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THE BEHAVIOUR OF AMORPHOUS SILICA-RICH ROCKS AS CEMENTITIOUS ADDITIVES IN SCREED MORTARS

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Abstract: The aim of the present study is to test Greek amorphous silica-rich rocks used as partial replacements of cement [25 and 50%] in cement mortars. The raw materials studied were diatomite rocks occurred in Zakynthos, Milos and Samos islands, and tuffite located in Milos Island. Cement substitutes participated in screed materials in percentages of 5% and 10% of the total dry mass. The raw materials were characterised chemically, mineralogically and technically. Microstructural analysis of raw materials and screed pastes was performed in order to specify reactions of silica phases in hydrated systems. The relationship between reactive silica of raw materials and compressive and flexural strength of the final products was also investigated. Properties of final products were examined and compared with commercial one. The water demand of pastes was increased by the addition of the siliceous raw materials, whereas their compressive and flexural strength was decreased. Conclusively, the siliceous rocks studied can be used as partial substitutes of cement in mortars only in ratios raw materials/cement lower than 1/2.

Keywords: Pozzolanic materials; Diatomite; Diatom frustules; Cement; Amorphous silica

1. Introduction

Screeding is a method of constructing a well profiled bedding layer onto which stones, bricks, ceramic tiles or any other paving can be directly laid onto with no further levelling. A screeded layer is approximately 5-10mm deep and usually applied in order to carry the final flooring or to obtain a defined level. Types of floor screeds are ready-mixed sand and cement, fibre and self-levelling screeds. Most common binder for screed mortars is cement.

In order to improve some basic screed properties as thermal and chemical resistance and to decrease density of the hardened mortar without negative results in strength values, chemical inert and lightweight aggregates are commonly used. In the present study diatomite rocks and tuffite rich in amorphous phases were used as substitutes of cement.

Diatomite is a sedimentary rock mainly composed of opal-A (biogenic amorphous silica) with the form of diatom frustules, sponge spicules, silicoflagellate skeletons and/or radiolarian cells. Besides opal-A, diatomite may also contain clay minerals, carbonates, quartz and/or feldspars.

The most common use of the high quality (opal-A-rich) diatomite is as filtrating material of liquids, due to its elevated porosity and good adsorption qualities (Dolley, 1991). Diatomite has also been used as a constituent for improvement in cement industry, because of its chemical stability and low weight. Being a heat resistant and chemically inert material, its use in fireproof cement is also known. Interest has also been given in using diatomite in Portland cement and mortars. Recent research has proved that using up to 20% of calcareous diatomite as an additive generally increases cement's strength (Yilmaz and Ediz, 2008; Degirmenci and Yilmaz, 2009), although significant drawbacks such as increased water demand should be expected (Stamatakis et al., 2003).

Volcanic tuffs and tuffites have been used since the antiquity as construction materials. Romans were of the first that produced mortars based on tuffs and their pozzolanic properties (Heiken, 2006). Modern researches have proved that the use of tuffs as cementitious material improves plasticity and durability against destructive factors without decreasing strength properties (Doodaran & Khiavi, 2009).

Both, diatomaceous and tuffaceous rocks occur in several places in Greece, sometimes in the same stratigraphic succession, having a genetic relationship. For the present study, diatomaceous raw materials originated from the islands of Zakynthos (Vougiato outcrop), Milos (Xylokeratia outcrop) and Samos (Chora outcrop), and tuffite from Milos Island (Xylokeratia outcrop) were examined. Several diatomaceous and tuffaceous rocks have been successfully tested as pozzolanic additives in cement, partially due to their reactive silica content (Fragoulis et al., 2002; Stamatakis et al., 2003).

The aim of the present study is to investigate the efficiency of the raw materials above, in application as partial substitutes of cement in screeds products. Screed mortars were prepared based on a commercial mixture provided from the company DUROSTICK S.A. Evaluation of laboratory screeds products with partial replacement of cement took place by comparing their basic properties with those of the relevant commercial product, hereinafter referred as the reference sample.

2. Materials and Methods

2.1. Raw materials

The raw materials used were Portland cement CEM I 52.5, obtained from TITAN Cement Company S.A and bulk diatomaceous and tuffaceous rocks.

All raw materials were crushed, homogenized and analyzed by X-ray fluorescence (PHILIPS PW1010 XRF spectrometer, TITAN S.A), X-ray diffraction (Siemens Model 5005 X-ray diffractometer, Cu-Ka rad., 40 kV, 40mA, NKUA) and evaluated by use of the EVA 10.0 program. Textural analysis of the raw materials and the final products was carried out by a Scanning Electron Microscopy (JEOL JSM-5600, NKUA). Granulometry of raw materials was kept under 106μm by grinding them in the standard period of 60sec. Granulometry was estimated by laser grain size analysis. The reactive silica content was determined after HCl and NaOH treatment, according to European regulation EN 197-2 (TITAN S.A.). The manufacturing and the measurement of the technical characteristics of the final products were carried out in DUROSTICK N. Choulis S.A. laboratories.

2.2. Methods

2.2.1. Preparation of screed mortars

The cement mortars–screeds were prepared according to European standard EN 13813. Reference sample was consisted of:

i) carbonate aggregates and mortar additives (75%) and
ii) cement (25%) per mass weight respectively.

Laboratory screeds were prepared by partial substitution of cement in percentage of 25 (trial A) and 50% (trial B) by weight. Water content remained stable at 20 % of total dry mass in all trials (Tab. 1).

Table 1: Composition % of laboratory and reference samples in total wet mass.

Samples	Composition	% w/w total wet mass
Trial A	Carbonate aggregates and mortar additives	62.5
	CEM I 52.5	15.63
	Amorphous silica-rich materials	5.21
	Water	16.66
Trial B	Carbonate aggregates and mortar additives	62.5
	CEM I 52.5	10.42
	Amorphous silica-rich materials	10.42
	Water	16.66
Reference	Carbonate aggregates and mortar additives	62.5
	CEM I 52.5	20.83
	Water	16.66

2.2.2. Testing methods

In order to examine properties of final products tests were performed for the evaluation of flowability and effectively water demand, compressive and flexural strength. The flowability was measured by a flow table test. For the compressive and flexural test, specimens were manufactured by blending all solid matters and water in the appropriate mixer, molding in steel moulds of 160 mm x 40 mm x 40 mm with vibration, curing in the moulds into a storage chamber at the temperature of 20 ± 2°C and humidity of 95 ± 5 % for two days and out of the mould in the same conditions for five more days and then storing in room conditions until testing. Strength tests were conformed to European standard EN 13892. Finally, mineralogical examination and microstructural analysis took place in different days of curing period.

3. Results and discussion

3.1. Raw materials characterization

Mineralogically, the material from Zakynthos is mainly composed of calcite, subordinate opal-A and traces of quartz and smectite, whereas Samos diatomite consists mainly of calcite with lower amounts of opal-A and feldspar, and trace amounts of quartz and aragonite (Tab. 2). Milos diatomite contains mainly opal-A and secondarily feldspar, and traces of detrital minerals. Milos volcanic tuff can be characterized as tuffite, due to its dolomite content. It consists mainly of volcanic glass and feldspar, with minor opal-CT, dolomite, quartz and smectite. Opal-A was detected in x-ray diffraction diagrams as a broad hump between 2θ 18° and 20°, whereas volcanic glass and the biogenic nature of the opal-A was confirmed by SEM analysis.

Table 2: Mineralogical evaluation of pozzolanic materials

Mineral	Zakynthos diatomite	Samos diatomite	Milos diatomite	Milos tuffite
Quartz	TR	TR		TR
Calcite	MJ	MJ		
Aragonite		TR		
Opal - A	MD	MD	MJ	
Dolomite				TR
Feldspar			MJ	MJ
Opal - CT				MD
Illite			TR	
Smectite	TR			MD
Volcanic glass				MJ

MJ = major component, MD = medium component, TR = minor or trace component.

Following the mineralogy, the chemistry of the diatomaceous rocks of Samos and Zakynthos is mainly influenced by CaO and SiO_2, whereas that of Samos diatomite and Milos tuffite by SiO_2 and Al_2O_3 (Tab. 3). All samples except the Samos diatomite satisfy requirements of European standard EN 197-1 (reactive silica > 25% by mass) and are characterized as natural pozzolanas.

Grain size distribution is presented in Diagram 1. Grindability of Milos tuffite and diatomite and Zakynthos diatomite is lower than that of Samos diatomite, the latter being closer to cement grain size distribution.

Microstructural analysis of raw materials showed that diatom frustules in Zakynthos diatomite, are large, broken and diagenetically altered (Stamatakis et al., 1989a) (Fig. 1). Their shape is mainly plate-like, with the characteristic sieve-like texture. Samos diatomite consists of reworked, mostly broken disk shaped and boat-like frustules (Fig. 2). Their degree of preservation is low due to the alkaline environment that they were exposed to, resulting to their partial dissolution (Stamatakis et al., 1989b). Milos island diatomite presents thread-like and disk shaped frustules (Fig. 3). In all three samples, rarely occurs other than diatom frustules amorphous silica phases. The ubiquitous presence of the microporous amorphous silica in the diatomaceous rocks studied is determinant for the properties of the final products. Milos tuffite is mainly consisted of volcanic glass. A typical structure of volcanic glass is shown in Figure 4.

Table 3: Chemical analysis of the raw materials studied and cement.

	Zakynthos Diatomite	Samos Diatomite	Milos Diatomite	Milos tuffite	Cement
SiO_2	34.7	22.9	62.63	54.96	20.47
Al_2O_3	1.98	2.24	11.83	12.06	4.7
Fe_2O_3	0.29	0.38	5.37	4.18	3.92
CaO	31.8	39.9	2.81	6.4	61.72
MgO	0.4	0.59	1.29	2.83	4.18
K_2O	0.05	0.14	0.79	1.57	0.59
Na_2O	0.07	0.12	2.39	2.19	0.18
SO_3	0	0.27	0.68	0.02	2.88
TiO_2	0.05	0.06	0.47	0.36	n.a.
P_2O_5	0.11	0.06	0.29	0.08	n.a.
Cl	0.01	0.05	0.49	0.1	n.a.
Free CaO	-	-	-	-	0.7
L.O.I.	31.44	10.32	10.12	15.16	2.08
Total	100.90	99.36	99.16	99.90	100.72
RS	28.28	19.17	45.53	42.59	-

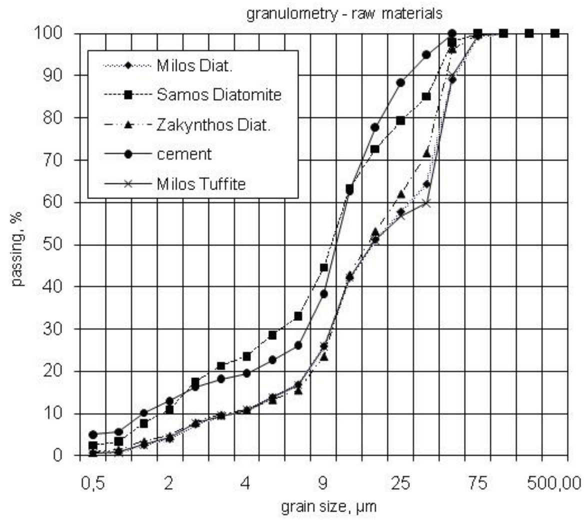

Diagram 1. Grain size distribution of raw materials.

3.2. Properties of products

3.2.1. Flowability

Rheological behavior of mixtures depends on water demand. Mortars of both trials in which cement was partially replaced by diatomite, needed more water in order to present the same rheological behavior. On the contrary, water demand of screed made with tuff ranges in the same level as reference sample. It is also observed that greater participation of diatomite is in screeds resulted to the increase of the water demand. Flowability of screeds is presented in Diagram 2.

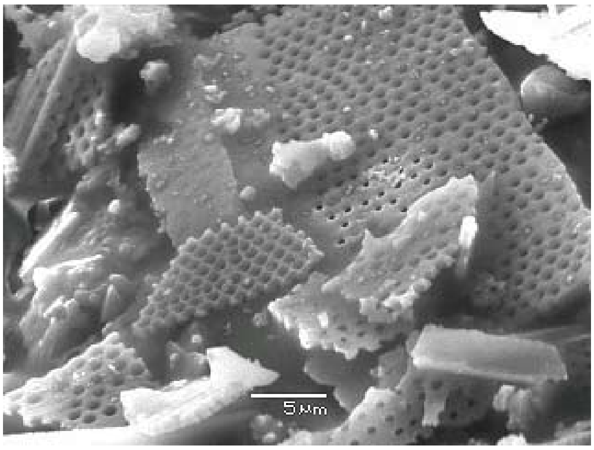

Fig. 1. Zakynthos diatomite composed of fragments of large diagenetically altered frustules.

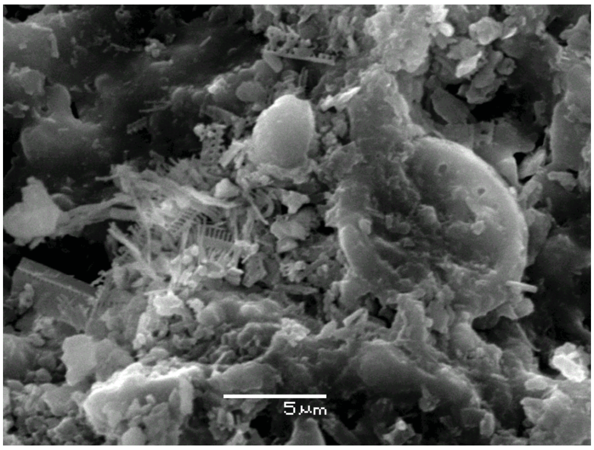

Fig. 2. Samos diatomite with intensely broken boat-like and partially preserved disk shaped frustules.

3.2.3. Compressive strength

Compressive strength values of screed products with partial replacement of cement are decreased in any case comparing with the reference sample. It is observed that partial replacement of cement at a ratio of 1/1 decreases strength values even more than 50%. This result is in good agreement with literature findings (Kastis et al., 2006; Degirmenci and Yilmaz, 2009).

3.2.4. Flexural strength

Flexural strength follows the trade of compressive strength, with value reduction as substitution of pozzolanic material increases.

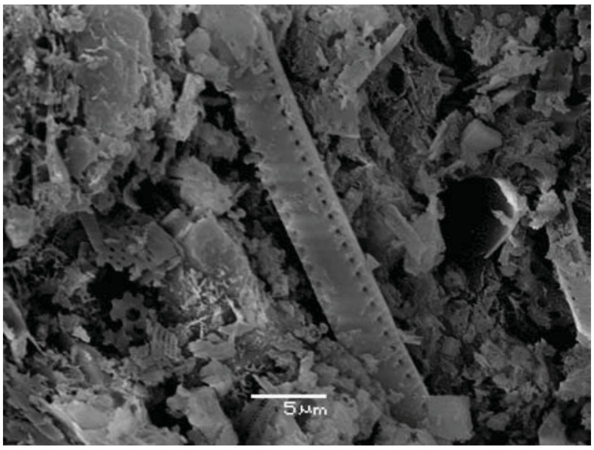

Fig. 3. Milos diatomite containing thread-like diatom frustules.

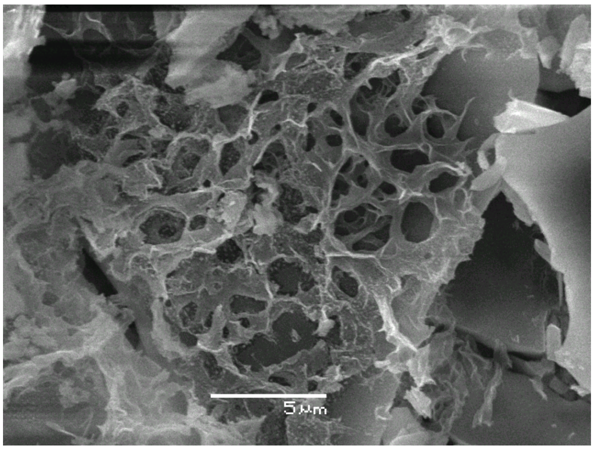

Fig. 4. Milos tuffite containing glass shards and pumice fragments with typical spongy texture.

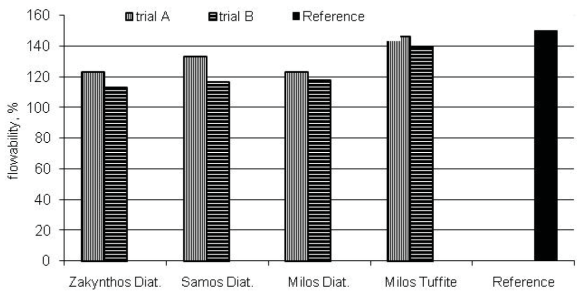

Diagram 2. Flowability of laboratory screeds (trial A and trial B) in regard to reference sample.

3.2.5. Relationship between reactive silica and strength values

It is noted that the screeds produced with Milos tuffite exhibit lower strength values than those produced by the diatomaceous samples in 14 and 28 days, despite the high content of reactive silica. It is probably due to the easier and faster dissolving of the opal-A than the volcanic glass and its reaction with the lime (Diag. 7 and Diag. 8).

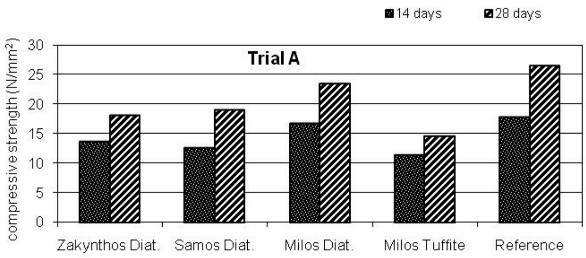

Diagram 3. Compressive strength of laboratory and reference screeds with partial replacement in cement/pozzolana ratio 3/1 (trial A)

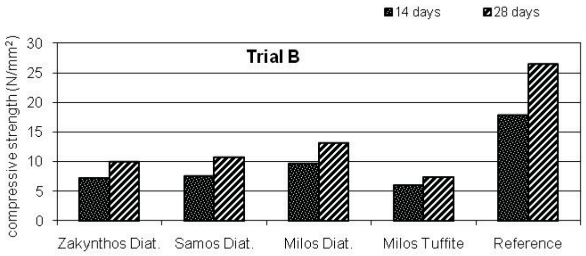

Diagram 4. Compressive strength of laboratory and reference screeds with partial replacement in cement/pozzolana ratio 1/1 (trial B)

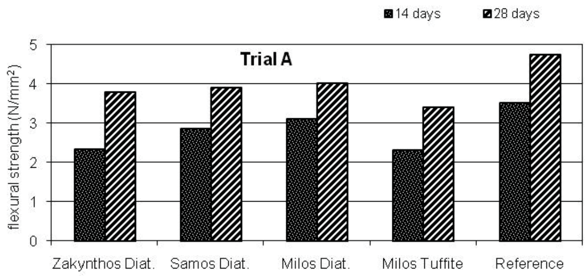

Diagram 5. Flexural strength of laboratory and reference screeds with partial replacement in cement/pozzolana ratio 3/1 (trial A)

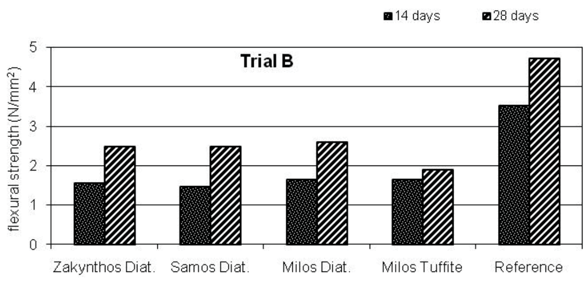

Diagram 6. Flexural strength of laboratory and reference screeds with partial replacement in cement/pozzolana ratio 1/1 (trial B)

3.2.6. Microstructural and mineralogical analysis

Micro-structure screed pastes were investigated through SEM analysis after 6 and 14 days of hydration. Figure 5 and Figure 6 present the early reaction of the diatom frustules surface for the formation of needle-like crystals of $Ca(OH)_2$ and ettringite $Ca_6Al_2(SO4)_3(OH)_{12}$•$26(H_2O)$ hexagonal crystals. At the 14th day of hydration of the pastes dominates the formation of calcium silicate hydrate (CSH) (Fig. 7 and Fig. 8). Shapes of diatoms are poorly preserved and hardly distinguished.

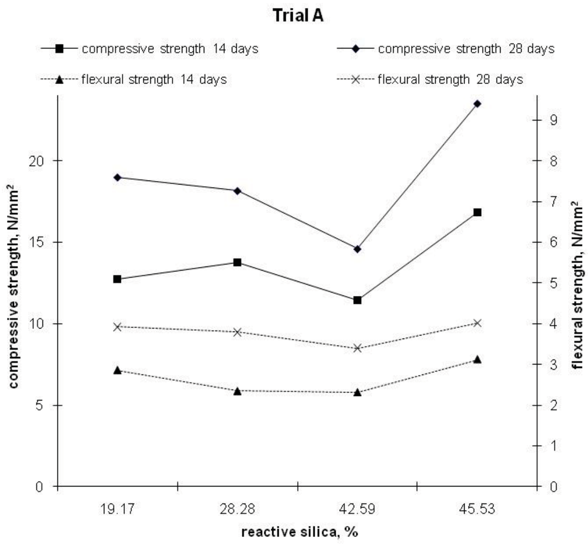

Diagram 7. Relationship between strength values and reactive silica content (trial A)

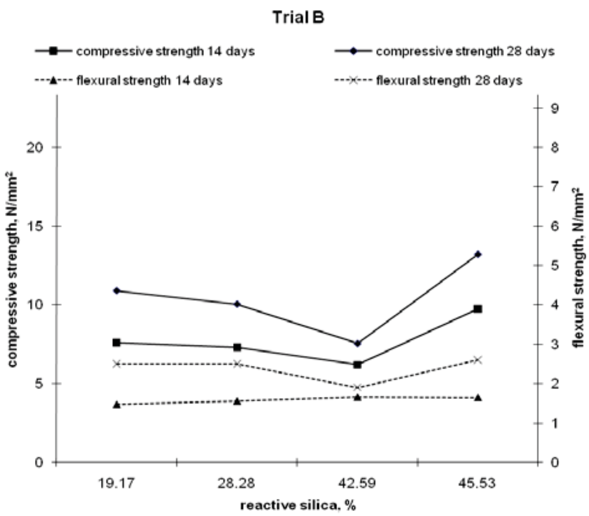

Diagram 8. Relationship between strength values and reactive silica content (trial B)

Differences on the amount of portlandite ($Ca(OH)_2$) after the 28th day of hydration process were observed. In mortar made of Milos tuffite and cement the participation of portlandite is clearly higher than in mortar made of Milos diatomite and cement. In X-ray diagram (Fig. 9) it is obviously illustrated that peak of portlandite is much lower in mortar of Milos diatomite than in mortar of Milos tuffite.

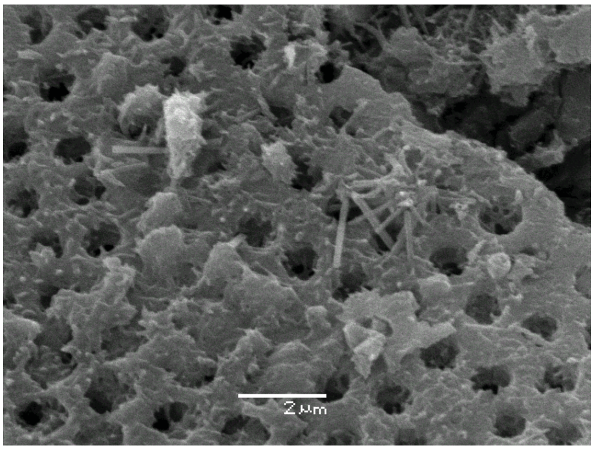

Fig. 5. Reaction of diatoms and formation of $Ca(OH)_2$ at the 6th day of hydration.

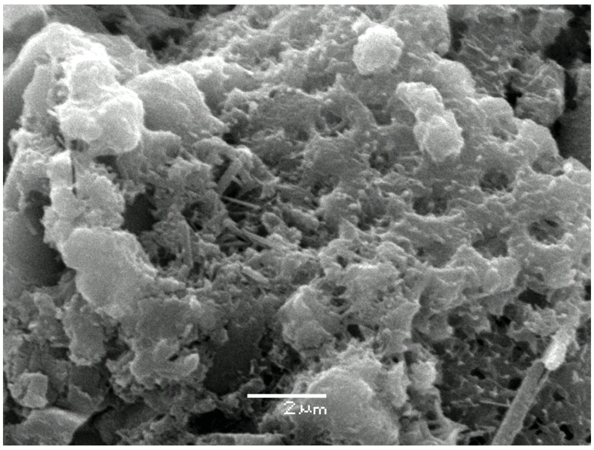

Fig. 6. Growing of ettringite on the surface of the diatom frustules at the 6th day of hydration.

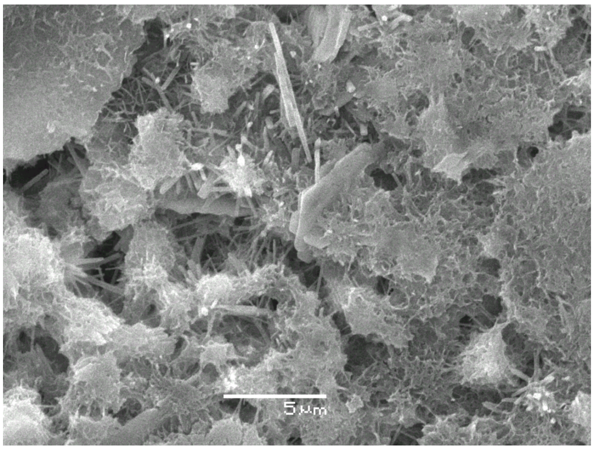

Fig. 7. Destruction of diatoms and formation of CSH, 14th day of hydration.

4. Conclusions

The following conclusions may be drawn from the conducted research:

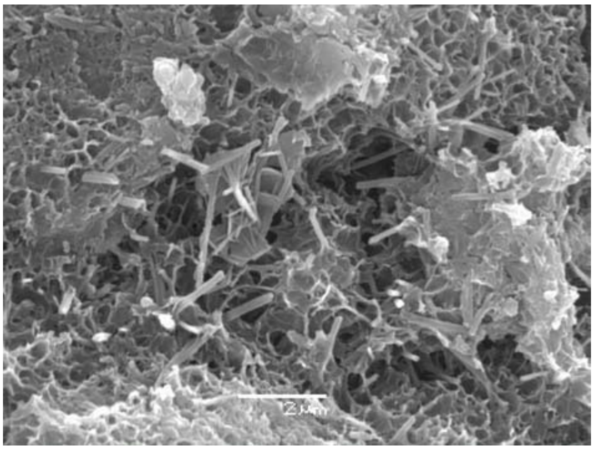

Fig. 8. Neoformed rod-like minerals (CSH) developed on poorly preserved diatom relics after hydration of 14 days.

- Water demand of pastes was increased by the addition of pozzolanic substitutes, whereas both compressive and flexural strength were decreased.
- Between the four cement substitutes, Zakynthos, Milos and Samos diatomite and Milos tuffite, screeds prepared with 25% replacement of cement with diatomite from Milos presented better results regarding strength properties, while those prepared with 50% substitution presented lower flow properties.
- No linear relationship between strength properties and reactive silica content was observed. Although, it is observed that the opal – A of diatomites is faster reactive than the volcanic glass and the opal –CT of the tuffite.
- In the previous also attributes the fact that the amount of portlandite in mortar made of tuffite after the 28th day of hydration was higher than this of Milos diatomite mortar. It seems that Portlandite reacts slower with volcanic glass and opal-CT in order to develop calcium-silicate phases, leading to lower strength values.
- Additionally, it seemed that grain size distribution is one of parameters that influence strength properties, as screeds prepared with diatomite from Zakynthos presented lower values than those with diatomite from Samos, despite the greater content of reactive silica.
- As a general conclusion, raw materials that contain significant amounts of either biogenic amorphous silica or volcanic glass can be used as partial substitutes of cement in mortars only in ratios raw materials/cement lower than 1/2. It is al-

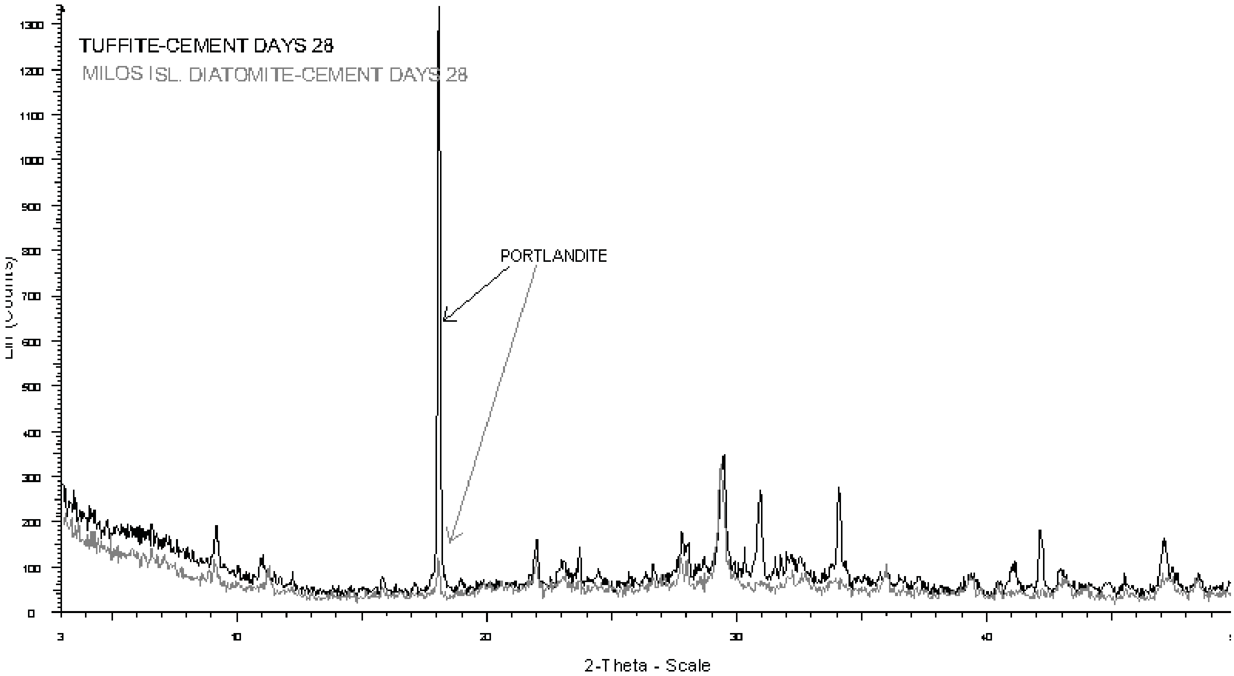

Fig. 9. X-ray diffraction diagram after 28 days hydration of Milos tuffite-cement (black) and Milos diatomite-cement (gray).

so expected that partial substitution of other types of cement with lower strength properties as the types CEM I 35.2 and CEM I 42.5 would favor the use of the raw materials studied.

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