A study of zeolitic tuffs associated with bentonite deposits from Almeria, Spain and Kimolos Island, Greece and their industrial potential as pozzolanas in the cement industry*

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ABSTRACT: Zeolite tuffs that represent co-products or by-products of quarrying originated from active bentonite quarries located in Kimolos Island Greece and Almeria Spain were studied in order to identify their efficiency for use as pozzolanas in the cement industry. The mineralogical, chemical and physical characteristics of four bulk zeolite-tuff samples were determined and compared to three glassy tuff samples extracted from a pozzolana quarry located in the SW part of Milos Island. From the analytical results, it is concluded that the Kimolos zeolite tuffs studied can replace the currently used volcanic glass-rich tuffites in Greece. The Almeria zeolitic tuff can find applications in the Spanish cement industry to replace the energy consuming Portland cement with naturally occurring Pozzolanas ["green" cement].

Key-words: *Zeolite, mordenite, tuff, pozzolanas, cement, compressive strength*.

ΠΕΡΊΛΗΨΗ: Ζεολιθικοί τόφφοι που συνδέονται γενετικά με τα μπεντονιτικά κοιτάσματα των περιοχών Αλμερίας Ισπανίας και της νήσου Κιμώλου και θεωρούνται παραπροϊόντα της εξόρυξης μπεντονίτη μελετήθηκαν με στόχο την πιστοποίηση της ικανότητάς τους να λειτουργήσουν ως ποζζολάνες στη βιομηχανία τσιμέντου. Για το σκοπό αυτό μετρήθηκαν οι ορυκτολογικές και χημικές παράμετροι και τα φυσικά χαρακτηριστικά τεσσάρων αντιπροσωπευτικών δειγμάτων από τις ως άνω περιοχές και τα αποτελέσματα συγκρίθηκαν με τα αντίστοιχα τριών αντιπροσωπευτικών δειγμάτων υελωδών τοφφιτών που προέρχονται από τη ΝΔ Μήλο και χρησιμοποιούνται ήδη από την τσιμεντοβιομηχανία. Από τα αναλυτικά αποτελέσματα προέκυψε ότι οι ζεολιθικοί τόφφοι που μελετήθηκαν μπορούν να αντικαταστήσουν τις ήδη χρησιμοποιούμενες ποζζολάνες στην Ελλάδα. Οι ζεολιθικοί τόφφοι της Αλμερίας μπορούν να βρουν εφαρμογή στην Ισπανική βιομηχανία τσιμέντου και να αντικαταστήσουν μέρος του ενεργοβόρου στην παραγωγή τσιμέντου Πόρτλαντ με φυσικές ποζζολάνες, δημιουργώντας έτσι ένα «πράσινο» τσιμέντο.

Λέξεις-κλειδιά: *ζεόλιθοι, τόφφος, ποζζολάνες, τσιμέντο, θλιπτική αντοχή*.

INTRODUCTION

Pozzolanas can be divided into two groups: natural such as volcanic rocks and diatomite, and artificial ones such as calcined clays, pulverized fly ash and ash from incinerated agricultural wastes. Natural pozzolanas are usually fine-grained rocks of volcanic or biogenic origin that have suitable chemical and mineralogical composition. Among them, the most common are glassy and pumice tuffs, zeolite tuffs and some qualities of diatomaceous rocks (Fragoulis *et al.*, 1997; Stamatakis *et al.*, 2000; Stamatakis *et al.*, 2001). Pozzolana itself is not cementitious but is latently hydraulic. In the presence of appropriate amounts of water, it reacts chemically with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Pozzolana-containing cements decrease the porosity of concrete and in the presence of moisture, promote self-healing of cracks. Moreover, both heat of hydration and alkali-aggregate reactivity are reduced, while sulfate resistance increases (Kontori *et al.*, 2009; Perraki *et al.*, 2010). Pozzolanas can be blended with OPC in percentages commonly up to 20%, considerably reducing cost, improving certain characteristics of OPC-based concretes such as long-term strength, resistance to sulphate attack and workability and to decrease CO_2 emissions.

Pozzolanas, either natural or artificial, are referred to siliceous and/or aluminosilicate raw materials. Eventhough most of the tuffs used as pozzolanas are glassy, zeolitic rocks have been successfully tested and used in cement applications (Huizhen, 1992; Kitsopoulos & Dunham, 1996; Stamatakis *et al.*, 2000). Zeolite minerals are characterized as framework aluminosilicate minerals. Their small particle size and their high specific surface area is the basis of their unique characteristics in industrial minerals applications. The behavior of the mordenite and/or clinoptilolite tuffs as pozzolanas has not been investigated thoroughly and

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* Ζεολιθικοί τόφφοι που συνδέονται με μπεντονιτικά κοιτάσματα από την Αλμερία, Ισπανία και τη Νήσο Κίμωλο και η δυνατότητα βιομηχανικής τους χρήσης ως ποζζολάνες στην παραγωγή τσιμέντου

controversial results have been obtained. It is being reported in literature that the introduction of zeolite up to 15% increases compressive strength at early ages (CANPOLAT *et al.*, 2004). On the other hand, the use of zeolitic tuffs in mortars results to late strengths similar to that of Portland cement mortars (JANOTKA *et al.*, 2003). This confirms that zeolitic cement can replace Portland cement in many applications with the advantage of higher resistance to acidic and sulfate attack (JANOTKA *et al.*, 2003). Other researchers have been led in diverse results, as the substitution of Portland cement by zeolites in percentage <50% leads in lower compressive strength (HEWLETT, 2007). The incorporation of zeolite in cement contributes to the consumption of $Ca(OH)_2$ and the formation of cement-like hydrated products formed during cement hydration (PERRAKI *et al.*, 2003; BLANCO VARELA *et al.*, 2006; SATO & TRISCHUK, 2008). According to KONTORI *et al.* (2009), the pozzolanic reaction of the zeolite is rather slow during the first days of hydration but accelerated after 28 days.

All these differences on the efficiency of zeolite rocks as pozzolanas could be attributed to the unspecified zeolite content of the samples, the degree of zeolite crystallinity, the crystal size and shape, and the presence of other active siliceous components (CANPLOAT *et al*., 2004; FRAGOULIS *et al*., 1997; KITSOPOULOS & DUNHAM, 1996; KONTORI *et al*., 2009; PERRAKI *et al*., 2010; YILMAZ *et al*., 2007) .

The aim of the present paper is to test zeolite [mordenite]-rich tuffs extracted as byproducts from bentonite quarries located in Greece and Spain. Correlation was made with currently used glassy tuffites originating from Milos Island which is close to Kimolos Island and also shares the same volcanic history. Besides their location in quarrying areas, an additional reason of selecting these two zeolite deposits for studying is that they present chemically and genetically similar raw materials.

GEOLOGICAL SETTING AND SAMPLING

Prassa, Kimolos Island, Greece

Kimolos volcanic rocks, along with that of the neighbouring Milos and Poliegos islands consist part of the South Aegean Volcanic Arc having Upper Neogene age [0.9-3.5 Myr]. The volcanic activity in these islands can be divided into two main periods, divided by a period in which epiclastic rocks were deposited (FRANCALANCI *et al.*, 2007). Basaltic to rhyolitic lavas and voluminous pyroclastic rocks formed from eruption during the first period, whereas rhyolitic pyroclastic deposits and perlitic lava domes characterize the second period of activity (FRANCALANCI *et al.*, 2007). The rock composition belongs to the calc-alkaline and high-K calc-alkaline series. The pyroclastic rocks and lavas have been locally transformed to opal-CT and /or cristobalite rich rocks, zeolite tuff, bentonite and kaolin. Most of the tuff and tuffite beds are unaltered, mainly composed of volcanic glass and pumice fragments.

Fig. 1. Prassa Quarry. The white bentonite active quarry confined between zeolitised tuffs, glassy pumiceous tuffs and overlaid by dark colored lapilli tuffs.

Fig. 2. View of the Prassa Quarry from the north. The benches are made on the white zeolite tuffs and the top two represent the dark colored lapilli tuffs.

Three samples up to 50 kg each were collected from the Prassa active quarry operating in the NE part of the island for the extraction of white bentonite (Figs 1 & 2). White to greenish zeolitic tuffs are located south of the bentonite deposit that is oriented almost in an east-west direction. Off-white to ivory colored pumiceous tuffs are developed north of the bentonite deposit, whereas, dark brown lapilli tuffs of small thickness overly the former deposits. The zeolitic tuffs are fine-grained and homogenous with only some traces of their original pumiceous character, whereas volcanic bombs or fragments of older rocks are absent. The zeolite-rich material is considered as by-product or co-product and it is sporadically used in admixtures with the bentonite for specific applications.

San Jose, Almeria, Spain

In San Jose, Almeria, Spain, a genetically similar zeolite tuff

Fig. 3. Off-white bentonitized and zeolitised pumice tuffs, confined between andesite lavas, Los Murcianos Quarry, San Jose Almeria, Spain.

Fig. 4. Los Murcianos Quarry. Pumice relics now transformed to bentonite patches into the zeolitised ash-tuff.

deposit has been located having Middle to Upper Miocene age [7-15 Myr] (Caballero *et al.*, 2005). An operating bentonite quarry at Los Murcianos is the only one that extracts zeolite tuffs as byproducts. The original rock was pumice and ash-tuff, as all the layers are fine-grained and there exist scant traces of volcanic rock fragments with residual pumiceous texture that is currently bentonitised (Figs 3 & 4). Similarly to the Prassa Kimolos deposit, the San Jose bentonite and the zeolite deposits have been formed by fluids of increased temperature, probably in two circles. The boundary of the zeolite/bentonite deposit is the Los Frailes volcanic complex and the deposits are emplaced between ignimbrites and tuffs (Regueiro *et al.*, 2007).

ANALYTICAL TECHNIQUES AND EXPERIMENTAL PROCEDURES

The bulk rock samples were crushed in a jaw crusher down to a size of less than 0.5 mm in diameter (TITAN SA). Furthermore, they were all ground with the use of the SIEBTECNIK gyratory lab mill to a grain size of less than 50 μm Their mineralogical and chemical composition were determined by the following methods:

- X-Ray Diffraction to determine the mineralogy of the volcanic tuffs and tuffites (TITAN SA). The measurements were carried out with the BRUKER D500 XRD apparatus under the following conditions:
- radiation source: Cu tube/Ka radiation
- range: 5-65^o 2θ
- measuring time: 5s
- step size: 0.04^o 2θ
- Textural analysis on the raw materials by SEM using the JEOL-JSM-5600, OXFORD LINK™ ISIS™ (NKUA, Athens).
- Chemical analysis by the XRF method in TITAN SA RDQ laboratory based in the Kamari Viotia Cement Plant (Elefsis). The BRUKER SRS 3400 sequential X-ray spectrometer was used operating at 50 kV, 69 mA with the AgRh tube and LIF, PET and OVE crystals.

Clinker and gypsum were co-grounded along with the raw materials at different percentages in a ball mill for the same period of time (45 min). The specific surface (Blaine) and the strength of the final products were determined according to the European regulations (EN 196-1). In addition, the water demand and the setting time (initial and final) of the laboratory-prepared cements were also determined (TITAN SA, Elefsis).

The results are shown in Tables 1, 2 and 3.

RESULTS AND DISCUSSION

Mineralogy and diagenetic implications

In Kimolos Island, the tuff deposits outcrop a significant part of it. However, most of the tuffs are glassy, pumiceous ash and lapilli tuffs and locally silicified. Diagenetic alterations of volcanic glass to zeolites have been located near Hellenica in the west Kimolos where both porous clinoptilolite tuffs and hard massive mordenite tuffs have been reported forming small deposits (Stamatakis *et al.*, 1996; Fragoulis *et al.*, 1997), and also in Prassa bentonite quarry in the north (Marcopoulos & Christidis, 1989).The zeolite deposits of Kimolos Island is assumed to have formed in an open hydrological system by the action of alkaline groundwater, under conditions of high heat flow rates (Stamatakis *et al.*, 1996; Fragoulis *et al.*, 1997). It is assumed that the fluids responsible for mordenite formation had probably higher temperature than that of clinoptilolite due to high heat flow rates originating from the emplacement of lavas in their vicinity (Fragoulis *et al.*, 1997).

The zeolite-bentonite deposit of San Jose Almeria occurs in a narrow area and it is tectonically controlled, as its contact with the neighboring andesite and dacite lavas is confined by normal faults. The deposit is composed of almost horizontal layers of interbedded epiclastic tuffs with volcanic

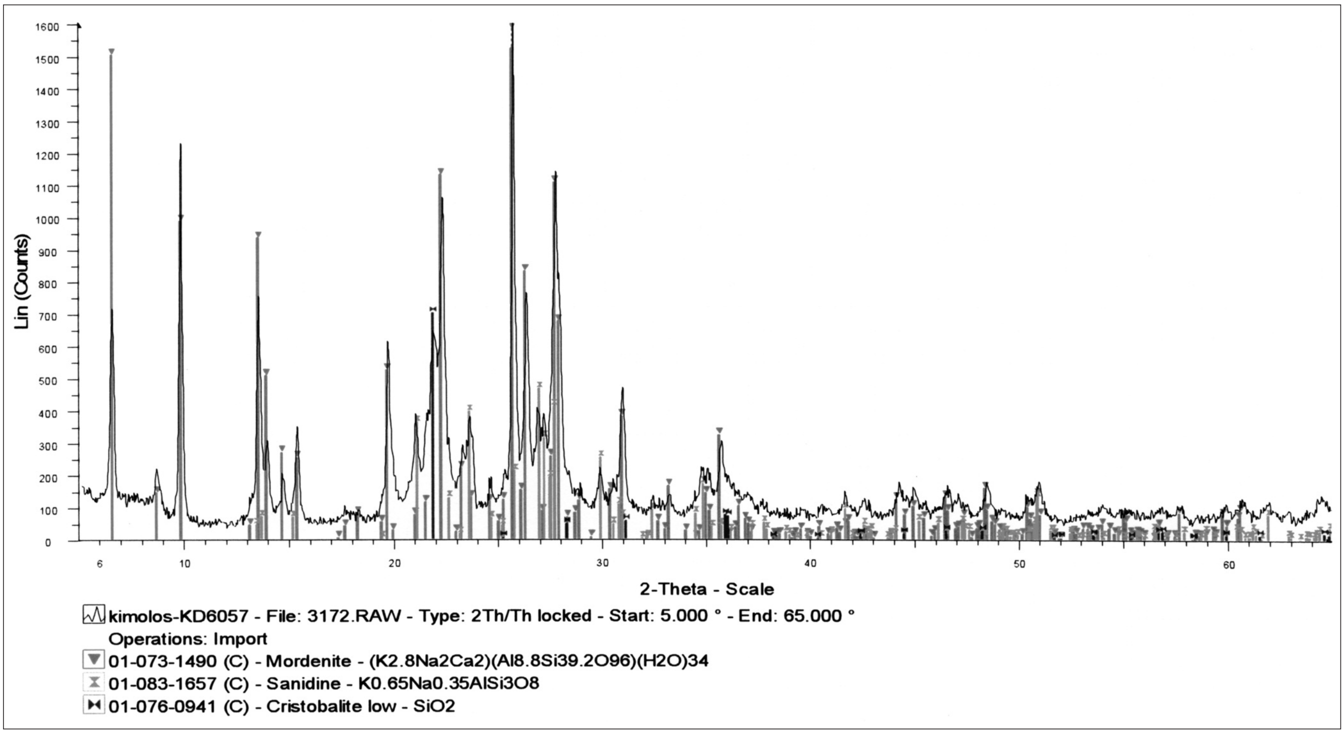

Fig. 5. XRD pattern of the Kimolos tuff sample Greenish mordenite-tuff-1.

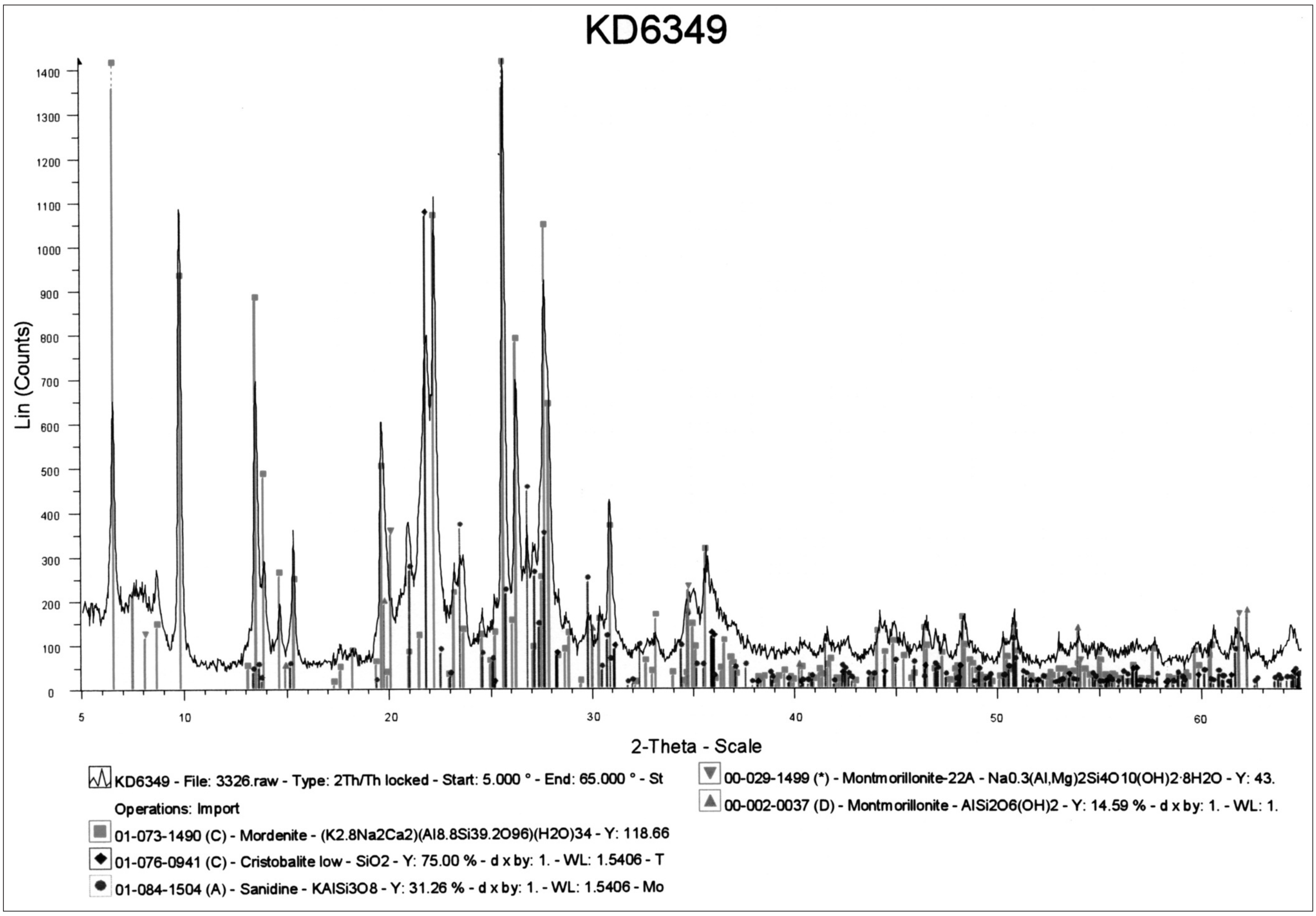

Fig. 6. XRD pattern of the Almeria tuff sample Greenish mordenite-tuff.

TABLE 1
XRD mineralogical analysis of the zeolitised tuff samples of Prassa, Kimolos and San Jose Almeria.

	Minerals				
Bulk zeolitic tuff samples	***Mordenite***	***Opal-CT, cristobalite, quartz***	***Smectite***	***Mafic minerals***	***Feldspars***
Kimolos white tuff	Major	Medium	Medium	Trace	Trace
Kimolos green tuff-1	Major	Medium	Trace	Trace	Medium
Kimolos green tuff-2	Major	Major	Trace	Trace	Trace
Almeria greenish tuff	Major	Medium	Medium	Trace	Trace
Reference samples	***Volcanic Glass***	***Quartz***	***Carbonates***	***Mafic minerals***	***Feldspars***
Glassy tuffite-1	Major	Medium	Trace	Trace - Minor	Medium
Glassy tuffite-2	Major	Medium	Trace	Trace - Minor	Medium
Glassy tuffite-3	Major	Medium	Trace	Trace - Minor	Medium

bentonitised materials which have been subjected to hydromagmatic activity (BENITO *et al*., 1998; CABALLERO *et al*., 2005). The harder layers are richer in either zeolites or volcanic and detrital constituents, whereas the bentonite-rich parts of the deposit are friable. It is assumed that the beds of originally glassy ash-tuffs have been devitrified by hydrothermal solutions forming initially bentonites and finally mordenite and cristobalite assemblages due to the action of silica-rich residual fluids (BENITO *et al*., 1998)

Mineralogical analysis

XRD analysis revealed that the Kimolos zeolite tuff is mainly composed of mordenite and secondarily by opal-CT or cristobalite, smectite and sanidine, whereas the Almeria sample is mainly composed of mafic minerals such as mordenite followed by minor amounts of quartz, opal-CT/cristobalite and smectite. In this sample, traces of augite and muscovite were also detected (Table 1). Sulphate minerals were absent from all zeolite tuff samples.

SEM analysis

SEM analysis of rock fragments has shown that both the zeolitised tuffs are mainly composed of cryptocrystalline zeolitic groundmass and only locally in fissures and pores the characteristic needle-like mordenite crystal assemblages and opal-CT lepispheres are grown on a massive matrix (Figs 7 & 8).

Chemical analysis

As it is concluded from the results shown in Table 2, the reference glassy tuffite samples, eventhough they contain sufficient amount of silica, they have low reactive silica content (~50% of the total). By contrast, both the zeolitised tuffs are richer in total and reactive silica. Furthermore, the greenish zeolite tuff-2 sample from Kimolos is richer in silica poly-

TABLE 2
XRF Chemical analysis of the reference samples and the zeolitic tuffs of Prassa, Kimolos Island and San Jose, Almeria.

Rock	**San Jose Almeria, Spain**	**Kimolos Greece**	**Kimolos Greece**	**Kimolos Greece**	*Reference sample-1*	*Reference sample-2*	*Reference sample-3*
	Greenish mordenite tuff	**White mordenite tuff**	**Greenish mordenite tuff-1**	**Greenish mordenite tuff-2**	*Glassy tuffite*	*Glassy tuffite*	*Glassy tuffite*
LOI	9.59	8,43	8,40	8,75	9,8	8,90	4,94
SiO_2	70.66	72,31	70,47	74,74	64,83	60,96	63,73
Al_2O_3	11.52	11,96	11,53	10,50	11,53	15,10	14,56
Fe_2O_3	1.14	0,63	0,44	0,54	3,17	3,40	6,46
CaO	1.35	0,98	1,20	2,00	4,6	6,10	5,51
MgO	1.04	0,68	0,36	0,64	1,64	1,30	1,41
SO_3	-	-	-	-	-	1,50	-
K_2O	2.18	2,45	3,99	1,90	2,11	2,10	1,13
Na_2O	2.60	1,62	2,27	1.48	2,57	0,60	2,2
Total	100.08	99.06	98.66	100.50	100,25	99.96	99.94
SiO_2 reactive	60	55	57,2	59	35	35	38,1

TABLE 3
Physical characteristics of laboratory produced cements.

Physical characteristic	*Reference sample-1 Milos*	**San Jose-Almeria, Spain**	**Kimolos Greece**	*Reference sample-2 Milos*	**Kimolos Greece**	*Reference sample-3 Milos*	**Kimolos Greece**
	Glassy tuffite	**Greenish mordenite tuff**	**White modenite tuff**	*Glassy tuffite*	**Greenish mordenite tuff-1**	*Glassy tuffite*	**Greenish mordenite tuff-2**
Grinding time [min]	45	45	45	45	45	45	45
Blaine cm^2/g	4230	5020	5350	4250	5320	4340	4940
Water demand %H$_2$O	28,4	29.6	34,4	28,1	32.2	28,8	33.0
Initial Setting Time [min]	160	165	130	170	140	140	110
Final Setting Time [min]	220	220	170	240	200	200	170
Strength 1day [Nt/mm^2]	12	12.3	13,7	9,3	13,7	11,9	12,2
Strength 2day [Nt/mm^2]	19,4	18.1	18,9	20,3	21,2	20,5	20
Strength 7day [Nt/mm^2]	29,4	31.2	27,9	33,6	33,0	31,3	30,6
Strength 28day [Nt/mm^2]	45,4	46.9	43,1	46,4	49.9	45	45.6

morphs, but that does not reflect significant changes in the reactive silica value ranging in all zeolite-tuff samples between 55-60%. The reactive silica values are significantly higher compared to the three reference volcanic glass-rich tuff samples ranging between 35-38%. The alkaline earths content of the reference tuff samples is higher than that of the zeolite tuffs, due to the carbonate minerals present (calcite and subsequently dolomite) of the glassy tuffs. The alumina content is higher in the glassy tuffs, whereas slightly less iron was detected in the Kimolos tuffs, with all other major elements fluctuating within a narrow range (Table 2).

Laboratory Cements

Laboratory cements were produced by co-grinding of 75%w/w clinker, 5% gypsum and 20%w/w of either glassy tuffite that is already used as pozzolana, which is located in the SW part of Milos Island [Reference Samples] or the zeolitic tuffs of Kimolos Island and San Jose, Almeria.

The grinding time was kept constant for all samples (45 min). All pozzolanas exceeded the lower limit of the reactive silica that is 25% (EN 197-1).

Table 3 shows that the setting time of the laboratory cements produced with either reference glassy tuffite samples or zeolite-tuff samples- have similar initial and final setting time. From the comparison of the cements produced with the reference glassy tuffite samples and the mordenite tuffs, it is concluded that the cements produced with the specific zeolite tuffs have equal or slightly higher compressive strength. However, the Greek zeolite tuffs have higher Blaine and thus higher water demand, a drawback that decreases compressive strength over time.

The cement produced with the Spanish zeolite tuff has a lower water demand and Blaine than those produced with the zeolite tuff from Kimolos, indicating that the Spanish pozzolanas are superior to Greek. If the Spanish sample was properly ground to obtain the same granulometry as the Kimolos zeolite tuff, it would be expected to obtain an extrapolated strength of more than 50 Nt/mm^2. Calvo *et al.* (2005) had similarly concluded that the use of 30-25% of the Almeria mordenite tuff in pozzolanic cements gives compressive strength values ranging between 45.7 to 51.8 N/mm^2

From the Figs 9-12 the following can be concluded:

1. The reactive silica was linearly correlated to total silica content of the samples. This close association of total and reactive silica is attributed to the fact that in both, the glassy tuffs of Milos and the zeolite tuffs of Kimolos and Almeria, the silica content is mainly correlated to the amorphous or neoformed easily decomposed silicate and aluminosilicate phases [opal-CT and zeolites] and not to the stable crystalline quartz or cristobalite. It is well known that feldspars [SiO$_2$ ~ 67%] and all quartz phases [SiO$_2$ ~100%], such as coarse

grained, microcrystalline and chalcedonic have reactive silica values of less than 10%, hence these mineral components does not yield detectable RS in the cement and are characterized as inert from the cement industry.

2. The reactive silica content was linearly correlated with the fineness of the samples [Blaine]. Based on SEM studies (Figs 7 & 8), it is obvious that the opal-CT and the zeolite grain size is very fine, hence this is another proof that these authigenic mineral phases play an important role on the supply of the samples with reactive silica. This correlation reveals also that the fine-grained material [high Blaine] decomposes easier to its reactive phases [silica].

The compressive strength of all samples studied was not linearly correlated with neither reactive silica nor Blaine. The strength of the cement is mainly due to the formation of hydrated products among which C-S-H is the most important. C-S-H is formed either from the direct hydration of C3S(3CaO.SiO_2) and C2S(2CaO.SiO_2) or from the reaction between $Ca(OH)_2$ and reactive silica (Naiqian, 1993; Taylor, 1997). The $Ca(OH)_2$ forms during the hydration of C3S and C2S while the reactive silica is contained in the pozzolanic materials (Fragoulis *et al.*, 1997).

It is noteworthy that even though the reactive silica of the glassy tuffs is much lower than that of the zeolite tuffs, it does not reflect the decrease of the respective compressive strength values. That could be explained by the assumption that the reactive silica of the zeolite tuffs is in excess, so a great part of it is not participating in the neoformation of cementitious substances formed during the hydration of cement. The slightly higher compressive strength of the mordenite tuffs compared with the glassy tuff-tuffite of Milos could be attributed to a combination of parameters such as, high reactive silica and Blaine. Similar results, concerning the efficiency of the mordenite tuffs in comparison with the glassy tuffs were obtained by using mordenite tuff from another deposit of Kimolos associated with clinoptilolite tuffs and located in the western part of Kimolos Island (Fragoulis *et al.*, 1997). In general, the high value of pozzolanic activity of the zeolite tuffs is an additional factor that may play an important role for the development of high late strengths in pozzolanic cements (Janotka *et al.*, 2003; Perraki *et al.*, 2003).

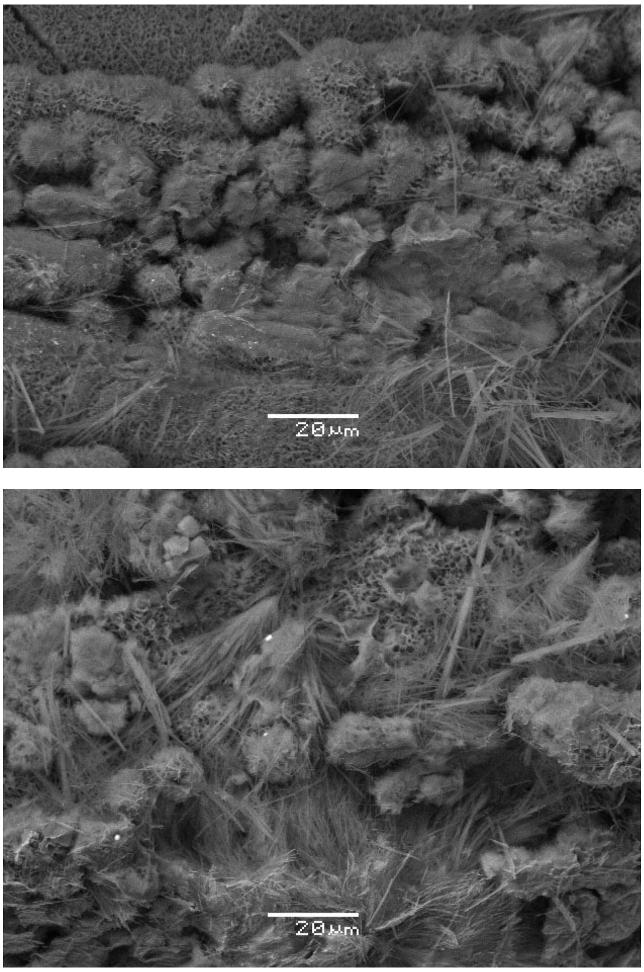

Fig. 7. SEM images of the mordenite tuff of Kimolos. Note the opal-CT lipispheres and the needle-like mordenite crystal assemblages [left] and the net-like montmorillonite background of the mordenite crystals [right].

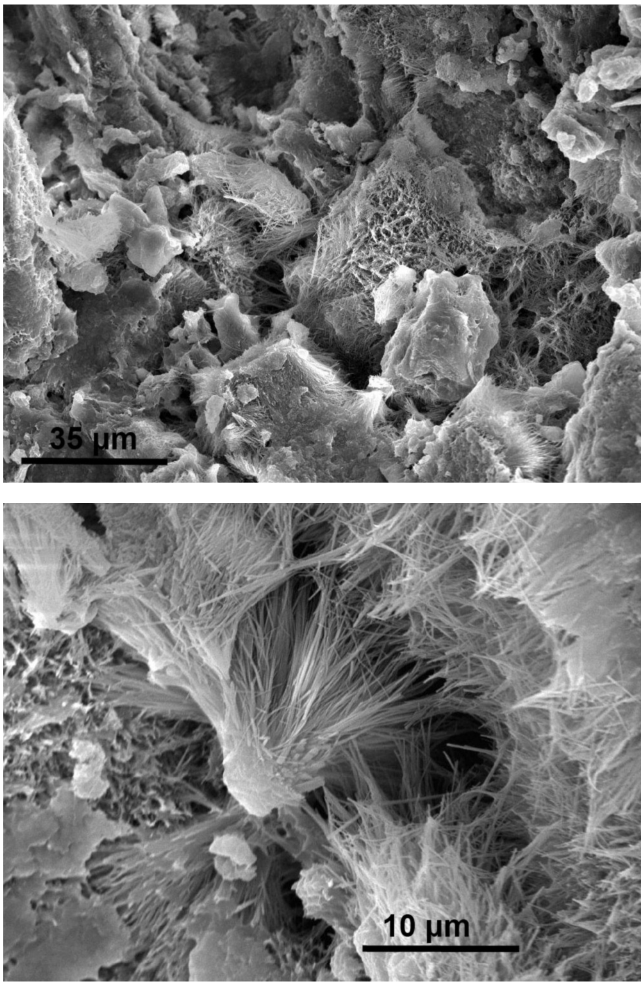

Fig. 8. Two SEM images of the mordenite tuff of San Jose. Mordenite fibrous crystal aggregates grown on a glassy precursor.

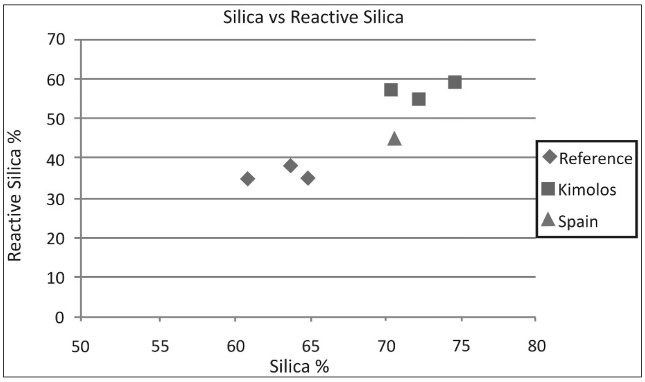

Fig. 9. Correlation between Silica and Reactive Silica of the samples.

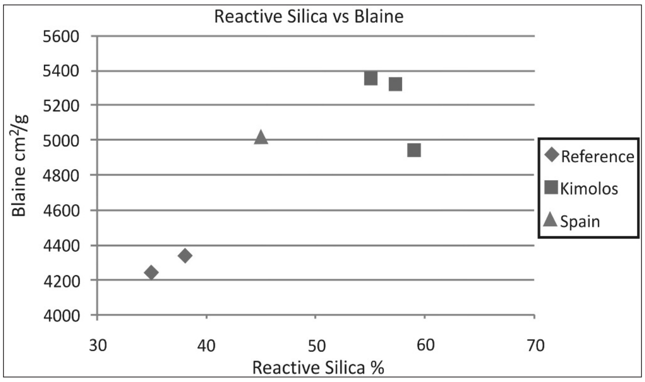

Fig. 10. Correlation between Reactive Silica and cement's Blaine.

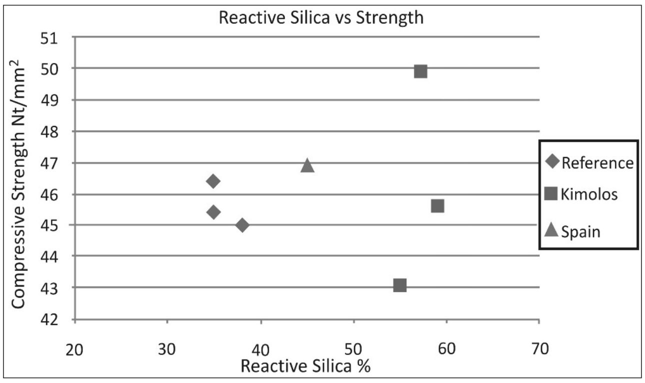

Fig. 11. Correlation between Reactive Silica and cement's Compressive Strength.

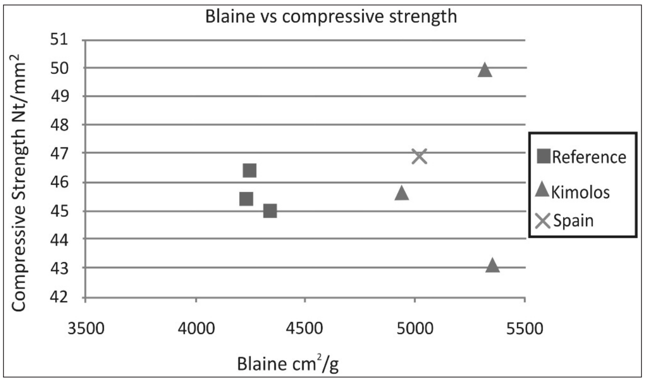

Fig. 12. Correlation between Blaine and cement's Compressive Strength.

CONCLUSIONS

- The reactive silica of the currently studied pozzolanas was linearly correlated to their total silica. That correlation requires further research to determine whether it was incidental or it followed a regular pattern that needs to be unveiled.
- The compressive strength of the laboratory cements was not correlated to either reactive silica content or Blaine, alone. Nevertheless, that does not excude the possibility of a correlation involving both reactive silica and Blaine together with other parameters related to cement and pozzolana characteristics.
- The Greek zeolite tuffs studied could replace the currently used volcanic glass-rich tuffs and tuffites of Milos. Alternatively, the Almeria zeolite tuffs can find applications in the Spanish cement industry to replace the energy consuming Portland cement with naturally occurring Pozzolanas ["green" cement].

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