Purification of mine water of radium — the implementation of the technology in a coal mine

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Abstract

In underground coal mines in the Upper Silesian Coal Basin there are inflows of highly mineralised waters containing radium isotopes. These waters cause radioactive pollution of the natural environment in mining areas. Therefore cleaning of saline waters of radium is very important. Two types of radium-bearing waters were distinguished - one type containing radium and barium ions, but no sulphates (type A) and another one in which radium and sulphate ions are present but no barium (type B).

A very efficient and inexpensive method of purification of saline waters of Ba^{2+} and Ra^{2+} ions was developed and implemented in two coal mines. As the result of used technology, based on application of phosphogypsum as the cleaning agent, a significant decrease of radium discharge was achieved - daily of about 120 MBq of ^{226}Ra and 80 MBq of ^{228}Ra.

Another type of radium waters does not contain barium ions, but contains sulphate ions SO_4^{2-}. There is no carrier for co-precipitation of radium so radium is transported with discharged waters to main rivers. Different method of purification from radium must be applied for such waters. Laboratory and field experiments were performed, and a cleaning method was chosen. For purification of saline waters - waste products from other industrial processes are applied. The method of purification have been applied in full technical scale in coal mine with very good results - of about 6 m^3/min of radium-bearing waters is cleaned. Whole this process takes place in underground old workings without any contact of mining crew with radioactive deposits, which are produced during the process. As a result radium amount released to the natural environment was significantly diminished - approximately of about 90 MBq of ^{226}Ra per day and 150 MBq of ^{228}Ra.

Introduction – Occurrence of radium-bearing waters in Polish coal mines

In coal mines, located in Upper Silesia, inflows of brines with enhanced natural radioactivity occur. In some cases, the total dissolved solids concentration (TDS) exceeds 200 kg/m^3, while radium concentration may reach 400 kBq/m^3. Therefore the assessment of the balance of radium isotopes in inflows showed, that amount of ^{226}Ra was of about 725 MBq per day, while the corresponding value for ^{228}Ra was roughly 700 MBq per day [5]. We found, that only 40% of radium remained in the underground galleries and gutters, while 60% were transported with waters to the settling ponds on the surface and later to rivers [6,7,8]. It was an important source of the contamination of the natural environment in the vicinity of coal mines.

The phenomenon of the radioactivity of saline waters from coal mines in Poland was discovered in 60's [2]. Later, investigations performed by Tomza and Lebecka showed, that radium concentration in water was correlated with the salinity [3]. Moreover, two types of brine were distinguished in coal mines. In waters type A ions of barium and radium are present, while in waters type B only radium ions and sulphate occur, but no barium [5]. From waters type A radium is very easily precipitated out with barium carrier as sulphates after mixing with waters rich in sulphate ions. In waters type B there is no carrier for radium, therefore precipitation of radium scales doesn't happen. Further investigations showed, that discharge of radium-bearing waters from coal mines caused in many cases contamination of the natural environment in the vicinity of these mines, especially small brooks and rivers. The highest levels of contamination were always connected with release of waters type A and precipitation of deposits with enhanced radium content. Such process occurs sometimes in underground galleries and sometimes on the surface in settling pond and small rivers, leading to the contamination of river's beds. Also purification of radium-bearing waters is based on the same process. In case of waters type B only a slow adsorption occurs, therefore the level of contamination is much smaller in comparison with waters type A.

In the past, the highest concentration of ^{226}Ra in discharge waters from coal mines in Upper Silesia was of about 25 kBq/m^3 [6]. **But due to the Polish regulations, waters in which radium content ^{226}Ra is higher than 0.7 kBq/m^3 should be treated as a waste material with enhanced radioactivity** [1]. In Poland, at the beginning of 90's in 10 out of 66 mines such waters were released into the rivers. Waters type A were discharged from seven collieries, and waters type B from 3 mines. As a result of application of purification methods, at present waters type A are dumped into rivers from two mines. The total activity of ^{226}Ra in these waters is only 30 MBq per day. The same number of mines (3) are sources of waters type B, but the amount of radium in such waters is much higher – for ^{226}Ra is of about 200 MBq [8]. Additionally, concentrations of another radium isotope, ^{228}Ra, are higher than that of ^{226}Ra, therefore the charge of that isotope in discharge waters is slightly higher than 300 MBq per day.

The difference between two types of radium-bearing can be explained on the example of two coal mines – Krupinski and Piast.

In Krupinski Colliery waters type A are present, and the maximum radium concentration of ^{226}Ra was as high as 100 kBq/m^3. In the past the coal mine released of about 150 MBq/day of both radium isotopes into the pipeline, collecting also salty waters from 11 other mines. The scaling of radium and barium sulphates in the pipeline caused severe problems with the exploitation of the pipeline. During several years, roughly 20 000 tons of deposits were formed inside pipes, and the average concentration of ^{226}Ra was 30 kBq/kg [9]. It was a first case, when the purification of mine waters from radium and barium was highly desirable. Investigations were undertaken in our laboratory and chosen method of cleaning was applied in the Krupinski Mine in 1990 [12]. Since that time, only 3 MBq out of 150 MBq is released on the surface due to the underground purification.

In Piast mine waters type B are present, in which maximum concentration of ^{226}Ra is as high as 12 kBq/m^3. Waters from the mine are released to the Vistula river, through Bojszowy reservoir and small river Gostynka. The assessment of radium balance in the mine gave the following results. Only small portion of radium remains underground, more than 99% is pumped out on the surface – of about 90 MBq/d ^{226}Ra and 150 MBq/day ^{228}Ra.

Piast Colliery together with two other mines - Czeczott and Ziemowit – are the main source of the contamination of waters in Vistula River. We found enhanced levels of radium 100 km downstream from the discharge points of mentioned above mines, close to Cracow [13].

Results of the investigations of the contamination of natural environment in the vicinity of coal mines forced us to think about the possibility of cleaning the mine waters from radium. At first we tried to design the method of purification for waters type A, which was relatively simple [12]. Such technology of radium removal have been implemented in two collieries – Krupinski (1990) and 1-Maja (1991).

As the effect of the undertaken measures, the amount of radium pumped out on the surface decreased significantly – more than 45% of the previous value during period 1990 - 1995 [13].

Removal of radium from waters type B

Investigations on possibilities to purify radium-bearing waters type B were started in Laboratory of Radiometry in the Central Mining Institute in late 80's. It was connected with two important factors. First of all, the Decree of the President of Polish Atomic Energy Agency, concerning waste products with enhanced radioactivity was issued in 1989 [1]. Due to this act, it is forbidden to release to the natural environment waters, in which ^{226}Ra concentration exceeds level 0.7 kBq/m^3. On the basis of the Decree, in the local authority (Voivodship) in Katowice a commitment was issued, that Piast Colliery was obliged to make efforts to diminish as low as possible concentrations of natural radionuclides (radium isotopes) in waters, discharged into rivers. Moreover, long-term release of radium-bearing waters caused in certain places a significant contamination of settling ponds and small rivers, so the ecological aspect of the possibility of radium removal from mine waters was also important.

Laboratory and field investigations on radium removal from mine waters were supported by Polish Committee of Scientific Research [4]. Results, obtained during tests (also in underground galleries), gave a basis to design the purification station in Piast Colliery [10]. In 1996 in Piast Mine the construction of the station have been started. Expenses were partly covered by National Fund of Environmental Protection and Water Resources. Construction of the installation was finished at the end of 1998 and the start-up of the implementation began [14].

As the sorbent, used for removal of radium, barium chloride was chosen. During laboratory and field test capabilities of this agent have been proved. Unfortunately, there are some limitations in use of that chemical. First of all, barium chloride is poisonous and the training of the mining crew had to be done to avoid any possibilities of intoxication. Moreover, we had to check the background of radiation level before implementation of the purification method in underground galleries as well as on the surface. Some other organising and research activities were completed.

And finally, during the period March – June 1999 the start-up of the purification installation, designed for removal of radium from saline waters have been done in Piast Colliery. It is a unique, first underground installation, built in a coal mine in a full technical scale. This installation is located at the depth 650 meters beneath the surface. Now the system is working in a routine way, therefore it is possible to purify 6 $m^3/min.$ of underground saline waters from radium. Implementation of the purification method in Piast Mine have been carried out by Central Mining Institute in co-operation with certain services from the colliery.

This work is just the first step of the purification of radium bearing waters in Piast Colliery, because till now only waters from the deepest horizon (650 meters) are a subject of radium removal. As the next stage the purification of waters from level 500 meters will be done. Later, the radium removal method will be implemented in two other collieries – Ziemowit and Czeczott. It should solve the problem of the radioactive contamination of the natural environment, caused by underground mining in Upper Silesia.

Hydrogeological situation in Piast Mine

In the overburden the most important layer is an impermeable, thick clay stratum. Therefore there is no hydraulic contact of mine working with the surface and no inflows of meteoric waters. Therefore water inflows into underground galleries of Piast Colliery are mainly due to the aquifers in carboniferous rocks. That are old waters, with high salinity. In 1998 at the level 500 meters the total inflow of brines was of about 5.7 m^3/min, and at the deeper horizon 650 m - 6.1 m^3/min.

The mineralization of the water varies in a very wide range. For instance, in shafts inflows of potable water are presents, while in other places inflows of waters with salinity close to the saturation, occur. The average concentration of Cl^- in brines from level 500 meters is approximately 40 g/dm^3, while in saline waters from level 650 meters the corresponding value is ca. 75 g/dm^3.

The average and maximum concentrations of radium isotopes in waters from Piast Mine are as follows:

^{226}Ra -	average concentration	6.3 kBq/m^3	maximum	12.4 kBq/m^3
^{228}Ra -	average concentration	10.2 kBq/m^3	maximum	19.3 kBq/m^3

THE DESCRIPTION OF THE PURIFICATION SYSTEM

The whole system is located in the central part of Piast Mine, in the vicinity of main shafts, at the depth 650 meters. This area was chosen by geological service accordingly to the following facts. First of all several development heading were driven in that area, moreover the structure of coal seams was too complicated for the exploitation. Additionally, the coal quality from that seem was low and numerous inflows of salty waters were found. Therefore the exploitation of coal in the area was stopped. Very convenient is also the fact, that existing galleries in chosen area are sublevel to the main galleries at the horizon, so no water hazard would be caused by purification.

At first, the small gallery was prepared for the purification station. It had to be located close to the shafts and transportation galleries, to enable easy transport of cleaning agent. Water from the eastern part of the mine (3.5 m^3/min) is pumped to the purification station through the pipeline with length 1500 meters, but water from the western part flows along gutters and the flow rate is a bit smaller – 2.6 m^3/min.

In the chamber of the purification station an automatic sorbent's feeder was installed. Water flows in the gutter under the feeder, and the sorbent is fed into the water. In the gauton several wards are built to make the water flow more turbulent. Under such conditions, the mixing of the sorbent with water is better and the dissolving of barium chloride is faster as well as the consecutive co-precipitation of radium with barium carrier as sulphates. Water is removed from the chamber through the pipeline with length 600 meters and diameter ϕ 600 to the system of settling galleries. That are five parallel galleries with length ca. 1050 meters each and a cross section is equal roughly 11.8 m^2. In these galleries the sedimentation of radium/barium deposits and of mechanical suspension takes place.

The settling galleries are isolated from the other parts of the mine. Special water dams were built, to ensure no leaking of the water to adjacent headings. Additionally, radioactive deposits in the system are confined and the radiation hazard for the mining crew is negligible.

From the settling galleries water flows out to the main water galleries near the exhausting shaft and is pumped out to the surface, to Bojszowy reservoir and finally discharged to Gostynka river.

THE START-UP OF THE PURIFICATION SYSTEM IN PIAST MINE

The purification of mine waters have been started in Piast Colliery in May 1999. As the settling galleries were full of waters with enhanced radium concentration, so the feed of sorbent during first ten days were done continuously, with the dose rate of about 100 grams per m^3. The volume of the settling galleries was assessed as 80000 m^3, and we supposed to obtain results at the outflow from the system after 6-8 days, because the daily inflow is approximately 10000 m^3.

The monitoring of radium content in water was done in several points of the system. Water samples were taken from the inflow (before purification), another sampling point was located at the outflow from the system. Moreover, samples of water pumped out on the surface and from the Bojszowy reservoir were taken from time to time.

On fig.1 preliminary results of purification during the period 5^{th} of May – 19^{th} of July are shown. The curve, describing radium concentration in outflow water, can be divided into few sections. Since 5^{th} of May till 11^{th} of May radium concentration in water was stable. But later, within few hours, we observed a rapid drop of the concentration of radium isotopes from ~ 15 kBq/m^3 to the value of about 3 kBq/m^3. Later on, it was a kind of stabilisation at that level until 19^{th} of May. On this day the concentration of radium isotopes (^{226}Ra+^{228}Ra)

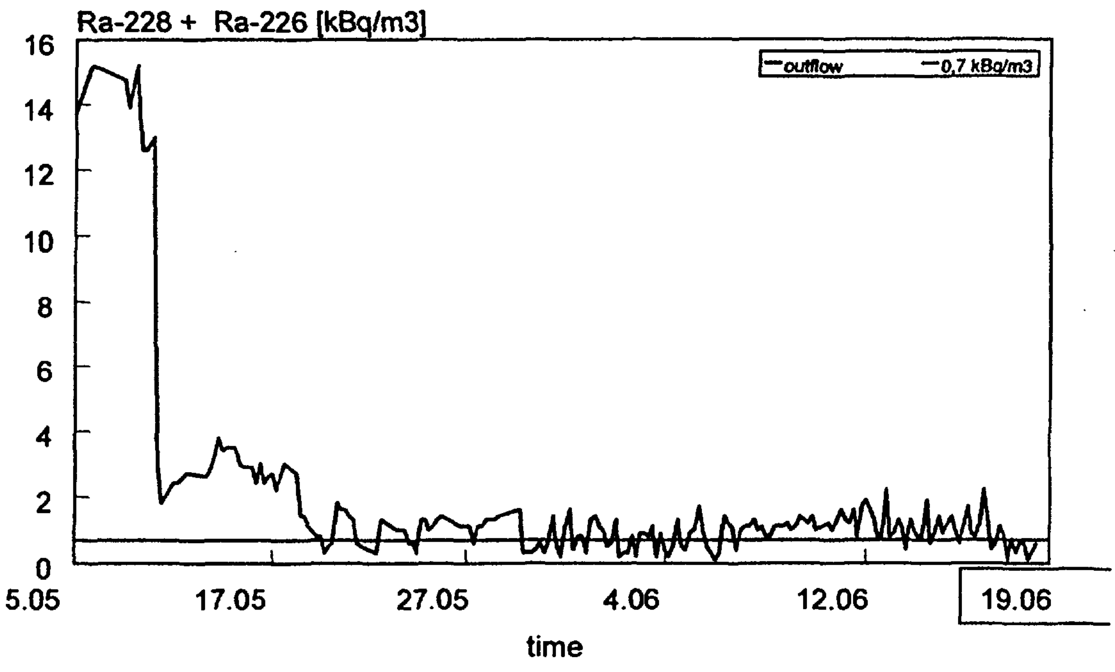

Fig.1. Results of the purification of waters in Piast Mine

decreased first time below 0.7 kBq/m^3. But during whole this period the feeder was working continuously and the dosage was two time higher as was planned (100 g/m^3 in comparison with planned 50 g/m^3).

Unfortunately, some problems with engine of the feeder caused the break of the feeding of the sorbent between 18^{th} and 20^{th} May. After reparation of the feeder the semi-continuous mode of dosage have been started, because we tried to reach the planned value of dosage. Probably both reasons caused the following effects - we observed variations of radium concentration at the outflow. During the period 19^{th} of May until 19^{th} of June we measured radium concentration in waters from the outflow in a range 0.2 - 1.5 kBq/m^3, and the average concentration was calculated as 0.7 - 0.9 kBq/m^3.

Concentrations of radium isotopes in water (^{226}Ra and ^{228}Ra) were measured by means of liquid scintillation counting, preceded by chemical separation of radium [11]. On fig.1. can be clearly seen, that in a very short time results of purification were excellent. Finally, after one month and a half, the radium content in water outflow from the purification system was below permissible value 0.7 kBq/m^3. We would like to emphasise the fact, that the efficiency of purification is better than 95%. As the result of the application of the method of radium removal from mine waters in that particular case, in Piast Colliery, amounts of radium pumped out onto the surface, decreased significantly.

THE EFFECTS OF THE PURIFICATION FOR THE NATURAL ENVIRONMENT

The influence of the purification on the radioactivity of discharged waters

We started to measure radium concentration in waters, released from Piast Mine into Gostynka, several years ago [7]. Also contamination in the vicinity of Bojszowy reservoir and of the river's bed was investigated [15]. During this period we gathered a lot of data, which gave the basis for the assessment of the effects of purification. On fig.2. results of measurements of radium concentration in waters from different sampling points are shown. We measured radium content in waters from main water galleries at level 650 meters, in discharge waters from Piast Mine to settling pond on the surface as well as in waters, released from settling pond into Gostynka river.

During the start-up of the purification, the effect of radium removal was significant. In cumulative waters from the horizon 650 meters concentration of radium isotopes $^{226}Ra+^{228}Ra$ decreased from 15 kBq/m^3 down to the value 1.5 kBq/m^3. Later on the decrease of radium content was even bigger – below 0.7 kBq/m^3. It means, that the amount of radium, pumped onto the surface from that horizon is more than ten time lower as before purification.

Fig.2. Effects of the purification - decrease of radium concentration in water

Such significant decrease of radium concentration in waters from level 650 meters caused similar effects in the waters from settling pond on the surface. On the surface the result of radium removal isn't so big, because waters from horizon 500 meters are not a subject of purification yet. The assessment of the radium balance showed, that the amount of radium released into the pond was lower of about 65% in comparison with previous values. Of course, the same pattern we observed at the outflow from the pond, but slightly retarded due to the retention time in the pond, roughly 8-9 days.

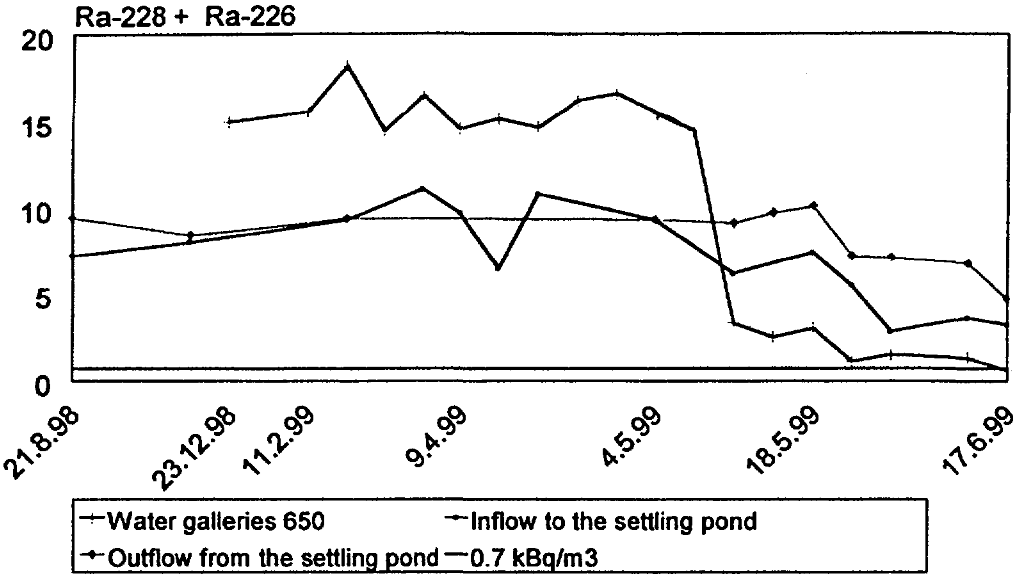

Fig.2. Piast Mine - effect of purification for the environment

Nonetheless, the radioactive contamination of waters, discharged into Vistula river was significantly diminished as a result of the implementation of the purification method. Calculations, made on the basis of obtained results of measurements, leads to the conclusion, that the total amount of ^{226}Ra, released through Gostynka to Vistula river is 60 MBq/day lower as before, while corresponding value for ^{228}Ra is equal 90 MBq/day. **The decrease of discharge of both radium isotopes from Piast Colliery into natural environment with saline waters is of about 150 MBq per day.**

SUMMARY

The purification station in Piast Colliery is a unique, first underground installation for the removal of radium isotopes from saline waters. Therefore no experiences, concerning construction, exploitation and management, have been known.

Implementation of the method of purification of radium bearing waters in non-uranium mine was difficult. All elements of the system – sedimentation galleries, feeders, control units etc. had to be designed without any comparison with other similar systems. Also the proper organisation of the transport of poisonous sorbent from the surface to the chamber in case of operating coal mine was very important. On the other hand, observations and experience gathered during the implementation of the method will be fruitful in the future, for the planning and improvement of similar systems in other coal mines.

During start-up of the installation in Piast Colliery good results of purification were reached after very short time. The most important effect of the purification is almost complete removal of radium from cumulative waters at level 650 meters – the effectiveness of the method is over 95%. Till the end of June 1999, the concentration of radium isotopes in outflow from the system decreased below 0.7 kBq/m^3. Of course, sometimes we found higher values of radium in these waters, but such variability at the very previous stage of implementation was predicted. We think, that in the future the average value of radium concentration will be even lower.

The ecological effect of the purification is also important. On the surface, at the inflow of saline waters into the settling pond as well as at the outflow from that pond, concentrations of radium isotopes are approximately 60-65% lower as in the previous period, before purification. It corresponds to the decrease of about 60 MBq for ^{226}Ra and 90 MBq for isotope ^{228}Ra of daily release from Piast Mine. It means, that the total amount of radium, discharged into Gostynka and Vistula is much lower, by value150 MBq/day.

To achieve the complete purification of mine waters in Piast Colliery, removal of radium isotopes from waters at level 500 meters must be done. We would like to use for this purpose the existing installation in the nearest future, at first for waters with highest concentrations of radium, later on for all radium-bearing waters from that horizon.

Full ecological effect would be reached in case of purification of radium-bearing waters type B from two other coal mines – Czeczott and Ziemowit. We are going to purify all these waters in Piast Mine, therefore the underground system of water transport must be build at first. Moreover, several additional settling galleries must be excavate. But the purification of saline waters from all these mines will solve the problem of the contamination of small tributaries of Vistula river. Laboratory experiments and field tests in Czeczott and Ziemowit mines proved the possibility of application of the same method of purification.

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