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IN-SITU APPLICATION OF THE MINERAL SORBENT CLINOPTILOLITE AS PERMEABLE BARRIER TO RADIOACTIVITY IN RIVER WATERS

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ABSTRACT. The natural zeolites as very effective mineral sorbents are often used for adsorption of many metals and other pollutants in the process of water purification. This study focused on the results of using the unique adsorption and chelating affinity of one of the most spread natural zeolites – clinoptilolite for reduction of radioactivity in river water ecosystems. For this purpose in-situ experiments were carried out in the river basin of the rivers Musalenska Bistritsa and Iskar from the Rila Mountain area. The dynamic of radioactive sorption of radioactive elements as ^{137}Cs, ^{7}Be, etc. is traced in the different river waters. The study could be useful in the developments of new safety and economically beneficial mode for reducing the harmful anthropogenic influences.

ПРИЛОЖЕНИЕ "ИН-СИТО" НА МИНЕРАЛНИТЕ СОРБЕНТИ КЛИНОПТИОЛИТИ КАТО ПРОПУСКЛИВА БАРИЕРА ЗА СТЕПЕНТА НА РАДИОАКТИВНОСТ В РЕЧНИТЕ ВОДИ

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РЕЗЮМЕ. Природните зеолити като много ефективни минерални сорбенти често са използвани за адсорбиране на много метали и други замърсители в процеса на очистване на води. Статията е фокусирана върху резултатите, които са получени на базата на уникалната адсорбция и естествения афинитет на най-разпространения природен зеолит – клиноптиолита за намаляване степента на радиоактивност в речните екосистеми. За тази цел бяха проведени експерименти "ин-сито" по поречието на реките Мусаленска Бистрица и Искър, извиращи от Рила планина. Това позволява да се проследи динамиката на изменение на степента на радиоактивност при сорбцията на радиоактивни елементи като ^{137}Cs, ^{7}Be, в различни речни води. Статията би могла да се използва за изследване на нов, безопасен и икономически изгоден метод за намаляване на вредните антропогенни въздействия.

Introduction

In the last decades the mineral sorbents "zeolites" have been intensively investigated for their adsorption properties. They are found in abundance in the world. In Bulgaria there are many deposits of natural zeolites near to the city of Kurdjali. The deposits of Beli Plast and Beli Bair are the most popular industrial of them. Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminum and oxygen in their framework and cations, water and/or other molecules within their pores. In all, over 130 different framework structures are now known. One of the most utilized zeolite is clinoptilolite because of his adsorption properties. About 40 natural occurring zeolites are known and more than 180 zeolite types have been synthesized. Many occur naturally as minerals but the others are synthetic, and are made commercially for specific uses, or produced by research scientists trying to understand more about their chemistry. Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tones per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. This is the reason zeolites often to be used to exchange their cations with the surrounding water because their cations are free to migrate in and out of zeolite structure. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.

The application of natural zeolites recently is more often environmentally related. Natural zeolites are being used for treating of low and intermediate aquatic waste. They even have been used in the clean-up at Chernobyl. Zeolites contribute to a cleaner, safer environment in a great number of ways. In fact

nearly every application of zeolites has been driven by environmental concerns, or plays a significant role in reducing toxic waste and energy consumption. More often the iindustrial and eenvironmental applications of zeolites are in the field of Gas adsorption (Nikolova, 2001a), ion exchange (Nikolova, 2001b), (Zhaohui Li, Bowman, 1997), (Helfferich, 1995), wastewater treatment (Korczak M., 1988), radioactive waste treatment (Ščerjan-Stefanović, Gurković, 1997), (Takagi, 1978), aquaculture (Cantrell et al., 1994), (Chmielewska et al., 2002), agriculture, etc.

The aim of this study was to investigate the possibility for in-situ application of zeolites (clinoptilolite) for river water purification from radionuclides.

Experimental; Materials and methods

Materials

The zeolites (clinoptilolite) used in the study are from the natural deposits in South-East Bulgaria near to the city of Kurdjali. Among the different varieties of zeolites the most-wide spread zeolite – clinoptilolite (size 0.8-1 mm) has been chosen for its adsorption properties. In the experiment it is placed in the permeable plastic containers (volume 250 ml).

Localities

In-situ experiments were carried out along the basin of river Iskar, Bulgaria. The experimental containers with zeolites have been placed at three points along the river – at the upper stream (Musalenska Bistritsa River), the middle stream and the lower stream of Iskar river.

Experiment.

At each locality 3 containers have been placed. For safety reasons the containers have been put in a netbox and tied to stones. After different periods of time (1week and 1 and 5 months) the containers have been removed. Prior the analyses the zeolite samples have been dried at 90˚C and homogenized. The radioactivity of ambient water and zeolite (control) also has been measured.

Methodology

Radioactivity in the different samples were measured with gamma-spectrometer with H.P.Ge-detector with relatively high effectiveness ~30%. Energy resolution is in the frame of ~2-2.2 KeV for energy ~1.3 MeV. For determination of absolute effectiveness was used standard prepared in INRNE with size ø 60x20 mm and density ~1.1 g cm^{-3}. For low activities is used low background system with typical lead protection. This one is giving possibility to measure activities lower then ~0.5 Bq kg^{-1} of the sample. For processing of the gamma-spectra is used program ANGES, developed in INRNE and recommended by IAEA. After full processing the final results are presented in Bq kg^{-1}.

Discussion

The comparative investigations for evaluation of adsorption capacity for ^{137}Cs in river waters show the different results. The content of ^{137}Cs in the water of Mussalenska Bistritsa River shows about 100 time lower radioactivity in comparison with the zeolite samples. The linear increasing indicates the potential possibility for accumulation of significant quantity of ^{137}Cs from the ambient water depending on the remaining period of time in the river (1-5 months). Nevertheless the slow flow velocity in the upper stream of the river a significant adsorption of ^{137}Cs with the time (50% higher for 5 months) in comparison with ^{137}Cs content in the control zeolites samples is observed (Fig. 1). In-situ experiments in the middle and lower stream of Iskar River show an accumulation of ^{137}Cs in the zeolites samples from the middle stream, which for 1 month is significantly higher than in Mussalenska Bistritsa River (Fig. 2). This fact is due to the higher flow velocity nevertheless the lower ^{137}Cs content in the water. The accumulation rate of ^{137}Cs in the lower stream of Iskar river is higher. For 1 month it increases double in comparison with the control zeolite samples. The reason for this result probably is due to the higher flow velocity in this part of the river (Fig. 3).

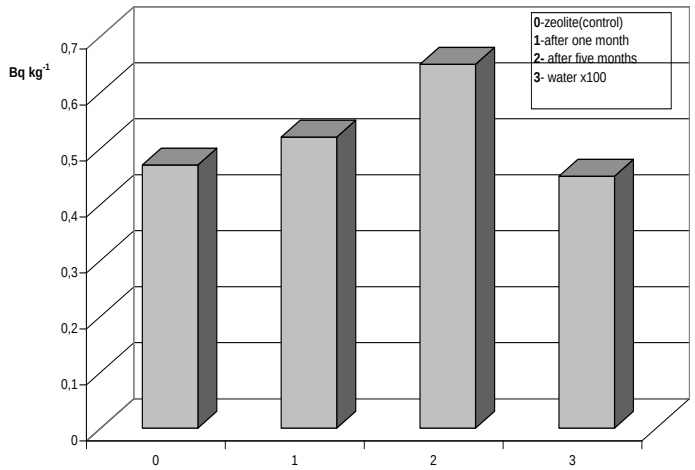

Fig. 1 Changes in the radioactivity (^{137}Cs) of zeolites (clinoptilolite) after different period of in-situ remaining in the water from Musalenska Bistrica river

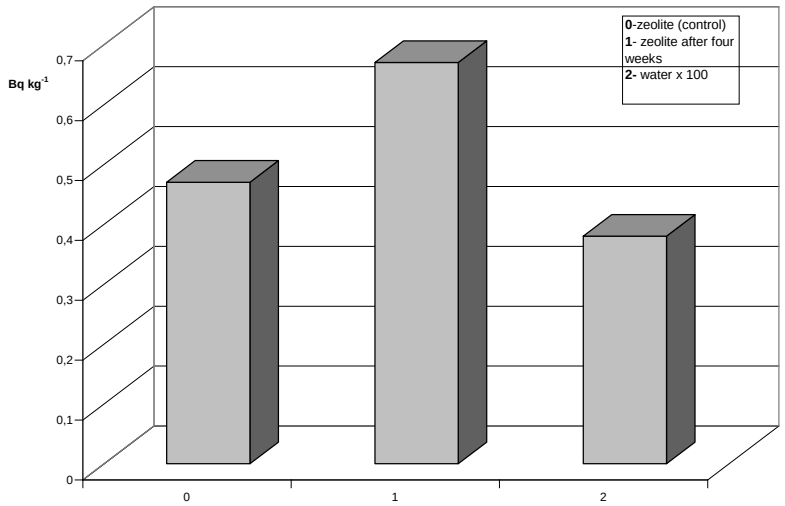

Fig. 2 Changes in the radioactivity (^{137}Cs) of zeolites (clinoptilolite) after remaining in the water from middle stream of Iskar river

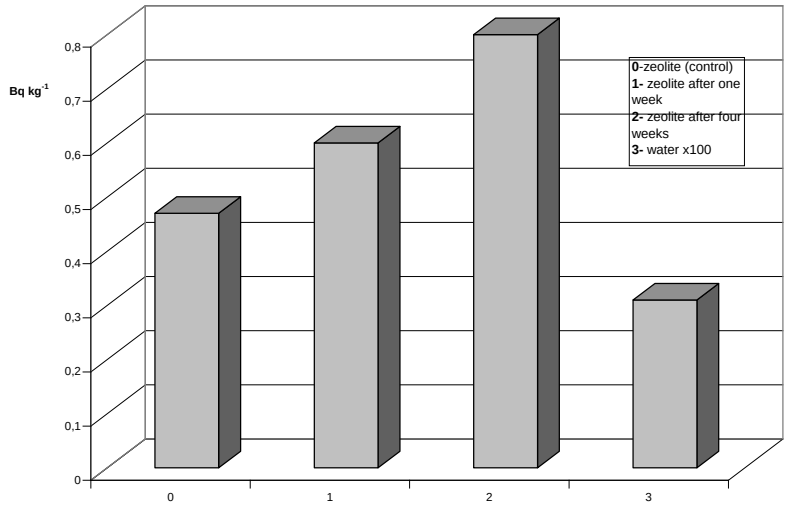

Fig. 3 Changes in the radioactivity (^{137}Cs) of zeolites (clinoptilolite) after remaining in the water from lower stream of Iskar river

Conclusions

Zeolites (clinoptilolite) present specific property to ^{137}Cs in natural river water. Despite the low level of ^{137}Cs in the river water the zeolites indicate a high capacity for adsorption from the ambient water probably due to their structure and adsorption properties. The adsorption capacity is high even at slow flow rate and has a tendency to increase with the increasing of the water velocity and the duration of their remaining in the running river waters.

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