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Radium in discharge waters from coal mines in Poland – effects of mitigation

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INTRODUCTION

Very often human activity, connected with the exploitation of mineral resources, leads to the contamination of the natural environment. Sometimes natural radionuclides are released or concentrated as waste material. In Poland the main source of waste and by-products with enhanced concentration of natural radionuclides is power industry, based on the coal exploitation and combustion. In hard coal mining industry 50 million tons of different waste materials are produced annually. As a result of coal combustion in power plants, the area of fly ash and sludge piles is increased by several km^2 per year (Michalik et al., 1995).

Upper Silesian Coal Basin (USCB) is located in the Southern-West part of Poland. Presently underground coal mines there extracting approximately 90 mln tons of coal per year. The depth of mine workings is from 350 to 1100 m. Upper Silesia is characterized by a very complicated and differentiated geological structure with numerous faults and other tectonic dislocations. Additionally, the area is very affected by mining. Two hydrological regions of the Coal Basin have been distinguished. First region is located in southern and western Silesia with thick strata of sediments covering carboniferous formation. This overlay is built mainly by Miocene clays and silts. The thickness of this rocks is up to 700 m. Such strata make almost impossible migration of water an gases. In the second region Miocene clays do not occur. Carboniferous strata are covered by and Quaternary sediments, slightly compacted. The oldest formations of this area form isolated sediments of Permian or Triassic limestone strongly fissured. There are numerous outcrops of coal seams. These formations enable very easy migration of water and gases.

An additional and unexpected component of the radioactive contamination of the natural environment, and different from that usually associated with this kind of industry, is caused by underground coal exploitation. In many of coal mines, located in Upper Silesian Coal Basin waters with enhanced radium content occur (Lebecka et al., 1986). Sometimes in radium-bearing brines barium ions are also present, in concentrations up to 2 g/l. Such waters were classified as radium-bearing type A waters. On the other hand, in the second kind of waters, which have been called type B, no barium can be found but radium and sulphate ions are present. The presence of barium in waters is the most important factor for the further behaviour of radium isotopes in mine galleries or on the surface. From type A waters radium and barium always co-precipitate as sulphates, when such waters are mixed with any water containing sulphate ions. As a result of the precipitation, barium sulphate deposits with highly enhanced radium concentrations are formed (Lebecka et al., 1986; Michalik et al., 1999). The total activity of radium isotopes in these sediments may sometimes reach 400 kBq/kg. In comparison, average radium content in soil is 25 Bq/kg (UNSCEAR, 1982). In case of radium-bearing type B waters, no precipitation occurs due to the lack of the barium carrier, and that is why the increase of radium content in sediments is much lower than ones originated from type A waters.

APPLIED METHODS AND INSTRUMENTATION

Radioactivity of waters from coal mines is mostly from radium isotopes — ^{226}Ra from the uranium series and ^{228}Ra from the thorium. A method of chemical separation of radium, developed by Goldin (Goldin, 1961), has been modified for liquid scintillation counting (Chałupnik, Lebecka, 1990; Chałupnik, Lebecka, 1993). Radium is co-precipitated with barium in form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (QUANTULUS, PerkinElmer). This counter is equipped in alpha/beta separation and anti-coincidence shield, which enables measurements of ^{226}Ra concentration above 3 Bq/m^3 with simultaneous measurements of ^{228}Ra (LLD = 30 Bq/m^3) and ^{224}Ra (LLD = 50 Bq/m^3). In addition, the procedure enables the simultaneous preparation of ^{210}Pb, which can separated from radium isotopes at the last stage of analysis and also measured in the LS spectrometer with a detection limit of 20 Bq/m^3.

SYSTEM OF MONITORING IN THE VICINITY OF COAL MINES

In the mining industry in Poland, monitoring of the radioactivity of mine waters, precipitates as well as gamma doses was obligatory since 1989.

Monitoring of radioactive contamination caused by effluents and tailings from coal mines must be done since 1986 (Guidelines, 1986). Due to these regulations the following measurements must be done in mine's vicinity:

1. 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.
2. 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.

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 (Report, 2004). In 80's 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. Contrary 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 maximum concentration of ^{228}Ra was as high as 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 (Report, 2004). 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 580 MBq/day of ^{226}Ra and 530 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. Although radium concentrations in waters type B were usually lower than in waters type A the total inflows to mines where radium-bearing waters type B occur were much higher. As a result the total activity of radium carried with water type B was higher. The highest values for a single mine (with waters type B) were: 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 were: 31 MBq of ^{226}Ra and 3 MBq of ^{228}Ra per day.

ASSESSMENT OF RADIUM BALANCE IN DISCHARGE WATERS

One of the biggest advantages of the monitoring system in Upper Silesia region is a possibility to make an assessment of radium balance in discharge waters periodically. For instance in years 1987, 1995, 2003 and 2006 such assessments have been prepared. For the calculations of about 300 results of mine waters have been taken as well as 40 analyses of river waters have been done. The term „mine waters” means not only mine waters but also river waters close to the discharge points. Term “river waters” is used for the samples taken at the sampling points of regional monitoring system of water quality. All the data are included in the mine waters database in the Laboratory of Radiometry as the element of the radiation hazard monitoring and environmental monitoring. A comparison of assessment results in chosen periods is shown in table 1.

Table 1. Radium balance assessment in rivers from Upper Silesia region

Catchment area	**Total activity 1995 [MBq/day]**		**Total activity 2003 [MBq/day]**		**Total activity 2006 [MBq/day]**	
	^{226}**Ra**	^{228}**Ra**	^{226}**Ra**	^{228}**Ra**	^{226}**Ra**	^{228}**Ra**
Inflows into “OLZA” pipeline from 11 mines	*9.8*	*6.7*	*6.8*	*6.8*	*6.5*	*6.5*
Olza River – discharge of „Olza” pipeline	1.6	1.4	2.5	1.8	2.3	1.6
Ruda-Nacyna Rivers (3 mines)	2.2	1.4	0.7	0.7	1.2	1.1
Bierawka River (5 mines)	1.6	1.2	2.7	3.2	1.8	1.4
Bytomka River (5 mines)	0.4	0.5	1.5	3.0	1.2	1.9
Kłodnica River (7 mines)	2.6	2.9	2.6	3.7	2.8	2.9
Rawa River (4 mines)	0.2	0.2	1.2	2.7	0.6	2.1
Black Przemsza River (4 mines)	1.6	3.1	1.3	2.3	1.5	2.8
Gostynka River (3 mines)	133.9	248.1	61.1	147.6	52.4	128.5
Mleczna River (2 mines)	1.3	2.4	1.5	3.3	1.5	3.3

The assessment of the total activity of radium released from coal mines in Upper Silesia with waste water is based on:

- results of determination of radium isotopes in waters released by collieries;
- 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 the 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.

Much more accurate were 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 settling ponds. In outflows from these ponds in 87% mines ^{226}Ra concentration exceeded 0.008 kBq/m^3, in 25% ^{226}Ra concentration was higher than 0.1 kBq/m^3 and in 8 % exceeded 0.7 kBq/m^3 (Decree, 1989). 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.

The significant decrease of daily discharge of radium was observed in the period 1987 -1995. Very first assessment of radium ^{226}Ra in mine effluents has been done in 1987, giving the value of the daily release at level 400 MBq. At that time no results of ^{228}Ra measurements were available. Results of another assessment, prepared in 1995 showed a significant decrease of radium activity in mine waters, released into natural environment, roughly by factor 2. There were two reason of this effect. Firstly, the purification of A type mine waters has been started in several coal mines in catchment areas of Olza river and Upper Vistula.

The another reason was due to economical changes in the mining industry – dewatering of deep mines was more and more expensive and hydro-technical solutions have been applied in numerous mines to reduce water inflows into underground galleries, with special emphasis on brines. In the last decade the decrease of radium activity in discharge waters is mainly due to the purification of B type brines in Piast Colliery (started in 1999) and construction of another treatment station in the year 2006 in Ziemowit Mine. In Piast Mine the implementation of the treatment technology on deeper of the horizons in the mine caused the decrease of radium release from the mine at level 150 MBq/day – 60 MBq/day of ^{226}Ra and 90 MBq/day of ^{228}Ra. Additionally, purification system for second horizon of Piast mine is under designing, and it will solve most of the problems with radium contamination of river waters in Upper Silesia region.

The process of water treatment is based on the dissolutionof barium chloride and immediate co-precipitation of barium and radium ions sulphates. This reaction is possible due to the surplus of sulphate ions in brines (30-50 times more than required for steichiometric reaction). This reaction is shown below:

$BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$

(dissolution of barium chloride)

$Ba^{2+} + Ra^{2+} + 2SO_4^{2-} \rightarrow BaRa(SO_4)_2$

(co-precititation)

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$

The solubility of barium sulphate is roughly 0.002 g/l, and presence of sulphate ions in the water makes the dissolution of barium sulphate impossible. Moreover, the solubility of radium sulphate is two orders of magnitude lower, therefore sediments are stable, and no back leaching is predicted.

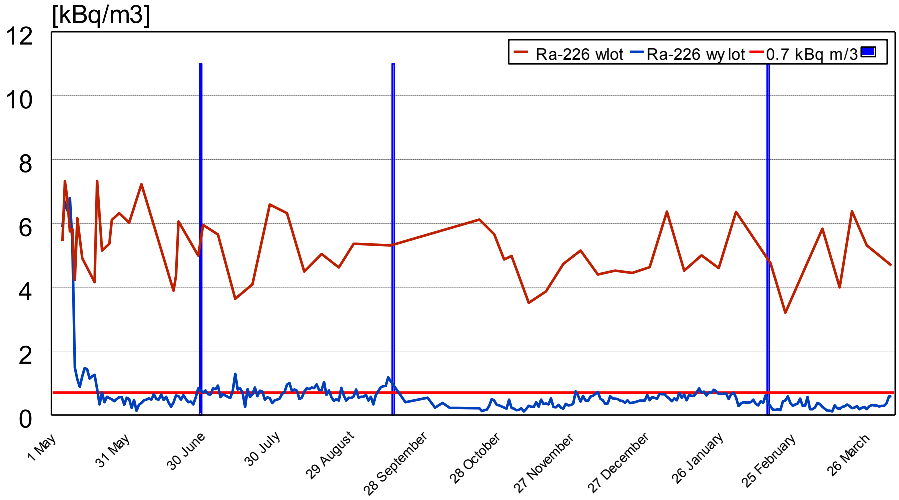

Figure1. Results of water treatment in Piast Mine in years 1999–2000.

In 90's enhanced radium concentrations were mainly observed in the Vistula river, into which most of the radium is discharged with B type waters — approximately 200 MBq of ^{226}Ra and 350 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. Some of these waters were not discharged directly to Vistula river, but to it's tributaries. The influences of singular inflows were very clearly. Moreover, waters from first mine were A type and the difference of radium behaviour (fast precipitation) in comparison with other 3 mines (waters B type) was 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 was much lower - 20 MBq per day of ^{226}Ra and 25 MBg/day of ^{228}Ra. As a result concentrations of radium in Oder were below 0.01 kBq/m^3. At the beginning of new century a treatment of mine waters (type B – without barium) has been started in underground galleries of Piast mine (1999). The total activity of radium isotopes in discharge waters decreased significantly, but still concentrations of radium isotopes in some rivers in Upper Silesia were 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.

One of the collieries, releasing radium isotopes into surface settling pond and finally into Vistula River was Ziemowit Mine. In this mine saline brines are very common, and the total inflow into mine galleries exceeds 20 m^3/min. Radium concentration in these brines is as high as 12 kBq/m^3 for ^{226}Ra and 20 kBq/m^3 for ^{228}Ra. Due to the lack of barium in brines (type B waters) from Ziemowit Mine the spontaneous coprecipitation of radium was negligible and only small part of radium remained underground as a result of adsorption on bottom sediments in underground water galleries. Therefore Ziemowit Colliery was the main source of the contamination of small brook, called Potok Golawiecki, a tributary of Vistula River and Vistula itself. In 2003 almost 50% of total activity released from all mines in USCB was dumped into surface waters from Ziemowit. Of about 60 MBq of ^{226}Ra and 100 MBq of ^{228}Ra was released daily, despite the fact, that concentrations of radium isotopes in effluents from Ziemowit Mine weren't very high, reaching 1.3 kBq/m^3 in case of ^{226}Ra and for ^{228}Ra - 2.5 kBq/m^3.

The ecological effect of the purification is the most important issue. At the outflow from the purification system, at the level -650 m the removal efficiency is above 95%. On the surface the efficiency is lower, due to mixing with untreated waters from level -500m, But at the inflow of saline waters into the settling pond, as well as at the outflow from that pond, concentrations of radium isotopes are approximately 80–85% lower than before purification. It corresponds to the decrease of about 40 MBq for ^{226}Ra and 60 MBq for isotope ^{228}Ra of daily release from the Ziemowit Mine. It means, that the total amount of radium, discharged into the Potok Golawiecki and Vistula rivers is much lower, by a value 100 MBq/day. 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. On the other hand we must take into account, the exploitation of deeper coal seams will cause more problems with inflows of radium-bearing brines into underground workings, even in these mines where no radium problems exist right now. Therefore periodical monitoring of discharge waters is necessary. Another legal problem must be also solved - responsibility for monitoring of waters, released from abandoned mines.

SUMMARY

Coal mining may cause significant pollution of the natural environment due to release of waste waters with enhanced concentrations of natural radionuclides (mainly radium isotopes. This phenomenon is well known not only in Upper Silesian Coal Basin but also in other regions of underground exploitation of coal (Ruhr Basin), oil and gas or other resources.

Due to mitigation measures, undertaken by mines, the significant improvement can be observed during last two decades. In most cases radium concentrations in discharge waters are low and surface waters are not contaminated. Moreover, further decrease of radium release is predicted as a result of underground mine water purification in two collieries.

Monitoring system of natural radionuclides in waste waters and river waters is an important element of the prevention against the pollution of the natural environment. Moreover, it is a source of data for optimization of ground reclamation of previously contaminated areas (mainly settling ponds) of abandoned coal mines.

Of course, further improvement of the system is required as well as solution of important legal problems, related with liquidation of coal mines, harmonization with EU regulations etc.

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