which is a composite material, derives from rocks and various amount mixes of industrial by-products. The general manufacture procedures of cement contain raw material mixing, burning, grinding, storage, and packaging. To make cement, aluminum, silicon, iron, and calcium are the vital elements. These elements exist in a form of limestone, clay, fly ash, iron ore, etc.—the chemistry of these materials determine the quality of the cement [2]. The amount of raw materials and industrial by-products determine the type of cement [3]. The raw materials used in cement production may contain traces of natural radioactive elements like $^{238}U$, $^{232}Th$, and $^{40}K$—the amount of these radioactive elements vary depending on the geochemical nature and geological site of the expended raw material [4–8]. Because of this, cement and its parent materials may have varying radioactive levels. When raw materials with radioactive elements are used in cement production, they cause external and internal radiation; external exposure is due to gamma radiations from $^{238}U$, $^{232}Th$, and $^{40}K$, while internal exposure is due to short-lived radiation materials produced by radon [9, 10].

Humans spend almost 80% of their time in enclosed parameter cement. Hence, to shield humans from radiation effects of construction material, it is imperative to determine the levels of radiation in cement and its parent materials. Upon establishment of these levels, guidelines and standards of the cement materials can be instituted. Therefore, this study assesses the radionuclide levels of radium (226), thorium (232), and potassium (40) in some cement materials produced in Turkey.

## Materials and Method

### *Sample Collection and Preparation*

A total of eight raw samples, two intermediate materials of cement production, and five different product cements were collected for gamma-spectrometric measurements of natural radioactivity levels in this study. Except for water, all the measured samples were in mass form either in granulated or grinded fine powder forms. Water sample was collected from tap water into a 500 mL polyethylene bottle from the cement factory production unit. All mass-formed samples were collected in polyethylene bags. Samples were all labeled, and their specifications and sources were noted on the labels. Mass-formed samples, except for the cement samples, were first pulverized, homogenized, and sieved by a sieve of 2 mm grid mesh before the measurement of activity concentration [11, 12]. Because of their homogeneous and powder form, cement samples were expended in their original state without any preceding processing (such as pulverization, homogenization, and sieving). All mass-formed samples were dried in a temperature-controlled furnace at 110 °C for 20–24 h until constant weight was obtained, ensuring complete removal of moisture from the samples. The weighted samples were kept in a plastic container of 250 $cm^3$ and hermetically sealed for 4 weeks. This process was performed to ensure secular equilibrium of $^{238}U$ and $^{232}Th$ in the sample with their respective daughters [13]. The natural radioactivity levels of present radionuclide in the samples were measured using a gamma-ray spectrometry with a high purity germanium (HPGe) detector [14]. All experiments were replicated twice—the means of the results are presented.

Cement mainly constitutes of clinker—clinker is formed after heating a mixture of limestone and clay between 1400 and 1500 °C. In addition, different types of cements are produced according to the other additives which are standardized EN-197-1:2011 [15]. CEM I, commonly branded as Portland cement, contains at least 95% clinker. Selected three types of CEM II such as A-W, B-M (L-W), and A-M (P-L) are produced by 80–94%, 65–79%, and 80–94% clinker with 6–20% (fly ash), 21–35% (trass and fly ash), and 12–20% (trass and limestone) additives, respectively. CEM IV/B (P-W) is produced by 45–64% clinker and 36–55% (trass and fly ash) additives, and all types of cements included minor additives such as natural gypsum (5–0%) EN-197-1:2011 [15].

## *Gamma-Spectrometric Measurements*

The gamma levels of the sampled cement raw materials and cement samples were performed in a Canberra Inc.-manufactured Extended Range Coaxial High-Purity Germanium (HPGe) detector, and its specifications and measurement procedures were given by Altun et al. [16].

## *Radiological Parameters and Hazard Indices*

### Radium Equivalent Activity ($Ra_{eq}$)

Radium equivalent activity ($Ra_{eq}$) is a term expended for adapting safety standards of radiation protection on human population [17–19]. This activity is calculated from radionuclide concentration such as $^{226}Ra$, $^{232}Th$, and $^{40}K$ in soil or other materials as given in Eq. (1). It is assumed that 370 Bq $kg^{-1}$ of $^{226}Ra$, 259 Bq $kg^{-1}$ of $^{232}Th$, and 4810 Bq $kg^{-1}$ of $^{40}K$ produce the same gamma-ray dose rate.

$$\mathrm{Ra}_{\mathrm{eq}} = A_{\mathrm{Ra}} + 1.43 A_{\mathrm{Th}} + 0.077 A_{\mathrm{K}} \quad (1)$$

where $A_{Ra}$, $A_{Th}$, and $A_K$ are the activity concentrations of $^{226}Ra$, $^{232}Th$, and $^{40}K$, respectively, in Bq $kg^{-1}$.

### Estimation of the Absorbed Gamma Dose Rate ($D_R$)

The $D_R$ in the indoor air of the gamma ray emitted by radionuclides ($^{226}Ra$, $^{232}Th$, and $^{40}K$) of cement and its parent materials was computed based on UNSCEAR (2000) [20] and the European Commission (1999) [21] guidelines. In addition, the dose conversion coefficients of a standard room were based on UNSCEAR and the European Commission standards—the size of a standard room was 4 m × 5 m × 2.8 m. The floor, ceiling, and concrete walls measured 20 cm thick with a density of 2350 kg $m^{-3}$. The values of $D_R$ were calculated expending Eq. (2):

$$D_{\mathrm{R}} \left( \mathrm{nGy\ h}^{-1} \right) = 0.92 A_{\mathrm{Ra}} + 1.1 A_{\mathrm{Th}} + 0.08 A_{\mathrm{K}} \quad (2)$$

where $A_{Ra}$, $A_{Th}$, and $A_K$ (in Bq $kg^{-1}$) are the activity concentrations of radium (226), thorium (232), and potassium (40), respectively. This study adopted 84.00 nGy $h^{-1}$ as a $D_R$ reference value. This $D_R$ value represents the external, terrestrial gamma radiation and the world's average population-weighted $D_R$ [20].

### Annual Effective Dose Equivalent (AEDE)

AEDE is the ratio of absorbed amount in air to effective quantity received by adults. The following Eq. (3) given by UNSCEAR (2000) was expended for the annual effective dose equivalent calculation. To estimate the AEDE, a conversion coefficient and the outdoor occupancy factor of 0.7 Sv $Gy^{-1}$ and 0.2 were used, respectively, as shown in the equation below.

$$\mathrm{AEDE} \left( \mu Sv\ \mathrm{year}^{-1} \right) = [D_{\mathrm{R}} \left( \mathrm{nGy\ h}^{-1} \right) \times 8760 \left( \mathrm{h}^{-1} \right) \times 0.7 \left( \mathrm{Sv\ Gy}^{-1} \right) \times 0.2 \times 10^{-3} \quad (3)$$

where $D_R$ (nGy $h^{-1}$) is estimated using Eq. (5), average worldwide value of AEDE as 480 μSv $y^{-1}$ [20].

### Annual Gonadal Dose Equivalent (AGDE)

Radiation can cause different negative effects such as death or mutation of all living cells or a whole organ [22]. According to UNSCEAR (2000) [20], the bone marrow, the bone surface cells, the thyroid, the lungs, and the gonads are among the organs that are much affected by radiations. Therefore, determining the annual gonadal dosage equivalent (AGDE) is very important—it is estimated using Eq. (4) [23, 24].

$$\text{AGDE}\ \left(\mu Sv\ \ \text{year}^{-1}\right) = 3.09 A_{\text{Ra}} + 4.18 A_{\text{Th}} + 0.3147 A_{\text{K}} \tag{4}$$

### Excess Lifetime Cancer Risk (ELCR)

The prolonged contact of radiation from natural radioactivity in the soil, especially settlement areas, can cause adverse effects such as cancer. Some regulatory agencies expend a quantitative risk index assessment procedure to identify ELCR [25]. This value is calculated according to the likelihood of cancer in a population of individuals for a certain lifetime expending projected intakes, exposures, chemical-specific dosage, and response data. ELCR is estimated using Eq. (5), as quoted by Ramasamy et al. [26, 27]:

$$\text{ELCR} = \text{AEDE} \times \text{DL} \times \text{RF} \tag{5}$$

where AEDE is the yearly effective dosage equivalent, DL is 70 years of life duration, and RF is fatal cancer risk per Sievert (0.05 $Sv^{-1}$) [28].

### Gamma Index ($I_\gamma$)

The European Commission (1999) [21] suggested an index named as the gamma index ($I_\gamma$) in order to provide the guidelines of the European Commission for building materials usage. According to the European Commission (1999), the exemption criterion of gamma dosage is 0.3 mSv $y^{-1}$, while the upper limit criterion stands at 1 mSv $y^{-1}$. The upper limit has been applied by numerous countries as a control limit [29]. The gamma index, $I_\gamma$, was defined in Eq. (6):

$$I_\gamma = \frac{A_{\text{Ra}}}{300\ \text{Bq kg}^{-1}} + \frac{A_{\text{Th}}}{200\ \text{Bq kg}^{-1}} + \frac{A_{\text{K}}}{3000\ \text{Bq kg}^{-1}} \tag{6}$$

where $A_{\text{Ra}}$, $A_{\text{Th}}$, and $A_{\text{K}}$ are the activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K, respectively, in Bq $kg^{-1}$.

### External Radiation Hazard ($H_{ex}$)

External radiation hazard, $H_{ex}$, has been accepted as a limit value of unity in order to be nonhazardous. It is given in Eq. (7):

$$H_{ex} = \frac{A_{Ra}}{370\ \text{Bq kg}^{-1}} + \frac{A_{Th}}{259\ \text{Bq kg}^{-1}} + \frac{A_{K}}{4810\ \text{Bq kg}^{-1}} \tag{7}$$

where $A_{Ra}$, $A_{Th}$, and $A_K$ are the activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K, respectively, in Bq kg$^{-1}$.

### Internal Radiation Hazard ($H_{in}$)

Internal radiation hazard, $H_{in}$, is shown in Eq. (8). A value ≤1 is favored [30].

$$H_{in} = \frac{A_{Ra}}{185\ \text{Bq kg}^{-1}} + \frac{A_{Th}}{259\ \text{Bq kg}^{-1}} + \frac{A_{K}}{4810\ \text{Bq kg}^{-1}} \tag{8}$$

where $A_{Ra}$, $A_{Th}$, and $A_K$ are the activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K, respectively, in Bq kg$^{-1}$.

## Results and Discussion

The measured activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K of the studied samples are shown in Table 1. Water and gypsum have the lowest activity concentrations of raw materials for $^{226}$Ra, $^{232}$Th, and $^{40}$K. The highest activity concentrations were captured in raw materials: coal (95.00 Bq kg$^{-1}$) for $^{226}$Ra and trass (270.00 Bq kg$^{-1}$ and 1990.00 Bq kg$^{-1}$) for $^{232}$Th and $^{40}$K, respectively. The studied clinker sample has completely lower activity concentrations (16.60 Bq kg$^{-1}$, 30.00 Bq kg$^{-1}$, and 380.00 Bq kg$^{-1}$, respectively) than the lowest activity concentration values of the cement samples of this study for $^{226}$Ra, $^{232}$Th, and $^{40}$K.

The least activity value of $^{226}$Ra in all cement samples was found in CEM II/A-M (P-L) (26.30 Bq kg$^{-1}$), while the maximum activity value of $^{226}$Ra was in CEM II/B-M (L-W)—47.0 Bq kg$^{-1}$ (Table 1). The value of $^{226}$Ra activity in CEM II/B-M (L-W) was still lower than both Turkey and Makedonia originated same type of cement samples in the literature (Table 2).

The highest activity values for $^{232}$Th (87.0 Bq kg$^{-1}$) and $^{40}$K (670.0 Bq kg$^{-1}$) were found in CEM IV/B (P-W), which has higher values than the other Turkish cement sample activity concentrations for these two radionuclides in the literature (Table 2). The lowest activity levels for $^{232}$Th and $^{40}$K (39.0 Bq kg$^{-1}$ and 430.0 Bq kg$^{-1}$, respectively) were reached for CEM I. These results show that the contents of radium

**Table 1** Activity concentrations of cement raw materials and cement

| Material type | Activity concentration (Bq kg$^{-1}$ ± relative error) | | |
|---|---|---|---|
| | $^{226}$Ra | $^{232}$Th | $^{40}$K |
| *Raw materials* | | | |
| Fly ash | 87.00 ± 8.70 | 133.00 ± 18.62 | 1090.00 ± 87.20 |
| Coal | 95.00 ± 10.45 | 72.00 ± 18.00 | 170.00 ± 85.00 |
| Iron ore | 26.90 ± 2.96 | 148.00 ± 17.76 | 310.00 ± 34.10 |
| Gypsum | 9.90 ± 1.09 | <MDA | <MDA |
| Clay | 23.70 ± 2.61 | 106.00 ± 13.78 | 1470.00 ± 102.90 |
| Limestone | 15.60 ± 1.72 | 12.30 ± 2.83 | 63.00 ± 14.49 |
| Trass | 42.00 ± 4.20 | 270.00 ± 29.70 | 1990.00 ± 139.30 |
| Water | 5.00 ± 0.55 | <MDA | <MDA |
| Raw materials mean | 38.14 | 92.66 | 636.63 |
| *Intermediate materials* | | | |
| Raw meal | 37.00 ± 4.07 | 40.00 ± 8.40 | 320.00 ± 48.00 |
| Clinker | 16.60 ± 1.83 | 30.00 ± 4.80 | 380.00 ± 34.20 |
| Int. materials mean | 26.80 | 35.00 | 350.00 |
| *Cement types* | | | |
| CEM I | 30.00 ± 3.30 | 39.00 ± 7.41 | 430.00 ± 47.30 |
| CEM II/A-W | 34.00 ± 3.74 | 46.00 ± 7.82 | 460.00 ± 50.60 |
| CEM II/B-M (L-W) | 47.00 ± 4.70 | 71.00 ± 11.36 | 550.00 ± 55.00 |
| CEM II/A-M (P-L) | 26.30 ± 2.89 | 48.00 ± 7.68 | 450.00 ± 45.00 |
| CEM IV/B (P-W) | 34.00 ± 3.40 | 87.00 ± 12.18 | 670.00 ± 60.30 |
| Mean | 34.26 | 58.20 | 512.00 |

(226), thorium (232), and potassium (40) depend on raw materials used, geological site, and geochemical nature. More or less, most parts of cements consist of a clinker. On the other hand, because of their higher activity concentrations, fly ash and/or trass should be taken into account as main origins of high amount of activity concentrations of measured radionuclides in the studied cement samples.

Radium equivalent activity, $Ra_{eq}$, levels of the raw materials and the studied cements were given in Table 3; 370 Bq kg$^{-1}$ was used as a specification reference limit to all samples [12]. $Ra_{eq}$ values of the raw materials were between 5.00 and 581.33 Bq kg$^{-1}$. With 581.33 Bq kg$^{-1}$ value, only the trass sample was higher than the limit value among the raw materials. Meanwhile, fly ash was critical with its near critical value, 361.12 Bq kg$^{-1}$. The intermediate materials were far from the limit value as given in Table 3. All the investigated cement samples had the least $Ra_{eq}$ ranging from 118.88 to 210.00 Bq kg$^{-1}$; these values are lower than their mild $Ra_{eq}$ levels.

Absorbed gamma dose rates ($D_R$) in indoor air were scattered between 4.60 and 494.84 nGy h$^{-1}$ for the raw materials, 78.67 and 103.64 nGy h$^{-1}$ for the intermediate materials, and 104.90 and 180.58 nGy h$^{-1}$ for the cement samples (Table 3). Most of the raw material values of $D_R$ were higher than the world average value 84.00 nGy h$^{-1}$. Raw meal was higher, but the clinker was lower than the world average.

**Table 2** Comparison of $^{226}Ra$, $^{232}Th$, and $^{40}K$ activity concentrations of some cement raw materials and cement

| Raw materials | $^{226}Ra$ | $^{232}Th$ | $^{40}K$ | Ref. |
|---|---|---|---|---|
| *Fly ash* | | | | |
| Turkey | 87.0 | 133.0 | 1090.0 | This study |
| Turkey | 232.3 | 117.1 | 466.2 | [31] |
| Macedonia | 140.0 | 80.0 | 540.0 | [32] |
| | 85.0 | 129.0 | 786.0 | |
| India | 45.1 | 39.9 | 88.4 | [33] |
| Bangladeshi | 117.8 | 157.3 | 1463.3 | [34] |
| *Iron (ore/oxide)* | | | | |
| Turkey | 26.9 | 148.0 | 310.0 | This study |
| Turkey | 41.6 | 11.4 | 152.6 | [31] |
| Egypt | 160.5 | 87.3 | 121.3 | [35] |
| Saudi Arabia | 37.2 | 28.8 | 44.8 | [36] |
| Saudi Arabia | 21.6 | 18.6 | 53.6 | [37] |
| *Gypsum* | | | | |
| Turkey | 9.9 | <MDA | <MDA | This study |
| Turkey | 8.0 | 11.0 | 35.0 | [38] |
| Turkey | 10.8 | 3.6 | 44.5 | [31] |
| Albania | 11.8 | 5.8 | 66.8 | [4] |
| Saudi Arabia | 9.0 | 6.5 | 184.8 | [37] |
| Saudi Arabia | 7.7 | 3.3 | 173 | [36] |
| Bangladeshi | 58.4 | 91.2 | 1101.1 | [34] |
| Tanzania | 9.8 | 4.4 | 81 | [1] |
| | 2.6 | 3.0 | 6.3 | |
| Pakistan | 8.2 | 16.2 | 187.7 | [39] |
| Egypt | 31.7 | 55.2 | 88.7 | [35] |
| Macedonia | 5.9 | 1.44 | 11.0 | [32] |
| Greece | 6.8 | <MDA | <MDA | [40] |
| *Clay* | | | | |
| Turkey | 23.7 | 106.0 | 1470.0 | This study |
| Turkey | 26.7 | 41.8 | 629.3 | [31] |
| India | 63.7 | 38.6 | 313.7 | [29] |
| Saudi Arabia | 15.8 | 13.8 | 70.7 | [37] |
| Saudi Arabia | 18.2 | 22.4 | 127 | [36] |
| Tanzania | 90.7 | 123.3 | 137.7 | [1] |
| | 23.4 | 43.2 | 21.2 | |
| Pakistan | 34.7 | 41.2 | 187.6 | [39] |
| Egypt | 33.7 | 68.9 | 130.7 | [35] |
| *Limestone* | | | | |
| Turkey | 15.6 | 12.30 | 63.0 | This study |
| Turkey | 16.5 | 7.7 | 88.1 | [31] |
| Saudi Arabia | 6.2 | 3.0 | 155.5 | [37] |

(continued)

**Table 2** (continued)

| Raw materials | $^{226}$Ra | $^{232}$Th | $^{40}$K | Ref. |
|---|---|---|---|---|
| Saudi Arabia | 42.8 | 0.9 | <MDA | [36] |
| Tanzania | 6.4 | 15.2 | 80 | [1] |
| | 25.2 | 1.3 | 13.2 | |
| Pakistan | 28.4 | 11.3 | 63.1 | [39] |
| Egypt | 19.7 | 39.0 | 61.2 | [35] |
| Greece | 6.0 | 6.6 | 101.0 | [40] |
| *Trass* | | | | |
| Turkey | 42.0 | 270.0 | 1990.0 | This study |
| Turkey | 67.9 | 76.7 | 681.6 | [31] |
| Clinker | | | | |
| Turkey | 16.60 | 30.00 | 380.0 | This study |
| Turkey | 28.3 | 15.9 | 219.0 | [31] |
| Albania | 55.5 | 17.0 | 160.3 | [4] |
| Bangladeshi | 49.8 | 75.7 | 856.4 | [34] |
| Saudi Arabia | 79.9 | 7.5 | 6.1 | [36] |
| Pakistan | 51.1 | 23.2 | 258.4 | [39] |
| Greece | 15.0 | 14.0 | 141.0 | [40] |
| Makedonia | 31.0 | 20.0 | 234.0 | [32] |
| *Cement types* | | | | |
| CEM I | | | | |
| Turkey | 30.0 | 39.0 | 430.0 | This study |
| Turkey | 34.0 | 13.0 | 208.0 | [41] |
| Turkey | 29.8 | 17.5 | 239.0 | [31] |
| Albania | 51.2 | 16.1 | 168.8 | [4] |
| India | 35.7 | 37.7 | 159.8 | [29] |
| Saudi Arabia | 11.2 | 10.0 | 117.1 | [37] |
| Makedonia | 30.0 | 20.0 | 222.0 | [32] |
| *CEM II* | | | | |
| Turkey CEM II/A-W | 34.0 | 46.0 | 460.0 | This study |
| CEM II/B-M(L-W) | 47.0 | 71.0 | 550.0 | |
| CEM II/A-M(P-L) | 26.3 | 48.0 | 450.0 | |
| Turkey CEM II | 51.0 | 18.0 | 221.0 | [41] |
| Turkey CEM II/A-LL | 22.4 | 12.6 | 157.1 | [31] |
| Albania CEM II/A-LL | 51.0 | 16.5 | 150.4 | [4] |
| CEM II/B-LL | 46.2 | 12.0 | 133.7 | |
| Makedonia CEM II/A-M | 45.0 | 29.0 | 272.0 | [32] |
| CEM II/B-M | 50.0 | 34.0 | 295.0 | |
| *CEM IV* | | | | |
| Turkey | 34.0 | 87.0 | 670.0 | This study |
| Turkey | 45.0 | 26.0 | 352.0 | [41] |

**Table 3** Radiological parameters and hazard indices of cement raw materials and cement samples

| Material type | $Ra_{Eq}$ (Bq kg$^{-1}$) | Dose rate ($D_R$) (nGy h$^{-1}$) | AEDE (μSv y$^{-1}$) | AGDE (μSv y$^{-1}$) | ELCR | $I_\gamma$ | $H_{ex}$ | $H_{in}$ |
|---|---|---|---|---|---|---|---|---|
| *Raw materials* | | | | | | | | |
| Fly ash | 361.12 | 313.54 | 384.53 | 1167.03 | 1.35E−03 | 1.32 | 0.98 | 1.21 |
| Coal | 211.05 | 180.20 | 221.00 | 647.89 | 7.73E−04 | 0.73 | 0.57 | 0.83 |
| Iron ore | 262.41 | 212.35 | 260.42 | 799.10 | 9.11E−04 | 0.93 | 0.71 | 0.78 |
| Gypsum | 9.90 | 9.11 | 11.17 | 30.59 | 3.91E−05 | 0.03 | 0.03 | 0.05 |
| Clay | 288.47 | 256.00 | 313.96 | 977.89 | 1.10E−03 | 1.10 | 0.78 | 0.84 |
| Limestone | 38.04 | 32.92 | 40.38 | 119.40 | 1.41E−04 | 0.13 | 0.10 | 0.14 |
| Trass | 581.33 | 494.84 | 606.87 | 1883.24 | 2.12E−03 | 2.15 | 1.57 | 1.68 |
| Water | 5.00 | 4.60 | 5.64 | 15.45 | 1.97E−05 | 0.02 | 0.01 | 0.03 |
| Raw materials mean | 219.67 | 187.95 | 230.50 | 705.07 | 8.07E−04 | 0.80 | 0.59 | 0.70 |
| *Intermediate materials* | | | | | | | | |
| Raw meal | 118.84 | 103.64 | 127.10 | 382.01 | 4.45E−04 | 0.43 | 0.32 | 0.42 |
| Clinker | 88.76 | 78.67 | 96.48 | 296.01 | 3.38E−04 | 0.33 | 0.24 | 0.28 |
| Int. materials mean | 103.80 | 91.16 | 111.79 | 339.01 | 3.91E−04 | 0.38 | 0.28 | 0.35 |
| *Cement types* | | | | | | | | |
| CEM I | 118.88 | 104.90 | 128.65 | 390.74 | 4.50E−04 | 0.44 | 0.32 | 0.40 |
| CEM II/A-W | 135.20 | 118.68 | 145.55 | 441.78 | 5.09E−04 | 0.50 | 0.37 | 0.46 |
| CEM II/B-M (L-W) | 190.88 | 165.34 | 202.77 | 614.71 | 7.10E−04 | 0.70 | 0.52 | 0.64 |
| CEM II/A-M (P-L) | 129.59 | 113.00 | 138.58 | 423.21 | 4.85E−04 | 0.48 | 0.35 | 0.42 |
| CEM IV/B (P-W) | 210.00 | 180.58 | 221.46 | 679.10 | 7.75E−04 | 0.77 | 0.57 | 0.66 |
| Mean | 156.91 | 136.50 | 167.40 | 509.91 | 5.86E−04 | 0.58 | 0.42 | 0.52 |
| | 370.00[a] | 84.00[a] | 480.00[a] | | 2.90E−04 | 1.00[b] | 1.00 | 1.00 |

[a]UNSCEAR (2000) [20] world average
[b]Council Directive (2014) [42]

However, all $D_R$ values of the cement samples were more or less higher than the world average 84.00 nGy h$^{-1}$.

AEDE values were calculated in the ranges of 6.64–606.87 μSv y$^{-1}$, 96.48–127.10 μSv y$^{-1}$, 128.65–221.46 μSv y$^{-1}$ for the raw and the intermediate product materials and the studied cement samples, respectively, as given in Table 3. Compared to the world average reference value of 480.00 μSv y$^{-1}$, all AEDE readings were below this value—except trass.

Annual gonadal dose equivalent (AGDE) values varied between 15.45 and 1883.24 μSv y$^{-1}$, 296.01 and 382.01 μSv y$^{-1}$, and 390.74 and 679.10 μSv y$^{-1}$, for the raw and the intermediate product materials and the cement samples, respectively (Table 3). The average value of AGDE is 509.91 μSv y$^{-1}$ for the studied cements.

Excess lifetime cancer risk (ELCR) values were obtained between $1.97 \times 10^{-5}$ and $2.12 \times 10^{-3}$, $3.38 \times 10^{-4}$ and $4.45 \times 10^{-4}$, and $4.50 \times 10^{-4}$ and $7.75 \times 10^{-4}$, for the raw and the intermediate product materials and the cement samples, respectively, as given in Table 3. Only water and gypsum remained lower than the limit reference value, $2.90 \times 10^{-4}$. It should be considered that according to their raw and intermediate materials' ELCR levels, all the studied cement sample values were higher than the limit level.

The gamma index ($I_\gamma$) values were calculated between 0.02 and 2.15, 0.33 and 0.43, and 0.44 and 0.77, for the raw and the intermediate product materials and the cement samples, respectively, as shown in Table 3. Fly ash, clay, and trass were higher than the limit value, 1.00. All the calculated samples for the raw and intermediate materials were stayed lower levels for this parameter. The samples' $I_\gamma$ values were below the reference point.

External radiation hazard ($H_{ex}$) values were found between 0.01 and 1.57, 0.24 and 0.32, and 0.32 and 0.57 for the raw and the intermediate product materials and the cement samples, respectively, as presented in Table 3. The limit reference value, 1.00, was only exceeded by trass among the raw and the intermediate materials. Fly ash drew attention on the boundary of the reference limit. Comparing the $H_{ex}$ results of the samples, their $H_{ex}$ values were below the standard limit.

In the latter of radiation hazard indices, internal radiation hazard, $H_{in}$, values were found between 0.03 and 1.68, 0.28 and 0.42, and 0.40 and 0.60 for the raw and the intermediate product materials and the cement samples, respectively, as given in Table 3. The limit reference value, 1.00, was only exceeded by trass and fly ash among the raw and the intermediate materials. All the cement samples of this study were lower than the limit value.

## Conclusions

In this study, cement factory raw materials, intermediate materials, and five different types of cement samples were investigated to determine the activity concentrations of their natural radionuclides and evaluated using some important radiation parameters, such as radiation indices. Gamma-ray spectrometry method was used to determine the activity concentration. Results indicated an average of 34.26 Bq kg$^{-1}$, 58.20 Bq kg$^{-1}$, and 512.00 Bq kg$^{-1}$ in $^{226}$Ra, $^{232}$Th, and $^{40}$K, respectively. Radium equivalent activity ($Ra_{eq}$) levels of the investigated cements varied between 118.88 and 210.00 Bq kg$^{-1}$, which were below the allowable concentration of 370 Bq kg$^{-1}$. The $D_R$ for the selected samples were between 104.90 and 180.58 nGy h$^{-1}$, which were higher than the world average value of 84.00 nGy h$^{-1}$. Annual effective dose equivalent (AEDE) values for the cement samples were in the range of 128.65–221.46 μSv y$^{-1}$, which were all lower than the world average reference value 480.00 μSv y$^{-1}$. Annual gonadal dose equivalent (AGDE) values varied between 390.74 and 679.10 μSv y$^{-1}$, and the mean value was 509.91 μSv y$^{-1}$ for the cement samples. Excess lifetime cancer risk (ELCR) values of the studied cements were between $4.50 \times 10^{-4}$ and $7.75 \times 10^{-4}$. All the studied cement sample values were higher than the limit level of $2.90 \times 10^{-4}$. The gamma index ($I_\gamma$) values of the cement samples were between 0.44 and 0.77. All the cement samples' $I_\gamma$ values were below the standard limit value, 1.00. External radiation hazard index ($H_{ex}$) values of the samples were in a range of 0.32 and 0.57. The internal radiation hazard index ($H_{in}$) values of the investigated cements were found between 0.40 and 0.60, which were lower than the limit value, 1.00.

This study shows that the raw materials could be effective on the natural radiation levels and amounts of the related parameters. Especially, levels of radionuclides of trass and fly ash are important among the raw materials of the investigated cements. Coal as fuel of cement production has also importance because of high amount of radionuclide content. Consequently, natural radioactivity levels of the product cements could be mainly affected by the raw materials related to their geological locations. When trass and/or fly ash added into the cement content, they could be effective constituents of natural radioactivity levels of the produced cements. Coal should be taken into account regarding the natural radioactivity evaluations. It can be stated that in order to decrease the natural radioactivity level of cements, raw material and fuel should be selected from lower radioactive originated locations and sources, considering the economic conditions, as well.

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