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Research paper

## Radium removal from mine waters with the application of barium chloride and zeolite: comparison of efficiency



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## ABSTRACT

In several coal mines in the Upper Silesian Coal Basin (USCB), in Poland, radium removal from mine water was necessary in order to mitigate the negative results of radium release with mine effluents. The most efficient method of radium removal was based on the application of barium chloride, implemented in full technical scale in two Polish collieries. Removal efficiency exceeding 95% of the initial activity was achieved. The technology was implemented in full technical scale in two collieries. The problem was that barium chloride is dangerous to health and moreover continuous use of the powdered chemical was required to achieve good results. Therefore, the possible application of zeolite for radium removal was tested in laboratory experiments. This passive technique would be less hazardous for miners and would not require full-time supervision meaning it would enable a reduction in workload. The main goal of the investigations described in this paper was to check the capability of zeolites to remove natural radionuclides from mine waters and compare the removal efficiency of radium isotopes with the results obtained from the application of barium chloride solution for the same purpose.

## 1. Introduction

For many years, numerous methods for pollutant removal from waste water have been used in different branches of industry (Doula, 2009; Fu & Wang, 2011; Gaikwad & Gupta, 2008). Often these pollutants consist of heavy metals or radioactive nuclides (Franus, Wdowin, Bandura, & Franus, 2015). The removal of such pollutants is usually based on: co-precipitation with specific carriers, filtration of the waste water through filters or barriers which are made out of the materials with desired properties, adsorption on sorbents, the use of ion exchange resins etc. Many different studies on the technologies and techniques mentioned above have demonstrated their effectiveness in reducing the concentrations of contaminants, such as heavy metals, anions and organic matter in water. However, research emphasise that the complexity of aquatic systems demands special attention in the selection and preparation of materials for water purification (Gaikwad & Gupta, 2008; Karmen, Zabukovec Logar, Šiljeg, & Farkas, 2013). According to Fu and Wang (2011), chemical precipitation is an effective, relatively simple and inexpensive method and is widely used in the industry. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates that may be separated from the water by sedimentation or filtration. For the removal of radionuclides from water in special installations, a gypsum (Feng, Aldrich, & Tan, 2000) or

phosphogypsum (Lebecka et al., 1994) can be applied, but the sedimentation of the fine crystals of precipitates usually requires a long period of time, even several days. In Poland, for example, investigations were conducted with mine water of enhanced radium content (Chałupnik & Wysocka, 2000), but such a process could be applied for any brines, contaminated with heavy metals and radium isotopes. Another mineral adsorbent which is used on a small scale in Polish collieries for radium removal was a barite (barium sulphate). The efficiency of implemented technologies for radium removal from coal mines, achieved during routine work of underground treatment installations was high, usually exceeding 90% (Chałupnik & Wysocka, 2000, 2008).

Over recent years, numerous papers, describing theoretical simulations, laboratory experiments and pilot tests, focused on the application of natural and synthetic zeolite materials for the removal of different pollutants from waste waters, drinking waters or liquid waste. Zeolites are aluminosilicate minerals which have a porous structure that reveals different properties such as sorption, ion exchange possibilities, the ability to act as molecular-sieves and catalytic abilities (Franus et al., 2015; Franus & Wdowin, 2010). Due to these properties, they are used in many branches of industry, such as: agriculture, medicine, chemical technology, environmental protection and engineering (Czurda & Haus, 2002; Doula, 2009; Franczyk & Garbulewski, 2013; Franus, 2012;

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Misaelides, 2011; Perego, Bagatin, Tagliabue, & Vignola, 2013; Yu, Han, & He, 2017). Zeolites are used, among others, to remove heavy metals (Tao et al., 2010) and natural and artificial radionuclides from waste waters, because they have the ability to capture a large number of different ions, including radionuclides, such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  (Stefanowa, 1999) or radium  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  (Chałupnik et al., 2013). The idea of the application of a zeolite based passive barrier for radium removal is particularly encouraging due to workload reduction and the limitation of radioactivity in wastes.

It is well known that the mining and processing of uranium ore leads to the release of waste water containing elevated levels of natural radionuclides. There are many reports about the application of the barium chloride precipitation process to treat acidic uranium industrial effluents (IAEA, 1976; IAEA-TECDOC-1419, 2004). Waste water from the processing of uranium is purified generally by means of an aqueous solution of barium chloride (Averill, Moffett, Webber, Whittle, & Wood, 1982; Huck, Anderson, & Andrews, 1985; Hynes, Meadley, & Thompson, 1985). It is one of the classic methods, used extensively in the uranium industry (Moffett & Barnes, 1974).

The technology of radium removal from underground brines with the application of barium chloride was implemented in two collieries in Poland several years ago (Chałupnik & Wysocka, 2008) with excellent results. For this purpose, powdered barium chloride was fed into the gutters which convey brines. Unfortunately, the feeding of the chemical agent must be done continuously as it was found to be impossible to make the feeding automatic. Therefore, the staff must maintain and supervise such installations continuously which means that they are consistently being exposed to poisoning. Consequently, the use of protective filter masks became necessary. Recently, the idea of using a barium chloride water solution was developed, enabling the fully automation of the process.

In this paper, we examine the efficiency of the employment of both methods (using zeolites and barium chloride), in the treatment of mine waters contaminated with radium isotopes. Under laboratory conditions, we have: i) tested the efficiency of both radium removal techniques, ii) assessed the influence of the contact time of water with zeolite on the removal efficiency, iii) assessed the effectiveness of different types of zeolite materials for the optimization of zeolite bed composition and, finally, iv) investigated the possibility of applying both methods in underground galleries of operating coal mines.

## 2. Materials and methods

### 2.1. Water samples for laboratory experiments

The first step of the project was the collection of mine waters for laboratory experiments. Three 100 L samples of brines were collected from two collieries. Two samples revealed mineralization (Total Dissolved Solids, TDS) exceeding 100 g/L, in one sample TDS was of about 45 g/L. In all samples concentrations of radium isotopes were enhanced. The samples contained a suspended matter, including coal and rock small particles of up to 30–40 mg/L, causing some problem with filtration through zeolite beds.

### 2.2. Zeolite materials

Two different zeolite materials were prepared for the experiments: natural zeolite – clinoptilolite, and synthetic zeolite – NaP1. Clinoptilolite is mined commercially in many parts of the world, for instance in Ukraine in Sokyrnytsia, which is in the Zakarpattia region (Shadrikov & Petukhov, 2014), in the Slovak Republic in Nizný Hrabovec (Macala & Pandova, 2007), and in Poland in Flysh Carpathian (Franus & Dudek, 1999). Clinoptilolite is a natural mineral that belongs to the class of microporous aluminosilicates which contain the exchange of metal cations and water molecules in their internal crystal-line lattice. Zeolites of this class are based on an open tetrahedral cage,

with a system of channels whose size is determined by the content of silicon. The cage of the structure is formed with a network of eight-membered and ten-membered rings. The clinoptilolite from Sokyrnytsia, Ukraine was used in our experiments and had an average diameter of mezzo-pores of 3.8 nm.

The synthetic NaP1 zeolite was prepared by using the conversion reaction of fly ash obtained during a hydrothermal reaction with sodium hydroxide. The NaP1 pore size distribution indicates the dominance of pores with a size of approximately 3.8 nm. The average pore diameter is approximately 9.0 nm (Adamczyk & Białecka, 2005; Bandura, Franus, Józefaciak & Franus, 2015; Franus, 2012; Franus, Wdowin, & Franus, 2014; Somerville, Blissett, Rowson, & Blackburn, 2013).

### 2.3. The barium chloride solutions

For the experiments 1 N and 0.1 N solutions of barium chloride were prepared. The aliquots of these solutions were mixed with treated water and shaken for 1 h. The reaction of barium with sulphate ions is immediate, but the settling of fine crystals of barium sulphate is a longer process (12 h).

### 2.4. Laboratory experiments and radium measurements

Several series of experiments of water purification with the use of synthetic and natural zeolites were performed. The contact time varied from 15 to 60 min. In experiments with brine samples, two different contact times were applied, these being one hour and six hours.

For the measurements of radium in water samples the radiochemical method was applied, based on the co-precipitation of radium isotopes with a barium carrier. The resulting precipitate is mixed with the gel scintillation cocktail InstaGel™ (PerkinElmer). The samples were measured in the Quantulus™ (Wallac PerkinElmer) low level liquid scintillation spectrometer. This method enables the simultaneous measurement of two radium isotopes  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ . The detection limits were very low: 0.002 kBq/m<sup>3</sup> in the case of  $^{226}\text{Ra}$  and 0.020 kBq/m<sup>3</sup> for  $^{228}\text{Ra}$ , when the initial sample volume was 1 L and the counting time was 1 h (Chałupnik & Lebecka, 1993).

The measurement of the radioactivity of zeolite prior to and after experiments was carried out with the application of low background gamma spectrometry. Samples were dried and then transferred to 0.6 L Marinelli beakers and measured within 24 h. The detection limit for gamma emitting radionuclides was below 1 Bq/kg.

The quality control of experiments was based on the application of certified materials for calibration – standard solutions for radium isotopes (liquid scintillation spectrometry) and reference materials for gamma spectrometry. Both methods were certified and accredited by the Polish Centre for Accreditation (PCA).

## 3. Results

### 3.1. The results of laboratory experiments of radium removal from mine waters with the application of zeolites

#### 3.1.1. Synthetic zeolite testing

The first stage of laboratory experiments was aimed at investigating the efficiency of radium removal by synthetic zeolites. Artificial zeolites NaP1 from the Technical University in Lublin, Poland were used for this purpose (see Fig. 1).

The preliminary laboratory experiments were performed in the manner described below. The chosen amount of the zeolite (2 kg) was mixed with sand and gravel (18 kg), which were added to increase the permeability of the sample. The mixture, made up of 10% zeolite and 90% sand and gravel, was placed in a column with a total volume of 60 L. The 30 L water sample was poured gently into the column. This water sample, collected in colliery A, revealed a pH value 6.8, salinity

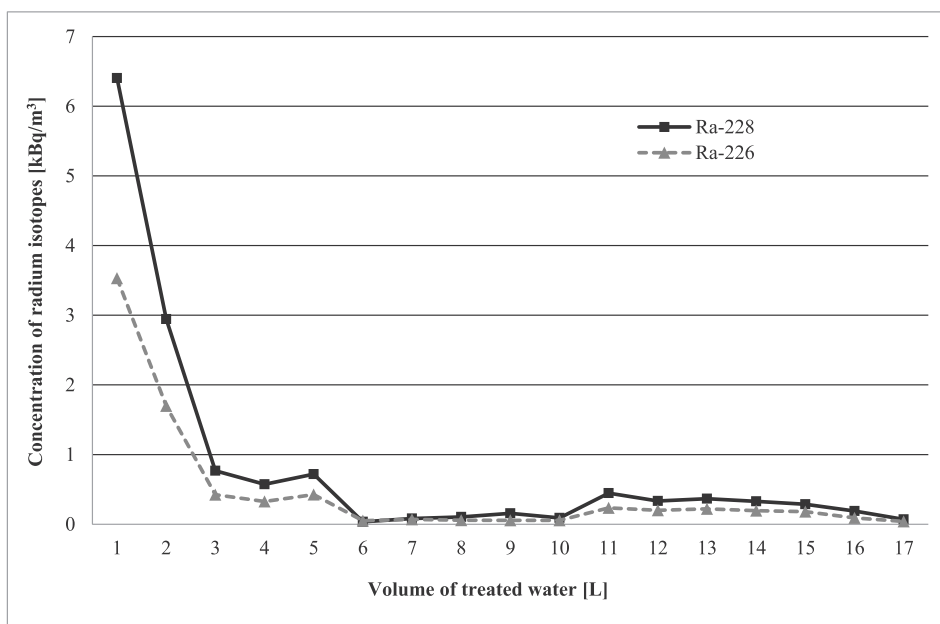


Fig. 1. Results of radium removal from the A colliery brine treated with the use of synthetic zeolite.

of about 45 g/L, and radium concentration of 3.6 Bq/L in the case of  $^{226}\text{Ra}$  and 6.4 Bq/L for  $^{228}\text{Ra}$ . Opening the valve at the bottom of the column allowed the filtration of the water sample through the bed and the removal of radionuclides and some stable elements by sorption on the zeolite. At the outflow aliquots of the volume of 1–1.5 L were collected and analysed. Sixteen samples were collected in this way (see Fig. 1). The estimated contact time was approximately 0.5 h at the beginning of the experiment and this increased up to 40 min.

It can be seen that the initial concentration of radium isotopes, equal to approximately 10.0 Bq/L decreased with time to 0.1 Bq/L, therefore the maximum removal efficiency was roughly 99% and the average radium removal efficiency exceeded 90%.

### 3.1.2. Experiments with natural zeolite

During the second stage of investigations the installation for laboratory experiments was modified in order to test natural zeolite – clinoptilolite. Small columns with a total volume of 0.8 L were used. There were loaded with 0.5 kg of the zeolite and gravel mixture, which had the same ratio of natural zeolite to gravel, i.e. 1:9. Again, water from colliery A was filtrated through the columns and 1 L aliquots of water were collected in order to measure the radium isotopes' concentration. The results are presented below (see Fig. 2).

In this case, a significant decrease in radium removal efficiency with the increase of the volume of treated water can be observed. Initially, the removal efficiency was approximately 99%, but after the treatment of about 30 L of water it decreased to just 40%. The decrease in radium concentration to values below LLD at the end was due to the use of deionized water to check the possibility of radium leaching from zeolite (not observed).

It was found that synthetic zeolite has much better adsorption efficiency in comparison with natural zeolite. This value for the synthetic zeolite was found to be at least ten times higher than for the natural zeolites, therefore the results agree with previous studies, which report the higher adsorption capacity of synthetic zeolite (Inglezakis, Loizidou, & Grigoropoulou, 2004). Unfortunately, synthetic zeolite is more expensive. Therefore, due to economic reasons, it was decided to apply mixtures of natural and synthetic zeolites in further experiments.

### 3.1.3. Radium removal with the use of the mixture of natural and synthetic zeolites

Due to the aforementioned reasons, during the third stage of

experiments mixtures of natural and synthetic zeolite materials were tested (Fig. 3). Due to the limitation of brine volumes, for these experiments the brine from colliery B was used, which had pH = 6.6, salinity 110 g/L, radium concentrations equal to 5.1 Bq/L for  $^{226}\text{Ra}$  and 8.0 Bq/L for  $^{228}\text{Ra}$ . Two different types of zeolite mixtures were used. The first type contained 10% of NaP1 zeolite and 90% of clinoptilolite, while the second consisted of 30% of artificial zeolite and 70% of the natural one. We found very similar results of the removal effects for both mixtures; the absorption efficiency exceeded 98% for the total water volume of 50 L in each experiment. Due to their similarity, just one series of the results of measurements is presented in Fig. 3.

The mass of the bed was approximately 500 g, of this 10% or 30% was a zeolite material mixture (50 or 150 g), thus the mass of NaP1 zeolite was 5 or 15 g only. The average contact time was 0.5 h, having the tendency to increase with time.

### 3.1.4. Discussion of the results of laboratory experiments with the use of zeolites

The laboratory experiments, performed over three stages of laboratory tests, confirmed the possibility of zeolite's application for the removal of radium from mine water.

During experiments with synthetic zeolite NaP1, it was observed that the efficiency of radium removal was high, exceeding 95–98%. The problem that emerged was the fast clogging of the bed, which was caused by the small size of the NaP1 grains (below 0.2 mm).

Results of experiments with the pure natural zeolite – clinoptilolite – clearly demonstrated that this material was not effective for water with enhanced content of suspended matter (within the range of 30–40 mg/L). The decrease in removal efficiency took place due to the settling of solid particles in the zeolite's bed. The efficiency of radium removal from water exceeded 90% initially, while at the end of the experiment the removal efficiency was just 40%. Mixed zeolite bed experiments showed that even an admixture of 10% of the artificial zeolite NaP1 increased the removal efficiency by a factor of 2, at least. The removal efficiency was found to be at the level of 98–99% for all mixtures of clinoptilolite and NaP1 zeolites. Moreover, no significant decrease in the efficiency (only 1–2%) was observed for a large volume (50 L) of treated water. This confirmed the high sorption capability of the mixture of zeolites.

The most important outcome of these experiments is that the adsorption capability of artificial zeolite is at least one order of magnitude

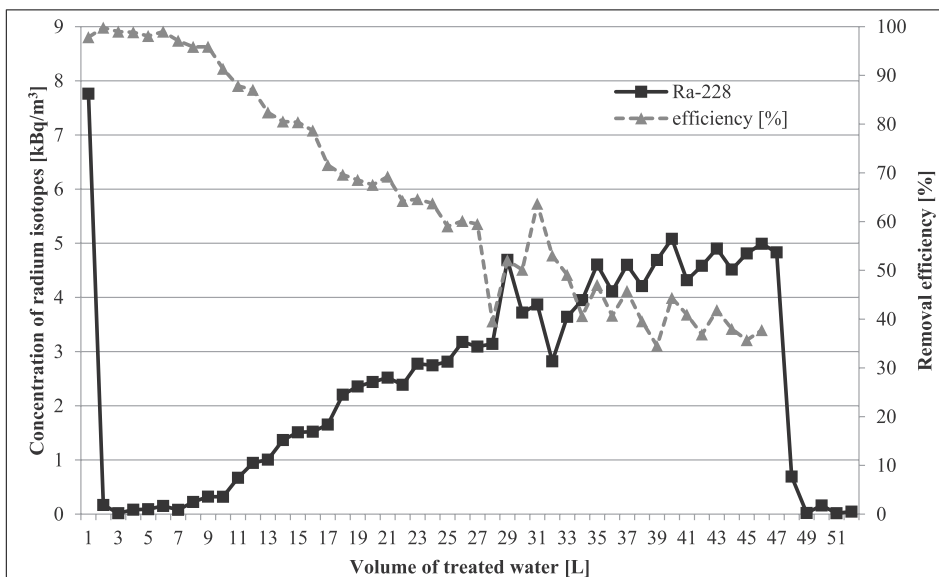


Fig. 2. Removal efficiency for a brine treated with the use of natural zeolite.

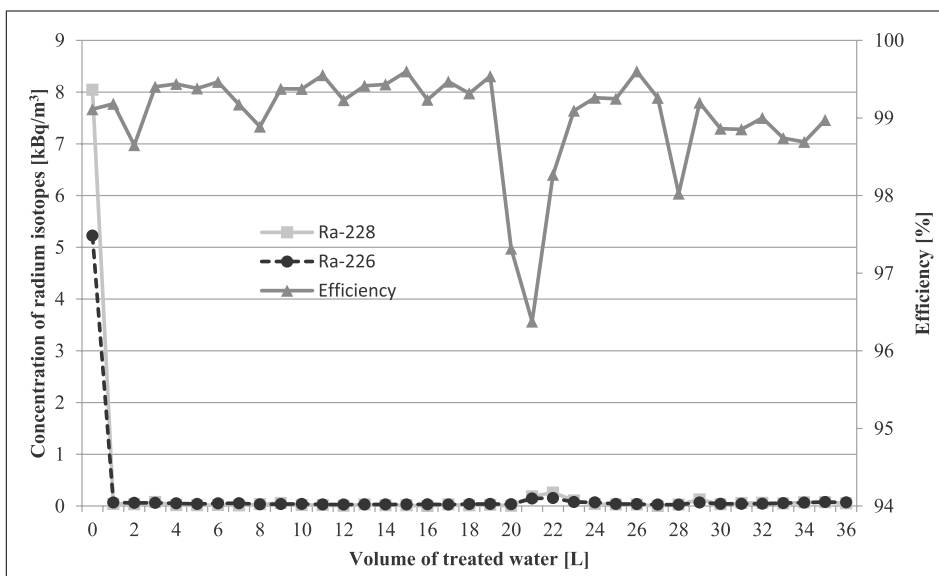


Fig. 3. Results of treatment with the application of the mixture of synthetic and natural zeolite (1:9 mass ratio).

higher than the natural one – clinoptilolite. On the other hand, the price of the artificial zeolite is much higher than the natural one. Several mixtures of natural and artificial zeolites were tested, which significantly improve radium removal. For further experiments and field application a mixture of optimal zeolite composition (90% natural zeolite and 10% artificial) was prepared. One of the most important goals of the investigations was to provide a laboratory basis for pilot tests in collieries.

The mine waters used in the experiments contained two other elements with a similar radius to Ra, these being Sr (50 mg/L) and Ba (0.05 mg/L). If <sup>226</sup>Ra activity concentration is recalculated into mass concentration the result is 0.0002 ng/L. Water treatment did not change the strontium concentration, but the barium level increased to 0.1 mg/L, while a significant decrease in radium concentration (95–98%) was observed. Thus, the removal efficiency of strontium and barium ions (despite similar radius and high concentration) was not effective.

Determination of the main ions (e.g. Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2+</sup>, Cl<sup>-</sup>) and heavy metals (Zn, Hg, Fe, Ni etc.) in the studied waters did not reveal any change in concentration during the treatment with the

zeolites. This is a surprising effect and confirms that the zeolite material is very selective for radium ions in brines. The results of the gamma spectrometric analyses of zeolite beds after sorption showed a high content of radium isotopes, reaching 1–2 kBq/kg, which confirms high selectivity and effectiveness in relation to radium ions, as was expected.

### 3.2. Radium removal from mine waters with the application of barium chloride solutions

The same water samples which were collected in two collieries were used for radium removal experiments using a barium chloride solution. The experiments were performed in the following way: the chosen amount of 1 N barium chloride solution (varying from 0.1 up to 0.8 ml) was added to the sample aliquot of a volume 0.5 L. For each batch of samples at least two parallel series was made, with different conditioning time (from 1 to 6 h) after the barium chloride solution was added. Finally, the samples were filtrated to separate the precipitate of barium and radium. Afterwards, radiochemical analysis was performed to determine the remaining ionic fraction of radium isotopes in the

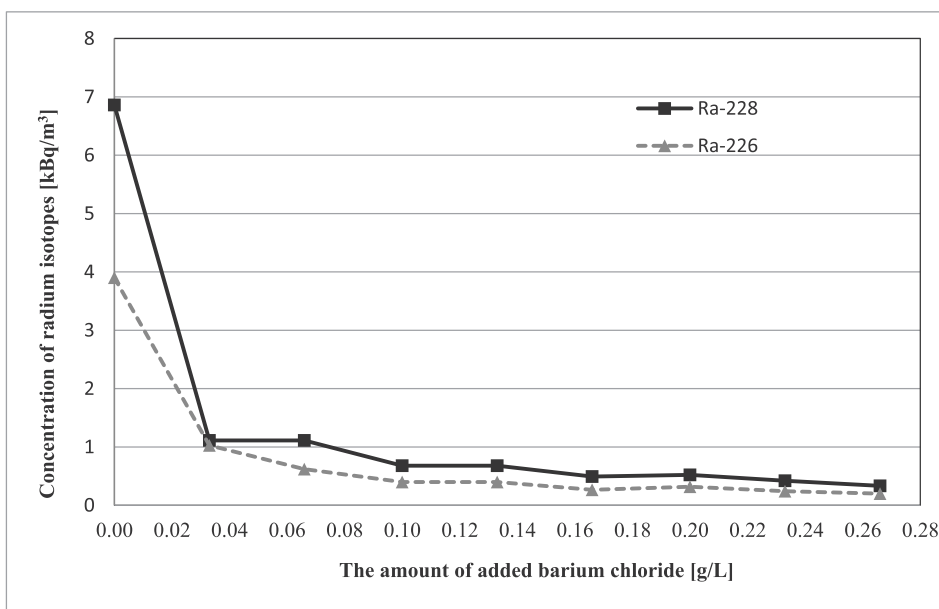


Fig. 4. Results of radium removal from colliery A brine. The contact time of barium chloride and the treated water was 1 h.

sample(s). A sample of raw, untreated brine was analysed within each batch to assess the removal efficiency.

Results of the investigations were analysed to find the correlation between the treatment effects of radium removal from mine waters and the level of salinity and radium content, as described below. Exemplary results for particular batches are shown in Figs. 4–7.

3.2.1. Experiments of radium removal from a brine

One of the brine samples was collected at the depth of 650 m in colliery A. The salinity of the brine exceeded 100 g/L, while the contents of radium isotopes were as follows: 6.96 kBq/m³ for <sup>228</sup>Ra and 3.95 kBq/m³ for <sup>226</sup>Ra. Two parallel series of radium removal experiments were performed, for the contact time 1 and 6 h and 1N BaCl<sub>2</sub> solution volume, increasing from 0.1 mL to 0.8 mL. A longer period of contact time was applied to check the contribution of small particles in the total mass of the precipitate. This experiment was repeated twice to check the accuracy of the results. Results of the experiments are shown in Figs. 4 and 5 and it can be clearly seen that the removal efficiency

was higher than 90%.

3.2.2. Radium removal from a brine – repetition

In the case of colliery B, brines from two horizons were sampled. At the deeper horizon (–650 m) the salinity (TDS value) of the brine was roughly 110 g/L, while radium concentrations were slightly higher, reaching 7.85 kBq/m³ for <sup>228</sup>Ra and 4.15 kBq/m³ for <sup>226</sup>Ra. Conditions for the experiments were the same as before. The results of the experiments were similar to those from mine A, therefore no graphic presentation is provided in this paper. The removal efficiency of radium was higher than 90%, in the case of a feeding ratio of 30 mg of barium chloride per one litre of the sample.

3.2.3. Radium removal from salty mine water

In the case of a water sample from another horizon (–500 m) from mine B, of lower salinity 45 g/L and lower radium concentrations (3.28 kBq/m³ of <sup>228</sup>Ra and 1.83 kBq/m³ of <sup>226</sup>Ra). It was necessary to extend the feeding ratio of barium chloride towards lower values, below

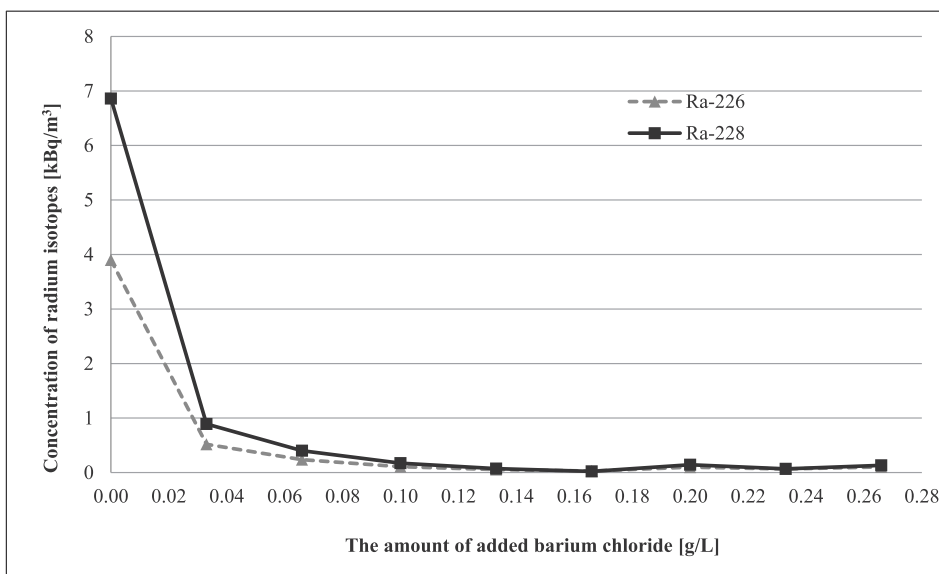


Fig. 5. Results of radium removal from colliery A brine. The contact time of barium chloride and the treated water was 6 h.

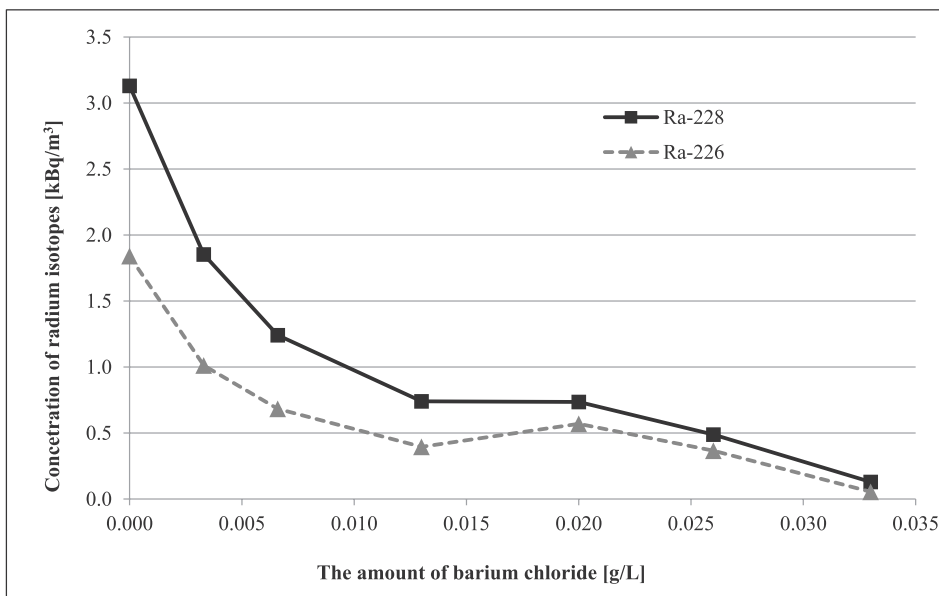


Fig. 6. Results of radium removal from colliery B brine. The contact time of barium chloride and treated water was 6 h.

0.1 mL per sample of 1N BaCl<sub>2</sub>. Therefore, it was necessary to diminish the feeding ratio of barium chloride and the 0.1N BaCl<sub>2</sub> solution was used.

In Fig. 6 the results of treatment with a low amount of barium chloride are given for the contact time of 6 h. It can be seen that even for the feeding ratio of 3 mg of barium chloride per litre of sample the removal efficiency was still high – it was estimated to be at least 40%.

The experimental data for the extended ratio of barium chloride feeding into treated water are shown in Fig. 7. It can be seen that removal efficiency exceeding 95% was estimated for the feeding ratio of 70 mg/L of barium chloride (of about 200 mL/L of 30% barium chloride solution).

#### 4. Discussion of the results of the laboratory experiments with the use of barium chloride

To date the technique of radium removal from brines in two

collieries (Chałupnik & Wysocka, 2008) was based on the application of powdered barium chloride. The use of a barium chloride solution requires a complete change to the existing installation, therefore laboratory tests are necessary. The results of the application of the barium chloride solution as the agent for radium removal were promising, as can be seen from the information presented above. The application of barium chloride as the cleaning agent in the form of a solution would allow the full automation of feeding and the remote control of the process, with no need for supervision and maintenance to be performed by the staff. We found that the removal efficiency should exceed 90%, as in existing underground installation.

Our experiments confirmed that the construction of the underground pilot installation at –500 m horizon in colliery B is expedient and it seems that it will work efficiently.

The next step of our investigation should be the design and construction of an underground treatment installation.

Our previous experiences suggested that the results of laboratory

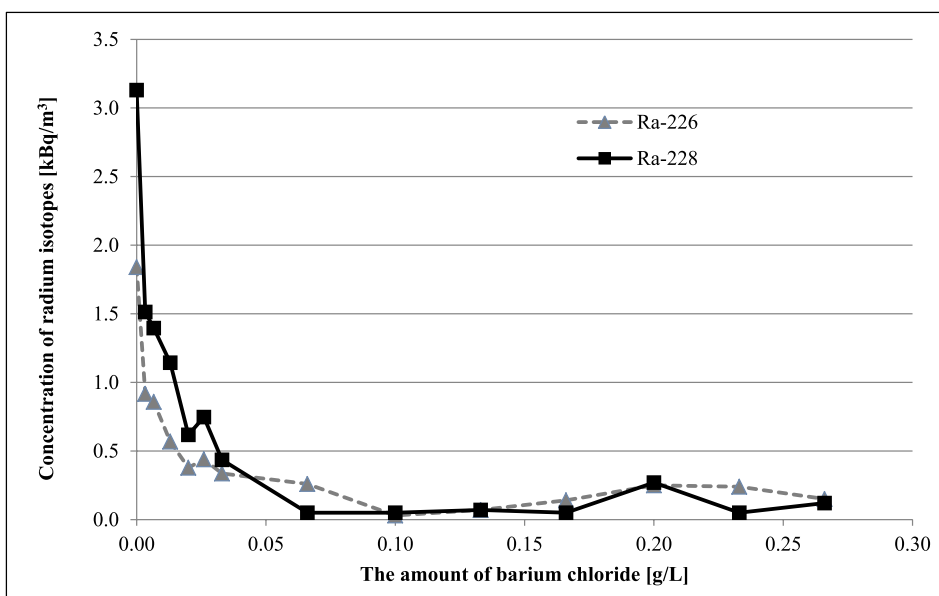


Fig. 7. Results of radium removal from colliery B brine. The contact time of barium chloride and treated water was 6 h, while the feeding ratio was from 1 mg/L up to 270 mg/L.

tests showed higher removal efficiency than those after implementation in real mines (Chałupnik & Wysocka, 2008). Therefore, further experiments should be performed in underground galleries, at the pilot installation.

It is necessary to highlight that no worsening of the mine water quality due to the radium removal was observed. Chemical analyses of raw and treated water showed that changes of the water chemical composition after the feeding of barium chloride is negligible. The only effect is an insignificant increase in chloride ion concentration and a decrease in sulphate ion content (at a level of 50 mg/L).

## 5. Conclusions

The investigations to compare two methods of radium removal from mine waters were performed under laboratory conditions. The first method was based on the application of zeolite, a solution promising better safety for the miners and lower radioactivity of waste materials. The second method is based on the use of a barium chloride solution, while this method is more selective towards the removal of radium isotopes, it also requires the continuous feeding of the solution into treated water and more stringent maintenance of the process. It was not possible to compare these two methods precisely, as zeolite experiments were performed as column ones, while barium chloride experiments were batch ones. Nonetheless, it was very important to estimate radium removal efficiency from different brines which were collected in several collieries. Therefore, we decided to compare two not fully compatible techniques.

The results of the laboratory experiments of the application of zeolite and barium chloride confirm the high ability of radium removal from mine waters for both methods. The biggest advantage is the high selectivity of the described methods, in most of the experiments the reduction factor for radium exceeded 90% of the initial concentrations. Concentrations of other ions were not affected by the water treatment. Laboratory experiments showed that no main component ions were removed from brines, the same pattern was found for trace elements, i.e. heavy metals.

### 5.1. Application of zeolite

The important findings of zeolite application for the radium removal from mine waters were:

- The content of mineral particles in the treated water is a crucial issue for its possible application in collieries: if the concentration of suspension exceeds 20–30 mg/L it would cause a decrease of purification efficiency.
- The mixture used for the barriers (beds) must be permeable enough to allow all treated water to flow through the barrier, but not too permeable so as to provide sufficient contact time. In our experiments the contact time was at least 45 min. The mixture must contain both artificial and natural zeolites, the former is to improve the efficiency and capability of the barrier, the latter is to keep the costs of treatment at a reasonable level.

### 5.2. Application of barium chloride in the form of a solution

The important results of the application of barium chloride solution for the radium removal from mine waters were:

- The method provides very good results of radium removal efficiency, exceeding 90–95%.
- Application of the barium chloride solution increases the safety of the staff dealing with the chemicals and decreases the possibility of the casual contamination of miners.

The comparison of the two possible methods of radium removal

from mine waters leads to the following constraints of their applications:

- The application of zeolite material may be difficult in active mine due to the problem with the elevated content of mechanical suspension in the water. It would lead to the clogging of the system and would cancel out the biggest advantage of the method – the fact that the method is passive and does not require maintenance for long periods.
- In the case of the barium chloride solution, the biggest disadvantage is the need of continuously feeding the barium chloride into water, although the use of the solution would enable fully automatic feeding and remote control of the process.

## Conflicts of interest

None declared.

## Ethical statement

Authors state that the research was conducted according to ethical standards.

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and Development of the natural radionuclides removal technology with application of zeolite materials “RATZEO”, PBS2/B2/14/2014, The National Centre for Research and Development.

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