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EVALUATING THE EFFICIENCY OF NATURAL AND SYNTHETIC ZEOLITIC MATERIALS FOR THE REMEDIATION OF POLLUTED MINING SOILS: A COMPARATIVE STUDY

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Abstract

The aim of the present study is to examine the effectiveness of natural and synthetic zeolitic materials as potential soil amendments for the rehabilitation of mine degraded areas. Thus, heavily polluted soil was sampled from the Lavrion old mining district in Greece. Two types of natural zeolite tuffs, clinoptilolite- and mordenite-rich, originating from Samos Island, Greece, were pulverized in the laboratory and used as low cost modifiers. Furthermore, a lignite-derived fly ash bulk sample collected from the electrostatic filters of the Meliti Lignite fired Power Station, west Macedonia, Greece, was modified by a low temperature alkaline hydrothermal treatment. The end-product was the zeolite Na-P1 ($Na_6Al_6Si_{10}O_{32} \cdot 12H_2O$), which is characterized by its high cation exchange capacity (CEC). Mixtures composed of 90% contaminated soil and 10% w/w of each of the three zeolitic materials was produced for analysis and tests. XRD and SEM methods were used for the characterization of the raw materials and the end-products. Estimation of water solubility and potential bioavailability with the EDTA extracting agent of heavy metals (Pb, Zn, Cu, Mn, Fe, Cd) was performed in those soil mixtures, following the European standard EN 12457-2. Furthermore, pot experiments that were implemented revealed that all three zeolite-bearing amendments have successfully decreased the potentially toxic elements uptake by the *Trifolium alexandrinum* crop. Soil mixtures containing synthetic zeolitic materials have displayed pH regulation, higher cation exchange capacity values, excellent growth of *T. alexandrinum*, as well as, a decrease of heavy metals content within the plant tissue. The results of the present study demonstrated that the fly ash synthesized zeolitic material exhibited the best results not only in the regulation of pH, in the increase of CEC, in the growth of *T. alexandrinum*, but also in reducing of potential bioavailability and water solubility of all 6 potentially toxic elements studied.
Keywords: Zeolites; fly ash; synthetic zeolites; contaminated soil; amendments; remediation.

1   INTRODUCTION

The extensive land pollution generated by old mining and metallurgical activities is considered as a major environmental issue in many European countries. Despite of 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 possibly toxic elements is greatly increased, natural attenuation may by limited and the contaminants can be mobilized. Such process may lead to serious contamination of natural water and agricultural products. Thus, it is necessary to take action to remediate the polluted soils. Various methods have been proposed and developed for the stabilization of contaminated soils. Methods including mixing of the contaminated soil or waste in situ, with appropriate amendments have been proposed and developed for the stabilization of contaminated soils (Conner, 1990).

In Lavrion (Laurium) mining district, south Attica, Greece, mining activities for silver and lead had started since 3000 BC and ended in 1978 (Konofagos, 1980). As a result of those activities, a huge quantity of mining and metallurgical waste was produced, including slag, flotation sand and coarser materials (Xenidis *et al.*, 2003). Despite of the fact that acid mine drainage from the mining galleries is limited due to geochemical and petrological controls (Vasilatos *et al.*, 2015) the tailings, with the combination of atmospheric factors (oxygen, rain) and bacteria, have polluted the soil and water of the area (Kontopoulos *et al.*, 1995). Nowadays, it has become a residential district, posing serious health threats caused by the presence of high concentrations of possibly toxic elements (Pb, Zn and Cd) in the soil. The economic limitations associated with the removal of the contaminated soil and its ex-situ treatment led to examination of possible in-situ treatment methods 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 those soils (Theodoratos *et al.*, 2000).

Zeolite is a group of alkaline porous alumino-silicate minerals with a negative charge, having a three-dimensional framework, neutralized by introducing exchanged cations in their structure sites. The crystal structure of zeolite grains constitutes the primary porosity (microporosity) of zeolites, while the grain sizes of zeolite and other minerals in the zeolite rocks are connected with the secondary porosity (mesoporosity and macroporosity) (Sprynskyy *et al.*, 2010). The primary porosity is defined as the microporosity displayed 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 zeolite bearing rocks. For example, the heterogeneity of the clinoptilolite bearing rocks porosity is influenced by the presence of associated authigenic and pyrogenic minerals (feldspars, clay minerals, other zeolite types) and heterogeneity of crystalline structure of those minerals, and unaltered volcanic glass (Mansouri *et al.*, 2013). The mesopores are active surfaces for catalysis, transport channels and adsorption of relatively large molecules. Besides some technological properties which may not be explained by adsorption in micropores, they might be explained by secondary porosity (Mansouri *et al.*, 2013). Clinoptilolite is a common zeolite, suitable as a sorbent easily extracted from open pits. Although many researchers classified it as a member of the heulandite family, its Si/Al ratio and thermal stability makes it different from heulandites (Mansouri *et al.*, 2013). Mordenite is a high-silica zeolite, often found as an alteration product of volcanoclastics and hydrothermal veins, fissures or amygdales of some igneous rocks. The ion exchanging efficiency depends on the micro-porosity and exchanging capacity of each particular zeolite. The application of zeolites as natural amendments for the remediation of hazardous metals polluted soils has been studied extensively. Moreover, zeolite applications in agriculture have been studied by

many researchers (e.g. Savvas *et al.*, 2004; Stamatakis *et al.*, 2001, 2017). It has been suggested that zeolites may be more suitable for rehabilitation of heavy metal-contaminated soils than other amendments, because they regulate soil pH value modestly and do not import any new pollutants (Castaldi and Santona, 2005)).

The aim of this study is to examine the effectiveness of natural and synthetic zeolitic materials as potential soil amendments for the rehabilitation of mine degraded soils such as in Lavrion, Greece.

2   MATERIALS AND METHODS

Polluted soil was sampled from the Lavrion mining area in Greece and two types of natural zeolitic tuffs, clinoptilolite- and mordenite-rich originating from Samos Island, Greece, were pulverized in the laboratory and used as low cost modifiers. The island of Samos contains two Neogene sedimentary basins, Karlovassi Basin at the west and Mytilinii Basin at 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 *et al.*, 1989; Stamatakis, 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, are well indurate. They are texturally homogeneous and often display a conchoidal fracture. 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 (Pe-Piper and Tsolis-Kataga, 1991). The needle-like mordenite crystals drapes across smectite; other silica mineral such as quartz and cristobalite are also present.

In addition, coal fly ash (CFA) sample derived from the electrostatic precipitators of the Meliti Lignite fired Power Station (Florina, Greece), was modified by a low temperature alkaline hydrothermal treatment, to produce a synthetic zeolitic material. The alkaline hydrothermal treatment, proposed by Koukouzas *et al.* (2010) and Itskos *et al.* (2015) took place at 90-100ºC, using 1M NaOH as an activation solution, In the present study, two interventions took place in the above method of zeolite synthesis: a) refilling with NaOH solution throughout the heating-stirring, so that the NaOH/fly ash ratio remained constant and b) increasing the heating-stirring period from 24 hours to 36 hours.

Mixtures of contaminated soil with the above natural and synthetic zeolitic materials were formed at a rate of 10% by weight. The following mixtures were prepared: i) 4 Kg contaminated soil + 400 g synthetic zeolitic material (FAZ), ii) 4 Kg contaminated soil + 400 g natural clinoptilolite-rich zeolitic material (ZCS), iii) 4 Kg contaminated soil + 400 g natural mordenite-rich zeolitic material (ZMS), iv) 4 Kg contaminated soil without any amendment (Lsoil), moistened with 40% of their water holding capacity and allowed to equilibrate for 1 week. After the equilibration period, pots were used on a laboratory scale, filled with each equilibration mix and *Trifolium alexandrinum* seeds were planted. Control pots with contaminated soil, without amendment (Lsoil), were also set up. All treatments were replicated 3 times. All plants potted exhibited growth. The experiment lasted ten weeks under natural environmental conditions. The moisture was maintained by irrigation twice a week. The mineralogical composition of natural and synthetic zeolitic materials was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Estimation of water solubility was measured with the European standard EN 12457-2 and potential bioavailability with the EDTA extracting agent of 6 heavy metals (Pb, Zn, Cu, Mn, Fe, Cd) was also performed in soil mixtures at the end of pot experiments. The growth of *Trifolium alexandrinum* was monitored visually during the

Table 1: Mineralogical composition of the materials used for the experimental procedure (ZCS: natural zeolite tuff rich in clinoptilolite, ZMS: natural zeolite tuff rich in mordenite, FAZ: synthetic zeolitic material, CFA: coal fly ash, Lsoil: heavily contaminated soil from Lavrio, Greece) (+: presence of mineral, -: absence of mineral, MJ: Major mineral phase).

Mineral species	Zeolitic materials			CFA	Lsoil
	ZCS	ZMS	FAZ		
Clinoptilolite	+ MJ	+	-	-	
Mordenite	+	+ MJ	-	-	
Zeolite P1, (Na)	-	-	+ MJ	-	
High Sanidine	+	+	-	-	
Anorthoclase	-	-	+	+	
Albite	-	-	+	+	
Opal CT	-	+	-	-	
Quartz	-	-	+ MJ	+ MJ	+ MJ
Hematite	-	-	+	+	+
Maghemite	-	-	+	+	
Lime	-	-	+	+	
Gypsum					+ MJ
Calcite					+
Muscovite					+
Illite					+
Plumbojarosite					+
Jarosite					+
Hemimorphite					+

experiment and measured by weighing the dried plant mass from each pot, after harvesting.

3   RESULTS AND DISCUSSION

The contaminated soil from Lavrion consists of quartz, calcite and clay minerals (illite), minerals usually present in soils (Table 1). However, mining activities in the region have contaminated the soil, and have enriched it, in gypsum jarosite, plumbojarosite, hematite, and hemimorphite originated by the weathering of the ores and slags of the area. As expected, the untreated contaminated soil from Lavrion presented acidic pH value (3.82). This soil showed high Fe_2O_3 and total S content (Table 2) due to the exploitation of the sulfur-containing minerals at the mines of the area. It also exhibits an increased content of all six possibly toxic elements studied: the soil content of Pb is 4.2%, of Zn is 3%, while the content of Fe is 21.6% (Table 2). It is noted that the content of those elements exceeds the Netherlands intervention values for the contaminated soil and the Canadian and the U.S. EPA standards for agricultural soils.

The two natural zeolite tuffs, Clinoptilolite-rich and Mordenite-rich, consist mainly of the minerals clinoptilolite and mordenite respectively (Table 1). It is noted that the mordenite-rich tuff ZMS contains high amounts of opal-CT and minor amounts of potassium feldspars and the clinoptilolite-rich tuff ZCS is richer in zeolite content, mainly clinoptilolite, containing only small amounts of mordenite and potassium feldspars, whereas opal-CT is not present. SEM images demonstrate the tabular texture of clinoptilolite crystals. 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. The needle-like mordenite crystals drapes across smectite while quartz and cristobalite are present.

The synthesized zeolitic material (FAZ) consists mainly of the synthetic zeolite Na-P1 ($Na_6Al_6Si_{10}O_{32}$·$12H_2O$), while the coal fly ash (CFA) consisted mainly of glass and quartz (Table 1). Both the quantity and quality of the synthetic zeolitic material produced by the above process were high. This is probably due to two interventions made in the method of Koukouzas *et al.* (2010) and Itskos *et al.* (2015). The Na-P1 zeolite has an affinity with the cations that are generally found in acid mine drainage effluents (Cardoso *et al.*, 2015). It is also exhibiting a high ion exchange capacity (CEC) due to the 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. The formation the synthetic zeolite was confirmed by SEM study, as microcrystals of Na-P1 zeolite grow on the typical glassy material of fly ash.

As about chemistry, the Mordenite-rich tuff (ZMS) exhibits higher Si, Na and K content compared to the Clinoptilolite-rich (ZCS) while the percentages of Al, Fe, Mg, Ca and Ti are greater in ZCS. Phosphorus and Chromium content is almost the same in both natural zeolitic materials (Table 2). The Fe values are very high in both materials (0.8% in ZMS and 1.3% in ZCS). The sample ZCS exhibits a higher content in Pb, Cu, Zn and Fe, while the Mn content is higher in ZMS. The Cd content of both natural zeolitic tuffs is the same, ($<$0.1 mg.kg^{-1}).

The Si, Al, Fe, Mg, Ca, K, Ti, P, Mn and Cr values were reduced in the synthetic zeolitic material (FAZ), while Na was the only major element that increased (Table 2). This is due to the treatment with the NaOH solution and, subsequently, the addition of Na in the solid to produce the Na-P1. Fe exhibited high values in both materials (4.6% in FAZ and 6.1% in CFA) (Table 2). Cadmium was minor, in both fly ash and synthetic zeolite ($<$0.1 mg.kg^{-1}). The synthesized zeolitic material exhibited higher pH values (12.25) compared to the natural zeolites samples (ZCS=8.1 & ZMS=7.5).

The untreated soil sample (Lsoil), used for the experiments, exhibited pH value as low as 4.52 but the amended soil mixtures presented increased pH. This was particularly evident in those samples amended with FAZ (pH 6.07). The higher pH value of the FAZ mixture is attributed to the higher pH of the FAZ component of the mixture. LSoil presented higher values after the equilibration. The pH values of all treatments increase after planting (from 4.37 at 4.52 for Lsoil, from 4.6 to 5.38 for the ZMS mixture, from 4.67 to 4.94 for the ZCS mixture and from 6.03 to 6.07 for the FAZ mixture, due to the soil equilibration with the zeolitic materials and the planting effect.

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 *et al.*, 2000). The newly formed phases may accommodate the metal pollutants either as major constituents (Chen *et al.*, 2000) or as minor components co-precipitated in hydroxides (Boisson *et al.*, 1999; Chlopecka and Adriano, 1997). 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. Shi *et al.*, 2009). Higher pH promotes the complexion of cations by stable bonds with the negative radicals on the mineral surfaces. Zeolite minerals may play a significant role in thus surface complexation because of their high specific surface (Sponer *et al.*, 2001). Moreover, the cation exchange properties of zeolite minerals may cause metal impoundment, regardless of pH value (Castaldi and Santona, 2005).

The greater growth of *Trifolium alexandrinum*was observed in the soil mixture amended with the synthetic zeolite FAZ. This is attributed to the higher pH values of this mixture, which as stated by Castaldi and Santona (2005) plays a key role both in phyto-toxicity and

Table 2: Major elements (%) and trace elements content of the materials used (ZCS: natural zeolite tuff rich in clinoptilolite, ZMS: natural zeolite tuff rich in mordenite, FAZ: synthetic zeolitic material, CFA: coal fly ash, Lsoil: heavily contaminated soil from Lavrio, Greece).

Major Elements (%)	Natural Zeolitic Materials		Coal Fly Ash	Synthetic Zeolitic Material	Contaminated soil
	ZCS	ZMS	CFA	FAZ	Lsoil
SiO_2	62.64	71.19	57.29	47.44	9.62
Al_2O_3	12.62	11.62	17.92	15.94	2.12
Fe_2O_3	1.91	1.20	8.69	6.65	30.87
MgO	1.18	0.20	2.25	2.05	0.25
CaO	3.22	1.63	7.30	6.77	8.04
Na_2O	0.67	1.05	1.40	6.62	0.11
K_2O	2.63	3.83	2.29	1.15	0.42
TiO_2	0.13	0.06	0.84	0.75	0.12
P_2O_5	0.02	<0.01	0.12	0.06	0.11
Cr_2O_3	<0.002	<0.002	0.020	0.016	0.045
Trace Elements $(mg.kg^{-1})$					
Pb	70.5	57.3	7.4	13.6	42000
Cd	<0.1	<0.1	<0.1	0.1	91.5
Cu	2.3	1.7	49.7	59.8	1366
Zn	47	5	27	38	29800
Mn	100	200	900	800	4600

in metal trace element availability reduction. Moreover, other authors (e.g. 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. The increase pH value of treated soil by the tested amendments confirmed the buffering effect (Radulescu, 2013) and suggested the opportunity of using zeolitic materials for conditioning and remediating contaminated soil in areas with sulfide mining.

Concerning the CEC, the synthetic zeolitic material (FAZ) exhibited the highest value (146 meq.100g^{-1}) among all tested zeolitic materials. The contaminated soil from Lavrion (Lsoil) presented the lowest CEC (28 meq.100g^{-1}) while the two natural zeolitic materials exhibited almost the same CEC values (80 meq.100g^{-1}). All mixtures with amendments exhibited higher CEC, compared to Lsoil. This demonstrates that zeolitic materials improved soil properties. Among the treatments with natural zeolitic materials, treatment with mordenite (ZMS) exhibited the higher CEC value (41 meq.100g^{-1}). Some authors have claimed that the remediation of polluted soils by zeolitic amendments may be mainly attributed to the cation exchange capacity rather than the pH value (e.g. Castaldi and Santona, 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 a higher CEC values is predicted to have a greater capacity to maintain adequate quantities of the above mentioned cations than a soil with a lower CEC. Zeolite is crystalline aluminum-silicates, 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 (Mondales *et al.*, 1995). Despite of 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 (ZMS) exhibits greater CEC value (41 meq.100g^{-1}). This may be attributed both by soil constitutes and combination of soil with amendments. Moreover Ross (1995) has referred 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+}).

Among all the pot experiments carried out in the present study, the treatments with the use of synthesized zeolitic material are the most efficient. Specifically, the growth of *Trifolium alexandrinum* in the treatment with FAZ, was higher compared to the treatments with the natural zeolitic materials (ZCS and ZMS), while in the application with unamended soil (Lsoil) the growth of *Trifolium alexandrinum* was negligible.

Furthermore, the water solubility % of heavy metals of all amended soil mixtures was measured to be lower than those of the untreated soil (Lsoil). Thus, in case of rainfall, the solubility of all 6 heavy metals studied will be lower if the synthetic zeolitic material (FAZ) was used as an amendment (0.001% for Pb, 0.27% for Cd, 0.32% for Zn, 0.003% for Cu, 0.16% for Mn, 0.001% for Fe) compared with the untreated soil (0.002% for Pb, 0.79% for Cd, 0.77% for Zn, 0.01% for Cu, 0.6% for Mn, 0.001% for Fe). Between the two natural zeolitic materials, more effective in reduction of water solubility of metals studied, was the mordenite-rich material (ZMS). FAZ addition has reduced the water solubility of Pb, Cd, Zn, Cu and Mn but not of Fe. The negative effectiveness for Fe of all and Pb of the rest treatments may be attributed to their release from the original amendments, as they exhibited high content of these metals (Table 2), in combination with their pH. Among the natural zeolites, the mordenite exhibited better effect in the reduction of the solubility of studied metals.

The potential bioavailability of heavy metals tested with the EDTA method, exhibited higher values. As the EDTA buffers a lower soil pH and, consequently, a higher percentage of the heavy metals content of the soil may be mobilized to the leachates. Between the two natural zeolites mixtures, the one with ZMS presented better performance, exhibiting the lowest potential bioavailability for all studied heavy metals. On the other hand, the synthetic zeolitic amendmend FAZ, exhibited lower potential bioavailability for Cd(3.9%), Cu(0.7%), Mn(1.3%)and Fe(0.02%). On the contrary the mixture with clinoptilolite exhibited higher plant growth, despite of the fact that pH and CEC values were lower. This is explained by the higher water holding capacity of this zeolite species which is a controversial factor in plant growth (Giannatou *et al.*, 2018).

The synthetic zeolitic material originated from the alkaline hydrothermal treatment of lignite fly ash, resulted a significant decrease of the contaminants leachability and potential bioavailability. The increase of pH may be the key factor for those potentially toxic elements immobilization. Among the natural zeolites, mordenite proved to be more effective in controlling the potential bioavailability of all studied heavy metals except Pb, in contrast to the clinoptilolite that presented a poor effect for almost all heavy metals. The potential bioavailability, as resulted by the EDTA method, of Pb and Zn in the amended samples was higher in comparison to the untreated soil. However, it is referred that the EDTA test may overestimate the bioavailable content of pollutants (e.g. Stouraiti *et al.*, 2002).

4 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 pot experiment conducted have resulted an improved performance in contaminated acid mining soil with zeolite

amendments for the *Trifolium alexandrinum* crop.

The pH increase of the amended soil confirmed the buffering effect of the zeolitic materials, along with the reduction of the heavy metals mobility, indicating their possible use in conditioning and remediating acid mining soils. Soil mixtures containing synthetic zeolitic materials as amendment displayed pH regulation, higher cation exchange capacity values, and excellent growth of *Trifolium alexandrinum*.

Synthetic zeolitic material resulted in a significant decrease of the potential bioavailability of Mn, Fe, Cd and Cu. Moreover, it has minimized the water solubility of Mn, Fe, Cd, Cu, Pb and Zn.

Between natural zeolitic materials originated from Samos Island, the most efficient was the clinoptilolite-rich tuff. Mordenite-rich tuff regulates better the pH and CEC, but exhibited less growth of the *Trifolium alexandrinum* plant compared with clinoptilolite-rich.

Both quantity and quality of the synthetic zeolitic material, originated from alkaline hydrothermal treatment of Meliti's lignite fly ash and produced during the present work effectively for amending the contaminated soil being the most effective among the tested amendments.

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