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Utilization of natural and synthetic zeolitic materials as soil amendments in abandoned mine sites.

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Abstract

The aim of this paper is to evaluate the effects of natural and synthetic zeolitic materials as soil amendments in contaminated soils. Two species of natural zeolites, clinoptilolite and mordenite, sampled from Samos Island, Greece, were used as low cost modifiers (amendments). Both of these materials show perfect XRD-patterns. Moreover, coal fly ash (CFA) derived from the electrostatic precipitators of the Meliti power plant (Florina, Greece) converted via an alkaline hydrothermal treatment with 1M NaOH was used to produce a synthetic zeolitic material. The mineralogical composition of natural and synthetic zeolites was tested and identified by X-ray diffraction (XRD) and scanning electron microscope (SEM). The amendments and original contaminated soils from a former mining area of Lavrion, were mixed and equilibrated for 1 week, hydrated up to 40% of their water holding capacity. After the equilibration, the growth of Trifolium alexandrinum both in amended and original soils was studied in a pot experiment. The increase in pH value of treated soil by the tested amendments, confirmed the buffering effect and suggested the opportunity of using zeolitic materials for conditioning and remedying contaminated acidic soils from sulphidic mining areas. Moreover the amended soils exhibited higher CEC values compared with unamended soil. Results showed that the synthetic zeolite produced by Meliti's power station fly ash, was the most effective for plant growth, among the tested amendments. Between natural zeolitic materials from Samos Island, *the most efficient was the clinoptilolite rich, probably because of its better water holding capacity compared with mordenite.*

Keywords: *zeolites, remediation, fly ash, plant growth, Trifolium alexandrinum, contaminated soil.*

Περίληψη

Ο σκοπός της παρούσας εργασίας είναι η μελέτη της δυνατότητας χρήσης και αξιοποίησης φυσικών και συνθετικών ζεολιθικών υλικών ως εδαφοβελτιωτικά για την αποκατάσταση ρυπασμένων εδαφών σε πρώην μεταλλευτικές περιοχές. Για το σκοπό αυτό χρησιμοποιήθηκαν δύο είδη ζεολιθικών τόφφων από τη Σάμο, το ένα πλούσιο σε κλινοπτιλόλιθο και το άλλο πλούσιο σε μορντενίτη, ως φυσικά εδαφοβελτιωτικά χαμηλού κόστους. Επιπλέον, ιπτάμενη τέφρα που προήλθε από τα ηλεκτροστατικά φίλτρα του ΑΗΣ Μελίτη στη Φλώρινα, μετατράπηκε σε συνθετικό ζεολιθικό υλικό μέσω μιας αλκαλικής υδροθερμικής επεξεργασίας με χρήση NaOH 1M. Η ορυκτολογική σύσταση των φυσικών και των συνθετικών ζεολιθικών υλικών μελετήθηκε και πιστοποιήθηκε με τη μέθοδο της περιθλασιμετρίας ακτίνων X και με το ηλεκτρονικό μικροσκόπιο σάρωσης. Τα εδαφοβελτιωτικά καθώς και δείγματα ρυπασμένου εδάφους από την μεταλλευτική περιοχή του Λαυρίου, αναμίχθηκαν και αφέθηκαν να εξισορροπήσουν για 1 εβδομάδα. Μετά την εξισορρόπηση, σε γλάστρες που περιείχαν τα παραπάνω μίγματα φυτεύτηκαν σπόροι του φυτού *Trifolium alexandrinum*. Η αύξηση της τιμής του pH στα μίγματα εδάφους - ζεολίθου, επιβεβαίωσε την ρυθμιστική ικανότητα των ζεολιθικών υλικών και έδειξε ότι υπάρχει δυνατότητα χρήσης ζεολιθικών υλικών για την αποκατάσταση όξινα ρυπασμένων εδαφών σε περιοχές εξόρυξης θειούχων μεταλλευμάτων. Επιπλέον, τα μίγματα που περιείχαν εδαφοβελτιωτικά παρουσίασαν υψηλότερες τιμές ιοντοανταλλακτικής ικανότητας (CEC) σε σύγκριση με το αρχικό έδαφος. Ο συνθετικός ζεόλιθος που παρήχθει από ιπτάμενη τέφρα, ήταν το πιο αποτελεσματικό εδαφοβελτιωτικό για την ανάπτυξη των φυτών από όλα τα υλικά που δοκιμάστηκαν. Μεταξύ των φυσικών ζεολιθικών υλικών από τη Σάμο, το πιο αποτελεσματικό ήταν το πλούσιο σε κλινοπτιλόλιθο, πιθανόν λόγω της καλύτερης ικανότητας του στη συγκράτηση του νερού.

Λέξεις κλειδιά: *ζεόλιθοι, αποκατάσταση, ιπτάμενη τέφρα, ανάπτυξη φυτών, Trifolium alexandrinum, ρυπασμένο έδαφος*

1. Introduction

Hazardous heavy metal pollution of soils is an increasingly urgent problem all over the world. The extensive land pollution generated by past old mining and processing activities actions has become a major environmental issue in many European countries. Despite the fact that soils have the natural capability to mitigate the bioavailability and mobility of metals mechanisms such as precipitation, adsorption process and/or redox reactions, when the concentrations of heavy metals is greatly increased, the soil's potential effects are limited, so the contaminants can be mobilized. This process may result to serious contamination of agricultural products or ground water. Thus, it is necessary to take action to remediate the heavily polluted soils.

Various methods have been proposed and developed for the stabilization of contaminated soils. They include mixing of the contaminated soil or waste in situ with appropriate amendments and curing for the reactions to proceed (Conner, 1990).

Lavrion, Greece (see Figure 1.1) is an extremely contaminated region, where mining activities were taking place from antiquity to the 20th century. The main products of the mining activity were lead, silver and zinc. These products were derived from the exploitation of sulphide ores (Ag-bearing galena, sphalerite and arsenopyrite) from the mining galleries of the area. As a result of the exploitation activities, a huge quantity of mining and metallurgical waste was produced, including slag, flotation sand and coarser materials (Xenidis, Papassiopi, and Komnitsas, 2003). These tailings with the combination of both atmospheric factors (oxygen, rain) and bacteria have polluted the soil and water of the area (Kontopoulos et al., 1995). Today, it has become a residential district, posing serious health threats caused by the presence of high concentrations of toxic heavy metals (Pb, Zn and Cd) in the soil (see Figure 1.2).

The economic limitations associated with the removal of the contaminated soil and its ex-situ treatment led to a closer examination of possible in-situ treatment technics including stabilization/solidification processes. Till now, stabilization techniques including the application of lime, cement, coal fly ash and phosphates among many other natural and synthetic additives employing various fixation mechanisms, have been tested in soils with varying degrees of contamination (Theodoratos et al., 2000).

Zeolite is a group of alkaline porous alumino-silicates minerals with a negative charge, having a three-dimensional framework, neutralized by introducing exchanged cations in their structure sites. The ion exchanging efficiency depends on the microporosity and exchanging capacity of each particular zeolite. The usage of zeolites as natural amendments for the remediation of hazardous heavy metal-polluted soils has been studied extensively during recent years. Moreover zeolite applications in agriculture have been studied by many researchers (e.g. Stamatakis et al., 2001; Savvas et al., 2004). Unlike any organic contaminants, heavy metals are generally immutable, not degradable and persistent in soils (Adriano et al., 2004; Shi et al., 2009; Sunarso and Ismadji, 2009; Peng et al., 2009). It has been referred that zeolites may be more suitable for rehabilitation of heavy metal-contaminated soils than other amendments, because it regulates soil pH value modestly and does not import any new pollutants (Castaldi, Santona and Melis, 2005; Kumpiene, Lagerkvist and Maurice, 2008).

The current study deals with the evaluation on a pilot plant scale of natural and synthetic zeolitic materials as amendments to the Lavrion contaminated soil.

2. Materials and Methods

Soil samples have been collected near the Lavrion harbor, about 55 km SSE of Athens (see Figure 1.1). Mining operations for silver and lead extraction had started around 3000 BC and ended in the 1980’s (Konofagos, 1980). The intensive mining and metallurgical development at the area, has resulted in serious contamination problems affecting the local community in the form of slags, sulfur compounds, smelting waste, etc, all rich in hazardous metals and metalloids (see Figure 1.2) (Moutsatsou and Protonotarios, 2006).

Fig. 1.1: Location map of Lavrion region and Samos Island

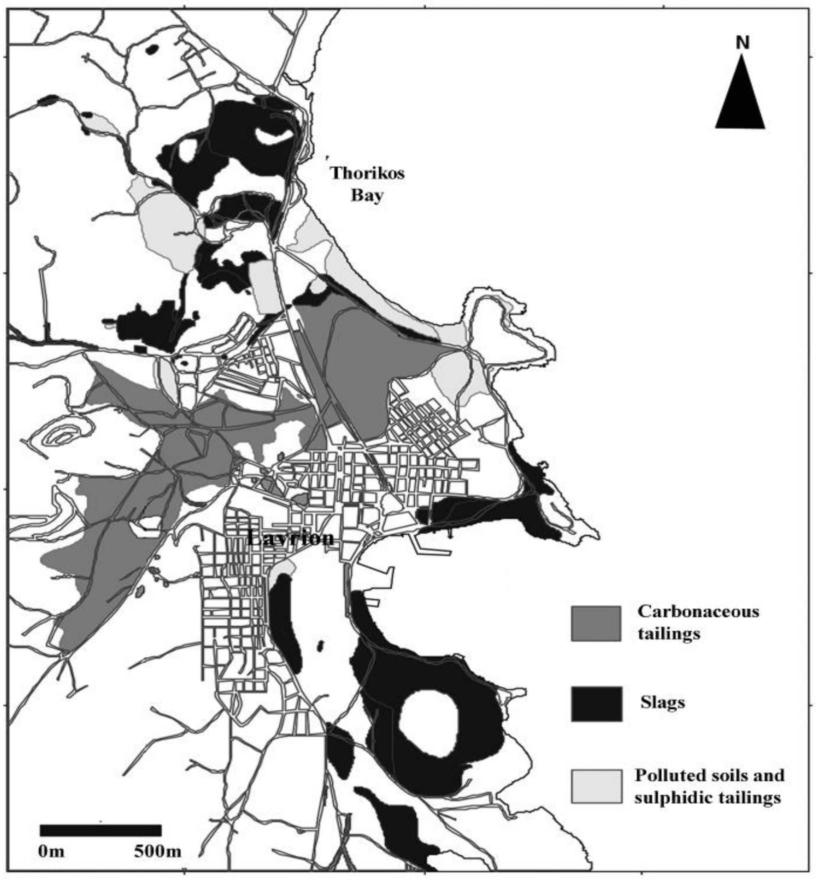

Fig. 1.2: Distribution of contaminant soils and mining tailings in the Lavrion area.

Two types of natural zeolite samples were collected from Samos Island, Greece (see Figure 1.1), [clinoptilolite (ZCS) and mordenite (ZMS)]. The island of Samos contains two Neogene sedimentary basins, Karlovassi in the west and Mytilini Basin in the east, separated by metamorphic basement rocks. Volcanic tuffs occur in the Late Miocene succession in both basins. Extensive diagenetic transformation of the tuffs/tuffites to zeolites (clinoptilolite, mordenite, analcime, chabazite), opal-CT and boron-bearing K-feldspar occurs in the Karlovassi Basin, whereas the volcanic tuffs are not zeolitized in the Mytilinii Basin (Stamatakis, 1989; Stamatakis, et al., 1989). The zeolitic rocks in the Karlovassi basin are usually very pale green and yellowish-brown in color. Even though they are exceptionally fine-grained and porous, they are well indurated. They are texturally homogeneous and often display a conchoidal fracture (Stamatakis, Hall and Hein, 1996).

Clinoptilolite is a common zeolite, suitable as a sorbent, easily extracted from open pits. Although many researchers classified it as belonging to theheulandite family (Breck, 1974), its Si/Al ratio and thermal stability makes it different from heulandites (Mansouri et al., 2013). The porous structure of the clinoptilolite has a heterogeneous nature. A primary porosity (microporosity) occurs because of the crystal structure of zeolite mineral grains, whereas a secondary porosity (mesoporosity and macroporosity) is connected with grain sizes of zeolite and other minerals in the zeolite rocks (Sprynskyy et al., 2010). The primary porosity is defined as the microporosity presented by the mineral 3-dimensional alumino-silicate framework. The mesoporosity is formed by slot pores determined mainly by cleavability of the zeolite crystals. The macropores consist of pores of various forms which are located between blocks of the zeolite crystallite and other minerals in the clinoptilolite bearing rocks. The heterogeneity of the clinoptilolite bearing rocks porosity is caused by the presence of associated minerals (albite, mordenite, etc.) and heterogeneity of the crystalline structure of those minerals (Mansouri et al., 2013). The mesopores are active surfaces for catalysis, transport channels and adsorption of relatively large molecules. Also some technological properties which may not be explained by adsorption in micropores might be explained by secondary porosity (Mansouri et al., 2013).

Mordenite is a high-silica zeolite, often found as an alteration product of volcanoclastic material and within veins, fissures or amygdales of some igneous rocks (Kitsopoulos and Dunham, 1998). Mordenite from Late Miocene rhyolitic tuffs in Samos is unusually rich in K and depleted in Na. This mordenite may have been formed by hydrothermal circulation of alkaline lake waters, rich in Ca and K, through the volcanic pile. The needle-like mordenite crystals drapes across smectite; other silica minerals such as quartz and cristobalite are also present. Mordenite rims holes and occurs in bands throughout the Platanos hydrothermally altered tuffs (Pe-Piper and Tsolis-Katagas, 1991).

Coal fly ash (CFA) samples are derived from the electrostatic precipitators of the Meliti (Florina, Greece) lignite-fired power plants. Many research works have focused on the utilization of fly ash as a low-cost sorbent for the removal of heavy metals (Srivastava et al., 2006; Pehlivan et al., 2006; Itskos et al., 2010), radionuclides, and organic pollutants, as well (Sun et al., 2010; Karagozoglu et al., 2007; Janosˇ et al., 2003). However, due to the fact that raw fly ashes have usually low sorption capacities, and physical or chemical modification, they have often been tested for their enhancement. Fly ash consists of alumino-silicate composites and thus presents a potential material for zeolite synthesis. The methodologies developed have been based on the dissolution of Al–Si bearing phases of the fly ash with alkaline solutions (mainly NaOH and KOH solutions) and the subsequent precipitation of zeolitic material (Querol et al., 2002; Koukouzas et al., 2010). Products of such alternation are characterized by better ion-exchange properties and several fold-enlarged surfaces (Remenarova et al., 2014).

The laboratory tests were conducted at the Economic Geology and Geochemistry Laboratory of the National and Kapodistrian University of Athens. CFA from Meliti Power Station, via an alkaline hydrothermal treatment with 1M NaOH was converted to synthetic zeolitic material (FAZ). The alkaline hydrothermal treatment, proposed by Koukouzas et al. (2010), took place at 90-100^{0}C, using 1M NaOH as an activation solution, in a 1L magnetic stirrer with a constant rate of raw material/ NaOH solution: 100gr/L. The incubation period was set overnight (about 30 hours) and mixing took place at 150 rounds per minute (rpm). After that period, the mixture was filtered and leached with water until no NaOH was detected. Finally, the solid residue was dried in an oven at 40^{o}C for about 3 days. The zeolite produced was Na-P1($Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$), a synthetic mineral with a high ion exchange capacity due to substitution of Si (IV) by Al (III) in its structure, which results in an overall negative charge, leading to applications as ion exchange or molecular sieve. This zeolite has an affinity with some metal ions, generally found in acid mine drainage effluents, and is an alternative for correcting this problem (Cardoso et al., 2015).

The mineralogical composition of all the materials used, including CFA and FAZ samples was identified by X-ray diffraction (XRD) and scanning electron microscope

(SEM). X-ray diffraction measurements were carried out on a Bruker Model 5005 X-ray diffractometer in combination with the DIFFRACplus software package. The diffractometer was operated using Cu K-a radiation at 40 kV and 40 mA, with graphite monochromator, and employing the following scanning parameters: 0.020° step size and 2.0 sec. step time. The output files were evaluated for mineralogical identifications by the use of the EVA 10.0 program of the Bruker DIFFRACplus software package. Electron probe microanalyses and SEM studies were carried out on a Scanning Electron Microscopy (SEM) JEOL JSM-5600. The system was operating at 20KV, 0.5nA and 50sec dead time.

The mineralogical composition of both natural and synthetic zeolites used in the current study is presented in Table 2.1. In the evaluated XRD patterns of the materials used, it should be noted that: a) the mordenite-rich tuff ZMS (upper pattern in blue) contains also high amounts of opal-CT and minor amounts of potassium feldspars. b) the clinoptilolite-rich raw material ZCS (lower pattern in black) is richer in zeolite content, mainly clinoptilolite, containing only small amounts of mordenite and potassium feldspars, whereas opal-CT is not present (see Figure 2.1a). c) the high degree of zeolitization of the coal fly ash (CFA) after the alkaline hydrothermal treatment (see Figure 2.1b); while the CFA (upper pattern in blue) consists mainly of quartz and feldspar, the synthetic zeolite (FAZ) (bottom pattern in black) consists mainly of Na-P1 zeolite, and the percentage of quartz and feldspar decreases.

The formation of the aforementioned FAZ zeolite was also confirmed by SEM investigation, as microcrystals of Na-P1 zeolite grows on the glassy material of fly ash (see Figure 2.2d). SEM images also demonstrate that the clinoptilolite crystals have tabular texture (see Figure 2.2a and b). In higher magnification, separate micro-plates or bars are detected. As a matter of fact, these micro-plates are not individual crystal grains of the clinoptilolite, but only aggregates presented by finer grains of the mineral. Such splitting of zeolite grains is typical for clinoptilolite cleavage and is a consequence of hydrothermal solution filtration. Heterogeneity of clinoptilolite grains is clearly presented in Figure 2.2a.

The measurement of pH in samples was performed by dilution of the solid in dionized water at a ratio of 1:1 solid: liquid. Finally, a Consort 561 multimeter was used for the pH determination. The pH values of all materials used, is presented in Figure 2.3.The synthetic zeolitic materials exhibit higher pH values in comparison with natural zeolite samples. As expected, the untreated contaminated soil from Lavrion (LSoil) is characterised by a pH value of 3.82.

Moreover, cation exchange capacity (CEC) was determined using the Rhoades (1982) method. As presented in Figure 2.4, the cation exchange capacity of the synthetic zeolitic materials exhibits higher values compared both with natural zeolites and contaminated soil LSoil.

In order to evaluate the natural and synthetic zeolitic materials as amendments in contaminated soils from abandoned mine sites, a pot experiment was conducted. A quantity of 4 kg of contaminated soil and each amendment (ZCS, ZMS and FAZ) at a rate of 10% by weight was used, to produce the CLS, MLS and FLS soil mixtures accordingly.After mixing the mixtures, they were equilibrated for 1 week, moistened to 40% of their water holding capacity. After the equilibration period, pots were used, filled with each equilibration mix and *Trifolium alexandrinum* seeds were planted. Control pots without any amendment (Control) were also set up. All treatments in the experiment were replicated 3 times. All plants potted were observed to have grown. The experiment has been performed for ten weeks under natural environmental conditions. The trifolium plants in all the trials were grown with sprinkler irrigation. At ten weeks, all the plants were harvested.

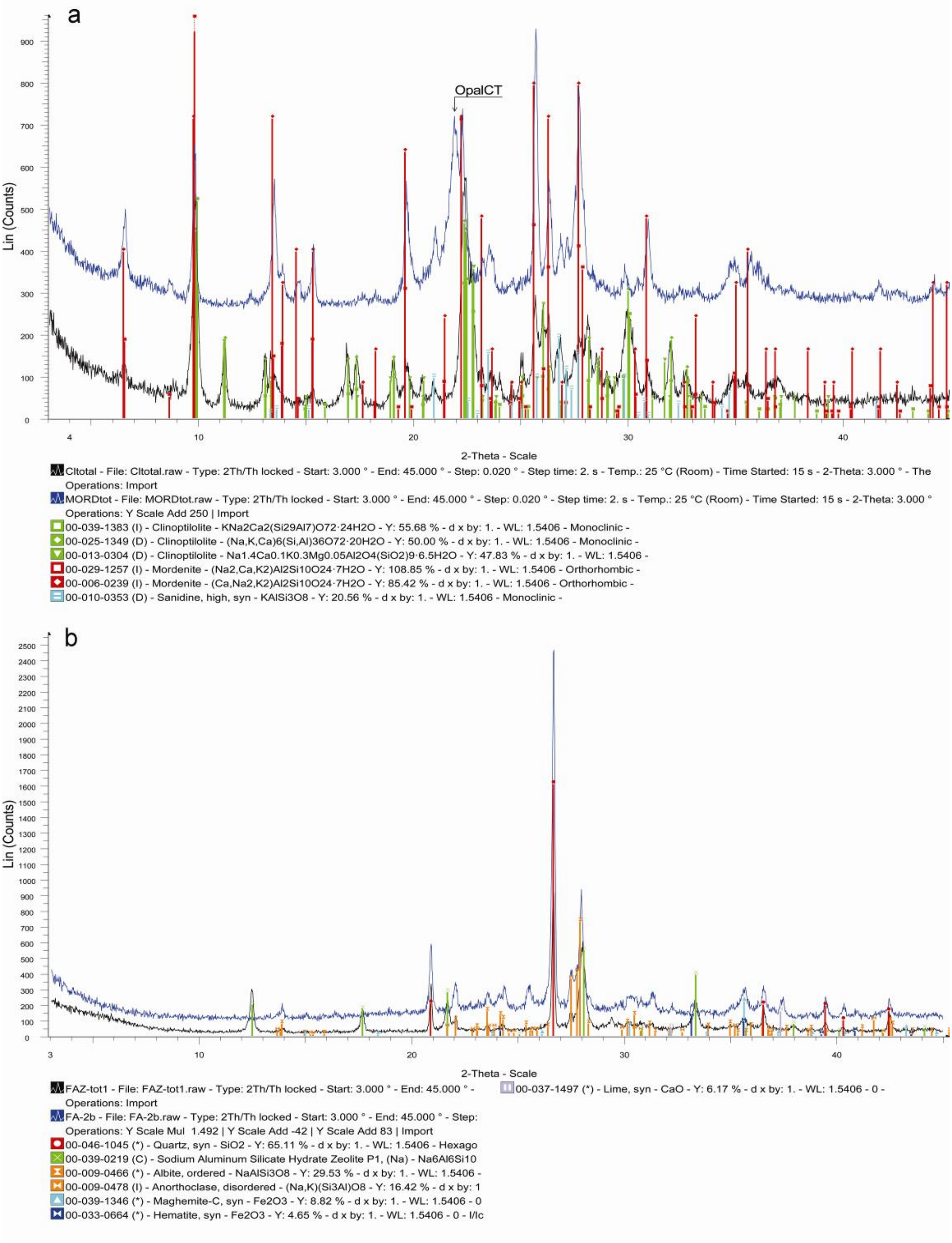

Fig. 2.1: XRD patterns of the materials used. a. Natural zeolitic tuffs from Samos Island. The upper pattern (in blue) is from the mordenite rich tuff ZMS and the lower (in black) is from the clinoptilolite rich row material ZCS. b. The upper pattern (in blue) is from the coal fly ash (CFA) before the alkaline hydrothermal treatment and the lower (in black) is from the synthetic zeolite rich material (FAZ) after the treatment.

Table 2.1: Mineralogical composition of soil amendments (+: presence of mineral, -: absence of mineral, MJ: Major mineral phase).

	Samples		
Mineral species	**ZCS**	**ZMS**	**FAZ**
Clinoptilolite	+ **MJ**	+	-
Mordenite	+	+ **MJ**	-
Zeolite P1, (Na)	-	-	+ **MJ**
Sanidine	+	+	-
Orthoclase	-	+	-
Anorthoclase	-	-	+
Albite	-	-	+
Opal CT	-	+	-
Quartz	-	-	+ **MJ**
Hematite	-	-	+
Maghemite	-	-	+
Calcite			+

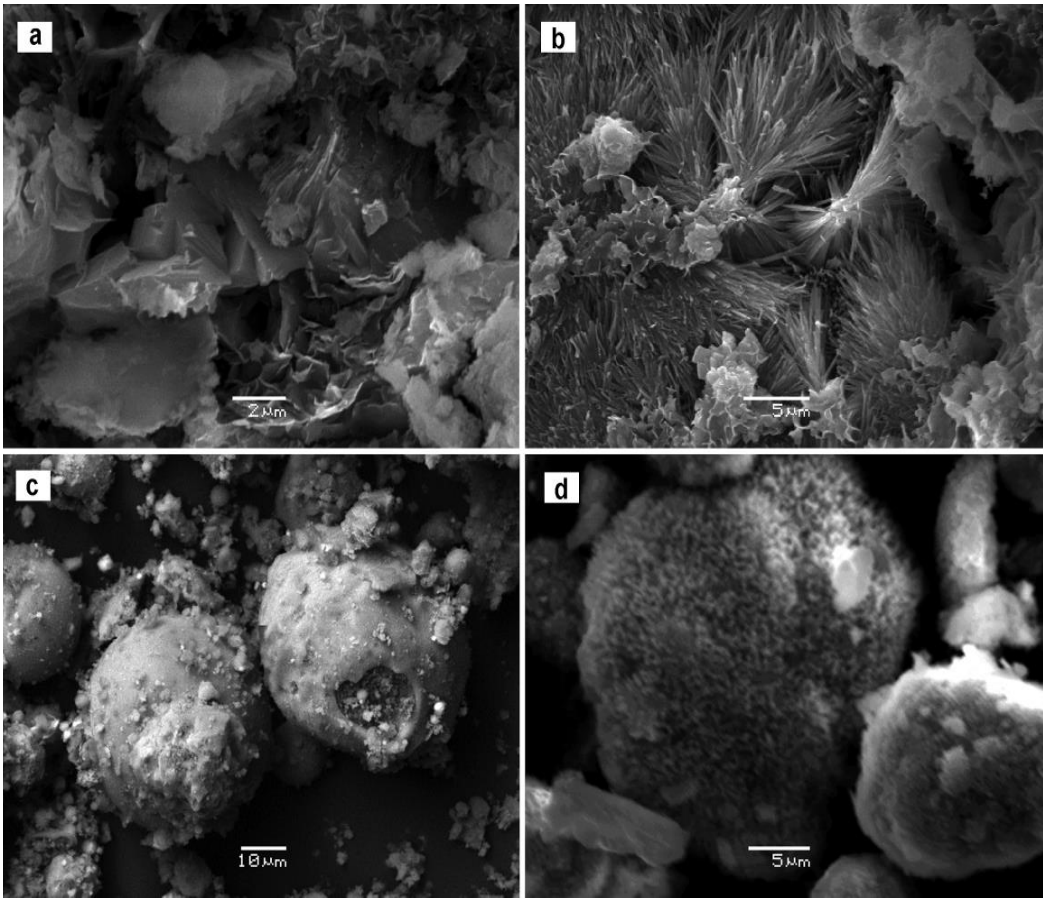

Fig. 2.2: SEM photographs of the materials used. a) Clinoptilolite-rich sample (ZCS) from Samos Island b) Fibrous mordenite in the ZMS sample from Samos Island also c) Fly ash glassy material in the CFA sample from the Meliti Power Station d) the glassy material of fly ash turns to microcrystals of NaP1 zeolite (FAZ) after the hydrothermal treatment.

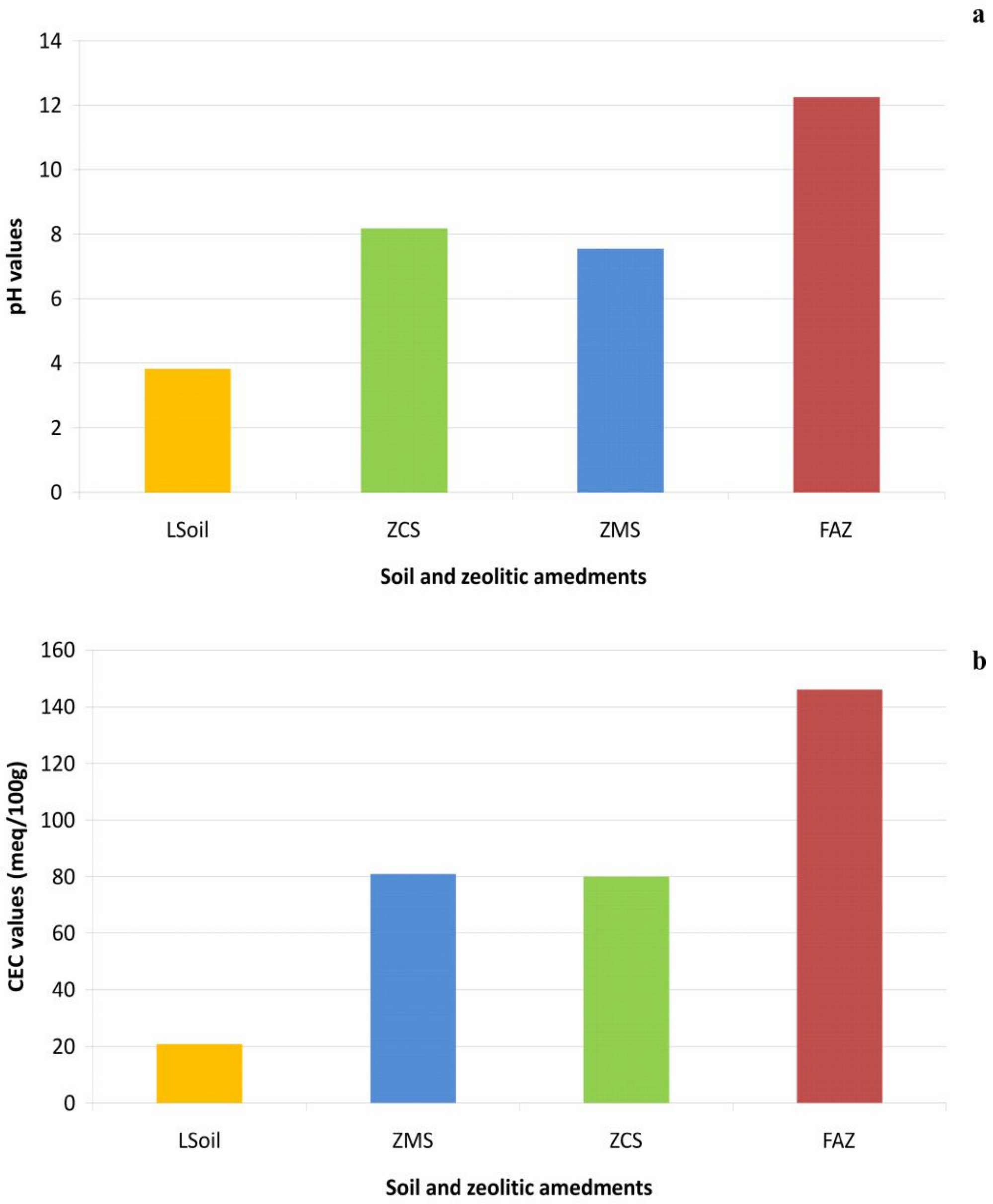

Fig. 2.3: pH (a) and Cation Exchange Capacity (b) values of natural and synthetic zeolitic materials along with the contaminated soil sample.

3. Results

The untreated soil sample (Control), used for the experiments, had a pH value as low as 4.52 (see Figure 3.1a). The amended soil mixture showed on the contrary an increased pH. This was particularly evident in the FLS sample (amended with synthetic zeolite) that had the highest pH value but close to the MLS pH value that follows. The highest pH value of the FLS is attributed to the high pH of the FAZ component used in the mixture. It is remarkable that the Control soil pH that has the same composition with LSoil presents higher values after the equilibration.

Figure 3.1b illustrates that amended soil samples have higher cation exchange capacity (CEC) values, compared with the non-amended soil sample (Control), which presents the lowest value. The greater value of CEC (40,87meq/100g) is evident in the MLS mixture with Samos mordenite.

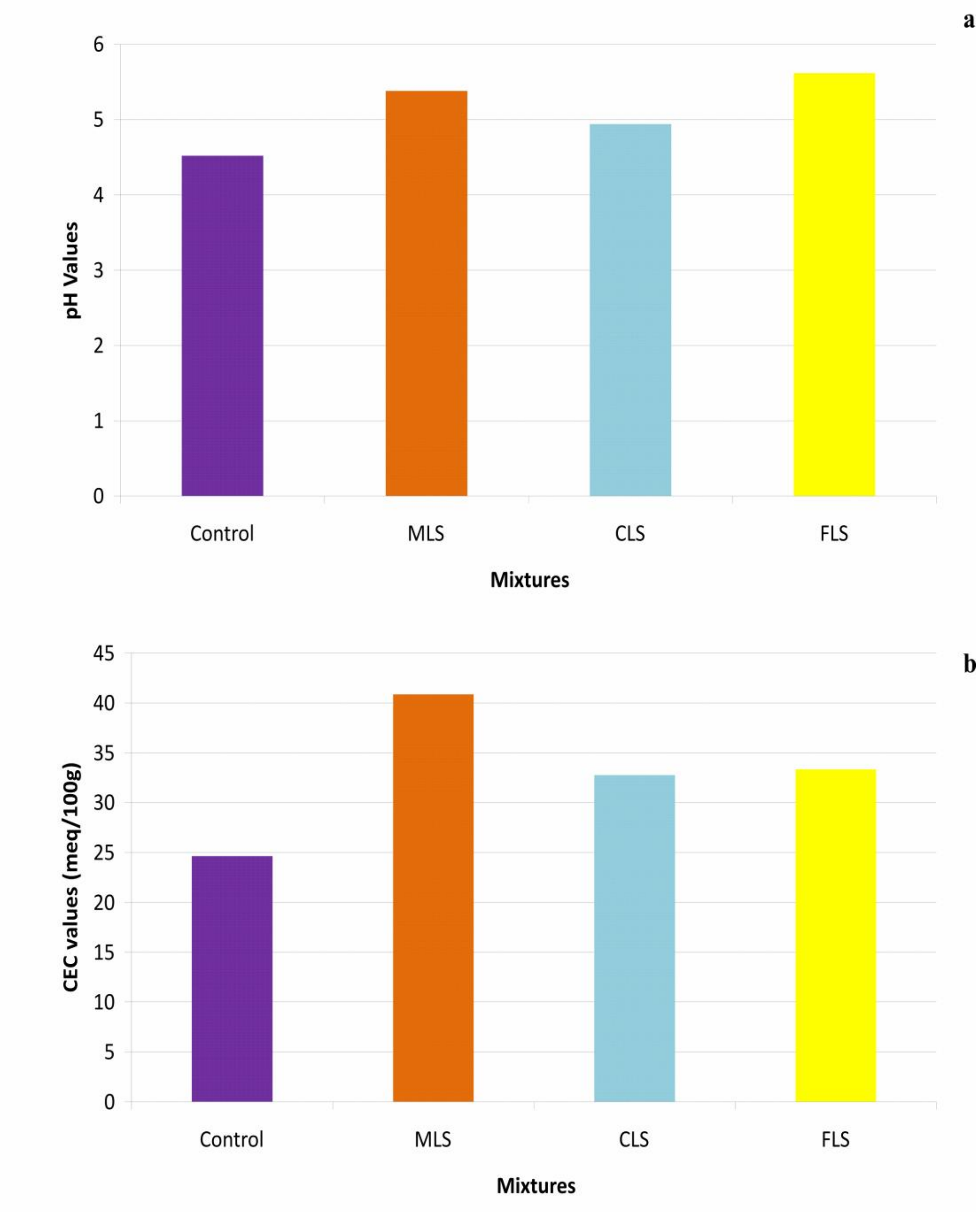

Fig. 3.1: pH (a) and Cation Exchange Capacity (b) values of mixtures produced for the pot experiment.

Table 3.1: Growth of *Trifolium alexandrinum* in soil treatments (+: presence of plant growth, -: absence of plant growth).

	Control	MLS	CLS	FLS
Plant Growth	-	+	++	+++

Table 3.1 presents the growth of *Trifolium alexandrinum* in soil mixtures. There was no plant growth in the Control mixture, while the FLS mixture with the synthetic zeolite produced by Meliti's fly ash exhibited the biggest plant growth, in comparison with the mixtures with natural zeolites, MLS and CLS, which gave a lower plant growth.

4. Discussion

It has been referred that zeolite as amendments in acidic soils may supply alkalinity to the acid polluted soils and cause the precipitation of insoluble phases (Chen, Lee and Liu, 2000). The newly formed phases may accommodate the metal pollutants either as major constituents (Chen, Lee and Liu, 2000) or as minor components co-precipitated in hydroxides (Chlopecka and Adriano, 1997; Boisson et al., 1999). The increase of alkalinity boosts the metal sorption via surface complexation processes. Even though mineral surfaces have a positive charge at low pH values due to the sorption of protons, as pH increases, owing to the deprotonation of the surface unsaturated bonds, they acquire a negative charge (e.g. Basaldella et al., 2007; Peng et al., 2009; Shi et al., 2009). Higher pH values promote the complexion of cations by stable bonds with the negative radicals on the mineral surfaces. Zeolite minerals may play a significant role in this surface complexation because of their high specific surface (Korkuna et al., 2006; Sponer et al., 2001). Moreover, the cation exchange properties of zeolite minerals may cause metal impoundment, regardless of pH value (Castaldi, Santona and Melis, 2005).

Trifolium alexandrinum growth, as observed during the current study, may be controlled by the physical and chemical characteristics of the amended soils (Castaldi, Santona and Melis, 2005). In the Control sample the trifolium showed absence of growth, although in all amended soil samples there was plant growth (see Table 3.1). This is probably due to the low pH value of the soil that makes it unsuitable for plant growth.

A greater growth was observed in the soil mixture (FLS) amended with the synthetic zeolite (FAZ). This is attributed to the higher pH values of this mixture, which as stated by Castaldi, Santona and Melis (2005) plays a key role both in phyto-toxicity and in metal trace element availability reduction. Moreover, other authors (e.g. Querol et al., 2002; Shi et al., 2009) have indicated that pH value is the major factor for the remediation of polluted soils and the immobilization of heavy metals by the addition of zeolitic material.

Other scientists have claimed that the remediation of such soils by zeolitic amendments may be mainly attributed to the cation exchange capacity rather than the pH value (Castaldi, Santona and Melis, 2005). As suggested by Ross (1995), the cation exchange capacity of a soil is a measure of the quantity of negatively charged sites on soil surfaces that can retain positively charged cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^{+}), by electrostatic forces. Cations retained electrostatically are easily exchangeable with cations in the soil solution so a soil with higher CEC values is predicted to have a greater capacity to maintain adequate quantities of the above-mentioned cations than a soil with a low CEC. Zeolite is a crystalline aluminum-silicate, with group I or II elements as counter ions. Its structure is made up of a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$tetrahedra linked to each other at the corners by sharing their oxygen. The substitution of Si(IV) by Al(III) in the tetrahedral accounts for a negative charge of the structure, which may give rise to a high cation exchange capacity (CEC) when the open spaces allow the access of cations (Breck, 1974; Mondales, Carland and Aplan, 1995). Despite the fact that the initial synthetic zeolitic material (FAZ) produced by fly ash has a significant higher CEC value, the soil mixture produced with natural zeolite mordenite (MLS) exhibits a greater CEC value (40,87meq/100g). This may be attributed both to soil constitutes and the combination of soil with amendments. Moreover, Ross (1995) suggested that a soil with a higher CEC may not necessarily be more fertile because a soil’s CEC can also be occupied by acid cations such as hydrogen (H^{+}) and aluminum (Al^{3+}).

Between natural zeolite mixtures, the one with clinoptilolite (CLS) exhibited higher plant growth, compared with the mordenite (MLS) despite the fact that pH and CEC values of CLS are lower than those of MLS. This can be explained by the water holding capacity of the clinoptilolite mineral phase, which is almost twice the water holding capacity of mordenite (Nguyen and Tanner, 1998). Water holding capacity is a controversial factor in plant growth, as the water is retained near the root and thus it enhances the availability for the plant uptake (Blum, 2011; Holbrook, 2010).

The need of a low-cost amendment for the in-situ remediation of polluted soils by the mining activities in the Lavrion region may be fulfilled effectively by the utilization of zeolitic materials on a large scale. In general, the results are very encouraging about the application of the synthesized zeolitic material. Additionally, the hydrothermal activation of fly ashes is a sustainable procedure that can be applied for the exploitation of the main by-product of power production in Greece.

5. Conclusions

Natural and synthetic zeolitic materials as soil amendments have proved to be promising for a low cost, in-situ treatment of contaminant soil in abandoned mine areas.

The pH increase of soil treated by the tested amendments, confirmed the buffering effect and suggested the opportunity of using zeolitic materials for conditioning and remedying acid soils.

The pot experiment we conducted has resulted to an improved performance in contaminated acidic soil with zeolite amendments for the *Trifolium alexandrinum* crop.

The synthetic zeolite produced by Meliti’s power station fly ash was the most effective among the tested amendments. This result renders those synthetic zeolites suitable for utilization as amendments for de-contamination procedures in abandoned mine sites.

Between natural zeolitic materials originated from Samos Island, the most efficient was the clinoptilolite-rich tuff, probably most likely because of its better water holding capacity compared to the mordenite rich one.

6. Acknowledgements

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