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COMPARATIVE STUDY OF THE CESIUM UPTAKE ABILITY BETWEEN HEU-TYPE (CLINOPTILOLITE-HEULANDITE) ZEOLITIC TUFF AND PURE HEULANDITE

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Abstract

Specific continuous layers of zeolitic tuff in Ntrista stream location of Petrota area of Evros region (NA11) and pure natural crystals of heulandite (HEU1) from the collection of the Department of Mineralogy-Petrology-Economic Geology, School of Geology, Aristotle University of Thessaloniki, have been investigated. The X-Ray Diffraction analyses showed that the sample NA11 consists of 86 wt% HEU-type zeolite, 4 wt% micas+ clay-minerals, 4 wt% quartz, 2 wt% christobalite and 4 wt% feldspars, while the sample HEU1 is pure heulandite crystal. The mineral-chemistry was determined by SEM-EDS microanalyses. The zeolite of the NA11 sample is Ca-rich clinoptilolite and its chemical formulae is $Ca_{1.8}K_{1.0}Mg_{0.7}Na_{0.5}Al_{6.4}Si_{29.5}O_{72} \cdot 21H_2O$, while the zeolite of the sample HEU1 is heulandite and its chemical formulae 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 samples was measured by the AMAS method (Ammonium Acetate Saturation). The two examined materials show high uptake ability. The measured value for the zeolitic tuff NA11 is 231 meq/100g, while for the heulandite crystal (HEU1) is 296 meq/100g. For the determination of the cesium sorption a $CsNO_3$ solution

(concentration 500 mg/L), labelled with small activity of ^{137}Cs , and pH 2-12 was used. The sorption of the cesium by the two materials, was determined by measuring the gamma radiation emitted by the ^{137}Cs tracer. The zeolitic tuff presents higher uptake ability of radioactive cesium than the pure heulandite crystal, whereas the sorption of radioactive cesium is not significantly affected by the pH values of the initial solutions in the range pH 2-12. The clinoptilolitic zeolitic tuff NA11 is suitable material for various environmental, agricultural and industrial applications.

Keywords: zeolitic tuff, clinoptilolite, heulandite, cesium, sorption

Περίληψη

Δείγματα ζεολιθικού τόφφου από τη θέση Ρέμα Ντρίστα των Πετρωτών του Ν. Έβρου (NA11) και καθαρού φυσικού κρυστάλλου ευλανδίτη (HEU1) από τη συλλογή του Τομέα Ορυκτολογίας-Πετρολογίας-Κοιτασματολογίας του Τμήματος Γεωλογίας, Α.Π.Θ. μελετήθηκαν ως προς την ορυκτολογική τους σύσταση, την ορυκτοχημεία του περιεχόμενου ζεόλιθου και τη δεσμευτική ικανότητα σε αμμώνιο και ραδιενεργό Cs. Η μελέτη της ορυκτολογικής σύστασης με τη μέθοδο της περιθλασιμετρίας ακτίνων-X έδειξε ότι το δείγμα NA11 περιέχει ζεόλιθο τύπου-HEU σε ποσοστό 86% κ.β., μαρμαρυγίες + αργιλικά ορυκτά 4% κ.β., χαλαζία 4% κ.β., χριστοβαλίτη 2% κ.β και αστρίους 4% κ.β., ενώ το δείγμα HEU1 διαπιστώθηκε ότι είναι καθαρός κρυστάλλος ευλανδίτη. Η ορυκτοχημεία προσδιορίστηκε με τη μέθοδο της ηλεκτρονικής μικροσκοπίας (SEM-EDS) και διαπιστώθηκε ότι ο περιεχόμενος ζεόλιθος του δείγματος NA11 είναι Ca-ούχος κλινοπτιλόλιθος με χημικό τύπο $\text{Ca}_{1.8}\text{K}_{1.0}\text{Mg}_{0.7}\text{Na}_{0.5}\text{Al}_{6.4}\text{Si}_{29.5}\text{O}_{72}\cdot 2\text{H}_2\text{O}$, ενώ ο ζεόλιθος του δείγματος HEU1 είναι ευλανδίτης με χημικό τύπο $\text{Ca}_{3.6}\text{Na}_{1.0}\text{K}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{Al}_{8.1}\text{Si}_{27.6}\text{O}_{72}\cdot 2\text{H}_2\text{O}$. Η δεσμευτική ικανότητα των δειγμάτων μετρήθηκε με τη μέθοδο του κορεσμού σε οξικό αμμώνιο (AMAS). Τα δύο εξεταζόμενα υλικά παρουσιάζουν υψηλή δεσμευτική ικανότητα, η οποία μετρήθηκε για το ζεολιθικό τόφφο NA11 231 meq/100g, ενώ για τον ευλανδίτη (HEU1) 296 meq/100g. Για τον προσδιορισμό της δέσμευσης του ραδιενεργού Cs, χρησιμοποιήθηκε διάλυμα νιτρικού καισίου (CsNO_3), ιχνοθετημένο με μικρή ποσότητα ραδιενεργού Cs (^{137}Cs), σε τιμές pH από 2 έως 12. Η μέτρηση της δέσμευσης του ραδιενεργού Cs από τα δύο υλικά πραγματοποιήθηκε με χρήση της

μεθόδου της φασματοσκοπίας ακτίνων-γ. Ο ζεολιθικός τόφος παρουσιάζει υψηλότερη ικανότητα δέσμησης ραδιενεργού καισίου σε αντίθεση με τον καθαρό κρύσταλλο ευλανδίτη, ενώ η δέσμηση του ραδιενεργού καισίου δεν επηρεάζεται σημαντικά από τις τιμές pH των αρχικών διαλυμάτων στο εύρος pH 2-12. Ο ζεολιθικός τόφος NA11 είναι κατάλληλος για ποικίλες περιβαλλοντικές, γεωργικές και βιομηχανικές εφαρμογές.

Λέξεις κλειδιά: ζεολιθικός τόφος, κλινοπτιλόλιθος, ευλανδίτης, καισίο, δέσμηση

1. Introduction

A zeolitic-rich volcanoclastic tuff corresponds to a rock which contains high amounts of one or more from the different (more than 65) phases of zeolites. The zeolitic rock with numerous applications is the high quality HEU-type (clinoptilolite-heulandite) zeolitic tuff. Zeolites characterized by significant capacities. They have the ability to absorb and desorb water without major structural changes and they show an enhanced high cation exchange capacity and selectivity for monovalent and bivalent cations. 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 SiO₂ 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). HEU-type zeolites (clinoptilolite-heulandite) show tabular crystals and contain micro/nano-pores in a framework of channels with 10- and 8- members rings, in dimensions of 7.5x3.1 Å, 4.6x3.6 Å, 4.7x2.8 Å (Baerlocher *et al.*, 2007; Mitchell *et al.*, 2012). The main exchangeable cations are Na⁺, K⁺, Ca²⁺ and Mg²⁺ (Tsitsishvili *et al.*, 1992; Colella & Mumpton, 2000; Baerlocher *et al.*, 2001; Bish & Ming, 2001; Kantiranis *et al.*, 2011). The HEU-type zeolite structure is characterized by the presence of five distinct extra-framework sites (A1, A2, A3,

B and C) that may host a variety of exchangeable cations (Kantiranis *et al.*, 2011). The positions of both the extra-framework cations and water molecules depend on the nature of the exchangeable cations of the zeolites (Armbruster and Gunter, 1991; Gunter *et al.*, 1994). However, the exact structural arrangement in the channels also depends on the specific Si/Al framework distribution and water content, which dependent on the water vapor pressure surrounding the sample. Therefore, zeolitic rocks have already been proposed and successfully applied to the removal of fission products (e.g., Cs⁺, Sr²⁺) and actinides (e.g., Th, U, Np, Pu) from effluents of the nuclear industry (Misaelides *et al.*, 1995a,b, 2018; Godelitsas *et al.*, 1996; Rajec *et al.*, 1999; Misaelides, 2011). Zeolitic rocks, containing clinoptilolite and 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 (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 (Filippidis & Kantiranis, 2007; Vogiatzis *et al.*, 2012; Filippidis *et al.*, 2015a,b; 2016a,b; Filippidis, 2016; Floros *et al.*, 2018; Kalaitzis *et al.*, 2019).

¹³⁷Cs and ¹³⁴Cs are two of the main fission products in radioactive wastes from industrial applications. ¹³⁷Cs and ¹³⁴Cs are considered potentially dangerous to human health and to the environment. The relatively high yield in nuclear power plants, long half-lives and high solubility of cesium, its migration through ground water to the biosphere is dangerous for environment and human life (Myttenaere *et al.*, 1993; Andersson *et al.*, 2002). Through the decades different types of natural microporous materials have been used for the removal of cesium from the environment and aqueous systems (Sikalidis, 2002). The selectivity of zeolites for specific radioactive nuclides depends on the kind of the cations of the zeolite, on the crystal framework of zeolite, on ion size and shape, on charge density, on the ion valency and on the electrolyte concentration in the aqueous phase (Sand and Mumpton, 1976; Barrer, 1978). The aim of this study is the comparison of the cesium sorption ability between pulverized high quality HEU-

type (clinoptilolite-heulandite) zeolitic tuff and pulverized pure heulandite crystals.

2. Materials and Methods

Sampling took place at Petrota area of Evros region. Petrota belongs to eastern Rodope massif. The high quality HEU-type zeolitic tuff was obtained from specific continuous layers of zeolitic tuffs in Ntrista stream (sample NA11) whereas pure heulandite crystals (sample HEU1) is from the collection of the Department of Mineralogy-Petrology-Economic Geology, School of Geology, Aristotle University of Thessaloniki.

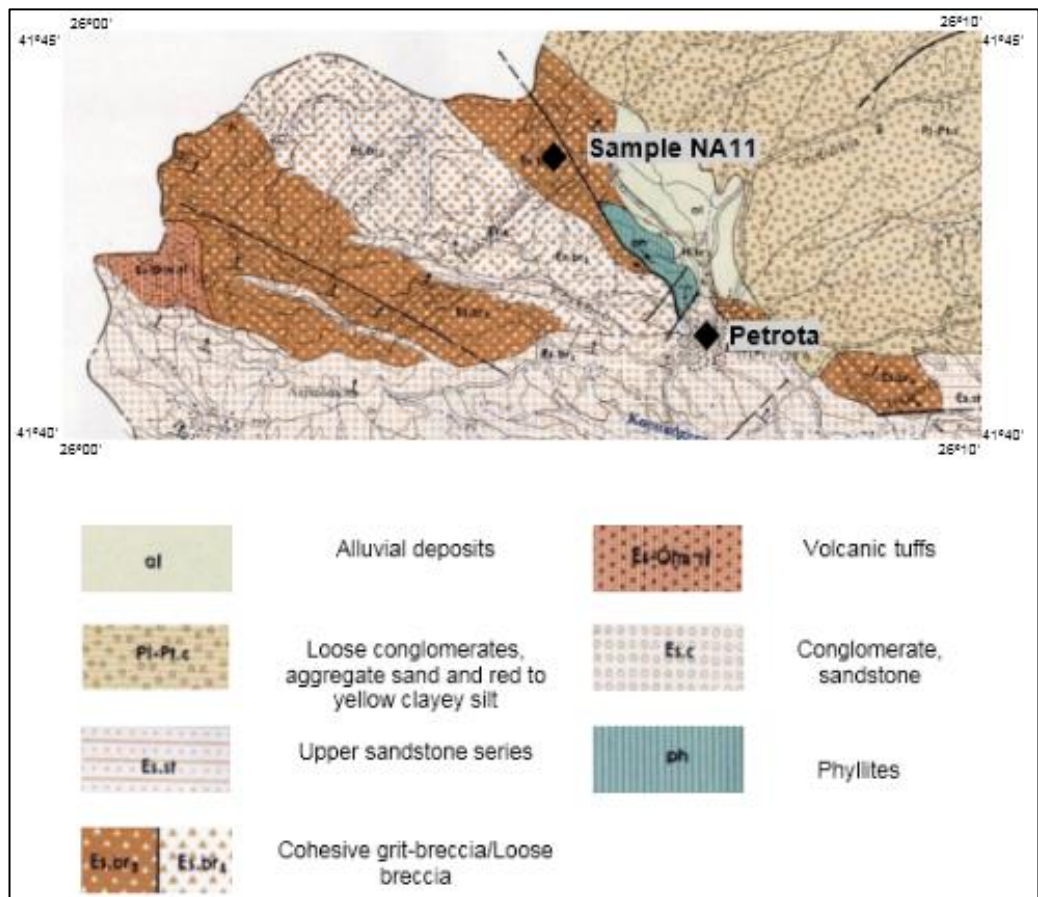


Fig 1: Geological map of sampling area (IGME, 1978).

The mineralogical composition of the samples was determined by X-Ray Diffraction (XRD). The XRD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered $\text{Cu}_{K\alpha}$ radiation on randomly oriented powder

samples. The samples were scanned over 3-63° 2θ interval at a scanning speed of 1.2 °/min. Furthermore, clay mineralogy was performed on oriented, glycolated and heated (550 °C/2.5 hours) samples scanned over 3-33° 2θ interval at a scanning speed of 0.24 °/min. The mineral-chemistry of the zeolites was determined by SEM-EDS microprobe analyses. SEM analyses performed using a Jeol JSM-840, equipped with a microanalyses system LINK AN10000. Measures have taken to minimize volatilization of alkali metals and alkaline earth metals. The uptake ability of the NA11 tuff sample, measured by the AMAS (Ammonium Acetate Saturation) method (Kantiranis *et al.*, 2011). The cesium sorption ability of the two materials (500 mg/L CsNO₃ aqueous solutions at different pH from 2 to 12 labelled with ¹³⁷Cs) 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 ¹³⁷Cs in the liquid phase). Different pH solution were chosen in order to define if the sorption ability is affected by the initial pH of the aqueous solutions.

3. Discussion and Conclusions

From the XRD analyses we found that sample NA11 from Ntrista stream consists of 86 wt% HEU-type zeolite, 4 wt% micas + clay minerals, 4 wt% christobalite, 4 wt% quartz and 4 wt% feldspars. Respectively, XRD analyses showed that the sample HEU1 is pure (100 wt%) heulandite. Also, in pretreated zeolite samples with cesium, XRD analyses showed that the mineralogy and the framework structure of samples remain unaffected after the adding of radioactive cesium cations. This is due to the fact that zeolites have an enhanced selectivity for monovalent cations such as Cs⁺ and NH₄⁺.

Microprobe analyses (Table1) showed that the chemical formula of the HEU-type zeolite of zeolitic tuff (NA11) is Ca_{1.8}K_{1.0}Mg_{0.7}Na_{0.5}Al_{6.4}Si_{29.5}O₇₂·21H₂O, whereas for pure heulandite (HEU1) the chemical formula is Ca_{3.6}Na_{1.0}K_{0.2}Sr_{0.2}Ba_{0.1}Al_{8.1}Si_{27.6}O₇₂·21H₂O. The contained zeolite of sample NA11 is Ca-clinoptilolite and its main exchangeable cations are Ca²⁺ and K⁺. Respectively, sample HEU1 is characterized as pure heulandite and its major

exchangeable cation is Ca^{2+} . Clinoptilolite and heulandite are the end members of HEU-type zeolite series. The Ammonium Acetate Saturation (AMAS) method showed that the uptake ability of sample NA11 is 231 meq/100g, while the corresponding value for pure heulandite crystals is 296 meq/100g. Results are in good agreement with the theoretical values of a typical clinoptilolite 220 – 254 meq/100g and of a typical heulandite 291 – 320 meq/100g uptake ability. The high uptake ability of sample NA11 is mainly due to the presence of clinoptilolite and to a lesser extent to clay minerals and micas. Also, the meso/macro pores of the zeolitic tuff contributes to the high uptake ability of sample NA11, while in sample HEU1 only the nano pores of the heulandite crystals contribute to the uptake ability. The high uptake ability measured for both samples indicates that the major process involved in NH_4^+ removal is the cation exchange.

Table1. Mineral-chemistry of pure heulandite crystal (sample HEU1) and of HEU type zeolite from the zeolitic tuff (sample NA11)		
average	23 analyses	22 analyses
	NA11	Pure HEU crystal
SiO_2	66,36	60,46
TiO_2	0,02	0,04
Al_2O_3	12,18	15,15
$\text{Fe}_2\text{O}_{3\text{tot}}$	0,12	0,15
MnO	0,04	0,07
MgO	1,02	0,07
CaO	3,82	7,29
SrO	0,07	0,89
BaO	0,05	0,81
Na_2O	0,59	1,16
K_2O	1,73	0,32
H_2O^*	14,00	13,59
Total	100,00	100,00
Number of cations in the basis of 72 oxygen atoms		
Si	29,5425	27,552
Ti	0,0112	0,0229
Al	6,3906	8,1368
Fe^{3+}	0,0134	0,0171
Mn	0,0151	0,0270
Mg	0,6768	0,0475
Ca	1,8221	3,5594
Sr	0,0181	0,2352
Ba	0,0087	0,1446
Na	0,5093	1,0249
K	0,9825	0,1860
H_2O	20,7869	20,6551
* Calculated by difference		

The results of gamma ray spectroscopy (Figure 2) showed that the cesium sorption ability of the HEU-type (Ca-clinoptilolite) zeolitic tuff (sample NA11) was higher than this of the pure heulandite (HEU1). The higher sorption ability of NA11 can be based on two main factors. The first factor is 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 second factor is the crystal framework of the zeolite and the chemical composition.

Chemical analyses (Table 1) showed that the zeolitic tuff is enhanced, apart from cations of Ca^{2+} 3.82, in monovalent cations such as $\text{K}^{+} + \text{Na}^{+} = 2.32$ and partially in $\text{Mg}^{2+} = 1.02$, while pure heulandite crystals are rich on bivalent cations such as $\text{Ca}^{2+} + \text{Sr}^{2+} + \text{Ba}^{2+} = 8.99$ and in lower amounts contain monovalent cations ($\text{K}^{+} + \text{Na}^{+} = 1.48$). According to Kantiranis et al. (2011) positions A1 and C in the crystal framework of HEU type zeolites occupied mainly by monovalent cations, while bivalent cations tend to occupy B places. The fact that A1 and C positions are bigger than B places and the size of dehydrated monovalent cations are smaller than the bivalent, have as a result the higher sorption ability of the zeolitic tuff.

Concerning the sorption ability in association with the pH on the initial aqueous solutions, it is obvious from figs. 2 and 3 that the sorption ability is not affected by the initial pH. This is due to the fact that 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. Between solutions with pH 4-10, materials neutralize the solutions approximately at pH 7 - 8. 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.

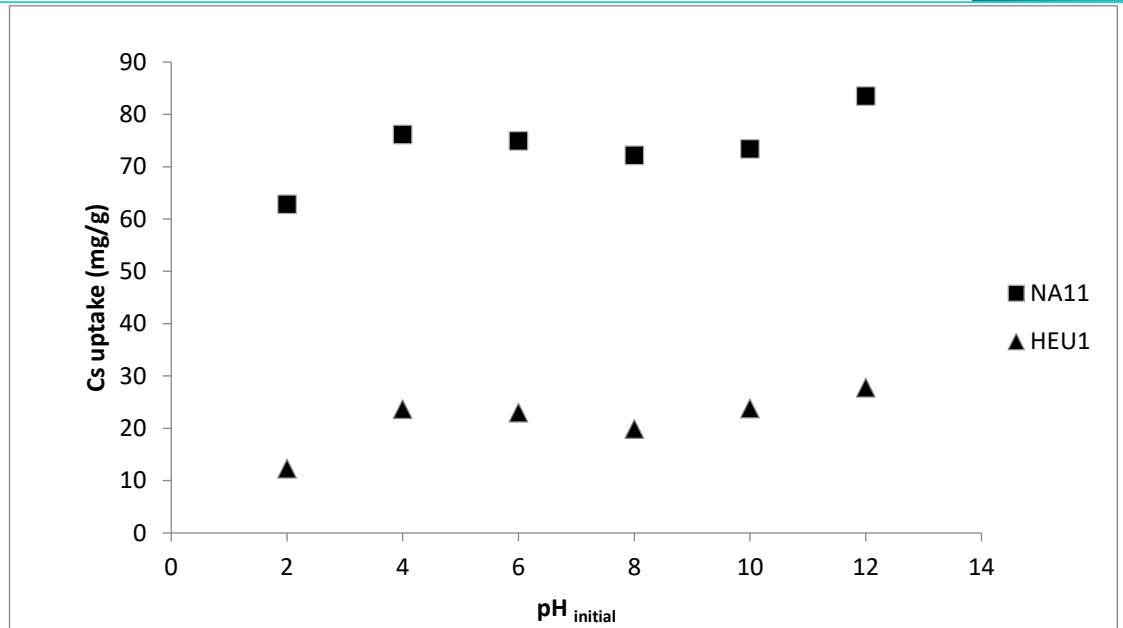


Fig. 2: Variation of Cs uptake capacity of zeolitic tuff (NA11) and of pure crystals of heulandite (HEU1) in accordance with the initial pH of the solutions.

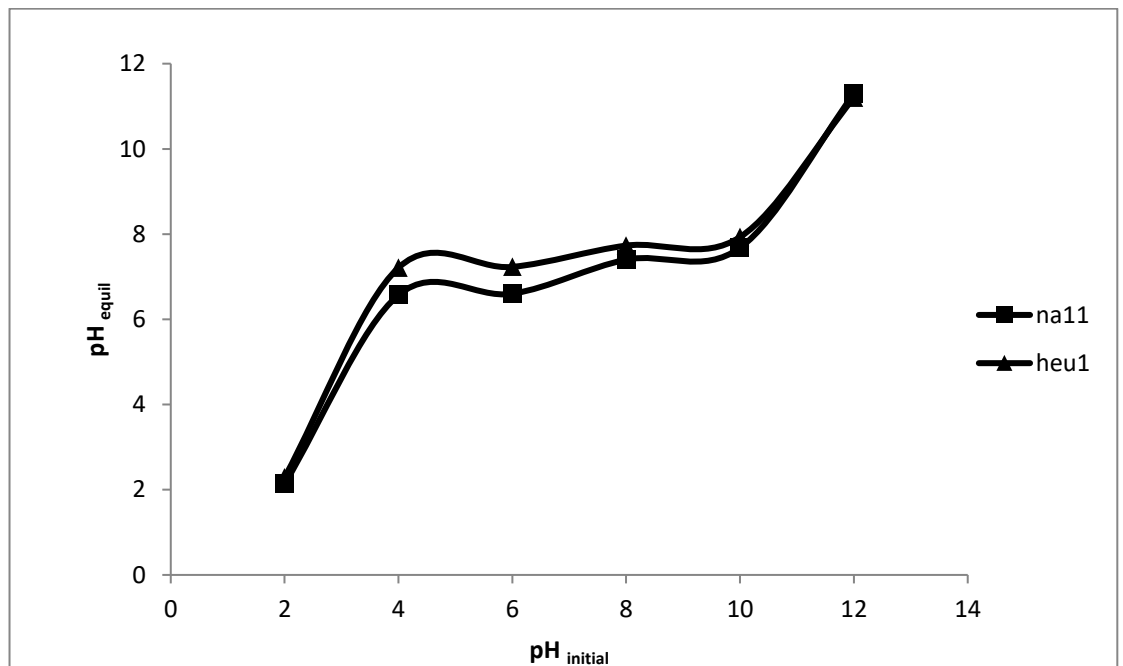


Fig. 3: Variation of pH in the solutions after using the zeolitic tuff (NA11) and the pure crystals of heulandite (HEU1), in comparison with initial pH of the aqueous.

To conclude, the zeolitic tuff characterized as a high quality zeolitic rock. The high cation exchange capacity, the mineralogical and chemical composition and the high capacity to bind efficiently radioactive cesium cations lay the zeolitic tuff suitable for environmental, agricultural and industrial uses particularly in the fixation of radionuclides.

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