URANIUM SORPTION FROM AQUEOUS SOLUTIONS ON SODIUM-FORM OF HEU-TYPE ZEOLITE CRYSTALS

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The uranium sorption from aqueous solutions (concentration range 50–20,000 mg/l) by the sodium-form (Na-form) of HEU-type zeolite crystals (particle-size < 20 μm) has been investigated by means of a batch-type method. The INAA, RI-XRF, powder-XRF, SEM-EDS and FT-IR techniques were used for the study of the experimental products. The absolute uranium uptake by the material reached the value of 11.68 mg/g in the case of initial concentration 20,000 mg/l. On the other hand the Kᵦ-values indicated that the relative uranium uptake, and consequently the percentage of removal, is higher for concentrations below 100 mg/l. The uranium uptake by the zeolite is attributed to different sorption processes such as ion-exchange, adsorption and surface precipitation, taking place both to the interior and the surface of the crystals and strongly depending on the pH of the solutions. The investigated zeolitic material was sufficiently resistant at the low initial pH of the solutions with dealumination phenomena only observed in the case of the most acidic solution used.

Although uranium is one of the naturally occurring actinides, its presence in the biosphere is not only attributed to natural sources (uranium-containing minerals and rocks) but also to certain human activities mainly related to the nuclear power production. Significant amounts of uranium are released to the environment during the entire nuclear fuel cycle, including the uranium ores processing and the final nuclear-waste disposal in geological repositories. Uranium anthropogenic contamination has been observed due to other reasons such as the phosphate fertilizers production and utilization, the coal burning in power stations and the copper ores processing.

The transport of uranium in the environment and its involvement in geochemical and biogeochemical cycles takes mainly place through aquatic pathways existing in the geosphere. However, the uranium mobility and accumulation in natural systems strongly depends on interactions with geological materials and immobilization processes such as sorption to rocks, minerals and suspended solid particles. Of especial interest are the interactions of dissolved uranium species with natural porous and particularly microporous solid phases (e.g. clay minerals, oxides/hydrous oxides/hydroxides/oxyhydroxides, zeolites, micas) showing the ability to sorb considerable uranium amounts from aqueous media. The investigation of the interactions between zeolites and uranium in aqueous environments is of increasing importance, because areas with zeoliferous rocks (mainly
tuffaceous sedimentary formations) have been considered as locations for direct disposal of high-level radioactive wastes. Most of the previous studies on the uranium sorption or uptake by natural zeolitic materials concern zeoliferous rocks, which are mixtures of zeolites and other minerals (clay minerals, SiO₂-phases, feldspars, micas, etc.), while the data for pure natural zeolite crystals are comparatively limited. Hafez et al. investigated, among other radionuclides, the uranium uptake by harmotome crystals, whereas Vochten et al. studied the interaction between raw zeolite crystals (scolecite, chabazite, heulandite, stilbite) and phosphoric-buffered solutions of constant uranyl-concentration 2x10⁻⁵ M. The effect of the pH on the uptake by solutions of 5x10⁻⁵ M constant concentration was also investigated in the last study using zeta-potential measurements.

The aim of the present study was to investigate the uranium sorption from unbuffered aqueous solutions of a wide concentration range (50-20000 mg/l) by the sodium-form (Na-form) of pure HEU-type zeolite crystals, using radioanalytical, diffraction, microscopic and spectroscopic techniques. The HEU-type zeolites (heulandite/clinoptilolite series) are the most common natural zeolites on the Earth, occurring mainly in sedimentary and volcanic rocks and constituting extensive deposits all over the world. The raw HEU-type zeolite crystals normally contain several exchangeable cations in their structure (Ca, K, Na, Mg, Sr, etc.) but homoionic metal-forms can be prepared by means of wet-chemical procedures. Particularly, the homoionic Na-form of the HEU-type zeolites has been postulated as the most convenient in order to study interactions with heavy metals in aqueous solutions, to prepare heavy metal-forms or even to produce more complex chemically modified crystals with distinguished chemical properties. It should be noted that no reference focused on the uranium sorption by the Na-form of pure HEU-type zeolite crystals has so far appeared in the literature.

EXPERIMENTAL

The HEU-type zeolite specimen selected for the present study was pure heulandite crystals developed into a cavity of a basaltic rock sample from Poona/India. Distinct zeolite crystals were crushed in an agate mortar and wet-sieved in analytical sieves for the separation of the 20-90 μm and <20 μm particle-size fractions. The coarse- and the fine-grained crystalline powder obtained was repeatedly treated with 4M NaCl solution at 100 °C in order to obtain the homoionic Na-form of the zeolite. The starting material was characterized by means of powder-XRD (PHILIPS 1820 PW diffractometer, CuKα radiation) and analyzed in thin-polished sections using SEM-EDS (JEOL, JSM 840-A with a LINK 10000 AN EDS, 20 μm defocused beam).

Both the coarse- (20-90 μm) and the fine-grained (<20 μm) zeolite crystals, in the Na-form, were used for preliminary uranium sorption experiments. These experiments