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RADIOACTIVE DEPOSITS IN POLISH COAL MINES AND THEIR INFLUENCE ON THE NATURAL ENVIRONMENT

B. Michalik, K. Skubacz, S.Chalupnik, J. Lebecka, A. Mielnikow

Central Mining Institute, 40-166 Katowice, Pl. Gwarkow 1, Poland

ABSTRACT

The paper describes results of investigation of sediments with enhanced natural radioactivity occurring in underground coal mines and in bottom sediments in rivers where mine waters have been dumped. The results of measurements show that these deposits contain mainly ^{226}Ra and ^{228}Ra and their progeny. Concentrations of ^{226}Ra in deposits occurring in underground mine workings are in some places high, reaching 378 kBq/kg. Concentrations of ^{228}Ra are usually lower, however the ^{228}Ra:^{226}Ra ratio varies from 0.3 to 3. Gamma dose rates due to presence of radioactive deposits in some underground galleries were as high as 30 μGy/h. Influence of bottom sediments with enhanced radium concentration on the natural environment in the vicinity of rivers and settlement ponds was studied on the example of a water reservoir where radium-bearing mine waters type B from two mines are released. The results show clearly enhanced radioactivity of bottom sediments and water in the settling pond and in the river, but no evident enhancement was found in the adjacent land. Bottom sediments with enhanced radium concentrations were found in Vistula river up to 70 km downstream from the discharge point.

INTRODUCTION

Brines with elevated radium concentration are well known to occur in oil fields [1,2]. Large inflows of such brines have been also found in underground coal mines in the Upper Silesian Coal Basin (USCB) in Poland [3]. Not only radium-bearing waters but also deposits with enhanced radium concentration cause contamination of the natural environment in the vicinity of coal mines [4] and sometimes also high gamma dose rates in underground mine galleries [5]. It has been found that the behaviour of radium during transportation of radium-bearing brines in the gutters of underground galleries, settling tanks and ponds, pipelines and rivers depends mainly on chemical composition of the brines and to some extend also on the conditions in the environment where the waters are transported through, for example on the presence of other waters of different chemical composition. Since the chemical composition of brines is so essential for further transportation of radium, two types of radium-bearing waters have been distinguished [4].

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Waters type A contain not only radium ions but barium ions as well. Concentration of barium in these waters is at least six orders of magnitude higher than that of radium and reaches 2 kg/m^3. High barium concentrations enable coprecipitation of radium sulphate with barium sulphate when radium-bearing water type A is mixed with another water containing sulphate ions, which are very common in nature. In case of radium-bearing waters type B, where barium ions are not present, concentration of radium ions is too low to enable precipitation of radium sulphate because concentration of $[Ra^{2+}] * [SO_4^{2-}]$ does not exceed the solubility product. Due to differences in their chemical proprieties, the effect of release of radium-bearing waters type A and type B into the natural environment is completely different. Radium from radium-bearing waters type A is precipitated out in underground mine workings and in settling ponds, pipelines and little rivers. Concentration of radium in such precipitates is usually high reaching 378 Bq/kg in underground galleries and 270 kBq/kg on the surface [4], but the precipitation and sedimentation takes place rather close to the point where radium-bearing waters type A mix with waters containing sulphates, so that in the distance over few or several kilometres downstream from the discharge point of mine water the river water is free of radium. In opposite, from radium-bearing waters type B radium is not precipitated but transported with water to large rivers. Although, concentrations of radium in bottom sediments are in this case not very high, contamination of river waters and bottom sediments is observed over a large distance even up to hundred kilometres from the discharge point [6].

The deposits with enhanced radium concentrations present in underground mine workings cause a radiation hazard for miners. Deposits located on the ground surface are a source of radioactive contamination of the natural environment. According to Polish regulations [7] solid waste materials with concentration of alpha emitters exceeding 10 kBq/kg should be treated as radioactive wastes. Due to Polish mining regulations [8] an underground work place with the gamma dose rate exceeding 3 µGy/h is considered as a workplace with radiation hazard. Monitoring and control of radiation hazard caused by natural radioisotopes is obligatory in Polish mines.

The aim of this work was to study the deposits formed out of different types of radium-bearing mine waters and their propagation in the environment. The work included a survey of deposits precipitated in underground waters from radium-bearing waters in Upper Silesian coal mines. To study the propagation of radioactive deposits in the natural environment two investigation sites where different types of radium-bearing waters are dumped from coal mines were chosen. The paper describes the first part of this work within which a water reservoir and it's vicinity was investigated where radium-bearing waters type B from two mines are released. Also one case of an underground mine gallery with radioactive deposits precipitated out from radium-bearing water type A was studied.

EXPERIMENTAL SECTION

Experimental methods

The study involved several experimental methods.

Determination of concentration of gamma emitters in solid samples, such as soil, deposits, vegetation was performed using gamma spectrometers with HPGe detectors and a multichannel analyser. The samples after drying at 105^0 C were placed in Marinelli beakers and measured. The gamma spectra were analysed by GENIE PC software from CANBERRA and EMCAPLUS from SILENA. The shielding - 40 cm of steel, 10 mm lead and 6 mm copper, assured very low

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background. Standards were made in the same type of beakers using Geological Certified Reference Materials for Radiometric Measurements from Analytical Quality Central Service (IAEA), and reference materials from National Brunswick Laboratory (NBL). The quality assurance procedure according the EN 45000 [9] implemented in the laboratory of gamma spectroscopy is described elsewhere [10]. Blank samples were measured once per month, while replications were done for each 10th sample. The laboratory is participating on permanent basis in the intercomparison programs organised by IAEA and by EPA.
Gamma dose rates were measured using a portable ratemeter FH 40F2 manufactured by FAG Kugelfisher, certified by Central Laboratory of Radiological Protection, Warsaw, Poland.
Concentrations of ^{226}Ra and ^{228}Ra in water samples were measured by liquid scintillation counting preceded by chemical separation. The method is described elsewhere [11]. Reliable results are assured by quality assurance program [12].
^{222}Rn in soil gas was measured using charcoal detectors and liquid scintillation technique. The measurements were performed by placing the vials containing charcoal in boreholes. After one week exposition samples were collected, transported to the laboratory, in which radon from charcoal was washed out, using toluene-based liquid scintillator. Later samples were measured in liquid scintillation spectrometer QUANTULUS (made by Wallac Oy, Finland).

Sampling and measurements

Deposits from underground mine workings of coal mines were taken within the obligatory sampling required by Polish mining regulations. The samples were taken by mine geologists from all mines where waters with ^{226}Ra concentrations over 1 kBq/m^3 were found. The sampling was done mainly in underground settling tanks and in galleries where radium-bearing waters type A are flowing - particularly in places where mixing of such water with other water takes place. In these mines also gamma dose rates or individual gamma doses obtained by miners cleaning the settling tanks or gutters were measured. During these investigations of about 250 samples of deposits were analysed and approximately 1500 measurements of gamma dose rates and gamma doses were done.

Investigation site - Bojszowy Reservoir

One of the biggest settlement tanks for waste waters from coal mines in Upper Silesia is the ***Bojszowy Reservoir***. This reservoir is situated near Gostynka river - 2 km from it's conjunction with Vistula river. The area of the reservoir is of about 160 000 m^2, the average depth - 1 m. Into this reservoir two coal mines release their saline waters type B. The reservoir has been used since 1980. Presently the average inflow is of about 25 000 m^3 per day and the average retention time is approximately 5-6 days. Waters discharged to Bojszowy Reservoir contain over 55% of radium released to the natural environment from all coal mines in Poland. These waters contain about 40 kg/m^3 of Cl^- ions and 2 kg/m^3 of SO_4^{2-} ions.

For assessment of radioactive contamination in the vicinity of Bojszowy reservoir following measurements were performed:

a) concentration of radium isotopes in waters:
- inflowing to the pond,
- present in the pond,
- discharged from the pond,
- from Gostynka and Vistula rivers;
- in shallow boreholes, located in the vicinity of the reservoir;

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b) concentration of natural radioisotopes in bottom sediments;
c) concentration of natural radioisotopes in soils;
d) concentration of ^{210}Po in soils and bottom sediments;
e) concentration of ^{222}Rn in soil gas.

We have collected 30 water samples from the pond. The distance between sampling points was 20 -30 m. Inflows from both collieries to the pond and water outflowing from the reservoir were sampled as well. In the same period samples from Gostynka river and Vistula rivers have been collected.

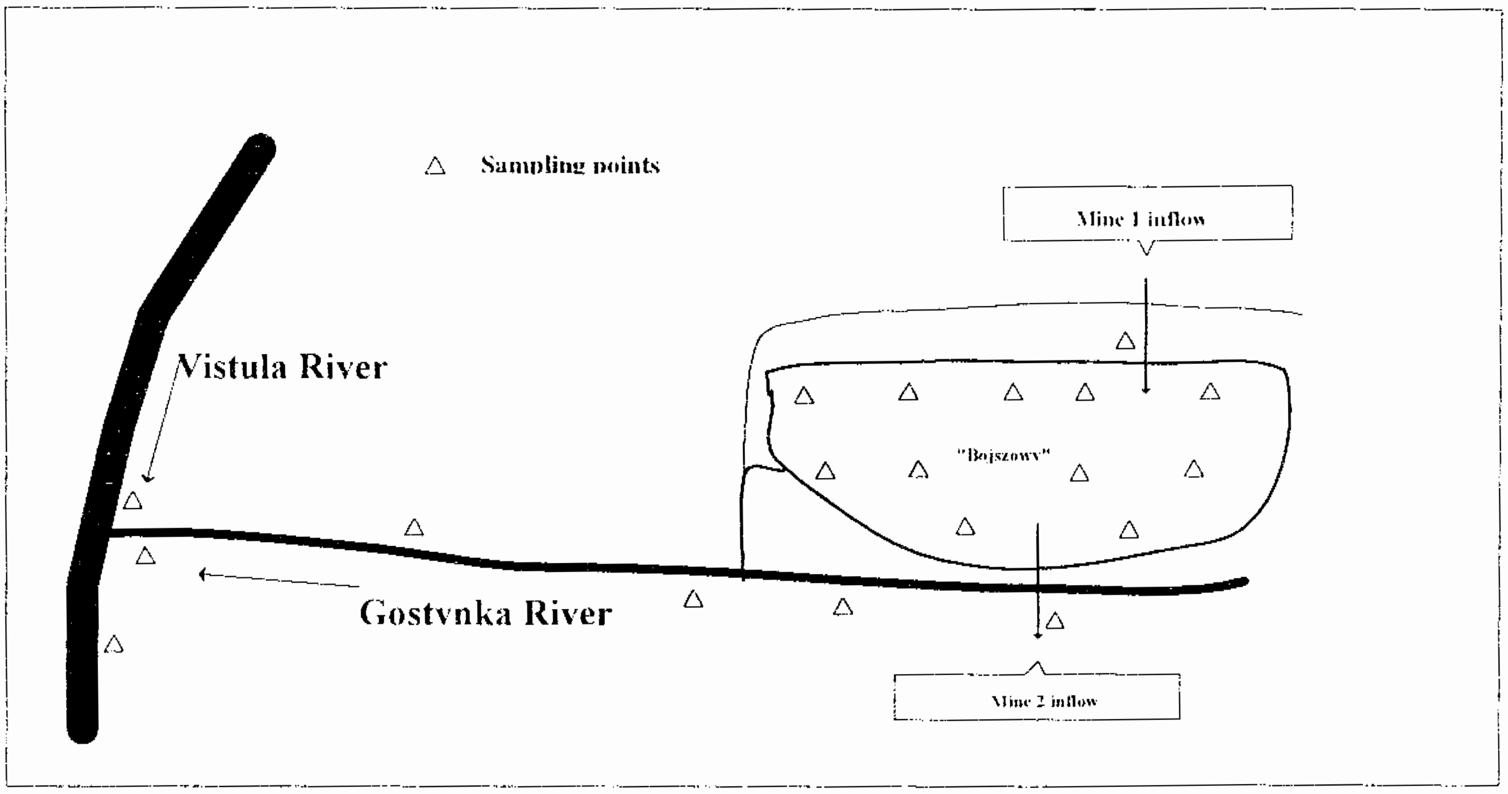

Fig.1. Schematic plan of the investigation site

We have collected samples of bottom sediments from Bojszowy reservoir from the same places as water samples. Also samples of river sediments and soils were taken in the vicinity of the reservoir. Measurements of ^{210}Po were done by alpha spectrometry and the uncertainty of a single measurements is approximately ±30%.

Gamma spectrometry was applied for measurements of ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{40}K, and uncertainties of these results were below 10%.

For measurements of natural radioisotopes in soil eight shallow boreholes were drilled and soil samples were taken at the depth between 0-50 cm and between 50-100 cm. Later in these boreholes radon measurements have been performed.

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RESULTS AND DISCUSSION

Deposits in underground mine workings

Deposits with radium concentration over 10 kBq/kg ($^{226}Ra+^{228}Ra$) were found in 19 out of 65 Upper Silesian coal mines. We found in underground galleries deposits with radium concentration over 100 kBq/kg in 5 coal mines and on the surface in the vicinity of two collieries. The highest concentration of radium isotopes was as high as 378 kBq/kg of ^{226}Ra and 182 kBq/kg of ^{228}Ra. The presence of such deposits at workplaces is resulting in increase of gamma dose rates and gamma doses, obtained by miners.

As an example of the influence of radioactive deposits on the gamma dose rate in underground galleries one coal mine have been chosen. In this particular mine an inflow of high radioactive brine was found - containing radium and barium ions. ^{226}Ra concentration was as high as 110 kBq/m^3, ^{228}Ra was of about 70 kBq/m^3, while barium concentration exceeds slightly 1.5 kg/m^3. This water is flowing in the gutter along the gallery. Another inflows in this gallery do not contain radium but sulphate ions. As a result of mixing of these waters spontaneous coprecipitation of radium and barium sulphates takes place. The results of measurements of gamma dose rate in this gallery are shown on fig. 1. Peaks of gamma dose rate up to 9 µGy/h as can be clearly seen, as a markers of places, where inflows of water with sulphates occur.

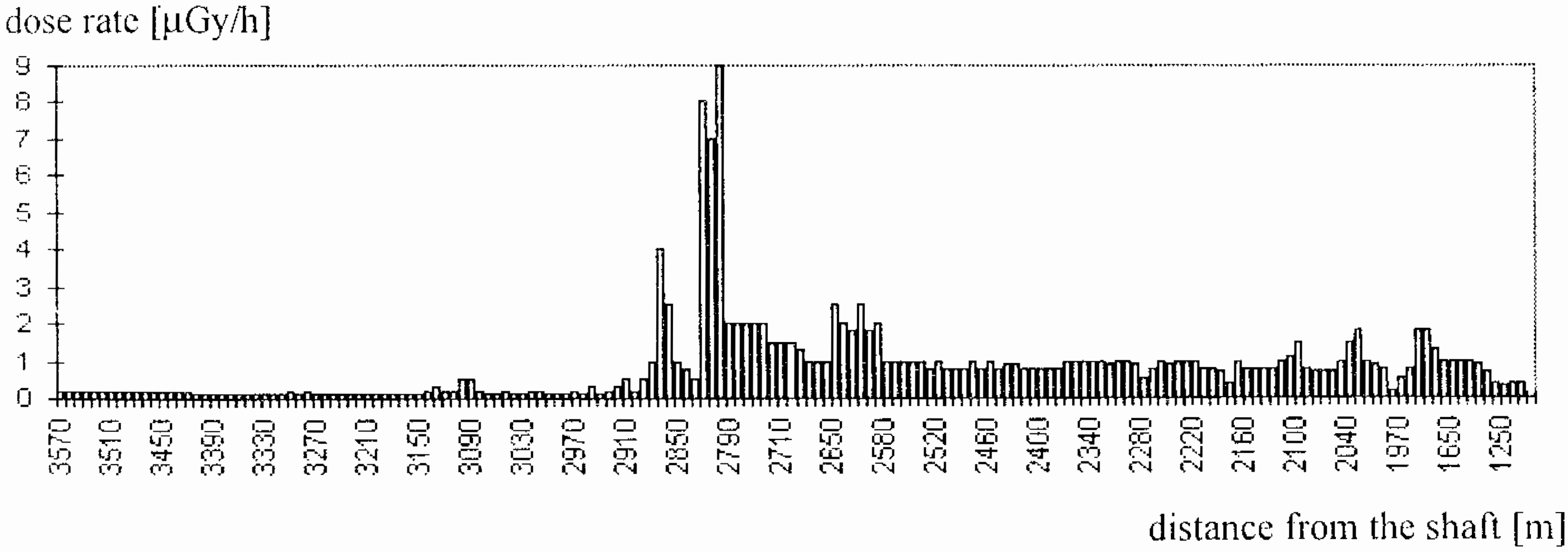

Fig.2. Gamma dose rates in a gallery with inflows of radium-bearing waters

In five coal mines in USCB gamma dose rates above 3 µGy/h have been discovered [13], mainly in water galleries (underground settlement tanks), which must be cleaned from time to time. In some cases, gamma dose rate can reach 30 µGy/h. Therefore not only environmental monitoring of gamma dose rates is necessary but sometimes also personal dosimetry of gamma doses must be done.

Area affected by radium-bearing brines released from coal mines
BOJSZOWY RESERVOIR

The values of radium concentration in water samples from Bojszowy reservoir are as follows (an uncertainty of a single measurement for ^{226}Ra ±8%, for ^{228}Ra ±15%):

- from 2.40 to 4.24 kBq/m^3 for ^{226}Ra

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- from 3.5 to 7.0 kBq/m^3 for ^{228}Ra.

In Gostynka river concentrations of radium isotopes from 0.006 kBq/m^3 (upstream from discharge point) to 0.64 kBq/m^3 (^{226}Ra) and from 0.01 kBq/m^3 to 0.99 kBq/m^3 (^{228}Ra) were found. It can be seen that according to Polish regulations waters from the reservoir should be treated as a liquid radioactive wastes.

All samples taken from boreholes were of low salinity and low radium concentration - ^{226}Ra below 0.005 kBq/m^3.

Results of measurements of natural radioisotopes in bottom sediments are shown in table 1.

Table 1

Isotope (range for earth crust) [ref. 16]	Concentration [Bq/kg]		
	reservoir sediments	river sediments	soils
^{226}Ra (7-50)	295-950	98- 661	6-54
^{210}Po (7-50)	100-150	-	6-67
^{228}Ra (10-50)	507-1705	78-811	9-54
^{224}Ra (10-50)	306-889	77-258	9-54
^{40}K (100-700)	168-665	332-535	180-661

It is clear, that concentrations of natural radionuclides in soils in the vicinity of Bojszowy reservoir are typical for the earth crust, while concentrations of radium isotopes in bottom sediments are enhanced. This is clearly the result of sorption of radium from radium-bearing waters stored in the reservoir. We observe this phenomenon in the reservoir and in Gostynka river as well.

Soil samples were taken from two layers: 0-50 cm and 50-100 cm. In deeper layers concentrations of polonium and radium ^{226}Ra are similar, while in surface layers polonium concentrations are slightly higher than radium due to fallout of radon daughters from air.

A quite different situation was observed in samples of bottom sediments where polonium concentrations are much lower than that of radium. This can be explained by the young age of sediments, not allowing to reach equilibrium between ^{226}Ra and ^{210}Pb and ^{210}Po. Moreover, there is no equilibrium between ^{228}Ra and ^{224}Ra in reservoir sediments, what makes an additional support for such conclusion.

As groundwater and soil samples collected in the vicinity of Bojszowy reservoir did not show high radium concentration we can draw a conclusion that water from the reservoir does not infiltrate into the ground.

During two months we have also measured radon concentration in these boreholes by means of charcoal detectors. The period of single measurement was set as one week. We found radon concentrations from 20 up to 2700 Bq/m^3. That are very previous results, done during testing the method of charcoal canisters. Very low radon concentrations were found in boreholes with high

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water table, partly as a result of high humidity influence on charcoal detectors. Partly such low values can be explained by low emanation factor due to high water table. Higher values are typical for soil gas in Upper Silesia region. Temporal variations of radon concentration may be explained as an influence of atmospheric pressure and humidity.

Assessment of balance of radium in waters and sediments in the BOJSZOWY reservoir

As radium concentrations in sediments are considerably higher than in average soil an assessment of total amount of radium deposited in the reservoir has been done. We made following assumptions:

- the depth of sediment layer - 0.5 m,
- average concentration of ^{226}Ra - 500 Bq/kg
- average concentration of ^{228}Ra - 700 Bq/kg
- area of the reservoir - 160 000 m^2
- density of the sediments - ca. 1 g/cm^3,
- water content in the sediments - ca. 50%.

On this basis, the total activity of radium isotopes in bottom sediments in the reservoir can be approximately calculated as:

^{226}Ra - 20 GBq,
^{228}Ra - 28 GBq.

Annual discharge of ^{226}Ra with water from the reservoir to the Gostynka river is of about 55 GBq, while the discharge of ^{228}Ra is 78 GBq. The Bojszowy reservoir has been exploited since 1980. The total discharge of ^{226}Ra up to now was about 770 GBq and of ^{228}Ra - 1100 GBq. It means, that the activity of ^{226}Ra adsorbed on bottom sediments in the reservoir makes only 2.6 % of the total activity of ^{226}Ra dumped to the natural environment since 1980. Corresponding figure for ^{228}Ra equivalent values is 2.5%. It shows that adsorption of radium on bottom sediments does not diminish substantially the total activity of radium dumped with type B radium-bearing waste waters from coal mines into natural environment.

In the vicinity of BOJSZOWY Reservoir radioactive contamination of the natural environment is observed in waters in rivers Gostynka and Vistula and in bottom sediments in the reservoir itself and in rivers. In Gostynka river concentration of radium isotopes in water sometimes exceeds 0.7 kBq/m^3 (permissible level for liquid radioactive waste in Poland). The major part of radium is transported to the Vistula and only a small portion has been deposited with suspension in the reservoir. Concentrations of radium isotopes in bottom sediments are substantially higher than the average values for earth crust, reaching 2700 Bq/kg.

High concentrations of radium observed in radium-bearing waters type A as well as in deposits precipitated out of these waters in underground mine workings and results of measurements performed earlier [14,15] in the vicinity of mines where radium-bearing waters type A were released into natural environment indicate that detailed investigations of such areas should be done.

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