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The influence of biogenic micro-silica-rich rocks on the properties of blended cements

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Abstract

Diatomaceous rock samples of a different origin and with amorphous, biogenic micro-silica (opal-A) as their major siliceous constituents were studied and their behaviour as a cement additive was determined. The raw materials were collected from Hungary, Romania and Greece. These diatomite rocks varied in geological age from Miocene to Pleistocene, and were deposited respectively in lacustrine, brackish and marine conditions. The depositional environment affected the size of the opal-A particles, those of lacustrine origin being the smaller (<10 μm). Most of the opal-A particles were represented by disk-shaped diatom frustules. Laboratory tests showed that these diatomite rocks exhibited good pozzolanic properties and could replace the most commonly used natural pozzolanas. The use of diatomaceous rocks as cement additives has drawbacks such as higher water demand, but the compressive strength of the laboratory produced cements exhibit higher values than OPC. The highest compressive strength values were obtained with the use of the Hungarian diatomite rock that had the greatest amount of reactive silica content reflecting its high opal-A content.

Keywords: Diatomite; Amorphous silica; Opal-A; Cement; Pozzolana; Compressive strength

1. Introduction

Pozzolanic materials used in the cement industry could include several qualities of diatomaceous rocks [1–5]. Such materials are sedimentary rocks of biogenic origin with high amorphous silica content. The amorphous silica is mainly in the form of diatom frustules, and secondarily in the form of sponge spicules, silicoflagellate skeletons and/or radiolarian cells. Beside its amorphous silica content, diatomite rocks may also contain carbonate and clay minerals, quartz, feldspars and volcanic glass. Pure diatomite rock is commonly used as a filtering agent, whereas calcareous or clayey diatomite is commonly utilised in the manufacturing of special fillers, absorbents and insulation products [6–9].

The natural pozzolanas currently used in Greece are volcanic tuffs with high amounts of volcanic glass providing the reactive silica needed for the formation of cementitious calcium silicate compounds (CSH). Biogenic silica-rich rocks, such as diatomites contain high amounts of reactive silica in the form of opal-A. Even though several diatomite deposits are located in Greece and other European countries, their usage as pozzolanic additives has not been established so far.

During a three-year European Research and Development project (Contract No ERBIC15-CT96-0712), several diatomaceous rocks originating in Greece, Romania and Hungary were tested and evaluated as cement additives. In the present study these materials were characterised and their potential as cement additives was evaluated taking into account their diversity in opal-A,

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reactive silica content and differences in diatom size, shape and morphology.

2. Geological setting

2.1. Hungary

The Hungarian diatomite sample was obtained from an active quarry operating for the production of diatomite granules used as absorbents, near to the village of Erdobenye, in NE Hungary. The Erdobenye sedimentary basin is located in the SSE margin of the volcanogenic Tokaj Mountains. The 70 m-thick sedimentary succession is of brackish to freshwater origin and consists of sandstone, tuffite, chert, claystone, and diatomite alternations of Sarmatian age [10–12]. Volcanic rocks of the same age occur at the edges of the basin.

2.2. Romania

The Romanian sample was obtained from a periodically operating diatomite quarry near the village of Adamclisi, southern Dobrogea. Middle Sarmatian age diatomite beds are 6–25 m thick with a dull-white to yellowish colour. They occur interbedded with green-grey clays and fossiliferous limestone and are genetically related to the presence of volcanic rocks of submarine origin that occur in the vicinity of the deposit [13].

2.3. Greece

Several diatomite deposits of diverse age, depositional environment and purity are present in Greece [14,15]. In the present study three representative deposits are studied, namely those of Alimia–Sarakiniko (Milos Island), Aitania (Crete Island) and Agios Nikolaos–Vougiato (Zakynthos Island).

2.3.1. Milos island

Milos Island is a member of the South Aegean Volcanic Arc. Most of the island is composed of lavas, ash-tuffs, tuffites, pumice-tuffs and volcanic breccio-conglomerates [16]. Even though diatomaceous rocks occur interbedded with tuffs in several places of the island, their thickest accumulation is reported in the northern part of the island, in the Alimia–Boundes–Sarakiniko area. Off-white to yellowish diatomite layers occur in three horizons with a total thickness of about 20 m [15,17–19]. They are of shallow marine origin and Pliocene–Pleistocene age [17]. The Milos sample was obtained from the uppermost horizon of this area, where the diatomite beds alternate with yellowish marlstone and grey pumice-tuffs.

2.3.2. Crete island

In Crete Island, Aegean sea, several occurrences of diatomite rocks have been described, with those of Pliocene age and shallow marine origin being the most important. These occur in the village of Aitania, near Heraklion town, North-Central Crete [14,20–22]. The respective deposits are white in colour, alternating with brownish sandstone and marlstone. Even though the diatomite-sandstone succession is $\approx$150 m in thickness, the individual diatomite layers do not exceed 7 m in thickness. The sedimentological structure of the diatomite layers revealed that most of the diatom frustules were re-deposited.

2.3.3. Zakynthos island

In the central part of Zakynthos Island, a white calcareous diatomite rock of lower Miocene age is present [23,24]. It has a thickness of about 50 m having been formed in a deep-sea environment [23]. Because of its high $CaCO_3$ content, the material is characterised as diatomaceous limestone instead of diatomite. The calcareous material is mainly of biogenic origin consisting of the tests of microfossils such as foraminifera [24].

3. Experimental procedures

The characterisation of the raw materials included chemical, mineralogical and morphological analyses. The materials were analysed with the PHILIPS PW1010 XRF spectrometer to determine their chemical composition. Their mineralogical analysis was performed on ground bulk samples with the Siemens D5000 diffractometer and the SEM analysis with the Philips XL30 E-SEM. 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 [25].

4. Results and discussion

4.1. Raw materials

4.1.1. Mineralogy

Opal-A, in the form of diatom frustules was the major constituent of the raw materials studied. Other biogenic silica components were silicoflagellate skeletons and sponge spicules (Plates 1–7). Opal-A was identified

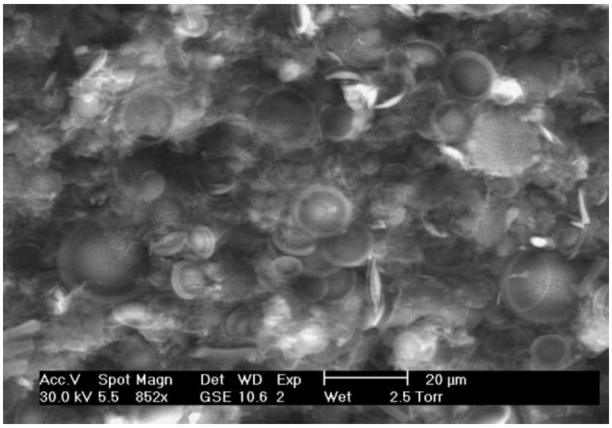

Plate 1. Well-preserved, small disk shaped diatom frustules in 'Erdobenye pure' diatomite sample, Erdobenye, Hungary.

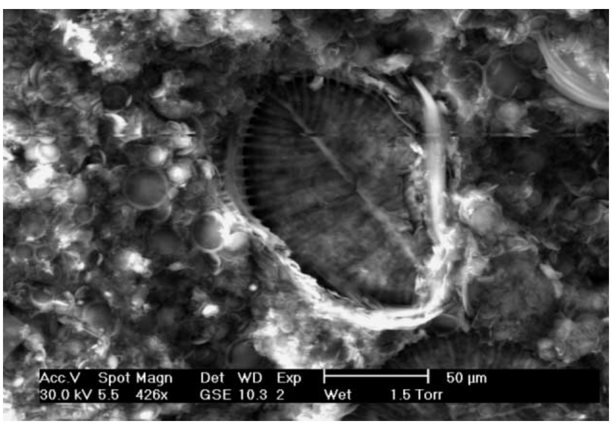

Plate 2. A large diatom frustule sunk in a matrix composed of abundant small diatom frustules, Erdobenye pure diatomite sample, Erdobenye, Hungary.

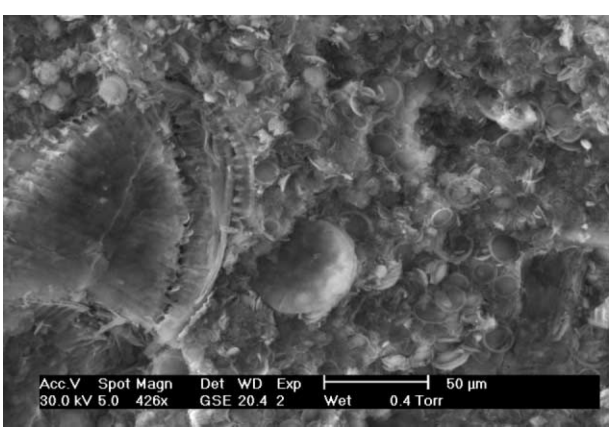

Plate 3. Progressive opal-A dissolution of large diatom frustules, Erdobenye pure diatomite sample, Erdobenye, Hungary.

in the XRD diagrams by the hump in the area of 20–26° 2θ and also by SEM. Calcite and quartz occurred in high amounts in the Zakynthos and Crete diatomite rocks.

Plate 4. Broken sponge spicules and pennate diatom frustules hosted in a clay matrix, Adamclisi deposit, Romania.

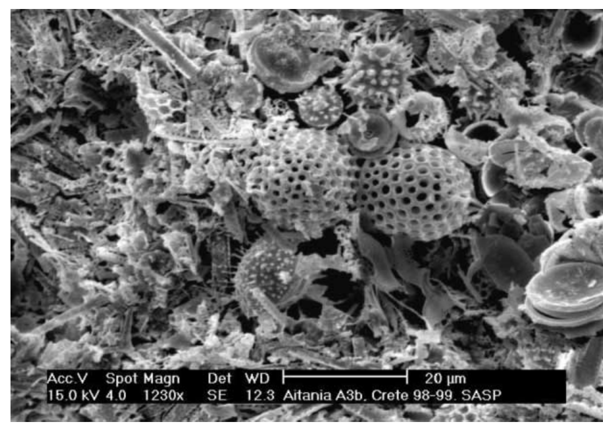

Plate 5. Well-preserved, disk-shaped diatom frustules, Aitania deposit, Crete Island, Greece.

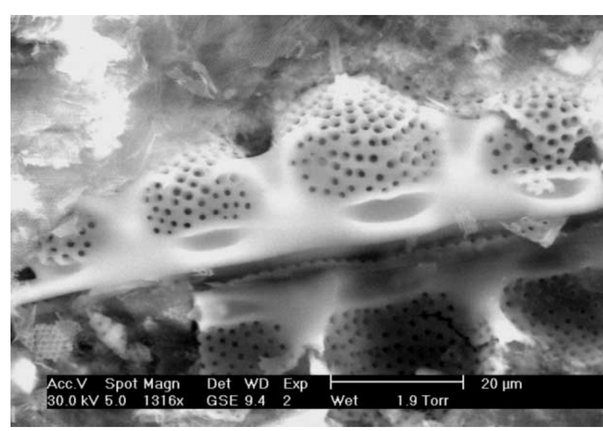

Plate 6. A well-preserved diatom frustule (detail), Alimia, Milos Island, Greece.

Smectite occurred in small amounts in the Hungarian and the Romanian diatomite rocks (Table 1). In general, Crete and Zakynthos diatomite rocks are the most

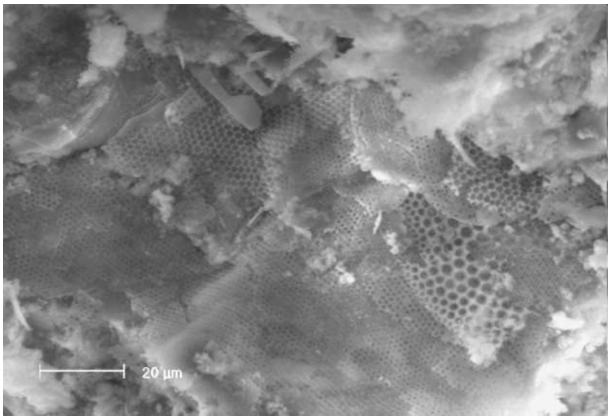

Plate 7. Closely packed sheet-like diatom assemblages alternated with calcite sheets, Zakynthos Island diatomite. Dissolution phenomena of opal-A are clearly shown due to its conversion to opal-CT (Stamatakis et al. [22]).

homogenous when compared with the Hungarian, the Romanian and the Milos Island diatomite deposits.

The Hungarian diatomite rock had the highest opal-A content of the raw materials analysed. Besides the amorphous silica phase, the sample contained minor amounts of clay minerals such as smectite and smectite-kaolinite, and also traces of quartz and feldspar.

The Romanian sample contained high amounts of opal-A but the broad peak on its XRD pattern was lower than that of the Hungarian sample, corresponding to a lower biogenic silica content. In addition to the amorphous phase, high amounts of detrital quartz and lesser amounts of feldspars were also present. Illite was a minor component of the rock, whereas carbonates such as calcite and dolomite were absent (Table 1).

The Milos bulk diatomite sample contained, besides opal-A, high amounts of clay minerals, calcite, feldspar and quartz (Table 1). Minor quantities of volcanic glass were also detected using SEM techniques.

The Crete diatomite sample contained, besides opal-A, variable amounts of quartz, feldspars, calcite, and clay minerals. Minor amounts of dolomite were also present.

In the Zakynthos diatomite sample, calcite was the major component, whereas opal-A was represented by a very weak hump in the XRD diagram. Quartz was also detected in trace amounts.

4.1.2. Chemistry of the raw materials

The major element analysis of the diatomaceous rocks revealed that they have diverse CaO content hence they could be divided in two groups. One group is the diatomaceous rocks from Zakynthos and Crete that had high CaO content, whereas the Hungarian, Romanian and the Milos sample comprise the other group that had a low CaO content.

The Hungarian diatomite had the highest SiO_2 content (77.68%). Most of it was attributed to opal-A. The low Al_2O_3 content of the sample corresponded to the relatively low amounts of alumino–silicate minerals such as clays and feldspars.

All samples had a low $K_2O + Na_2O$ content, and especially the biogenic silica-rich Hungarian sample, due to the low amounts of feldspars and other alkali-rich minerals (Table 2).

The Romanian sample had a SiO_2 content of about 75%, attributed to the presence of opal-A, quartz and alumino–silicate minerals. The Al_2O_3 content of that sample was the highest among all samples due to the presence of alumino–silicate minerals (Table 1).

In addition to the major elements chemical analysis, the insoluble residue (IR) and the RS content of the raw materials were determined. According to the Greek regulations concerning cement types, the IR should be between 20% and 40% for pozzolanic cements [25]. Recent European regulations (EN197-1) state that the RS content of a pozzolanic material should be at least 25% of the material [26]. As shown in Table 2, all samples have $RS > 25\%$, so they both comply to the Greek and the EU regulations. However, the Hungarian diatomite had the highest RS content while the Zakynthos and Crete diatomite rocks had the lowest.

Even though the Romanian sample had a high content of total SiO_2, its RS content was only the 67% of the total SiO_2. This could be attributed to the presence of non-reactive silica minerals in the rock (Table 2). The presence of clay minerals and feldspars in the Milos

Table 1
Mineralogical analysis of the diatomaceous rock samples

	Greece			Hungary	Romania
	Zakynthos	Milos (Alimia)	Crete (Aitania)	Erdobenye	Adamclisi
Opal-A	mj	mj	mj	mmj	mj
Quartz	tr	md	mj	tr	mj
Calcite	mj	md	mj		
Dolomite			tr		
Feldspar		md	tr	tr	tr
Smectite			md	md	md
Illite		md	md		tr
Smectite-kaolinite		md		md	

Explanatory notes: mmj: predominant, mj: major, md: medium, tr: minor/trace component blank cells means not detected mineral phases.

Table 2
Chemical analysis of the diatomaceous rock samples

	Greece			Hungary	Romania
	Zakynthos (%)	Milos (Alimia) (%)	Crete (Aitania) (%)	Erdobenye (%)	Adamclisi (%)
SiO_2	30.25	59.90	48.59	77.68	75.00
Al_2O_3	2.02	7.68	5.66	4.14	9.80
Fe_2O_3	1.01	2.36	3.48	3.23	3.85
CaO	32.97	9.50	16.79	1.09	0.70
MgO	1.07	1.55	2.42	1.98	1.98
K_2O	0.17	1.78	1.01	0.39	1.34
Na_2O	0.11	1.00	0.67	0.12	0.50
LOI	32.68	16.48	22.27	11.23	6.91
Total	100.28	100.25	99.89	99.86	100.08
IR	22.64	56.10	39.06	56.50	67.64
RS	25.50	45.02	28.20	69.07	50.49
RS/TS	0.84	0.75	0.58	0.89	0.69

Explanatory notes: RS = reactive silica, TS = total silica, IR = insoluble residue, LOI = loss on ignition.

diatomite accounted for its high Al_2O_3 content (Tables 1 and 2).

4.1.3. SEM studies

The examination of the samples with the E-SEM confirmed the existence of the various diatom types and microfossils (Plates 1–7). The Hungarian sample consisted of small disk-shaped diatom frustules (Plate 1). Most of them were smaller than 10 μm and their degree of preservation was good. The small size of the diatom frustules is a characteristic feature of lacustrine diatomite deposits. Some larger diatom frustules randomly occurring in the fine grain matrix exhibited an early stage of opal-A dissolution starting from the rim of the frustules (Plates 2 and 3). The diatom association in the Romanian sample was dominated by pennate-type frustules that were the main component of the rock. Consequently, disk-shaped frustules were not abundant. Silicoflagellate skeletons and sponge spicules were also part of the opaline silica phase. In most cases, the diatomite frustules were enclosed in a clayey matrix (Plate 4). Reworked diatom frustules and silicoflagellate skeletons constituted the opaline phase in the Crete diatomite. The predominance of the broken frustules was indicative of transportation and re-deposition of most of the micro-silica particles. Crystals of detrital minerals such as quartz and feldspars existed in the groundmass of the samples. However, some layers contained well-preserved diatom frustules that had not been transported a great distance (Plate 5).

The Milos diatomite contained broken diatom frustules, due to reworking and mixing with tuffaceous materials. However, in most of the diatomite beds the diatom frustules were well preserved retaining their detailed structure (Plate 6).

Closely packed assemblages composed of sheet-like large diatom frustules with dissolved, sharp edges constituted most of the Zakynthos micro-silica phase (Plate 7). The degree of preservation of the diatom frustules was low because of their gradual transformation to opal-CT at shallow depths and to chalcedonic quartz at greater depths [23,24]. By contrast, radiolarian cells and sponge spicules exhibited a higher degree of preservation due to their thicker skeleton.

4.2. Laboratory produced cements

Blended cements were produced by grinding each one of the diatomite rocks with clinker and gypsum. Fifteen different mixtures were produced by adding 10%, 15% and 20% of each of the five diatomite rocks that replaced clinker. All mixtures were ground for 42 min. Following their production, their specific surface area (Blaine), setting time and 1, 7 and 28-day compressive strengths were measured. The results, summarised in Table 3 indicate the following:

- The addition of diatomite rocks in cement had a great effect on its grain size increasing its fineness. Diatomite rocks are very soft materials and as such, grinding with clinker and gypsum resulted into a dramatic increase of the specific surface area (Blaine) of the cement. Cements produced with the Hungarian diatomite had the highest Blaine; this diatomite was characterised by the most reactive silica and therefore the highest content of diatoms. Among the diatomite rocks, the one from Zakynthos was the hardest to grind. This difference in hardness could be attributed to its high calcite content.
- The blended cements produced with the Hungarian diatomite had the highest strength. It is likely, that the diatomite quality and the high specific surface area of the final products (blended cements) had a great influence on their properties (Figs. 1 and 2).
- The addition of diatomite rocks to cement drastically increased its water demand. As shown in Table 3,

Table 3
Physical characteristics of laboratory produced cements and mortars

	% Clinker replacement by diatomite	Specific surface mm^2	Water demand (%)	Initial setting time (min)	Final setting time (min)	1 Day strength (MPa)	7 Days strength (MPa)	28 Days strength (MPa)	Strength change (%)
Hungary	0[a,b]	3030	25.2	125	165	14.6	38.6	53.40	0.0
	10	5830	29.6	140	165	20.1	43.8	62.95	17.9
	15	7480	32.0	145	180	19.0	42.7	63.85	19.6
	20	8890	36.0	155	190	17.5	38.8	59.60	11.6
Romania	0	3290	25.0	140	170	15.4	39.7	52.80[b]	0.0
	10	5160	28.4	135	175	18.0	41.9	58.10	10.0
	15	6000	31.0	145	190	17.1	40.6	58.80	11.4
	20	6850	31.4	150	190	16.1	39.1	57.46	8.8
Milos	0	3320	25.0	140	170	15.4	39.7	52.50[b]	0.0
	10	4870	27.6	140	165	22.2	46.0	57.40	9.3
	15	5780	28.6	140	170	20.8	44.0	56.80	8.2
	20	5910	29.4	140	170	19.7	42.9	56.30	7.2
Crete	0	3320	25.0	140	170	15.4	39.7	52.50[b]	0.0
	10	4700	28.8	140	165	18.7	43.9	55.40	5.5
	15	5710	30.2	140	170	16.2	41.1	55.20	5.1
	20	5820	31.0	145	175	13.4	36.4	53.00	1.5
Zakynthos	0	3340	26.2	110	130	19.8	42.7	55.00[b]	0.0
	10	4800	28.2	175	195	18.0	43.7	57.00	3.6
	15	5400	28.4	185	220	18.8	43.0	56.10	2.0
	20	6560	28.8	190	230	17.2	41.8	55.10	0.2

[a] Control sample: clinker 95%, gypsum 5%.
[b] The five reference samples used (0% addition) were of slightly different characteristics, as shown in this Table.

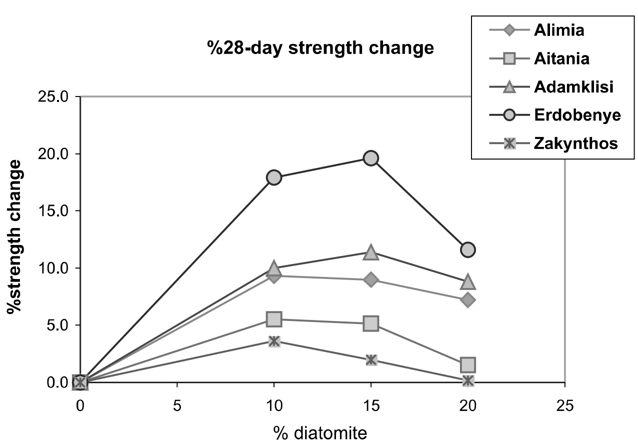

Fig. 1. Percentage of strength change vs. diatomite addition.

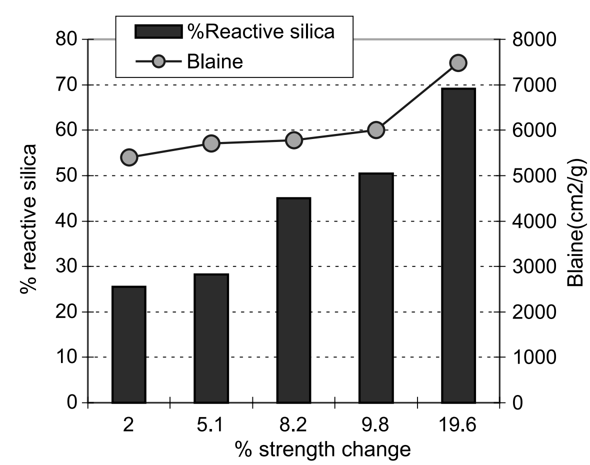

Fig. 2. Percentage of strength change for blended cements with 15% diatomite vs. RS content and Blaine.

their addition in quantities exceeding 15% was almost prohibited since this caused the average water demand to increase by ≈20%. However, any problems related to water demand that might occur during concrete manufacturing could be overcome by the incorporation of small quantities of superplasticisers into the mix. However, these substances would increase the cost of the concrete, but this may be acceptable if a special concrete were to be produced.

- As shown in Fig. 1, the highest strengths were obtained with the 10–15% addition of diatomite rock. It is known that the pozzolanic cements manufactured using pozzolanic tuffs or synthetic additives exhibit slightly lower compressive strength than the OPC. By contrast, the addition of all types of the aforementioned diatomite rocks in cement resulted in blended cements with a higher strength than that of the reference Portland cement (Table 3). Other natural pozzolanas used in blended cements and exhibiting higher strength than that of OPC are zeolite (clinoptilolite)-rich ash tuffs [27,28]. However, cements produced with most of the natural pozzolanas have a lower compressive strength than OPC [29,30].

- Satisfactory cement strength was obtained even with the addition of impure, calcareous diatomite rocks of Zakynthos Island that has relatively low content of total and reactive silica. It is likely, that the small grain size of the biogenic calcite present in the calcareous diatomite acts as a filler lowering the porosity of the cement pastes and therefore improving their strength. It is known that calcareous cements produced with 10–15% limestone, clinker and gypsum yield compressive strengths, similar or higher than those of OPC [31].
- Due to the small grain size of the diatom frustules that compose the diatomite rock, the cements produced by diatomite addition had a specific surface area that was almost twice than that of the reference sample. The positive correlation between the RS content of each diatomite and the strength of the blended cements is shown in Fig. 2. In the diatomaceous rocks studied, the increase of the compressive strength of the diatomaceous cements is probably due to the high amounts of the amorphous, easily released silica they contain. In the same figure, the positive relationship between Blaine of these cements and % strength change is also shown.

5. Conclusions

The aforementioned tests and measurements of the behaviour of the diatomite containing cements leads to the following conclusions:

- The small grain size and the friability of diatomaceous rocks contribute to the high specific area of the respective blended cements, which in turn is responsible for the drastic increase of the water demand.
- The Hungarian (Erdobenye) diatomite is the purest diatomite rock studied and it is composed by the smallest micro-silica diatomite particles. Cement produced with this rock has the highest compressive strength.
- The Zakynthos Island calcareous diatomite is composed of small particles of calcareous and siliceous microfossils. Its compressive strength is also higher than that of OPC.
- The higher the RS content of the diatomite, the higher the strength of the blended cement. However, the type and morphology of the amorphous silica (diatom frustules) and the presence of friable, fine grained biogenic calcite are additional parameters that need to be taken into consideration since they might also affect the strength of the resulting cements.
- In summary, diatomite rocks could be used for the production of blended cements with a high strength. Problems in concrete manufacturing arising from the high water demand of these cements could be overcome by the use of superplasticisers. The next step in studying these diatomite rocks would require concrete manufacturing and determination of its properties.

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