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APPLICATION OF ZEOLITIC VOLCANIC TUFFS FROM GREECE (LEFKIMI-DADIA, METAXADES, AND SANTORINI ISLAND, GREECE) AS POZZOLANIC MATERIALS

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ABSTRACT

Volcanic tuffs of Oligocene age rich in zeolite minerals coming from three different areas in Greece (Lefkimi-Dadia area, Metaxades area, Santorini Island) were examined as an industrial commodity.

The zeolite minerals present in these tuffs belong to the heulandite group of minerals. Minerals of the types 2 and 3 were found in the Lefkimi-Dadia tuffs, minerals of the types 1 and 2 in the Metaxades tuffs and minerals of the type 3 (clinoptilolite) were found in Santorini tuffs. The Lefkimi-Dadia tuffs have the highest amount of SiO_2 and the tuffs from Santorini have the lowest.

The investigation of some of their properties shown that they can reach an optimum pozzolanic activity if they have first been calcined.

Finally this ability to act as pozzolanic materials in real conditions was tested. For this purpose they were added in concrete mixture as replacements of the ordinary Portland cement. Tested, after a 28 day period, concrete cubes with 10% replacement by Lefkimi-Dadia, Metaxades and Santorini pozzolanic materials reached 99.03%, 97.46% and 92.01% respectively of the compressive strength of a cube contain 100% Portland cement.

INTRODUCTION

Zeolites have been known almost for more than 250 years and 30-40 different minerals have recognised. The most common of all these species are the clinoptilolite, mordenite, chabazite and the erionite. The commercial term 'zeolites' applies to occurrences of usually volcanic tuffs which contain from one up to four or five zeolite minerals, along with quartz, clays, micas and feldspars. Deposits have been recorded in more than fifty countries all over the world but the massive occurrences are located in the United States, Japan, Mexico, Italy, Bulgaria and Yugoslavia (Lefond, 1983).

Breck (1974) showed that the various applications of the zeolites are dependent on different physical and chemical properties, such as :

a. Ion exchange capacity
b. High degree of hydration
c. Low density and large void volume when dehydrated
d. Stability of the crystal structure of many zeolites when dehydrated
e. Uniform molecular-sized channels in the dehydrated crystals
f. Electrical conductivity
g. Adsorption of gases and vapours
h. Catalytic properties

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In this work the possibility of using zeolitic tuffs from Greece as Pozzolanic materials was examined.

POZZOLANIC MATERIALS AND POZZOLANIC ACTIVITY

Pozzolans can be either natural or artificial material and they are defined as siliceous and aluminus substances which are not cementitious themselves but which react with lime in the presence of water at atmospheric temperatures to produce cementitious compounds. They have been known since the Roman times where they have been used extensively by the Romans for the construction of roads, public buildings and aqueducts. They took their name from the village of Pozzuoli, a place near Napoli, Italy where the Neopolitan Yellow tuff can be seen, (Sersale, 1958).

The pozzolans are used in the manufacture of Portland cement clinker, for making lime-pozzolana mortars, as replacement of the Portland cement in concrete and for making pozzolanic cements, which are mixtures of ground pozzolana and Portland cement clinker. They found excellent application in the hydraulic cements where higher protection from the water corrosion is required.

The mechanism by which pozzolans accomplish changes in the properties of concrete is not known fully. However, the action of pozzolans is in part physical and in part chemical. The physicals effects relate particularly to specific gravity, particle shape, fineness and water absorption capacity

The pozzolanic reaction proceeds slowly; the portland-pozzolan cement concrete hardens slowly and usually increases progressively in strength and durability for long periods of time. Those pozzolans which inhibit or prevent cement-aggregate reaction in the concrete do so by chemical reaction with the absorption of the alkalies(Na_2O and K_2O) released by the hydrating Portland cement. The alkalies thus bound by the pozzolan are unable to attack the aggregates (Drury, 1954). The pozzolanic activity can be induced by heating. Price (1975) showed that the activity can be the result of the presence of:

(a.) Volcanic glass
(b.) Opal
(c.) Clay minerals
(d.) Zeolites
(e.) Hydrated oxides of aluminium

So volcanic tuffs may owe their activity not only to glass but also to opal, clays and zeolites. The latter material are classed as mixed activity type pozzolans.

Pozzolans with activity type (a.) obtain their maximum after calcining at 550°C to 900°C, materials with activity type (b.) after calcining at 750°C to 1000°C and with type (d.) calcination at about 760°C will give the maximum activity (Mielenz, 1950).

Fig 1: Map of Greece showing the locations of the areas studied (1: Metaxades, 2: Lefkimi - Dadia, 3: Santorini.).

The addition of altered volcanic tuffs consisting mainly of zeolites gives to the concrete satisfactory compressive

Table 1: Minerals detected by X-ray Diffraction.

LEFKIMI - DADIA								
S	**Heul Typ 2,3**	**Mo**	**Cr**	**Alb**	**Mi**	**Qz**	**Sm**	**K-Feld**
KL20	+	—	+	+	+	+	+	—
KL21	+	+	+	+	+	+	+	—
KL22	+	—	+	+	+	+	+	—
KL23	+	+	+	+	+	+	+	—
KL24	+	—	—	+	+	+	—	—
KL25	+	+		+	+	+	+	—
KL26	+	+	+	+	+	+	+	+
KL27	+	+	+	+	+	+	+	+
KL29	+	+	+	+	+	+	+	—

METAXADES				
S	**Heul Typ 1,2**	**Mo**	**Cr**	**Sm**
KM1	+	+	+	—
KM2	+	+	+	+
KM3	+	+	+	+
KM4	+	+	+	—
KM5	+	+	+	—
KM6	+	+	+	+
KM7	+	+	+	+

SANTORINI					
S	**Heul Typ 3**	**Mo**	**Cr**	**Alb**	**Sm**
KS11	+	+	—	—	+
KS12	+	+	+	+	+
KS13	+	+	+	+	+
KS14	+	+	+	—	+
KS15	+	+	+	+	+
KS16	+	+	+	+	+
KS17	+	+	+	+	+

(S:Sample, Heul:Heulandite, Mo:Mordenite, Cr:Cristobalite, Alb:Albite, Mi:Mica, Qz:Quartz, K-Feld:K-Feldspar, Sm:Smectite, Typ:Type, + : Detected, — :Not detected.)

strength in early stages, and exceeds the strength of 100% Portland cement after one year if the concrete is kept under water. It also gives satisfactory tensile strength and resistance to attack by sodium sulphate solution.

MATERIALS AND METHODS

The samples used in this investigation come from Lefkimi-Dadia and Metaxades, Thrace, and Santorini island, Aegean Sea, Greece. They represent different horizons of the zeolitic deposits (Fig.1).The mineralogy of the tuffs was examined by X-Ray diffraction (XRD) and Scanning Electron Microscopy (SEM) and the geochemistry by X-Ray Fluorescence Spectroskopy (XRF).The free-lime estimation was carried out as described in BS 4550. The construction and the testing of the concrete cubes was undertaken in accordance with BS 1881.

Table 2: Major element analysis of the zeolitic tuffs.

LEFKIMI - DADIA	KL20	K121	K122	K123	K124	K125	KL26	KL27	KL28
SiO_2	71.17	68.22	76.35	74.76	70.67	73.38	74.12	70.69	74.13
TiO_2	0.14	0.22	0.22	0.23	0.13	0.14	0.19	0.15	0.13
Al_2O_3	12.82	10.54	10.81	11.72	10.49	12.07	10.62	12.56	12.86
Fe_2O_3	1.63	2.32	1.28	1.19	164	0.60	1.23	1.69	0.81
MnO	0.06	0.05	0.03	0.03	0.11	0.02	0.08	0.05	0.05
MgO	0.78	0.98	0.62	0.80	1.48	0.74	0.70	1.13	0.32
CaO	3.01	3.68	1.94	3.01	3.21	2.56	2.19	2.81	2.10
Na_2O	1.73	2.24	1.28	1.51	0.67	0.87	1.61	1.19	2.04
K_2O	3.63	2.59	2.56	2.73	2.33	3.55	3.50	4.36	3.91
P_2O_5	0.03	0.04	0.08	0.08	0.02	0.02	0.03	0.03	0.02
LOI	5.80	6.29	3.84	4.02	7.43	5.68	4.17	5.84	4.16
Total	100.80	99.16	99.01	100.08	98.18	99.63	98.44	100.52	100.53

METAXADES	KM1	KM2	KM3	KM4	KM5	KM6	KM7
SiO_2	70.25	72.89	71.13	70.04	69.41	69.78	72.06
TiO_2	0.10	0.13	0.13	0.11	0.10	0.10	0.11
Al_2O_3	13.14	10.56	11.82	12.68	12.31	12.07	11.69
Fe_2O_3	0.94	1.09	0.92	0.76	0.83	0.74	0.67
MnO	0.02	0.09	0.06	0.05	0.10	0.03	0.01
MgO	0.61	0.46	0.48	0.60	0.46	0.54	0.59
CaO	2.60	2.97	3.26	3.33	3.30	3.28	2.20
Na_2O	1.94	1.56	1.50	1.26	1.53	1.32	0.75
K_2O	2.92	2.63	3.09	3.17	3.46	3.15	4.49
P_2O_5	0.02	0.03	0.02	0.02	0.02	0.02	0.02
LOI	7.43	7.01	8.07	9.58	8.98	9.23	7.97
Total	99.97	99.42	100.48	101.60	100.50	100.26	100.56

SANTORINI	KS11	KS12	KS13	KS14	KS15	KS16	KS17
SiO_2	66.27	64.95	62.78	62.30	64.32	66.83	62.41
TiO_2	0.20	0.23	0.35	0.43	0.22	0.30	0.32
Al_2O_3	12.05	14.34	12.02	13.48	13.76	12.59	12.98
Fe_2O_3	1.39	1.57	2.37	3.16	1.56	2.44	2.56
MnO	0.05	0.08	0.05	0.19	0.05	0.03	0.04
MgO	1.24	1.64	1.46	1.11	0.97	1.27	1.65
CaO	2.26	2.51	2.78	3.05	1.82	2.79	2.93
Na_2O	3.25	2.85	3.51	4.38	3.94	2.48	3.02
K_2O	1.69	1.61	2.22	0.88	2.94	1.75	1.82
P_2O_5	0.25	0.27	0.06	0.09	0.06	0.10	0.04
LOI	11.18	9.48	10.86	10.08	10.57	10.02	11.95
Total	99.83	99.53	98.46	99.15	100.21	100.60	99.72

MINERALOGY AND GEOCHEMISTRY

The zeolitic tuffs consist of cryptocrystalline glass mass with phenocrysts. The examination of the glassy matrix with the aid of SEM showed that it had undergone extensive devitrification with authigenic minerals such as clays and zeolites as end products. The zeolitic minerals recognised were heulandite type of minerals along with mordenite. The phenocrysts were quartz, plagioclase, mica and rare K-feldspar. These observations were confirmed when the samples were examined by XRD and the results are shown in Table 1. The different types of the heulandite minerals were clarified by thermal tests proposed by Boles (1972) and Allieti (1972,1977). The different types identified were type 1, 2 and 3. Type 1 is the Ca member of the heulandite group and its crystal lattice can be destroyed at temperatures less than 550^{o}C. Type 3 (clinoptilolite) is the Na-rich, K member and its crystal lattice is stable at temperatures up to 760^{o}C. Finally type 2 are the heulandite type of minerals with an intermediate thermal behaviour.

The major element geochemistry of the samples is shown in Table 2. By having just major element analysis there is evidence about the origin of the volcanic tuffs. Hay and Sheppard(1977) showed that the replacement of rhyolitic glass by zeolites introduced a gain of H2O, Ca and Mg and the loss of Si, Na, K and Fe. Surdam (1977) showed that it is not always the rule because the genesis of zeolites and consequently the mineral chemistry depends on cations ratios, the Si/Al ratio and the presence of H2O along with the level of salinity and/or the alkalinity of the system. A first approximation can be that the original tuffs should be intermediate to acid in composition .

Tsolis-Katagas & Katagas (1989,1990) have worked on the mineralogy, geochemistry and the origin of the Santorini and Metaxades tuffs. They suggested that the Santorini tuffs had undergone hydrothermal alteration while those of Metaxades burial diagenesis. Skarpelis and Marantos (1987) and Skarpelis et al. (1993) have worked similarly with the Lefkimi-Dadia tuffs and suggested burial diagenetic procedures responsible for the zeolites origin.

FREE-LIME ESTIMATION AND CONCRETE TESTS

After the mineralogy and the geochemistry were examined the samples from each location were mixed together in absolutely random proportions to create three different samples from the three different locations and they marked as L for Lefkimi-Dadia area, M for Metaxades area and S for Santorini island. This was done in order to examine the deposits as one unit which could be the source for the pozzolanic material. The proportion of each initial sample taking part in the total weight of the bulk sample are shown in Table 3 and the final chemistry of these samples in Table 4.

The next step was to try to find out critical temperature and time duration for which the sample should be calcined so that the optimum pozzolanicity can incurred.

As was already known the ability of the tuffs to act as pozzolanic materials depends on the fixation of the calcium hydroxide released by the settling cement (Drury, 1954). For that reason the samples were heated in a range from 660^{o} C up to 1060^{o} C at 100^{o} C intervals and for 4 and 12 hours and then left to react for seven days with lime at a one lime to three parts of Pozzolana ratio and under water saturated conditions. At the end of this period the free lime content(calcium oxide and calcium hydroxide) was estimated according to the BS 4550 : Part 2 : 1970. The results are shown in Table 5 and Fig. 2. This test helped the decision to calcine the pozzolans from Metaxades and Santorini at 860^{o} C and these from Lefkimi-Dadia at 1060^{o} C all for 12 hours.

At the final stage of this work, standard Portland cement concrete cubes and concrete cubes which contained pozzolana in replacement of the ordinary

Table 3: Proportions of each initial sample participating in the L,M and S samples.

Sample	%	Sample	%	Sample	%
KL20	12.50	KS11	15.39	KM1	9.45
KL21	10.42	KS12	3.10	KM2	20.47
KL22	3.12	KS13	14.67	KM3	18.11
KL23	11.46	KS14	11.41	KM4	7.87
KL24	2.08	KS15	18.26	KM5	14.17
KL25	10.42	KS16	30.00	KM6	18.11
KL26	16.66	KS17	7.17	KM7	11.81
KL27	10.42				
KL28	10.42				
KL29	12.50				
TOTAL	100.00	TOTAL	100.00	TOTAL	99.99

Table 4: Chemical analysis of L, M, and S samples.

	S	M	L
SiO_2	63.43	68.29	69.48
TiO_2	0.30	0.11	0.16
Al_2O_3	11.09	11.23	11.57
Fe_2O_3	2.19	0.86	1.22
MnO	0.03	0.05	0.04
MgO	1.33	0.47	0.70
CaO	2.35	2.90	2.57
Na_2O	3.39	1.48	1.49
K_2O	1.81	2.92	3.09
P_2O_5	0.10	0.02	0.04
LOI	12.78	12.21	9.76
Total	98.80	100.54	100.13

Table 5: Free lime values in mixtures made with pozzolan from Lefkimi-Dadia (L), Metaxades, (M) and Santorini (S). (660:660°C, temperature, 4 or 12: duration of calcining in hours)

Sample	Free Lime%	Sample	Free Lime%	Sample	Free Lime%
S/000/0	10.72	M/000/0	12.61	L/000/0	10.03
S/660/4	9.63	M/660/4	11.25	L/660/4	9.92
S/760/4	8.42	M/760/4	7.28	L/760/4	9.91
S/860/4	7.22	M/860/4	7.02	L/860/4	9.06
S/960/4	7.68	M/960/4	7.40	L960/4	9.24
S/1060/4	7.88	M/1060/4	7.65	L1060/4	8.30
S/660/12	8.72	M/660/12	7.78	L/660/12	9.72
S/760/12	8.16	M/760/12	7.71	L760/12	8.12
S/860/12	6.21	M/860/12	5.43	L/860/12	6.62
S/960/12	8.41	M/960/12	6.38	L/960/12	7.16
S/1060/12	8.61	M1060/12	7.75	L/1060/12	6.24

Table 6:Compressive strength for cubes made with 100 % Portland Cement (P/100/*) and different substitutions of pozzolans. (L:Lefkim-Dadia, M:Metaxades,S:Santorini. 10,20,30 :% substition for pozzolana. 3,7,14,28:Days of testing after moulding)

Concrete cube	Compressive Strength(N/mm^2)
P/100/3	24.0
P/100/7	33.4
P/100/14	41.7
P/100/28	51.3
L/10/3	21.6
L/10/7	30.5
L/10/14	39.4
L/10/28	50.8
L/20/3	17.5
L/20/7	24.8
L/20/14	31.2
L/20/28	42.6
L/30/3	13.3
L/30/7	19.7
L/30/14	26.9
L/30/28	37.4
M/10/3	20.5
M/10/7	29.5
M/10/14	38.2
M/10/28	50.0
M/20/3	15.4
M/20/7	22.4
M/20/14	32.7
M/20/28	41.9
M/30/3	11.3
M/30/7	16.4
M/30/14	23.1
M/30/28	28.8
S/10/3	19.0
S/10/7	28.5
S/10/14	36.9
S/10/28	47.2
S/20/3	15.0
S/20/7	22.7
S/20/14	31.2
S/20/28	39.8
S/30/3	9.7
S/30/7	14.9
S/30/14	20.9
S/30/28	27.4

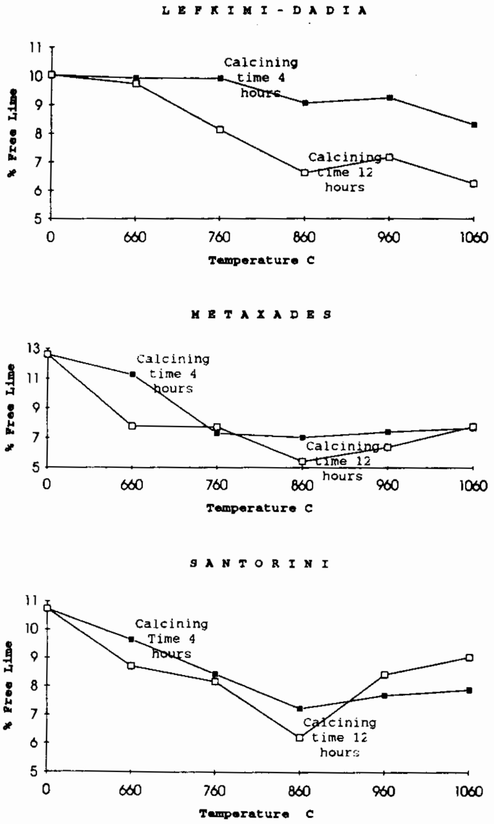

Fig. 2: % Free-lime for the different pozzolanas

Portland cement by 10%, 20% and 30% were made. The procedure followed for making all the cubes is in accordance with the British Standard 4550. All the materials used are those recommended by the BS 4550 and for testing the cubes the procedure described in the British Standard 1881: Part 116: 1983 were followed. All tests were done in the Concrete laboratory of the Engineering Department of Leicester University.

The failures of the concrete cubes can be characterised as satisfactory failures according to the descriptions given in BS : 1881 : Part 116 : Paragraph 7 : 1983. Explosive failures were recorded for the cubes: L/10/7, S/20/28, M/10/14, M/20/14, L/10/14, L/20/14, L/

Table 7: Percentages of the compressive strength of 100% Portland Cement cubes reached by using different additions of pozzolan from different places

	10% pozzolan	20% pozzolan	30% pozzolan
Lefkimi-Dadia			
3 days	90.00	72.92	55.42
7 days	91.32	74.25	58.98
14 days	94.48	74.82	64.51
28 days	99.02	83.04	72.90
Metaxades			
3 days	85.41	64.17	47.08
7 days	88.32	67.06	49.10
14 days	91.61	78.42	55.39
28 days	97.46	81.68	56.14
Santorini			
3 days	79.16	62.50	40.42
7 days	85.33	67.96	44.61
14 days	88.49	74.82	50.12
28 days	92.01	77.58	53.41

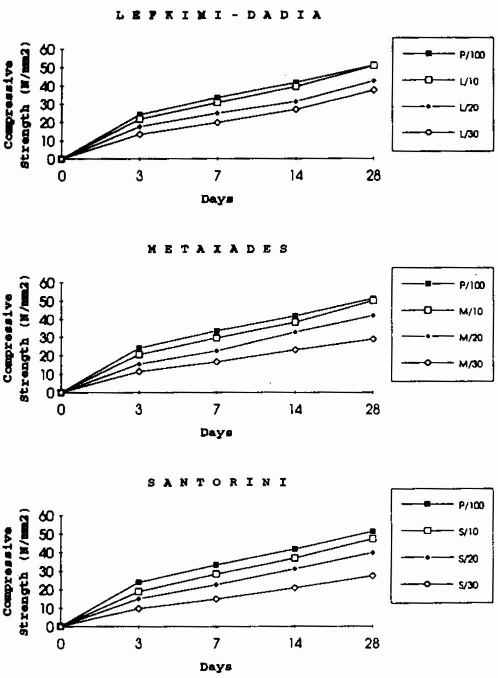

Fig. 3: Compressive strength curves for the different pozzolanas

20/28, L/30/7, L/30/14. There were not any unsatisfactory failures.

All the results are expressed as absolute values of compressive strength in N/mm^2 (Table 6) and as percentages of the value of the compressive strength which was reached in the same period of time by the 100% Portland cement concrete cubes (Table 7). The compressive curves are given in Fig. 3.

DISCUSSION-CONCLUSIONS

The estimation of the free-lime percentage in the lime-pozzolana mixtures proved the necessity of calcining the materials which are going to be used as pozzolans. The calcined material reduced the percentage of the free-lime to 60%, 43% and 57% of the free-lime recorded in the unheated samples, for Lefkimi-Dadia, Metaxades and Santorini respectively.

The temperature around which the optimum pozzolanicity can be achieved is the same for Metaxades and Santorini although the heulandite type of mineral present is different. For the Metaxades and the heulandite type of minerals, group 1 and 2 the recorded temperature is the one where the crystal structure of the specific type of heulandite is completely destroyed. In the other hand for the Santorini and the heulandite type of mineral, group 3, the same recorded temperature of 860^0 is just over the 760^0 where this type of mineral (clinoptilolite) is reported to be ultimately stable.

Over that temperature and for that period of time a crystal structure destruction is likely for this type too. So the pozzolanicity in both cases is incurred just after the crystal structure destruction.

For the Lefkimi-Dadia pozzolanic material there were two minima observed. The minimum at 860^0 should be related to the presence of the heulandite and the other at 1060^0 to the presence of unaltered glass which was found in this tuffs. In this case the glass probably needs higher calcining temperature to became active. The problem though with these temperatures is that they are getting close to melting points, and the handling of the calcined material could be very difficult in an industrial application.

The compressive strength tests were revealed very clearly that we can not replace cement for more than 10% of the mass required in the concrete mixture. In all the cases a replacement of about 10% worked satisfactory. The concrete cubes of the 10% replacement maintained over 90% of the strength of an ordinary Portland cement concrete cube and with the Lefkimi-Dadia material almost reached the same strength.(99.02% of the original). As it is known for the pozzolanic concrete that is hardening slowly it is likely that the strength over the 3, 6 and 12 months period should reached and overtake the strength of ordinary Portland cement concrete.

Any further investigations should deal with the mineralogy of the lime-pozzolana mixtures trying to find out the compounds being responsible for the additional strength and of course at the other hand the testing time for the concrete cubes should be extended.

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