MONITORING AND CONTROL OF RADIUM CONTENT IN DISCHARGE WATERS FROM COAL MINES IN POLAND

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Abstract
Saline waters from underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from the uranium decay series and ^{228}Ra from the thorium series. More than 70% of the total amount of radium remains underground as radioactive deposits due to spontaneous co-precipitation or water treatment technologies, but several tens of MBq of ^{226}Ra and even higher activity of ^{228}Ra are released daily into the rivers along with the other mine effluents from all Polish coal mines. Mine waters can have a severe impact on the natural environment, mainly due to its salinity. Additionally high levels of Ra concentration in river waters, bottom sediments and vegetation were also observed. Sometimes Ra concentrations in rivers exceeded 0.7 kBq/m^3, which was the permitted level for waste waters under Polish law. The investigations described here were carried out for all coal mines and on this basis the total Ra balance in effluents has been calculated. Measurements in the vicinity of mine settling ponds and in rivers have given us an opportunity to study Ra behaviour in river waters and to assess the degree of contamination. Technical measures such as inducing the precipitation of Ra in gobs, decreasing the amount of meteoric inflow water into underground workings etc., have been undertaken in several coal mines, and as a result of these measures the total amount of Ra released to the surface waters has diminished significantly during the last 15 years.

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 there are 35 underground coal mines extracting approximately 100 mln tons of coal per year. The depth of mine workings is from 350 to 1050 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 mainly consists of Miocene clays and silts. The thickness of this rocks is up to 700 m. Such strata make almost impossible migration of water and gases. In the second region Miocene clays do not occur. Carboniferous strata are covered by slightly compacted Quaternary sediments. 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 USCB waters with enhanced Ra content occur (Lebecka et al., 1986). Sometimes barium ions are also present in concentrations up to 2 g/L in Ra-bearing brines. Such waters were classified as Ra-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 Ra and sulphate ions are present.
In the area of USCB about 35 underground coal mines are active. The total water outflow from these mines is about 750000 m^3/day. The salinity of these brines is far higher than that of ocean water. The total amount of salt (total dissolved solids - TDS) carried with mine waters to the rivers is about 10000 tonnes/day. The commonest ions in these brines are Cl^- and Na^+ with concentrations up to 70 g/L and 40 g/L respectively, additionally brines usually contain several grams per litre of Ca^{2+} and Mg^{2+} and significant amounts of other ions (Tomza and Lebecka, 1981). Waters with high Ra 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 (Rozkowski and Wilk, 1992). These saline waters cause severe damage to the natural environment, owing mainly to their high salinity (sometimes > 200 g/L), but also to their high Ra concentration, reaching 390 kBq/m^3 (Skubacz et al., 1990).
The presence of barium in waters is the most important factor for the further behaviour of Ra 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 Ra concentrations are formed (Lebecka et al., 1986; Michalik et al., 1999). The total activity of Ra isotopes in these sediments may sometimes reach 400 kBq/kg. In comparison, average Ra content in soil is 25 Bq/kg (UNSCEAR, 1982). In case of Ra-bearing type B waters, no precipitation occurs due to the lack of the barium carrier, and that is why the increase of Ra content in sediments is much lower that ones originated from type A waters.

Applied methods and instrumentation

Radioactivity of waters from coal mines is mostly from Ra isotopes, ^{226}Ra from the uranium series and ^{228}Ra from the thorium series. A method of chemical separation of Ra, developed by Goldin (1961), has been modified for liquid scintillation counting (Chalupnik and Lebecka, 1990; 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 be separated from Ra 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 till 2003. 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: a) 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; b) 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 Ra 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 1980s waters with Ra concentration above 1.0 kBq/m^3 were found in 43 out of 65 coal mines in USCB. The highest concentrations of Ra were measured in highly mineralised waters from deeper levels in Ra-bearing waters type A. The ratio of ^{226}Ra to ^{228}Ra in Ra-bearing waters type A was in average of about 2:1. On the contrary in Ra-bearing waters type B there was more ^{228}Ra than ^{226}Ra, and 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 Ra-bearing waters belong to the waters with highest known Ra 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 Ra 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 Ra flowing with water to different parts of mines and to different mines were calculated. These results were compared with values obtained using Ra 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 Ra 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 Ra 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 (i.e. 255 GBq per year). Although Ra concentrations in waters type B were usually lower than in waters type A, the total inflows to mines where Ra-bearing waters type B occur were much higher. As a result the total activity of Ra 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 Ra 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 Ra balance in discharge waters periodically. For instance in years 1987, 1995, 2003 and 2006 such assessments have been prepared. For the calculations 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. The 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.
The assessment of the total activity of Ra released from coal mines in Upper Silesia with waste water is based on (i) results of determination of Ra isotopes in waters released by collieries and (ii) data on amount of water released by individual mines. We have also made an estimation of total activity of Ra which remains in underground workings in a form of deposit precipitated out of Ra-bearing waters either due to unintended mixing of natural waters of different chemical composition or due to the purification of Ra-bearing waters. This estimation has been done basing on (i) results of determination of Ra isotopes in original waters inflowing to the underground mine workings from the rocks; (ii) rough estimation of the amounts of water inflows from different sources or parts of mines; (iii) calculated value of the total activity of Ra pumped out from underground mine workings with waste waters by individual mines.

Table 1. Comparison of 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
Krynica River (4 mines)	0.7	0.7	1.4	2.4	1.2	1.8
Przemsza River (2 mines)	0.4	0.4	2.3	5.6	1.2	2.4
Bobrek River (3 mines)	0.2	0.2	0.3	1.2	0.8	1.5
Black Przemsza River (4 mines)	1.6	3.1	1.3	2.3	1.5	2.8
Gostynia 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
Upper Vistula (4 mines)	73.0	117.2	42.9	84.2	8.9	19.8
Total: 35 active mines 30 abandoned	219.1	380.1	120.1	258.2	77.4	169.5

Much more accurate were the results of calculations of the total activities of Ra present in water pumped out from individual mines. These values were calculated basing on the Ra 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 exceeds 0.008 kBq/m^3, in 25% ^{226}Ra concentration is higher than 0.1 kBq/m^3 and in 8 % exceeded permissible level, i.e. 0.7 kBq/m^3 (Decree, 1989). In rivers enhanced concentrations of Ra can be observed many kilometres down from the discharge points. This is mainly true for Ra-bearing waters type B, because out of these waters Ra 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 its conjunction with Vistula river.
The significant decrease of daily discharge of Ra was observed in the period 1987-1995. Very first assessment of ^{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 Ra activity in mine waters, released into natural environment, roughly by factor 2. There were two reasons 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 second 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 period the decrease of Ra 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 horizons in the mine caused the decrease of Ra release from the mine at level 150 MBq/day (60 MBq/day of ^{226}Ra and 90 MBq/day of ^{228}Ra). The application of the purification technology in another mine should further reduce Ra discharge. Additionally, purification system for second horizon of Piast mine is under designing, and it will solve most of the problems with Ra contamination of river waters in Upper Silesia region.
In 1990s enhanced Ra concentrations were mainly observed in the Vistula river, into which most of the Ra 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 its tributaries. The influences of singular inflows were very clear. Moreover, waters from first mine were A type and the difference of Ra 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 Ra 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 Ra 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. The total activity of Ra isotopes in discharge waters decreased significantly, but still concentrations of Ra isotopes in some rivers in Upper Silesia were clearly enhanced as compared with natural levels. In comparison with data from other locations, concentrations of Ra isotopes in rivers in USCB are significantly higher. Enhanced concentrations of Ra in river waters in Upper Silesia are caused solely by the influence of mine waters. One of the collieries, releasing Ra 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 Ra was negligible and only small part of Ra 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. About 60 MBq of ^{226}Ra and 100 MBq of ^{228}Ra were released daily, despite the fact that concentrations of Ra isotopes in effluents from Ziemowit Mine were not very high, reaching 1.3 kBq/m^3 of ^{226}Ra and 2.5 kBq/m^3 of ^{228}Ra.
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 -500 m, but at the inflow of saline waters into the settling pond, as well as at the outflow from that pond, concentrations of Ra 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 Ra discharged into the Potok Golawiecki and Vistula rivers is much lower by a value 100 MBq/day. This station is still in preliminary period of activity and more detailed reports will be published later. Due to release of Ra-bearing mine waters from coal mines there is a contamination of river waters. As a result Ra 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 its tributaries. On the other hand we must take into account that the exploitation of deeper coal seams will cause more problems with inflows of Ra-bearing brines into underground workings, even in these mines where no Ra 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 Ra isotopes). This phenomenon is well known not only in USCB 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, a significant improvement can be observed during last two decades. In most cases Ra concentrations in discharge waters are low and surface waters are not contaminated. Moreover, further decrease of Ra 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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