# ABSTRACT

Some radioactive nuclides are naturally present in the environment, usually as members of a radioactive series whose parent nuclides are $^{238}U$, $^{235}U$ and $^{232}Th$. Increased content of natural radionuclides occurs in specific types of rocks or groundwater. Human activities related to the extraction, processing and storage of mine waste may lead to an increase in the content of radionuclides in the extracted raw materials, by-products and all types of waste generated in mining and processing processes. Moreover, such activity, changing the natural conditions in which radionuclides are found and subjecting them to technological processes, often leads to an increase in the availability of radionuclides and their ability to spread in the environment after deposition on the surface.

Radiation hazard is caused not only by the parent nuclides of radioactive series, such as uranium and thorium, but also or mostly by decay products, such as radium and radon. Due to the different mobility of radium and its parent nuclides, as well as the long half-lives of radium isotopes, their presence can sometimes be detected irrespective of the presence of the parent nuclides. For example, the presence of radium isotopes in groundwater is caused by the natural processes of interaction of water in the aquifer with matter: rocks, soil or even metal ores. Migration of radium from rocks to water occurs with different efficiency, depending on the availability and solubility of rocks, the presence of oxygen, acidity, concentration of radioisotopes in rocks and their mobility under given conditions. The uranium mining and processing industry as well as the extraction of crude oil, gas, metal ores and hard coal are the main sources of water with increased radioactivity, most often also with high salinity. Also thermal and mineral waters, waters used for balneological purposes and those intended for consumption, may contain increased concentrations of radium, but it should be emphasized that the concentrations of radium isotopes in such waters are usually much lower than in brines.

The Upper Silesian Coal Basin, exploited due to the hard coal seams located in its area, is characterized by staggered aquifers. For this reason, the mineralization and chemical composition of the waters change with the depth. There are radium-bearing brines in the coal mines of the Upper Silesian Coal Basin. High concentrations of radium and large volumes of salty waters drained and pumped to the surface may not only lead to contamination of surface watercourses with salts of stable elements, but also contamination of the environment with radium isotopes and their decay products (e.g. $^{210}Pb$ with a half-life of over 20 years). Not only surface waters may be contaminated, but also bottom sediments due to the formation of radioactive sediments. The main process responsible for the formation of sediments is the co-precipitation of radium and barium in the form of barium-radium sulphate, however, adsorption of radium isotopes by bottom sediments may also take place. The lack of control over the release of liquid or solid waste to the environment and the lack of supervision over the conditions of solid waste storage may cause environmental contamination to spread, even over a large area. Considering the long half-lives of radium isotopes, especially $^{226}Ra$ ($T_{1/2}$ about 1600 years), and their high radiotoxicity, the contamination may be long-lasting.

Purification of water from radioactive nuclides has been the subject of numerous studies, also at the Central Mining Institute, in the Silesian Centre for Environmental Radiometry. Many different methods of water purification have been developed and tested: co-precipitation of $RaSO_4$ with $BaSO_4$, water filtration, suspension coagulation and flocculation, adsorption and ion exchange, reverse osmosis, selective retention on mineral membranes, aeration. Some of them were used on an industrial scale, including in Silesian mines, but most of them did not go beyond the experimental phase. It should be emphasized that many studies were carried out with the use of synthetic waters with an uncomplicated matrix, positively influencing the treatment efficiency.

One of the possible methods of purifying water from pollutants, including radium isotopes, is the use of zeolites. Zeolites are microporous aluminosilicates, belonging to the group of inorganic porous materials, characterized by an open structure of channels and chambers and a very large specific surface. Zeolites differ in the sizes of chambers, cells, channels, type of connections, chemical composition, type of exchangeable cations. In addition, distortions of the crystal lattice and possible zeolite modifications after the synthesis process have a significant impact on the properties of a given material.

**Scientific purpose of the work:**

The scientific aim of this dissertation was to study the process of radium adsorption and desorption on zeolite materials. This doctoral thesis contains the results of research on sorption and desorption of radium isotopes from water with the use of various types of zeolite materials. Based partly on the previous research carried out at the Central Mining Institute, the author for the purposes of the study proposed the division of the mine waters, containing radium, into 3 types: radium-sulphate, radium-barium, radium-strontium. The author has carried out research on the efficiency of the radium water purification process for several selected types of real waters, characterized by different chemical compositions. For this purpose, the author examined water samples before and after treatment, analysing the content of radium $^{226}Ra$ and $^{228}Ra$ isotopes in these waters, the content of anions and cations, electrolytic conductivity and total hardness. Not only zeolites but also other sorption materials were selected: 11 zeolite samples, 2 fly ash samples and alumina trioxide, with different zeolite phase contents, different synthesis methods, chemical composition and granulation. Selected sorption materials were additionally tested and characterized, granulation analyses were performed, the mineralogical composition and zeolite phase content in individual samples were determined, the main ion exchange cations and the Si:Al ratio were determined, and the analysis of textural properties was performed.

The author designed 3 different types of tests to study the radium water purification process. The process of radium desorption from used zeolites was also investigated. The author studied the influence of the chemical composition of the treated water on the efficiency of the process of removing radioactive contaminants from it and determined the usefulness of individual types of zeolites for the process of purifying water from radium.

**Utilitarian purpose of the work:**

The utilitarian goal was to develop the principles of using zeolites to remove radium from waters in various areas of the economy. The author outlined the possibilities of using zeolites to remove radium isotopes from water intended for consumption, used for health purposes in health resorts or reservoir waters from other branches of the mining industry, such as copper mines or the production of oil and gas, including shale gas. For this purpose, the author performed additional research and assessed the impact of the use of zeolites in the purification of radium water on their other parameters, such as the content of barium or strontium. The conducted research enabled the development of rules for the use of zeolites for the removal of radium from water in various areas of the economy.

**The main achievements of the work:**

The author has carried out extensive research on various types of zeolites for the removal of radium isotopes from the actual mine waters selected for this purpose, but also, on a smaller scale, performed tests for synthetic waters. The author showed that individual types of zeolite materials are characterized by significantly different effectiveness in removing radium isotopes from treated waters, the best results were obtained with the use of NaP1 and NaX zeolites.

**The subject of research as part of the work was:**

- study of the efficiency of the water purification process from radium $^{226}Ra$ and $^{228}Ra$ isotopes,
- evaluation of the influence of zeolite parameters on the efficiency of the radium removal process,
- assessment of the impact of the chemical composition of water on the efficiency of the radium removal process,
- analysis of the impact of the radium water purification process with the use of zeolites on the chemical composition of water,
- evaluation of the possibility of using zeolites for water purification in various branches of the economy,
- study of the radium desorption process from spent zeolites.

**The scope of the research carried out included:**

- purification efficiency tests for 11 zeolites, 2 fly ash and $Al_2O_3$ samples,
- treatment efficiency tests using 5 types of real mine water,

- radium desorption test from NaP1 zeolite,
- barium adsorption test on NaP1 zeolite,
- studies of zeolite properties (zeolite phase content, textural properties, mineralogical composition, main ion exchange cations, Si:Al ratio),
- testing the parameters of treated waters before and after the purification process (radium concentration of $^{226}Ra$ and $^{228}Ra$, chemical composition (cations, anions, electrolytic conductivity, pH, total hardness).

Thanks to the research carried out during the preparation of the dissertation, it was possible to achieve both the scientific goal and the utilitarian goal set by the author when he started working on his doctorate.