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№ 1431

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August 25, 2019

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Abstract. In the formation waters, occurring in coal mines in the Upper Silesian Coal Basin, Poland different pollutants are present which may cause damages to the environment, among them radium isotopes. In several collieries the radium removal from mine water was necessary to mitigate negative results of radium release with mine effluents. The most efficient method of radium removal is based on application of barium chloride, implemented in full technical scale in two of Polish collieries. Another possibility of removal radium isotopes from salty waters is an application of zeolites. In this paper a review of different techniques is given, showing possibilities of application of different methods of radium removal, its advantages and drawbacks.

1 Introduction

Problem of enhanced concentrations of radium in effluents has been found in uranium mines and mills at first [1, 2, 3]. It was necessary to treat waste waters before disposal into environment to remove radium and avoid contamination of watercourses [4, 5, 6]. Similar problem of enhanced radium content in formation waters was found in oil and gas industry [7, 8]. Finally, it became obvious, that any underground exploitation may lead to release of brines with enhanced concentration of radium isotopes [9, 10, 11]. Radium isotopes can be found in drinking waters, coming from underground aquifers, too [12. 13]. The problem of high radium content in brines in Polish coal mines has been discovered in early 70's of last century [11]. Enhanced concentrations of radium in effluents from coal mines in Upper Silesian Coal Basin (USCB) are leading to the contamination of surface waters [14]. Therefore not only monitoring but control of radium concentrations in these waters is required [15]. In the past enhanced radium activities have been measured in waters, released from eleven out of sixty six coal mines in USCB. Nowadays, due to mitigation measures, applied in some mines, this number is down to five mines. Within 15 years, between 1990 and 2005, the total activity of radium isotopes, released by mining industry to the natural environment was lower of about 70% than previously [16]. Despite that, the total release of radium activity was at the end of 2005 equal 120 MBq/day for ^{226}Ra and 220 MBq/day in case of ^{228}Ra [16]. That was one of the reasons, that further measures were required to solve the problem of radioactive pollution entirely. Unfortunately, due to deepening of the mines in the period 2000-2015, the new inflows of radium rich brines appeared in USCB collieries, therefore the total activity of radium isotopes, released to the environment, started to rise again [17].

The more stringent environmental regulations concerning radioactive discharges [18, 19], introduced into Polish legal system at the end of 80's of last century, caused the need to investigate the possibility of decontaminating the mine waters. The first task was to design the method for treatment of waters containing radium and barium, which was relatively simple [20]. 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 [15].

More difficult problem was the radium removal from sulphate rich brines, without a carrier for radium. In one of the such collieries, releasing radium isotopes into surface settling pond and finally into Vistula River saline brines are very common, and the total inflow into mine galleries exceeds 20 m^3/min. Radium concentration in these brines was as high as 12 kBq/m^3 for ^{226}Ra and 20 kBq/m^3 for ^{228}Ra. Due to the lack of barium in brines the spontaneous co-precipitation of radium was negligible and only small part of radium remained underground as a result of adsorption on bottom sediments in underground water galleries [14].

2 Radium removal from water

The treatment for removal of radium from waters has been introduced at first in uranium mining and milling [21, 22]. The purification of radium waters has been the subject of numerous studies mainly due to the fact that sewage from mines and uranium ore processing plants was a very serious source of environmental contamination with the ^{226}Ra isotope. Many different methods of water treatment were studied. Some of them have been used on an industrial scale. The following methods of removing radium from water can be mentioned:

co-precipitation of $RaSO_4$ with $BaSO_4$,
filtration,
coagulation and flocculation,
adsorption and ion exchange,
reverse osmosis,
selective retention on mineral membranes,
aeration,
chelating agents + ion exchange,
foam separation,
co-precipitation with nitrate lead,
extraction in solvents.

Most of the above-mentioned methods have not gone beyond the experimental phase, some are only used as supportive techniques (like filtration, coagulation, etc.), yet others (for example aeration) are only used for drinking water. There are some reports of using the above mentioned methods on a technical scale. Adsorption on barite was used to purify waters from the uranium processing plant in the United States and Canada in the 1960's [23], but later this method has been changed for the co-precipitation of radium-barium sulphate. Ion exchangers were used for the purification of water from uranium mines in Czechoslovakia [24], as well as in one installation in Canada [23], where this method was the final stage of wastewater treatment from the processing plant, after neutralization, applied simultaneously with the barium chloride treatment and filtration. Of all the above-mentioned methods of radon wastewater treatment, co-precipitation with barium sulphate is the most widespread because it is relatively simple and cheap.

As it has been mentioned, the most common technique was use of barium chloride leading to the co-precipitation of barium and radium sulphates. Removal of radium is based on chemical reactions. These reactions are as follows. When barium chloride is used for this purpose, at first the barium chloride dissolves in the water.

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

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

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

As a result of the latter reaction, small crystals of barium sulphate are formed, but its need a certain time for sedimentation. Other option in uranium mining was the use of ion exchange resins [25] to remove radium from effluents, usually very efficient but expensive.

Different problem has been encountered in oil and gas industry, where the formation waters usually contain not only radium but also barium and strontium. In such cases, when formation waters were mixed with any waters, containing sulphate ions, the spontaneous co-precipitation of radium, barium and strontium occurred and deposits with high radium activity concentration were formed [26]. It was leading to scaling in pipelines and other elements of oil rigs, but also contamination of the environment.

In coal industry in Poland there were technical but also legal reasons to start development of radium removal techniques from brines [18, 19]. At first the treatment technology was developed for radium and barium rich waters and implemented in two coal mines [20]. It was based on use of the waste product from fertilizers' industry – phosphogypsum. Later on the technique of radium removal from sulphate and radium rich waters was developed, patented and finally introduced in two collieries [15]. This method is based on continuous feeding of powdered barium chloride into treated water, which flows into sedimentation galleries, where barium and radium sulphate is deposited.

A specific type of wastewater are mine waters, for example barium and radium rich waters (it means waters containing Ba^{2+} ions, but no sulphate ions), occurring in some hard coal mines in Upper Silesia. They are heavily mineralized brines. The method for cleaning such waters was developed by Lebecka and co-workers [20]. It involved the feeding of gypsums to the waters for purification. Gypsum was slowly dissolved and the sulphate ions thus supplied reacted with the barium and radium ions present in the water, causing coprecipitation of radium and barium sulphate. Barium ion concentrations in these waters ranged from several dozen mg/L to 2 g/L, so it was quite sufficient to ensure the precipitation process. Waste gypsums such as phosphogypsums or gypsum from the mine water desalination plant were used for this purpose. The process was carried out in underground excavations of mines, and possibly supplemented in a settling pond on the surface. In some cases, a water flow through the phosphogypsum layer was used. The amount of gypsum (or phosphogypsum) needed to clean 1 m^3 of water was about 1 kg.

This method was implemented in full scale in two coal mines. In one of them, about 6.0 m^3/min of water was purified in which the initial concentration of radium (^{226}Ra) was approximately 20 kBq/m^3 and after the purification, the water discharged into the settling pond did not contain more than 0.3-0.4 kBq/m^3 of ^{226}Ra. In the second mine, the initial concentration of radium ^{226}Ra in water was of about 12 kBq/m^3, and after purification it was below 0.7 kBq/m^3. The amount of treated water was about 1.5 m^3/min. Radium waters from hard coal mines are characterized not only by the presence of radium ^{226}Ra but also ^{228}Ra. In the case of barium and radium rich waters, the ratio of concentration of ^{228}Ra is usually 0.5-0.8 in comparison with the concentration level of ^{226}Ra. In the case of sulphate and radium rich waters (it means containing no barium, but sulphates ions) the ratio of ^{228}Ra to ^{226}Ra activity can reach even value about 3. Then the critical problem was to bring down the total ^{226}Ra and ^{228}Ra concentrations below 0.7 kBq/m^3 in the purification process, which level was a permissible concentration due to legislation in this period.

The problems with the feeding of hygroscopic material enforced the investigations of other possible methods of radium removal from mine waters [27]. The use of zeolite material has been tested in surface installation in one of the collieries in the period 2015-2016, but results were not sufficient, mostly due to presence of mechanical suspension in treated waters. Therefore for treatment the mine waters the solution of barium chloride was finally chosen as the best, while zeolite beds can be used for treatment of drinking waters, spa waters etc.

The purification of radium from drinking water is usually carried out together with other water treatment processes, these processes are not particularly effective in removing radium, but generally allow the achievement of satisfactory results.
The following processes should be mentioned here:
- aeration (15-30% of radium removal efficiency),
- filtration and sedimentation (50% efficiency),
- iron and manganese removal (efficiency 10 to 85%),
- coagulation and sorption (80% efficiency),
- demineralization (high efficiency for some processes, exceeding 90%),
- reverse osmosis (efficiency of 96%),
- ion exchange (95% efficiency),
- softening (85% efficiency),

the use of acrylic fibers, impregnated with MnO2, (efficiency reaching 96%).

Particularly noteworthy was the method used by Friedman and coauthors [28] for treatment of mineral waters from radium using barite, applied in full scale in the health resort of Helein near Salzburg. The cleaning effect was satisfactory, a significant reduction in the concentration of radium was achieved while maintaining all the other parameters that determine the healing properties of mineral waters.

Problems with enhanced radium content in drinking water supplies may lead to formation of slags with enhanced radioactivity. It occurs in cases, when aeration is used to remove iron and manganese from water. In this way iron hydroxide and manganese dioxide are produces and radium isotopes are adsorbed on these materials. Afterwards, the disposal of slugs into the environment without any restrictions may be problematic.

3 Underground treatment installations in Polish collieries

The initial concept of radium-bearing waters treatment in collieries was based on the following assumptions:
- first of all, formation waters from the entire mine must be treated;
- then the water should be directed to the feeding station, where phosphogypsum or barium chloride will be added;
- after the chemical reaction of co-precipitation of radium and barium, the water will be directed to the system of sedimentary galleries or mined out zones, where sedimentation of radium-barium sulphate and the non-radioactive suspension will occur;
- from the sedimentation system, clarified waters will go to water galleries and pumping stations, and be pumped to the surface from there.

The treatment of sulphate and barium rich waters has been started in the Colliery A since 1999 and in the Colliery B since 2006. During this time, a lot of experience in the maintenance of the purification plant was gathered, which confirmed the previously formulated criteria for efficient functioning of the radium-bearing water treatment system. First of all, the assumption was made that the use of barium chloride and continuous feeding of the chemical would allow to achieve very good cleaning effects, especially if all waters, flowing to a particular horizon or to whole mine, are treated. It also turned out that as a result of the isolation of the mine area where the treatment is carried out, the radiation exposure of the mine crew can be kept at the low level (as before cleaning). It should be mentioned, that the Polish treatment installation was the first one worldwide, built in non-uranium mine [15].

In A Colliery, the radium-bearing water treatment system was constructed in the central part of the mine at the level of -650 m. The feeding station of the barium chloride was located in the intersection between the main roadways of the level. A gravitational inflow of water to the site from the western part of colliery was constructed. From the eastern part of the colliery, water was supplied via a pipeline from a pumping station, built specifically for this purpose. In the feeding chamber, a doubled barium chloride feeder was installed. The water to be treated was flowing in the sewage channel underneath and the barium chloride was feeding continuously with dosage 50 g/m^3. Special barriers were installed in the channel, increasing the turbulence of the flowing water, which ensured better conditions for mixing of the cleaning agent with water. The reason of such a construction was to accelerate the dissolution of barium chloride, and thus the subsequent reaction of the precipitation of barium and radium sulphate. From the channel, the water was gravitationally drained by a pipeline Ø 600 mm and a length of about 600 m to the sedimentation galleries, where the mechanical, non-radioactive suspension and sediments were deposited. These settling system consisted of five parallel galleries with a length of about 1050 m each, an average cross section of each gallery was approximately 18 m^2.
The sedimentation system was isolated from the remaining part of the mine, water dams were built to prevent the leakage of water from the system to other workings in this area.
During the first 4 years of operation (1999 - 2003), the radon water treatment system at level -650m was operating properly. Unfortunately, in the following years, there were problems with maintenance of the installation. These problems were solved on a regular basis, but caused temporary deterioration of the cleaning results. In 2007, the capacity of the system was so limited that only half of the water flowing in to the level of 650 m was flowing through the system. The operation of the purification system did not ensure the assumed parameters of removing radium from waters at level -650 m, despite the high costs and workload incurred by the mine, over its maintenance. Then the system was completely blocked (at the end of 2009) and for this reason it was necessary to improve the existing technology. In 2007, the reasons for blocking the system were identified: the pipeline discharging water from the feeding station was partially blocked. The reason for blocking was the improper constructional solution of the connection of downpipes with the pipeline leading to the insulating dam. This resulted in a blind end, where the accumulation of barium sulphate followed, resulting in the gradual scaling of the downpipes and finally the decrease in the flow. This problem was solved only in 2010, when the employees of the colliery disassembled the pipeline. After cleaning the pipes, the pipeline was reassembled and the radium water treatment system was put back into operation.

The experiments with the use of barium chloride solution for radium removal has been started in the year 2016 in Colliery A. The feeding station was designed and built at the level -500m to treat medium salty waters at that level. Preliminary results of the treatment were very good, described elsewhere [26]. Future treatment installations in other mines should be based on this technology.

The exploitation of the treatment installation in Colliery B has been started in the year 2006, at the -650m horizon. This was the second installation of this type in Polish coal mines, therefore the research plan and their scope, as well as the schedule for the implementation of the treatment technology was based on the experience acquired during the implementation of the method in the A Colliery. The start-up period lasted several months and confirmed very good results of water treatment. The calculations, carried out after a year of operation of the system, showed the following effects. The average concentration of radium ^{228}Ra in the water before purification was of about 5.5 kBq/m^3 while radium ^{226}Ra concentration was lower - 3.0 kBq/m^3. The measurements, done during the implementation showed that in the water discharged to the surface, the average concentrations of these isotopes were respectively 0.4 kBq/m^3 for ^{228}Ra while for ^{226}Ra approximately 0.2 kBq/m^3. Assuming that about 13,000 m^3 of saline water was discharged to the surface within 24 hours, the initial daily activity of radium isotopes in these waters was approximately 75 MBq for ^{228}Ra and almost 40 MBq for ^{226}Ra. After treatment, the radium isotopes activity in water decreases 10 times - down to only 6 MBq/day for ^{228}Ra and 3 MBq/day for ^{226}Ra. At the end of first year of exploitation of the installation discharge of radium isotopes was reduced by more than 100 MBq per day, or nearly 40 GBq per year.

As the part of the RATZEO [PBS/B2/14/2014] research project. investigations were conducted on the possibility of using a mixture of zeolites for the treatment of radium-bearing waters. These tests were performed in a pilot modular installation in which water was cleaned after sedimentation of the mechanical suspension in the surface settling. These studies have shown that the use of a zeolite deposit in underground excavations will be complicated due to the filling of the bed by a mechanical suspension and a gradual decrease in the purification efficiency.

The zeolite based installation was built on the surface in the vicinity of the settling pond of Colliery B in the year 2015 [see Fig.1.], preceded by long term laboratory experiments [29]. Results of laboratory investigations were very promising, the achieved radium removal efficiency was of about 95-98% for a mixture, containing only 10% of zeolite materials. The pilot tests lasted 15 months, from October 2015 till December 2016. In total, during the pilot tests about 1320 water samples were collected and tested, about 40 samples of zeolite mixtures were taken and measured before and after their use, environmental tests of possible changes in gamma background and doses received by employees were also conducted. Experimental research has shown that in installations for removing radium from mine waters it will be necessary to use a zeolite bed with a much higher content of zeolite mixture, at a level of at least 40% of the total mass of the deposit. For such a mixture the radium removal efficiency was at level 60-70%. Such a deposit should provide purification of underground water for several months. During this time the suspension in the treated waters would have a significant impact on decrease of adsorption and filtration efficiency. If the concentration of suspension at the inlet to the system will not exceed 10-15 mg/L, the system should work of about half of a year. Unfortunately, with the increase of the suspension content the possible time of effective removal of radium by zeolites would decrease significantly. The results of the field tests clearly show that the underground water should have to undergo the process of removing the mechanical suspension, before treatment in the radium removal system.

Fig.1. Surface installation for radium removal from brines

4 Summary

Water treatment technologies, aimed at removal of natural radionuclides (mostly radium), are applied in different industrial branches, not only in uranium mining.

One of the possible application is drinking water treatment in these countries, where limits of radionuclides concentrations are set – for example USA or European Union. Very important issue is not to worsen any other parameters of treated water.

Removal of radium from formation waters in oil and gas industries is important, especially when contamination of marine environment is possible, like at North Sea Norwegian or Brithish platforms.

It must be taken into account that any type of underground mining and processing of minerals may lead to realease of effluents with enhanced concentrations of natural radionuclides and often mitigation measures are necessary.

One of the examples of non-uranium industry, causing environmental pollution is Polish coal mining industry. In several collieries mitigation measures were applied to prevent the technical problems with dewatering systems exploitation and contamination of the environment.

Implementation of treatment technologies in active collieries proved, that the best method of radium removal from sulphate rich water is the use of barium chloride. Application of this technology will ensure the high efficiency of radium removal, excedeeing 90% in two installations in Polish collieries. Moreover, the use of barium chloride solution instead of powdered chemical is a way to full automation of the process, lower workload and much lower risk of contamination for the staff. Of course, the risk assessment and radiation hazard calculations must be done. In case of barium rich waters the cleaning agent must be a soluble sulphate chemical (gypsum, sodium sulphate) in amounts high enough to ensure complete removal of barium and co-precipitation of radium.

It can be seen, that for removal of radium isotopes from mine waters, specific methods must be applied, due to high salinity of brines and the presence of other contaminants. Therefore the chosen methods must be robust, applicable for treament huge volumes of water (up to few tens of m^3 per minute) and selective for removal just radium isotopes.

The research was partly supported by Polish Ministry of Higher Education, within a RATZEO project PBS2/B2/14/2014 - Opracowanie technologii oczyszczania wód kopalnianych z naturalnych nuklidów promieniotwórczych z wykorzystaniem materiałów zeolitowych. „The development of the technology for removal of natural radionuclides from mine waters with application of zeolite materials”

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