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The physical and mechanical properties of composite cements manufactured with calcareous and clayey Greek diatomite mixtures

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Abstract

The aim of the present study is to test diatomite rocks as alternative pozzolanic materials that could be used for the manufacturing of pozzolanic cements in Greece. The diatomite rocks used occur in Samos Island and in the Elassona, Greece. The Samos diatomites were mainly consisted of calcite and opal-A, whereas the Elassona diatomite consisted of opal-A, clay minerals, feldspars and quartz. As a result, the Samos samples were rich in CaO and SiO_2, while the Elassona ones were rich in SiO_2, Al_2O_3 and Fe_2O_3. The specific surface of the laboratory-produced cements was high, with the grindability of the Elassona diatomites being lower than that of Samos. The water demand of all blended cements was higher than that of the laboratory produced OPC. The late compressive strength of most diatomite cements studied was improved with respect to the lab OPC.

Keywords: Diatomite; Diatom frustules; Pozzolana; Cement; Amorphous silica

1. Introduction

Amorphous silica is found in nature in the form of siliceous microfossils such as diatoms, radiolarians, silicoflagellates and sponge spicules constituting the diatomaceous earth. Volcanic glass is another source of natural, amorphous silica-rich material. This type of SiO_2 occurring either in the diatomaceous earth or in the volcanic glass reacts with $Ca(OH)_2$ and produces CSH that is mainly responsible for the development of strength. In order for a material to be used as a pozzolana for cement production, specific requirements—regarding the material itself—have to be fulfilled [1,2]. Furthermore, numerous tests on the cement/pozzolana mixtures (blended cements) are necessary in order to evaluate their performance [3–5]. Presently, the Milos glassy tuff is used as the primary pozzolanic material for the manufacturing of blended cements in Greece. The aim of the present study is to test new, alternative pozzolanic materials such as the amorphous, biogenic silica-rich rocks from Samos Island, Aegean Sea and Elassona, Central Greece for the production of laboratory cements (LPC). These cements were evaluated by determination of their specific surface (Blaine), water demand, initial and final setting time and compressive strength.

2. Geology and mineralogy of the diatomaceous rocks of Samos and Elassona

The diatomaceous rocks of Samos occurring in the Upper Miocene lacustrine basin of Mytilinii, in the eastern part of the island are characterized as calcareous diatomite and diatomaceous limestone due to their high $CaCO_3$ content. The biogenic silica had been deposited in a closed lake with saline–alkaline character that led to the partial dissolution of the siliceous tests at the lower stratigraphic levels [6,7]. The diatomite layers overlie a porcelaneous limestone and are partially covered by a greenish pumice tuff.

The diatomaceous rocks of Elassona are characterized as clayey diatomites, due to their high clay content [8]. They compose most of the Upper Miocene sedimentary rocks of the Sarantaporo–Elassona basin, which is part of the NW–SE oriented chain of lacustrine

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basins extending from the southern Yugoslavia to the Central Greece.

3. Rock sampling and experimental procedures

Four bulk diatomaceous rock samples of 70 kg each were collected from Samos (2) and Elassona (2). The Samos samples were collected from two sites of Mytilinii basin, one located near Mavratzei village and the other located in Kazania, an area between Mytilinii and Mavratzei villages. The Elassona samples were collected from two sites of the Sarantaporo–Elassona basin, one near Giannota village located at the eastern part of the basin and the other from a location close to the Lykoudi village at the SE part of the basin. The thickness of the visible outcrop from Giannota was about 5 m, while that of Lykoudi was 30 m, approximately.

The characterization of the diatomite rocks included chemical, mineralogical and textural analyses. The rock samples were crushed, homogenized and mineralogically analysed with the Siemens D5000 diffractometer (Table 1). Their chemical analysis was performed on ground bulk samples with the PHILIPS PW1010 XRF spectrometer (Table 2). SEM analysis was performed on diatomite rock chips with the Philips XL30 E-SEM (Figs. 1–4). The reactive silica (RS) was measured according to the established procedure of chemical treatment of the samples with concentrated HCl (36–37% w/w) and KOH (European Norm EN 196-2). The aforementioned pozzolanic raw materials, clinker and gypsum were used for the production of blended cements by co-grinding. The resulting cements were subjected to specific surface area, setting time (initial and final) and compressive strength measurements, according to Greek Regulations EN196-1, 3 & 6.

Water demand refers to the amount of water that has to be added in the cement to produce a paste of a specific consistency (penetration depth of 35 mm). Curing of the mortars bars took place in a moisture chamber at room

Table 1
Semi-quantitative XRD mineralogical analysis of Samos and Elassona diatomite rocks

Mineral	Samos		Elassona	
	Kazania	Mavratzei	Lykoudi	Giannota
Quartz	TR	MD	MD	TR
Calcite	MD	MJ		
Illite			TR	TR
Feldspars			TR	TR
Aragonite	TR			
Clinochlore			MD	MD
Smectite		TR	MD	MD
Vermiculite			MD	MJ
Opal-A (diatoms)	MJ	TR	MD	MJ

Explanatory notes: MJ = major component, MD = medium component, TR = minor/trace component. Blank cells means not detected mineral phases.

Table 2
XRF chemical analyses of diatomite rocks from Samos and Elassona

Oxides	Elassona		Samos	
	Giannota (% w/w)	Lykoudi	Mavratzei	Kazania
SiO_2	59.52	64.44	20.70	49.17
Al_2O_3	17.83	16.68	2.42	0.66
Fe_2O_3	8.08	5.90	1.03	1.62
CaO	1.82	1.35	38.08	24.15
MgO	1.79	1.81	0.40	0.90
K_2O	2.58	1.92	0.40	0.46
Na_2O	1.28	0.48	0.30	0.32
LOI	7.27	7.30	36.58	22.90
TOTAL	100.17	99.88	99.91	100.18
Reactive SiO_2	36.7	31.7	8.24	36.22

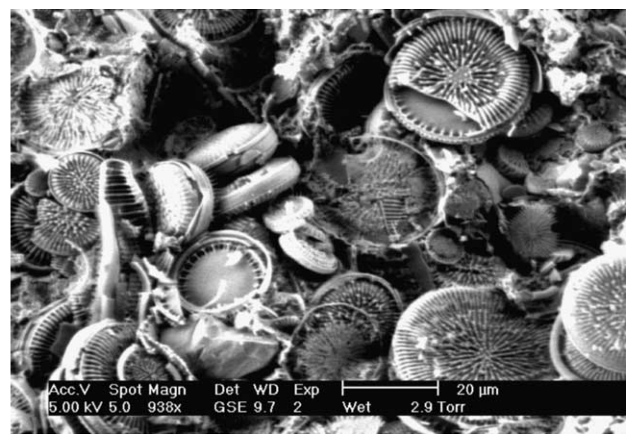

Fig. 1. Disk-shaped diatom frustules from Giannota area, Elassona basin retaining their minute structure.

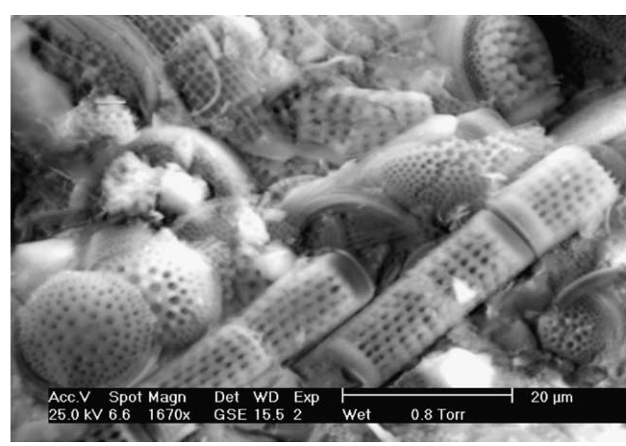

Fig. 2. Colonies of well preserved cylindrical diatoms hosted in a clay matrix along with disk-shaped diatoms from Lykoudi area, Elassona basin.

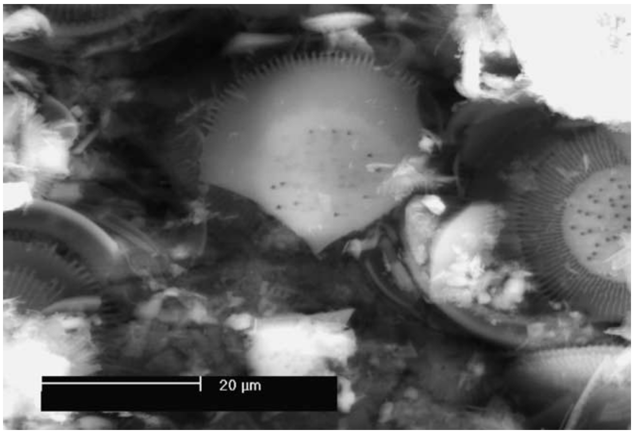

Fig. 3. Broken and dissolved disk-shaped diatom frustules from Kazania/Samos.

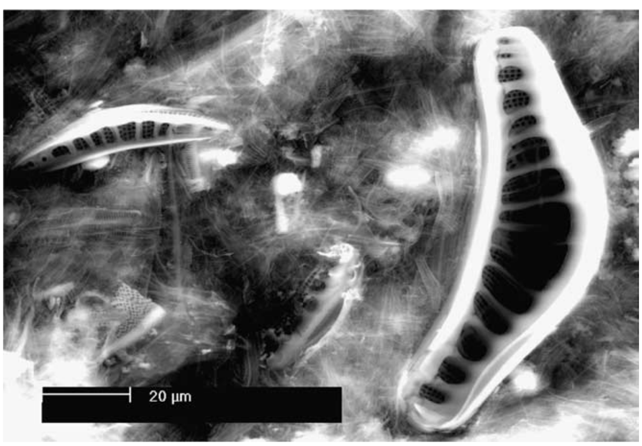

Fig. 4. Bow-like thick diatom frustules retaining their morphology due to their thickness from Mavratzei/Samos.

temperature. The size of specimens used for compressive strength measurements was 4×4×16 cm. The test results are summarised in Table 3.

4. Results and discussion

4.1. Mineralogical and chemical analyses of raw materials

All four samples contained, besides the crystalline constituents, an amorphous silica phase (opal-A) as shown by the presence of a broad peak (hump) between 20° and 26° 2θ in the X-ray diffractogram.

The XRD analysis of the Lykoudi and Giannota Elassona samples revealed that they were rich in clay minerals, opal-A, and detrital minerals such as feldspar and quartz (Table 1). Calcite or other carbonates were not identified. Because of their high clay content, both samples are characterized as clayey diatomite.

By contrast, the main constituent of the Samos samples was calcite followed by variable amounts of silica polymorphs (quartz and opal-A). Aragonite was also present in the Kazania sample. According to their mineralogy, the Mavratzei sample could be categorized as diatomaceous limestone and the Kazania sample as calcareous diatomite (Table 1).

Based on the XRF analysis, the SiO_2 content of the four samples varied considerably ranging from 15% to 65%, approximately.

Samos samples were very rich in CaO. On the other hand, their Al, Mg, Fe, K and Na content was very low (Table 2). On the contrary, the Elassona samples were rich in Al_2O_3 and Fe_2O_3, whereas their CaO content was very low. Their Fe_2O_3 concentration is mainly related to the Fe-rich chlorite clinochlore (Table 1).

4.2. Optical microscopy

The samples were examined under the transmitted light of the optical microscope. Kazania and Lykoudi samples had a high content of siliceous microfossils, mainly diatom frustules. Diatoms are single-celled algae belonging to the Class Bacillariophycae and in the deposits studied ranged from 2 to 30 μm in size. Even though there were well preserved diatom frustules in the samples studied, some of them were broken due to diagenetic alteration. Sponge spicules were rarely observed (Giannota sample).

4.3. SEM studies

The study of the diatomaceous material with SEM showed that the Elassona diatom frustules were well preserved and had a disk or cylindrical shape (Figs. 1 and 2). The degree of preservation of the frustules in the rock was high; the frustules occurred as assemblages hosted in a clayey groundmass. The cylindrical diatoms were 5×15 μm in size whereas the disk-shaped diatoms had a diameter of less than 30 μm.

By contrast, the degree of preservation of the Samos diatom frustules was low, due to the alkaline environment they were exposed to, leading to their partial dissolution [6]. The morphology of the diatom frustules was predominated by the disk and bow-shaped forms (Figs. 3 and 4). In general, the Samos diatom frustules were larger than those of Elassona.

4.4. Blended cements

The composition, the specific surface (Blaine), the water demand, the setting time and the compressive strength of the studied cements are presented in Table 3.

The results from the tests on the blended diatomite cements indicated that:

Table 3
Physical properties of tested cements

Diatomite origin	Diatomite content (%)	Blaine (cm^2/gr)	Water demand (%)	Setting Time (min)		Compressive Strength (MPa)				% Strength change regarding to the lab OPC		
				Initial	Final	1 day	2 days	7 days	28 days	2 day	7 days	28 days
Lab. OPC	0	3320	24.6	110	140	15.4	25.9	40.0	52.5	0	0	0
SAMOS	10	4100	25.8	135	175	17.0	27.5	40.5	52.0	6.2	1.5	−1
(Mavratzei)	15	4500	26.2	135	175	16.2	26.5	39.9	50.2	2.3	0	−4.4
	20	4900	26.6	140	180	15.7	25.0	36.5	47.6	−3.5	−8.5	−9.3
Lab. OPC	0	3320	24.6	110	140	15.4	25.9	40	52.5	0	0	0
SAMOS	10	5550	26.4	110	150	17.6	28	41.3	56.1	8.1	3.5	6.9
(Kazania)	15	6440	27.4	120	160	17.4	27.5	40.5	57.7	6.2	1.5	9.9
	20	7430	29	140	180	15.9	25	37.5	57.6	−3.5	−6	9.7
Lab. OPC	0	3150	25	100	150	13.0	22.5	36.0	50.0	0	0	0
ELASSONA	10	4880	29	110	140	18.2	27.3	42.2	55.8	21.3	17.2	11.6
(Giannota)	15	5560	30.8	120	160	15.9	24.3	36.4	64.1	8	6.7	8.2
	20	6380	33.4	145	185	14.6	21.6	34.6	50.6	−4	−3.9	1.2
Lab. OPC	0	3150	25	100	150	13.0	22.5	36.0	50.0	0	0	0
ELASSONA	10	4720	28	120	165	17.5	25.5	40.0	52.9	13.3	11.1	5.8
(Lykoudi)	15	6140	30	145	185	14.3	22.1	36.3	50.8	−1.8	0.8	1.6
	20	5730	32	160	210	13.2	20.4	33.8	48.0	−9.3	−6.1	−4
Lab. OPC	0	3000	25.4	135	165	14.0	23.5	39.1	55.0	0	0	0
MILOS	10	3270	26.6	140	175	14.0	20.7	35.4	51.6	−11.9	−9.5	−6.2
(Xylokeratia)	15	3350	27.0	140	180	12.8	19.2	32.4	45.2	−18.3	−17.1	−17.8
	20	3500	27.6	150	190	12.3	17.7	30.0	43.6	−24.7	−23.3	−20.7

The calcareous diatomite of Kazania, Samos was easier to grind than the diatomaceous limestone of Mavratzei and the clay diatomites of Elassona, due to the abundance of brittle diatom frustules in the Kazania sample. On the other hand, the morphology and size of calcite grains in the Mavratzei sample and the microstructure of the platy clay particles of the Elassona samples hindered their grindability (Table 3). The addition of the diatomaceous rocks in cement resulted in the drastic increase of its specific surface because of their high grindability (Table 3). Their unusually high specific surface was mainly due to the nature of the rock that was composed of very fine-grained particles such as diatom frustules, clay particles and calcareous grains. The specific surface of these cements was considerably higher than that of the currently produced cements with the Milos Island pozzolanic tuff (Table 3 and [9]). The water demand of the clayey diatomites of Elassona was higher than the calcareous diatomites of Samos (Table 3). The most calcite-rich sample of Mavratzei exhibited the lowest water demand. However, the water demand of the diatomite cements was much greater than that produced with the Milos Island pozzolana (Table 3). This could present a problem to the concrete manufacturer since a greater amount of water has to be added in the mixture to produce cement pastes of satisfactory rheology. Alternatively, to solve this problem, plasticizers or superplasticizers could be used. The delay that was observed in the initial and final setting time of the LPC's was expected due to their pozzolanic nature.

The effect of the pozzolana addition on the cement strength is shown in Figs. 5 and 6. Among the cements

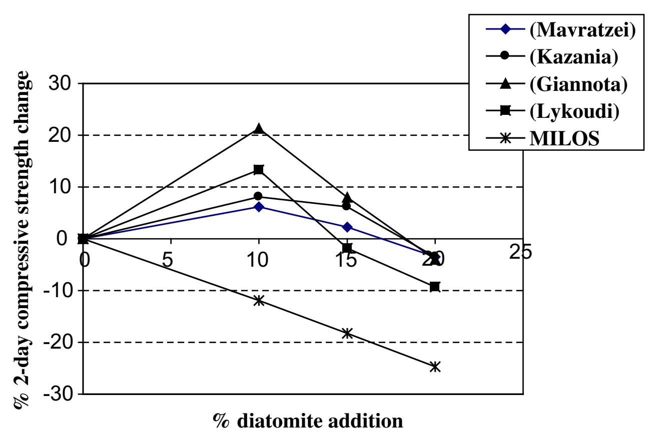

Fig. 5. Effect of diatomite addition on the 2-day strength. Mavratzei and Kazania samples are from Samos Island. Giannota and Lykoudi samples are from Elassona. The glassy pozzolanic tuff exploited in Xylokeratia SW Milos Island, is presented as MILOS.

produced with CaO-rich diatomites, the ones containing the Samos/Kazania diatomite exhibited the highest late strength. This could be attributed to its very high Blaine and also to their sufficient amorphous silica content (expressed as reactive silica also). Similar behaviour with regard to strength was observed in calcareous diatomites that had similar SiO_2 content, derived from Zakynthos Island, Greece [3,5].

The Elassona clayey diatomite exhibited good compressive strength due to its high reactive silica content expressed as opal-A, and also to its fineness. The reactive silica to total silica ratio of the two Elassona samples was different indicating the presence of excessive

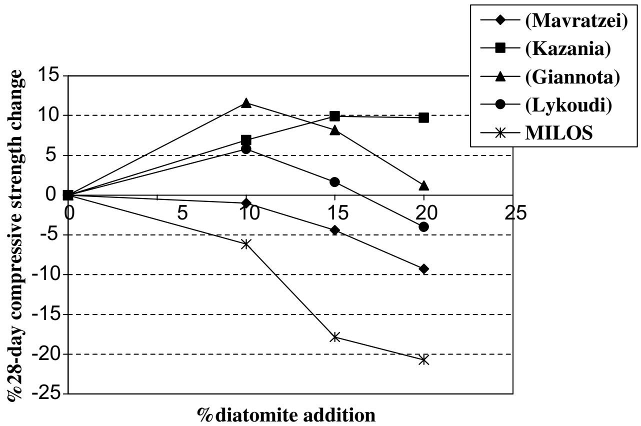

Fig. 6. Effect of diatomite addition on the 28-day strength. Samples details as in Fig. 5.

amounts of non-reactive silica in the form of quartz, clays and feldspars in the Lykoudi rock. The Giannota rock had a high opal-A content (diatom frustules) and hence higher reactive silica content (Tables 1 and 2).

The late strength of the LPC's containing diatomites was higher than that of the cements produced with the Milos Island pozzolana (Table 3). This was probably due to their considerably greater specific surface and possible higher reactivity—and therefore pozzolanic activity—exhibited by the siliceous microfossils compared to that of the glassy phase of the tuff.

The preliminary study of the diatomaceous rocks under investigation indicated that the Kazania (Samos) and Elassona diatomites could be utilised for cement production. However, further investigation is needed in order to study the behaviour and properties of the concrete manufactured with these cements. The main drawback of the diatomite addition to cement is the drastic increase in the water demand of the produced cements. Therefore, the addition of a superplasticizer to concrete is necessary if these diatomites are to be used for cement production. The performance of the diatomaceous cements in concrete should include certain trials and tests such as porosity, chloride permeability, freezing and thawing and seawater resistance.

5. Conclusions

The diatomite rocks studied were light in weight and soft materials, rich in amorphous silica, which is mainly present in the form of diatom frustules. The amount and type of these microfossils play an important role in the strength development of the blended cements since they are a source of reactive silica.

The addition of diatomite in cement results into a drastic increase of the specific surface (Blaine). The diatomite cements produced have a higher water demand than the lab OPC and Milos blended cements due to their higher specific surface. The initial and final setting time increase with respect to the lab OPC and Milos pozzolana cement. For those cements with a Blaine exceeding 5000 cm^2/gr, the compressive strength is higher than the lab OPC and considerably higher than the Milos tuff pozzolanic cement.

It is likely that the combination of reactive silica and high Blaine results in cements with improved mechanical properties.

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