

UPTAKE ABILITY OF ZEOLITIC ROCK FROM SOUTH XEROVOUNI, AVDELLA, EVROS, HELLAS

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Abstract

Zeolitic rock samples from South Xerovouni contain on average, 57 wt.% HEU-type zeolite, 6 wt.% clay minerals, 3 wt.% mica (total of 66 wt.% microporous minerals), 19 wt.% feldspars, 10 wt.% cristobalite and 5 wt.% quartz (total of 34 wt.% non-microporous minerals). Chemically the zeolitic rock consists mainly of 69.9 wt.% SiO₂, 13.2 wt.% Al₂O₃, 1.2 wt.% Fe₂O₃, 1.0 wt.% MgO, 3.0 wt.% CaO, 1.5 wt.% Na₂O and 2.2 wt.% K₂O. The zeolitic rock shows an average ammonia ion exchange capacity of 150 meq/100g. HEU-type zeolite accounts for the most of the uptake ability, while clay minerals and mica contribute to a relative small extent only. The uptake ability of the five zeolitic rock samples showed positive correlations with the content of HEU-type zeolite as well as with the total content of microporous minerals (zeolite + mica + clay minerals). Such materials could be used in a wide range and scale of agricultural, aquacultural, and environmental applications.

Key words: zeolite, HEU-type, Xerovouni, CEC, mineralogy.

1. Introduction

Zeolites constitute a major class of crystalline hydrated aluminosilicate microporous minerals including both natural and synthetic species (Breck, 1974). The crystalline framework of the zeolites is based on a three dimensional network of (Si,Al)O₄ tetrahedral and extra-framework alkali and alkaline-earth cations, which are loosely bound to the anionic charges within this framework structure and can be exchanged for other cations, including H⁺. High quality natural zeolites have many applications in industry, agriculture and the environment (e.g., Merkle and Slaughter, 1968; Barrer, 1978; Mumpton, 1978; Pond and Mumpton, 1984; Gottardi and Galli, 1985; Dyer, 1988; Tsitsishvili et al., 1992; Misaelides et al., 1993; Holmes, 1994; Ming and Mumpton, 1995; Misaelides et al., 1995a,b; Filippidis et al., 1996; Godelitsas et al., 1996a,b; Filippidis and Kassoli-Fournaraki, 2000; Bish and Ming, 2001; Kantiranis et al., 2002; Filippidis, 2008; Filippidis et al., 2008, 2009). The great majority of these applications employs their cation exchange capabilities and involves the replacement of the existing extra-framework cations with other cations from the surrounding environment. Due to the favourable ion-exchange selectivity of natural zeolites for certain cations, these minerals have been studied for potential use in the treatment of nuclear, municipal and industrial

wastewaters and acid mine drainage waters. It is of economic importance that natural zeolites are used in their natural state so that expensive purification is avoided.

Zeolite-bearing rocks occur in a variety of geologic settings; mostly as alteration or authigenic minerals, low temperature-pressure minerals in metamorphic systems, secondary minerals in weathering zones or in vein-deposits. Commercially interesting zeolites are presently limited to authigenic and alteration settings in finely crystalline sedimentary rocks (Mumpton, 1978). Zeolites are widespread in Greece and clinoptilolite is the most common type (e.g., Tsolis-Katagas and Katagas, 1989, 1990; Stamatakis et al., 1996; Filippidis and Kassoli-Fournaraki, 2000; Kantiranis et al., 2002). Clinoptilolite is a high silica member of the heulandite group of natural zeolites and occurs in abundant and easily mined, sedimentary deposits in many parts of the world (Mumpton, 1988). The composition and purity of natural clinoptilolites and therefore their physicochemical properties vary widely between deposits and may even vary within the same deposit (Mercer and Ames Jr, 1978; Kassoli-Fournaraki et al., 2000).

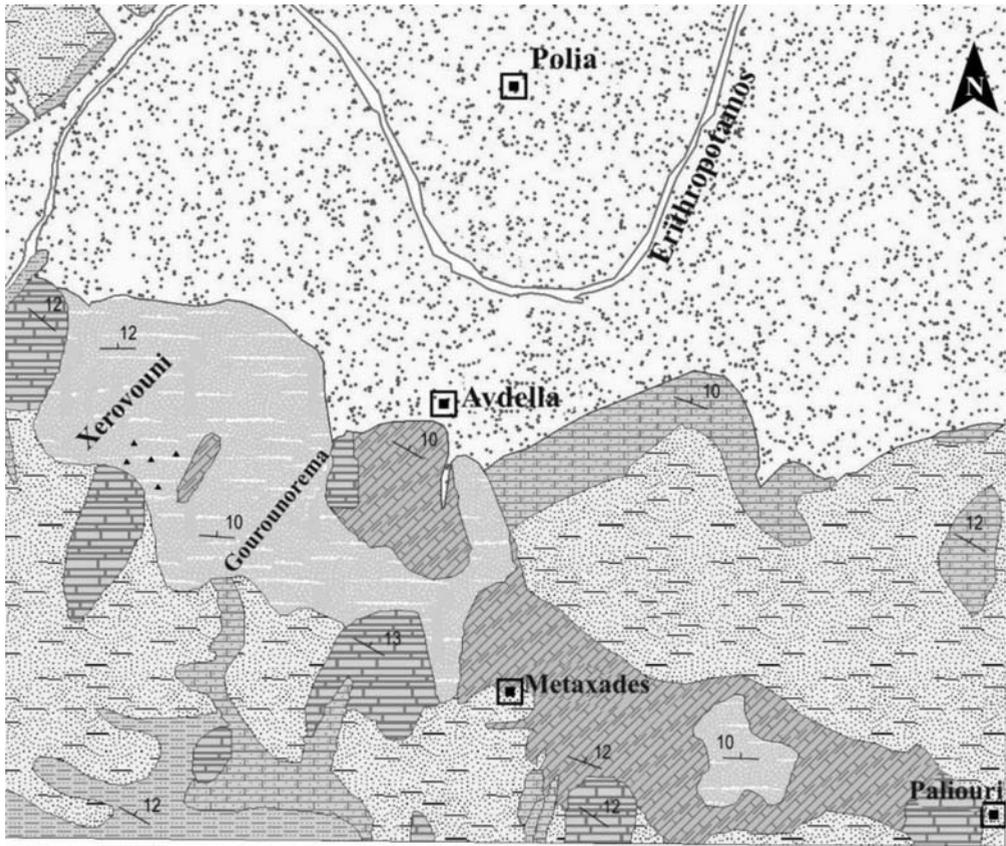
The present study investigates the relationship between the mineralogy and the uptake ability of HEU-type zeolite-bearing tuffs from south Xerovouni, Avdella, Evros, Hellas.

2. Geological setting

The Metaxades upper Eocene zeolite-bearing volcanoclastic sediments belong to the Orestias Tertiary molassic basin of the northeastern Thrace in Greece. This meta-Alpine basin has an elongated shape and extends into Bulgaria. It is dominated by sediments of Eocene to Pleistocene age, deposited unconformably on the crystalline basement of the Rhodope massif. In the investigated area (Fig. 1) the formations recognized are (Koutles et al., 1995): Eocene formations consisting of: a) breccias-conglomerates (10-15 m thick), which lie unconformably upon the metamorphosed basement. Their composition is phyllitic, gneissic, amphibolitic, quartzitic or andesitic; they display a grading from coarser to finer fragments upwards, b) gray siltstones (~100 m thick) with psammitic and marly interlayers, c) mostly semi-loose sandstones (40-50 m thick) of varying grain-size, including very thin clayey interlayers, d) white to pale gray, yellow or green zeolite-bearing volcanoclastic tuffs (20-25 m of visible thickness) conformably deposited on the sandstones or siltstones; a thin layer of gray marl is discernible on the upper part of the tuffs, e) loose white-yellowish marly limestone (510 m thick) and f) limestone (less than 30 m thick) rich in fossils. Oligocene formations of relatively great thickness, unconformably deposited on the Eocene formations. They consist of gray clays, red-yellowish sandstones, white-yellow siltstones and interlayers of marly limestone. Quaternary sediments of varying thickness, deposited over all previous formations. The complete sequence of the above formations is not always present in all sites of the basin. One or more formations may be locally absent due to tectonic activity, erosion or non-deposition. In the broader area, two main visible faults and several fractures have been observed.

3. Materials and Methods

Five zeolitic tuff samples were taken from South Xerovouni of Avdella-Metaxades area (Fig. 1), in order to determine their mineralogical and chemical composition, petrographic characteristics, and uptake ability. The samples were studied in their bulk form, ground (<125 μm) and homogenized. Samples for mineralogical and chemical analyses were ground further in an agate mortar, while thin sections were prepared for microscopic study. Chemical analyses of samples were carried out by AAS on a Perkin Elmer 5000 spectrometer equipped with a graphite furnace.



LEGEND

-  Holocene fluvio-terrestrial formations
-  Plio-Pleistocene formations
-  Limestones
-  Marly limestones
-  Volcaniclastic tuffs
-  Sandstones
-  Siltstones
-  15 Strike and dip of beds
-  Samples location
-  Village



Fig. 1: Geological map and samples locations (modified, Koutles et al., 1995).

The mineralogical composition of the samples was determined by X-ray Powder Diffraction (XRPD) method. The XRPD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuK_α radiation on randomly oriented samples. The counting statistics of the XRPD study were: step size: $0.01^\circ 2\theta$, start angle: 3° , end angle: 63° and scan speed: $0.02^\circ 2\theta/\text{sec}$. Quantitative estimates of the abundance of the mineral phases were derived from the XRPD data, using the intensity of certain reflections and external standard mixtures of minerals (Kantiranis et al., 2004).

In order to determine the sorption ability of each zeolite-rich sample, the samples were treated with 1M ammonium acetate (NH_4OAc) aqueous solution, according to the AMAS method (Bain and Smith, 1987). Approximately 125 mg of each $<125\ \mu\text{m}$ sample was added to a centrifuge tube with 10 mL of the 1N NH_4OAc solution. The suspensions were well shaken, agitated for 24 hours, and then centrifuged. The clear liquid was discarded and the NH_4OAc -saturation procedure repeated 9 times, adding fresh 10 mL of NH_4OAc solution each time. After the completion of the 10-day NH_4OAc -saturation, the excess NH_4OAc was washed with 10 mL of 99% isopropyl alcohol, well shaken, and centrifuged. The clear supernatant liquid was discarded and the procedure repeated five times. The samples then were dried in room temperature. Following the NH_4OAc saturation, the NH_4^+ ions retained by the zeolite-rich samples, are converted using a strong base to NH_3 and analysed by an ammonia electrode. The NH_3 concentration was determined using an Orion potentiometric ammonia gas electrode combined with a Jenway 3045 pH/mV/ion analyser. Each air-dried NH_4^+ -saturated sample was placed in a 100 mL Pyrex beaker containing a Teflon covered stirring bar. Deionised nitrogen-free water (50 mL) was added and the solution was stirred to suspend the sample. The electrode was immersed into the suspension taking care to prevent entrapment of air under the concave tip. By addition of 0.5 mL of 10M NaOH, the NH_3 measurements were taken at constant level achievement. The electrode calibration was performed daily using ammonium calibrating solutions of 10, 100 and 1000 ppm provided by Jenway and hourly using the 10 ppm ammonium solution.

4. Results and Discussion

The study of the thin sections show the presence of zeolite, mica (biotite), clay minerals (mainly smectite), feldspars, quartz and amorphous material (Fig. 2). Also, were recognized glass shards, i.e. sites of altered volcanic glass, which consist from outer to inner of clay minerals and fine zeolite crystals (Fig. 3).

The semi-quantitative mineralogical composition (wt. %), the total micro-porous mineral content (wt. %) and the uptake ability of all samples are presented in Table 1. The major mineral phase present in the studied samples is found to be HEU-type zeolite, with percentages varying from 42 wt.% (sample X1) to 67 wt.% (sample X4), with an average amount of 57 wt.%. These results are in good agreement with previous studies on the zeolitic tuffs of Metaxades Area, which report an average amount of 58 wt.% in HEU-type zeolite (Marantos et al., 1989; Tsirambides et al., 1989, 1993; Tsirambides, 1991; Filippidis, 1993; Misaelides et al., 1994a,b, 1995a,b; Koutles et al., 1995; Symeopoulos et al., 1996; Haidouti, 1997; Tserveni-Gousi et al., 1997; Sikalidis, 1998; Yannakopoulos et al., 1998; Vlessidis et al., 2001; Filippidis and Kassoli-Fournaraki, 2002; Katranas et al., 2003; Papadopoulos et al., 2004; Filippidis and Kantiranis, 2005; Kantiranis et al., 2006; Filippidis et al., 2007). In minor amounts plagioclase (5-21 wt.%), K-feldspar (4-19 wt.%), cristobalite (3-17 wt.%), quartz (3-8 wt.%), micas (3-4 wt.%) and clay minerals (4-11 wt.%), were also determined. The total percent of micro-porous minerals (zeolite + micas + clays minerals) vary from 49 wt.% (sample X1) to 75 wt.% (sample X4), while feldspars + quartz + cristobalite constitute the non-microporous content of the samples varying between 25 wt.% (sample X4) and 51 wt.% (sample X1).

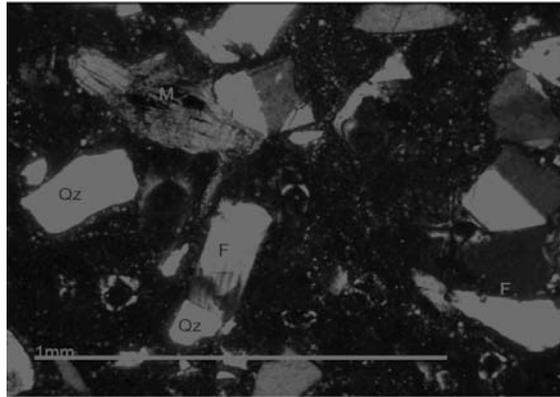


Fig. 2: Representative microphotograph of the studied samples. Qz=Quartz, M=Mica (biotite), F=Feldspars (Nicols +).

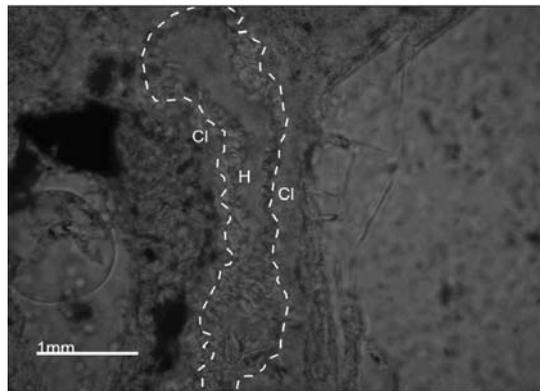


Fig. 3: A glass shard (white line). H=HEU-type zeolite, Cl=Clay minerals (Nicols //).

The chemical compositions of the zeolite-bearing rock samples are presented in Table 2. All samples contain high amounts of SiO₂ varying between 69.24 wt. % (sample X1) and 70.63 wt. % (sample X4). The Al₂O₃ content measured from 12.12 wt. % (sample X4) to 14.57 wt. % (sample X1). Low amounts of TiO₂, MnO and Fe₂O_{3T} were also found. The total percentage of oxides of the exchangeable cations Mg, Ca, Na, and K vary between 6.84 wt. % (sample X4) and 9.11 (sample X1) with a mean value of 7.75 wt.%. These cations mainly came from the zeolite framework, but also high amounts of feldspars and /or micas + clays may affect their content, especially in sample X1. Loss of ignition varies between 6.07 wt.% (sample X1) and 9.42 wt.% (sample X4).

The chemical formula of the HEU-type zeolite in the studied area, calculated from microprobe analyses of prior studies (Tsirambides et al., 1993; Koutles et al., 1995; Kantiranis et al., 2006) is Ca_{2.1}K_{0.5}Mg_{0.3}Na_{0.3}Al_{6.3}Si_{29.9}O₇₂·18.9H₂O.

The measured uptake ability varies between 111 meq/100g (sample X1) and 176 meq/100g (sample X4), with an average value of 150 meq/100g for all five samples (Table 1). This value is in very good agreement with the theoretical value of 152 meq/100g calculated taking in considerations the mineralogical composition of the samples and the theoretical ion exchange capacity values of clinop-

Table 1. Semi-quantitative mineralogical composition (wt.%) and uptake ability (meq/100g) of the South Xerovouni samples.

Sample	X1	X2	X3	X4	X5	Average
HEU-type zeolite	42	62	52	67	59	57
Micas (Biotite)	3	3	4	3	4	3
Clay Minerals	4	6	11	5	5	6
K-Feldspars	19	8	9	6	4	9
Plagioclases	21	8	9	6	5	10
Quartz	8	3	4	3	6	5
Cristobalite	3	10	11	10	17	10
Micro-porous minerals	49	71	67	75	68	66
Uptake ability	111	164	143	176	156	150

Table 2. Whole rock chemical analyses (wt.%) of South Xerovouni samples.

Sample	X1	X3	X4	Average
SiO ₂	69.24	69.91	70.63	69.93
TiO ₂	0.08	0.10	0.07	0.08
Al ₂ O ₃	14.57	12.81	12.12	13.17
Fe ₂ O ₃ t	1.25	1.30	0.92	1.16
MnO	0.09	0.09	0.11	0.10
MgO	0.89	1.22	0.92	1.01
CaO	2.75	2.89	3.33	2.99
Na ₂ O	2.47	1.21	0.90	1.53
K ₂ O	3.00	1.98	1.69	2.22
L.O.I.*	6.07	8.63	9.42	8.04
<i>Total</i>	<i>100.41</i>	<i>100.13</i>	<i>100.10</i>	<i>100.23</i>

*LOI=Loss of Ignition

tilolite (254 meq/100g, Mumpton, 1977), smectite (100 meq/100g, Deer et al., 1992) and biotite (25 meq/100g, Deer et al., 1992).

The comparison between the mineralogical composition and the uptake ability, results in positive correlation between the uptake ability and the wt.% composition in zeolite and total micro-porous minerals. The correlation coefficients were found 0.99 and 0.95 respectively (Figs 4 and 5).

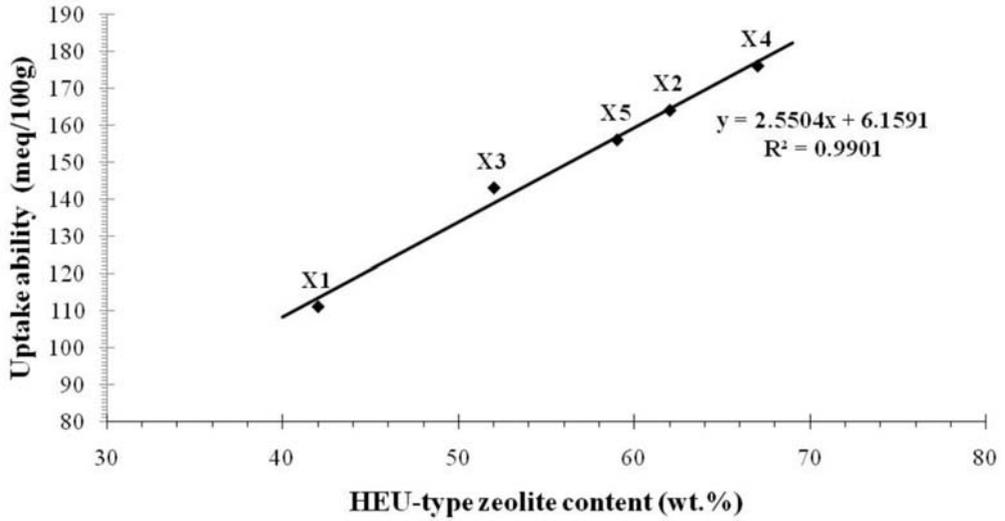


Fig. 4: Correlation of HEU-type zeolite content vs uptake ability of South Xerouvouni samples.

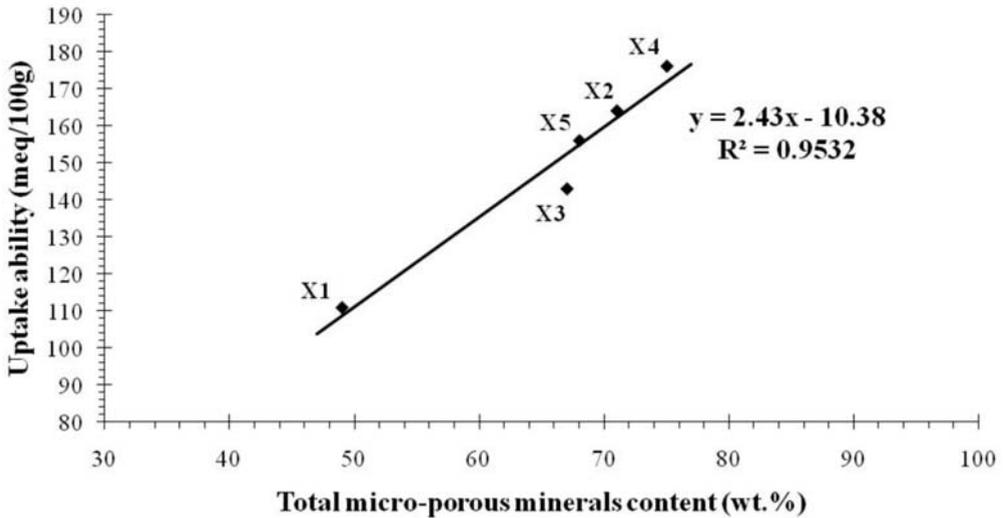


Fig. 5: Correlation of total micro-porous minerals content vs uptake ability of South Xerouvouni samples.

The measured uptake abilities gives the opportunity of utilizing the studied South Xerouvouni zeolitic tuffs in a wide range of environmental applications, such as: improvement of drinking water, purification of municipal and industrial wastewaters and wastewater treatment units, conversion of sewage sludge and manure to odourless fertilizer, oxygen enrichment of aqua, fishery and fish breeding for production of healthier food, soil amendment, odour control and gas purification and drying systems.

5. Conclusions

Five zeolitic tuff samples were taken from South Xerovouni of Avdella-Metaxades area, in order to determine their mineralogical and chemical composition, petrographic characteristics, and uptake ability. The major mineral phase present in the studied samples is found to be HEU-type zeolite, with an average amount of 57 wt.%. In minor amounts plagioclase, K-feldspar, cristobalite, quartz, micas and clay minerals, were also determined. The total percent of micro-porous minerals (zeolite + micas + clay minerals) vary from 49 to 75 wt.%, while the non-microporous content between 25 and 51 wt.%. All samples contain high amounts of SiO₂ varying between 69.24 and 70.63 wt. %. The Al₂O₃ content measured from 12.12 to 14.57 wt. %, while low amounts of TiO₂, MnO and Fe₂O_{3T} were also found. The total percentage of oxides of the exchangeable cations Mg, Ca, Na, and K vary between 6.84 and 9.11 wt.% with a mean value of 7.75 wt.%. These cations mainly came from the zeolite framework, but also high amounts of feldspars and /or micas + clays may affect their content. Loss on ignition vary between 6.07 and 9.42 wt.%. The measured uptake ability varies between 111 and 176 meq/100g, with an average value of 150 meq/100g for all five samples, showing a positive correlation with the zeolite and total micro-porous minerals content.

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