Behaviour of radium discharged with waste waters into the surface settling pond

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Abstract: As a result of a discharge of radium-bearing waters from coal mines into settlement ponds and later into rivers a significant increase of radium concentration in bottom sediments can be observed. Sometimes there is also a contamination of river banks, soils and vegetation. Mine waters contain mainly two radium isotopes i.e. ^{226}Ra from uranium series and ^{228}Ra from thorium series in chloride rich solution. Due to the chemical properties of such discharged brines, these waters contain usually no uranium, no thorium but occasionally elevated concentration of other radio-isotopes as ^{210}Pb and ^{210}Po. It is only after fixing by deposition or adsorption of radium isotopes that the built-up of the activity of their progeny begins. Therefore concentrations of radium isotopes are higher than the decay products. The paper describes results of investigation of waters and sediments with enhanced natural radioactivity, that occur in settling pond, where mine waters have been dumped. The results of measurements show that these deposits contain mainly ^{226}Ra and ^{228}Ra (in the form of sulphates) and radium progeny. The influence of bottom sediments with enhanced radium concentration on the natural environment in the vicinity of settlement ponds was also studied. The results show clearly enhanced radioactivity of pond bottom sediments and water in the settling ponds and in the river, into which the water drains, but no evident enhancement was found in the adjacent land. The investigated coal mine is located in the drainage area of the Vistula river, and river sediments with enhanced radium concentrations were found in the Vistula several kilometres downstream from the discharge point.

1 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].

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 that ones originated from type A waters.

The precipitation of radium and barium sometimes occurs in surface settling ponds. It may cause the enhancement of the radiation hazard for inhabitants of adjacent areas. That is on of the reasons of numerous conflicts between local authorities and communities with coal mines. For our investigations one of the most polluted settling ponds was chosen.

2 THE DESCRIPTION OF THE CHOSEN SETTLING POND

For our investigations a settling pond was chosen, for which emergency measurements had already been done as a result of the protects of local communities. Inspectors of Polish Atomic Energy Agency were invited to measure gamma dose rates in the vicinity of the pond. Monitoring had been performed at 37 points around the reservoir. In their report a significant increase of dose rates was quoted, up to 42 μGy/h near the point of inflow of waters into the settling pond. With the increase of the distance from the discharge point the decrease of dose rate was observed – down to 2 μGy/h at 15 metres from the end of the pipeline. That area is presently secured against casual entry of non-authorised persons. On the remaining part of the area lower values of gamma dose rates were measured, not exceeding the level 1.2 μGy/h. In comparison, the background of gamma dose rate in Poland is within the range 0.02 – 0.09 μGy/h [Radiological Atlas of Poland, 1998].

Since 1977 the pond has been used for the sedimentation of the suspended solids from mine waters. Approximately 70 million cubic metres of saline waters has been discharged into the pond during last 22 years. The content of the suspension varied from 0.3 up to 2.4 g/dm^3. The area of the pond is very large – about 36 ha.

Radium-bearing type A waters have been pumped into reservoir [Michalik et al., 1999] – along with significant amounts of barium and traces of sulphate ions. For example in 1998 about 5600 m^3/day of such waters were released into the pond. The co-precipitation of radium and barium took place spontaneously and as a result insoluble deposits of $BaSO_4$ + $RaSO_4$ have settled out at the bottom of the pond. Such scales are characterised by highly enhanced levels of radium isotope concentrations.

Nowadays the degree of radium precipitation in lower than in the past owing to the fact that about half 50% of the emerging waters has its radium removed underground.

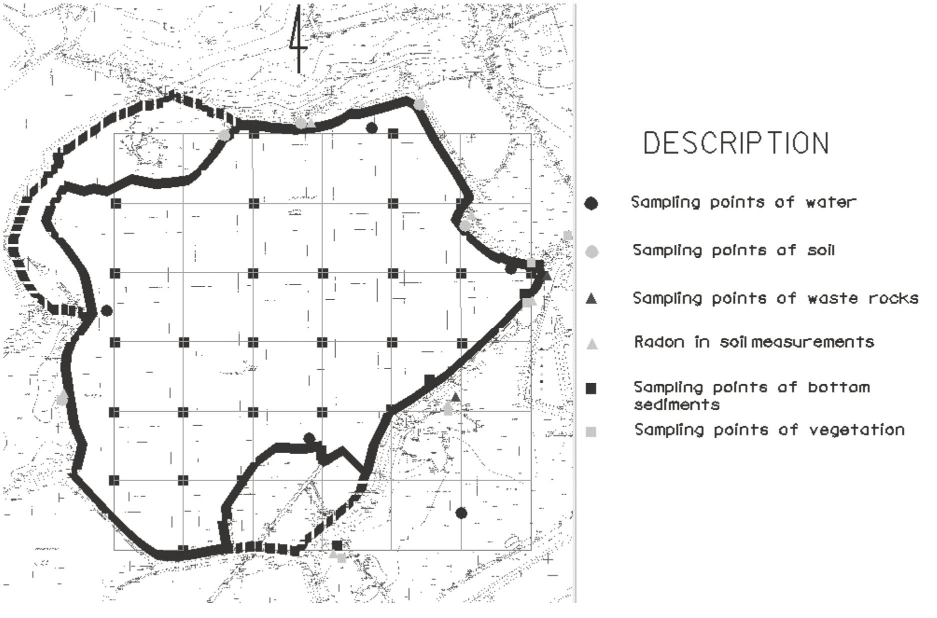
Analyses from 1999 showed that the average concentrations of the two radium isotopes in saline waters discharged into the pond were equal:

- Ra-226 – 2.27 kBq/m^3
- Ra-228 – 2.37 kBq/m^3

It has been calculated that about 9.5 GBq/year of both radium isotopes are released into the pond. Due to the high rate of the deposition of radium, the pond bottom sediments were investigated more carefully. During the measurements the radiation hazard was also assessed. Shortly the pond will be rebuilt, therefore so that an investigation of the current situation is very important. The sketch plan of the pond and surrounding area is shown in Figure 1.

Figure 1 Sketch plan of the reservoir (with sampling points)

3 APPLIED METHODS OF MEASUREMENTS



The reliability of the results in measurements of natural and artificial radioactivity is critical. An internal quality assurance system has been implemented in radiometric laboratory and was initiated in the early 1990's according to PN-EN 45001 standard.

For the purpose of this work we applied high resolution gamma spectrometry for the measurements of natural radionuclides in solid samples (^{226}Ra, ^{228}Ra, ^{224}Ra, ^{40}K) and liquid scintillation counting for the measurements of radium isotopes (^{226}Ra and ^{228}Ra) in water [Lebecka et al., 1993] . The investigations of gamma doses and dose rates have been done by means of dosemeters with thermoluminescent detectors (TLD), while radon in soil was measured using Lucas cell after soil gas sampling.

4 RESULTS OF MEASUREMENTS

Water and sediment samples from the reservoir were collected from 28 chosen sampling points on a regular grid. In each sampling point following measurements were done:

- The thickness of the bottom sediments layer;
- The depths of water above the sediments;
- The shape of the bottom (by bathymetric scanning);
- Gamma dose rate above the water surface.

Bottom deposits were sampled at each point for further gamma spectrometry (natural and artificial radionuclides). Since bottom sediments were very soft and water laden, it was impossible to sample the different layers of deposits that represents different ages of sediments.

Results of radium measurements in water and solid samples

In Table 1 summarises the results of measurements of radium activity in bottom sediments, performed by gamma spectrometry.

It can be clearly seen, the measurements show big differences of radium content in sediments. Results of radium analysis in water samples are quoted in Table 2, whilst Figure 2 shows the pattern of the total radium concentration in water.

In the central part of the reservoir (distant from the inflow point) both radium isotopes (^{226}Ra and ^{228}Ra) are more uniformly distributed. There is a little exchange between waters in this area and the rest of the pond. Usually, where sediments with a higher radium content were found, radium content in water is lower than average.

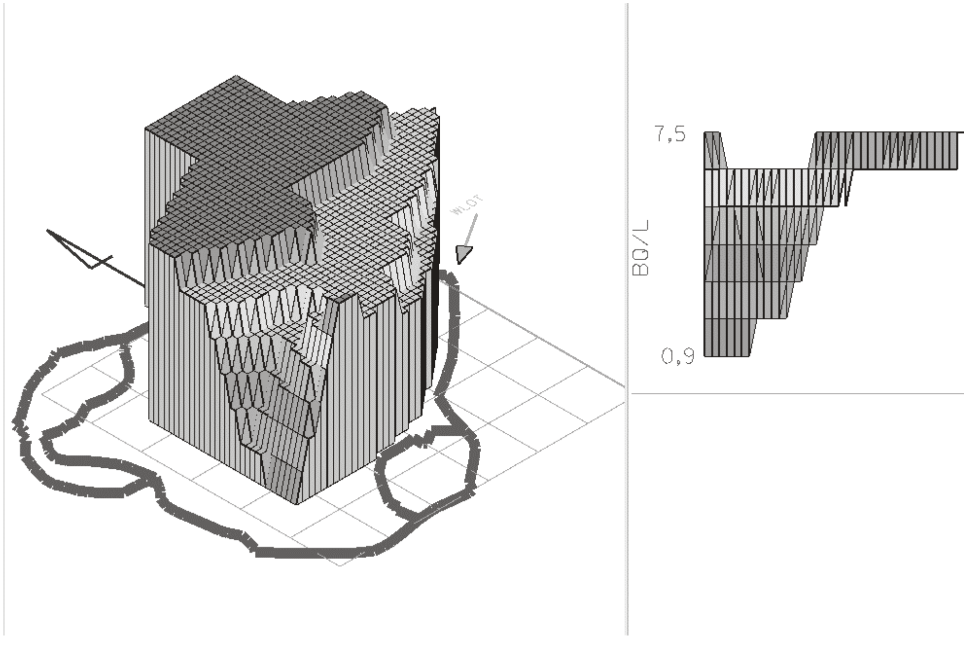


Figure 2 Radium concentration in waters from the pond

Bottom sediments	*28 samples*	
	^{226}Ra [Bq/kg]	**^{228}Ra [Bq/kg]**
Average	**5105**	**1407**
Median	**1191**	**593**
Maximum	**49151**	**6388**
Minimum	**67**	**62**

Table 1 Results of radium measurements in bottom sediments from the pond

Water	*28 samples*	
	^{226}Ra [Bq/m^3]	**^{228}Ra [Bq/m^3]**
Average	**3176**	**2931**
Median	**3609**	**3220**
Maximum	**3996**	**3740**
Minimum	**337**	**520**

Table 2 Results of radium measurements in water samples from the pond

Additionally, in order to assess the pollution of the banks of the pond, we took soil samples as well as samples of waste rock, that was used for the construction of the banks. Results of gamma spectrometric measurements are shown in Table 3. At one particular site, the radium concentration in waste rock was clearly enhanced, probably due to the contamination with mine sediments. Caesium-137 concentration in soil samples is however higher, due to pollution after Chernobyl accident, which is still palpable.

Table 3 The activity of chosen radionuclides in waste rocks and soil samples from the banks of the settling pond

	Concentrations of radionuclides			
	^{226}Ra [Bq/kg]	**^{228}Ra [Bq/kg]**	**^{40}K [Bq/kg]**	**^{137}Cs [Bq/kg]**
The range of the concentration for waste rocks	**30 –3508**	**40 -2482**	**414 -645**	**<2 – 79**
The range of the concentration for soil	**29 - 74**	**33 - 77**	**377 - 811**	**77 – 238**

In the close vicinity of the pond a swamp with the deposit of mud, used for the therapeutic purposes, is located. This is a source of the mud for the medical treatment in the near-by spa, and therefore it was very important to check the possible pollution in the swamp. Three samples were taken for the analysis and results are shown in Table 4.

Table 4 Activities of radionuclides in samples of therapeutic mud

Sample number	**Concentrations of radionuclides**			
	^{226}Ra [Bq/kg]	**^{228}Ra [Bq/kg]**	**^{40}K [Bq/kg]**	**^{137}Cs [Bq/kg]**
Sample 1	**22±3**	**17±3**	**102±13**	**119±3**
Sample 2	**25±3**	**20±3**	**114±17**	**278±8**
Sample 3	**27±3**	**25±3**	**137±15**	**335±10**

We found no contamination from radium isotopes, leaking from the settling pond, but there were still remnants of fallout of caesium-137 from May 1986.

Radon concentration in soil gas

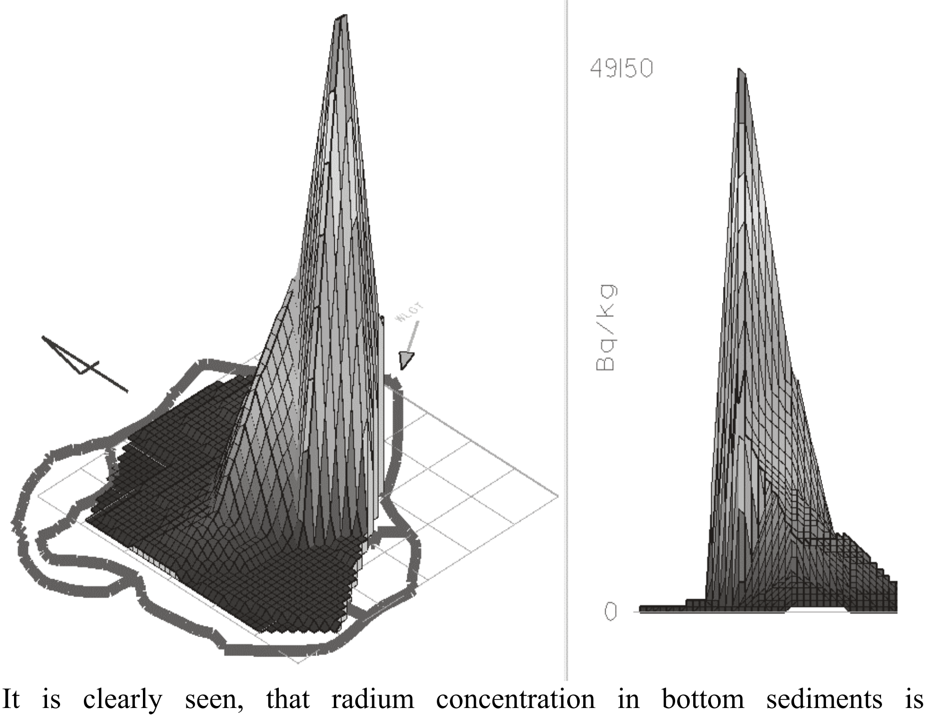
The contamination of pond's banks, caused by waste rocks and sediments with enhanced radium concentration would be expected to lead to increase of radon in soil. Therefore we investigated radon concentrations in soil gas along the banks of the pond. The soil gas was sampled from the depth 1 metre, transferred into Lucas cells and measured. Sampling points are shown on the sketch plan of the area (Figure 1). The maximum value of radon concentration in soil gas was 12.7 kBq/m^3. However in numerous sampling points radon concentration was very low, probably due to the high water table in the ground around the pond.

5 ANALYSIS OF THE RESULTS OF INVESTIGATION

The influence of the deposition of radium in the reservoir on the contamination of the adjacent land

Accordingly to the UNSCEAR report [UNSCEAR, 1982], the normal range for radium isotopes in earth's crust is 10 - 50 Bq/kg, whilst the range for the potassium K-40 is 100-700 Bq/kg. In the table 5 the range of measured values for particular radionuclides in the present study are shown and compared with the average values for the natural environment.

Figure 3 Radium-226 in bottom sediments



It is clearly seen, that radium concentration in bottom sediments is significantly higher than the average value for the Earth's crust. The source of the enhancement are radium-bearing mine waters. Radium is co-precipitated with barium as insoluble sulphates and settles at the bottom of the pond together with non-radioactive suspended matter, dumped into the pond with mine waters.

Table 5 The summarised results of the investigation of natural radionuclides in solid samples in the area of the settling pond

Rad onuclide	**Activity [Bq/kg]**		
(the range of conce trations in	*Bottom sediments*	*Wa te rocks*	*Soil and*
^{226}Ra (7-50)	67 - 49151	30 - 3508	22 – 74
^{228}Ra (10-50)	62 - 6388	40 - 2482	17 – 47
^{224}Ra (10-50)	65 - 8990	38 - 1791	17 – 44
^{137}Cs	<2 - 1014	<2 - 79	77 – 238
^{40}K (100-700)	155 - 848	414 - 664	102 – 811

The rate of co-precipitation can be assessed from the activity of radium isotopes in the sediment. A very wide range of radium concentration in sediments and the distribution pattern shows, that the co-precipitation and sedimentation of radium and barium takes place mainly near the discharge point of saline waters into the pond. On the other hand, there are large areas in the pond, where pond sediment contamination is very low, even where there is enhanced radium content in water.

High radium content in waste rocks can be seen only near the inflow point. The contamination is possibly caused by dredging of sediments from the bottom onto the banks of the pond. We found no contamination of soils on the adjacent lands. Another important result of the survey is that there is no radioactive pollution in the swamps which supply the therapeutic mud. Finally, the following conclusion can be drawn, that except for a very small area near the outlet of the pipeline, which carries saline waters from mine to the settling pond, contamination is limited to the sediments at the bottom of the reservoir.

The caesium radioisotope, ^{137}Cs, is an artificial nuclide with half-life of about 30 years. Therefore it shouldn’t be present in the natural environment. However, in many samples we found elevated activity of this isotope. This is a result of radioactive fallout after the Chernobyl accident in 1986. ^{137}Cs is not present nn samples of bottom sediments from deeper layers, or in freshly excavated waste rocks. However in soil samples and in samples of bottom sediments from places with low rates of sedimentation, enhanced levels of ^{137}Cs have been measured.

Radium concentration in these sediments is also low and it supports a thesis, that these sediments have been carried into the pond from fields in the vicinity. Additional support for this theory is a fact, that similar ratio of activities of radium and ^{137}Cs have been found in samples of therapeutic mud.

Assessment of the radium balance in bottom sediments in the settling pond

The radium concentration in bottom sediments is non-uniform and in many localities there is a considerable enhancement above the average level. This may cause serious problems during reclamation. In attempting to resolve this problem, an assessment of the amount of affected sediments at the bottom of the settling pond was done. The mass balance of total activity due to precipitated radium nuclides, has also been considered.

During sampling, measurements of the thickness of the sediment and the depth of water above the bottom were done. We were thus able to prepare a computer generated bathymetric chart, and to calculate the thickness of bottom sediments for whole area of the pond. We found that the maximum thickness of that layer occurs in the southern-east part of the reservoir, close to the place of discharge of mine waters from pipeline (Figure 1). The maximum thickness is about 1.2 metres. The area, where the layer of deposits is thicker than 0.4 m, seems to be only a small part of the pond, roughly 2.5 ha. For the remaining 33 ha the thickness of sediments layer varies from 0.1 to 0.4 m and minimum thickness of precipitates can be found in northern and western parts of the pond. It is likely that in this part of the reservoir only small inflows of fresh water occur and as a result there is a very slow precipitation of radium and barium from water. Moreover, no coal remains were found here and the radium content in sediments from this part was rather low, below 500 Bq/kg.

The bathymetric map shows also, that in the northern and eastern parts of the pond there is a subsidence, caused by underground mining. In the remaining area the depth of the water layer is very shallow, therefore the bottom sediments are found just below the water surface or sometimes even above the water – especially near the outflow from the pond to the Vistula River.

Table 6 Amount and total activity of the bottom sediments, settled in the pond

The area of the reservoir [m^2]	***Deposits volume [m^3]***	***Water volume [m^3]***	***Total activity of ^{226}Ra [Bq]***	***Total activity of ^{228}Ra [Bq]***	***Total activity of ^{226}Ra+ ^{228}Ra [Bq]***
360000	**113107**	**262084**	**240×10^9**	**74×10^9**	**314×10^9**

The maximum activity of radium isotopes in sediments (about 55 kBq/kg of ^{226}Ra+^{228}Ra) was discovered in the southern part of the pond – midway between inflow of mine waters and the outflow from the pond to the Vistula (Figure 3). Near the inflow from the pipeline the average activity of radium isotopes is 10 kBq/kg. The most probable reason of that phenomenon is the faster deposition of non-radioactive suspended matter and much slower settlement of fine crystals of barium and radium sulphates.

On the large part (35-40%) of the bottom, situated mainly in the north and west, there the average radium concentration is lower as 350 Bq/kg in case of ^{226}Ra and 230 Bq/kg of ^{228}Ra. In guidelines [Michalik et al., 1995], concerning the storage of waste material with enhanced natural radioactivity on the surface, these values were proposed as maximum permissible values of radium concentrations in such deposits and waste rocks.

That the total activity of radium isotopes, deposited in the pond, is roughly equal 315 GBq. The major part of that activity (at least 240 GBq) is due to the presence of ^{226}Ra, with a half-life of 1620 years. There are 74 GBq of the activity from ^{228}Ra, with a half-live of only 6 years. It means, that technologically enhanced radioactivity will be present in this area centuries after the end of mining activity. Without proper techniques of ground reclamation, deposits from the reservoir may endanger people, now and in the future, in the vicinity of the pond.

In 1997 a Decree of the President of Polish Atomic Energy Agency (PAA) was issued, concerning maintenance and handling of radiation sources [Decree, 1997]. Accordingly to this Decree, exemptions from the necessity to apply for a permit for disposal are possible only for mass products or waste materials, if the maximum dose equivalent doesn't exceed 10 μSv per year for any person. Additionally, derived limits are: 10 kBq/kg (concentration of natural radionuclides) and 10 kBq (the total activity of natural radioisotopes) per permit. In the event that any of these limits are exceeded, the procedure must obtain the approval of the PAA. It seems most likely, the reclamation of the area wouldn't be possible without major restrictions.

In our opinion, the critical parameter, during handling and storage of mining waste with enhanced natural radioactivity, is the radium concentration. Established guidelines indicate that waste rocks and deposits might be stored as the surface piles without any restriction, if the ^{226}Ra concentration is lower than 350 Bq/kg and corresponding concentration of ^{228}Ra is below 230 Bq/kg. In other cases, the assessment of possible hazard for the environment and inhabitants of adjacent areas must be carried out. It means, that during the reclamation of that particular settling pond, the analysis of radiation hazard for members of local community must be undertaken.

6 CONCLUSIONS

During our investigations we found clear evidence, that the settling pond has been contaminated by radium-bearing brines, pumped from the mine, where type A waters (with barium and radium ions) occur. Co-precipitation of radium and barium from water in a form of sulphates resulted in deposition of significant amounts of radium isotopes, together with non-radioactive suspended matter onto the bed of the reservoir.

he assessment of total activity of radium isotopes gave the following results: total activity of ^{226}Ra in bottom sediments is roughly equal 240 GBq, while the corresponding activity of ^{228}Ra is about 74 GBq. Fortunately, results of investigations on the banks of the pond, show that the pollution is mostly confined in the pond, except for the Vistula river, which is contaminated by the outflow of waters with enhanced radium concentration from the reservoir.

he contamination of the soil and waste rocks in the adjacent area is insignificant, except for few hot spots near the point of inflow of mine waters into the pond. Important conclusion, drawn on the basis of bottom sediments investigation, is that for 1/3 of the area of the reservoir, radium activity is only slightly enhanced. On the other hand, the amount of sediments and activity of radium, would cause severe problems during reclamation of that area.

It is very important to choose suitable techniques to diminish the influence on the natural environment and to minimise the radiation hazard in the future. The best solution would be a transfer of sediments from the pond into underground galleries and gobs inside the mine. The consistence of sediments (very soft, not compact) suggests the potential for hydro-transport technology. Moreover, it would ensure the radiation safety of the crew during whole process. If this technology would be applied, the possibility, that deposits would be spread in an uncontrolled way is non-significant. Other technologies for the removal of deposits from the pond before underground storage are unsafe for workers and may lead to the contamination of the ground in the vicinity of the pond and along transport roads.

An alternative solution is to leave the deposits in the reservoir. However measures must be implemented to ensure that there is radiation hazard, not only within a short time but over a long period of time (due to the relatively long half-life of ^{226}Ra). Radium is present in sediments in an insoluble form of radium (and barium) sulphate, so the probability of the re-entry of this isotope from sediments into ground waters is extremely low. Nevertheless, a long-term stability of that compound must be checked [Rajaretnam & Spitz, 2000]. It seems to be sufficient to bury sediments under a thick layer (a metre or two) of inactive material with “normal” radium content, to reduce the gamma dose rate to the background level. Another possibility is to apply capping materials with a low permeability deposits (for example clay) to limit any radon exhalation from deposits. Onto this cover any type of backfilling can be used.

It is possible also to develop an impermeable cover before the ground reclamation, by simply leaving the reservoir intact for some time to continue as a settling pond. Newly deposited material should make a good barrier for gamma radiation as well as for radon, but only provided that there was to be no radium inputs. Therefore, the purification of radium-bearing waters must be undertaken elsewhere, in underground galleries to achieve this purpose.

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Zachowanie się radu w powierzchniowym osadniku wód dołowych

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Streszczenie: Oprócz soli, wody występujące w kopalniach węgla kamiennego na Górnym Śląsku często zawierają izotopy promieniotwórcze, a przede wszystkim izotopy radu. Stężenia ^{226}Ra w wodach dopływających do podziemnych wyrobisk kopalń mogą sięgać nawet 390 kBq/m^3, podczas gdy stężenia tego izotopu w wodach powierzchniowych zazwyczaj nie przekraczają 0,1 kBq/m^3. Tak wysokie stężenia radu jakie występują w polskich kopalniach są rzadko spotykane w przyrodzie, jednakże wody ze zbliżonymi stężeniami radu stwierdzono w Iranie, Australii, Ukrainie, Niemczech i Rumunii. Z radonośnych wód wytrącają się promieniotwórcze osady. Takie zjawisko może zachodzić nie tylko pod ziemią, ale także na powierzchni w osadnikach, rurociągach, małych ciekach powierzchniowych. Wytrącanie się osadów zawierających podwyższone zawartości izotopów radu uwarunkowane jest rodzajem wód z których powstają. W niektórych przypadkach radonośne wody kopalniane prócz radu zawierają również jony baru, których stężenie może sięgać 1.5 kg/m^3. Wody zawierające zarówno rad i bar zostały nazwane wodami radowymi typu A. Drugi typ wód radowych, dla odróżnienia nazwany typem B, nie zawiera jonów baru a zawiera jony siarczanowe SO_4^{2-}. Obecność baru w wodach odgrywa kluczową rolę w zachowaniu radu. Z wód typu A (zawierających bar) rad prędzej czy później

ulegnie współstrąceniu wraz z barem po zmieszaniu się tych wód z wodami siarczanowymi, które są bardzo pospolite w przyrodzie. Stężenie ^{226}Ra w tworzących się w taki sposób osadach może sięgać 400 kBq/kg, podczas gdy średnie stężenie tego izotopu w glebie wynosi około 25 Bq/kg.