

# Application of zeolites for radium removal from mine water

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Received: 7 February 2013 / Accepted: 28 May 2013 / Published online: 24 July 2013  
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**Abstract** For removal of radium from saline waters in Upper Silesian mines, several methods of purification have been developed. The most efficient one is based on application of barium chloride, which was implemented in full technical scale in two Polish coal mines several years ago. Very good results of purification have been achieved—the removal efficiency exceeding 95 % of the initial activity. Another possibility for the removal of different ions from salty waters and brines is the application of zeolites. We found that technique as a very promising method for removal of not only radium isotopes from mine waters but also other ions (barium, iron, manganese). Treatment of several various water samples has been done to assess the removal efficiency for natural radionuclides. Preliminary results show very good effects for radium isotopes as well as for barium ions. In the paper, a short description of laboratory results of the purification of mine waters with application of synthetic zeolites is presented.

**Keywords** Natural radioactivity · Radium · Radioactive waters · Brines · Coal mines · Purification · Zeolites

## Introduction

The Upper Silesian Coal Basin (USCB) is located in the southwestern part of Poland (Fig. 1). Presently, Silesian underground coal mines extract about 90 million tons of coal

per year. The depth of mine workings is from 350 to 1,100 m. The geological structure of the Upper Silesian Coal Basin is very complicated and differentiated with numerous faults and other tectonic dislocations. The mining activity is causing destruction of the strata, leading to the increase of permeability. Two hydrological regions of the Coal Basin are recognized. The first region is located in southern and western Silesia, where there are thick strata of sediments covering carboniferous formation. The cover of up to 700 m is built mainly by Miocene clays and silts. Such strata restrict migration of water and gases. In the second region located in the northern and eastern part, Miocene deposits do not occur. Carboniferous strata are covered either by slightly compacted Quaternary sediments or numerous outcrops of coal seams. The oldest formations of this area comprise strongly fissured and isolated sediments of Permian or Triassic limestone. These formations enable very easy migration of water and gases (Rózkowski 1978).

Underground coal exploitation in Upper Silesia is a source of an additional and unexpected contaminant of the natural environment—radioactivity. In many coal mines, located in USCB, waters with enhanced radium content occur (Tomza and Lebecka 1981). Sometimes in radium-bearing brines, barium ions of concentrations up to 2 g/l are also present. Such waters—not often met in nature—are classified as radium-bearing type A waters. In the so-called type B waters, barium ions do not occur, but there are  $\text{SO}_4^{-2}$  ions (<5 g/l). The presence of barium ( $\text{Ba}^{2+}$ ) in the waters is the most important factor for the further behavior of radium isotopes in mine galleries or on the surface. From type A waters, radium and barium always co-precipitate as sulfates, when mixed with any water containing sulfate ions. As a result of the precipitation, barium sulfate deposits with highly enhanced radium concentrations are formed (Lebecka et al. 1985; Lebecka et al. 1994; Michalik et al. 2002; Chałupnik and Wysocka 2009). The total activity of radium isotopes in these sediments may sometimes reach

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Responsible Editor: Philippe Garrigues.

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**Fig. 1** Location of Upper Silesian Coal Basin

400 kBq/kg, while the average radium content in soil is 25 Bq/kg (UNSCEAR 2000). Due to the lack of barium carrier in radium-bearing type B waters, precipitation does not occur. It is the reason why the increase of radium content in sediments is much lower than the ones which originated from type A waters.

In the last decade, the decrease of radium activity in discharged underground waters is mainly due to the purification of B-type brines in Piast Colliery which started in 1999 and the construction of another treatment station in Ziemowit mine in 2006. In Piast mine, the implementation of the treatment technology on deeper horizons in the mine caused the decrease of radium release from the mine to the level of 150 MBq/day to 60 MBq/day of  $^{226}\text{Ra}$  and 90 MBq/day of  $^{228}\text{Ra}$  (Chałupnik and Wysocka 2008). Similar results have been achieved in the second underground coal mine, Ziemowit. Additionally, the purification system for the second horizon of Piast mine is under design, and it is expected to solve most of the problems with radium contamination of river waters in that part of the Upper Silesia region. The process of water treatment is based on the dissolution of barium chloride and immediate co-precipitation of barium and radium ions as sulfates. This reaction is possible due to the surplus of sulfate ions present in brines in concentrations 30–50 times higher than required for stoichiometric reaction. The only problem is due to chemical properties of barium chloride. This chemical is potentially dangerous for miners. It is hygroscopic, causing technical problems during feeding in a very humid mine atmosphere. Therefore, another option has been tested: the application of zeolites for removal of radium isotopes and some heavy metals from mine waters and drinking waters. The results seem to be very promising.

#### Different techniques of water treatment

Water treatment technologies for removal of natural radionuclides (radium) have been developed at first for the uranium mining and milling industry (Nixon et al. 1983). This problem is well known since for many years, it was a very important issue to diminish the environmental pollution caused by the uranium industry. Usually, treatment techniques are based on the application of barium chloride, which is added as a carrier for further radium co-precipitation as sulfate (Gordon and Lowley 1957). The radioactive suspension is removed in sand filters or other mechanical ones (Ring et al. 1982; Hynes et al. 1985). Very common is also the application of cheaper methods like bioremediation (Luan et al. 2012), but the removal efficiency for such a solution is often unstable and dependent on different factors, such as atmospheric conditions (Groudev et al. 2008). Methods for treatment of effluents from the uranium industry are under continuous improvements; a lot of experiments are performed to test new and sometimes rather expensive techniques, like titanate nanofibers (Yang et al. 2008). This material can be used for the removal of radium, strontium, barium, and lead radionuclides from wastewater, being a potential adsorbent not only in the uranium industry.

Water treatment for removal of pollutants and radioactivity is often necessary for drinking water supplies, especially from underground aquifers. In different countries, like Finland, Sweden, or Austria, this problem is so important that a lot of investigations have been done to solve it (Annamäki and Turtiainen 2000). In some of these waters, radium and uranium are present together, becoming a potential threat for the local communities (Drinking Water Directive 1998; Stehlik and Friedmann 1989). In the USA, the Environmental Protection Agency enforced regulations concerning maximum radium concentration in drinking water (CFR40 2000); therefore, treatment technologies had to be applied for water supplies throughout the country. Drinking water treatment is done usually with the application of aeration. Mn- and Fe-oxyhydrates, the byproduct from treatment processes, are excellent scavengers for radium isotopes (Annamäki and Turtiainen 2000). Other methods of drinking water treatment involve ion exchange resins by adsorption on special filters with manganese dioxide, with application of reverse osmosis or polymeric columns. Radium ions are being removed during this process (Miro et al. 2008; Baeza et al. 2012; Deng 2005). An application of zeolite for removal of radionuclides from drinking water has been reported by scientists from Estonia (Lumiste et al. 2012).

In non-uranium industries, like coal mining, radium removal from mine water is not very common (Patent 1996; Chałupnik and Wysocka 2008). It may be important in oil and gas exploitation but mostly due to the technical problem with scaling of pipelines; therefore, removal of radium

(together with non-radioactive barium and strontium) is done (Abo-Elmagd et al. 2010), or just the opposite—special chemicals are used to prevent this process (Varskog et al. 2004). In mining industries, special features of mine water must be taken into account when investigations or development of treatment technologies are performed. A very important issue is the high salinity of brines, reaching or even exceeding 100 g/l (Lebecka et al. 1992). Another problem is related with the volume of water required for purification. In some Polish coal mines, the outflow from a single horizon in the mine may reach 15–20 m<sup>3</sup> per minute (roughly 30,000 m<sup>3</sup> per day). Additionally, the treatment should be done in underground galleries to prevent pollution of the natural environment, even at the settling ponds on the land surface. Due to these circumstances, costs of the treatment installations are high; for instance, the cost of construction of the treatment station in one of the coal mines was as high as 5 million euro. Moreover, the application of barium chloride (a very poisonous material) and the need of continuous feeding of the reagent into the treated water (up to 1,000 kg per day) make the exploitation of the treatment station expensive.

A possible solution for a passive technology might be the application of zeolite materials (natural and synthetic ones) for the removal of not only radium but also some other pollutants from mine water. Application of zeolites is expected to be significantly cheaper than the methods used so far; however, a detailed financial study has to be done in the future. Zeolites have been applied for removal of heavy metals from groundwater (Lumiste et al. 2012) and similar pollutants from different wastewaters (Wang and Peng 2010; Shevade and Ford 2004; Payne and Abdel-Fattah 2005), while applications for mine water treatment are relatively rare (Wingenfelder et al. 2005). In some technologies, zeolite is being used as a “supporting medium” for additional cleaning after application of a main treatment method like wetlands, sand filters, limestone pebbles, etc. (Lizama et al. 2012; Lumiste et al. 2012).

### Properties of zeolites

Natural zeolites are aluminosilicate minerals having a porous structure, which can adsorb a lot of stable cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Ba<sup>2+</sup>), gases, and also radionuclides, for instance, radium isotopes. Therefore, such materials are known as “molecular sieves”. The most common natural zeolites are as follows: mordenite, chabazite, clinoptilite, natrolite, and stilbite. Until now, more than 40 different natural zeolites have been identified. Due to contamination with other minerals, natural zeolites are excluded from certain applications. For such purposes, synthetic zeolites are produced (Panek et al. 2011; Franus 2012). Zeolites are used for water purification as catalysts in nuclear industry, although their largest application is the production of softeners for laundry detergents.

Nowadays, more than 150 types of synthetic zeolite are known. The most important types are NaP and Na-X zeolites due to the presence of interconnected systems of microchannels. At Technical University in Lublin, Poland, a prototype device for the production of synthetic zeolites has been constructed. In this system, up to 30 kg of zeolitic material can be produced in each cycle from fly ash (Franus and Wdowin 2009). As some of the fly ash may contain an elevated concentration of natural radionuclides, the natural radioactivity of synthetic zeolites should be monitored. The concentration of zeolitic minerals in the final product varies from 50 to 95 %. The highest purity can be achieved for sodalite, but the average diameter of pores in this material is rather low (0.25 nm), reducing significantly the applicability of this product. Lower efficiency of production (50–65 %) has been achieved for other types of zeolite, like the NaP1 material (average diameter of pores 0.45 nm) and Na-X zeolite, in which pores are having an average size of 0.70 nm. These materials are more suitable for industrial applications, like water treatment. Other minerals present in the final product are mulite and quartz. For the laboratory tests, the zeolite NaP1 has been chosen.

### The scope of purification laboratory tests

For the measurements of radium in the liquid sample, the radiochemical method has been applied based on coprecipitation of radium isotopes with a barium carrier. The resulting precipitate is mixed with the gelling scintillating cocktail LumaGel™. The samples are measured in a low-level liquid scintillation spectrometer Quantulus™. This method enables simultaneous measurement of two radium isotopes, <sup>226</sup>Ra and <sup>228</sup>Ra. The detection limits are very low: 0.002 kBq/m<sup>3</sup> in the case of <sup>226</sup>Ra and 0.020 kBq/m<sup>3</sup> for <sup>228</sup>Ra, when the initial sample volume is 1 l and the counting time is 1 h (Chałupnik and Lebecka 1993).

Measurements of radioactivity of the zeolite prior to experiments and afterwards have been performed with the application of low-background gamma spectrometry. Samples have been dried at first, then transferred to 0.6-l Marinelli beakers and measured; the counting time for a single sample equalled 24 h. The detection limit for gamma-emitting radionuclides is below 1 Bq/kg (Michalik et al. 2002).

### Laboratory experiments

The laboratory experiments have been performed in the following way. The chosen amount of the mixture of zeolite with the sand and gravel (to increase the permeability) has been placed in a column with a total volume of 60 l. The

water sample with a volume of 30 l was poured gently into the column. The opening of the valve at the bottom of the column allowed the filtration of the sample through the bed, leading to the removal of radionuclides and some stable elements by the zeolite. The aliquots with a volume of 2–3 l have been collected and analyzed. Table 1 describes the water samples used in the tests.

**Radium removal from “synthetic” drinking water**

For the production of the filtration mixture, 20 kg of sand, 12.5 kg of gravel, and 1.5 kg of NaP1 zeolite have been used. This mixture has been placed in the column, and 30 l of synthetic drinking water (low conductivity) was used for the first experiment. The average volume of samples after filtration was 2.5 l, and results of the treatment are shown in Table 2.

It can be clearly seen that the results of treatment are very good. The efficiency of radium removal from water exceeds 90 % for all samples, except the last one. Even in this case, the efficiency is higher than 80 %. The most difficult problem in this experiment was leaching very fine particles of zeolite from the mixture. Therefore, at the end of the experiment, the drop of the efficiency was probably caused by this effect, and there was a need to improve the quality of zeolites, i.e., to produce coarser grains of the material. Despite those problems, results of the treatment proved the capabilities of the application of zeolites for removal of radionuclides from drinking water, which is very important for some underground drinking water supplies (Drinking Water Directive 1998; Decree 2007; Vornehm 2009).

**Radium removal from “synthetic” barium-bearing water**

In this experiment, the most important issue was to assess the capacity of the zeolite for barium removal. Barium is sometimes present in saline mine waters in significant concentrations, reaching 2–3 g/l. In this case, the barium content in the sample was even higher, 6 g/l. Additionally, radium isotopes have been added to the water sample with a total volume of

30 l. In this case, the filtration mixture consisted of 34.5 kg of quartz sand and 2.2 kg of zeolite. The results of purification are shown in Table 3. Also, in this case, the average volume of the sample aliquot was 2.5 l.

It can be seen that about 12.5 l of the barium-bearing water has been very finely purified, and only traces of radium and barium were present in the water after filtration. The removal efficiency exceeded 98 %. Afterwards, the purification efficiency dropped very quickly, showing the saturation of the zeolite in the column with barium. The amount of the zeolite in the column was 2.2 kg, and approximately 80 g of barium has been removed from the solution. The rough estimation shows that 1 kg of zeolite is able to remove 40 g of barium from the water and possibly similar amount of other stable elements from the solution like manganese or iron. The experiment assured us that the problem with overload of the column capacity can happen in cases when stable pollutants are present in water in elevated concentrations and the volume of filtrated water is significant, too. This is a proof that treatment of radium- and barium-bearing waters would be difficult or impossible due to the high barium content and fast loss of adsorption capabilities of the zeolite. If the concentration of barium in mine water is low, then the applicability of zeolite is possible and should lead to the positive results of purification.

**Radium removal from mine water**

The water sample for experiments has been collected in the underground water galleries of one of the collieries in the Upper Silesian Coal Basin. The salinity (TDS) exceeds 100 g/l, and the concentration of radium isotopes is clearly enhanced. The water contains few grams per liter of sulfate ions, but barium is not present in the water. The filtration mixture consisted of 20 kg of sand, 12.5 kg of gravel, and 1.5 kg of NaP1 zeolite. Results of the water treatment are presented in Table 4.

For the experiment, 30 l of mine water was used, and the average volume of the treated water was 3 l. Except for the two first samples, the purification efficiency exceeded 98 %, despite the fact that the total volume of purified water was

**Table 1** Description of water samples used in experiments

No.	Sample description	Ra-226 (kBq/m <sup>3</sup> )	Ra-228 (kBq/m <sup>3</sup> )	Remarks
1	Synthetic drinking water (sample A)	0.216±0.034 <sup>a</sup>	1.01±0.27	Deionized water with added radium standard solutions
2	Artificial “barium-bearing” water (sample B)	1.059±0.045	1.97±0.47	Barium conc. 6 g/l, conductivity 9,650 μS/cm
3	Mine water C	1.833±0.296	3.16±0.51	Conductivity 112,400 μS/cm
4	Mine water D	4.216±0.534	7.81±1.46	Conductivity 119,000 μS/cm

<sup>a</sup> Budget of uncertainty is defined as the sum of the uncertainty of the sample volume, the uncertainty of the activity of the standard solution, the uncertainty in counting of the standard solution, and the uncertainty of the corrected count rates of the measured sample

**Table 2** Results of purification of synthetic drinking water

No.	Sample description	Ra-226 concentration (kBq/m <sup>3</sup> )	Ra-228 concentration (kBq/m <sup>3</sup> )
1	Raw water (before treatment)	0.216±0.034	1.01±0.27
2	Sample A-1/1	<0.003	<0.06
3	Sample A-1/2	<0.003	<0.06
4	Sample A-1/3	<0.007	<0.06
5	Sample A-1/4	0.019±0.008	<0.06
6	Sample A-1/5	0.041±0.009	0.07±0.06
7	Sample A-1/6	<0.003	<0.08
8	Sample A-1/7	<0.003	<0.06
9	Sample A-1/8	<0.007	<0.03
10	Sample A-1/9	0.008±0.007	<0.03
11	Sample A-1/10	0.013±0.008	0.07±0.06
12	Sample A-1/11	0.041±0.011	0.09±0.07

30 l. The result was a confirmation of the possibility of radium removal from very salty waters (brines) with application of a zeolite material.

### Radium removal from mine water—second experiment

Another water sample has been collected from the outflow in one of the underground galleries of the same mine as the previous sample, but this time, the total volume of the water sample was 150 l. Again, the salinity of the water was higher than 100 g/l, and the water contained no barium but sulfate ions and radium isotopes. The filtration mixture consisted of 26.5 kg of sand and 2.0 kg of zeolite NaP1. The total volume of the treated water was 140 l, and the average volume of the sub-sample was 5 l. Results are presented in Table 5.

In this experiment, a larger water sample has been used. The sample was the largest one possible to be collected in the

**Table 3** Radium removal from synthetic barium-bearing water

No.	Sample description	Ra-226 concentration (kBq/m <sup>3</sup> )	Ra-228 concentration (kBq/m <sup>3</sup> )
1	Synthetic barium bearing water	1.059±0.084	1.97±0.47
2	Sample B-4/1	0.025±0.008	<0.06
3	Sample B-4/2	0.029±0.008	<0.06
4	Sample B-4/3	<0.007	<0.06
5	Sample B-4/4	0.009±0.007	<0.05
6	Sample B-4/5	0.040±0.009	<0.06
7	Sample B-4/6	0.292±0.034	0.55±0.16
8	Sample B-4/7	0.485±0.057	1.14±0.32

**Table 4** Results of purification of mine water C

No.	Sample description	Ra-226 concentration (kBq/m <sup>3</sup> )	Ra-228 concentration (kBq/m <sup>3</sup> )
1	Sample C (mine water from water galleries)	1.833±0.296	3.16±0.51
2	Sample C-2/1	0.151±0.010	0.20±0.05
3	Sample C-2/2	0.070±0.007	0.11±0.04
4	Sample C-2/3	0.022±0.005	<0.03
5	Sample C-2/3	0.024±0.005	<0.03
6	Sample C-2/4	0.027±0.005	<0.03
7	Sample C-2/5	0.013±0.004	<0.03
8	Sample C-2/6	0.033±0.005	<0.03
9	Sample C-2/7	0.013±0.004	<0.02

underground mine and transported to the surface. The main purpose of the experiment was the estimation of the adsorption capacity of the zeolite during the long-term treatment. It can be clearly seen that very good purification efficiency has been achieved—above 98 % for both radium isotopes. The gamma spectrometry measurements of the filtration bed showed that the total activity of radium, adsorbed on zeolite, was approximately 1,500 Bq (500 Bq of Ra-226 and 1,000 Bq of Ra-228); in mass units, it equals roughly  $2 \times 10^{-11}$  g. It means that the overload of zeolite could be only the result of adsorption of stable elements like strontium or manganese. The chemical analysis of these pollutants showed that this effect may occur after filtration of at least 1.2 m<sup>3</sup> of such brine.

In the conditions in underground galleries, the main problem would be the mechanical suspension present in brines as

**Table 5** Results of purification of mine water D

No.	Sample description	Ra-226 concentration (kBq/m <sup>3</sup> )	Ra-228 concentration (kBq/m <sup>3</sup> )
1	Sample D (brine from the underground gallery)	4.216±0.534	7.81±1.46
2	Sample D-2/1	0.038±0.009	0.10±0.06
3	Sample D-2/3	0.014±0.007	<0.05
4	Sample D-2/5	0.024±0.008	0.06±0.06
5	Sample D-2/7	0.055±0.009	0.07±0.06
6	Sample D-2/9	0.025±0.008	<0.05
7	Sample D-2/11	0.032±0.009	<0.05
8	Sample D-2/13	0.035±0.009	0.09±0.06
9	Sample D-2/15	0.032±0.009	0.09±0.06
10	Sample D-2/17	0.007±0.007	<0.05
11	Sample D-2/19	0.016±0.007	<0.05
12	Sample D-2/21	0.011±0.007	<0.05
13	Sample D-2/23	0.037±0.009	0.10±0.06
14	Sample D-2/25	0.007±0.007	<0.05

a result of exploitation. Therefore, to estimate the possibility of application of a zeolite material for underground treatment of mine waters, it will be necessary to perform underground tests of the method.

### Conclusions

The aim of the laboratory experiments was to check the possibility of zeolite application for removal of radium from mine water. For the experiments, four different water samples were used: two artificial ones and two brines from a chosen colliery.

It can be clearly seen that the results of purification were very good. The efficiency of radium removal from water exceeded 90 % for all samples, except the synthetic barium-bearing water, when the purification efficiency dropped significantly after overloading of the filtration bed. The most difficult problem in these experiments was the leaching of very fine particles of zeolite from the column. Therefore, there is a need to improve the quality of zeolite and produce coarser grains of the material.

The estimation of the capacity of zeolite for radium isotopes showed that it would be possible to use such method for the treatment of radium-bearing waters. On the other hand, in underground galleries, the main problem would be the mechanical suspension present in brines as a result of exploitation. Therefore, it will be necessary to perform underground tests of the method.

The main goal of these experiments was to find an inexpensive passive method for the treatment of a huge volume of mine waters to remove radium isotopes and some other stable pollutants. Additionally, the method must fulfill specific requirements of the mining industry—waste waters in underground mines contain high concentrations of mechanical suspension, clogging very efficiently all filters. The application of zeolite materials together with fly ash for the construction of passive barriers seems to be such a solution. As the spoils after treatment are having enhanced radioactivity, it is necessary to dump such a material to old galleries or exploited out zones (gobbins). The mixture of zeolite with fly ash and sand must be treated as a disposable material. No recovery is predicted to avoid additional radiation hazard for miners. Therefore, any application of ion exchange resins, nanofibers, or polymers in the mining industry is excluded, mostly due to the costs.

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