Natural Radioactivity of Selected Sedimentary Rocks from the Krzeszowice Area

Grzegorz LIZUREK and Aleksandra SITAREK
University of Silesia, Faculty of the Earth Sciences
ul. Będzińska 60, 41-200 Sosnowiec, Poland
e-mail: glizurek@us.edu.pl; asitarek@us.edu.pl

Abstract
Sedimentary rocks from the borders of Krzeszowice graben have been the most popular origin of building materials in the whole Kraków region since the Middle Ages to the present day. Apart from using these rocks for building purposes, they are also used in road construction industry and as a part of sorbent for desulphurisation of combustion gases. It is vital to know the background radiation of these rocks. In situ gamma ray spectrometry was used to determine the activity concentrations of nuclides from U series, Th series and potassium ⁴₀K in selected rocks that were mostly of the Paleozoic age.

Geology of the Krzeszowice Graben

Investigated area is the S-E edge of Silesian-Krakowian monocline, which forms a layered plate whose complex consists of Permian to Cretaceous rocks. This complex is inclined towards N-E. This unit was folded and faulted during geological history and in the Neogene the Krzeszowice graben was formed. The bottom of the graben is filled with the Miocene marine sediments, but the edges of this elongated depression are limited by almost parallel faults. In these edges, different types of rocks belonging to Silesian-Krakowian monocline crop out. The outcrops of sedimentary rocks were selected as measurement sites for in situ gamma ray spectrometry. Seven rock surfaces were measured in six locations; one of them is magmatic rock and the rest are sedimentary rocks (five Paleozoic rocks and one Mesozoic).

The first location was the outcrop of Permian Myslachowice conglomerate from Filipowice formed from solid rock particles originated from older rocks surroundings. The conglomerate consists of well rounded particles of Carboniferous limestones mainly, but also Devonian dolomites, limestones, porphyry and sandstone pebbles. The cement has iron compounds (Gradziński 1972).
The second measurement site was Czatkowice quarry of Carboniferous limestone. These rocks are part of coal deposit, and have dark beige colour. This limestone is characterized by variable consistence of CaO, MgO and SiO$_2$ (Pinińska 1989).

Next location was closed quarry of black bituminous limestone of Devonian age in Dębnik. Black color of this limestone is caused by occurrence of distorted pyrite (Bednarczyk and Hoffmann 1989). This rock, also called “marble”, has been exploited since XVth century.

The fourth measurement site was Dubie quarry of Devonian dolomite, also called dolomite from Zbrza. In this place, two rocks were measured – dolomite and trachyandesite dyke of Permian age, that cut the carbonates.

The dolomites are the oldest formation outcropping in studied area (Silesian-Krakowian monocline). Trachyandesite is the exception of sedimentary rock selection to this work, but it was chosen due to its position – vertical cut through the carbonates, that may influence the surrounding dolomite.

Next rock chosen for measurements was hardly weathered Carboniferous sandstone from Tenczynek, the location is popularly known as “rock below the pine”.

The last investigated rock was Jurassic platy limestone from Nielepice quarry. This is the most popular outcropping rock in the studied area. This rock is currently used for cement and lime production, but formerly it was used for monument construction in the Middle Ages.

Fig. 1. Location of measurement points on the background of geological map of the Krzeszowice vicinity (according to Gradiński 1972); 1 – Filipowice, 2 – Czatkowice, 3 – Dębnik, 4 – Dubie (dolomite), 5 – Dubie (trachyandesite), 6 – Tenczynek, 7 – Nielepice.
Methods

The EG&G ORTEC spectrometry system consists of a HPGe detector (30% efficiency, crystal length: 59 mm, diameter: 58.6 mm) with cryostat filled with liquid nitrogen mounted on a tripod, a multichannel buffer DART, and a laptop. The resolutions of the detector are 0.67 keV at 122 keV and 1.73 keV at 1.33 MeV. Software used for determination of the radionuclides and their activity concentration M-1B32 (EG&G ORTEC) use the one-meter geometry, in situ analysis methods developed by the U.S. DOE Environmental Measurements Laboratory (Beck et al. 1972). The software consists of two parts: the supervisor program which uses the programs M-1 Setup and Gamma Vision-32, and the operator program M-1 for Windows. In field conditions, the detector was placed 1 m above the rock surface. In this case, detector view for gamma emitters was approximately 10 m in radius to a depth of 30 cm, depending on the ground and energy source (Helfer and Miller 1988). The determination of the presence of radionuclides and calculation of their activities was based on the following gamma-ray transitions (in keV): $^{40}$K (1460.8), $^{208}$Tl (583.1 and 860.5), $^{212}$Pb (238.6 and 300.1), $^{212}$Bi (727.2 and 1620.6), $^{214}$Pb (241.9, 295.2 and 351.9), $^{214}$Bi (609.3, 1120.3, 1238.1 and 1764.5) and $^{228}$Ac (338.3, 911.1 and 968.9) (Debertin and Helmer 1988). The energy tolerance for library file (1Meter.lib) was stated as 1.75 keV. Counting live time was set on 3 h for each measurement point. Powdered mixture calibration sources of $^{40}$K (840 Bq), $^{226}$Ra (218 Bq) and $^{232}$Th (127 Bq) were used for calibration of the spectrometer. The vertical distribution of particular radionuclides is described within M-1 software by parameter $\alpha/\rho$, where $\alpha$ is the reciprocal of the relaxation length (flux reduction by factor $e$) for the gamma energy line being observed (cm$^{-1}$) and $\rho$ is the soil (rock) density (g cm$^{-3}$) (EG&G ORTEC 2000). The general source distribution is represented with three cases: $\alpha/\rho < 0.1$, uniform source distribution (natural radionuclides), $\alpha/\rho > 0.5$, planar source distribution (fresh fallout) and $0.1 < \alpha/\rho < 0.5$, not uniform or planar. Values of $\alpha/\rho$ ranging from 0.1 to 0.5 have been found to describe realistic fallout distributions most adequately, the more aged fallout will be represented by the smaller values. In our work we assumed $\alpha/\rho = 0$ for distributions of $^{40}$K, $^{208}$Tl, $^{212}$Pb, $^{212}$Bi, $^{214}$Pb, $^{214}$Bi and $^{228}$Ac (manufacturer’s recommended value), EG&G ORTEC (2000) and ORTEC (2000).

Results and Discussion

Measured values of $^{40}$K, $^{208}$Tl, $^{212}$Pb, $^{212}$Bi, $^{214}$Pb, $^{214}$Bi, $^{228}$Ac and calculated activity concentration of $^{226}$Ra for all measured rocks are given in Table 1. The uncertainty value (Table 1) consists of the random and systematic errors in all of the factors involved in calculating the final nuclide concentration result (ORTEC 2000). The error can be expressed as:

$$\sigma_r = \sqrt{\sum \sigma_{i}^2 + \frac{1}{3} \sum \sigma_{s}^2},$$

where $\sigma_r$ is the uncertainty, $\sigma_i$ is the individual random error and $\sigma_s$ is the individual systematic error. The random uncertainties are counting, random summing and ab-
sorption correction, whereas the systematic uncertainties are nuclide uncertainty from library, efficiency fitting uncertainty, calibration source uncertainty and geometry correction. The random summing uncertainty is estimated to be 10% of the Eq. 1 (ORTEC 2000).

Table 1
The results of in situ γ-ray measurements of $^{40}$K, $^{208}$Tl, $^{212}$Pb, $^{212}$Bi, $^{214}$Pb, $^{214}$Bi and $^{228}$Ac at different locations at the Krzeszowice graben area. The uncertainty means one standard deviation ($\sigma$), Eq. (1)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Filipowice</th>
<th>Czatkowice</th>
<th>Dębniak</th>
<th>Dubie</th>
<th>Dubie</th>
<th>Tenczynek</th>
<th>Nielepice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock (age)</td>
<td>Conglomerate (C)</td>
<td>Limestone (C)</td>
<td>Limestone (D)</td>
<td>Dolomite (D)</td>
<td>Trachyandesite (P)</td>
<td>Sandstone (C)</td>
<td>Limestone (J)</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>423.2±6.1</td>
<td>53±2</td>
<td>473±9</td>
<td>85±4</td>
<td>184±3</td>
<td>129.5±4</td>
<td>82±3</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>11.4±1.1</td>
<td>2.5±0.3</td>
<td>11.4±0.9</td>
<td>2.4±0.3</td>
<td>3.3±0.6</td>
<td>9.2±0.7</td>
<td>3.4±0.5</td>
</tr>
<tr>
<td>$^{212}$Pb</td>
<td>17.8±1</td>
<td>5±0.5</td>
<td>30.3±0.8</td>
<td>&lt; DL</td>
<td>6.9±0.4</td>
<td>18±0.9</td>
<td>7.8±0.3</td>
</tr>
<tr>
<td>$^{212}$Bi</td>
<td>14.9±1.7</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>15.2±2</td>
<td>4.6±0.7</td>
</tr>
<tr>
<td>$^{228}$Ac</td>
<td>34±3.6</td>
<td>6.6±1.4</td>
<td>30.9±5.6</td>
<td>7.2±1.3</td>
<td>9.7±1.7</td>
<td>28.8±3.4</td>
<td>9.5±2</td>
</tr>
<tr>
<td>$^{214}$Pb</td>
<td>19.7±2.4</td>
<td>35.1±1.7</td>
<td>42.2±4.8</td>
<td>20.3±2.6</td>
<td>23.6±4.8</td>
<td>18.3±1.9</td>
<td>13.7±1.8</td>
</tr>
<tr>
<td>$^{214}$Bi</td>
<td>28.5±4.1</td>
<td>36.4±2.2</td>
<td>44.3±6.7</td>
<td>18.1±3.3</td>
<td>20.4±5.7</td>
<td>23.5±2.9</td>
<td>11.9±2.7</td>
</tr>
<tr>
<td>$^{226}$Ra*</td>
<td>24.1±3.3</td>
<td>35.7±2.4</td>
<td>43.2±6.8</td>
<td>19.2±3.7</td>
<td>22±6.4</td>
<td>20.9±2.4</td>
<td>12.8±2.8</td>
</tr>
</tbody>
</table>

* Based on activity concentrations of $^{214}$Bi and $^{214}$Pb

DL – detection limit

In this work the radioactive equilibrium in $^{232}$Th $\rightarrow$ $^{228}$Ac and $^{238}$U $\rightarrow$ $^{226}$Ra $\rightarrow$ $^{222}$Rn $\rightarrow$ $^{214}$Pb $\rightarrow$ $^{214}$Bi series was assumed. Exhalation of $^{222}$Rn from the rock can produce 10-20% reduction in the gamma emitting $^{214}$Pb and $^{214}$Bi on the surface. However in field conditions that exhalation is compensated in most part by the contribution of the flux from the same nuclides in the ambient air (Helfer and Miller 1988).
The highest value of $^{40}$K activity concentration was noted in Devonian limestone from Dębnik and in Carboniferous conglomerate from Filipowice amounting to $473 \pm 9$ Bqkg$^{-1}$ and $423.2 \pm 6.1$ Bqkg$^{-1}$ respectively. Limestone (C) from Czatkowice is characterized by the lowest $^{40}$K activity concentration of $53 \pm 2$ Bqkg$^{-1}$. In the case of intrusion influence on the dolomite in the Dubie quarry there is no evidence that trachyandesite enriched intruded dolomite in potassium. The activity concentration of $^{40}$K in Permian trachyandesite ($184 \pm 3$ Bqkg$^{-1}$) is distinctly higher than $^{40}$K concentration noted in Devonian dolomite ($85 \pm 4$ Bqkg$^{-1}$). In Fig. 3 the comparison of $^{40}$K activity concentration in rocks of studied area with average concentrations in soil and continental crust is shown. The average activity concentration of $^{40}$K in the continental crust amounting to 850 Bqkg$^{-1}$ (Eisenbud and Gesell 1997), was not exceeded by any of measured rocks. In the case of soil average activity of $^{40}$K amounting to 400 Bqkg$^{-1}$ (Eisenbud and Gesell 1997), a higher value was noted for two rocks: Devonian limestone from Dębnik and Carboniferous conglomerate from Filipowice ($473 \pm 9$ Bqkg$^{-1}$ and $423.2 \pm 6.1$ Bqkg$^{-1}$). These values exceed the average concentration clearly above the standard deviation gap, but it can be said that these rocks have activity concentration of $^{40}$K on the soil level.

**Th series**

Measured activity concentration values of particular nuclides from Th series are presented in Table 1. There is very good radioactive equilibrium between $^{228}$Ac and
$^{208}$Tl in $^{232}$Th series at each measurement location. It is clearly visible after multiplying concentration value of $^{208}$Tl by 2.77 factor, that is deduced from the decay channel distribution in Th series. The highest activity concentration was noted in conglomerate (C) from Filipowice (34 ± 3.6 Bqkg$^{-1}$), Devonian “marable” from Dębni (30.9 ± 5.6 Bqkg$^{-1}$) and sandstone (C) from Tenczynek (28.8 ± 3.4 Bqkg$^{-1}$). The difference between these concentration values is smaller than uncertainty gap. The smallest activity concentrations with values ranging from 6.6 ± 1.4 Bqkg$^{-1}$ to 9.7 ± 1.7 Bqkg$^{-1}$ characterize rest of the carbonates and trachyandesite. In the case of the dyke from Dubie and its influence on the surrounding dolomite for Th series there is not significant difference in activity concentration of $^{228}$Ac and other nuclides from this series noted in dolomite (7.2 ± 1.3 Bqkg$^{-1}$) and in trachyandesite (9.7 ± 1.7 Bqkg$^{-1}$). This difference is within the standard deviation gaps. The lack of difference can be caused by opposite influence of the dolomites on trachyandesite or by the small thickness of the dyke – about 2-3 m. The clastic rocks from the studied area have higher Th series activity concentration than most of the carbonates (except of the limestone from Dębni). There is no correlation between Th series concentration and the age of the rock observed. The comparison of activity concentration of Th series obtained for sedimentary rocks and trachyandesite with the average activity concentration of Th in continental crust (44 Bqkg$^{-1}$) is shown in Fig. 3. This average activity concentration is clearly higher than any noted concentration in sedimentary rocks from Krzeszowice area.

U series

As it was mentioned above, the activity concentration of U series was based on $^{226}$Ra activity concentration that was deduced from $^{214}$Bi and $^{214}$Pb concentrations. The highest $^{226}$Ra activity concentration was noted in two dark bituminous limestone’s Devonian “marble” from Dębni (43.2 ± 6.8 Bqkg$^{-1}$) and in limestone (C) from Czatkowice quarry (35.7 ± 2.4 Bqkg$^{-1}$). The lowest U series activity concentration characterises Jurassic limestone from Nielepice: 12.8 ± 2.8 Bqkg$^{-1}$. The highest concentrations are probably caused by the reductive deposition environment. In such case, uranium comes to the sediment from surroundings (Polański 1979). It is distorted pyrite that produced dark colour and characteristic "bitouminous" smell of the limestone from Dębni (Bednarczyk and Hoffmann 1989). This appearance of pyrite may be an indication of reductive deposition environment.

Comparison of U series activity concentration measured in the Krzeszowice area with average activity concentration of this series in the continental crust (Fig. 3) shows that the highest noted value exceeds the average (36 Bqkg$^{-1}$) and the U series activity concentration value in Carboniferous limestone from Czatkowice is close to crustal average activity concentration value. The other U series activity concentrations presented in this work are clearly lower than continental crust average activity concentration.

At the same figure, a comparison of U series activity concentration measured in sedimentary rocks from borders of Krzeszowice graben with average activity concentration in the carbonates (25 Bqkg$^{-1}$) is presented. This comparison shows that two
highest values noted in limestones from Dębnik and Czatkowice clearly exceed the average activity concentration in the carbonates, when other measured activity concentrations of U series in carbonates from studied area are clearly below this average. There is an interesting dependence between the age of limestone from studied area and its activity concentration – the oldest limestone has the highest activity concentration. It is hard to tell whether this connection is global because of small number of measured limestones (only three), but it is more likely that this age–concentration dependence is characteristic for the studied area.

In the case of the influence of dyke from Dubie on the surrounding dolomite for U series, there is no significant difference in activity concentration of $^{226}$Ra and other nuclides from this series noted for dolomite (19.2 ± 3.7 Bqkg$^{-1}$) and trachyadesite (22 ± 6.4 Bqkg$^{-1}$). This difference is again within the standard deviation gaps. It is strange that U series concentration is higher than Th series concentration in trachyandesite from the Dubie quarry; such a situation is common for carbonates but not for magmatic rocks (Eisenbud and Gesell 1997). This fact suggests that dolomites surrounding the trachyandesite dyke have greater influence on it or the size of the dyke is not sufficient to measure the activity concentration of radionuclides in situ with the one meter geometry method.

Conclusions

In most of the studied rocks, the U series activity concentration is higher than the Th series activity concentration. Only clastic sedimentary rocks, such as sandstone
and conglomerate, had higher Th series activity concentration than the U series concentration. The average activity concentrations of U and Th series in the continental crust are 36 Bq kg\(^{-1}\) and 44 Bq kg\(^{-1}\), respectively, so our results contradict the expected prevalence of the Th series concentration. This can be explained by the origin of the rocks. Clastic rocks are composed mostly of grains of other weathered rocks, which were transported to the deposition site. Since the Th minerals are hard to dissolve, the grains composed of thorium minerals are deposited and compose the clastic sedimentary rocks. In the case of carbonates, it is unlikely for thorium minerals to come into deposition in such an amount as in clastic rocks. Carbonates from the Krzeszowice graben borders show an interesting dependence between the age of rock and the activity concentration of nuclides from U series – the older the rock, the higher the U series activity concentration. This dependence characterizes probably only these local carbonates; because of a small number of measurements and lack of similar cases in literature it is impossible to treat this dependence as a global rule. It is to be said that sedimentary rock gamma ray background radiation level in the Krzeszowice area does not exceed the average continental crust gamma radiation level. Therefore, there is no reason to stop using these rocks as building or other industrial material sources even in the case of the rock that is “richest” in U series activity; i.e., the Dębniak limestone. This rock has a higher activity concentration (43.2 ± 6.8 Bq kg\(^{-1}\)) than the continental crust average activity concentration (36 Bq kg\(^{-1}\)), but the difference between these values is not higher than the uncertainty gap, so in the case of sedimentary rocks from the Krzeszowice area the highest activity concentration level is comparable to average continental crust background radiation level.

References


EG&G ORTEC, 2000, In situ spectroscopy M-I-B32 M-I Setup supervisor program. Software user’s manual, EG&G ORTEC Part No. 779980, Oak Ridge.


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