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Properties and hydration of blended cements with calcareous diatomite

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Abstract

In this paper the effect of diatomite addition on blended cement properties and hydration was studied. Calcareous diatomaceous rocks of Zakynthos Island, Ionian Sea, containing mainly $CaCO_3$ and amorphous silica of biogenic origin with the form of opal-A were used. Cement mortars and pastes, with 0%, 10%, 20% and 35% replacement of cement with the specific diatomite, were examined. Strength development, water demand and setting time were determined in all samples. In addition, XRD, SEM and weight loss at 350 °C were applied in order to study the hydration products and the hydration rate in the cement–diatomite pastes. Blended cements, having up to 10% diatomite content, develop the same compressive strength, as the corresponding Portland cement, while the presence of diatomite leads to an increase of the paste water demand. Diatomite is characterized as natural pozzolana, as it satisfies the requirements of EN 197 1 concerning the active silica content. The pozzolanic nature of the diatomite results to the formation of higher amounts of hydrated products, specifically at the age of 28 days.

Keywords: Diatomite; Blended cements (D); Mechanical properties (C); Physical properties (C); Hydration (A)

1. Introduction

The use of pozzolanic materials in the manufacture of concrete has a long, successful history, as their use predates the invention of Portland cement by, at least, 20 centuries. However, during the last decades there has been an increasing interest from most cement industries worldwide to incorporate pozzolanic materials to their products. A pozzolana is defined as a material, which is capable of reacting with lime in the presence of water at ordinary temperatures to form compounds with cementitious properties ("cementitious compounds"). The pozzolanic materials used in the cement industry nowadays include natural products, such as volcanic products with high amounts of volcanic glass (tuffs, ash, pumice), zeolites, diatomites, metakaolin, calcined shales, calcined clays (the latter three require heat treatment prior use) or by-products, such as fly ash, silica fume and slag. Among all of them, several qualities of diatomaceous rocks are also used [1–5].

Diatomaceous rocks are sedimentary rocks of biogenic origin with high natural amorphous silica content. The amorphous silica (opal-A) is mainly in the form of diatom frustules, and secondarily in the form of sponge spicules, silicone–flagellate skeletons and/or radiolarian cells. This type of SiO_2 can react with $Ca(OH)_2$ and produce calcium silicate hydrates (CSH), which are responsible for the development of strength. Beside opal-A, the diatomite rocks commonly contain carbonate and clay minerals, quartz and feldspars. Pure diatomite ($SiO_2 > 95\%$) is widely used as filtering agents and supplementary cementing materials, whereas calcareous or clayey diatomites are commonly used as abrasives, special fillers, absorbents and insulation products [6–9].

The aim of this study was to test and evaluate the diatomaceous deposits of Zakynthos Island, Ionian Sea, as an additive (main constituent) in blended cements. More specifically, the effect of diatomite on blended cement's properties and hydration was studied.

2. Geological setting and mineralogy of Zakynthos' diatomaceous rocks

It is well known that several diatomite deposits of diverse age, depositional environment and purity are present in Greece [10–12].

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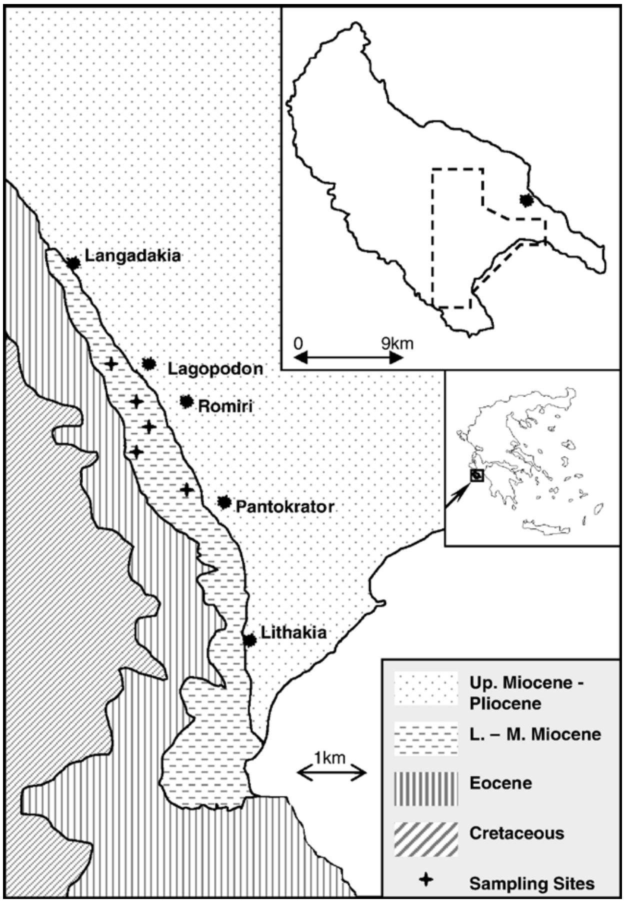

Fig. 1. Simplified geological map of the southern part of Zakynthos Island showing sampling locations [11].

One of them is located in the central part of Zakynthos Island, Ionian Sea, where white-colored calcareous diatomaceous rocks of Lower–Middle Miocene age are present (Fig. 1). The thickness of the sequence, occurring in a continuous NNW–SSE belt from Langadakia to Lithakia villages, is approximately 50 m having been formed in a deep-sea environment [12,13]. Because of its high $CaCO_3$ content, the material could be characterized as calcareous diatomite or diatomaceous limestone instead of diatomite. Most of the opal-A particles are represented by disk-shaped diatom frustules, while the calcareous material is also of biogenic origin, consisting of the tests of microfossils such as foraminifera [13]. In general, Zakynthos diatomites are quite homogenous, mainly consisted of calcite and biogenic silica (opal-A), while quartz is present in trace amounts.

Table 1
XRF chemical analyses of diatomite (%)

SiO_2	37.58
Al_2O_3	–
Fe_2O_3	1.10
CaO	32.99
MgO	0.74
K_2O	0.03
Na_2O	–
SO_3	–
LOI	26.74
Total	99.18
Reactive silica	31.68
Ratio of reactive silica to total silica	0.84

Table 2
Diatomite fineness characteristics

Fineness characteristics			Rosin–Rammler parameters	
d_{20} (μm)	d_{50} (μm)	d_{80} (μm)	*n*	pp (μm)
15.0	6.3	2.0	0.97	9.2

3. Experimental

3.1. Materials

The diatomite samples were crushed, homogenized and mineralogically analysed with the Siemens D5000 diffractometer. XRD patterns showed that calcite is the main crystalline mineral of the diatomite rock. In addition, an amorphous silica phase (opal-A) is present, as it is shown by broad peak (hump) between 20° and 26° 2θ. Quartz is also identified in very low concentration. Chemical analysis of diatomite was performed on ground bulk samples with the PHILIPS PW1010 XRF spectrometer (Table 1). The reactive silica was measured according to the established procedure of chemical treatment of the samples with concentrated HCl (36–37% w/w) and KOH (EN 196-2).

The fineness characteristics of the diatomite are given in Table 2. Diatomite is a very fine material with a mean particle size of 6.3 μm.

Table 3
Chemical analysis of PC and characteristics of clinker

Cement	
Chemical analysis	(%)
SiO_2	21.54
Al_2O_3	4.83
Fe_2O_3	3.89
CaO	65.67
MgO	1.71
K_2O	0.60
Na_2O	0.07
SO_3	2.74
Cl^-	0.00
Clinker	
Mineralogical composition	(%)
C_3S	57.8
C_2S	18.1
C_3A	6.2
C_4AF	11.8
Moduli	
Lime saturation factor (LSF)	0.949
Silica ratio (SR)	2.47
Alumina ratio (AR)	1.24
Hydraulic modulus (HM)	2.17

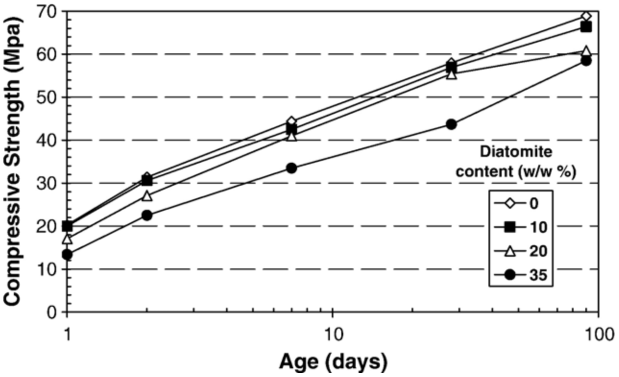

Fig. 2. Compressive strength development of diatomite cements in relation to the diatomite content.

Portland cement (PC) of industrial origin (CEM I 52.5) was used for the production of the mixtures. The chemical analysis of PC and the clinker characteristics are given in Table 3.

3.2. Cement properties and hydration

Blended cements were produced by replacing PC with 10% w/w, 20% w/w and 35% w/w of diatomite. The compressive strength of mortar samples, cured for up to 90 days (EN 196-1) as well as the water demand and the setting time (EN 196-3) was determined. In addition, normal mortar flow was measured according to ASTM C1437.

The hydration process of the cements containing diatomite was studied according to the following procedure. The cements were mixed with deionized water at a water-to-cement ratio (W/C) of 0.4 to produce pastes. The pastes were cast in cubic moulds ($20\times20\times20\ \mathrm{mm}^3$). The specimens were left in the moulds for 6 h, and then were put with water in polyethylene containers, sealed hermetically and cured at 20 °C. Samples hydrated for periods of 1, 2, 7 and 28 days were crushed, subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum at laboratory temperature (approximately 20±2 °C). The hydrated samples were ground to pass through a 54 μm sieve and were studied by means of XRD in order to identify the crystalline hydration products. The water bound in the hydrated products was determined based on the weight loss of the dried pastes after thermal treatment at 350 °C for 1 h. The weight loss in the range 350–500 °C was also measured (treatment time: 1 h) and was expressed as $Ca(OH)_2$. The texture of the hydration products was studied using a Siemens XL30 scanning electron microscope (E-SEM) interfaced to an energy dispersive X-ray spectrometer (EDS) OXFORD LINK ISIS 300.

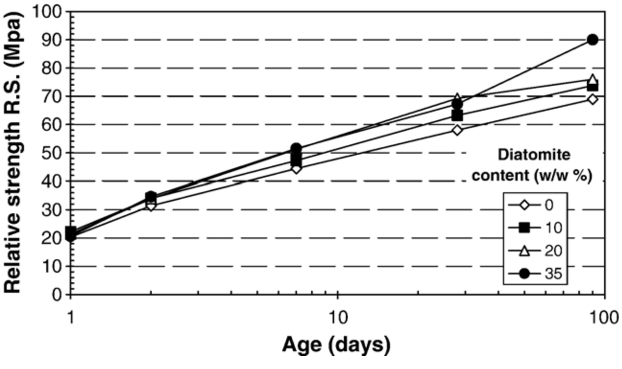

Fig. 3. Relative strength of diatomite cements in relation to curing age and the diatomite content (relative strength (RS): diatomite cements strength based on the pure cement content).

4. Results and discussion

4.1. Cement properties

Fig. 2 shows the compressive strength development of diatomite cements in relation to the cement replacement level. It is observed that the addition of 10% diatomite does not significantly alter the compressive strength at any age. Further increase of the diatomite content leads to cements having compressive strength lower than the PC.

The rate of strength development in Portland cement is mainly dependent on the hydration rate of clinker, while in cement–diatomite systems it is dependent on the combination of clinker hydration and the pozzolanic activity of diatomite. The main factors that affect the contribution of diatomite in strength are: a) the filler effect, b) the dilution effect, and c) the pozzolanic reaction of diatomite with CH. The filler effect, which is depended on the fineness and the amount of mineral (diatomite) used, leads to the improvement of the initial porosity of the mix due to the obstruction of pores and voids by the action of the finer grains. The dilution effect, which is inversely proportional to the mineral addition, leads to less hydrated compounds due to the less clinker content of the blended cement. The pozzolanic reaction between the amorphous silica of the mineral addition and the calcium hydroxide produced by the cement hydration reactions makes the paste more homogeneous and dense.

Fig. 3 shows the relative strength of diatomite cements in relation to curing age and the diatomite content. Relative strength (RS) is a corrected value of diatomite cements strength, taking into account the pure cement content. It is derived from the relation $(RS)=(S\times100)/C$ where S: compressive strength of diatomite cement and C: pure cement content of the above cement. (RS) presents the diatomite cement strength, expressed on the basis of "pure cement" content instead of "pure cement + diatomite" content. In fact (RS) indicates the effect of diatomite addition on the hydration process of the cement. (RS) values greater than pure cement strength, indicate that the diatomite addition

Table 4
Physical properties of diatomite cements

Sample	Diatomite (% w/w)	Water demand (% w/w)	Setting time (min)		Flow of normal mortar (%)
			Initial	Final	
PC	–	27.1	110	160	104.0
D-10	10	27.6	120	160	102.5
D-20	20	28.2	110	150	101.0
D-35	35	28.9	120	170	99.0

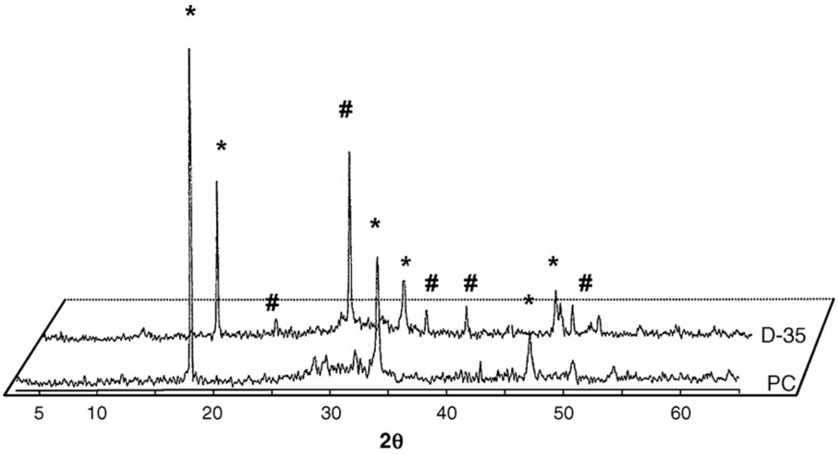

Fig. 4. XRD patterns of PC and D-35 pastes after 28 days of hydration (*: $Ca(OH)_2$, #: $CaCO_3$).

favors the hydration and improves the strength development of the cement. As it is seen from Fig. 3, diatomite cements have (RS) greater than pure cement strength at all ages. At ages of 1 and 2 days, the filler effect overlaps the dilution effect and leads to slightly higher relative strength. At ages more than 7 days, the relative strength shows a clear increase, due mainly to the pozzolanic reaction of the diatomite. In the case of cements containing 35% diatomite, the relative strength significantly increases after 28 days. This strength increase is attributed to the cessation of the pozzolanic reaction at higher ages than the other blended cements, as the less cement content leads to less available calcium hydroxide for the pozzolanic reaction.

Table 4 gives the water demand and the setting times of the cement pastes. The "water demand" is the quantity of water that is required in order to prepare a cement paste of standard consistency as specified in EN 196-3. The diatomite cements demand more water than the PC. The water demand of diatomite cements varies from 27.6% to 28.9%, while the PC has a water demand of 27.1%. The increase in water demand is mainly attributed to the high fineness of diatomite (Table 2, d_{50}=6.3 μm). The flow tests (Table 4) confirm the above results and show that the diatomite addition impairs the mortar workability. Diatomite cements exhibit similar setting times to that of PC (Table 4).

4.2. Cement hydration

As it is known, the principal hydration products in blended cements are essentially similar to those in Portland cement. Of course, in blended cement pastes, $Ca(OH)_2$ content is lowered, both by the dilution of clinker and by the pozzolanic reaction. The hydration products of Portland cement do not have very clear diffraction peaks, due mainly to their semi-amorphous nature. Besides there is an overlapping of the peaks of the hydrated and anhydrous compounds. Modifications of the composition of hydration products may probably occur in blended cements, but they cannot be clearly evaluated by means of XRD.

Table 5
Water bound in hydration products in relation to diatomite content and hydration time

Sample	Hydration time (days)			
	1	2	7	28
PC	6.84	6.89	8.65	10.13
D-10	6.31	6.88	8.52	10.03
D-20	6.04	6.23	8.47	9.9
D-35	5.09	5.33	8.27	9.26

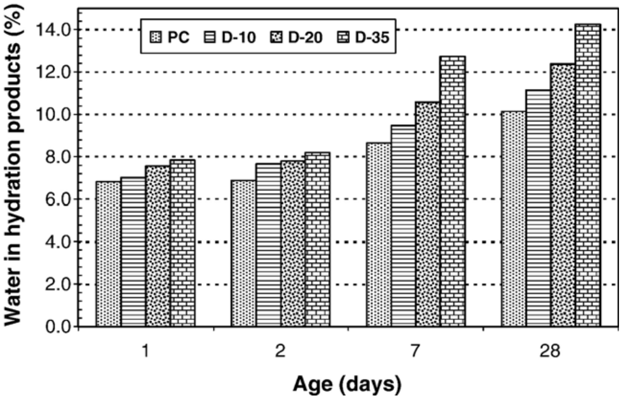

Fig. 5. Bound water in hydration products (expressed based on pure cement).

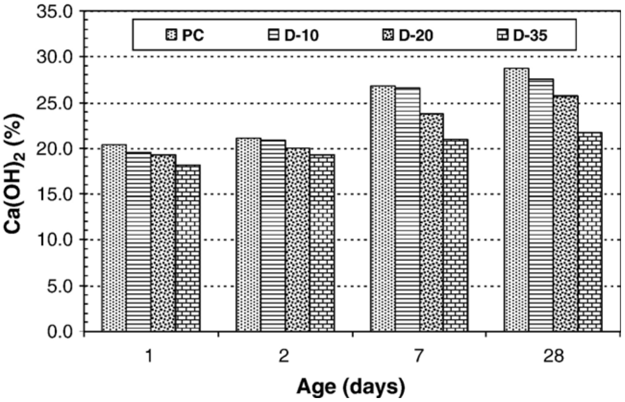

Fig. 6. $Ca(OH)_2$ in the pastes in relation to the diatomite content and the age of hydration.

Fig. 4 indicates the X-ray patterns of PC and D-35 pastes after 28 days of hydration. In both samples, the main crystalline product is $Ca(OH)_2$, while the anhydrous clinker phases have almost completely reacted. In the sample with diatomite, calcite, which is one of the diatomite's main constituent, is also present. The carbonate ions incorporate in calcium aluminate hydrates and carboaluminates are formed, as it is indicated by the peak at $d=7.5712$ Å, which corresponds to $Ca_4Al_2O_6CO_3 \cdot 11H_2O$. In PC a small amount of $Ca_4Al_2O_6SO_4 \cdot 14H_2O$ ($d=9.5478$ Å) has also been detected.

Table 5 presents the weight loss of the pastes at 350 °C, which corresponds to the water in hydrated calcium aluminate and silicate phases. Fig. 5 presents the water of hydrated products expressed on the basis of "pure cement" content instead of "pure cement + diatomite" content. As it is seen, the bound water increases proportionally to the diatomite content. This fact indicates the formation of higher amounts of hydrated products due to the pozzolanic reaction of diatomite. The effect of diatomite is more intense at the age of 28 days, as it was expected, since the pozzolanic reaction of natural materials is a rather slow reaction.

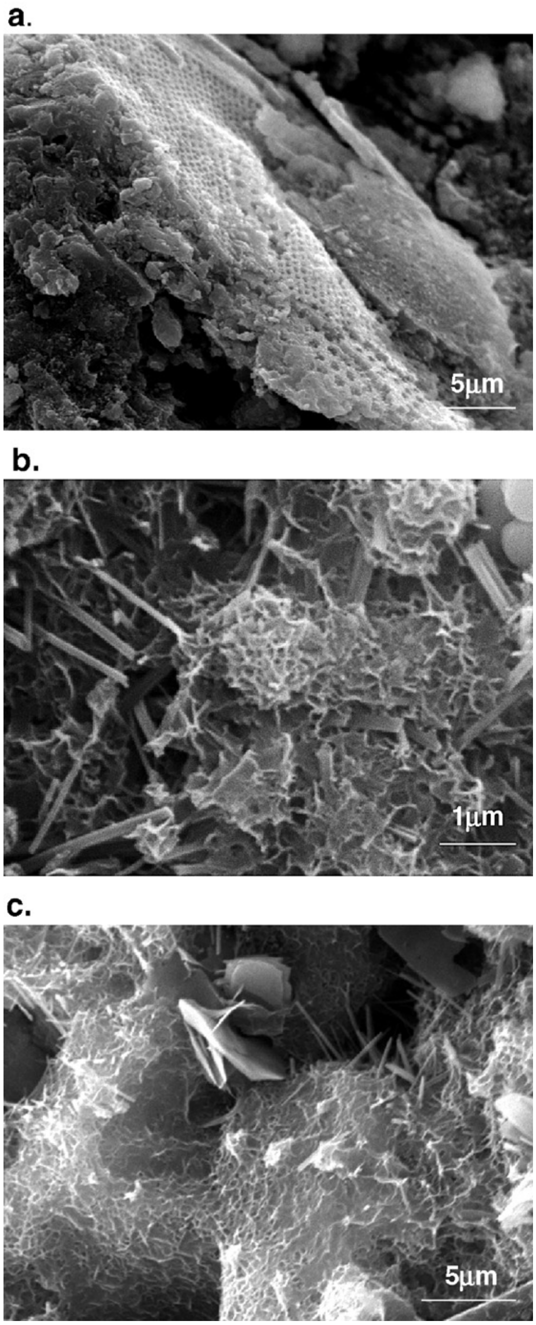

Fig. 7. SEM photos of the sample D-20 (a: 1 day; b, c: 28 days).

The most appropriate way to evaluate the pozzolanic reactivity of materials is the determination of $Ca(OH)_2$ in blended cements pastes, in relation to the age of hydration. This determination can be easily performed using thermogravimetry. However, calcium hydroxide is easily carbonated and transformed to calcium carbonate, therefore the amount of calcium hydroxide which is equivalent to calcium carbonate (decomposition peak ~700 °C) must be counted in. This cannot be done when the materials added in blended cements contain considerable amounts of carbonate as in the case of diatomite. Fig. 6 presents $Ca(OH)_2$ in the pastes in relation to the diatomite content and the age of hydration. It is obvious that the $Ca(OH)_2$ content of the samples is decreased as the diatomite content is increased, especially at the higher age. This fact indicates the pozzolanic activity of the added material.

Fig. 7 presents some SEM photos of D-20 sample. Fig. 7a is from the sample hydrated for 1 day and shows a well preserved diatomite cell having the characteristic honeycomb texture. Fig. 7b and c show the surface of diatomite in the sample hydrated for 28 days. As it is seen, the honeycomb surface has been weathered due to the pozzolanic reaction and needle-like hydration products have been developed. $Ca(OH)_2$ in the form of hexagonal plates is clearly seen in these pictures.

All the above measurements confirm the pozzolanicity of diatomite and its incorporation in the hydration procedure of Portland clinker. It must also noticed, that dolomite is characterized as natural pozzolana (P) according to the EN 197 1. This standard specifies that the reactive SiO_2 content shall be not less that 25% by mass and diatomite satisfies this requirement (Table 1).

5. Conclusions

The following conclusions can be drawn from the present study:

- Diatomite is characterized as natural pozzolana, as it satisfies the requirements of EN 197 1 concerning the active silica content.
- Blended cements, having up to 10% diatomite content, develop the same compressive strength, as the corresponding Portland cement.
- The addition of diatomite results to a higher paste water demand.
- The pozzolanic reaction of diatomite leads to the formation of higher amounts of hydrated products, especially at the age of 28 days.

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