Removal of radium from mine waters – the experience from the coal mine

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Abstract: Inflows of highly mineralised waters, containing high levels of radium isotopes, occur frequently in underground mines in the Upper Silesian Coal Basin (USCB). These waters not only result in an increase in the radiation hazard for miners but also cause radioactive pollution of the natural environment in mining areas. Therefore removal of radium is important. Two types of radium-bearing waters were found in USCB - one type containing radium and barium ions, but no sulphates (type A) and another one in which radium and sulphate ions are present but only traces of barium (type B). A very simple, efficient and inexpensive method of purifying saline waters of Ba^{2+} and Ra^{2+} ions has been developed and implemented in two coal mines. The type B water however, does not contain barium ions, but has sulphate ions SO_4^{2-}. There is no available carrier for co-precipitation of radium therefore radium would normally be transported with discharged waters to rivers. A method of purification for such waters has been developed. Laboratory and pilot scale field experiments were performed at first, and involved the use of waste products from other industrial processes. The method of purification has now been applied at the full technical scale in coal mine, with very good results - about 6 m^3/min. of radium-bearing waters is purified. The whole process takes place in underground old workings without the need for any miners coming into contact with radioactive deposits. As a result the radium levels released to the natural environment has been significantly diminished – from 90 MBq down to 40 MBq per day of ^{226}Ra from 120 MBq/day down to 50 MBq/day of ^{228}Ra.

1 INTRODUCTION – OCCURRENCE OF RADIUM-BEARING WATERS IN POLISH COAL MINES

In the coal mines of Upper Silesia, inflows of brines with enhanced natural radioactivity occur. In some cases, the total dissolved solids concentration (TDS) exceeds 200 kg/m^3, whilst the radium concentration may reach 400 kBq/m^3. The analysis of the radium isotopes in inflows showed, that the input of ^{226}Ra was of about 725 MBq per day, while the corresponding value for ^{228}Ra was roughly 700 MBq per day [Lebecka et al., 1986]. Only 40% of radium remained in the underground galleries and gauntons, whilst 60% were transported in pumped waters to the settling ponds on the surface and later to rivers [Lebecka et al., 1993, Lebecka et al., 1994]. It was an important source of contamination of the natural environment.

The phenomenon of the radioactivity of saline waters from coal mines in Poland was discovered in the1960's [Sałdan, 1965]. Later, investigations showed, that radium concentration in water was correlated with the salinity [Tomza & Lebecka, 1981]. Moreover, two types of brine were distinguished in coal mines. In type A waters ions of barium and radium are present, while in type

B waters only radium ions and sulphate occur, but no barium [Lebecka et al., 1986]. From type A waters radium is very easily precipitated out with barium carrier as sulphates after mixing with waters rich in sulphate ions. In type B waters there is no convenient carrier for radium, therefore no precipitation of radium scales occur. Further investigations showed, that discharge of radium-bearing waters from coal mines caused many cases of contamination of the natural environment, especially small brooks and rivers in the vicinity of these mines. The highest levels of contamination were always connected with release of type A waters and precipitation of insoluble deposits with enhanced radium content. Such process sometimes occurred in underground galleries but sometimes on the surface in settling ponds and small rivers, leading to the radioactive contamination of river beds. The purification of radium-bearing type A waters is based on the same chemical process. From waters pf B type only a slow adsorption occurs, therefore the level of contamination is much smaller in comparison with type A waters.

In the past, the concentration as high as about 25 kBq/m^3 of ^{226}Ra in discharge waters from coal mines in Upper Silesia has been measured – and the total discharge approximately 900 MBq/day [Skubacz et al., 1990]. However new regulations demand that waters in which content of ^{226}Ra is more than 0.7 kBq/m^3 must be treated as a waste material with enhanced radioactivity [Decree of the Polish Atomic Energy Agency, 1989]. In Poland, at the beginning of 1990's in 10 out of 66 mines, such waters exceeded these limits. Type A waters were discharged from seven collieries, and type B waters from three. As a result of application of purification methods, at present two of the mines are allowed to discharge type A waters to the surface settling ponds. The total activity of ^{226}Ra in type A waters is only 30 MBq per day (reduced from 220 MBq/day). Three mines are sources of type B waters, but the amount of radium in such waters is much higher – about 200 MBq of ^{226}Ra per day [Wysocka et al., 1999]. Additionally, concentration of another radium isotope, ^{228}Ra, is even higher than that of ^{226}Ra, the total amount of this isotope in discharge waters is slightly more than 300 MBq per day.

The more stringent environmental regulations concerning radioactive discharges forced us to investigate the possibility of decontaminating the mine waters. The first task was to design the method for treatment of type A waters, which was relatively simple [Lebecka, Lukasik & Chałupnik, 1994]. Such method of radium removal have been implemented in two collieries in early 1990's, and have resulted in a substantial reduction in the amount of radium pumped to the surface – less than 55% of the previous value during period 1990 - 1995 [Michalik et al., 1999].

2 REMOVAL OF RADIUM FROM TYPE B WATERS

Investigations of techniques to purify radium-bearing type B waters were started in Laboratory of Radiometry in the Central Mining Institute in late 1980's. It was connected with an important factors. On the basis of new regulations [The Decree of Polish Atomic Energy Agency, 1989], the local authority in Katowice issued a decision, that Piast Colliery was to make every effort to reduce as low as possible concentrations of natural radionuclides (radium isotopes) in waters, before discharging into Gostynka river. Moreover, the long-term release of radium-bearing waters that caused significant local contamination in settling ponds and small rivers, required the assessment of the ecological impact of radioactive pollution. Therefore this 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 [Lebecka, Lukasik & Chałupnik, 1994]. Results, obtained during tests (also in underground galleries), gave a firm basis for the design of the purification station in Piast Colliery [Chalupnik, 1999]. By 1996 the construction of the station had started, partly supported by National Fund of Environmental Protection and Water Resources. The construction of the installation was finished at the end of 1998 and testing started.

To aid the co-precipitation of radium, barium chloride was chosen as agent. During laboratory and field testing the capabilities of this agent have been proved. The chemical reaction is as follows:

$$BaCl_2 \Rightarrow Ba^{2+} + 2\ Cl^-$$

Firstly, the barium chloride dissolves in the water. Next step of the reaction is the co-precipitation of radium and barium ions as sulphates (in case of radium reaction is not stoichiometric):

$$Ba^{2+} + Ra^{2+} + 2SO_4^{2-} \Rightarrow BaRa(SO_2)_4$$

Unfortunately, there are some limitations on the use of that chemical. First of all, barium chloride is poisonous and the mining crew had to be trained in relevant safety procedures. Furthermore as well as other organisational and research activities, the background radiation level had to be checked prior to implementing the purification process both in underground galleries and on the surface.

Finally, during the period March – June 1999 the purification installation went on stream. It is unique, the 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 and is now working routinely. It is possible to treat 6 m^3/min. of underground saline waters. Construction of the purification method in Piast Mine have been carried out by certain services from the colliery in co-operation with the Central Mining Institute.

This work is only the first step in purifying of radium bearing waters in Piast Colliery, because until now only waters from the deepest level (650 meters) are subject of radium removal. The next stage involves the purification of waters from the 500 meters level. Later, the radium removal process will be initiated in two adjoining collieries, where radium-bearing type B waters also occur. It should solve the problem of the radioactive contamination of the natural environment in Upper Silesia, caused by underground mining.

3 HYDROGEOLOGICAL SITUATION IN PIAST MINE

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

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

The average and maximum concentrations of radium isotopes in waters from the 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

4 THE DESCRIPTION OF THE PURIFICATION SYSTEM

The whole system is located in the central part of the Piast Mine, in the vicinity of main shafts, at a depth 650 meters. This area was chosen by mine's geological service accordingly to the following reasons. First of all, although several development heading were driven in that area, the structure of coal seams was too complicated for the exploitation. Additionally, the coal quality from those seams was poor and numerous inflows of salty waters were found. Therefore the exploitation of coal in the area was stopped. Also very conveniently, that existing galleries in chosen area are beneath to the main galleries at the horizon, so no flooding 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 1500 metre long pipeline, but water

from the western part flows along gutters and the flow rate is smaller – 2.6 m^3/min.

In the chamber of the purification station an automatic sorbent feeder was installed. Water flows in the trough under the feeder, and the sorbent is fed into the water. In the gauton several baffles are built to make the water flow more turbulent. Under such conditions, the mixing of the sorbent with water is better and the dissolution of barium chloride is faster as is the resulting co-precipitation of radium with barium carrier as sulphates. Water is removed from the chamber through a 600 metre pipeline (600 mm internal diameter) to the system of settling galleries. That are five parallel galleries each about 1050 m long and with a cross section of 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 miners is negligible.

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

5 ONE YEAR EXPERIENCE WITH THE MAINTENANCE OF THE PURIFICATION SYSTEM IN PIAST MINE

The purification of mine waters were started in the 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 carried out continuously, at the dose rate of about 100 grams per m^3. Since the volume in the settling galleries was assessed as 80000 m^3 and the daily inflow is approximately 10000 m^3 we did not expected to record any changes at the outflow until 6-8 days had passed.

The radium content in water was monitored at several locations in the system. Water samples were taken from the inflow (before purification), and at the outflow from the system and from waters pumped to the surface. The Bojszowy reservoir was sampled every three months. 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 [Chałupnik & Lebecka, 1993].

In Figure 1 preliminary results from the purification process during the period May – July are shown. The curve, describing radium concentration in outflow water, can be divided into several sections. During the first few days of May, radium concentration in water was stable. But later, within just a few hours, there was a rapid drop of the concentration of radium isotopes from ~ 15 kBq/m^3 to the value of about 3 kBq/m^3. It stabilised at that level until the 19th of May, and on this day the concentration of radium isotopes (^{226}Ra+^{228}Ra) decreased for the first time below 0.7 kBq/m^3. During this initial period the feeder was working

continuously and the barium chloride input was twice as high as planned for routine use (100 g/m^3 in comparison with 50 g/m^3).

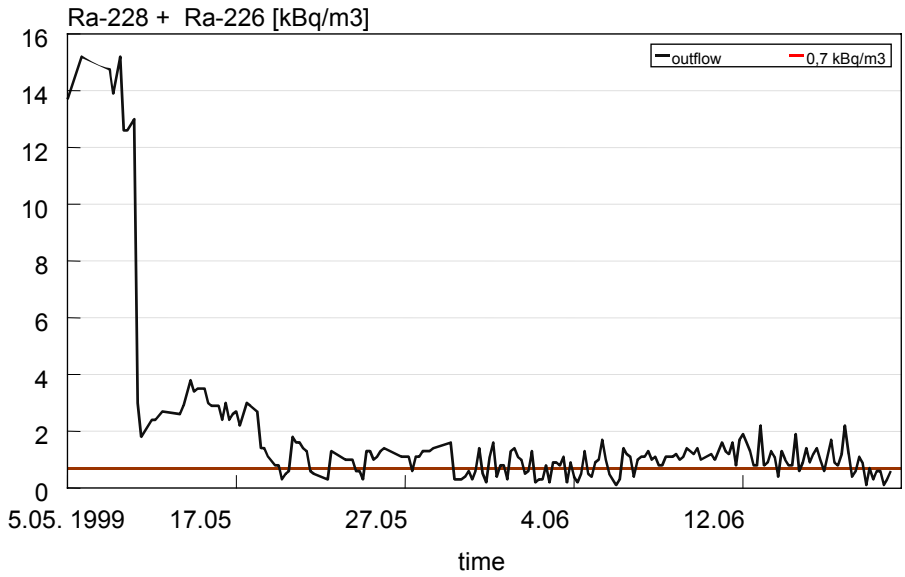

Figure 1 Preliminary results of the underground purification

Unfortunately, some problems with motor of the feeder machine caused a break of the feeding of the sorbent between 18th and 20th May. After repairs a semi-continuous mode of dosage was started, in order tp attempt to achieve the planned value. We observed increased variations of radium concentration at the outflow, probably as a result of these two changes. During the period 19th of May until 19th of June we measured radium concentration in waters from the outflow in the range 0.2 - 1.5 kBq/m^3, and the average concentration was calculated as 0.7 - 0.9 kBq/m^3.

It can be clearly seen, that in a very short time results of purification were excellent (Figure 1.). After one month and a half, the radium content in water outflow from the purification system was below permissible value of 0.7 kBq/m^3. We would like to emphasise the fact, that the efficiency of purification is better than 90% and the amount of radium pumped out onto the surface, decreased significantly.

Figure 2 shows a summary of the results for the past year. It can be seen, that except for some minor problems, caused mainly by "human factor", results of purification are very good. The efficiency of purification stabilised at level 90%. About 50 MBq of ^{226}Ra and ca. 70 MBq of ^{228}Ra is settled in underground storage galleries each day. During the exploitation of the purification station much experience has been gained which will further increase the efficiency of mitigation measures for other mines.

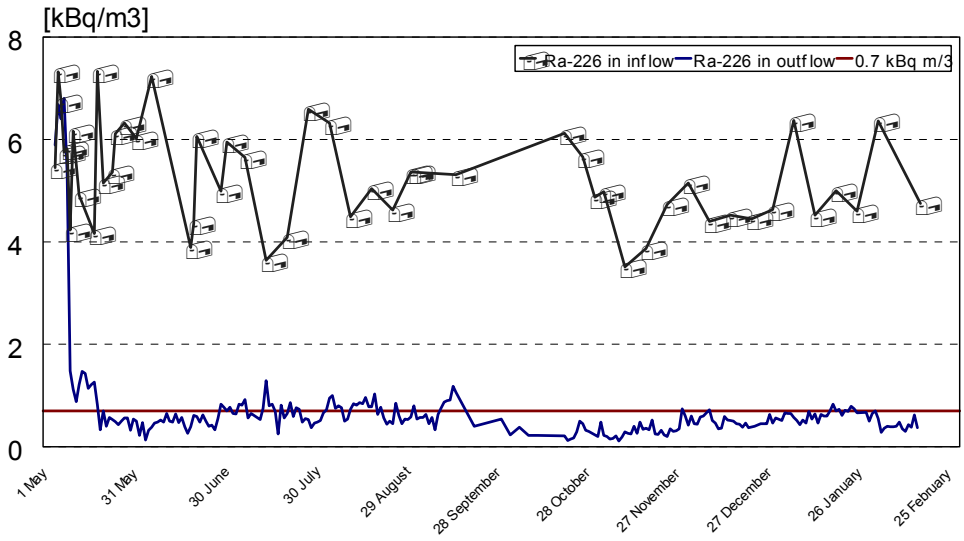

Figure 2 Purification of radium-bearing waters in Piast Mine

6 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, discharged from the Piast Mine into the Gostynka River, several years ago [Lebecka et al., 1986] and the contamination in the vicinity of Bojszowy reservoir and of the river's bed has been investigated more recently [Wysocka et al., 1999]. During this period we gathered a lot of data, on which we can assess the effects of purification. In Figure 3. 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 650 meters level, in discharge waters from the Piast Mine at its settling pond on the surface, as well as in waters released from settling pond into the Gostynka river, and the results are shown in Figure 3.

During the start-up of the purification, the effect of radium removal was significant. In cumulative waters from the 650 meters level the concentration of radium isotopes $^{226}Ra+^{228}Ra$ decreased from 15 kBq/m^3 down to the value 1.5 kBq/m^3. It means, that the amount of radium, pumped onto the surface from that horizon is reduced by a factor of ten.

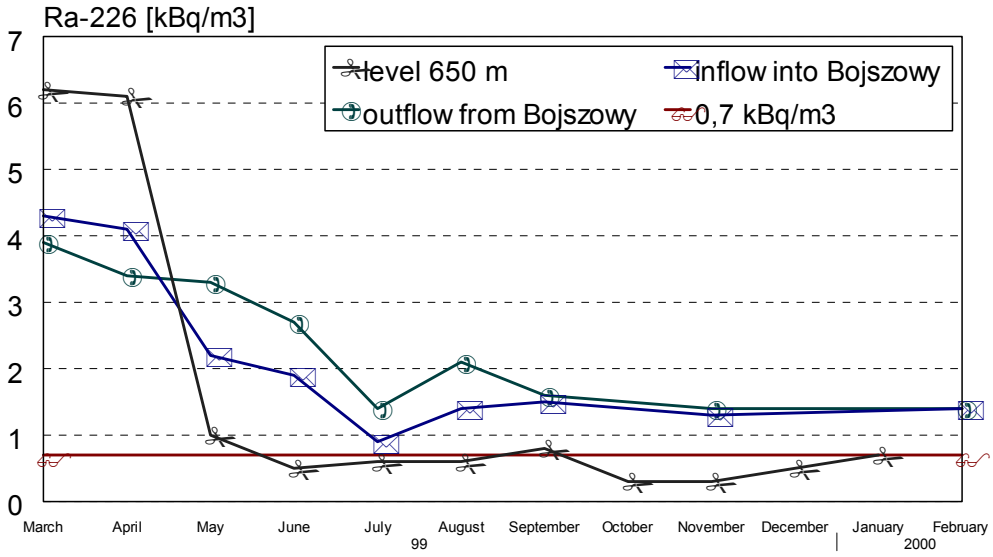

Figure 3 Effects of the purification

Such a major decrease of radium concentration in waters from 650 meters level resulted in a decrease in the waters from settling pond on the surface. However the results are not commensurate, because 500 meters level waters are not treated yet. The assessment of the radium balance showed, that the amount of radium released into the pond was about 65% lower compared with previous values. As expected, the same pattern was observed at the outflow from the pond, but slightly retarded due to the retention time in the pond of roughly 8-9 days.

Nonetheless, the radioactive contamination of waters, discharged into the Vistula river was significantly diminished as a result of the implementation of the purification method. Calculations, made on the basis of actual measurements, leads to the conclusion, that the total amount of ^{226}Ra, released through Gostynka to the Vistula river is 50 MBq/day lower than before, whilst corresponding value for ^{228}Ra is 70 MBq/day. The decrease in discharge of both radium isotopes from the Piast Colliery into the natural environment by saline waters is about 120 MBq per day.

7 SUMMARY

The purification station in Piast Colliery is unique, it being first underground installation for the removal of radium isotopes from saline waters. Therefore there was no previous experience to fall back on concerning construction, application and management.

The implementation of this 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. In particular the proper organisation of the transport of poisonous sorbent from the surface to the chamber within an operating coal mine was very important. On the other hand, observations and experience gathered during the implementation of the method will be advantageous in the future, and will aid in the planning and development of similar systems in other coal mines.

During start-up of the installation in the Piast Colliery good results for purification were reached after very short time. The most important effect of the purification is almost complete removal of radium from waters at 650 meters level – the effectiveness of the method is over 90%. The average concentration of radium isotope ^{226}Ra in outflow from the system decreased to below 0.7 kBq/m^3. Of course, sometimes we found higher values of radium in these waters, but such variability at the very early 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 than before purification. It corresponds to the decrease of about 50 MBq for ^{226}Ra and 70 MBq for isotope ^{228}Ra of daily release from the Piast Mine. It means, that the total amount of radium, discharged into the Gostynka and Vistula rivers is much lower, by a value 120 MBq/day.

To achieve the complete radium reduction in mine waters from the Piast Colliery, the removal of radium isotopes from waters at 500 meters level must be undertaken. We plan to use the existing installation for this purpose in the near future, firstly for waters with the highest concentrations of radium, later on for all radium-bearing waters from that horizon.

The full ecological effect would be achieved when the radium-bearing type B waters from two adjacent coal mines are treated. All waters would be treated at the Piast Mine, therefore the underground system of water transport must first be built and several additional settling galleries must be excavated. The purification of saline waters from all these mines will solve the problem of the contamination of small tributaries of the Vistula river. Laboratory scale experiments and field tests in adjoining mines proved the possibility of using of the same method of purification.

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ZASTOSOWANIE TECHNOLOGII UZDATNIANIA RADIOAKTYWNYCH WÓD W WARUNKACH KOPALŃ GŁĘBINOWYCH

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Streszczenie: W kopalniach śląskich występują wpływy silnie zmineralizowanych wód o zawartości soli niekiedy przewyższających 200 kg/m^3 i wysokich zawartościach izotopów radu, sięgających 400 kBq/m^3. Jedynie około 40% radu obecnego w wodach kopalnianych pozostaje w wyrobiskach podziemnych w postaci osadów, podczas gdy pozostałe ponad 60% radu trafia na powierzchnię a stamtąd do rzek, powodując skażenia środowiska naturalnego wokół kopalń. W polskich kopalniach występują dwa typy wód radowych. Wody jednego typu (zwane wodami typu A) zawierają rad i bar, a nie zawierają jonów siarczanowych, podczas gdy wody drugiego typu (Typ B) zawierają rad i jony siarczanowe, ale nie zawierają baru. Z wód typu A rad łatwo współstrąca się z barem w postaci siarczanów po zmieszaniu z innymi wodami, które zawierają jony siarczanowe. W przypadku wód radowych typu B, nie występuje w nich nośnik dla radu (bar), dlatego wytrącanie osadów radowych nie zachodzi. Kopalnia „Piast" wraz z KWK „Czeczot" i KWK „Ziemowit" stanowią główne źródło skażeń promieniotwórczych Wisły. Oczyszczanie wód radowych typu A, rozpoczęte na początku lat 90-tych doprowadziło do znaczącego ograniczenia skażeń powierzchni poprzez wody radowe tego typu a ładunek radu

odprowadzanego na powierzchnię obniżył się o około 45-50%. Jednakże problem oczyszczania wód radowych typu B okazał się znacznie trudniejszy. Konieczne było znalezienie substancji (tzw. sorbentów), pozwalających na usuwanie radu z tych wód. Badania te , rozpoczęte w Laboratorium Radiometrii GIG, pozwoliły na wyselekcjonowanie tego typu substancji oraz określenie skuteczności ich działania.