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Environmental impact of coal mining on the natural environment in Poland

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Abstract. Saline waters occurring in underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from uranium series and ^{228}Ra from thorium series. Approximately 40% of total amount of radium remains underground in a form of radioactive deposits, but 225 MBq of ^{226}Ra and 400 MBq of ^{228}Ra are released daily to the rivers with mine effluents. Technical measures as spontaneous precipitation of radium in gobs, decreasing of amounts of water inflows into underground working etc. have been undertaken in several coal mines and as the result total amount of radium released to the surface waters diminished of about 60% during last 5-6 years. Mine waters can cause a severe impact on the natural environment, mainly due to its salinity. But also the enhancement of radium concentration in river waters, bottom sediments and vegetation is observed. Sometimes radium concentration in rivers exceeds 0.7 kBq/m^3, which is due to Polish law a permissible level for waste waters. The extended investigations were performed in all coal mines and on this basis the radium balance in effluents has been calculated. Measurements done in the vicinity of mine water's settling ponds and in rivers gave us an opportunity to survey radium behaviour in river waters and the range of contamination. Solid waste materials with enhanced natural radioactivity have been produced in huge amounts in power and coal industries in Poland. There are two main sources of these waste products. As a result of combustion of coal in power plants low radioactive waste materials are produced, with ^{226}Ra concentration seldom exceeding few hundreds of Bq/kg. Different situation is observed in coal mines, where as a result of precipitation of radium from radium-bearing waters radioactive deposits are formed. Sometimes natural radioactivity of such materials is very high, in case of scaling from coal mines radium concentration may reach 400 000 Bq/kg - similar activity as for 3% uranium ore. Therefore maintenance of solid waste with technologically enhanced natural radioactivity (TENR) is also a very important subject.

Enhanced natural radioactivity

The occurrence of the natural radioactivity in uranium mines became a known phenomenon early on. In other types of mines (as coal or phosphate ones) enhanced levels of natural radioactivity have been observed, but unfortunately this phenomenon is not known as well.

The enhanced levels of gamma radiation in Polish coal mines have been discovered by Saldan in early 60's [1], but regular investigations have been started in 70's by Tomza and Lebecka [2], concerning mainly radium-bearing waters and radioactive deposits. In one case in a coal mine in Poland the radium concentration (^{226}Ra) in such scale reached 400 kBq/kg, which corresponds to an activity of 3% U ore. Similar problem in Ruhr Basin was reported by Gans [3], which found high radium concentration in waste waters from coal mines. Natural radioactivity enhanced by effluents from phosphate industry has been investigated in Brazil by Paschoa and Nobrega [4]. Recently very high radium concentrations have been found in the USA in brine sludge - a mineral waste water produced by oil and gas industry. As a result of radium precipitation from such waters in pipes etc. high radioactive scales are formed. Problem of radioactive contamination causing by such materials (called NORM - naturally occurring radioactive materials) is presently investigated [5]. Similar situation is observed in

Romania [13] in oil industry, which causes the contamination of the natural environment. Some reports from coal industry [11] give a suggestion, that similar situation - occurrence of radium-bearing saline waters - could takes place also in coal mines in United States. In fact, the consensus from many presentations at the Natural Radiation Environment Meeting in Montreal, June 1995 seems to be that in most mines and deep wells waters contain enhanced natural radioactivity.

The Upper Silesian Coal Basin (USCB) is located in southern part of Poland and there are of about 50 underground coal mines. Total outflow of water from these mines is of about 800 000 m^3/day. The salinity of these brines if far higher than that of the ocean water. The total amount of salt (total dissolved solids - TDS) carried with mine waters to the rivers is about 10 000 tonnes/day. The dominating ions in these brines are Cl^- and Na^+ with concentrations up to 70 g/l and 40 g/l accordingly, but these waters contain also usually several grams per litre of Ca^{2+} and Mg^{2+} and significant amounts of other ions [2]. Waters with high radium concentration occur mainly in the southern and central part of the coal basin, where coal seams are overlaid by a thick layer of impermeable clays [1]. Saline waters occurring in coal mines in Upper Silesia cause severe damages to the natural environment. It is mainly an effect of their high salinity, sometimes higher than 200 g/l, but additionally, these waters often have high radium concentration, reaching 390 kBq/m^3 [8].

Investigation done by Tomza and Lebecka [2] showed that concentration of radium in water is correlated with it's salinity. As the salinity of mine waters is usually increasing with the depth, waters with higher radium concentration occur in deeper horizons. Later two different types of radium-bearing water were found in coal mines [8]. One type (type A) of water contains radium and barium, but no sulphate ions, whilst in another type of water (type B) there is no barium but radium and sulphate ions. From waters type A radium is easily co-precipitated with barium as sulphates when mixed with other natural waters containing sulphate ions. In case of radium-bearing waters type B, there is no carrier for radium, therefore precipitation does not occur. Further investigation [12] showed that radium bearing waters released from coal mines sometimes cause widespread contamination of small and larger rivers in their vicinity. This contamination is caused by radium present in an ionic form in water as well as by radium present in suspended matter and in deposits. Radioactive deposits are formed particularly by co-precipitation of barium and radium as sulphates from radium-bearing waters type A [2]. This process results in diminishing of the total activity released into rivers because part of radium remains in underground mine workings as deposits. Precipitation of barium and radium sulphates in underground mine workings takes place either spontaneously or as a result of applied purification technologies which are aimed to reduce the radium concentration in waste waters below the permissible level [9].

In the past the highest concentration of ^{226}Ra in discharge waters from a single coal mine in USCB was as high as 25 kBq/m^3 [8]. **According to Polish regulations discharge waters with radium ^{226}Ra concentration over 0.7 kBq/m^3 should be treated as a liquid radioactive waste** [9]. Such waters were released from ten out of sixty six underground hard coal mines in Poland, in which radium-bearing waters were dumped from settlement ponds to the natural environment. Waters type A were discharged from 7 coal mines (now from 3 collieries). The total activity of ^{226}Ra released with these waters is of about 30 MBq per day. Although waters type B have been discharged also from only 3 mines, but the total output of ^{226}Ra is higher than in waters type A - approximately 200 MBq per day [10]. The occurrence of the enhanced natural radioactivity in Polish coal mines causes the radiation hazard for mining crews. In the mining industry in Poland, monitoring of the radioactivity of mine waters, precipitates as well as gamma doses is obligatory since 1989.

Monitoring of radioactive contamination caused by effluents and tailings from coal mines must also be provided since 1986 [9]. Due to these regulations the following measurements must be done in mine's vicinity:
I. The concentration of ^{226}Ra and ^{228}Ra in effluent from the settlement pond, in river above and below the discharge point, in water supplies nearby discharge point.
II. The concentrations of natural radionuclides in solid samples, dumped onto the piles.
Such complex monitoring system gives an opportunity to obtain a complete picture of the influence of a certain mine on the underground and surface employees as well as on inhabitants of adjoining areas.

Applied methods and instrumentation

(A) Measurements of radium isotopes and ^{210}Pb in waters

Radioactive waters from coal mines contain mainly radium isotopes - ^{226}Ra from uranium series and ^{228}Ra from thorium series. A method of chemical separation of radium, developed by Goldin [6], have been modified for liquid scintillation counting [7, 8]. In this method, radium is co-precipitated with barium in form of sulphates and this precipitate is mixed with liquid gelling scintillator. The measurements of prepared samples have been performed by means of a low background liquid scintillation spectrometer QUANTULUS (Wallac Oy, Finland). This counter is equipped in feature of alpha/beta separation and anti-coincidence guard, which enables measurements of ^{226}Ra concentration as low as 3 Bq/m^3 and simultaneous measurements of ^{228}Ra (LLD = 30 Bq/m^3) and ^{224}Ra (LLD = 50 Bq/m^3). In addition, this method enables a simultaneous preparation of ^{210}Pb, which can be measured in LS spectrometer from 20 Bq/m^3.

(B) Measurements of gamma emitting natural isotopes in solid samples

Solid samples (radioactive deposits from settlement ponds, river beds but also soils, solid wastes, ashes) contain mainly isotopes from uranium and thorium series, ^{40}K and sometimes ^{137}Cs (as a result of Chernobyl disaster). For the measurements a gamma spectrometry system have been used - it contains HPGe detector (45%, PGT), multichannel analyser built-in computer (CANBERRA) and software for spectrum analysis GENIE-PC (CANBERRA). This instrumentation enables measurements of ^{226}Ra concentration (as low as 1 Bq/kg), ^{228}Ra and ^{224}Ra, ^{40}K and other natural and artificial isotopes [14].

Investigations of the contamination of the natural environment, caused by coal mining industry

The assessment of the total activity of radium released from coal mines in Upper Silesia with waste water was done basing on:

- results of determination of radium isotopes in waters released by all coal mines;
- data on amount of water released by individual mines.

We have also made an estimation of total activity of radium which remains in underground workings in a form of deposit precipitated out of radium-bearing waters either due to unintended mixing of natural waters of different chemical composition or due to purification of radium-bearing waters. This estimation has been done basing on:

- results of determination of radium isotopes in original waters inflowing to the underground mine workings from the rocks;
- rough estimation of the amounts of water inflows from different sources or parts of mines;
- calculated value of the total activity of radium pumped out from underground mine workings with waste waters by individual mines.

Analysis of inflows of radium-bearing waters into underground workings

Concentration of radium isotopes in original water samples from different coal mines varies in a very wide range - from 0 to 110 kBq/m^3 for ^{226}Ra and from 0 to 70 kBq/m^3 for ^{228}Ra [10]. Waters with radium concentration above 1.0 kBq/m^3 were found in 43 out of 65 coal mines in Upper Silesian Coal Basin. The highest concentrations of radium were measured in highly mineralised waters from deeper levels in radium-bearing waters type A. The ratio of ^{226}Ra to ^{228}Ra in radium-bearing waters type A was in average of about 2:1. In opposite in radium-bearing waters type B there were more ^{228}Ra than ^{226}Ra, the ratio ^{226}Ra: ^{228}Ra was from 1:2 up to 1:3. Concentration of ^{226}Ra in these waters reached 20 kBq/m^3, while concentration of ^{228}Ra reached 32 kBq/m^3. These values justify the statement that Upper Silesian radium-bearing waters belong to the waters with highest known radium concentration.

Original waters flowing into mine workings from the rocks from different aquifers are collected in gutters in underground galleries, brought together from different parts of the mine, clarified and pumped out to the surface. Radium concentration in these mixed waters was lower than in original water and did not exceed 25 kBq/m^3 of ^{226}Ra and 14 kBq/m^3 of ^{228}Ra [10].

Basing on the results of measurements of radium concentration in the original waters inflows into the mine workings and on data on the flow rates of water provided by the mine hydrologists, the total activities of both radioisotopes of radium flowing with water to different parts of mines and to different mines were calculated. This results were compared with values obtained using radium concentrations in mixed waters taken from the drainage system (from gutters) from different parts of mines and corresponding flow rates obtained from the mines. The difference is indicating the activity of radium remaining in underground mine workings due to spontaneous precipitation of radium and barium sulphates or due to applied purification of water. The calculated activity of radium remaining in underground mine workings as deposits in all Upper Silesian coal mines is 425 MBq/day of ^{226}Ra and 300 MBq/day of ^{228}Ra. These values can not be considered as very accurate, since the uncertainty of measurements of flow rates of small inflows is rather large. The approximate amount of ^{226}Ra in **water inflows in coal mines** in USCB have been calculated as high as 650 MBq/day (i.e. 230 GBq per year) while for ^{228}Ra this value is of about 700 MBq/day or 255 GBq per year (see fig.1.). Although radium concentrations in waters type B are usually lower than in waters type A the total inflows to mines where radium-bearing waters type B occur are much higher. As a result the total activity of radium carried with water type B is higher. The highest values for a single mine (with waters type B) are: 78 MBq per day of ^{226}Ra and 145 MBq per day of ^{228}Ra.

In comparison corresponding values of inflows of radium with saline waters in 4 copper mines in Poland are: 31 MBq of ^{226}Ra and 3 MBq of ^{228}Ra per day.

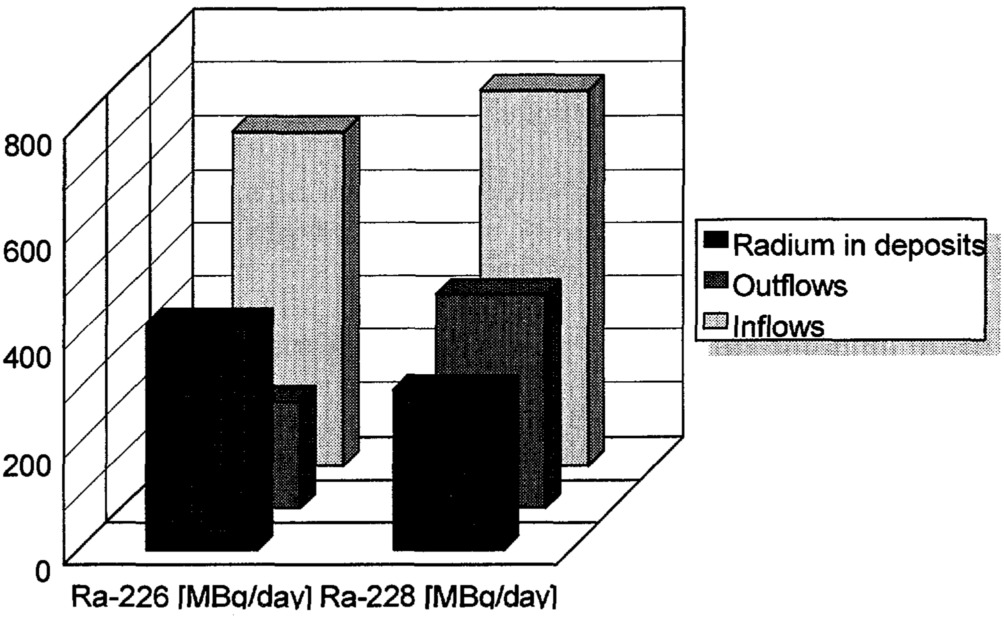

FIG. 1. Radium balance in coal mines.

Analysis of outflows from coal mines

Much more accurate are the results of calculations of the total activities of radium present in water pumped out from individual mines. These values were calculated basing on the radium concentration determined in these waters and on data of amount of water provided by mines.
Samples of discharged waters were taken from settlement ponds. We found that the amount of radium ^{226}Ra, **released with saline waters** to the rivers is approximately equal 225 MBq per day (75 GBq/year) and for ^{228}Ra - 400 MBq/day (145 GBq per year).

In outflows from settlement ponds in 87 % mines ^{226}Ra concentration exceeds 0.008 kBq/m^3, in 25% ^{226}Ra concentration is higher than 0.1 kBq/m^3 and in 8 % exceeds permissible level - i.e. 0.7 kBq/m^3 [9].

In rivers enhanced concentrations of radium can be observed many kilometres down from the discharge points. This is mainly true for radium-bearing waters type B, because out of these waters radium is not easily precipitated. The highest value of ^{226}Ra concentration was as high as 1.3 kBq/m^3 - it was found in a small stream near it's conjunction with Vistula river.

Enhanced radium concentrations are mainly observed in the Vistula river, into which most of the radium is discharged with B type waters - approximately 180 MBq of ^{226}Ra and 375 MBq of ^{228}Ra per day. Concentration of ^{226}Ra (0.035 kBq/m^3) was observed in Vistula in Cracow - 70 km downstream from Upper Silesia. The concentration of ^{226}Ra in Vistula river is shown on fig.2a and 2b. Bars show the concentrations of radium in discharge waters from mines. Some of these waters are not discharged directly to Vistula river, but to it's tributaries. In this case bars are located in places of conjunction of these rivers. The influences of singular inflows can be seen very clearly. Moreover, waters from first mine are A type and the difference of radium behaviour (fast precipitation) in comparison with other 3 mines (waters

B type) is very evident. Different situation was observed in the vicinity of Oder river, where in coal mines occur mainly waters type A. The amount of radium discharged into this river is much lower - 20 MBq per day of ^{226}Ra and 10 MBg/day of ^{228}Ra. As a result concentrations of radium in Oder ***are below 0.1 kBq/m³.***

Concentrations of radium isotopes in some rivers in Upper Silesia are clearly enhanced as compared with natural levels. In comparison with data from other locations, concentrations of radium isotopes in rivers in USCB are significantly higher. Enhanced concentrations of radium in river waters in Upper Silesia are caused solely by the influence of mine waters.

Due to release of radium-bearing mine waters from coal mines there is a contamination of river waters. As a result radium concentration in some small rivers exceeds permissible level for radioactive wastes. Therefore development and application of purification methods is justified and further efforts should be done to reduce the contamination of rivers, particularly of Vistula River and it's tributaries.

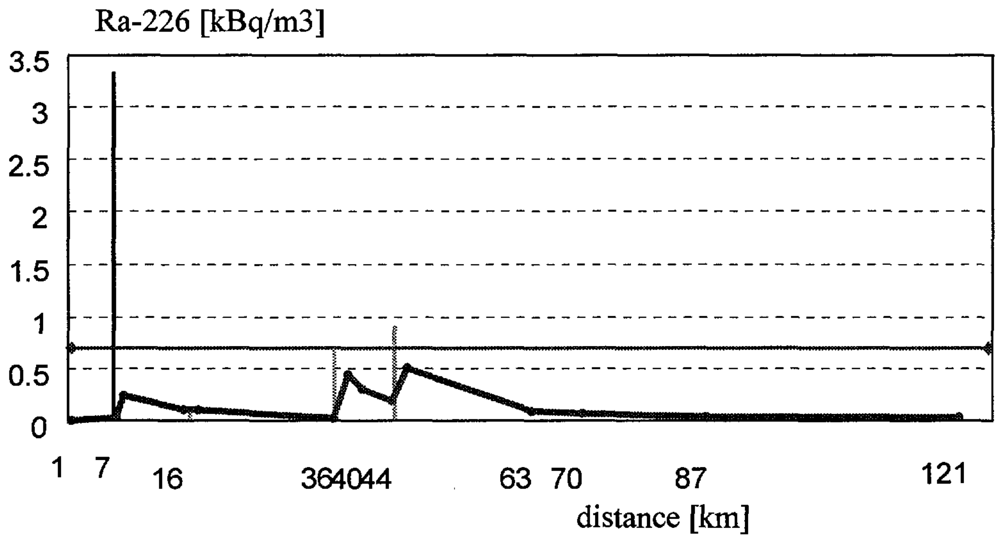

FIG. 2a. Radium in Vistula — during hot summer.

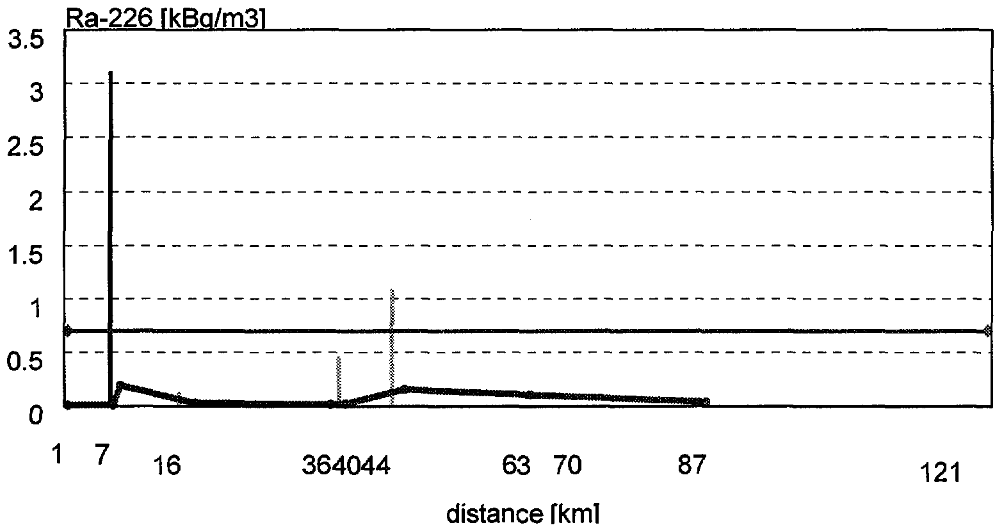

FIG. 2b. Radium in Vistula - during autumn and winter.

It can bee seen that in Cracow, which is 80 km downstream from the last point of mine waters discharge, radium content is about 0.04 kBq/m^3 of ^{226}Ra, while the average value for other Polish rivers is only 0.004 kBq/m^3 [16].

In one of small tributaries of Vistula, in Gostynka river concentrations of radium isotopes from 0.006 kBq/m^3 above discharge point to 0.635 kBq/m^3 (^{226}Ra) and from 0.01 kBq/m^3 to 0.99 kBq/m^3 (^{226}Ra) were found. The values of radium concentration in water samples from settling pond Bojszowy, from which mine waters were discharged into that river, varied from 2.397 to 4.236 kBq/m^3 for ^{226}Ra and from 3.51 to 7.01 kBq/m^3 for ^{228}Ra. Due to Polish regulations waters from the reservoir and from Gostynka should be treated as a waste with enhanced natural radioactivity. Therefore implementation of the purification methods in coal mines is so important.

Natural radioisotopes in bottom sediments

Enhancement of concentrations of natural isotopes in bottom sediments takes place in different places and under different conditions. First of all the level of the enrichment of radium isotopes in sediments depends on the type of saline water. Therefore three different sites were chosen for the investigations.

First site was a large settling pond into which waters type A were dumped in the past (before 1990). At that time ^{226}Ra concentration reached 21 kBq/m^3, while ^{228}Ra - 12 kBq/m^3 [17]. Co-precipitation of radium and barium caused a severe problems on that area. But now the radium content in mine waters released into that pond is below 0.1 kBq/m^3 [18]. That is the main reason, that the concentrations of radium isotopes in bottom sediments are not very high.

The second site is a small river, into which waters type B are released from one of coal mines. Maximum concentration of ^{226}Ra was as high as 2 kBq/m^3, while the maximum of ^{226}Ra was of about 4 kBq/m^3 [19].

As a third site a large settling pond with waters type B was chosen. Concentration of ^{226}Ra may reach 4 kBq/m^3, while concentration of ^{228}Ra is even higher - up to 7 kBq/m^3 [7]. The main process of the contamination is the sorption of radium isotopes on bottom sediments, therefore radium concentration in it is lower than in the first case.

Several samples of bottom sediments were taken from all sites. For each sample gamma spectrometric analysis was made. Also soil samples were collected at the banks of reservoirs and rivers. . In most cases a strong disequilibrium in $^{226}Ra/^{210}Po$ and $^{228}Ra/^{224}Ra$ sub-series can be observed.

The impact of bottom sediments on the contamination of the river's banks is usually negligible. Only in places where due to the flooding of river banks or as a result dredging and removal of bottom sediments, contamination took place, we can observe the increase of gamma dose rates.

It is clear, that concentrations of natural radionuclides in soils in the vicinity of reservoirs are typical for the earth crust [15]. Though, concentrations of radium isotopes in bottom sediments in settling ponds and in rivers are enhanced. This is clearly the result of deposition or sorption of radium from radium-bearing waters. We observe these phenomena in ponds and rivers as well.

Table 1. Concentrations of natural radioisotopes in bottom sediments from different investigation sites

Sampling place	^{226}Ra [Bq/kg]	^{228}Ra [Bq/kg]	^{224}Ra [Bq/kg]	^{210}Pb [Bq/kg]
Jankowice settling pond	350 - 4400	215 - 2400	190 - 2250	210 - 3400
Golawiecki river	70 - 543	163 -1229	89 - 531	12-86
Bojszowy reservoir	295 - 950	417 -1750	306 - 889	90 - 522

Conclusions

- The underground mining of coal causes sometimes a significant enhancement of the natural radioactivity in the environment. It is mainly a result of the release of radium-bearing waste waters from coal mines as well as a storage on the surface solid waste products with enhanced natural radioactivity. This phenomenon is observed not only in the Upper Silesian Coal Basin (USCB) but also in Germany and in other countries.
- In Upper Silesia the annual release of radium with mine waters to the natural environment can be assessed as of about 75 GBq of ^{226}Ra and approximately 145 GBq of ^{228}Ra.
- We found, that different types of radium-bearing waters (A and B) have the different impact on the natural environment. Not only the range of the transport and contamination of river waters is bigger in case of brines type B but also a possibilities of a further migration of radium are different. Probably radium adsorbed on bottom sediment from waters type B is far more mobile than radium precipitated in a form of a barium and radium sulphates from waters type A. This problem needs further investigations.
- As a result of the monitoring of the contamination of the natural environment we can draw conclusions concerning methods of ground reclamation and methods of the control of the radioactive contamination:
  - a complete investigation of the range and a level of the contamination must be done before the ground reclamation;
  - the method of the reclamation must be adequate to the range and level of the contamination and must diminish the possible impact on the inhabitants of the adjacent lands;
  - during and after the reclamation a continuous monitoring must be performed to assure the achievement of the desired parameters of the radiation level and to avoid any possibilities of spread of the sediments along the transportation routes;
  - after the reclamation measurements of the gamma radiation and radon concentration must be done.

Due to the fact, that the problem of the radioactive contamination of the natural environment is only partly regulated by Polish law, a certain actions must be undertaken to solve this problem.

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