

Environmental, industrial and agricultural applications of Hellenic Natural Zeolite*

Anestis A. Filippidis

Department of Mineralogy-Petrology-Economic Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Hellas
e-mail: anestis@geo.auth.gr

ABSTRACT: The Hellenic Natural Zeolite (HENAZE) from Ntrista stream of Petrota village (Evros), contains 89 wt.% HEU-type zeolite and exhibit an ammonia ion exchange capacity (sorption ability) of 226 meq/100g. The commixture of sewage sludge originated from Arta town with the HENAZE, resulted to odorless and cohesive zeo-sewage sludge. The treatment of Kilkis City urban wastewaters with the HENAZE resulted to production of clear water with improved quality parameters by 92% for the color, 94% for the suspended particles, 95% for the chemical oxygen demand, 950% for the dissolved oxygen, 96% for the P_2O_5 , 99% for the NH_4 , 97% for the SO_4 , 92% for the NO_3 , 82% for the NO_2 , 90% for the C_{total} , 94% for the Mn and 93% for the Ni contents. Simultaneously, a precipitate of odorless and cohesive zeo-sewage sludge was produced. The treatment of Thessaloniki textile industry wastewaters with the HENAZE resulted to production of clear water with improved quality parameters by 97% for the color, 93% for the suspended particles, 95% for the chemical oxygen demand, 98% for the P_2O_5 and for the NH_4 contents. Simultaneously, a precipitate of odorless and cohesive zeo-sludge was produced. The values of the quality parameters, measured in the clear waters, are fulfilling the requirements for disposition as downstream, irrigation, swimming and fish waters. HENAZE removed 55% of NO_3 from well groundwater, as well as 74% of Pb, 79% of Ag and 57% of NO_3 from their aqueous solutions. The treatment of Koronia Lake water with the HENAZE, resulted to clear water with improved quality parameters by 93% for the color and 96% for the chemical oxygen demand. HENAZE also removed 51-92% of cyanobacteria from Doirani Lake water and their culture. The odorless and cohesive zeo-sewage sludge produced, either by the commixture of sewage sludge with the HENAZE or as precipitate from HENAZE-treatment of urban waste waters, is suitable for the reclamation of agricultural soils. The odorless and cohesive zeo-sewage sludge, as well as the odorless and cohesive zeo-sludge, is suitable for safe deposition, since their dangerous species are not leached with deionised water. The addition of HENAZE in the agricultural soils, increases the crops yield by 17-66 % and improves the quality by 4-46 % of agricultural products, reduces the use of fertilizers by 56-100 %, reduces the usage of irrigation water by 33-67 %, prevents the seepage of dangerous species into the water environment (e.g., NO_3 by 55-92 %), protecting thus the quality of surface and groundwater. The usage of HENAZE in vivarium units and in the animal nutrition increases the production (e.g., 17% of cow milk, 7% of broilers body weight) and improves the quality of their products, reduces the feed cost, the animal diseases, animal medication, the new-born animal's death-rate and the malodor, converting thus the manure to odorless fertilizer. The mineralogical composition and the physico-chemical properties, make HENAZE suitable material for numerous environmental, industrial and agricultural applications, such as, animal nutrition, soil amendment for agriculture, conditioning of acid and basic soils, greenhouse and flowers substrates, durability and health improvement of lawn, purification of industrial and urban wastewaters, treatment of sewage sludge, odor control, fish farming, gas purification and drying, oxygen enrichment of aqua ecosystems, improvement of drinking water, constructed wetlands and wastewater treatment units.

Key-words: Natural zeolite, zeo-sewage sludge, zeo-sludge, groundwater, surface-waters, urban wastewaters, industrial wastewaters, cyanobacteria.

ΠΕΡΙΛΗΨΗ: Ο Ελληνικός Φυσικός Ζεόλιθος (ΕΛΦΥΖΕ) από το ρέμα Ντρίστα του χωριού Πετρωτά του Νομού Έβρου, περιέχει 89 %κ.β. ζεόλιθο τύπου-HEU και παρουσιάζει ικανότητα ανταλλαγής ιόντων αμμωνίας (ικανότητα απορρόφησης) 226 meq/100g. Η ανάμειξη λυματολάσπης της πόλεως της Άρτας με τον ΕΛΦΥΖΕ, είχε ως αποτέλεσμα την παραγωγή άοσμης και συνεκτικής ζεο-λυματολάσπης. Η κατεργασία αστικών λυμάτων της πόλεως του Κιλκίς με τον ΕΛΦΥΖΕ έδωσε διαυγές νερό με βελτιωμένες τις ποιοτικές παραμέτρους κατά 92% για το χρώμα, 94% για τα αιωρούμενα στερεά, 95% για το χημικά απαιτούμενο οξυγόνο, 950% για το διαλυμένο οξυγόνο, 96% για τα P_2O_5 , 99% για την NH_4 , 97% για τα SO_4 , 92% για τα NO_3 , 82% για τα NO_2 , 90% για το C_{total} , 94% για το Mn και 93% για το Ni. Ταυτόχρονα, η κατεργασία έδωσε ως ίζημα άοσμη και συνεκτική ζεο-λυματολάσπη. Η κατεργασία υγρών αποβλήτων βαφείων της Θεσσαλονίκης, έδωσε διαυγές νερό με βελτιωμένες τις ποιοτικές παραμέτρους κατά 97% για το χρώμα, 93% για τα αιωρούμενα στερεά, 95% για το χημικά απαιτούμενο οξυγόνο, 98% για τα P_2O_5 και για την NH_4 . Ταυτόχρονα, η κατεργασία έδωσε ως ίζημα άοσμη και συνεκτική ζεο-λάσπη. Οι τιμές των παραπάνω ποιοτικών παραμέτρων στα διαυγή νερά, είναι μικρότερες από το ανώτατο επιτρεπόμενο όριο των πρότυπων νερών για διάθεση σε φυσικό αποδέκτη, για άρδευση, κολύμβηση και διαβίωση ψαριών. Ο ΕΛΦΥΖΕ απομάκρυνε το 55% των NO_3 από υπόγειο νερό γεώτρησης, καθώς επίσης το 74% του Pb, το 79% του Ag και το 57% των NO_3 από τα υδατικά τους διαλύματα. Η κατεργασία νερού της λίμνης Κορώνειας με τον ΕΛΦΥΖΕ, έδωσε διαυγές νερό με βελτιωμένες τις ποιοτικές παραμέτρους κατά 93% για το χρώμα και 96% για το χημικά απαιτούμενο οξυγόνο. Ο ΕΛΦΥΖΕ απομάκρυνε επίσης το 51-92% των κυανοβακτηρίων από νερό της λίμνης Δοϊράνης και από καλλιέργειες τους. Η άοσμη και συνεκτική ζεο-λυματολάσπη που παράγεται, είτε με την ανάμειξη της λυματολάσπης με τον ΕΛΦΥΖΕ, είτε ως ίζημα με την κατεργασία των αστικών λυμάτων με ΕΛΦΥΖΕ, είναι κατάλληλη για χρήση ως εδαφοβελτιωτικό στις γεωργικές καλλιέργειες. Η άοσμη και συνεκτική ζεο-λυματολάσπη, καθώς και η άοσμη και συνεκτική ζεο-λάσπη, είναι κατάλληλες για ασφαλή απόθεση, επειδή τα επιβλαβή συστατικά τους δεν εκπλύνονται με απιονισμένο νερό. Η προσθήκη του ΕΛΦΥΖΕ στα αγροτικά εδάφη, αυξάνει τις σοδειές κατά 17-66% και βελτιώνει την ποιότητα των αγροτικών προϊόντων κατά 4-46%, μειώνει τη χρήση λιπασμάτων κατά 56-100 %, μειώνει την κατανάλωση του νερού άρδευσης κατά 33-67 %, αποτρέπει την έκπλυση επιβλαβών ουσιών στο υδάτινο περιβάλλον (π.χ., NO_3 κατά 55-92 %), προστατεύοντας έτσι την ποιότητα των επιφανειακών και υπόγειων υδάτων. Η χρήση του ΕΛΦΥΖΕ ως υλικό δαπέδου κτηνοτροφικών μονάδων και πρόσθετο ζωοτροφών, αυξάνει την παραγωγή (π.χ., 17% στο γάλα αγελάδων, 7% στο βάρος κρεο-παραγωγών ορνιθίων) και βελτιώνει την ποιότητα των προϊόντων, μειώνει την κατανάλωση τροφής, τις ασθένειες και τη φαρμακευτική αγωγή των ζώων, τη θνησιμότητα των νεογνών και τη δυσοσμία, μετατρέποντας την κοπριά σε άοσμο λίπασμα. Η ορυκτολογική σύσταση και οι φυσικο-χημικές ιδιότητες, καθιστούν τον ΕΛΦΥΖΕ κατάλληλο

* Περιβαλλοντικές, βιομηχανικές και αγροτικές εφαρμογές του Ελληνικού Φυσικού Ζεόλιθου

υλικό για πολυάριθμες περιβαλλοντικές, βιομηχανικές και αγροτικές εφαρμογές, όπως ζωοτροφές, εδαφοβελτιωτικό γεωργικών καλλιεργειών, βελτιωτικό όξινων και αλκαλικών εδαφών, υπόστρωμα θερμοκηπίων και ανθοκομικής, ανθεκτικότερο και υγιέστερο γρασίδι, καθαρισμό βιομηχανικών και αστικών υγρών αποβλήτων, κατεργασία λυματολάσπης, αποσημητικό υλικό, ιχθυοκαλλιέργειες, καθαρισμό και ξήρανση αερίων, οξυγόνωση υδάτινων οικοσυστημάτων, βελτίωση ποιότητας πόσιμου νερού, τεχνητούς υδροβιότοπους και μονάδες διαχείρισης υδάτων.

Λέξεις-κλειδιά: Φυσικός ζεόλιθος, ζεο-λυματολόαση, ζεο-λάσπη, υπόγειο νερό, επιφανειακά ύδατα, αστικά λύματα, βιομηχανικά υγρά απόβλητα, κωνοβακτήρια.

INTRODUCTION

Zeolite comprises a special solid crystalline microporous material, with open structure and void space. Some high quality HEU-type natural zeolites, displays unique physical and chemical features and have a great variety of environmental, industrial and agricultural applications. The large natural zeolite deposits and the low cost of mining, gave access to large-scale utilization (e.g., MUMPTON, 1977; SAND & MUMPTON, 1978; POND & MUMPTON, 1984; GOTTARDI & GALLI, 1985; TSITSISHVILI *et al.*, 1992; HOLMES, 1994; COLELLA & MUMPTON, 2000; COLELLA *et al.*, 2001; KALLO, 2001; MING & ALLEN, 2001; TCHERNEV, 2001; HARBEN, 2002).

Around the village of Petrota (Northeastern Greece), seven different zeolitic occurrences show varying zeolite content and cation exchange capacity (CEC). The Livadakia location on average, contains 39 wt.% HEU-type zeolite with CEC of 101 meq/100g, the Palestra location 47 wt.% HEU-type zeolite with CEC of 91 meq/100g, the Toponymio Petrota location 53 wt.% HEU-type zeolite with CEC of 115 meq/100g, the Mavri Petra location 74 wt.% HEU-type zeolite with CEC of 186 meq/100g, the Fylakio Omega location 45 wt.% mordenite with CEC of 101 meq/100g and the Gkazomylos location contains 59 wt.% HEU-type zeolite with CEC of 167 meq/100g (Table 1).

In the Ntrista stream location of Petrota village has been located a zeolite deposit, the Hellenic Natural Zeolite (HENAZE) of GEO-VET N. Alexandridis & Co O.E. concession, containing on average 89 wt.% HEU-type zeolite with CEC of 226 meq/100g (Table 1). The present study investigates the production of odorless and cohesive zeo-sewage sludge by treatment of sewage sludge originated from Arta town with the HENAZE. Some other environmental, industrial and agricultural uses of HENAZE are also reported.

MATERIALS AND METHODS

The Hellenic Natural Zeolite (HENAZE) sample used was selected from a vertical profile of the Ntrista stream within the GEO-VET's concession. The sample was ground < 0.5 mm and homogenized (Fig. 1).

A part of the sample was ground further in an agate mortar in order to determine its mineralogical composition by X-ray Powder Diffraction (XRPD) method. The XRPD analysis was performed using a Philips diffractometer, Ni-filtered $\text{CuK}\alpha$ radiation on randomly oriented samples. The samples were scanned from 3° to 65° 2θ at a scanning speed of



Fig. 1. The < 0.5 mm grain-size of HENAZE used for the present study.

1.2°/min. Semi-quantitative estimates of the minerals were derived from the XRPD data, using the intensity (counts) of certain reflections, the density and the mass absorption coefficient for $\text{CuK}\alpha$ radiation of the minerals (FILIPPIDIS & KANTIRANIS, 2007). The morphology of the HEU-type zeolite was studied by Scanning Electron Microscopy (SEM).

The sewage sludge originated from Arta town (Western Greece) was commixed with the HENAZE at high-speed shaker, in nine different proportions of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90 (sewage sludge: HENAZE). A part of the produced zeo-sewage sludge was left to dry at room temperature and another part was left to dry at a temperature of 105 °C.

RESULTS

The semi-quantitative mineralogical composition of HENAZE is presented in Table 2. The HENAZE contains 89 wt.% HEU-type zeolite, 3 wt.% mica + clay-minerals, 5 wt.% feldspars and 3 wt.% quartz. The total microporous minerals content is 92 wt.%.

The typical platy crystals of HEU-type zeolite have a grain-size of approximately 5 to 25 μm (Fig. 2). The HENAZE contains microporous in the HEU-type zeolite crystals), mesoporous and macroporous. The commixture of sewage sludge originated from Arta town with the HENAZE resulted to odorless and cohesive zeo-sewage sludge (Figs 3-6).

DISCUSSION AND CONCLUSIONS

The Hellenic Natural Zeolite (HENAZE), contains 89 wt.% HEU-type zeolite, 3 wt.% mica + clay-minerals, 5 wt.% feldspars and 3 wt.% quartz. The chemical formula of the HEU-type zeolite is $\text{Ca}_{1.5}\text{K}_{1.4}\text{Mg}_{0.6}\text{Na}_{0.5}\text{Al}_{6.2}\text{Si}_{29.8}\text{O}_{72}\cdot 20\text{H}_2\text{O}$ and ammonium exchange capacity of HENAZE is 226

TABLE 1

The content and type of zeolite, as well as the Cation Exchange Capacity (CEC, meq/100g) of zeolites occurring in locations around Petrota village (North-eastern Greece).

Location	wt.% Zeolite	CEC	Reference
Livadakia	35 HEU-type	101	FILIPPIDIS & KASSOLI-FOURNARAKI (2002)
	43 HEU-type	101	FILIPPIDIS <i>et al.</i> (2007c)
	39	101	<i>Average</i>
Palestra	47 HEU-type	82	MARANTOS & PERDIKATIS (1994)
	HEU-type	-	STAMATAKIS <i>et al.</i> (1996)
	HEU-type	-	STAMATAKIS <i>et al.</i> (1998a)
	HEU-type	-	STAMATAKIS <i>et al.</i> (1998b)
	HEU-type	-	HALL <i>et al.</i> (2000)
	HEU-type	-	STAMATAKIS <i>et al.</i> (2000)
	HEU-type	100	STAMATAKIS <i>et al.</i> (2001)
	47	91	<i>Average</i>
Toponymio Petrota	42 HEU-type	80	MARANTOS & PERDIKATIS (1994)
	HEU-type	-	STAMATAKIS <i>et al.</i> (1998a)
	54 HEU-type	132	FILIPPIDIS & KASSOLI-FOURNARAKI (2002)
	54 HEU-type	-	KANTIRANIS <i>et al.</i> (2006)
	63 HEU-type	132	FILIPPIDIS <i>et al.</i> (2007c)
	53	115	<i>Average</i>
Mavri Petra	76 HEU-type	-	KIROV <i>et al.</i> (1990)
	54 HEU-type	-	MARANTOS & PERDIKATIS (1994)
	HEU-type	-	STAMATAKIS <i>et al.</i> (1998a)
	HEU-type	-	BARBIERI <i>et al.</i> (2001)
	79 HEU-type	185	FILIPPIDIS & KASSOLI-FOURNARAKI (2002)
	79 HEU-type	-	KANTIRANIS <i>et al.</i> (2006)
	83 HEU-type	186	FILIPPIDIS <i>et al.</i> (2007c)
	74	186	<i>Average</i>
Fylakio Omega	45 Mordenite	101	KIROV <i>et al.</i> (1990)
	45	101	<i>Average</i>
Gkazomylos	41 HEU-type	-	KIROV <i>et al.</i> (1990)
	43 HEU-type	-	MARANTOS & PERDIKATIS (1994)
	HEU-type	-	STAMATAKIS <i>et al.</i> (1998a)
	HEU-type	-	HALL <i>et al.</i> (2000)
	HEU-type	-	BARBIERI <i>et al.</i> (2001)
	69 HEU-type	167	FILIPPIDIS & KASSOLI-FOURNARAKI (2002)
	69 HEU-type	-	KANTIRANIS <i>et al.</i> (2006)
	75 HEU-type	167	FILIPPIDIS <i>et al.</i> (2007c)
	59	167	<i>Average</i>
Ntrista Stream	89 HEU-type	226	FILIPPIDIS & KANTIRANIS (2002)
	89 HEU-type	226	FILIPPIDIS (2005a)
	89 HEU-type	226	FILIPPIDIS (2005b)
	89 HEU-type	226	FILIPPIDIS (2007)
	89 HEU-type	229	FILIPPIDIS & KANTIRANIS (2007)
	89 HEU-type	226	FILIPPIDIS (2008)
	89 HEU-type	226	VOGIATZIS <i>et al.</i> (2008)
	89	226	<i>Average</i>

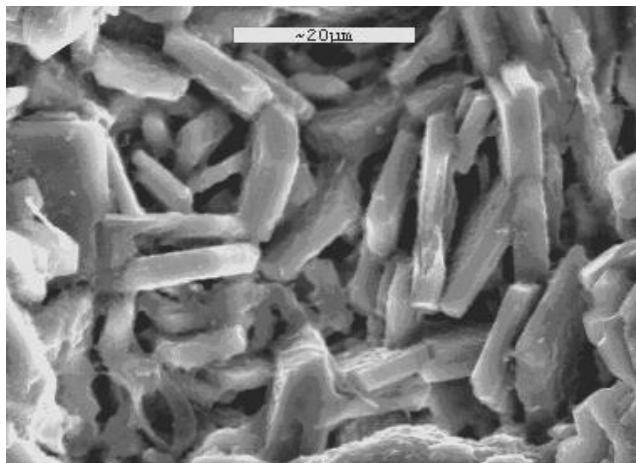


Fig. 2. SEM microphotograph of typical platy crystals of HEU-type zeolite of the HENAZE.



Fig. 3. Starting sewage sludge (external deposition) originated from Arta town.



Fig. 4. Odorless and cohesive zeo-sewage sludge (proportions 80:20, after 18 hours at 105 °C).

meq/100g. The chemical composition of HENAZE is 68.62 wt.% SiO₂, 11.80 wt.% Al₂O₃, 2.92 wt.% K₂O, 2.14 wt.% CaO, 1.13 wt.% Na₂O and 0.75 wt.% MgO. HENAZE shows a remarkable ability to neutralize the pH of basic water (pH 9.5) from the lake Koronia (Prefecture of Thessaloniki) and of acidic stream mine water (pH 5.5) from NE Chalkidiki Prefecture, exhibiting an amphoteric character (FILIPPIDIS &



Fig. 5. Odorless and cohesive zeo-sewage sludge (proportions 50:50, after 36 hours at RT).

KANTIRANIS, 2002, 2007; FILIPPIDIS, 2005b).

The commixture of sewage sludge originated from Arta town with the HENAZE resulted to odorless and cohesive zeo-sewage sludge, suitable for the amendment of agricultural soils, but also for safe deposition.

The treatment of urban wastewaters of pH 8.4 (Table 3) with the HENAZE, resulted to production of clear water (Fig. 7) of pH 7.5, free of odors and improved quality parameters by 92 % for the color, 94 % for the suspended particles, 95 % for the chemical oxygen demand (COD), 950 % for the dissolved oxygen, 96 % for the P₂O₅, 99 % for the NH₄, 97 % for the SO₄, 92 % for the NO₃, 82 % for the NO₂, 90 % for the Cr_{total}, 94 % for the Mn and 93 % for the Ni contents (Table 3). Simultaneously, a precipitate of odorless and cohesive zeo-sewage sludge was produced, dried overnight at room temperature (Fig. 7). The values of the pH and of the quality parameters, measured in the clear water, are fulfilling the requirements for disposition as downstream, irrigation, swimming and fish waters. Leaching experiments of the zeo-sewage sludge by deionised water, proved the fixation of dangerous species by the HENAZE, preventing them to be transported into the water environment and consequently protecting the quality of surface and groundwater (FILIPPIDIS *et al.*, 2008f).

The treatment of textile industry wastewaters of pH 8.6 (Table 4) with the HENAZE resulted to production of clear water (Fig. 8) of pH 8.0, free of odors and improved quality parameters by 97 % for the color, 93 % for the suspended particles, 95 % for the chemical oxygen demand (COD), 98 % for the P₂O₅ and for the NH₄ contents (Table 4). Simultaneously, a precipitate of odorless and cohesive zeo-sludge was produced, dried overnight at room temperature (Fig. 8). The values of the pH and the quality parameters, measured in the clear water, are fulfilling the requirements for disposition as downstream, irrigation, swimming and fish waters.

The HENAZE removed 55 % of NO₃ from well groundwater, as well as metals and anions for their aqueous solutions, 74 % of Pb, 79% of Ag and 57% of NO₃ (Table 5). The treatment of Koronia Lake water (Thessaloniki Prefecture, Northern Greece) of pH 9.6 (Table 6) with the HENAZE, resulted to production of clear water of pH 7.3,

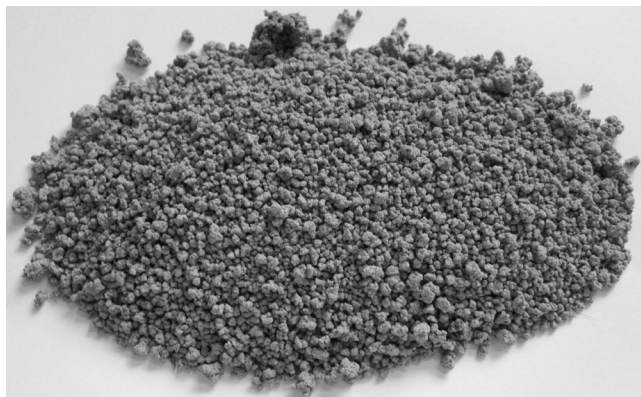


Fig. 6. Odorless and cohesive zeo-sewage sludge (proportions 30:70, after 36 hours at RT).

free of odors and improved quality parameters by 93% for the color and 96% for the chemical oxygen demand (COD, Table 6). The HENAZE removed 51% of *Colonial Mycrocystis* cyanobacteria, 75% of *Filamentous* cyanobacteria from Doirani Lake water (Kilkis Prefecture, Northern Greece), as well as 92 % *Chroococcus* cyanobacteria from their culture (Table 7).

The natural zeolites show a remarkable ability to remove inorganic, organic, organometallic compounds, gas species, metals and radionuclides from their aqueous solutions. The sorption of the different species from their solutions by the micro- meso- and macroporous of natural zeolite can be attributed to absorption (mainly ion exchange), adsorption and surface precipitation processes (e.g., TSITSISHVILI *et al.*, 1992; MISAILIDES *et al.*, 1995; GODELITSAS *et al.*, 1999, 2001, 2003; KALLO, 2001). The sorption of gas phases results to oxygen enrichment of the air and to the remarkable decrease of the malodor. Also, they show an ability to neutralize the pH of acidic and basic waters, acting either as a proton acceptor or donor, exhibiting thus an amphoteric character (e.g., FILIPPIDIS *et al.*, 1996; CHARISTOS *et al.*, 1997).

The Hellenic Natural Zeolite (HENAZE) is of very high quality (>85 wt.% HEU-type zeolite), removes inorganic, organic, organometallic, gas species, metals, cations and anions from their aqueous solutions. Also, shows an ability to neutralize the pH of acidic and basic waters. The increase of the pH in the acidic pH-range could mainly be attributed to the binding of the protons to the Lewis basic sites of the zeolite. The decrease of the pH in the basic pH-range could be the result of the removal of protons from surface Brønsted acidic sites or even of the detachment of protons from water molecules surrounding the exchangeable cations, caused by OH attack on the zeolite (e.g., FILIPPIDIS *et al.*, 1996; CHARISTOS *et al.*, 1997; GODELITSAS *et al.*, 1999, 2001, 2003).

The mineralogical composition and the physico-chemical properties, make the HENAZE suitable material for numerous environmental, industrial and agricultural applications, such as: Animal nutrition, soil amendment for agriculture, conditioning of acid and basic soils, greenhouse and flowers substrates, durability and health improvement of

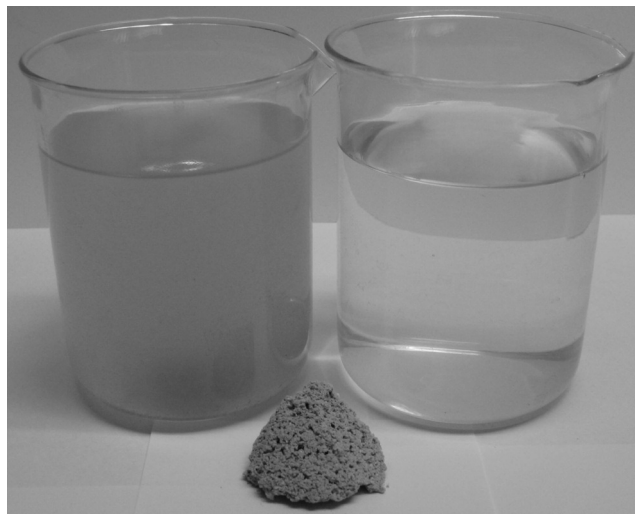


Fig. 7. Left: Starting urban wastewater, Centre: Odorless and cohesive zeo-sewage sludge and Right: Clear water after the HENAZE treatment.



Fig. 8. Left: Starting textile industry wastewater, Centre: Odorless and cohesive zeo-sludge and Right: Clear water after the HENAZE treatment.

lawn, purification of industrial and urban wastewaters, treatment of sewage sludge, odor control, fish farming, gas purification and drying, oxygen enrichment of aqua ecosystems, improvement of drinking water, constructed wetlands and wastewater treatment units.

The odorless and cohesive zeo-sewage sludge produced, either by the commixture of sewage sludge with the HENAZE or as precipitate from HENAZE-treatment of urban waste water, is suitable for the reclamation of agricultural soils, but also for the safe deposition, since the dangerous species are not leached from the zeo-sewage sludge by deionised water (FILIPPIDIS *et al.*, 2008f), preventing them to be transported into the water environment and thus protecting the quality of surface and groundwater.

The addition of HENAZE in the agricultural soils (Table 8), increases the yield by 17-66 % and improves the quality

TABLE 2
Semi-quantitative mineralogical composition of Hellenic Natural Zeolite (HENZA).

Minerals	Wt. %	Minerals	Wt. %
HEU-type zeolite	89	Total microporous minerals	92
Mica + Clays	3		
Feldspars	5	Total non-microporous minerals	8
Quartz	3		
Total	100	Total	100

TABLE 3
Chemistry of starting urban wastewater, clear water after the HENZA treatment and relevant improvement (average values*).

Parameter (Detection limit)	Starting urban wastewater	Clear water	Improvement (± %)
pH (0.1)	8.4	7.5	- 11
Color, mg/L, Pt scale (5)	1292	97	- 92
Suspended Particles, mg/L (5)	263	16	- 94
Chemical Oxygen Demand (COD) mg/L O ₂ (15)	493	25	- 95
Dissolved Oxygen, mg/L (0.1)	0.6	6.3	+ 950
P ₂ O ₅ , mg/L (0.02)	12.26	0.43	- 96
NH ₄ , mg/L (0.02)	48.50	0.35	- 99
SO ₄ , mg/L (0.02)	0.74	0.02	- 97
NO ₃ , mg/L (0.02)	46.50	3.90	- 92
NO ₂ , mg/L (0.02)	0.11	0.02	- 82
Cr _{total} , mg/L (0.02)	0.20	0.02	- 90
Mn, mg/L (0.02)	0.31	0.02	- 94
Ni, mg/L (0.02)	0.28	0.02	- 93

* Average values: FILIPPIDIS *et al.* (2007a, 2008a-c, e-g, 2009a, b, 2010a).

TABLE 4
Chemistry of starting textile industry wastewater, clear water after the HENZA treatment and relevant improvement (average values*).

Parameter (Detection limit)	Starting textile industry wastewater	Clear water	Improvement (± %)
pH (0.1)	8.6	8.0	- 7
Color, mg/L, Pt scale (5)	1264	40	- 97
Suspended Particles, mg/L (5)	127	9	- 93
Chemical Oxygen Demand (COD) mg/L O ₂ (15)	432	23	- 95
P ₂ O ₅ , mg/L (0.02)	8.56	0.18	- 98
NH ₄ , mg/L (0.02)	20.05	0.42	- 98

* Average values: FILIPPIDIS *et al.* (2008c, d, e).

TABLE 5
Chemistry of starting well groundwater and solutions, clear water after the HENZA treatment and relevant improvement.

Parameter (Detection limit)	Starting underground well-water	Clear water	Improvement (± %)
NO ₃ , mg/L (1) *	98	44	- 55
	Starting solution		
Ag, mg/L (1) **	100	21	- 79
Pb, mg/L (1) **	100	26	- 74
NO ₃ , mg/L (1) **	100	43	- 57

* FILIPPIDIS *et al.* (2006), ** FILIPPIDIS (2005a).

TABLE 6
Chemistry of water from Lake Koronia (Thessaloniki Prefecture, Northern Greece),
clear water after the HENAZE treatment and relevant improvement (average values*).

Parameter (Detection limit)	Starting Koronia lake water	Clear water	Improvement (± %)
pH (0.1)	9.6	7.3	- 24
Color, mg/L, Pt scale (5)	348	23	- 93
Chemical Oxygen Demand (COD) mg/L O ₂ (15)	770	28	- 96

* Average values: FILIPPIDIS (2005b), FILIPPIDIS *et al.* (2006, 2007b).

TABLE 7
Density of Cyanobacteria of starting Lake water and Culture, of overflowed water after the the HENAZE treatment
and relevant improvement (average values*).

Bacteria type (unit) Lake or culture	Starting Cyanobacteria Density	Cyanibacteria Density after the HENAZE treatment	Improvement (± %)
Colonial Mycrocystis (colonies/mL) Doirani Lake Water	320	157	- 51
Filamentous (filaments/mL) Doirani Lake Water	8254	2069	- 75
Chroococcus (cells/mL) Culture	955909	80441	- 92

* Average values: FILIPPIDIS *et al.* (2010b, c).

TABLE 8
Agricultural uses of HENAZE.

Species	Fertilizer		Irrigations		Production (Kg/acre)		±%
	Kg/acre	± %	Nr.	± %	Without HENAZE	With HENAZE	
Wheat **	20				170		+29
	0	-100				220	
	10				70	110	
Rice **	90				880		+34
	40	-56				1180	
Maize **	120		3		800		+50
	0	-100	2	-33		1200	
	0	-100	1	-67		800	
Production increase (%) by addition of HENAZE in agricultural soils							
Species			%		Species	%	
Grapes			48 - 66		Carnation (florescence increase) *	25	
Tomato **			48 - 52		Cotton *	17	
Actinides *			45				
Quality improvement of tomato by HENAZE addition in agricultural soils							
Quality parameters					Produced		±%
					Without HENAZE	With HENAZE	
Soluble solids (%) **					4.20	4.35	+4
Vitamin C (mg/100g) **					6.81	8.61	+26
Firmness (Kg) **					0.619	0.906	+46
HENAZE as feed additive and farm floor material							
17 % increase of milk production in cows *				Taste and quality improvement of products (meat, milk, eggs, etc)			
7 % increase of body weight in broilers *				Reduction of new-born animals death-rate			
Reduction of feed cost				Reduction of the malodour			
Reduction of animal diseases				Conversion of manure to odourless fertilizer			
Reduction of animal medication							

* FILIPPIDIS (2007), ** FILIPPIDIS *et al.* (2007d).

by 4-46 % of agricultural products, reduces the use of fertilizers by 56-100 %, reduces the usage of irrigation water by 33-67 %, prevents the seepage of dangerous species into the water environment (e.g., NO₃ by 55-92 %, Tables 3 and 5), protecting thus the quality of surface and groundwater. The usage of HENAZE in vivarium units and in the animal nutrition increases the production and improves the quality of their products, reduces the feed cost, the animal diseases, animal medication, the new-born animal's death-rate and the malodor, converting thus the manure to odorless fertilizer (Table 8).

ACKNOWLEDGEMENTS

I express my gratitude to the company GEO-VET N. Alexandridis & Co O.E., for the supply and treatment of HENAZE, as well as for their economical support.

REFERENCES

- BARBIERI, M., CASTORINA, F., MASI, U., GARBARINO, C., NICOLETTI, M., KASSOLI-FOURNARAKI, A., FILIPPIDIS, A. & S. MIGNARDI (2001). Geochemical and isotopic evidence for the origin of rhyolites from Petrota (Northern Thrace, Greece) and geodynamic significance. *Chemie der Erde*, 61, 13-29.
- CHARISTOS, D., GODELITSAS, A., TSIPIS, C., SOFONIOU, M., DWYER, J., MANOS, G., FILIPPIDIS, A. & C. TRIANTAFYLIDIS (1997). Interaction of natrolite and thomsonite intergrowths with aqueous solutions of different initial pH values at 25° C in the presence of KCl: Reaction mechanisms. *Applied Geochemistry*, 12, 693-703.
- COLELLA, C. & F.A. MUMPTON (2000). *Natural Zeolites for the Third Millennium*. De Frede Editore, Napoli, 481pp.
- COLELLA, C., DE GENNARO, M. & AIELLO, R. (2001). Use of zeolitic tuff in the building industry. In: BISH, D.L. & D.W. MING (Eds), *Natural Zeolites: Occurrence, Properties, Applications*. Reviews in Mineralogy and Geochemistry, Vol. 45, Mineralogical Society of America, Washington DC, 551-587.
- FILIPPIDIS, A. (2005a). Mineralogy and physicochemical characteristics of five natural zeolite samples on behalf of N.Alexandridis & Co O.E. *Report, Thessaloniki*, 10p (in Greek).
- FILIPPIDIS, A. (2005b). Improvement and protection of Lake Koronia waters with natural zeolite. *Proc. 13th Sem. Environ. Protection, Thessaloniki*, 73-84 (in Greek).
- FILIPPIDIS, A. (2007). Zeolites of Trigono Municipality of Evros Prefecture in industrial, agricultural, cattle-raising and environmental technology. *Proc. Development Perspectives of Northern Evros, Petrota*, 89-107 (in Greek).
- FILIPPIDIS, A. (2008). Treatment and recycling of municipal and industrial waste waters using Hellenic Natural Zeolite. *AQUA, Proc. 3rd Intern. Conf. Water Science and Technology, Athens*, 5p.
- FILIPPIDIS, A., GODELITSAS, A., CHARISTOS, D., MISAEELIDES, P. & A. KASSOLI-FOURNARAKI (1996). The chemical behavior of natural zeolites in aqueous environments: Interactions between low-silica zeolites and 1M NaCl solutions of different initial pH-values. *Applied Clay Science*, 11, 199-209.
- FILIPPIDIS, A. & N. KANTIRANIS (2002). Morphology, mineralogy, chemistry, mineralchemistry and ion exchange capacity of five natural zeolite samples for N. Alexandridis & Co O.E. *Report, Thessaloniki*, 5p (in Greek).
- FILIPPIDIS, A. & A. KASSOLI-FOURNARAKI (2002). Management of aquatic ecosystems using Greek natural zeolites. *Proc. 12th Sem. Environ. Protection, Thessaloniki*, 75-82 (in Greek).
- FILIPPIDIS, A., KANTIRANIS, N., DRAKOULIS, A. & D. VOGIATZIS (2006). Improvement and protection of the lake Koronia using natural zeolite. *Proc. 2nd Congress Environment Council of Aristotle University, Thessaloniki*, 273-279 (In Greek with English summary).
- FILIPPIDIS, A. & N. KANTIRANIS (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., APOSTOLIDIS, N., FILIPPIDIS, S. & I. PARAGIOS (2007a). Purification of urban wastewaters and production of odorless sewage sludge using porous Hellenic natural zeolite of Petrota (Evros). *Proc. 3rd Panhellenic Symp. Porous Materials, Thessaloniki*, 23-25 (in Greek).
- FILIPPIDIS, A., APOSTOLIDIS, N., FILIPPIDIS, S. & I. PARAGIOS (2007b). Improvement and protection of the lake Koronia using Hellenic natural zeolite of Petrota (Evros). *Proc. 3rd Panhellenic Symp. Porous Materials, Thessaloniki*, 110-112 (in Greek).
- FILIPPIDIS, A., KANTIRANIS, N., STAMATAKIS, M., DRAKOULIS, A. & E. TZAMOS (2007c). The cation exchange capacity of the Greek zeolitic rocks. *Bull. Geol. Soc. Greece*, 40(2), 723-735.
- FILIPPIDIS, A., SIOMOS, A., BARBAYIANNIS, N. & S. FILIPPIDIS (2007d). Agricultural and environmental applications using Hellenic Natural Zeolite of Petrota (Evros). *Proc. Jean Monnet Congress, Veria*, 557-569 (in Greek with English summary).
- FILIPPIDIS, A., APOSTOLIDIS, N., FILIPPIDIS, S. & I. PARAGIOS (2008a). Purification of urban wastewaters, production of odorless and cohesive zeo-sewage sludge using Hellenic Natural Zeolite. *Proc. 8th Intern. Hydrogeological Congress of Greece, Athens*, 2, 789-798 (in Greek with English abstract).
- FILIPPIDIS, A., APOSTOLIDIS, N., FILIPPIDIS, S. & I. PARAGIOS (2008b). Purification of industrial and urban wastewaters, production of odorless and cohesive zeo-sewage sludge using Hellenic Natural Zeolite. *Proc. 2nd Intern. Conf. Small Decentralized Water and Wastewater Treatment Plants, Skiathos*, 403-408.
- FILIPPIDIS, A., APOSTOLIDIS, N., PARAGIOS, I. & S. FILIPPIDIS (2008c). Production of odorless sewage sludge, purification of dye-work and urban waste-waters, using Hellenic Natural Zeolite. *Proc. 3rd Environ. Conf. of Macedonia, Thessaloniki*, 8p (in Greek with English abstract).
- FILIPPIDIS, A., APOSTOLIDIS, N., PARAGIOS, I. & S. FILIPPIDIS (2008d). Purification of dye-work wastewaters and production of cohesive zeo-sludge using Hellenic Natural Zeolite. *Proc. 8th Intern. Hydrogeological Congress of Greece, Athens*, 2, 783-788 (in Greek with English abstract).
- FILIPPIDIS, A., APOSTOLIDIS, N., PARAGIOS, I. & S. FILIPPIDIS (2008e). Purification of dye-work and urban wastewaters, production of odorless and cohesive zeo-sewage sludge, using Hellenic Natural Zeolite. *Proc. 1st Intern. Conf. Hazardous Waste Management, Chania*, 8p.
- FILIPPIDIS, A., APOSTOLIDIS, N., PARAGIOS, I. & S. FILIPPIDIS (2008f). Safe management of sewage sludge, produced by treatment of municipal sewage with Hellenic Natural Zeolite. *AQUA, Proc. 3rd Intern. Conf. Water Science and Technology, Athens*, 5p.
- FILIPPIDIS, A., APOSTOLIDIS, N., PARAGIOS, I. & S. FILIPPIDIS (2008g). Zeolites clean up. *Industrial Minerals*, April, 68-71.
- FILIPPIDIS, A., APOSTOLIDIS, N., FILIPPIDIS, S. & I. PARAGIOS (2009a). Purification of sewage effluents and production of odorless-cohesive sewage sludge, using Hellenic Natural Zeolite. *Faculty of Engineering, Aristotle University, YDROGALIA*, 425-434 (in Greek with English abstract).
- FILIPPIDIS, A., PAPASTERGIOS, G., APOSTOLIDIS, N., PARAGIOS, I., FILIPPIDIS, S. & C. SIKALIDIS (2009b). Odourless and cohesive zeo-sewage sludge produced by Hellenic Natural

- Zeolite treatment. *AMIREG, Proc. 3rd Intern. Conf. Resource Utilization and Hazardous Waste Management, Athens*, 96-100.
- FILIPPIDIS, A., PAPASTERGIOS, G., APOSTOLIDIS, N., FILIPPIDIS, S., PARAGIOS, I. & C. SIKALIDIS (2010a). Purification of urban wastewaters by Hellenic Natural Zeolite. *Bull. Geol. Soc. Greece*, 43(5), 2597-2605.
- FILIPPIDIS, A., MOUSTAKA-GOUNI, M., PAPASTERGIOS, G., KATSIAPIS, M., KANTIRANIS, N., KARAMITSOU, V., VOGIATZIS, D. & S. FILIPPIDIS (2010b). Cyanobacteria removal by Hellenic Natural Zeolite. *Proc. 3rd Intern. Conf. Small Decentralized Water and Wastewater Treatment Plants, Skiathos*, 383-387.
- FILIPPIDIS, A., MOUSTAKA-GOUNI, M., KANTIRANIS, N., KATSIAPIS, M., PAPASTERGIOS, G., KARAMITSOU, V., VOGIATZIS, D. & S. FILIPPIDIS (2010c). *Chroococcus* (Cyanobacteria) removal by Hellenic Natural Zeolite. *Proc. 8th Intern. Conf. Occurrence, Properties and Utilization of Natural Zeolites, Sofia*, 91-92.
- GODELITSAS, A., CHARISTOS, D., DWYER, J., TSIPIS, C., FILIPPIDIS, A., HATZIDIMITRIOU, A. & E. PAVLIDOU (1999). Copper (II)-loaded HEU-type zeolite crystals: characterization and evidence of surface complexation with N,N-diethyldithiocarbamate anions. *Microporous and Mesoporous Materials*, 33, 77-87.
- GODELITSAS, A., CHARISTOS, D., TSIPIS, A., TSIPIS, C., FILIPPIDIS, A., TRIANTAFYLIDIS, C., MANOS, G. & D. SIAPKAS (2001). Characterisation of zeolitic materials with a HEU-type structure modified by transition metal elements: Definition of acid sites in Nickel-loaded crystals in the light of experimental and quantum-chemical results. *Chemistry European Journal*, 7, 3705-3721.
- GODELITSAS, A., CHARISTOS, D., TSIPIS, C., MISAEILIDES, P., FILIPPIDIS, A. & M. SCHINDLER (2003). Heterostructures patterned on aluminosilicate microporous substrates: Crystallisation of cobalt (III) tris(N,N-diethyl-dithiocarbamate) on the surface of HEU-type zeolite. *Microporous and Mesoporous Materials*, 61, 69-77.
- GOTTARDI, G. & E. GALLI (1985). *Natural Zeolites*. Springer-Verlag, Berlin, 409pp.
- HALL, A., STAMATAKIS, M.G. & J.N. WALSH (2000). The Pentolofos zeolite tuff formation: A giant ion-exchange column. *Annales Geologiques des Pays Helleniques*, 38, 175-192.
- HARBEN, P.W. (2002). *The Industrial Minerals HandyBook: A Guide to Markets, Specifications & Prices*. Pensord, Blackwood, UK, 374-379.
- HOLMES, D.A. (1994). Zeolites. In: D.D. CARR (Ed), *Industrial Minerals and Rocks*. Braun-Brumfield Inc, Ann Arbor, Michigan, 1129-1158.
- KALLO, D. (2001). Applications of natural zeolites in water and wastewater treatment. In: BISH, D.L. & D.W. MING (Eds), *Natural Zeolites: Occurrence, Properties, Applications*. Reviews in Mineralogy and Geochemistry, Vol. 45, Mineralogical Society of America, Washington DC, 519-550.
- KANTIRANIS, N., CHRISAFIS, C., FILIPPIDIS, A. & K. PARASKEVOPOULOS (2006). Thermal distinction of HEU-type mineral phases contained in Greek zeolite-rich volcanoclastic tuffs. *European Journal of Mineralogy*, 18(4), 509-516.
- KIROV, G.N., FILIPPIDIS, A., TSIRAMBIDIS, A., TZVETANOV, R.G. & A. KASSOLI-FOURNARAKI (1990). Zeolite-bearing rocks in Petrota area (Eastern Rhodope Massif, Greece). *Geologica Rhodopica*, 2, 500-511.
- MARANTOS, I. & V. PERDIKATSI (1994). Study of the mineralogical composition, dehydration / adsorption of water and ion exchange capacity of zeolitic tuffs from Petrota-Pentalofos area, N. Evros. *Bull. Geol. Soc. Greece*, 30(3), 311-321 (in Greek with English abstract).
- MING, D.W. & E.R. ALLEN (2001). Use of natural zeolites in agronomy, horticulture and environmental soil remediation. In: BISH, D.L. & D.W. MING (Eds), *Natural Zeolites: Occurrence, Properties, Applications*. Reviews in Mineralogy and Geochemistry, Vol. 45, Mineralogical Society of America, Washington DC, 619-654.
- MISAEILIDES, P., GODELITSAS, A., FILIPPIDIS, A., CHARISTOS, D. & I. ANOUSIS (1995). Thorium and uranium uptake by natural zeolitic materials. *The Science of the Total Environment*, 173/174, 237-246.
- MUMPTON, F.A. (1977). Utilization of natural zeolites. In: F.A. MUMPTON (Ed), *Mineralogy and Geology of Natural Zeolites*. Short Course Notes, Vol. 4, Mineralogical Society of America, Blacksburg, Virginia, 177-204.
- POND, W.G. & F.A. MUMPTON (1984). *Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture*. International Committee on Natural Zeolites, Brockport, New York, 305pp.
- SAND, L.B. & F.A. MUMPTON (1978). *Natural Zeolites: Occurrence, Properties, Use*. Pergamon, Oxford, 546pp.
- STAMATAKIS, M.G., HALL, A. & J.R. HEIN (1996). The zeolite deposits of Greece. *Mineralium Deposita*, 31, 473-481.
- STAMATAKIS, M.G., HALL, A., LUTAT, U. & J.N. WALSH (1998a). Mineralogy, origin and commercial value of the zeolite-rich tuffs in the Petrota-Pentalofos area, Evros County, Greece. *Estudios Geologicos*, 54, 3-15.
- STAMATAKIS, M.G., FRAGOULIS, D., PAPAGEORGIOU, A. & E. CHANIOTAKIS (1998b). Zeolithic tuffs from Greece and their commercial potential in the cement industry. *World Cement Research and Development*, July, 98-103.
- STAMATAKIS, M.G., FRAGOULIS, D., CHANIOTAKIS, E., BEDELEAN, I. & G. CSIRIC (2000). Clinoptilolite-rich tuffs from Greece, Romania and Hungary and their industrial potential as cement additive. *Proc. 3rd Congress Mineral Wealth, Technical Chamber of Greece, Athens*, B, 451-457.
- STAMATAKIS, M., KOUKOUZAS, N., VASSILATOS, Ch., KAMENOU, E. & K. SAMANTOUROS (2001). The zeolites from Evros region, Northern Greece: A potential use as cultivation substrate in hydroponics. *Acta Horticulturae*, 548, 93-103.
- TCHERNEV, D.I. (2001). Natural zeolites in solar energy heating, cooling and energy storage. In: BISH, D.L. & D.W. MING (Eds), *Natural Zeolites: Occurrence, Properties, Applications*. Reviews in Mineralogy and Geochemistry, Vol. 45, Mineralogical Society of America, Washington DC, 589-617.
- TSITSISHVILI, G.V., ANDRONIKASHVILI, T.G., KIROV, G.N. & L.D. FILIZOVA (1992). *Natural Zeolites*. Ellis Horwood, New York, 295pp.
- VOGIATZIS, D., CHRISTARAS, B., FILIPPIDIS, A., KASSOLI-FOURNARAKI, A., KANTIRANIS, N., MOROPOULOU, A. & A. BAKOLAS (2008). Evaluation of the Cement-Sand-Hellenic Natural Zeolite Mortars Hardening using Ultrasonic Techniques. *Proc. 1st Panhellenic Congress Building Materials, Athens*, B, 1099-1110 (in Greek).

