15th International Congress of the Geological Society of Greece
Athens, 22-24 May, 2019 | Harokopio University of Athens, Greece
Bulletin of the Geological Society of Greece, Sp. Pub. **7** Ext. Abs. GSG2019-130

Comparative Study of the Cesium Uptake Ability between HEU-type (Clinoptilolite-Heulandite) Zeolitic Tuff and Pure Heulandite

C. Mytiglaki[1], N. Kantiranis[1], P. Misaelides[2], F. Noli[2] and A. Filippidis[1]

(1) Aristotle University, Faculty of Sciences, School of Geology, Dept. of Mineralogy-Petrology-Economic Geology
(2) School of Chemistry, 54124 Thessaloniki, Greece, michristi@geo.auth.gr, kantira@geo.auth.gr, misailid@chem.auth.gr, noli@chem.auth.gr, anestis@geo.auth.gr

Introduction and Objectives

The zeolitic volcaniclastic rock deposit corresponds to a rock which contains high amounts of one or more from the different (more then 65) phases of zeolites. The zeolitic rock with numerous applications is the high quality HEU-type (clinoptilolite-heulandite) zeolitic tuff. Among other quality characteristics, only HEU-type zeolitic tuff with ≥80 wt% clinoptilolite-heulandite, ≤20 wt% clay minerals, free of fibres (e.g., fibrous zeolites such as erionite, mordenite, roggianite, mazzite, etc) and free of SiO_2 minerals (quartz, cristobalite, tridymite) can be used as feed additive for all animal species and consequently as nutrition supplement for humans. For all other environmental, industrial and agricultural applications, the zeolitic tuff, among others, should contain ≤20 wt% clay minerals (except for the uses in construction and cement industry) and ≥80 wt% clinoptilolite-heulandite (EU Regulation No 651/2013; Filippidis *et al.*, 2016a; Filippidis, 2016 and references therein). The HEU-type (clinoptilolite-heulandite) shows tabular crystals and contains micro/nano-pores in a framework of channels with 10- and 8-memers rings, in dimensions of 7.5x3.1 Å, 4.6x3.6 Å, 4.7x2.8 Å (Baerlocher *et al.*, 2007; Mitchell *et al.*, 2012). Natural zeolites are characterized by enhanced high cation exchange capacity and selectivity, higher for monovalent cations and lower for bivalent cations. Therefore, zeolitic rocks have already been proposed and successfully applied to the removal of fission products (e.g., Cs, Sr) and actinides (e.g., Th, U, Np, Pu) from effluents of the nuclear industry (e.g., Misaelides *et al.*, 1995a,b, 2018; Godelitsas *et al.*, 1996; Rajec *et al.*, 1999; Misaelides, 2011). Zeolitic rocks, ontaining e.g. clinoptilolite, chabazite, were used for the remediation of the consequences of the Three Miles Island, Chernobyl and Fukushima nuclear accidents and, along with clay minerals, were proposed as potential hosts for nuclear waste and as permeable reactive barriers for the cleaning of contaminated ground waters (e.g., Misaelides 2019). HEU-type (clinoptilolite-heulandite) zeolitic tuffs have effectively been used, to remove trace elements from wastewaters, and other different environmental, industrial and agricultural applications (e.g., Filippidis & Kantiranis, 2007; Vogiatzis *et al.*, 2012; Filippidis *et al.*, 2015a,b; 2016a,b; Filippidis 2016; Floros *et al.*, 2018; Kalaitzis *et al.*, 2019). The aim of this study was the comparison of the cesium sorption ability between pulverized high quality HEU-type (clinoptilolite-heulandite) zeolitic tuff and pulverized heulandite crystals.

Materials and methods

The high quality HEU-type (clinoptilolite-heulandite) zeolitic tuff (sample NA11) was obtained from specific continuous layers of zeolitic tuff in Ntrista stream location of Petrota area of Evros region (sample NA11) whereas pure heulandite crystals (sample HEU1) from the collection of the Dept. of Mineralogy-Petrology-Economic Geology (Aristotle Univ.). The mineralogical composition of the samples was determined by X-Ray Diffraction (XRD). The sample NA11 consists of 86 wt% HEU-type zeolite, 4 wt% micas + clay minerals, 4 wt% christobalite and 4 wt% feldspars, while the sample HEU1 is pure (100 wt%) heulandite. The combined methods of SEM-EDS, thermal treatment and XRD (Kantiranis *et al.*, 2006, 2011) applied in the sample NA11, revealed that the HEU-type zeolite presents characteristics of group 1 zeolite (clinoptilolite) and of group II (Intermediate heulandite). The mineral-chemistry of the zeolites was determined by SEM-EDS microanalyses. The chemical formula of the HEU-type zeolite (NA11) is $Ca_{1.8}K_{1.0}Mg_{0.7}Na_{0.5}Al_{6.4}Si_{29.5}O_{72}$ $21H_2O$, whereas that of pure heulandite (HEU1) is $Ca_{3.6}Na_{1.0}K_{0.2}Sr_{0.2}Ba_{0.1}Al_{8.1}Si_{27.6}O_{72}\cdot 21H_2O$. The uptake ability of the NA11 tuff sample, measured by the AMAS (Ammonium Acetate Saturation) method (Kantiranis *et al.*, 2011), was 231 meq/100g, while the corresponding value for the heulandite (HEU1 sample) 296 meq/100g. The cesium sorption ability of the two materials (500 mg/L $CsNO_3$ aqueous solutions of pH 2-12 labelled with ^{137}Cs) was determined, after equilibration for 24 hours and separation of the solid and liquid phase by filtration and centrifugation, using a gamma-ray spectroscopy (measurement of the 661 keV radiation emitted by ^{137}Cs).

Experimental results and conclusions

The experimental results showed that the cesium sorption ability of the HEU-type (clinoptilolite-heulandite) zeolitic tuff (sample NA11) was higher than this of the pulverized pure heulandite (HEU1) (Fig. 1). This is most probably due to the contribution of the nano/micro of the HEU-type zeolite (86 wt%) and the micas+clay minerals (4 wt%), as well as the meso/macro-pores of the zeolitic tuff to cesium cation sorption, while in the case of pure heulandite only the micro/nano-pores of the crystals contributed to the cesium removal from the solutions. The chemical composition of the zeolites (zeolite chemistry) can also influence their uptake ability. The cesium sorption ability was not significantly affected by the solution pH. The lower uptake value observed in the case of solutions with initial pH 2 is, most probably, due to the competition of the Cs^+- with H^+- cations. HEU type zeolites exhibit an amphoteric character having the ability to neutralize the solutions acting either as a proton acceptor or as a proton donor (Fig. 2). Cesium is present in aqueous solutions of pH 2-12 always in Cs^+ cationic form.

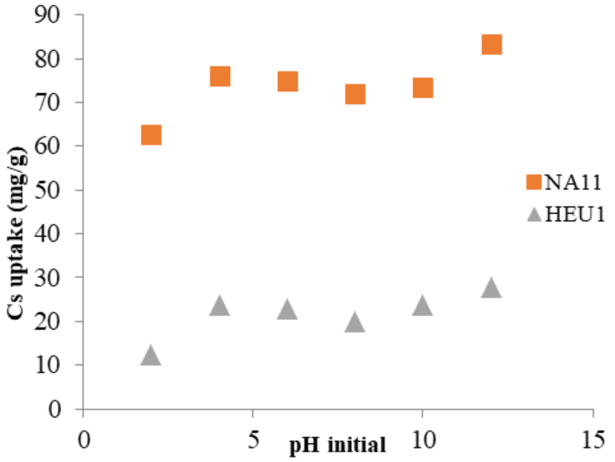

Fig 1. Variation of Cs uptake capacity of zeolitic tuff (NA11) and of pure crystals of heulandite (HEU1) in accordance with the initial pH of the solutions.

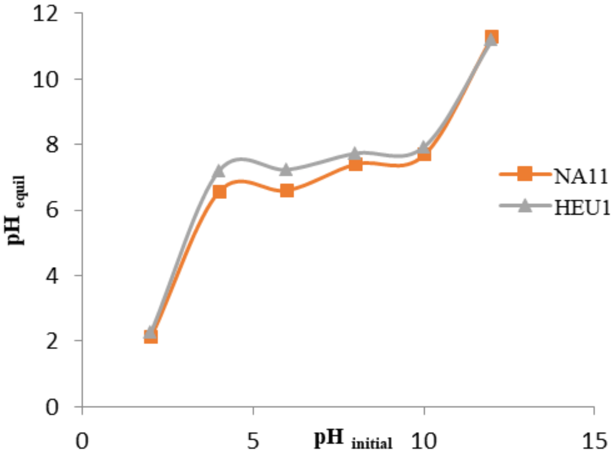

Fig 2. Variation of pH in the solutions after using the zeolitic tuff (NA11) and the pure crystals of heulandite (HEU1), in comparison with initial pH of the Cs traced aqueous solutions.

References

Baerlocher, Ch., McCuster, L.B., Olson, D.H., 2007. Atlas of zeolite framework types. Amsterdam, Elsevier, 301p.

EU Regulation No 651/2013. Commission Implementing Regulation (EU) No 651/2013 of 9 July 2013 concerning the authorization of clinoptilolite of sedimentary origin as a feed additive for all animal species and amending Regulation (EC) No 1810/2005.

Filippidis, A., 2016. Applications of the Hellenic Natural Zeolite (HENAZE) and specifications of zeolitic tuffs. Bull. Geol. Soc. Greece, 50(4), 1809-1819.

Filippidis, A., Kantiranis, N., 2007. Experimental neutralization of lake and stream waters from N. Greece using domestic HEU-type rich natural zeolitic material. Desalination, 213, 47-55.

Filippidis, A., Kantiranis, N., Papastergios, G., Filippidis, S., 2015a. Safe management of municipal wastewater and sludge by fixation of pollutants in very high quality HEU-type zeolitic tuff. J. Basic & Applied Research Intern., 7(1), 1-8.

Filippidis, A., Papastergios, G., Kantiranis, N., Filippidis, S., 2015b. Neutralization of dyeing industry wastewater and sludge by fixation of pollutants in very high quality HEU-type zeolitic tuff. J. Global Ecology & Environment, 2(4), 221-226.

Filippidis, A., Kantiranis, N., Tsirambides, A., 2016a. The mineralogical composition of Thrace zeolitic rocks and their potential use as feed additives and nutrition supplements. Bull. Geol. Soc. Greece, 50(4), 1820-1828.

Filippidis, A., Tziritis, E., Kantiranis, N., Tzamos, E., Gamaletsos, P., Papastergios, G., Filippidis, S., 2016b. Application of Hellenic Natural Zeolite in Thessaloniki industrial area wastewater treatment. Desalination & Water Treatment, 57(42), 19702-19712.

Floros, G.D., Kokkari, A.I., Kouloussis, N.A., Kantiranis, N.A., Damos, P., Filippidis, A.A., Koveos, D.S., 2018. Evaluation of the natural zeolite lethal effects on adults of the bean weevil under different temperatures and relative humidity regimes. J. Economic Entomology, 111(1), 482-490.

Godelitsas, A., Misaelides, P., Filippidis, A., Charistos, D., Anousis, I., 1996. Uranium sorption from aqueous solutions on sodium-form of HEU-type zeolite crystals. J. Radioanal. Nucl. Chem., 208, 393-402.

Kalaitzis, A., Stoulos, S., Melfos, V., Kantiranis, N., Filippidis, A., 2019. Application of zeolitic rocks in the environment: assessment of radiation due to natural radioactivity. J. Radioanal. Nucl. Chem., 319, 975-985.

Kantiranis, N., Chrissafis, C., Filippidis, A., Paraskevopoulos, K., 2006. Thermal distinction of HEU-type mineral phases contained in Greek zeolite-rich volcaniclastic tuffs. European J. Mineralogy, 18(4), 509-516.

Kantiranis, N., Sikalidis, K., Godelitsas, A., Squires, C., Papastergios, G., Filippidis, A., 2011. Extra-framework cation release from heulandite-type rich tuffs on exchange with NH_4^+. J. Environmental Management, 92, 1569-1576.

Misaelides, P., 2011. Application of natural zeolites to the environmental remediation: A short review. Microporous Mesoporous Materials, 144, 15-18.

Misaelides, P., 2019. Clay minerals and zeolites for radioactive waste immobilization and containment: A concise overview. In: Mercurio, M., Sarkar, B. and Langella, A. (eds). Modified clay and zeolite nanocomposite materials: Environmental and pharmaceutical applications. Elsevier, Amsterdam, pp. 243-274.

Misaelides, P., Godelitsas, A., Filippidis, A., 1995a. The use of zeoliferous rocks from Metaxades-Thrace, Greece, for the removal of caesium from aqueous solutions, Fresenius Environ. Bull., 4, 227-231.

Misaelides, P., Godelitsas, A., Filippidis, A., Charistos, D., Anousis, I., 1995b. Thorium and uranium uptake by natural zeolitic materials. Sci. Total Environ., 173-174, 237-246.

Misaelides, P., Sarri, S., Kantiranis, N., Noli, F., Filippidis, A., de Blochouse, B., Maes, A., Breynaert, E., 2018. Investigation of chabazitic materials as Cs-137 sorbents from cementitious aqueous solutions. Microporous Mesoporous Materials, 266, 183-188.

Mitchell, S., Michels, N.L., Kunze, K., Perez-Ramirez, J., 2012. Visualization of hierarchically structured zeolite bodies from macro to nano length scales. Nature Chemistry, 4, 825-831.

Rajec, P., Macasec, F., Misaelides, P., 1999. Sorption of heavy metals and radionuclides on zeolites and clays. In: Misaelides, P., Macasek, F., Pinnavaia, T.J., Colella, C. (Eds.) Natural microporous materials in environmental Technology. Kluwer, Dordrecht, 353-363.

Vogiatzis, D., Kantiranis, N., Filippidis, A., Tzamos, E., Sikalidis, C., 2012. Hellenic Natural Zeolite as a replacement of sand in mortar: Mineralogy monitoring and evaluation of its influence on mechanical properties. Geosciences, 2, 298-307.