RADIUM IN MINE WATERS IN POLAND: OCCURRENCE AND IMPACT ON RIVER WATERS

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ABSTRACT

A regional survey of contamination of river waters by natural radioisotopes released with mine waters from underground coal mines in Upper Silesia is described. In these mines there are inflows of water with high salinity reaching over 200 kg/m^3 and high radium concentration up to 400 kBq/m^3. During the survey, performed in 1993-1995, all mines and rivers where the mine waters are dumped, were investigated. Waters from different aquifers were sampled as well as inflows to settlement ponds, discharges to small streams and rivers and river waters in chosen places. Over 800 samples were collected and analysed. As a result a balance of radium in outflows from coal mines and in discharges into rivers was prepared. The total amount of ^{226}Ra inflowing with water into underground mines is of about 625 MBq/day while the amount of ^{228}Ra is about 700 MBq/day. It was found that less than 40% of radium present in waters inflowing into underground mine workings remains there as deposits while over 60% is pumped out to the surface and later is dumped to the natural environment.

INTRODUCTION

In coal mines in the Upper Silesian Coal Basin (USCB) saline waters occur with elevated natural radioactivity, mainly radium isotopes. This phenomenon was mentioned by Saldan [1] and later investigated and described by Tomza and Lebecka [2]. Such waters have been found also in another regions, sometimes as a natural radium-bearing waters - in Iran [3] and Japan [4] - mainly as mineral hot springs. Also oil extraction industry in Australia [5], Ukraine [6] as well as coal mining (for example in Germany [7]) produce saline waters with enhanced radium concentration. Concentrations of ^{226}Ra in these waters are rather high, for example concentration of this radioisotope in hot springs in Iran reaches 330 kBq/m^3 [3]. In comparison in the Netherlands an average concentration of ^{226}Ra in rivers is of about 0.003 kBq/m^3 [15], while waters with

concentration exceeding 0.008 kBq/m^3 are stated as waters with elevated radioactivity. Gans [7] found in surface waters in Germany an average value 0.004 kBq/m^3.

The Upper Silesian Coal Basin is located in southern part of Poland and there are 60 underground coal mines. Total outflow of water from these mines is of about 900 000 m^3/day. The salinity of these brines if 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 11 000 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 [18] 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 in an ionic form present in water as well as by radium present in suspended matter and in deposits. Radioactive deposits are formed particularly by coprecipitation of barium and radium 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 water 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. The total activity of ^{226}Ra released with these waters was of about 140 MBq per day. Although waters type B have been discharged only from 3 mines, but the total output of ^{226}Ra is higher than in waters type A - approximately 300 MBq per day [10].

The aim of this work was to investigate the concentrations and total activities of ^{226}Ra and ^{228}Ra in waters inflowing into underground mine workings, dumped from coal mines into rivers, in river waters and remaining in underground workings as deposits. Also investigations of propagation of radium in river waters was planned.

EXPERIMENTAL SECTION

Measurements of radium isotopes in water samples.

Measurements of concentration of radium isotopes in water samples was performed by liquid scintillation (LS) technique. preceded by chemical separation of radium with barium carrier. The method is based on Goldin's procedure [14] with modifications for LS counting. This method enables simultaneous determination of ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{210}Pb. Thanks to high counting efficiency of LSC the method is not time consuming and therefore can be applied for large number of samples. In this work only ^{226}Ra and ^{228}Ra were determined, because other investigation show that there is not much of ^{210}Pb in water. ^{224}Ra was not determined because the radiotoxicity of this isotope is lower than that of ^{226}Ra and ^{228}Ra, and the short half time (3.6 days) of this isotope would cause serious organisation problems with collecting and processing the samples. Detailed description of this method is published elsewhere [12]. The main steps are following. To the water sample solutions of $BaCl_2$ and $PbCl_2$ are added to serve as carriers for radium and radioactive lead. Then barium, radium and lead are coprecipitated using sulphates. Afterwards lead is removed by subsequent dissolution and reprecipitation of sulphates at the pH=4.5. The remaining precipitate is rinsed to remove other compounds including other radioactive materials. As a result in the precipitate remains only radium sulphate with the barium sulphate as a carrier. The precipitate is mixed with a gelling scintillator in a scintillation vial. After one month the vial is placed in a liquid scintillation spectrometer where alpha and beta particles emitted by radium and it's daughter products are counted. In order to determine ^{226}Ra and ^{228}Ra the measurement is performed after decay of ^{224}Ra (about 30 days) in two channels, low energy channel used for measurements of beta particles emitted by ^{228}Ra, high energy channel used for measurement of alpha and beta particles emitted by ^{226}Ra and its daughter products. Since there is an interference due to the continuous spectra of beta particles, cross calculations are used to determine the concentrations of ^{228}Ra and ^{226}Ra. Since the samples were filtrated before chemical treatment only radium dissolved in water was measured.

The measurements were performed by means of liquid scintillation spectrometer QUANTULUS (Wallac Oy, Finland) with an anticoincidence shielding and alpha-beta discrimination feature. Using this instrument and the described above method following detection limits for 1 l sample and 1 hour counting time were achieved:

^{226}Ra - 2 Bq/m^3; ^{228}Ra - 10 Bq/m^3

The detection limits were calculated according to Currie [16]. The determination of ^{226}Ra is performed with accuracy ± 8%, while ^{228}Ra is determined with accuracy ± 20%.

A quality assurance program, described elsewhere [17] was applied according to EN 45000 [18]. To assure good quality of analysis every 5th sample was doubled (randomly chosen). Samples were analysed in series of 16. Always a blank sample was included as well as at least two standards and one reference sample. Standard of ^{226}Ra solution was manufactured by Amersham. ^{228}Ra standard was supplied by US EPA. As reference samples mine waters with very well known chemical composition and concentration of radium isotopes were used. The laboratory participated also since 1993 and 1994 on regular basis in the EPA intercomparison programme of measurements of ^{226}Ra and ^{228}Ra in water samples with very good results [17].

Sampling

Sampling of underground waters and outflows from mines was done by mining staff as a routine required by Polish regulations. River waters were taken during national and regional sampling of

environmental water monitoring, which is done by services of Water Authorities. For determination of radium isotopes 800 water samples collected during the sampling campaign from '93 to '95 were used. About 400 water samples were taken in underground mine workings. These were mainly samples from different parts and exploitation levels of mines, but also samples of original water flowing out directly from rocks were taken. Other 400 samples were taken on the ground surface from the outlets of the mine drainage systems, settling ponds and rivers. The sampling was done only in these rivers where radium-bearing waters from coal mines were released. The sampling was done as upstream and downstream from the discharge point. Totally 250 water samples from rivers were taken.

RESULTS AND DISCUSSION

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 inflowing 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 inflowing 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 inflowing 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 275 MBq/day of ^{226}Ra and 150 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 625 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 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.

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 350 MBq per day (125 GBq/year) and for ^{228}Ra - 555 MBq/day (200 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.

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 300 MBq of ^{226}Ra and 545 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.1. 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 affluents. 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/m^3.***

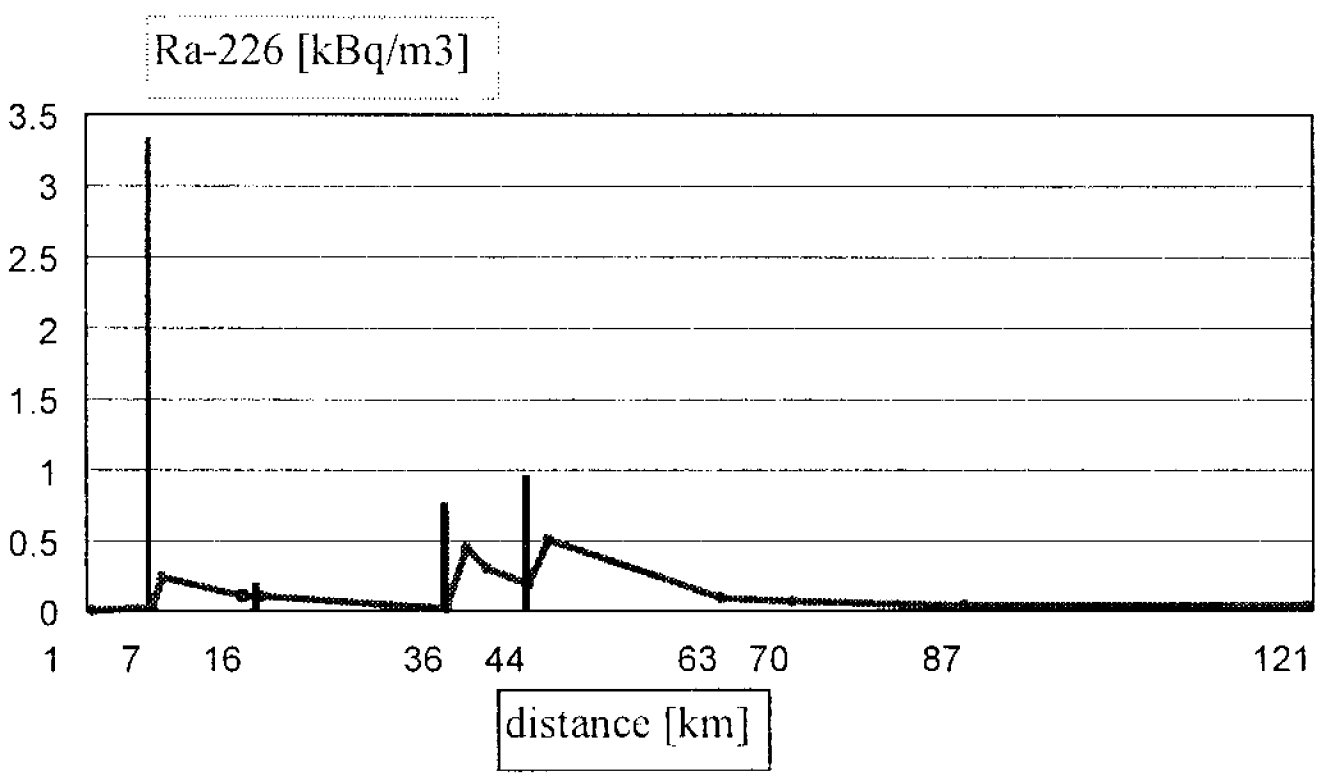

Fig.1. Radium in Vistula river during summer

Concentrations of radium isotopes in some rivers in Upper Silesia are clearly enhanced as compared with natural background. 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 its affluents.

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