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Mineral composition and heavy metal contamination of sediments originating from radium rich formation water

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HIGHLIGHTS

- A complex analysis of sediments arose from formation water was carried out.
- Data concerning radioactivity, mineral composition and metals content are provided.
- Correlations observed indicate the main mechanism of contaminants accumulation.
- Mineral composition is crucial for further behavior of radium in sediments.

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ABSTRACT

Radium rich formation water is often associated with fossil fuels as crude oil, natural gas and hard coal. As a result of fossil fuels exploitation high amount of such water is released into environment. In spite of the high radium content such waters create a serious radiation risk neither to humans nor biota directly. First and foremost due to very high mineralization they are not drinkable at all. But after discharge chemical and physical conditions are substantially changed and sediments which additionally concentrated radium are arising. Due to features of technological processes such phenomenon is very intensive in underground coal mining where huge volume of such water must be pumped into surface in order to keep underground galleries dry. Slightly different situation occurs in oil rigs, but finally also huge volume of so called process water is pumped into environment.

Regardless their origin arising sediments often contain activity concentration of radium isotopes exceeding the clearance levels set for naturally occurring radioactive materials (NORM) (Council Directive, 2013). The analysis of metals and minerals content showed that besides radioactivity such sediments contain high amount of metals geochemically similar to radium as barium, strontium and lead. Correlation analysis proved that main mechanism leading to sediment creation is co-precipitation radium with these metals as a sulfate. The absorption on clay minerals is negligible even when barium is not present in significant quantities. Owing to very low solubility of sulfates radium accumulated in this way should not migrate into environment in the neighborhood of a site where such sediment were deposited.

1. Introduction

Co-occurrence of radium rich formation water with fossil fuels is quite common phenomenon in nature. In almost all cases of crude oil exploitation the presence of heavy mineralized formation water containing radium in concentrations significantly exceeding levels observed usually in fresh water is reported (IAOGP, 2008). Waters having similar properties are also often associated with deep hard coal seams. This phenomenon is very well known in case of the Upper Silesian Coal Basin (USCB), southern Poland (Michalik et al.,2002; Chałupnik et al., 2001). Besides Upper Silesia, the occurrence of the formation water with enhanced concentration of radium was overhauled in the Ruhr Coal Basin, Germany, where the mine "Auguste Victoria" had been discharging water containing ^{226}Ra at the level of 13 kBq m^{-3}. It resulted in a serious contamination of the river Lippe catchment area, including water, soil and biota (Wiegand, 2004). In spite of the lack of well documented cases, the occurrence and discharge of radium rich water is highly probable in other regions where hard coal is exploited.

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2. Problem formulation

Formation water with high radium concentration is dangerous to humans only in case of intake; however, due to its high content of salt, such kind of water is not consumable at all. Crucial for the creation of enhanced exposure to radiation is additional concentration of radium during sedimentation of a matter suspended in such waters. Such a process can be very efficient and results in sediments with radium activity concentration increased by a few orders of magnitude in comparison to the average value observed in the Earth crust. Finally, exposure to the external radiation due to such a waste can create a significant radiation risk. In case of a coal mine (and crude oils rigs as well) the main process responsible for such an efficient sediment creation is co-precipitation of Ra^{2+} ions together with other ions occurring in formation water e.g. Ba^{2+}, or Sr^{2+}, which leads to creation of indissoluble barium or strontium sulfate. The co-precipitation of Ra^{2+} ions with calcium carbonate has been also reported (Zielinski et al., 2001). When radium-like ions are not present, the adsorption on the clay minerals suspended in water is supposed. Finally, solids created from formation water vary in their chemical and mineral composition due to the origin of parent formation water.

In the underground coal mine the formation water released into underground galleries due to the coal extraction process must be pumped onto ground surface. In order to minimize a possible detrimental impact on environment, mainly related to the high salinity of such waters, a special system of settling and retention ponds is applied, where the waste water from the mine is kept before discharging into fresh water *i.e.*, a river. The main purpose of this system is to remove a suspended matter from the mine water and control the dilution process in order to keep the appropriate salt content in the destination fresh water. Additionally, such a system creates favorable conditions for the creation of bottom sediments and scales with enhanced concentration of radium isotopes in the settling pond as well as in the entire mine dewatering system. Concentration of high activity radium is the source of the exposure to external radiation in the vicinity of the sediments. However, when a potential radiation risk to surrounding environment is concerned, the radium and the migration of long lived radium progenies as well as their transfer to biota turn out to be crucial. These agents depend on a mineral composition of the sediments and the speciation bounded radionuclides. In general, chemical composition of the sediments precipitated from the mine water is similar to the carboniferous rock associated with coal seams. However, the mineral composition can be altered by a process leading to their creation.

The analysis of activities of various radium isotopes and their decay products in the sediments, their mineral composition as well as contaminations by metals allows to predict the behavior of the sediments in the environment as well as to optimize methods of disposal. Furthermore, such analysis can provide essential data required for the identification of their origin. And last but not least, results collected on base of easily available sediments from coal mining can be also broadened and used for the prediction of radium final fate in case of sediments created from water discharged by oil industry that in overwhelming majority are deposited on seabed.

3. Material and methods

In order to analyze mineral composition and content of heavy metals in the sediments, 21 samples from 10 coal mines located in the Upper Silesian Coal Basin (USCB), have been taken (Fig. 1). Selected coal mines discharge formation waters varying significantly in their chemical composition, especially when the barium content is considered. The samples of the sediment were selected among the samples analyzed routinely in the frame of the monitoring of a radiation risk in underground coal mines. The measurements of radionuclides activity concentration were undertaken using a high-resolution HPGe gamma-spectrometer with a detection limit lower than 1 Bq kg^{-1}. According to the certified by Polish Accreditation Centre (PCA) internal procedure of the Laboratory of Radiometry (Central Mining Institute), the given uncertainty lead to 1-sigma reliability. The radium isotopes were determined by measurements of their progenies after equilibrium had been reached at the following gamma energies: ^{226}Ra directly at 186 keV and by ^{214}Pb (295 and 351 keV) and ^{214}Bi (609 keV), ^{228}Ra by ^{228}Ac at 911 keV, ^{228}Th and ^{224}Ra (that are in secular equilibrium) by ^{212}Pb (238 keV) and ^{208}Tl (583 keV) corrected for the decay ratio.

Mineral composition of the sediments was tested by the powder X-ray diffraction (XRD) method. X'PERT PRO-PW 3040/60 PANALITICAL and D8 DISCOVER BRUKER diffractometers were used. Each sample was measured using Co Kα or Cu Kα characteristic X-ray radiation. Analyses were carried out in the Department of Mineralogy, Geochemistry and Petrology, Faculty of Earth Sciences of the University of Silesia and the Department of Environmental Monitoring of the Central Mining Institute in Katowice. For the qualitative analysis the standard database ICDD (The International Centre for Diffraction Data, 2012) PDF-4+ were used. The quantitative analysis was carried out based on the full pattern analysis technique known as the Rietveld method (Rietveld, 1969); Rodriguez-Carvajal, 1997) and the structural standard from the database ICSD (The Inorganic Crystal Structure Database, 2013).

Determination of the content of metals As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sn Sr, Zn, was carried out by atomic emission spectroscopy with induced coupled plasma by means the Optima 5300DV spectrometer produced by Perkin Elmer (Bzowski and Bojarska, 2003). The content of Hg was determined by the method of high-temperature combustion coupled with the method of cold steam atomic absorption spectroscopy by means of the mercury analyzer MA 2000 produced by Nippon Instruments Corp. The analyses were performed in the Laboratory of Solid Waste Analyses, Department of Environmental Monitoring, Central Mining Institute in Katowice.

4. Results

4.1. Radionuclides activity concentration

Activity concentration of radium isotopes in the investigated samples varies from values of the level typical for a natural background observed in unaltered environment, up to values several times higher than the clearance level set for NORMs (Council Directive, 2013). Due to the fact that all investigated samples were taken from the sediments precipitated from mine waters, the assumption can be made that in the moment of sedimentation only very few amounts of decay products of radium isotopes were present. In other words, activity concentration of all radium decay products was negligible when compared with the initial radium concentration. Owing to that, the age of the sampled sediments can be assessed by the ratio of ^{224}Ra and ^{228}Ra (Table. 1). In time of the measurements the age of the investigated samples was between 2 and 5 years.

4.2. Mineral composition

In investigated samples the following crystalline solids have been identified: